SCHOOL OF ENGINEERING

CRESP

Short Course
Introduction to Nuclear Chemistry and Fuel Cycle Separations

Vanderbilt University School of Engineering
Department of Civil and Environmental Engineering
Nashville, TN
December 16-18, 2008

COURSE MONOGRAPH

Speakers Affiliations

Acknowledgements

ORGANIZING COMMITTEE:

Raymond G. Wymer, Chair, Vanderbilt University
David S. Kosson, Vice-Chair, Vanderbilt University
Cynthia Atkins-Duffin, Lawrence Livermore National Laboratory
David DePaoli, Oak Ridge National Laboratory
Kathryn Higley, Oregon State University
Terry Todd, Idaho National Laboratory

SPEAKERS:

Cynthia Atkins-Duffin, Lawrence Livermore National Laboratory
Allan Croff, ORNL, ret., and USNRC
David DePaoli, Oak Ridge National Laboratory
B. John Garrick, NWTRB Chairman
Mark Gilbertson, Department of Energy
Mike Goff, Idaho National Laboratory
Clarence Hardy, Nuclear Fuel Australia, Ltd
Kathryn Higley, Oregon State University
Gordon Jarvinen, Los Alamos National Laboratory
Robert Jubin, Oak Ridge National Laboratory
David S. Kosson, Vanderbilt University
Jack Law, Idaho National Laboratory
Frank L. Parker, Vanderbilt University
Robert Sindelar, Savannah River National Laboratory
Lawrence Tavlarides, Syracuse University
John Vienna, Pacific Northwest National Laboratory
Raymond G. Wymer, Chair, Vanderbilt University

STAFF:

Lisa Bliss, Assistant Director CRESP III
Randi Hall, Administrative Assistant
Kevin Brown, Senior Research Scientist

This course is based on work supported by the U. S. Department of Energy, under Cooperative Agreement Number DE-FC01-06EW07053 entitled 'The Consortium for Risk Evaluation with Stakeholder Participation III' awarded to Vanderbilt University. The opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily represent the views of the Department of Energy or Vanderbilt University.

This course is also partially supported by Nuclear Education Grant Program from the U.S. Nuclear Regulatory Commission.

About CRESP

CRESP

Consortium for Risk Evaluation with Stakeholder Participation III

Co-Principal Investigators:	David S. Kosson, Ph.D.	david.kosson@vanderbilt.edu	615-322-1064
	Charles W. Powers, Ph.D.	charles.w.powers@vanderbilt.edu	201-214-4937

About CRESP

The Consortium for Risk Evaluation with Stakeholder Participation CRESP III is primarily a five year (2006 - 2011) Department of Energy cooperative agreement awarded to Vanderbilt University. The multi-university consortium is working to advance cost-effective, risk-based cleanup of the nation's nuclear weapons production facility sites and cost effective, risk-based management of potential future nuclear sites and wastes.

CRESP III Mission

The mission of CRESP III is to advance cost-effective, risk-based cleanup of the nation's nuclear weapons production facility sites and cost effective, risk-based management of potential future nuclear sites and wastes. This will be accomplished by seeking to improve the scientific and technical basis for environmental management decisions by the Department of Energy and other public entities and by fostering public participation in that search.

Scope

The CRESP III projects help define and assess the technical and regulatory scope and approaches useful for the nation as it strives to undertake its cleanup and stewardship responsibilities in a protective and cost-effective manner at contaminated sites, and plan and manage potential future nuclear sites and wastes. The project effort focuses on supporting independent and collaborative research, reviews, methods, data gathering and stakeholder participation needed for effective evaluation and communication of DOE related health, environmental and other risks. The effort seeks responsively to address on important cleanup-related challenges at the sites, on the end states which cleanups seek to achieve, and planning and management challenges for potential future nuclear sites and wastes. CRESP III is committed to accomplishing these outcomes by:

- performing targeted studies on specific risk related issues important to the long-term management of environmental problems;
- contributing to risk evaluation and assessment, or to the development of related methodologies, relevant to risk issues at a number of DOE sites;
- focusing on the collection and analysis of data needed for effective risk evaluation, and on the definition and assessment of relevant technical and regulatory approaches valuable in resolving risk-related issues;
- providing an independent mechanism to support the assessment of DOE'S needs for research, to critique current research, and to develop data relevant to the concerns of the public, to support planning and to be responsive to evolving regulatory commitments; and
- supporting efforts to improve working relationships and communications with the public and stakeholders at sites and across the DOE complex.

The CRESP Membership

The CRESP III consortium member universities, led by Vanderbilt, now include Howard University, New York University School of Law, Oregon State University, Robert Wood Johnson Medical School, Rutgers, The State University of New Jersey, University of Arizona, the University of Pittsburgh and the University of Washington.

Table of Contents

Spent Nuclear Reactor Fuel Reprocessing: Past, Present, and Future

Raymond G. Wymer
Vanderbilt University

Why Should We Care About Reprocessing?

Today's technologically advanced world is absolutely dependent on available, abundant, environmentally acceptable and affordable energy. Nearly all of today's major sources of energy are based on fossil fuels that are either becoming environmentally unacceptable because of solid and gaseous waste products, will become depleted in the foreseeable future, or are vulnerable to adverse manipulation, both in price and availability. Energy sources such as sunlight and wind can and will make a worthwhile contribution to the energy supply mix, but they will not by themselves adequately address the problems just noted. Another major energy source has already being added to the list of viable energy sources: nuclear energy. The use of nuclear must be increased if the serious problems noted above are to be minimized or avoided entirely.

Nuclear energy is not without its drawbacks, most notably the radioactive wastes that attend nuclear energy production. There is as yet nowhere in the world a licensed and operating high-level radioactive waste repository for the spent fuel wastes from nuclear power reactors. This true whether the wastes are intact spent nuclear reactor fuel elements or are wastes from spent nuclear reactor fuel reprocessing. However, progress is being made in several countries to establish geologic repositories for High-level radioactive wastes. A repository already exists in the U.S. for alpha wastes.

In addition to the radioactive wastes there are other very serious potential drawbacks to obtaining energy from nuclear power reactors as exemplified by the catastrophic Chernobyl reactor accident in Russia and the relatively benign Three-Mile Island Reactor accident in the U.S. Major advances have been made in nuclear power reactor design in recent years that significantly reduce the likelihood of recurrence of such accidents, and reactor licensing requirements that militate against such accidents have become more stringent. In any case, the need for the energy that can be obtained from fissioning the atom must be balanced against the dangers inherent in its use. The national and international consequences of an inadequate energy supply are simply unacceptable; safe and affordable nuclear energy is subject to continuing technological advances and improvements that make its production both acceptably safe and reliable.

As informed citizens it is incumbent on us to understand the pros and cons of nuclear energy and to weigh the many and complex benefits against the risks and costs of its production and use. These are issues too important to be uninformed about. Among the most important of these issues is that of spent fuel reprocessing. To understand this issue it is necessary to know how the U.S. got to where it is.

Spent Nuclear Fuel Reprocessing: U.S. History

The U.S. entry into spent nuclear reactor fuel reprocessing came about because of the desire to create an arsenal of nuclear weapons, first for use by the U.S. to defeat its enemies during World War II (WWI), and second as a counter-force to Russia's nuclear weapons buildup during the subsequent Cold War. In the course of WWII the U.S. built and operated a large spent nuclear fuel reprocessing plant at Hanford in the southeastern corner of the state of Washington. The purpose of the reprocessing plant was to separate plutonium from irradiated uranium fuel rods. The plutonium was to be used in the manufacture of atomic bombs that it was hoped would help bring to the wars with Japan and Germany to a successful conclusion. In fact, that is what happened with Japan.

The reprocessing carried out in the Hanford plant was the first large-scale spent nuclear fuel reprocessing in the world, and for the next 25 years the U.S. led the world in developing spent nuclear fuel reprocessing.

Reprocessing to recover plutonium began with the scale up of a laboratory-scale process developed by Seaborg and associates and was based on co-precipitation of plutonium with bismuth phosphate. Although the process did work, as it turned out it was an unfortunate choice because of the large amount of phosphate ion that wound up in the reprocessing plant waste stream. The presence of phosphate significantly complicates treatment and final disposal of the reprocessing wastes. It was soon found that solvent extraction of plutonium along with uranium was a much simpler and more efficient process, and solvent extraction processes with several different organic solvents was adopted both in the U.S. and abroad. In the U.S. a process based on methyl isobutyl ketone succeeded the bismuth phosphate process, and it in turn eventually was replaced by the Purex process. The Purex process proved to be highly successful and has been used universally throughout the world for recovering plutonium both for manufacture of nuclear reactor fuel and for nuclear weapons production.

Plutonium production and its separation from uranium and fission products continued after WWII in order to build a stockpile of nuclear weapons based on plutonium. Another large reprocessing plant to recover plutonium for the same purpose was built in South Carolina. Concurrently nuclear weapons based on ^{235}U produced by gaseous diffusion were produced as was fuel for the U.S. naval fleet, notably submarines and aircraft carriers. The naval fuels were more refractory than those used in plutonium production reactors and were reprocessed in a special plant built in Idaho. None of these three reprocessing plants is now reprocessing spent fuel to produce plutonium. Two of them are totally shut down.

In addition to the U.S. government reprocessing plants there were several abortive attempts to establish commercial spent fuel reprocessing in the U.S. Initially these attempts were encouraged by the U.S. Atomic Energy Commission (AEC), the forerunner of the today’s Department of Energy (DOE). A small reprocessing plant was operated for a short time in upstate New York. This plant, the West Valley Reprocessing Plant, reprocessed both commercial spent fuel and fuel for the AEC. It is now decommissioned and the site awaits cleanup. Construction of two other plants was completed or started. One, the General Electric plant in Morris, IL, was built but never operated. Construction of the other plant, the Allied General Services Plant was never completed because of the moratorium placed on U.S. reprocessing by the Carter administration. As a consequence of these actions there is at present no commercial spent nuclear fuel reprocessing carried out in the U.S.

Reprocessing has continued unabated elsewhere in the world, and as will be discussed later, there is an initiative underway by DOE to reestablish commercial spent nuclear fuel reprocessing in the U.S. as part of a larger initiative to provide complete fuel recycle services internationally.

Foreign Spent Nuclear Fuel Reprocessing

Although all attempts at spent nuclear fuel reprocessing was forcibly discontinued in the U.S. in the mid-1970s this was not the case overseas. France, Great Britain, and Russian continued major reprocessing activities in the ‘70s and beyond, and smaller countries like Japan and Belgium operated smaller reprocessing plants, all eventually based on the U.S. Purex process.

Today there are significant (of the order of 800 tonnes or more per year of heavy metal[1]) reprocessing plants in operation in countries ranging from those mentioned above to India and China, both of whom have large and growing nuclear energy programs. In most cases the plants have been used both for commercial power reactor spent fuel reprocessing and for spent fuel reprocessing related to government, i.e., military, activities. Japan has a large (800 metric tonnes per year of heavy metal) commercial spent fuel plant just starting operation. The current major spent fuel reprocessing capacity world-wide is given in table 1 below.

Table 1. Major Current Commercial Light Water Spent Fuel Reprocessing Capacity

Commercial Plant	**Nominal Capacity, tonnes Heavy Metal/year**
France, LaHague	1700
UK, Sellafield (THORP)	900
Russia, Mayak	400
Japan Tokai Rokkasho	 ~100 800
Approximate Sub-Total	**~3900**
Other	
UK	1500
India	275
Approximate Sub-Total	**1775**
Total Commercial Capacity	**5675**
(U.S. commercial capacity)	(0)

A U.S. Spent Nuclear Fuel Reprocessing Renaissance?

Very important changes have taken place since the 1970s in the world's energy supply situation, and in particular in the energy supply situation of the U.S., the world's largest energy user. Energy supply problems in the form of excessive reliance on oil from the comparatively unstable middle-eastern countries and from Venezuela; concerns about global warming due to carbon dioxide generated by burning fossil fuels; concerns about the eventual depletion of fossil fuel resources and reserves; concerns about radioactive wastes; and concerns about nuclear weapons proliferation have all arisen and brought about a major reappraisal of the energy supply situation in the U.S. and abroad. A desire to avoid as nearly as possible reliance on external energy suppliers has become a major driver toward energy independence among the major energy users, and to a large extent this has lead them to move toward establishment of indigenous nuclear energy in the form of large nuclear power plants.

In the year 2001 an international forum was convened to discuss the next generation of nuclear power reactors with the goal of making available safer, more reliable, more versatile and more proliferation resistant reactors to help address the large and growing energy supply problems. In addition, this forum, the Generation IV International Forum, discussed the potential eventual need for spent nuclear reactor fuel recycle when the cost of uranium reached levels making recycle economically viable or the cost of recycle itself was low enough to make recycle viable.

---

[1] By convention reprocessing plant capacity is stated in terms of the amount of uranium present in the spent fuel before irradiation, which is referred to as "heavy metal."

The Forum settled on development of five reactor types that it felt could best meet the spectrum of reactor properties likely to be needed for the future supply of commercial nuclear energy. These needs include reliability, low cost, safety, high-temperature heat (for industrial applications), actinide burning[2], and ease of reprocessing. Table 2 lists the reactors selected by the Forum and some characteristics related to their selection.

Table 2. Generation IV Reactors Selected by the International Forum

Reactor Type	Characteristics
PWR PWR	Universal acceptance and ease of evolutionary development
FBR	Breeds Pu from ^{238}U; efficient actinide burner
HTGR	Produces high temperatures useful industrially and for thermochemical hydrogen production; graphite-based fuel
MSR	Circulating molten salt fuel; very proliferation resistant; on-line reprocessing

Fuel Cycle Studies and Initiatives

Concurrent with the cessation of all commercial spent nuclear fuel reprocessing activity in the U.S. in the ‘70s, a study called International Nuclear Fuel Cycle Evaluation, INFCE, was started. This was a multi-nation study that produced a series of documents on all aspects of nuclear fuel cycles, including both the uranium and the thorium fuel cycles[3]. The five elements of the study were:
An assessment of the nuclear fuel cycles
Improving availability to developing nations of plutonium for use in nuclear reactor fuel
Providing secure spent nuclear fuel storage
Improved nuclear safeguards
Alternatives to a plutonium and highly enriched uranium economy
A major conclusion of INFCE was that plutonium in excess of current national needs should be safeguarded by the International Atomic Energy Agency (IAEA).

Although INFCE did nothing to change the situation with respect to fuel reprocessing in the U.S. it did make a thorough study of the above elements of the study and produced valuable documents for future reference. The results of the study are as relevant today as they were when they were written. In fact, two current new initiatives to establish international fuel recycle centers contain much of what was studied and reported in INFCE, although there s little if any attribution to the earlier study.

There are two new initiatives to establish international fuel recycle centers, one being promoted primarily by the U.S. and the other by Russia. However, these initiatives are not entirely separate, and they have essentially the same goals and substantial collaboration exists.

---

[2] The term “actinide burning” refers to the destruction of actinide elements by fissioning them in reactors. This destroys the long-lived actinides and produces the more manageable fission products. Actinide destruction is beneficial both because of the additional energy produced by fission and because their destruction helps reduce the heat load in a geologic repository from actinide alpha decay. Reducing the heat load permits emplacement of more waste in a given volume of repository.

[3] The uranium fuel cycle uses uranium as its essential element and produces additional fuel as plutonium by irradiation of uranium in reactors. The thorium fuel cycle uses thorium as its essential element and produces additional fuel as ^{233}U by irradiation of thorium in reactors.

The U.S. initiative is called Global Nuclear Energy Partnership (GNEP). The Russian initiative is called Global Nuclear Infrastructure (GNI). The central idea of both is establishment of fuel recycle centers within the major nuclear weapons countries that already have fuel recycle activities. These centers would for a fee provide fuel recycle to countries possessing nuclear power reactors, but having no indigenous recycle capability. Recycle activities would include fuel fabrication, spent fuel reprocessing and uranium enrichment. The issue of waste disposal has not yet been addressed in any detail. Russia has already designated a uranium enrichment plant at Angarst in Siberia. This plant is already under IAEA supervision.

The stated goals of GNEP are as follows:

- Expand domestic use of nuclear power
- Demonstrate proliferation-resistant fuel cycles
- Minimize nuclear waste
- Develop and demonstration fast burner reactors[4]
- Establish international lease and return fuel cycle services
- Demonstrate small-scale, modular power reactors
- Design nuclear safeguards into nuclear fuel recycle facilities and reactors

An important part of GNEP is the Advanced Fuel Cycle Initiative (AFCI) whose goal is to develop reprocessing and waste management approaches that will help meet the GNEP broader goals listed above. AFCI is primarily a U.S. domestic program. At the outset of GNEP construction and operation of a large U.S. reprocessing plant (at least 800 MTHM per year) was envisioned, but as a consequence of a National Academies report and Congressional actions the reprocessing plant was put on hold.

The stated goals of the Russian BNI are as follows:

- Establish full-service international fuel cycle centers
- Have nuclear centers only in nuclear weapons states
- Plan a shareholding structure for countries involved in centers
- Coordinate with the U.S. GNEP initiative

As can be seen, the Russian initiative is more sharply focused on the international fuel cycle center concept than the U.S. initiative is. The major difference is that the U.S. initiative has a strong focus on re-establishing the nuclear energy fuel cycle within the U.S. in addition to establishing international. Russia does not need this focus because it never abandoned the fuel cycle.

Reprocessing

Types of Commercial Power Reactor Fuel

The reason for commercial reprocessing is to recover valuable materials from spent nuclear reactor fuel and separate them from the wastes that are produced by reprocessing. The valuable materials are uranium, plutonium, and in some cases, other actinide elements such as neptunium, which is the feed material for ^{238}Pu production.[5] Although not practiced to a significant extent there is some reason to believe that other material of value may also be

---

[4] Fast burner reactors are liquid-metal-cooled reactors with fast neutron energy spectrums that are designed specifically to burn (fission) actinide elements such as Np, Pu, Am and Cm to produce the more manageable fission product waste.

[5] ^{238}Pu is used as a heat source for thermoelectric power generation in space applications.

recovered during reprocessing. Such material includes the Zircaloy cladding which potentially could be recovered for use in fabricating new fuel. Also, radioisotopes such as cesium-137 could be recovered for use in gamma irradiators.

Reprocessing wastes include the fission products and, for the time being, spent fuel cladding. The cladding is Zircaloy in the case of LWRs and stainless steel in the case of fast reactors, whether burners or breeders. In the future as fuel burnup goes to higher levers it is very likely that new, more refractory alloys will be needed for fast reactor fuel cladding. In the case of more advanced reactors such as the high-temperature-gas-cooled reactors graphite replaces metal as the fuel material containment material.

The principle reactors and their reactor fuel types are listed in Table 3.

Table 3. Principle Commercial Power Reactors and Reactor Fuel Types

Reactor Type	Fuel Type	Operating Properties
LWR		
PWR	UO_2/Zircaloy clad	Water cooled and moderated
BWR	UO_2/Zircaloy clad	Water cooled and moderated
FBR		
LMFBR	UO_2/PuO_2/SS clad	Liquid metal cooled
GCR	UO_2/PuO_2/SS clad	Gas cooled
HTGR		
Pebble bed	UO_2/graphite balls	Gas cooled/graphite moderated
Prismatic	UO_2 graphite prisms	Gas cooled/graphite moderated

The type of head-end treatment used to prepare the several fuel types differ significantly (see, *Head-end operations hot cell and equipment* below) but after the head-end treatment the rest of the reprocessing operations are very similar. The major differences are whether or not PuO_2 is present initially in the fuel and the degree of fuel burnup. In the case of FBR fuel the PuO_2 fraction may be as high as 20%, and this higher Pu content must be taken into consideration. The degree of burnup is typically in the 35 to 55 MWD/te for LWR fuels, and may exceed 100 MWD/te for FBR fuels. HTGR fuels also tend to have higher burnups than LWR fuel. The higher burnups produce larger amounts of fission products whose higher radiation intensity is more damaging to the organic extractants.

Features of Reprocessing

The two major classifications of nuclear fuel reprocessing are 1) aqueous and 2) non-aqueous. Aqueous reprocessing can be by either of two approaches, viz., solvent extraction or precipitation. As noted earlier the first large-scale nuclear fuel reprocessing was by precipitation to recover plutonium from irradiated fuel rods. Subsequently solvent extraction replaced precipitation as the reprocessing method of choice.[6]

Non-aqueous reprocessing typically employs molten salts, molten metals, or volatilization. Separation of the desired substances is usually effected either by selective chemical, electrochemical, or volatility methods. Although non-aqueous methods have found some

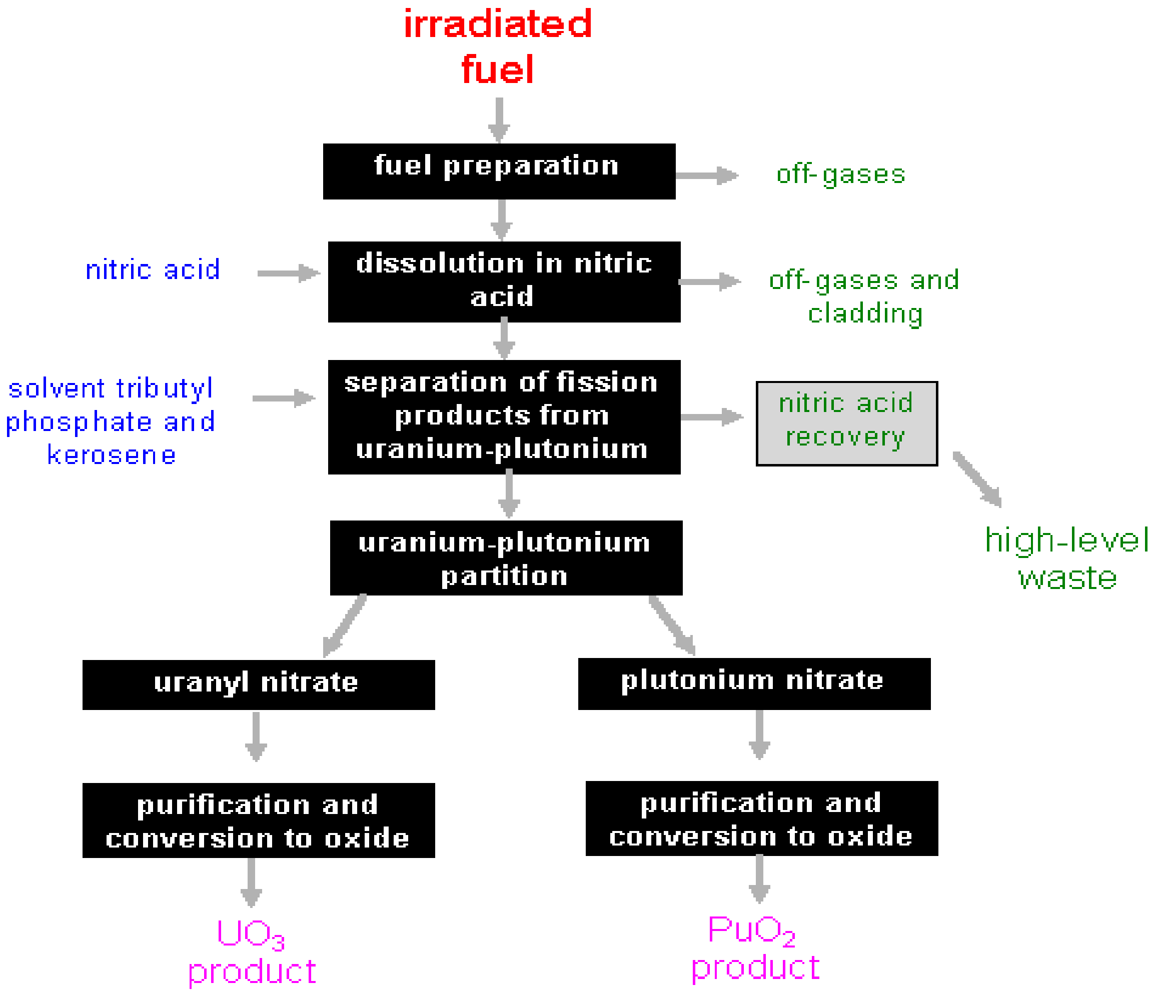
---

[6] Solvent extraction is a method whereby one or more substances in one liquid phase move selectively into a second, immiscible liquid phase during contact between the two phases.

applications, at present by far the largest amount of spent nuclear fuel reprocessing is by an aqueous method, i.e., solvent extraction.

The Purex process is the reprocessing method most used. It is an aqueous solvent extraction process that employs an acidic aqueous phase and an immiscible organic phase made of tri-n-butyl phosphate (TBP) mixed with an organic diluent such as dodecane or kerosene. The concentration of TBP is about 30% by volume. Figure 1. is a very simplified representation of the Purex process. It does, however, show all of the basic operations of the process.

Figure 1. Greatly Simplified Purex Process Flowsheet



There are nine major process areas and their related process steps associated with reprocessing plants based on the Purex process. These are discussed below:

Spent fuel receiving and interim storage areas
Spent fuel is received from reactors in shipping casks. Typically the shipping casks are unloaded under water where the spent fuel is inventoried and stored until it is time to reprocess it. Water is a convenient storage medium because it is easily cleaned up if it becomes contaminated and it inexpensive and versatile.

Head-end operations hot cell and equipment

Head-end operations are carried out in a heavily shielded hot cell[7] to protect the plant operators from the intense radiation from the spent fuel. The primary purpose of the head-end operations is to dissolve the fuel material. To accomplish this, the fuel element may be disassembled and/or segmented and chopped into small pieces that will fit in a dissolver vessel. The purpose of chopping the spent fuel into small pieces, typically one to two inches long, is to expose the actual fuel material, which is nearly always an oxide composed primarily of UO_2. The oxide is charged into the dissolver and dissolved in nitric acid. Any of several configurations and types of dissolvers may be used. The current movement is toward continuous dissolving. The first major waste stream is produced in the form of pieces of cladding hulls in this operation.

Solvent extraction hot cell and equipment

After dissolution in nitric acid the resultant solution is assayed to determine its composition, especially the amounts of uranium and plutonium. The acidic solution of uranium, plutonium, other actinide elements and fission products is then transferred to a hot cell where it is treated by solvent extraction of the desired actinides into the TBP solvent to separate them as products from fission product wastes and other actinides if desired. Additional process steps are carried out to further purify and solidify the products.

Solvent extraction equipment may be pulse columns, centrifugal contactors or mixer-settlers, depending on the level of radiation (centrifugal contactors minimize radiation exposure), presence of solids (pulse columns handle solids well and have few mechanical parts subject to failure) and nature of the separation needed (mixer-settlers are sometimes used for solvent cleanup and recycle).

Solvent cleanup/recycle equipment

Solvent cleanup is an important operation and is necessary for efficient separation of products (actinides) from wastes (fission products). Some TBP/kerosene destruction occurs due to radiolysis and chemical attack during the extraction step and liquid waste streams are produced when the degradation products are washed out of the extractant. These aqueous streams are customarily concentrated by evaporation to reduce their volume. Solvent cleanup equipment can consist of liquid-liquid contactors to bring solvent and wash solution, often sodium carbonate, into contact or of columns of solid sorbent such as silica gel that selectively remove fission contaminants such as zirconium and ruthenium.

Off-gas treatment equipment

Large amounts of water vapor and nitrogen oxides come off the dissolver and are mixed with air that is circulated through the head-end operations hot cell. Volatile fission products such as iodine, oxides of ruthenium and of technetium, krypton-85, carbon-4 dioxide and tritiated water are also present in the off-gas. In addition, a large volume of air that circulates though other process hot cells enters the off-gas stream. In the past off-gas treatment was limited to removal of iodine and recover of oxides of nitrogen to reconstitute nitric acid for further use. In the future it is probable that tritium will be removed and recovered from the spent fuel before it is dissolved and that krypton-85 will be recovered from the dissolver off-gas.

---

[7] A hot cell is a fairly large room surrounded by thick concrete shielding walls that are usually fitted with manually operated manipulators that can perform operations within the cell while the operators are safely outside the shielding.

Equipment used for off-gas treatment includes traps such as sodium hydroxide solutions for iodine recovery and column scrubbers to sorb the nitrogen oxides. Cryogenic processes equipment is being considered for krypton-85 recovery.

Uranium product storage area

Uranium from the TBP extraction process is converted to UO_2 and stored in a designated storage area for further disposition. Because the uranium is still slightly enriched some attention must be paid to criticality.

Plutonium product storage area

Plutonium from the TBP extraction process is converted to PuO_2 and stored in a designated storage area for further disposition. Because the plutonium is highly fissionable great attention must be paid to criticality. This is achieved through use of specially designed containers whose construction maintains safe spacing between them.

Waste treatment area

The Purex process produces a variety of waste types, as do all reprocessing methods. The exact nature of the wastes depends somewhat on the type of fuel reprocessed. However, for most LWRs the wastes are very similar, varying mostly in the amount and nature of the metal cladding and fuel element structural materials that become waste. Besides these metal wastes there are high-level liquid wastes that contain the fission products, solvent recycle wastes, ion exchange resin wastes (primarily from plutonium final purification and fuel element storage pool water cleanup), off-gas cleanup wastes and a variety of wastes produced in cleanup operations throughout the reprocessing plant. An area is designated for treating these wastes to put them into a form suitable storage pending their final disposition. Treatment consists of evaporation of high-level wastes and solvent recycle wastes to reduce their volume before transfer to storage tanks, and solidification of most other wastes in concrete.

Waste storage and shipping areas

An area is designated for storing all but the liquid wastes prior shipping them to an off-site disposal area such as the Envirocare waste site in Utah.

Commercial Reprocessing Plant Requirements and Considerations

There are important legal requirements as well as important considerations that must be factored into any plans to build and operate a spent commercial nuclear reactor fuel reprocessing plant. Some of the most important of these are listed in Table 4 below.

Table 4. Commercial Reprocessing Plant Requirements and Considerations

Legal Requirements
An environmental impact statement
An NRC license for construction and operation
Meeting EPA radioactivity release limits at the plant site boundary
Decontamination and decommissioning friendly
Considerations
Factors impacting plant siting
Plant design considerations
Anti-terrorism features
Nuclear non-proliferation attributes
Economical
Minimal waste production
Storage and shipment of high-level wastes, low-level wastes, alpha wastes and mixed wastes

The legal requirements must be promulgated in federal regulations that have yet to be modified or written for reprocessing plants. Both the Nuclear Regulatory Commission (NRC) and the Environmental Protection Agency (EPA) will be involved in this exercise.[8]

Some of the more important physical and geographic plant siting considerations and issues are listed in Table 5 below.

Table 5. Plant Siting Considerations and Issues

Proximity to nuclear reactors: relates to transportation of spent fuel and wastes
Geology/nature of rock/soil: relates to ease of transport of radionuclides
Hydrology: the principle pathway for radionuclide transport
Seismology – fault lines; history of earthquakes: impacts siting and construction
Climatology – rainfall: relates to atmospheric inversions; transport of radionuclides
Topography – natural and man-made features of the land: relates to drainage of water and containment
Demographics – population distribution and density: relates to extent of impact of radioactivity release
Agriculture – magnitude of farming and nature of crops: relates to ingestion of contaminated food
Proximity to industry: relates to cost of an accident; interruption of supply of vital materials

---

[8] NUREG-1909 is an NRC document written in part specifically to address problems associated with licensing reprocessing plants.

Wastes

Typical Reprocessing Plant Waste Streams

Reprocessing plants produce wastes in liquid, solid and gaseous forms. Each type of waste must be dealt with an environmentally acceptable, economical and safe manner and in accordance with regulations. This is a challenging task because there are many difficulties with managing each type of waste. The reprocessing waste types are listed in Table 6.

Table 6. Typical Reprocessing Plant Waste Streams and possible Treatments

Waste Type	**Source**	**Possible Treatment**
Liquids		
HLW	First extraction cycle raffinate	Vitrify
LAW	Solvent scrub solution	Evaporate to concentrate
Gases		
Krypton-85	Dissolver off-gas	Remove cryogenically
Iodine-129	Dissolver off-gas	Capture on zeolite or in caustic solution
Carbon-14	Dissolver off-gas	Capture as the carbonate
Hydrogen-3 (T)	From voloxidation or as HTO	Capture as a hydrate or in concrete
Solids		
HLW	Contaminated cladding hulls	Compact as metal
LAW	Miscellaneous process wastes	Fix in concrete

Managing Plant Wastes

Management of plant wastes depends on the type and properties of the waste. It is anticipated that the wastes will ultimately be disposed of in a geologic repository, in a near-surface disposal site or stored until radioactive decay has reduced the radioactivity to innocuous levels.

In the past at the government reprocessing sites and under the pressures of WWII and then of the Cold War with the USSR many wastes, both radioactive and toxic, were managed poorly. High-level acidic radioactive liquid wastes were put into large (million gallon) tanks where sodium hydroxide was added to neutralize the waste to prevent corrosion of the tanks by the acid. Most of the fission products and residual actinides formed insoluble solids that precipitated to the bottom of the tanks. In addition neutralization of the nitric acid produced sodium nitrate the formed salt crystals. The result of this type of treatment of high-level wastes was that a very large amount of solids was formed in many of the tanks. The internal structure of the tanks is such that there are many obstacles to removing the solids. A variety of expensive and complex approaches, both physical and chemical, are being resorted to remove the solids so that they can be vitrified in preparation for final disposal.

Many of the lower activity wastes and toxic wastes were simply put into “cribs”, ponds and pits. In most cases these were large excavations in the ground, most of which were unlined with any sort of membrane to contain the wastes other than clay linings in some cases. Hanford for example has 21 cribs and 19 ponds. Types of waste ranging from alpha contaminated wastes to carbon tetrachloride were handled in this way, in some case many tonnes.

Table 7 lists current representative management approaches and waste treatment and disposition methods according to waste types and properties.

Table 7. Current Representative Waste Management Approaches

Waste Type	Property	Treatment	Disposition
Liquid HLW	Highly radioactive	Vitrify as borosilicate glass	Interim storage and final geologic disposal
LAW	Low level of radioactivity; some may not fit NRC waste categories (GTCC)	Stabilize in concrete	Send to Envirocare or a DOE site
Alpha	Alpha activity >100 nCi/gram	Convert to solid	Send to WIPP
Various, mostly FPs	Decays to innocuous level quickly	Convert to a safe form	Store until decayed to an innocuous

Waste Transportation

Transportation of wastes from the reprocessing plant site to disposal sites is an issue that, although not specifically a reprocessing plant waste issue, is nonetheless a very important issue closely related to reprocessing and to wastes. A reprocessing plant cannot operate indefinitely without disposing of its wastes. In the past and up to the present time liquid high-level wastes have been stored on site in large metal tanks. This is true of the liquid wastes at the government reprocessing plants at Hanford, Savannah River and Idaho Falls and it was true of the partially commercially operated reprocessing plant at West Valley. Progress is being made with the current stored tank wastes. They are being vitrified to put them into a concentrated solid glass and await establishment of permanent disposal sites for their final disposal. Low-level wastes and alpha wastes are already being sent to existing disposal sites. In all case, transportation is required to get the wastes to the disposal sites.

Transportation issues center about licensable shipping casks and containers, methods of transportation such as trains, trucks and barges, and transportation routes over which the wastes must travel. The NRC, federal and local departments of transportation, and citizens groups all have a stake in and bear responsibility to see that waste transportation is carried out safely, legally, and with due regard for the rights, economical well being, and desires of the citizens directly impacted by the waste transported.

Major Conclusions

- Spent nuclear fuel reprocessing is an established industry world-wide
- DOE has launched a major initiative to institute international centralized fuel cycle services and to re-establish indigenous reprocessing
- Waste management and disposal remains as an important issue
- There are significant licensing issues both for commercial spent nuclear fuel recycle and for waste disposal

References

1. “Background, Status, and Issues Related to the Regulation of Advanced Spent Nuclear Fuel Recycle Facilities,” NUREG-1909, A.G. Croff, R.G. Wymer, L.L. Tavlarides, J.H. Flack, H.G. Larson June 2008.
2. “Actinide Separation Chemistry in Nuclear Waste Streams and Materials,” R.G. Wymer, Principle Author, EA/NSC/DOC(97)19. December 1997.
3. “Chemical Aspects of the Nuclear Fuel Cycle: A Special Issue,” Radiochimica Acta, vol.25, No.3/4, 1978.
4. “Compatibilities of Technologies with Regulations in the Waste Management of H-3, I-129, C-14, and Kr-85, Part II, Analysis,” ANL-83-57, Part II, November 1983.
5. “Environmental Radiation Requirements for Normal Operations in the Uranium Fuel Cycle,” Title 40, Part 190 of the Code of Federal Regulations, 1977.
6. “Light Water Reactor Nuclear Fuel Cycle,” R.G. Wymer and B.L. Vondra, Eds., CRC Press, 1981.

Management of Nuclear Waste

Mark A. Gilbertson
Deputy Assistant Secretary for Engineering and Technology
Office of Environmental Management
U.S. Department of Energy

Steven L. Krahn, DPA
Director
Office of Waste Processing
U.S. Department of Energy

Steven L. Ross, PhD
Office of Waste Processing
U.S. Department of Energy

Introduction

The Office of Environmental Management (EM) provides environmental remediation clean-up progress today, along with potential energy solutions for the future. Although much clean-up progress has been made, EM is still facing management challenges and site remediation efforts that will require the ability to continue to make technological leaps forward. Solving these challenges is inherently dependent upon understanding the underlying chemistry and how to separate and (im) mobilize radionuclides. With completion dates extending past 2050, EM will continue to need a cadre of managers, engineers, and scientists, who will be able to make informed decisions based on the best engineering and scientific understanding of the clean-up issues.

EM was established in November 1989 as the first step toward correcting contamination problems resulting from over 50 years of nuclear energy research, uranium enrichment, isotope production, weapons production, and fuel processing activities. Creation of this office consolidated several U.S. Department of Energy (DOE) organizations previously responsible for the handling, treatment, and disposition of radioactive and hazardous waste. At the time of its creation, waste management and clean-up activities were occurring at more than 137 contaminated installations in 34 states and territories. At these installations, there were 3,700 specific sites with more than 10,500 hectares with hazardous or contaminated surface or groundwater, soil, or structures, and the number was growing as new sites were defined. In addition, 500 surplus facilities awaited decontamination and decommissioning and approximately 5,000 peripheral properties (residences, businesses) had soil contaminated with uranium tailings (Ref. 10).

EM's mission is to complete the safe cleanup of the environmental legacy brought about from government-sponsored nuclear energy research and nuclear weapons development. This environmental clean-up effort is complex and demanding. Therefore, the first item discussed in this paper is the scale and scope of this effort. Next, the management practices and clean-up methods used to achieve its mission are described. These procedures have achieved several successes and these successes are recounted next. Following that, several current activities are described. Then several of the significant challenges are related. The paper concludes with a description of the management improvements implemented over the last three years. Throughout this paper, DOE will be identified as the Unites States agency responsible for the activities described. However, it is EM that effects the actions.

DOE recognizes the enormity of this clean-up task. EM has been engaged in this clean-up activity since its inception, nearly two decades ago. DOE believes the time required to complete these clean-up activities continues to be measured in decades, possibly four or five. Approximately $ 70 billion (US) has been spent cleaning up this legacy of the cold war and it may be that the final cost is three to four times the amount already invested. The magnitude of this effort is great; however, the mission of "closing the cycle" on nuclear materials is a vital one.

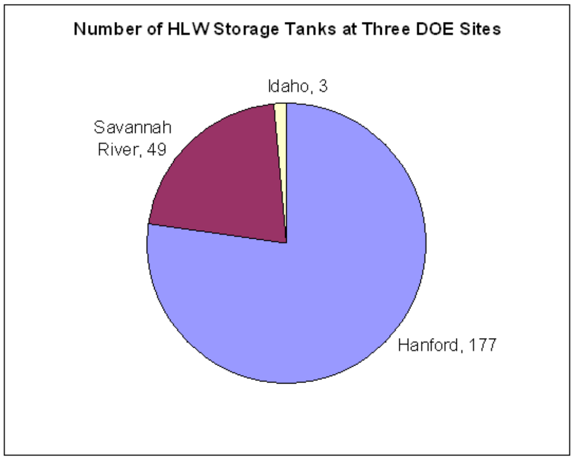
Description of Clean-Up Effort

The processes that resulted in wastes included the separation and enrichment of uranium, forming this enriched uranium into a fuel element, irradiation in a reactor, separation of the resulting plutonium, and forming the plutonium for use in a weapon. Along this route, each step resulted in both the desired product and in a quantity of waste. In some cases, the quantity of waste generated was very large. Furthermore, since the overall route from uranium ore to finished nuclear weapons was complex, the waste falls into a number of diverse categories.

Each of these waste categories has a specific definition and legislative history in the United States. This paper focuses on six of those categories.

High-Level Waste

The first waste type is High-Level Waste (HLW). HLW is defined, in part, as "the highly radioactive material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste …" (Ref. 1). Note that this definition is functional and is based on how the waste is produced rather than on the radionuclide content of the waste. HLW is a major waste stream at three DOE sites: Hanford, Savannah River, and Idaho. At each site, this liquid waste is stored in underground tanks. Table 1 shows the current status of HLW storage:



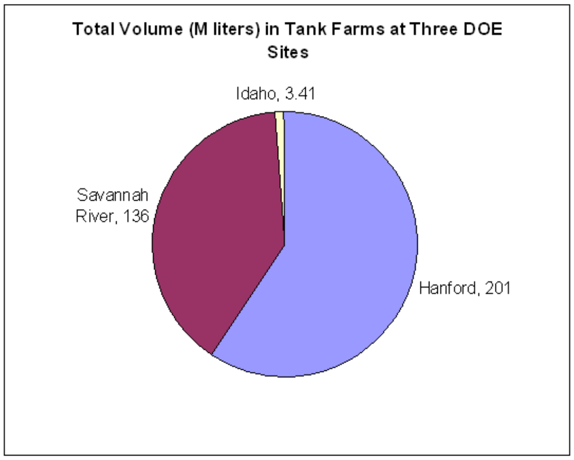


Table 1. HLW Storage at DOE Sites (Ref.2)

Site	Number of Tanks	Total Volume in Tank Farm (M liters) ***	Total Capacity in Tank Farm (M liters)
Hanford	177	201	473
Savannah River	49	136	222
Idaho	3*	3.41	12.5 **

* A fourth tank is empty and available for use if needed;

** Of this total installed capacity, only 4.6 M liters in four tanks are usable. All remaining tanks have been filled with an engineered grout (Ref. 39).

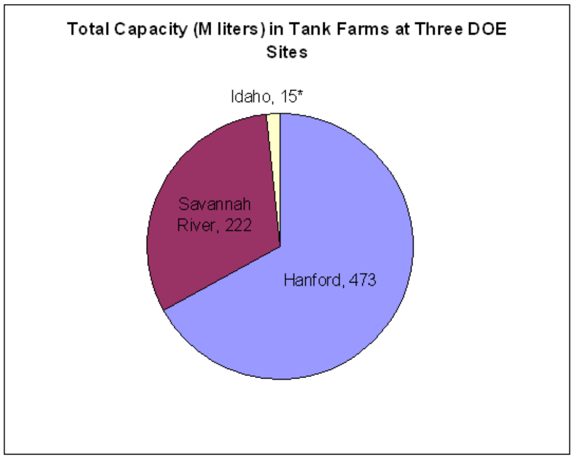
*** M liters = 1,000,000 liters

The first tanks were built at Hanford starting in 1943 (Ref. 2). These tanks were of single shell construction and had a design life of 20 years. That design life is now exceeded. As a result of this longer than anticipated use, some tanks have leaked liquid HLW to the surrounding environment. Prompted by leaks in some of the single shell tanks, DOE pumped the free and drainable liquids from those tanks into double shell tanks and implemented a remedial investigation program to determine the nature and extent of past leaks. Double shell tank construction started in 1968 and these tanks have a design life of 20-50 years. Underground tanks for high-level waste were also built at the Savannah River site in the State of South Carolina, and at the Idaho National Laboratory in the State of Idaho. The tank farm at Savannah River site is nearly as old as that at Hanford; the first tanks at Savannah River site were built in the early 1950's and a total of 51 tanks were constructed. These tanks ranged in size from 2.84 M liters to 4.92 M liters. Of this total, two have been closed, the first in 1997, leaving 49 in operation. There have been smaller leaks from twelve of these tanks, typically on the order of tens of liters. Because of leaks at these two sites, coupled with agreements with the States of Washington, Idaho, and South Carolina, DOE is addressing the issue of tank closure and how it can be done safely and efficiently. The tanks at the Idaho National Laboratory were fabricated with stainless steel, thus they have a lower risk of leaking.

DOE processes these high-level wastes at Savannah River at the Defense Waste Processing Facility (or DWPF) which is a vitrification plant operated to treat high-level liquid radioactive waste. The plant receives liquid waste feed material from the underground tanks via underground transfer lines. The feed material is pretreated, blended with a glass-forming frit and fed into a Joule-heated Melter where it is heated into a molten glass and poured into stainless steel canisters. The material solidifies inside the canister into a glass form that encapsulates the waste. In addition, DOE currently has under construction the Waste Treatment Plant (WTP) at Hanford. The WTP will be the world's largest radioactive waste treatment plant and will be used to treat Hanford's underground tank waste. The WTP also uses a vitrification process.

DOE has another tank waste management process in construction at Savannah River that works in parallel with the DWPF, the Salt Waste Processing Facility (SWPF). When construction is complete, the SWPF will process high-curie salt waste currently stored in underground tanks into waste streams that are suitable for immobilization at downstream facilities. The high-level waste component--actinides, strontium, and cesium--will be separated and sent to the DWPF for vitrification and eventual transfer to an offsite national repository. The decontaminated salt solution, the low activity but high volume component, will be solidified in a cementitious grout mixture. The grout, while in liquid form, is transferred to storage vaults for permanent disposal in the Saltstone Facility. Recently, DOE has commissioned operations of an interim salt removal process, using a similar technology to the SWPF but on a smaller scale, to be used until the SWPF comes on line in 2013.

The Idaho National Laboratory and the Savannah River site have each begun their tank grouting projects to permanently close tanks that have been satisfactorily emptied of their contents. At Savannah River, a development project investigating the best ways to fill an underground tank with grout was initiated after considering several other possibilities. This process initially cleans the tanks to the extent economically and technically feasible, adds a grout to stabilize the residual contents, and then fills the void space with grout to provide long-term, internal physical support. Savannah River selected four tanks for this preliminary project. Idaho National Laboratory, which has the smallest tank farm, is farthest ahead in the area of tank closure. A total of eleven tanks have been emptied, cleaned, and filled with grout to prevent future collapse (Ref. 29). The largest of these tanks has a capacity of 1,140,000 liters. In comparison, the largest of the Hanford tanks is about 3,790,000 liters and presents additional challenges due to its larger capacity.



At Hanford, whose 177 tanks make it by far the largest of the tank farms, grouting of the entire tank farm (473 M liters, Table 1) would be a much more expensive solution (Ref. 17). Hanford is planning a tank closure demonstration on one of the smaller tanks after completion of waste retrieval from that tank. The purpose of the demonstration is to verify tank stabilization (by core sampling of the grout layer). This work will also include characterizing contaminated soil outside the tank and stabilizing it by impermeable barrier installation; characterizing and stabilizing one diversion box and direct buried pipelines by in-situ grouting; and characterizing and isolating in-trench pipelines.

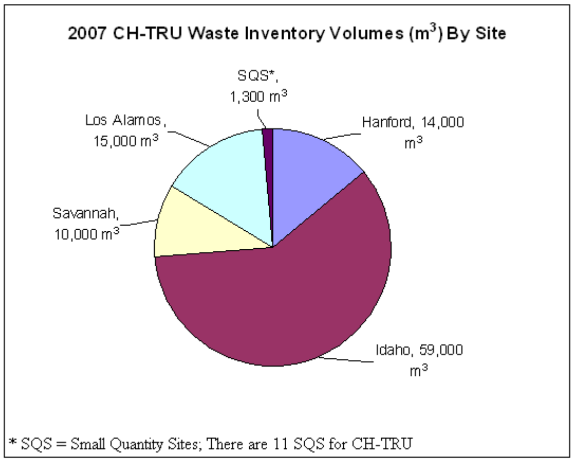
All of these projects are expected to provide DOE with invaluable knowledge and background on the path forward for tank closure.

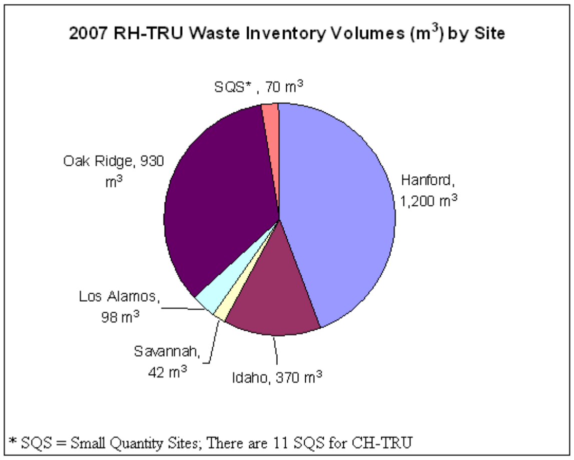
Transuranic Waste

The next waste type to consider is transuranic waste, known as TRU waste. A DOE manual (Ref. 4) defines transuranic (TRU) waste as waste that contains more than 100 nanocuries per gram of alpha-emitting isotopes with atomic numbers greater than uranium (92) and with half-lives greater than 20 years.

The management of TRU waste has a long history. In 1957, the National Academy of Sciences concluded that the most promising method of disposal of radioactive waste was in salt deposits (Ref. 18). Congress passed the Waste Isolation Pilot Plant (WIPP) Land Withdrawal Act in 1992 which placed WIPP under U.S. Environmental Protection Agency (EPA) regulation. Subsequently, the U.S. EPA established radioactive waste disposal regulations specifically addressing transuranic waste and WIPP. In 1996, President Clinton signed legislation amending the WIPP Land Withdrawal Act (Ref. 3). The first shipment of TRU waste was received at WIPP on March 26, 1999 – making WIPP the first geologic repository to go into operation, worldwide.

Most TRU waste in the DOE inventory is contaminated with plutonium-239, which has a longer half-life (24,000 years) than most fission products present in spent nuclear fuel. Due to the low level of contamination allowed, the sources of TRU waste are numerous: shoe covers, packaging, or used storage containers, workers gloves, etc. TRU waste at these levels of contamination can be contact handled. As the level of contamination increases, the dose to the worker increases and more elaborate and complex methods of handling TRU contaminated materials are required to protect worker safety and health. As procedures become more complicated, more TRU waste is created. These charts show the amounts of contact-handled TRU waste around the DOE complex.





If the combined beta, gamma, and neutron dose rate anywhere on the surface of a TRU waste container exceeds 200 millirems (0.002 sieverts) per hour (the "contact-handled," CH-TRU, limit), remote handling methods are required. The methods involve shielding to protect the worker and/or automation of certain steps to reduce the potential for radiation exposure. The chart above shows the amounts of remote-handled TRU (RH-TRU) waste around the DOE complex.

As these two charts illustrate, TRU waste presently is located at 15 sites in the DOE complex and the total amount is 100,000 m^3. Placing all this waste on a typical soccer field, the field would be covered to a depth of about 20 meters. This total compares to the greater than 55,500 m^3 already disposed at WIPP near Carlsbad, New Mexico (Ref. 25).

Low-Level Waste

Continuing with the description of wastes types, the next category is low-level waste (LLW). The definition of low-level waste is exclusionary in nature: low-level waste is radioactive waste that is neither high-level radioactive waste, nor spent nuclear fuel, nor transuranic waste, nor byproduct material (Ref. 4). The situation with commercial LLW is similar, with the exception that commercially-generated LLW must be disposed of in a U.S. Nuclear Regulatory Commission-licensed facility (Ref. 5). Note: this regulation goes a step further and subdivides commercially-generated low-level waste into classes).

Commercially-generated waste containing radionuclide concentrations exceeding those given in Table 1 of paragraph 61.55 in Part 61 (Ref. 5) of the Code of Federal Regulations (CFR), usually are referred to as “Greater Than Class C” wastes or GTCC. While the U.S. Nuclear Regulatory Commission regulates the disposal of GTCC, it is DOE that must execute its disposition. The fact that GTCC is not classified as a high-level waste but must be disposed in the same manner as high-level waste (deep geologic burial) presents an enigma. DOE currently is developing an Environmental Impact Statement on GTCC disposal alternatives. Deep geological burial is one option considered. Another is an enhanced near surface facility and another is a deep borehole facility. As the legislation and regulations stand currently, the geologic repository proposed for Yucca Mountain cannot accept GTCC wastes and, unless the GTCC waste is contaminated with transuranic isotopes, it cannot be accepted by WIPP.

LLW may be characterized as “low dose but high volume.” LLW consists of slightly contaminated cleaning materials, tools, and other miscellaneous items associated with operations in and around nuclear facilities. In some ways, it is like TRU waste, except the concentration of transuranic isotopes is not allowed to exceed 100 nanocuries per gram. Furthermore, there are limits set on the content of several specific isotopes to protect the health and safety of workers and the public (Ref. 6).

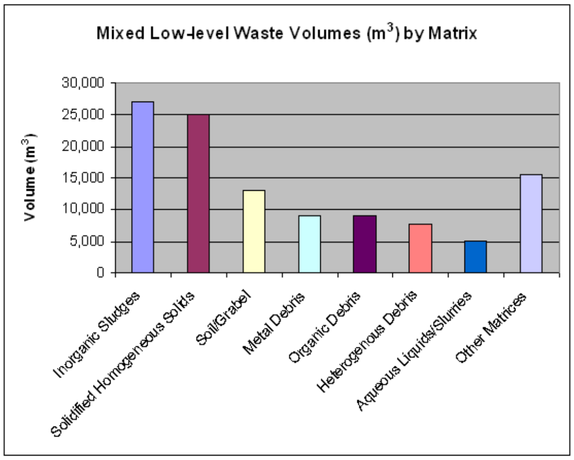
Mixed Low-Level Waste

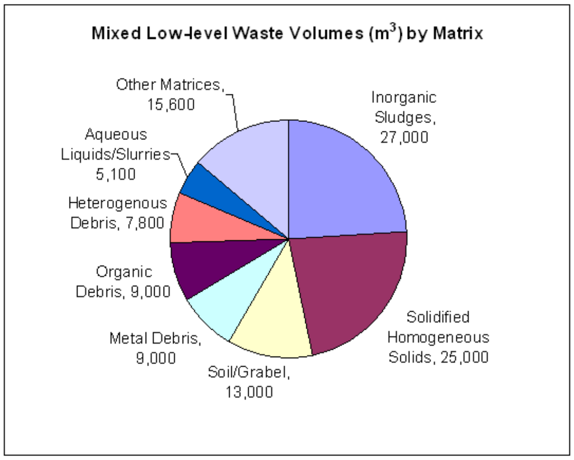
Mixed low-level waste is another category similar to LLW. It is also a low dose, high volume waste type. Mixed low-level waste contains materials that are chemically hazardous and have a low level of radioactive contamination (Ref. 7). Chemically hazardous materials are regulated under the *Resource Conservation and Recovery Act (RCRA) of 1976* (Ref. 8). A chemical is hazardous if it exhibits any of the following characteristics: ignitability, corrosiveness, chemically reactive, toxicity, or meets other specific criteria in the rule.

DOE tracks the composition of mixed low-level waste by assigning each waste stream to one or more of more than 100 treatability groups. The groups take into account the physical matrix of the waste form, the presence of hazardous constituents and characteristics, and the radiological characteristics of the waste. The major categories of treatability groups, which identify the physical waste matrix and the volumes of each, are presented in the following table:

Table 2. Mixed Low-level Waste by Matrix

Physical Matrix	**Volume (m^3)**
Inorganic Sludges	27,000
Solidified Homogeneous Solids	25,000
Soil/Gravel	13,000
Metal Debris	9,000
Organic Debris	9,000
Heterogeneous Debris	7,800
Aqueous Liquids/Slurries	5,100
Other Matrices	15,600
Total	111,500





Hazardous constituents present in mixed low-level waste include toxic heavy metals, organic and halogenated organic chemicals, cyanides, inorganic chemicals and elements, explosive compounds, and corrosive chemicals and solutions.

Plutonium Disposition

The Department stores plutonium that the United States no longer needs for nuclear weapons. This plutonium is currently located at Hanford, Lawrence Livermore National Laboratory, Los Alamos National Laboratory, Savannah River, and Pantex. The majority is in the form of pits (the spherical core of a nuclear weapon), while the remainder is in non-pit forms such as contaminated metal, and oxides remaining from the nuclear weapons production process. DOE plans to dispose of the surplus plutonium that is in pit, clean metal and oxide forms, by fabricating it into mixed uranium and plutonium oxide fuel (MOX) fuel that can be used in commercial nuclear power plants. This process will take place in a new MOX Fuel Fabrication Facility that is currently under construction at the Savannah River site. Some of DOE's non-pit plutonium, however, is not suitable to be converted to MOX fuel. This plutonium would be processed in the H-Canyon facilities at Savannah River, where the plutonium will be dissolved and vitrified in the Defense Waste Processing Facility.

Spent Nuclear Fuel

The last category of waste to be discussed is spent nuclear fuel. Up to this point in the paper, the Atomic Energy Act of 1954 (Ref. 29) has kept DOE activities essentially separate from commercial nuclear issues. For the category of spent nuclear fuel (and its companion high-level waste discussed earlier) that separation changed with the promulgation of the *Nuclear Waste Policy Act of 1982* (Ref. 1). This legislation defines spent nuclear fuel as fuel that has been withdrawn from a nuclear reactor following irradiation, the constituent elements of which have not been separated by reprocessing.

The act also requires that both spent nuclear fuel and high-level waste be disposed by deep geologic burial. That is fine in the commercial sector where the number of reactor designs is limited and the physical characteristics of spent fuel fall within a narrow range. However, a major function of DOE has been research into reactor design, into fuel design and fabrication, irradiated fuel examination and so forth. DOE manages an inventory of more than 250 fuel types which means that DOE also manages an inventory of more than 250 spent fuel types. This inventory ranges from intact commercial spent fuel (from the commercial reactors at Big Rock Point and R.E. Ginna generating stations) to rubble from the Three Mile Island accident, to research reactor fuels from universities, to spent fuel from foreign nuclear energy research programs, and to spent fuel from DOE's own research and production reactors. These different fuels come in a wide variety of shapes and sizes. DOE has developed a standard, no-breach canister to be used in the management of this great variety of spent fuels. DOE's spent fuels will be placed in these canisters, the canisters will be transported to the repository (when it becomes available), and the canisters will be disposed in a waste package underground for permanent isolation from the environment.

Management and Processing Methods

Role of Technology

Although the Department has made great progress toward safely disposing of its legacy nuclear waste (e.g., the completed cleanup of the Fernald, Rocky Flats, and Mound sites), much remains to be done. While past accomplishments often provide a guide for future success, the unique nature of many of the remaining challenges will require a strong and responsive applied research and engineering program. In the Fiscal Year 2007 House Energy and Water Development Appropriations Report, EM was directed to "prepare a DOE technology roadmap that identifies technology gaps that exist in the current program, and a strategy with funding proposals to address them." This report was sent to Congress in March 2008 and listed several initiatives aimed at reducing technical risk and uncertainty in the areas of waste processing, groundwater and soil remediation, and deactivation and decommissioning and facility engineering (Ref. 11). From this Roadmap came the Multi-year Program Plan, prepared by DOE Headquarters staff in collaboration with the National Laboratories (Ref. 15). This plan addresses priorities, budget, schedule, major products and deliverables, and performance metrics. As such, it provides the detailed plans for implementing the program area's initiatives.

The Engineering and Technology Program reduces the technical risk and uncertainty in the Department's clean-up programs and projects. Risks are known technical issues that could prevent project success. Uncertainties are indefinite or unpredictable technical aspects of a project. To reduce those risks and uncertainties, the program will provide technical solutions where none exist, improved solutions that enhance safety and operating efficiency, or technical alternatives that reduce programmatic risks (cost, schedule, or effectiveness).

Management Tools

In addition to the Roadmap, several corporate boards were established. Each board studies and analyzes issues and problems within a specific waste category. There are corporate boards for High-Level Waste, Transuranic Waste, and Low-Level Waste. These boards have several functions. First, they serve as a consensus building body to integrate DOE waste management and disposition activities across the DOE program. Second, they identify the need for and develop policies, planning, standards, and guidance to implement an effective and efficient national waste management program. Finally, these boards evaluate the implications of waste management issues and their potential impact across the DOE complex and recommend solutions to senior DOE management.

Implementing Best Available Technologies and Processes

We have developed and are developing waste management processes and methods that are "best-in-class" techniques. Examples of these techniques are found in the way DOE manages its high-level waste, its tank farms, and its waste storage.

The *Nuclear Waste Policy Act of* 1982 requires that the disposal path for high-level waste should be vitrification followed by burial in a deep geological repository (Ref. 1). Vitrification is widely recognized throughout the world. The *Resource Conservation and Recovery Act* (Ref. 8) lists vitrification as the only means of safely storing, transporting, and disposing of high-level radioactive waste. DOE has been vitrifying high-level waste successfully at the Savannah River site in the Defense Waste Processing Facility for more than a decade.

The high-level waste tank farms managed by DOE all will be closed permanently. DOE already has initiated steps to determine which closure methods provide the optimum combination of performance, efficiency, and economy. Several tanks at both Savannah River and Idaho have been filled with grout to immobilize any residual radioactivity and to provide structural stability long into the future. The staff at Savannah River site is doing extensive work in developing grout formulations for tank wastes and estimating how these grouts might perform. Historically, grout has been one of the most commonly used materials for solidifying and stabilizing radioactive waste.

One process DOE can be certain of using is deep geologic burial. DOE already has one such repository in operation near Carlsbad, New Mexico. It is the Waste Isolation Pilot Plant (WIPP). DOE began work on WIPP in 1979. By law (Ref. 12) WIPP presently is limited to accepting TRU waste and proscribed from accepting high-level waste or spent nuclear fuel. Since March, 1999, WIPP has set the standard for permanent disposal of long-lived radioactive defense wastes in the United States. WIPP also has an impressive safety record that includes receiving 6,734 shipments, which were collectively transported almost 7.9 million miles (13.6 million km). WIPP receives, on average, 21 shipments per week of contact-handled TRU waste and 5 shipments per week of remote-handled TRU waste. Shipments to WIPP are tracked by satellite along their entire route. Training for numerous Emergency Response Teams operated by communities along the routes was provided by DOE.

Successes

At this time, DOE has several notable successes.

High-Level Waste

In the area of high-level waste management, the efforts at West Valley, Savannah River, and at Hanford have made and are making considerable strides forward. The vitrification campaign is complete at West Valley and 275 canisters are stored on-site, ready for disposal. The high-level waste in these canisters represents 632.5 metric tons of heavy metal recovered from the reprocessing of commercial spent nuclear fuel before West Valley ceased reprocessing operations in 1976. At Savannah River, as of October 2007, nearly 2,400 canisters (Ref. 24) of vitrified high-level waste have been produced at the DWPF and transferred to interim on-site storage. At Hanford, the largest nuclear waste processing plant ever planned, the Waste Treatment and Immobilization Plant, is making substantial progress; at the end of June 2008, plant design was 78 percent complete, procurement was 43 percent complete and construction was 30 percent complete. When the Waste Treatment Plant is in full operation (scheduled in 2019), it will be producing more than 6 metric tons of glass per day (Ref. 22).

Low-Level and Mixed Low-Level Waste

Every DOE site generates LLW. The good news is that DOE has closed 86 of 108 sites nationwide (Ref. 7); this produces a substantial reduction in waste sources. DOE has a long history of LLW management (Ref. 8). During this time, DOE has disposed of 1,000,000 m^3 of low-level waste from around the complex and 3,860 metric tons of contaminated scrap metal from Portsmouth, Ohio. Within DOE, the low-level waste management plan is shallow land burial at one of two locations: Nevada Test Site or Hanford Reservation.

In the area of mixed low-level waste, the DOE *Radioactive Waste Management Manual* (Ref. 4) identifies disposal of mixed low-level wastes on the site where generated as the preferred alternative. If this is not possible, then disposal at another DOE facility is preferred. If conditions prevent this second option, then disposal at a commercial facility is allowed. DOE uses all three modes of mixed low-level waste disposal. DOE estimates that it will have disposed of 315,000 m^3 of mixed waste by the year 2010 (Ref. 14). This volume represents contaminated materials recovered from the environment.

Transuranic Waste

It cannot be overstated that the primary accomplishment in the area of transuranic waste, one that enables complex-wide progress to be made, was the opening of WIPP in March 1999. Since its opening, more than 55,500 m^3 of TRU has been delivered and emplaced at WIPP (Ref. 25) as of 2008. This total includes contact-handled and, since January of 2007, more complex, remote-handled TRU waste.

The cleanup of the Melton Valley area at the Oak Ridge site in Tennessee has made impressive progress, and there are several portions of the clean-up task that deserve mention. Remedial actions included construction and capping of collection and diversion trenches at shallow land burial sites and liquid waste seepage pits; excavation of transuranic waste trenches; removal of contaminated sediments from waste ponds; grouting and abandonment of hundreds of wells; excavation and disposal of contaminated soil and equipment; and in-situ treatment of two liquid waste seepage trenches. The High Flux Isotope Reactor waste tank was closed in place by removing the liquid contents and stabilizing the tank and residual sludge in place using grout. Two transuranic waste tanks were closed by removing approximately 114,000 liters of transuranic sludge from the tanks using pulse jet mixing equipment and transferring the sludge to the LLW system. The empty tank shells were stabilized in place by filling them with grout (Ref. 30).

Cleanup of Major Weapons Component Site

In 1951, Rocky Flats Plant was given the mission to manufacture nuclear weapons components from materials such as plutonium, beryllium, and uranium. When operations ceased, large amounts of plutonium, plutonium compounds, and metallic residues remained at the various site facilities. Significant volumes of hazardous and radioactive waste generated during production operations were also present throughout numerous buildings and soil was contaminated, resulting in the site being placed on the National Priorities List. The National Priorities List is the list of hazardous waste sites in the United States eligible for long-term remedial action financed under the federal Superfund program (Ref. 9). In 1991, the Rocky Flats Plant and the site transitioned to a new mission: cleaning up the contamination and waste from past production activities. It was at this time that the Rocky Flats Plant became the Rocky Flats Environmental Technology Site. By the end of 2005, all site facilities were demolished, all waste was removed, and contamination was reduced to regulatory agreed-upon levels. The site became a National Wildlife Refuge under a Memorandum of Understanding with the U.S. Department of Interior (Ref. 23).

Spent Nuclear Fuel

EM safely stores approximately 2,500 metric tons of spent nuclear fuel at the Hanford site, the Idaho National Laboratory and the Savannah River site as well as the Fort St. Vrain site in Colorado. There are two disposition paths applicable to this fuel: (1) spent nuclear fuel at Hanford and the Idaho National Laboratory would be packaged into disposable canisters, interim stored, pending transportation to the geologic repository; and (2) aluminum-clad spent nuclear fuel either at the Savannah River site or planned to be transferred from the Idaho National Laboratory, would be processed through H-Canyon. The resulting high-level waste would be processed through the Defense Waste Processing Facility, and stored in the Glass Storage Building until it could be shipped to the repository.

Of the approximately 2,500 metric tons of spent nuclear fuel managed by DOE, 2,100 metric tons were at one facility, the shut down K-reactor basins at Hanford. These 2,100 metric tons have been successfully retrieved, placed inside stackable baskets inside a canister, dried, sealed, and placed in storage several miles away from the Columbia River (Ref. 26). Best-in-class practices were used to successfully retrieve and store this fuel.

Technology Development and Demonstration

Along with these clean-up activities, DOE has brought a number of new technology developments to fruition. Recent examples, which are discussed in more detail below, include the following: cold crucible induction melter technology (Ref. 16), continuous sludge leaching, rotary microfilter, Near Tank Cesium Removal, Sludge Mass Reduction, and Small Column Ion Exchange.

The cold crucible induction melter technology may offer several advantages over the ceramic-lined, Joule-heated melter at the Savannah River vitrification facility. A ceramic lined, Joule-heated melter heats the glass by passing an electric current directly through the glass forming materials in the melter. These melters are lined with materials that are slowly corroded by the molten glass, and the lining needs replaced periodically. The cold crucible induction melter is different in two ways. First, it heats the glass forming materials by placing the melter body within an induction coil and inducing an electric current. This approach results in higher melt temperatures than achievable by the Joule-heated melter. The second difference is reflected in the name, cold crucible. The melter body is surrounded by cooling coils. Because these cooling coils remove heat from the walls, a layer of glass forms on the inside surfaces of the melter. This layer of glass separates the molten glass from the melter walls and prolongs the service life of the melter lining. Thus, the cold crucible melter is shut down less frequently.

These advantages include a potential increased waste loading to greater than 50 weight percent (versus the usual maximum of 34 to 38 weight percent), a higher waste throughput and melt rate, possible extension of melter service life, and higher tolerance for noble metals. Because of these advantages, the cold crucible induction melter has the potential to result in substantial life cycle cost and schedule reduction and provide assurance that regulatory agreements and closure dates can be met. DOE has considerable international collaboration in this area. In the Russian Federation, DOE works with SIA “Radon” to maximize the loading of high-iron feeds and with the Khlopin Radium Institute to improve the solubility and retention of troublesome waste stream components such as aluminum and chromium. DOE also works with both the French and the South Koreans to evaluate cold crucible induction melter throughput.

Continuous Sludge Leaching (CSL) is designed to leach a mineral form of aluminum present in significant quantities in the HLW sludges at both the Savannah River and Hanford sites. This particular mineral form is not effectively leached by current baseline technologies at either site. Research by DOE indicates that cross-flow filtration removes the aluminum from the HLW sludge. Lab scale testing of this process began in 2008. CSL is expected to reduce dramatically the quantity of HLW canisters produced at both the Savannah River site (35%) and at the Hanford site (55%) in comparison to the current technology baselines. This could result in billions of dollars in savings.

The processes that Savannah River and Hanford use for solid-liquid separation are rate limiting and require a large working area. Savannah River National Laboratory has been developing a rotary microfilter to perform the solid-liquid separation step. A full scale 25-disk prototype has been tested with Savannah River simulated waste. By deploying the rotary microfilter as the solid-liquid separation process, the Savannah River and Hanford sites can treat additional radioactive liquid waste using processes such as Small Column Ion Exchange, and Bulk Vitrification, and Sludge Washing. This additional waste treatment would accelerate tank closure.

Current retrieval activities at Hanford are constrained by the limited availability of Double Shell Tank space. Current milestones require that all waste be removed from the Single Shell Tanks by 2018. A process called Near Tank Cesium Removal (NTCR) would allow the low activity waste stream to go to a Supplemental Treatment System. This could possibly accelerate both retrieval and tank closures activities. DOE has completed Proof of Principle experiments to test resin destruction and dissolution in nitric acid. Deployment of the NTCR process could accelerate the start of the Hanford Waste Treatment Plant Low Activity Waste Vitrification Facility up to 6 years.

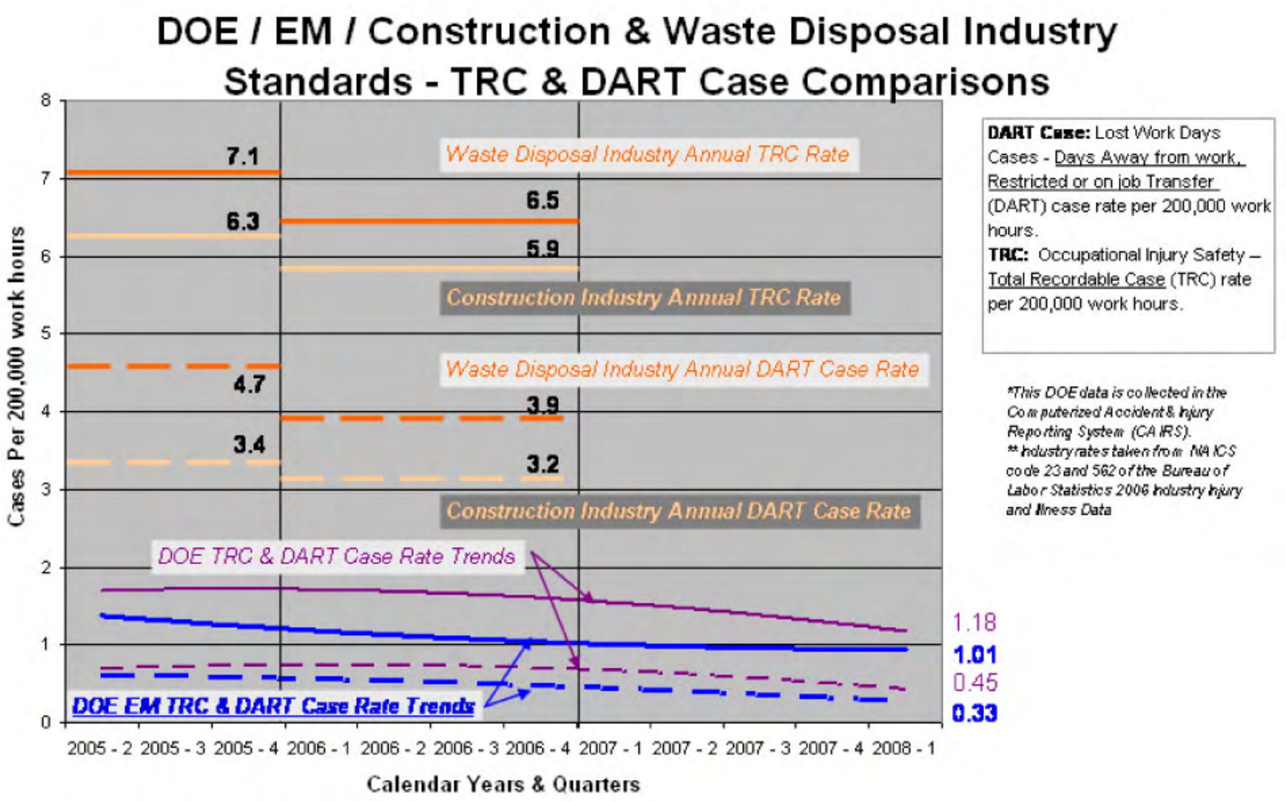
Another newly developed technology is Sludge Mass Reduction. The current understanding of the actual mass of sludge contained in the Savannah River site HLW tanks indicates that about 7,900 canisters could be produced, at the high end of the range. This is higher than projected in prior years, and there is a risk that the 2028 completion date could be missed. One method to reduce the mass of sludge to be vitrified is to remove aluminum present in the sludge. Savannah River developed a simple low temperature caustic leaching process that can be deployed in an existing waste tank with minimal modifications. The process was recently demonstrated at full scale in Tank 51. This process will be used on future sludge batches and is expected to reduce sludge mass by the equivalent of 900 canisters.

DOE is developing methods to increase the rate at which radioactive liquid waste is treated and waste tanks are closed. The largest fraction of the waste to be processed is salt waste (90% of the Savannah River site volume). Processes that remove cesium and allow the waste to be disposed of as LLW are required. Savannah River National Laboratory and Oak Ridge National Laboratory are developing the Small Column Ion Exchange (SCIX) process for two resins: non-elutable crystalline silicotitanate and elutable resorcinol formaldehyde. This additional waste treatment would accelerate tank closure by decreasing the life cycle associated with salt waste processing. The SCIX equipment can be mounted in existing waste tank risers thus reducing the shielding and infrastructure needed for the process (and the construction and installation cost).

Current Activities

With this record of achievements, it would be easy for DOE to relax its efforts and take pride in its accomplishments. Rather than reducing its intensity, DOE has maintained or even increased the intensity of its efforts. Some of our current activities (Ref. 16) include:

<u>Conducting cleanup with a “Safety First” culture that integrates environment, safety and health requirements, and controls into all work activities to ensure protection of the worker, public, and the environment:</u> DOE has made great strides in implementing effective Worker Safety Health Programs that have resulted in substantial decrease in our injuries (as shown in the figure below). Safety is the dominant characteristic and value of DOE. Safety comes first and is valued above production, budget, and schedule. Safety overrides every other priority.



DOE / EM / Construction & Waste Disposal Industry Standards - TRC & DART Case Comparisons

DART Case: Lost Work Days Cases - Days Away from work, Restricted or on job Transfer (DART) case rate per 200,000 work hours.
TRC: Occupational Injury Safety – Total Recordable Case (TRC) rate per 200,000 work hours.

*This DOE data is collected in the Computerized Accident & Injury Reporting System (CAIRS).
** Industry rates taken from NAICS code 23 and 562 of the Bureau of Labor Statistics 2006 Industry Injury and Illness Data

As depicted in the chart above, DOE Total Recordable Case rate (TRC) and Days Away, Restricted or on Job Transfer (DART) (i.e. “lost time”) rate for the fourth quarter of 2007 were 0.95 and 0.33, respectively, as compared to the 6.3 and 3.4 in the 2006 Department of Labor benchmarks for the construction industry. Even with the hazardous nature of the work, DOE workers are performing better than national averages. A number of our DOE sites have received special recognition for their worker safety and health programs through the Voluntary Protection Program. DOE provides continuous emphasis on safety by DOE management at all levels.

<u>Establishing a disposition capability for radioactive liquid tank waste and spent nuclear fuel:</u> This capability includes the development of performance measures that tell DOE how well it is doing. For radioactive liquid tank waste (and other forms such as sludge and saltcake), the measure is volume which only is counted when the inventory is reduced. This measure refers to waste traditionally called "high-level" waste, such as waste in the 177 tanks at Hanford. The performance measure for spent nuclear fuel is the heavy metal mass of SNF ready for final disposition. Packaging for transport is not included unless no further packaging is required after transport.

<u>Securing and storing nuclear material in a stable, safe configuration in secure locations to protect national security:</u> DOE is making significant strides in consolidating its special nuclear materials to fewer locations to minimize the number of facilities with special nuclear material. Today, Hanford and Savannah River each have only one such facility. In addition, Personnel Security Programs ensure the continued reliability of employees having access to classified matter and special nuclear material at all DOE sites.

Transporting and disposing of transuranic and low-level wastes in a safe and cost-effective manner to reduce risk**:** EM safely transported more than 10,000 radioactive shipments in 2005 and again in 2006. As a result of DOE's work, the National Academy of Sciences is utilizing DOE's approach to develop its own Commodity Flow Survey Guide for community groups throughout the United States. DOE received the Transportation Community Awareness and Emergency Response (TRANSCAER) Chairman's Award, one of the industry's most prestigious transportation safety awards. The TRANSCAER Chairman's Award is awarded only when the National TRANSCAER Committee determines an exceptional effort should be recognized. DOE is the first federal agency to receive this award and is one of only two recipients of the Chairman's Award in its 15-year history. EM was presented the U.S. Transport Council's Special Achievement Award for the successfully completed shipments of the WIPP program.

Remediating soil and groundwater in a manner that will assure long-term environmental and public protection: DOE is actively investigating, developing, and implementing permanent and cost-effective remediation technologies to remove and/or immobilize technetium-99, strontium-90, uranium, metals, and chlorinated organics in groundwater and soil. Sophisticated groundwater and fate and transport models are being used throughout the complex. DOE is developing and institutionalizing new technical contract performance measures for remediation activities and ensuring that all source terms of contamination are fully identified and all contaminated sites are appropriately characterized. The Department controls the clean-up investments for remediating contaminated groundwater and soil and is integrating successfully implemented remediation technologies and regulatory approaches across the complex to reduce the risk of duplicative efforts.

Along with these important tasks, DOE is focusing its efforts on (Ref. 16):

Decontamination and Decommissioning of Test Area - North at Idaho: Test Area North covers about 1 km^2 at the north end of the Idaho National Laboratory site. In October 2008 DOE demolished the last major facility in Test Area North as part of the Idaho Clean-up Project. What remains is the remediation of contaminated soils and tanks and to continue the remedial pump-and-treat activities of the groundwater.

Demolition of the Hanford K-Basins: This project significantly reduces environmental risk because of the basins proximity to the Columbia River. In 2009, the K-East Basin will be completely demolished and the remediation of the contaminated soil started. The K-West Basin will be demolished and soil remediated at a later date.

Demolition of the West Wing of the Oak Ridge K-25 building: This former gaseous diffusion plant comprises one of the largest building complexes in the world. In 2009, EM will continue to clean up the east and north wings while the west wing will be demolished.

Challenges

There are still significant challenges remaining before DOE can complete the cleanup (Ref. 17). The clean-up program depends upon annual appropriations, and the actual funding may be more or less than the projections used in the planning stages for cost and schedule. Thus, it is also important to recognize that some upcoming clean-up milestones could be missed due to technical, performance, or level of funding issues.

Moreover, some of the relevant agreements with federal and state regulators were negotiated many years ago, with incomplete knowledge by any of the parties of the technical complexity and magnitude of costs that would be involved in attempting to meet the requirements. This incomplete knowledge, coupled with other issues including technical performance, optimistic planning assumptions, and emerging technical or regulatory barriers, also have impeded the Department in meeting all milestones and obligations contained in the environmental compliance agreements.

In planning its environmental clean-up efforts, EM is challenged to focus on work that will meet its compliance commitments, maximize risk reduction, and maintain a safe environment for its workers and the public. EM also faces the challenge of investing in developing solutions for meeting outyear technical challenges. The Department strongly believes that setting priorities and establishing work plans in this way is the most effective use of taxpayer funds and will have the greatest benefit, at the earliest possible time, to the largest number of people.

Management Improvements to Strengthen Performance

Project Management Principles and Processes

When DOE began its clean-up program, and until fairly recently (circa 2004), the clean-up work at the sites was performed as “level of effort” matched to the funding provided each year. The clean-up programs were not conducted under a standard project management schedule and cost methodology, as is the case with capital construction projects. The Department undertook, in 2005, an intense program to infuse the standard project management methodologies and tools into the management of its clean-up program.

The elements of this project management process are similar to those the Department was already using for its capital construction projects (including those capital construction projects needed for the clean-up program), and were tailored to suit the unique nature of decontamination, decommissioning, demolition, soil and groundwater remediation, etc.

Essentially, each project has five “critical decision” (CD) points. This information is summarized from the Department’s applicable directive, and its accompanying manual and guidance: (Ref. 31).

- CD-0 Establishment of mission need, i.e. purpose of the project
- CD-1 Determination of preferred alternative, from both a business and a technical perspective; identification of the cost and schedule range.
- CD-2 Establishment of the cost and schedule “baselines” for the project, subsequent to an external audit and verification of the cost and schedule
- CD-3 Authority to commence actual field work at the site
- CD-4 Conclusion of the field work/actual work on the project

Evaluation of Alternatives

Leading up to CD-1, the governmental staff performs an evaluation of alternatives, considering both technical aspects and business case aspects. They may employ the expertise of the appropriate contractor, insuring no conflict of interest. The Environmental Management Program may incorporate a standard technical maturity assessment, and a risk assessment methodology, as a part of this decision process, to be discussed below. Also approved at CD-1 is the proposed cost and schedule range. To a great degree, the range itself is determined by the amount of technical and programmatic uncertainty.

Establishment of Scope, Performance, Cost and Schedule Baselines

After the technical and business approaches are selected at CD-1, the project is now permitted to begin engineering design and development. The preference is that sufficient engineering be completed (nominally considered to be 35 percent) to permit a rather definitive estimate of scope, performance, cost and schedule to be developed. Before the proposed cost and schedule can be presented for approval, an independent review must be performed to validate that the proposed cost and schedule baseline is considered to be legitimate. It is still possible, at this point, to have unresolved technical issues, but there must be specific recognition of any such issues, along with a risk assessment. A factor for contingency, both cost and schedule, is normally included in the baseline. At this point, the approval official can approve CD-2, the scope, performance, cost and schedule baseline. Engineering work is permitted to continue uninterrupted pending this decision.

Approval of Construction or Commencement of Field Work (i.e. cleanup)

Once engineering is nominally or essentially completed, the project would be ready for approval of CD-3, which enables actual work on site to begin. In a number of instances, for both construction and cleanup, approval for work on site to begin has been granted even though engineering work is not essentially completed. In the United States, when construction is performed without all engineering design being completed, the overall process is called “design build,” and the Department is using this approach to construct several of its process facilities to chemically process waste to transform it into a physical form suitable for disposal. For example, the Department is utilizing this approach for significant design and construction efforts for such process facilities at the Savannah River site, the Hanford site, and the Idaho National Laboratory.

Technology Maturity and Readiness

EM has begun to incorporate a technology maturity and readiness assessment into its projects at various stages. The most applicable points would be leading up to CD-1, the selection of technical alternative, but this methodology can be used even during construction and field work, since as stated above, engineering is typically proceeding as field work is ongoing. The intent is to resolve technical issues before performance of the cleanup or processing stage, and it is not uncommon to have technology issues throughout the life of a clean-up project. For example, a technology that may work well to remotely remove residual highly radioactive material from the bottom of one or several tanks, may not work at all in a tank where the physical characteristics of the residual are different. Or a groundwater remediation method that has been successful at a particular location may become less successful after time, so a revised approach may be indicated.

We have adopted a standard technology maturity tool which defines technology maturity and assigns a numerical rating, from 1 to 9, with 1 being the least mature, and 9 being the most mature. The table below gives the narrative description to correlate with the numeric ratings (Ref. 32).

Table 3. Technology Readiness Levels

Relative Level of Technology Development	**Technology Readiness Level**	**TRL Definition**	**Description**
System Operations	**TRL 9**	Actual system operated over the full range of expected conditions.	The technology is in its final form and operated under the full range of operating conditions. Examples include using the actual system with the full range of wastes in hot operations.
System Commissioning	**TRL 8**	Actual system completed and qualified through test and demonstration.	The technology has been proven to work in its final form and under expected conditions. In almost all cases, this TRL represents the end of true system development. Examples include developmental testing and evaluation of the system with actual waste in hot commissioning. Supporting information includes operational procedures that are virtually complete. An ORR has been successfully completed prior to the start of hot testing.
	TRL 7	Full-scale, similar (prototypical) system demonstrated in relevant environment	This represents a major step up from TRL 6, requiring demonstration of an actual system prototype in a relevant environment. Examples include testing full-scale prototype in the field with a range of simulants in cold commissioning[1]. Supporting information includes results from the full-scale testing and analysis of the differences between the test environment, and analysis of what the experimental results mean for the eventual operating system/environment. Final design is virtually complete.
Technology Demonstration	**TRL 6**	Engineering/pilot-scale, similar (prototypical) system validation in relevant environment	Engineering-scale models or prototypes are tested in a relevant environment. This represents a major step up in a technology's demonstrated readiness. Examples include testing an engineering scale prototypical system with a range of simulants.[1] Supporting information includes results from the engineering scale testing and analysis of the differences between the engineering scale, prototypical system/environment, and analysis of what the experimental results mean for the eventual operating system/environment. TRL 6 begins true engineering development of the technology as an operational system. The major difference between TRL 5 and 6 is the step up from laboratory scale to engineering scale and the determination of scaling factors that will enable design of the operating system. The prototype should be capable of performing all the functions that will be required of the operational system. The operating environment for the testing should closely represent the actual operating environment.
	TRL 5	Laboratory scale, similar system validation in relevant environment	The basic technological components are integrated so that the system configuration is similar to (matches) the final application in almost all respects. Examples include testing a high-fidelity, laboratory scale system in a simulated environment with a range of simulants[1] and actual waste[2]. Supporting information includes results from the laboratory scale testing, analysis of the differences between the laboratory and eventual operating system/environment, and analysis of what the experimental results mean for the eventual operating system/environment. The major difference between TRL 4 and 5 is the increase in the fidelity of the system and environment to the actual application. The system tested is almost prototypical.

Relative Level of Technology Development	Technology Readiness Level	TRL Definition	Description
	TRL 4	Component and/or system validation in laboratory environment	The basic technological components are integrated to establish that the pieces will work together. This is relatively "low fidelity" compared with the eventual system. Examples include integration of ad hoc hardware in a laboratory and testing with a range of simulants[1] and small scale tests on actual waste[2]. Supporting information includes the results of the integrated experiments and estimates of how the experimental components and experimental test results differ from the expected system performance goals. TRL 4-6 represent the bridge from scientific research to engineering. TRL 4 is the first step in determining whether the individual components will work together as a system. The laboratory system will probably be a mix of on hand equipment and a few special purpose components that may require special handling, calibration, or alignment to get them to function.
Research to Prove Feasibility	**TRL 3**	Analytical and experimental critical function and/or characteristic proof of concept	Active research and development (R&D) is initiated. This includes analytical studies and laboratory-scale studies to physically validate the analytical predictions of separate elements of the technology. Examples include components that are not yet integrated or representative tested with simulants.[1] Supporting information includes results of laboratory tests performed to measure parameters of interest and comparison to analytical predictions for critical subsystems. At TRL 3 the work has moved beyond the paper phase to experimental work that verifies that the concept works as expected on simulants. Components of the technology are validated, but there is no attempt to integrate the components into a complete system. Modeling and simulation may be used to complement physical experiments.
Basic Technology Research	**TRL 2**	Technology concept and/or application formulated	Once basic principles are observed, practical applications can be invented. Applications are speculative, and there may be no proof or detailed analysis to support the assumptions. Examples are still limited to analytic studies. Supporting information includes publications or other references that outline the application being considered and that provide analysis to support the concept. The step up from TRL 1 to TRL 2 moves the ideas from pure to applied research. Most of the work is analytical or paper studies with the emphasis on understanding the science better. Experimental work is designed to corroborate the basic scientific observations made during TRL 1 work.
	TRL 1	Basic principles observed and reported	This is the lowest level of technology readiness. Scientific research begins to be translated into applied R&D. Examples might include paper studies of a technology's basic properties or experimental work that consists mainly of observations of the physical world. Supporting Information includes published research or other references that identify the principles that underlie the technology.

[1] Simulants should match relevant physical and chemical properties.

[2] Testing with as wide a range of actual waste as practicable; and consistent with waste availability, safety, ALARA, cost, and project risk is highly desirable

EM has recently initiated this process and has applied the technology maturity tool to assist with decision making. EM is still in the early stages of its use, but has found it to be useful to better understand the options, to help go beyond vendor claims of maturity, and to make better decisions.

Identification and Management of Risk

Coupled with the use of a technology maturity tool is identification and management of risk. For the clean-up program, not all risk is technical in nature. Other forms of risk can be uncertainty on the disposition path for certain wastes, uncertainty concerning the future regulatory regime, or regulatory decisions and requirements, or programmatic uncertainty such as performance, and availability of funding in future years. A few examples of such risks follow.

It may become necessary to provide a greater degree of worker protection, such as self-contained breathing air, if vapors prove to present a sufficient hazard. The extra protective devices will likely require more time to apply and remove, may restrict time available to work in the affected area, and reduce productivity.

It may become necessary to further treat a particular waste to enable it to be dispositioned at a certain location. Or a commercial disposal facility may fail to obtain, or may fail to retain, its license to accept certain types of waste.

Because of migration of groundwater that was unanticipated, the Department and the applicable regulator may deem it necessary to install either more monitoring wells, or a more aggressive remediation regime, than was originally planned.

The approach EM takes to managing risk is to develop a risk management plan. The plan includes identification of risk, contingency funds to cover that risk, and identification of strategies to mitigate and overcome the risks. EM provides recognition of the risks inherent in the projects by identification of both cost and schedule contingency.

Summary

This paper has described the actions of the U. S. Department of Energy in the cleanup of America's nuclear legacy remaining from early weapons production and the ensuing Cold War. Particular attention was paid to a description of the clean-up effort and the management and processing methods. Included in the discussion were comments on DOE's successes, its current efforts, and some of the challenges faced by the Department.

DOE nuclear waste management provides environmental cleanup today and energy solutions for tomorrow. DOE's record proves that safe, effective nuclear waste management is possible. DOE has effectively reduced risk to the environment and the community and each year our knowledge and skill base grows. DOE's investment in environmental cleanup provides global benefits beyond nuclear cleanup, including advancing nuclear power during a stagnant time for the nuclear industry and enhancing global security and nuclear non-proliferation. Enormous challenges lie ahead, e.g., the ability to continue to make technological leaps forward, and the willpower of societies to continue to pursue difficult, expensive work.

References

1. *Nuclear Waste Policy Act of 1982,* 42 U.S.C. 10101 et seq.
2. *Tank Waste Retrieval, Processing, and On-Site Disposal at Three Department of Energy Sites, Final Report*. National Research Council, The National Academies Press, Inc. 500 Fifth Street, N.W., Washington, D.C. 20001, 2006.
3. *WIPP Land Withdrawal Act (LWA) of 1992*, P. L. No. 102-579, 106 Stat.
4. DOE M 435.1-1, *Radioactive Waste Management Manual*, U. S. Department of Energy, Washington, D.C., August 1999.
5. 10 CFR Part 61, *Licensing Requirements for Land Disposal of Radioactive Waste*.
6. 10 CFR Part 961, *Standard Contract for Disposal of Spent Nuclear Fuel and/or High- Level Radioactive Waste.*
7. *Research Opportunities for Managing the Department of Energy's Transuranic and Mixed Wastes*. National Research Council, The National Academies Press, Inc. 500 Fifth Street, N.W. Washington, D.C. 20001, 1999.
8. *Resource Conservation and Recovery Act of 1976*.
9. *Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980*.
10. "*FY 1994 Program Summary*," DOE/EM-0216, U.S. Department of Energy Office of Environmental Management, Washington, D.C. 20585, October 1994.
11. "Engineering and Technology Roadmap: Reducing Technical Risk and Uncertainty in the EM Program," U.S. Department of Energy Office of Environmental Management, Washington, D.C. 20585, March 2008.
12. The Waste Isolation Pilot Plant Land Withdrawal Act, P.L. 102-579.
13. *Melton Valley Clean-up Status and Strategy*, The Advocate, Oak Ridge Site Specific Advisory Board, Issue #26, April 2007.
14. *Waste and Materials Disposition Update*, Douglas Tonkay, Office of Commercial Disposition Options, U.S. Department of Energy Office of Environmental Management, Washington, D.C. 20585, April 2006.
15. *Integrated Multi-Year Program Plan (FY 2008 – FY 2010)*, Office of Engineering and Technology, U.S. Department of Energy, Washington, D.C. 20585, March 2008.
16. Rispoli, James A. Statement to the Senate Subcommittee on Energy and Water Committee on Appropriations, *Budget Request for the Department of Energy's Office of Environmental Management,* Hearing, April 9, 2008.
17. Radioactive Tank Waste from the Past Production of Nuclear Weapons: Background and Issues for Congress, D.M. Andrews and A. Andrews, Congressional Research Service. Washington, D.C.
18. *The Disposal of Radioactive Waste on Land*, National Academy of Sciences, Publication 519, Washington, D.C., September 1957.
19. *Final Environmental Impact Statement for a Geologic Repository for the Disposal of Spent Nuclear Fuel and High-Level Radioactive Waste at Yucca Mountain, Nye County, Nevada, Appendix A: Inventory and Characteristics of Spent Nuclear Fuel, High-Level Radioactive Waste, and Other Materials,* DOE/EIS-0250, Office of Civilian Radioactive Waste Management, U.S. Department of Energy, Washington, D.C. 20585.
20. *Startup of Second Nuclear Waste Storage Facility at the Savannah River Site*, Department of Energy, Savannah River Operations Office, http://sro.srs.gov/.
21. *Savannah River National Laboratory, Russia Collaborate to Advance Melter Technology*, Department of Energy, Oak Ridge National Laboratory Pulse, No. 241, August 13, 2007, http://www.ornl.gov/info/news/pulse/pulse_v241_07.htm.
22. *Comprehensive Review of the Hanford Waste Treatment Plant Flowsheet and Throughput*, Hanford Waste Treatment and Immobilization Plant Project, March 2006.

http://www.hanford.gov/orp/uploadfiles/WTP%20Flowsheet%20Background%20Report_FINAL%20Draft_March06.pdf.

23. *Closure Legacy, from Weapons to Wildlife*, U.S. Department of Energy, Rocky Flats Project Office, August 2006, http://rockyflats.apps.em.doe.gov/.
24. *Life-Cycle Liquid Waste Disposition System Plan*, LWO-PIT-2007-00062, Washington Savannah River Company, Aiken, South Carolina 29808, October 2007.
25. Shipments and Disposal Information, Waste Isolation Pilot Plant, Carlsbad Field Office, U.S. Department of Energy, Carlsbad, New Mexico, June, 2008, http://www.wipp.energy.gov/shipments.htm.
26. *Multi-Canister Overpack Topical Report*, HNF-SD-SNF-SARR-005, Revision 3, Project Hanford Management Contractor for the U.S. Department of Energy under Contract DE-AC06-96RL13200, Fluor Hanford, P.O. Box 1000, Richland, Washington, January 2002.
27. *Agreement Between the Government of the United States of America and the Government of the Russian Federation Concerning the Management and Disposition of Plutonium Designated as No Longer Required for Defense Purposes and Related Cooperation, 2000.* Quoted in *Troubled Disposition: Next Steps in Dealing with Excess Plutonium*, Matthew Bunn, Arms Control Today, Washington, DC 20005, April 2007.
28. *Tank Closure Progress at the Department of Energy's Idaho National Engineering Laboratory Tank Farm Facility,* K. A. Lockie in a presentation to the National Academies Committee on Development and Implementation of a Clean-up Technology Roadmap, August 27, 2007, www.em.doe.gov/pdfs/INL_08.27.08_Keith_A._Lockie_.pdf.
29. *Atomic Energy Act of 1954* (AEA), 42 U.S.C. 2011 et seq.
30. *Melton Valley Remediation Completed,* DOE Oak Ridge Environmental Management Program, April 2008, www.bechteljacobs.com/pdf/factsheets/melton_valley.pdf.
31. *Program and Project Management for the Acquisition of Capital Assets*, DOE Order 413.3, U.S. Department of Energy, Washington, D.C. 20585, March 2008.
32. *Technology Readiness Assessment (TRA)/Technology Maturation Plan (TMP) Process Guide*, Office of Environmental Management, U.S. Department of Energy, Washington, D.C. 20585, March 2008.

An Overview of the Nuclear Separations Course Presentations

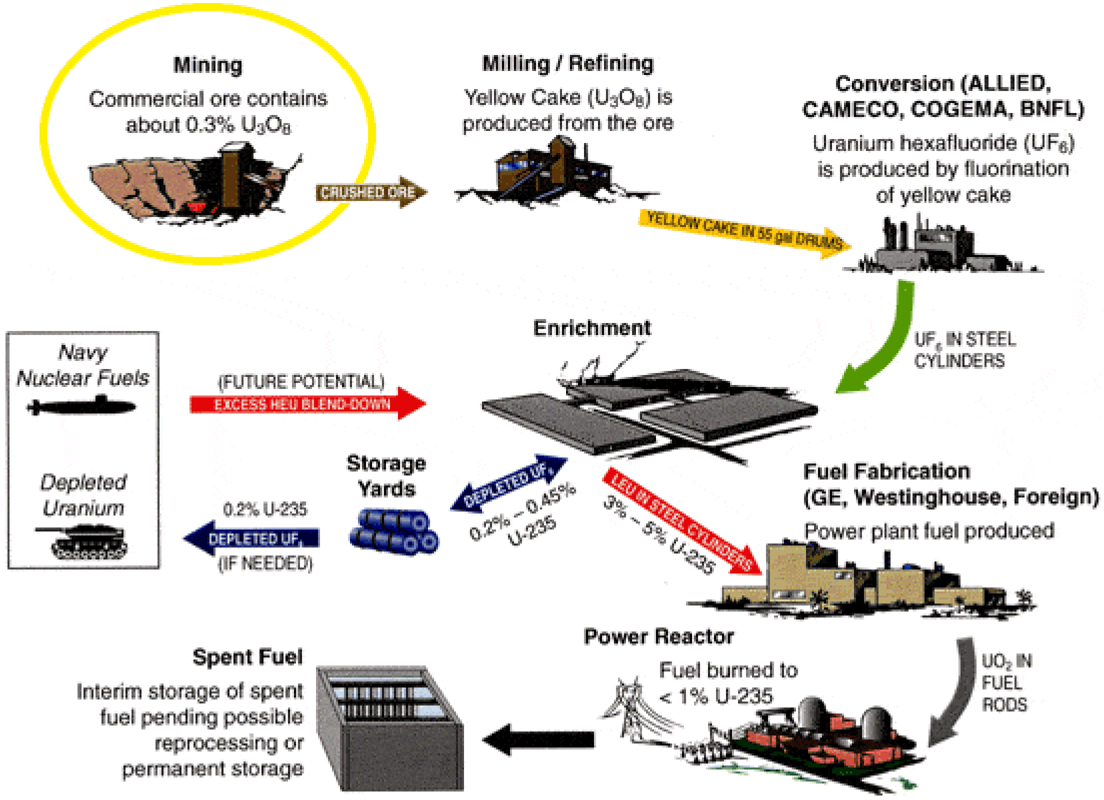
Raymond G. Wymer
Vanderbilt University

Introduction

This paper is an overview of the remainder of the course presentations. Its purpose is to put the remainder of the presentations into the context of the nuclear fuel cycle. Extensive use has been made of excerpts from the individual presentations (usually with some modifications).

Separations are at the heart of all nuclear fuel cycles, whether the cycle is the uranium-plutonium or the thorium-uranium cycle and whether the cycle is the once-through cycle or complete spent fuel recycle. The various parts of the uranium fuel cycle, with the exception of waste management and reprocessing are shown in figure 1. At present in the U.S. only interim storage is practiced.

Figure 1. The Uranium Fuel cycle



A very wide variety of separations processes that support the uranium fuel cycle have been studied since the beginning of the nuclear era in the 1940s in order to meet the requirements of nuclear energy production and military applications, i.e., naval vessel propulsion and nuclear weapons production. Many separations have been studied at the very small scale, e.g., the very earliest separation of plutonium; others have reached the laboratory bench scale; and others have been carried to engineering-scale demonstration. A few have reached very large industrial-scale application throughout the world.

The fissioning of uranium and plutonium produces elements and their isotopes of nearly all the elements in the periodic table as well as neutron capture reactions in uranium and plutonium to produce elements not found in nature[1]. The extremely large number of elements produced during fission has required chemical separations studies that are very extensive in order to complete the fuel cycle. To develop, demonstrate, and implement the necessary fuel cycle separations processes it has been necessary to study many aspects of fundamental chemistry as well as sophisticated chemical engineering unit operations.

Chemistry of Fuel Cycle Elements

A necessary first step in the development of separations processes is an understanding of the chemistry of chemical elements whose separation is sought. Understanding the chemistry includes a knowledge of the solid, liquid and gaseous (or vapor) chemical species of the elements. The earliest separations of plutonium, for example, were based on co-precipitation of plutonium species; purification of uranium has been based almost entirely on liquids, i.e., on solution chemistry[2]; uranium enrichment has been based entirely on the gaseous compound UF_6.

Additionally, there are important subdivisions of chemical behavior within the three material phases noted above. Especially important subdivisions are the formation of complex ions and compounds in the liquid phase, and both co-precipitation and sorption on surfaces of ions and compounds in the solid phase.

The paper by Jarvinen discusses the important roles played in nuclear separations by precipitation and crystallization; Wymer discusses the key roles played by complexation reactions.

Precipitation and Crystallization

The distinction between precipitation and crystallization may be based on the speeds of the process and the size of the solid particles produced. The term precipitation commonly refers to a process resulting in rapid solid formation that can give small crystals that may not appear crystalline to the eye, but still may give very distinct x-ray diffraction peaks. Amorphous solids (as indicated by x-ray diffraction) may also be produced. Agglomeration describes the tendency of small particles in a liquid suspension to coalesce into larger aggregates. Other terms used in the literature include aggregation, coagulation, and flocculation.

Crystallization often involves “aging.” The term aging refers to a variety of other processes that change a precipitate after it forms. Aging usually results in larger particle sizes and may be referred to with terms such as digestion or “ripening” of the precipitate. The details of performing the precipitation or crystallization process can be very important to produce a pure product and one that separates well from the liquid phase.

For actinide metal ions limiting the amount of added precipitating agent such as oxalic acid (e.g., to form $Pu_2(\text{oxalate})_3$) is used both to control initial super-saturation and to get larger particle sizes that are readily filtered and to limit the formation of soluble anionic complexes of the actinide element that may form in the presence of excess precipitant and reduce the yield of the product.

---

[1] Actually, trace amounts of many of the so-called “new” elements have been found in the natural environment, possibly produced by cosmic radiation.

[2] A noteworthy exception is purification of uranium by distillation of UF_6 prior to enrichment.

Co-precipitation refers to the variety of ways that other solutes in a multi-component solution may associate with a precipitate or crystal. This includes surface adsorption, incorporation of other anions or cations in the lattice of a growing crystal as part of a stable solid solution, or by entrapment. There may also be physical inclusion of pockets of "mother liquor." Co-precipitation is a very important method for recovering small amounts of a solute that may be far below its solubility limit. In this case the solute sought precipitates with a major solute component (sometimes referred to as the carrier). Co-precipitation has been a crucial separation process to isolate traces of radionuclide, e.g., plutonium and some transplutonium elements, and to investigate their chemical behavior. The bismuth phosphate process used for the first large-scale purification of plutonium from neutron-irradiated uranium is an example of co-precipitation. Precipitated $BiPO_4$ from acid solutions carries the trivalent and tetravalent actinides (especially Pu(IV)), but not the pentavalent and hexavalent ions. The $BiPO_4$ solid carries only small amounts of the fission products.

The different oxidation states of the actinide ions (particularly U, Np, and Pu) in aqueous solution show large differences in precipitation chemistry that facilitates their separation and purification. Table 1 lists examples of the decontamination factors[3] achieved by precipitation for common contaminants of plutonium in oxidation states III-IV. Because of the relatively low decontamination factors, precipitation is generally not selective enough to be used as the primary process for separation and purification of plutonium or other actinides from fission products in irradiated fuel or targets[4]. Multiple precipitations may be used to achieve greater separation, but the nature of the precipitates and the handling difficulties often makes this approach infeasible.

Table 1. Decontamination factors for plutonium precipitated from an irradiated plutonium alloy dissolved in nitric acid

Element	Pu(III) oxalate	Pu(IV) oxalate	Pu(IV) peroxide	Pu(III) fluoride
Fe	33	10	50	1.4
Co	47	> 95	30	8.6
Zr	3.5	> 44	1	1.1
Mo	> 13	> 15	> 140	1.1
Ru	> 38	33	> 14	36
Ce	1	1	6	1.1

Many solid materials have been used as sorbents for final purification of products of separation. Activated charcoal, silica, alumina, clays, and iron hydroxides are among the many materials used to sorb ions from solutions. The negatively charged surfaces of oxide materials can sorb cations from solution sometimes with surprisingly good selectivity.

---

[3] Decontamination factor is defined as the ratio of concentration of the substance of interest in a phase before separation to its concentration in that phase after separation.

[4] Decontamination factors of 10^6 or higher are typically required to produce a U or Pu product of adequate purity.

Complexation reactions

Complexation reactions are chemical reactions wherein a chemical species, usually a metallic cation, combines chemically with another species, usually an anion of an acid, to form a chemical entity having chemical properties unlike either of the initial reactants. Complexation of elements is very strongly dependent on the valence states of the elements. Changing the valence of an element dramatically changes its chemistry and consequently changes its complexation reactions and its separations chemistry. Table 2 lists common valence states of the elements of interest here as well as some of their important features. The most common valence states are in bold face font.

Table 2. Important features of Some Common Valence States

Element	**Valences**	**Features**
Tc	+**4**, *+5*, *+6*, **+7**	Environmentally mobile as TcO_4^-; Tc_2O_7 is volatile at relatively low temperatures
U	*+3*, **+4**, +5, **+6**	UO_2^{2+} forms extractable species; U^{+4} is used in oxide fuels; UF_6 is volatile and is used in enrichment processes
Np	*+3*, *+4*, **+5**, *+6*, *+7*	Environmentally mobile as NpO_2^-; forms extractable species
Pu	*+3*, **+4**, **+5**, **+6**, **+7**	Environmentally Mobile as Pu^{+4} colloid; Pu^{+4} is extractable; Pu^{+4} is used in oxide fuels
Am	**+3**, *+4*,*+5*, *+6*	Am^{+3} is very stable in aqueous media; Am^{6+} is potentially useful in separations from other actinides
Cm	**+3**, *+4*	Cm^{+3} is the only common valence state in aqueous solution; it behaves much like rare earths

Uranium

Uranium is at the heart of commercial nuclear power and is vital to the entire nuclear enterprise. Its presence and use worldwide has resulted in a vast literature, not only on uranium complexation and separations reactions, but also on all aspects of the uranium fuel cycle: mining and, milling; isotope enrichment; reactor fuel manufacturing; spent reactor fuel reprocessing; and weapons production. The number of valence states of uranium that are easily obtainable under ordinary conditions make possible a wealth of compounds and complexation reactions that present almost unparalleled opportunities for separations processes, both of uranium from contaminants and of uranium isotopes.

A very useful and extraordinarily stable uranyl tricarbonate complex anion, $UO_2(CO_3)_3^{-4}$, forms with carbonate anions. This extraordinary anionic uranyl tricarbonate complex finds use in uranium solution mining, in fuel fabrication, and in separations from a host of cations that do not form such anionic complexes.

Plutonium

Plutonium has the unique property of existing in significant amounts in four valence states simultaneously in aqueous solutions. It is, however, possible to stabilize it in essentially pure in each of its valence states. The variety of valence states of plutonium presents ample opportunities for it to engage in complexation reactions and for a range of separations processes. Its proclivity to form very strong complexes with fluoride ion provides a method for the dissolution of the very refractory plutonium dioxide as well as a chemical form useful in the formation of plutonium metal. In high nitrate ion concentrations anionic nitrate complexes of Pu^{+4} are formed. These complexes are readily sorbed on organic anion exchange resins. This reaction is used as a means of separating plutonium from other actinides that do not form anionic complexes with nitrate ion.

Neptunium

The similarity in the chemistries of neptunium and plutonium complicates their separation from each other in the Purex process. However, it has been found that by careful control of redox conditions it is possible to maintain in-extractable NpO^{2+} in the presence of extractable Pu^{4+} and thus to effect their separation. By careful manipulation of redox conditions it is also possible to co-extract uranium, neptunium and plutonium into TBP and in this way to produce an actinide stream that is both somewhat proliferation resistant and also useful for recycle into reactors.

The Front End of the Fuel Cycle

All fuel cycles start with separation of the desired chemical elements from ores. These elements include such diverse materials as uranium, thorium, zirconium, iron, rare earths, carbon, lead, fluorine, sodium, aluminum, and other less widely known elements such as lithium, beryllium, boron, molybdenum, and others. Uranium is the most important element in the nuclear fuel cycle.

Mining, milling, conversion and enrichment of uranium

The paper by Hardy discusses the location of uranium ore bodies, uranium mines and mining, uranium milling and refining, uranium conversion to other chemical forms, e.g., UF_6, and enrichment, and touches on fabrication of reactor fuels.
There are four basic methods of obtaining uranium from its ores or from other materials:

- Underground mining
- Open-pit mining
- In-situ leaching
- Recovery from mining other materials, e.g., phosphate rock, mineral sands, coal ash, etc.

Underground mining employs vertical shafts down to the depth of the ore-body or inclined access tunnels from the surface if the ore-body is not at a great depth. Open-pit (or open-cut) mining involves excavation of overburden to reach the ore-body. Analysis of the depth of overburden, the depth of the ore-body or related ore bodies, the grade (quality) of the ore, the inclination of the ore bodies to the surface, and many other factors are required to decide which method is the most economic.

In underground and open-pit mining, the coarse primary ore is milled. In this process the ore is crushed in a primary crusher and then reduced in a secondary crusher to a fine powder suitable for a leaching process. This leaching process can use dilute sulfuric acid or dilute sodium hydroxide or sodium carbonate. The leachant choice depends on the chemistry of the uranium ore and the host rock. Ores containing high concentrations of carbonate minerals are usually not suitable for acid leaching because of excessive consumption of acid. The leach product is usually called Uranium Ore Concentrate (UOC) or yellowcake and can have a yellow to dark brown color.

Uranium enrichment

After milling, the uranium is typically enriched in the fissionable isotope ^{235}U. For most common reactor fuels the enrichment is of the order of 4 to 5 % ^{235}U. One of the first uranium enrichment methods was the Calutron method. This method was followed by enrichment by gaseous diffusion and then by gas centrifugation. Later, methods of isotope enrichment using laser excitation and chemical exchange methods were developed. A major consideration in choice of enrichment process is energy consumption. Calutrons and gaseous diffusion are very energy intensive.

Calutrons

Calutrons are basically electromagnetic mass separators. The separation is effected by ionizing the uranium atoms and injecting them into a magnetic field where the ionized isotopes move in arcs of differing radii depending on their masses. They are collected individually in separated spots on a collector and the separated isotopes are separately recovered.

Gaseous diffusion

Gaseous diffusion relies on the ability of uranium to form molecules of uranium hexafluoride (UF_6) that are gaseous at ambient temperatures. The molecules are pumped through a barrier with very small pores. The lighter $^{235}UF_6$ molecules travel through the pores faster than the $^{238}UF_6$, thus effecting a small isotopic separation. Many successive passes through the barrier (called stages) pores are required to achieve useful isotopic separation.

Gas centrifugation

Gas centrifugation also relies on gaseous UF_6. The UF_6 is spun very rapidly in vertical cylinders, forcing the heavier UF_6 to move preferentially to the inner wall of the cylinder where it is continuously removed by a small scoop. Many stages are required to achieve a useful separation.

Lasers

Laser separation has not reached commercial application. It is based on the use of laser light to selectively ionize ^{235}U isotopes of vaporized uranium atoms or molecules of a volatile uranium compound. The ionized uranium species is selectively removed by attraction to a charged surface. Powerful lasers are required to achieve useful separations.

Chemical exchange

Chemical exchange relies on very small differences in the affinity for either ion exchange resins or organic solvents of uranium chemical isotopic species in solution. It has been demonstrated on a large scale with organic solvents, but has not reached commercial application.

Nuclear reactors and their fuels

The paper by Croff discusses fuels for existing and possible future U.S. civilian nuclear power reactors. After irradiation this fuel could constitute the material feed for a fuel reprocessing plant. His paper also has some discussion of the characteristics of the reactors in which the fuel is irradiated. A large number of reactor types and fuels have been studied in the course of development of practical nuclear power production.

Reactors

The most prevalent power reactors are light water reactors (LWRs). These are reactors in which the "core" containing the fuel is cooled with water. The hydrogen in the water also slows (moderates) the fission neutrons produced by the nuclear reactor which allows it to operate using fuel having fissile material (^{235}U or plutonium) concentrations less than 10%. All U.S. power reactors are LWRs of which there are two variants:

- Pressurized-water reactors (PWRs) in which the water in the reactor vessel is under sufficiently high pressure so that it does not boil. Steam is generated in a heat exchanger and routed to the turbine generator.
- Boiling-water reactors (BWRs) in which the water in the reactor vessel is allowed to boil and the resulting steam is routed direction to the turbine generator.

A large amount of development has been carried out on an additional reactor type: fast reactors. These are reactors in which the core is cooled with a molten metal such as Na, Na/K, Bi, or Pb, or by helium gas. Because these elements are relatively heavy (or, in the case of He, having a low density) fission neutrons are not significantly slowed. Because the neutrons are not significantly slowed these reactors are known as "fast" reactors. Such reactors require fissile material concentrations around 20%. Relatively few of these reactors have operated but they are being further developed for future use in the U.S. and elsewhere.

Another much less common reactor type uses graphite-based fuels where the major constituent of the core is the graphite form of carbon. Most of these reactors are cooled by He but some designs have considered molten salt coolants such as mixtures of light-element fluorides. These reactors can operate at much higher temperatures than other reactor types and consequently are more thermodynamically efficient.

Fuel Fabrication

Conventional nuclear fuel fabrication involves converting enriched uranium to uranium dioxide powder and then going through a series of steps to produce pellets, elements, and assemblies. Fabrication is enriched uranium hexafluoride that is reacted to yield uranium dioxide powder that is pressed to form a fuel pellet suitable for constituting nuclear fuel (subject to inspection which yields scrap for recycle). A Zircaloy cladding tube is loaded with fuel pellets by sliding them into the tube by force and/or gravity. Helium is injected into the tube, a top end spring is inserted, and end plugs are welded in place. A "cage," composed of grid spacers and guide thimbles (tie rods), is constructed on a horizontal table. The fuel elements are then pushed into the cage. The end pieces (nozzles) are then attached. The resulting assembly is inspected and loaded into special carriers for transportation to the reactor.

MOX fuel

All mixed oxide (MOX) fuels made and used to-date have been composed oxides of uranium and plutonium. Such fuels have been irradiated in LWRs and fast reactors, primarily in Europe and Japan. The U.S. is building a plant at Savannah River that will convert plutonium metal from dismantled nuclear weapons to plutonium oxide to make fuel for U.S. LWRs. Test assemblies are presently being irradiated in U.S. LWRs. Advanced fuel cycles may add Np, Am, and/or Cm to the U-Pu oxides.

Sol-gel fuel

Sol-gel approaches to fuel fabrication have also been studied. They are liquid-based and, as a consequence, do not involve blending powders, thus producing a very homogeneous product. The process yields small spheres having a diameter of tens to a thousand microns.

Sol-gel spheres can then be made into a pellet fuel using a consolidation fabrication process called DIPRES. An alternative to DIPRES is the Sphere-Pac process in which spheres are sintered and made in three sizes designed when mixed to achieve maximum packing density. The spheres are simply mixed and poured into cladding tubes where "smear" densities of about 85% can be achieved. Sphere-Pac fabrication may be particularly useful in the manufacture of fuels containing high-activity actinides.

Advanced fuels

Advanced metal-clad fuels in which the fuel matrix is composed of actinide carbide, nitrides, and metals are being developed. Fabrication of carbides and nitrides is similar to that for oxide fuels with the exception that these fuels are very sensitive to the presence of oxygen and humidity and so must be fabricated under carefully controlled inert atmospheres. Fabrication development efforts are in their early stages. Metal matrix fuels have been made on a small scale for decades and irradiated in demonstration reactors such as EBR-I and II at Idaho National laboratory.

In reactors using graphite fuels the graphite serves as both a structural material that partially substitutes for metal cladding as well as being a neutron moderator. Two types of graphite-based fuels are under development: prismatic fuel assemblies for the high-temperature gas-cooled reactors.

Radiation effects

Neutron irradiation causes many changes in the fuel. Some of the most important changes are:

- Fissioning uranium and/or plutonium to produce energy and fission products. Fuel burnups[5] for PWRs and BWRs are now approaching 50 GWd/MTHM and 45 GWd/MTHM, respectively.
- Capturing neutrons to produce a variety of radionuclides
  - Other actinide isotopes:$^{232,\ 236}$U,^{237}Np, $^{238\text{-}242}$Pu, $^{241\text{-}243}$Am, ^{244}Cm (U-Pu fuel cycle) and ^{232,233}U (U-Th fuel cycle)
  - Radionuclides from activation of hardware
    - Main constituents: ^{60}Co (stainless steel and Inconel), ^{93}Zr (Zircaloy), ^{14}C (graphite)
    - Trace constituents: transuranics from U, ^{3}H from lithium, ^{14}C from nitrogen

Spent Fuel Reprocessing

Reprocessing used nuclear reactor fuel is undertaken to 1) recover valuable fissile constituents (primarily ^{235}U and plutonium) for subsequent reuse in recycle fuel; 2) reduce the volume of high-level waste (HLW) that must be placed in a geologic repository; and 3) recover special isotopes. There are two broad approaches to reprocessing: aqueous and electrochemical. The

---

[5] Burnup is a term used to express the amount of fuel that has been consumed as a result of the neutron irradiation it has received.

paper by Jubin covers aqueous reprocessing. Law's paper discusses liquid/liquid solvent extraction equipment. Goff's paper addresses non-aqueous reprocessing.

Aqueous reprocessing

There are two primary separation processes used in aqueous fuel reprocessing: solvent extraction and ion exchange. Aqueous reprocessing is a sequence of chemical and engineering steps carried out in acidic aqueous and organic solvents to separate desired materials from waste materials present in spent nuclear reactor fuel and to recover in a purified form the desired materials, specifically uranium and plutonium and perhaps a few other materials such as neptunium. This separation process is called solvent extraction. There are a number of process areas and equipment pieces required to carry out reprocessing by solvent extraction.

Solvent extraction

Solvent extraction has been utilized in numerous industrial applications, including the petroleum, hydrometallurgical, pharmaceutical, and nuclear industries. Solvent extraction involves bringing two immiscible phases into intimate contact, typically an aqueous phase and an organic phase. When this occurs, the extractable components will distribute between the two phases. Assuming sufficient contact time, equilibrium will be established between the two phases. The ratio of the concentrations in the resulting phases is referred to as the distribution coefficient, D, defined as

$$D_i = y_i / x_i,$$

where

y_i = concentration of constituent i in the organic phase and
x_i = concentration of constituent i in the aqueous phase .

Solvent extraction is a very versatile process that is easily adapted to multistage operations. This is highly desirable when very high purification is needed or when the properties of materials to be recovered are so similar that single-stage precipitation or crystallization would not result in acceptable separations. Ion exchange, which will be discussed later, can also be used to achieve high degrees of separation, but is generally best suited for situations where small quantities or low concentrations are involved and batch operation is acceptable.

Facilities

The facilities needed for aqueous reprocessing are: 1) spent fuel receiving and interim storage areas, 2) head-end operations hot cell and equipment, 3) solvent extraction hot cell and equipment, 4) solvent cleanup/recycle equipment, 4) off-gas treatment equipment, 5) uranium product storage area, 6) plutonium product storage area, 7) waste treatment area, and 8) waste storage and shipping areas.

Figure 2 is a greatly simplified flowsheet of the most widely used aqueous solvent extraction process, the Purex process. Although highly simplified it does show the principal reprocessing steps.

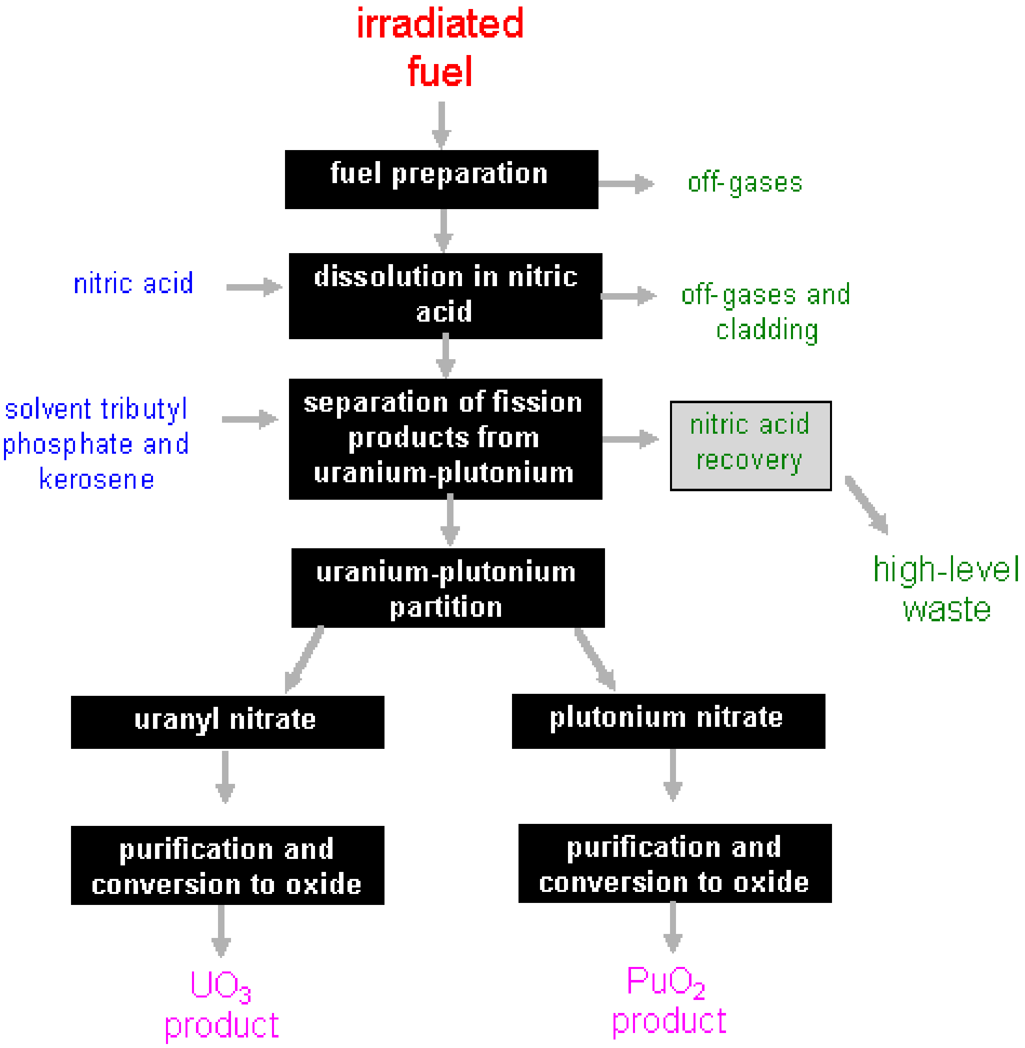


Figure 2. Simplified Purex Reprocessing Flowsheet

Solvent extraction contacting equipment has been extensively studied and employed for the past 50 years. Each type of equipment has been proven over many years of operation and each has inherent advantages and disadvantages. The type chosen for a particular process application should be based on several factors including: criticality, process (holdup) volume, process complexity (operability), reliability, maintenance philosophy, throughput, costs and performance such as solvent exposure (contact time), solids tolerance, flow rates, equilibrium upset resistance, and process kinetics. A summary of comparisons of various types of contactors is shown in Table 3.

Table 3. Comparison of Mixer-Settler, Pulse Column and Centrifugal Contactors

	Ratings[a]			
Criteria	**Mixer-settler**	**Pulse Column**	**Centrifugal Contactor**	**Comments**
Long residence time[b]	5	4	1	
Short residence time[c]	1	2	5	
Hot cell headroom	5	1	5	
Floor space required	1	5	3	May be small percentage of total floor area.
Instrumentation/control	5	4	5	
Ease of scale-up	3	3	5	
Low hold-up volume	2	3	5	
Equipment reliability	4	5	3	
Equipment capital cost	4	5	4	May be insignificant in relation to building cost.
Process flexibility[d]	4	3	5	
High throughput	2	5	5	Based on criticality safe by geometry equipment.
Solids tolerance	2	5	2	
Rapid steady state	2	3	5	
Rapid restart	5	2	5	After temporary shutdown.

a. 5 = superior, 4 = good, 3 = average, 2 = below average, 1 = poor.
b. Considered an advantage when process chemistry requires long residence time.
c. Considered an advantage when solvent degradation is a concern.
d. Process flexibility includes such factors as the range of organic-to-aqueous (O/A) flow ratio, the "turndown" in flow rate, and the ease with which the location of feed and product streams can be changed.

Non-aqueous reprocessing

Although there are many non-aqueous reprocessing methods, for the purposes of this discussion non-aqueous reprocessing is restricted to pyrochemical reprocessing.

Pyrochemical methods

Pyrochemical reprocessing methods use high-temperature oxidation/reduction reactions in non-aqueous media to separate the actinides, especially uranium and plutonium, from the fission products. These methods exploit the differences in both the volatilities and thermodynamic chemical activities of compounds of actinides and fission products to achieve the separation.

Pyrochemical separations can be achieved by using electrochemical methods instead of or in addition to chemical equilibrations.

Development of electrochemical treatment of spent fuel is focused on recovery of transuranium elements as a group. Because of the chemical similarity of the rare earth fission products with the transuranium elements, a portion of these and some uranium are also recovered with the transuranium elements. This product will have a significant radiation field associated with it so that fabrication of fuel for recycle will have to be performed remotely in a hot cell. This aspect of the technology provides a potential nonproliferation benefit.

Pyrochemical technologies offer some potential advantages compared to traditional aqueous separation technologies like Purex. The solvents used in non-aqueous technologies are typically fused salts and so are not subject to radiation damage. Larger quantities of fissile material can be handled in a single operation, since water, a neutron moderator, is not present. These technologies are potentially more compact than aqueous technologies. However, the equipment is typically batch equipment, and consequently pyro-processes do not have the important advantage of continuous operation that aqueous processes have. Pyrochemical technologies have typically resulted in incomplete separation of fissile material from fission products and transuranium elements

The attributes of pyrochemical technologies have made them good candidates to recycle fast reactor fuels, which generally have higher radiation fields than LWRs due to increased burnups and have much higher fissile material concentrations. In general they are not suitable as separation technologies for recycle of fuel to thermal reactors because they do not remove enough of the fission products that act as neutron poisons in a thermal spectrum. These fission products are not neutron poisons in a fast neutron spectrum.

Volatilization

Volatilization is an important class of non-aqueous separations technology. Volatilization takes advantage of the different vapor pressures of the elements or compounds in spent nuclear fuel. In general, the fuel is heated to release gaseous fission products, and when taken to even higher temperatures, some of the more volatile fission products like cesium and technetium can also be removed. This process is called “voloxidation.”

The volatility of the halides of many elements is a separation technology that has been used. Halides (typically fluorides or chlorides) can form volatile compounds of the actinides, most notably UF_6. By converting spent fuel into halides, the actinide halides can be separated from the bulk of the fission products as gases. This technology works best in systems that are primarily uranium based. The volatility of $ZrCl_4$ has been used to separate and purify zirconium which is used as fuel cladding in LWR fuel manufacture.

Management of Nuclear Waste

Nuclear wastes are a nettlesome problem and, along with reprocessing, their treatment, management and disposal comprise what is called the “back end” of the fuel cycle. The papers by Gilbertson and Viena address nuclear waste management. Gilbertson addresses the broad issues related to waste management in a national sense from a DOE Environmental Management (DOE/EM) perspective. Viena’s paper is more tightly focused and addresses problems related to waste classifications and treatment methods related specifically to waste forms for reprocessing wastes.

Broad waste management issues

DOE/EM was established to provide environmental remediation clean-up along with potential energy solutions for the future. At the time of its creation waste management and clean-up activities were occurring at more than 137 contaminated installations in 34 states and territories. At these installations there were 3,700 specific sites with more than 10,500 hectares with hazardous or contaminated surface or groundwater, soil, or structures, and the number was growing as new sites were defined. In addition, 500 surplus facilities awaited decontamination and decommissioning and approximately 5,000 peripheral properties (residences, businesses) had soil contaminated with uranium tailings. Re-establishment of reprocessing in the U.S. will add to the wastes to be managed in the future. Regardless of the reprocessing method chosen for reactor spent fuel there will be radioactive and non-radioactive wastes produced. Processes, waste forms, and waste management approaches must be available to deal with them.

In the US radioactive wastes are defined according to level of radioactivity and type of radioactivity and other materials present. Radioactive wastes are classified into the following categories: high-level wastes (HLW), low-level waste (LLW), greater than Class C waste (GTCC), transuranic waste (TRU) and mixed waste. Following is a brief discussion of the waste categories.

HLW

HLW is defined from the source of waste rather than the radioactivity. The source includes the waste resulting from the first cycle raffinate of spent nuclear fuel (SNF) reprocessing. The *Nuclear Waste Policy Act of 1982* defines spent nuclear fuel as fuel that has been withdrawn from a nuclear reactor following irradiation, the constituent elements of which have not been separated by reprocessing. The act requires that both spent nuclear fuel and high-level waste be disposed by deep geologic burial.

LLW

LLW is classified either as Class A, B, or C. Class A is the least radioactive and Class C the most. Class C waste is LLW that not only must meet more rigorous requirements on waste form than classes A or B to ensure stability but also requires additional measures at the disposal facility to protect against inadvertent intrusion. Waste that is not generally acceptable for near-surface disposal is waste for which form and disposal methods must be different, and in general more stringent, than those specified for Class C waste. In the absence of specific requirements such waste must be disposed of in a geologic repository unless proposal for disposal of such waste in a disposal site is approved by the Nuclear Regulatory Commission.

GTCC

Those materials that exceed Class C activity levels, but do not meet the source definition for HLW, are known as greater-than-class C wastes (GTCC). There is no clearly defined regulation for its disposal.

Transuranic

If waste contains more than 100 nanocuries per gram of alpha-emitting isotopes with atomic numbers greater than uranium (92) and with half-lives greater than 20 years it is classified as transuranic waste and must be treated and disposed of according to NRC regulations for that type of waste. If the combined beta, gamma, and neutron dose rate anywhere on the surface of a TRU waste container exceeds 200 millirems (0.002 sieverts) per hour it is designated "remote-handled," (RH-TRU) waste and remote handling methods are required for worker protection. Otherwise it is called “contact-handled” (CH-TRU).

Mixed

The final category of radioactive wastes is mixed wastes, defined as “…any hazardous waste containing radioactive waste.” It is a low-dose, high volume waste type.

Vitrification

The *Nuclear Waste Policy Act of* 1982 requires that the disposal path for high-level waste should be vitrification followed by burial in a deep geological repository. Vitrification, incorporation of waste in a glass matrix, is widely recognized and accepted throughout the world. The *Resource Conservation and Recovery Act* (RCRA) lists vitrification as the only means of safely storing, transporting, and disposing of high-level radioactive waste.

Vitrification of wastes into borosilicate glass is the current baseline technology for HLW treatment in the U.S. and in most countries conducting spent fuel reprocessing. DOE has been vitrifying high-level waste successfully at the Savannah River site in the Defense Waste Processing Facility for more than a decade.

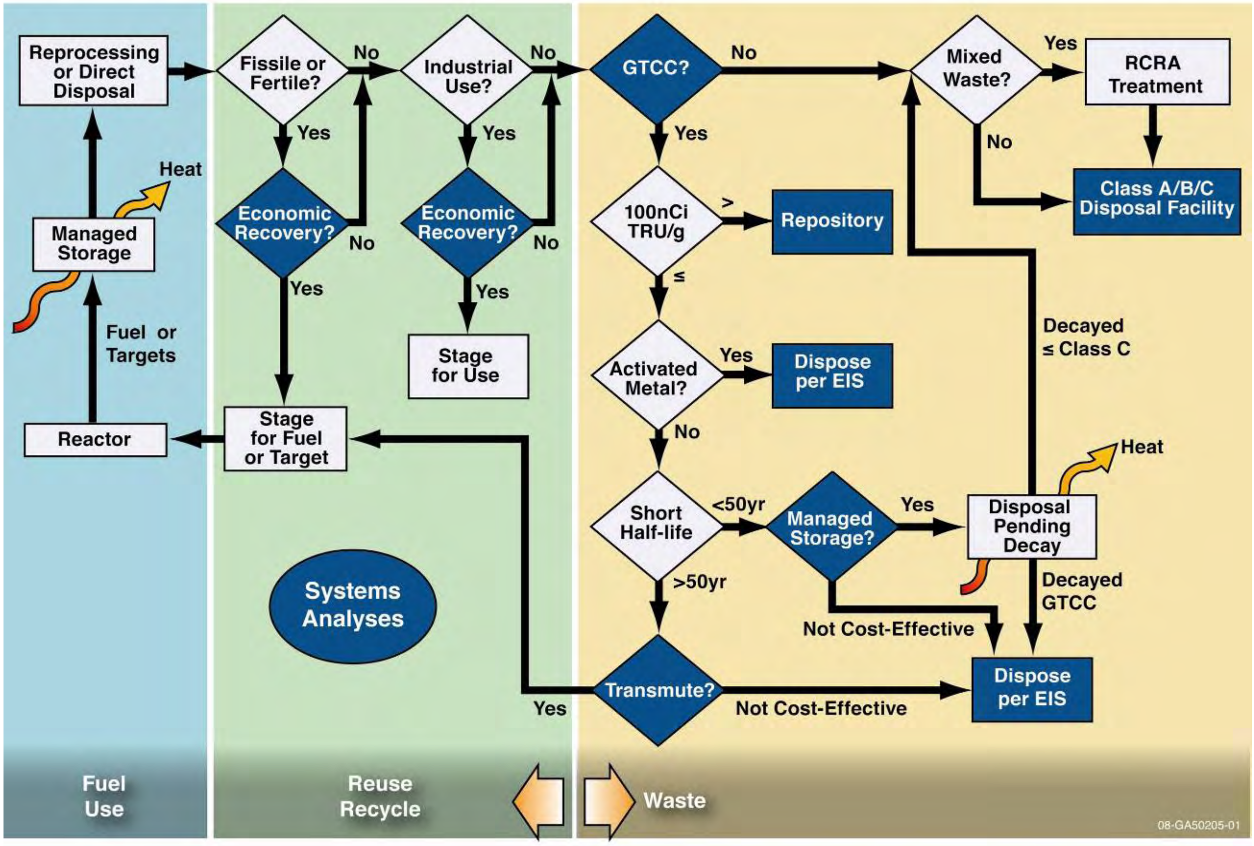
This process and waste form was selected based on the following attributes:

- continuous, high-throughput, operation of glass melters
- acceptable solubility of waste components in the glass, i.e., acceptable waste loading
- tolerance of the waste form to variations in waste composition
- low raw materials costs
- durable waste form
- technology based on extensive commercial application of glass fabrication
- resistance to damage from radiation and radioactive decay

Waste management philosophy

Figure 3 illustrates the general philosophy proposed to evaluate waste management. The philosophy is four-fold: 1) promote the reuse of materials if economically viable (considering waste management costs as part of the economic evaluation), 2) classify wastes on a risk basis, 3) develop disposal systems for classes of waste with radioactive risks described by the classification, and 4) allow all wastes within a risk classification to be disposed of in facilities designed to protect against those risks.

Figure 3. Integrated Waste Management Strategy Logic Diagram



Nuclear Radiation

The paper by Sindelar addresses the important issue of nuclear radiation. The nuclear fuel cycle has radiation as an integral component of nearly all of its parts. Protection of workers and the public from adverse effects of radiation is a very important requirement of all aspects of nuclear separations activities as well as management of all parts of the fuel cycle.

Radiation comes both as electromagnetic radiation and as particulate radiation. Electromagnetic radiation may be present at frequencies from that of soft x-rays to the very high frequencies of gamma radiation. Particulate radiation may be electrons, alpha particles, neutrons, and positrons.

The effects of radiation must be considered in the design of a nuclear materials separations facility in terms of:

- personnel exposure;
- adverse effects on the chemical processes; and
- degradation of the materials of construction.

Shielding against ionizing radiation must be provided in separations facilities for spent nuclear fuel due to the attendant radiation from radioisotopes produced via fission or neutron capture reactions during irradiation of the fuel. Properties of radiation, simplified shielding approaches, and hazards are given in Table 4. The table indicates that, without shielding, gamma and neutron radiation travel hundreds of feet in air.

Table 4. Range in air and shielding for various ionizing radiation sources

Type of Ionizing Radiation	**Characteristics**	**Range in Air**	**Shield**	**Hazards**	**Source**
Alpha	**Large mass, +2 charge**	**Very short, 1- 2 inches**	**Paper, skin**	**Internal**	**Pu, U**
Beta	**Small mass, -1 charge**	**Short, 10 feet**	**Plastic, glass, metal**	**Internal, external skin & eyes**	**Fission & activation products**
Gamma/x-ray	**No mass or charge, photon**	**Several 100 feet**	**Lead, steel, concrete**	**Whole Body internal or external**	**Fission & activation products**
Neutron	**Mass, no charge**	**Several 100 feet**	**Water, concrete, plastic**	**Whole Body internal or external**	**Cf, neutron sources**

Radiolysis

Radiolysis, the molecular breakdown of a material as a result of radiation absorbed dose, can strongly and adversely affect chemical separations processes. The radiolytic production rate of species is characterized by the G-value, that is, the number of molecules of the species produced per 100 eV of absorbed energy. The G-value is typically dependent on the radiation type. Radiation that deposits its energy in a short linear path of material is referred to as high Linear Energy Transfer (LET) radiation whereas particles, or gamma rays, that deposit their energy along a greater length in a material are low LET radiation.

Tri-n-butyl-phosphate

Any proposed separations process should be thoroughly reviewed, and any new process should be evaluated for radiolysis issues prior to full operations to ensure process conditions are as expected and are manageable. Tri-*n*-butyl Phosphate (TBP) is an ester used widely in solvent extraction in the PUREX process. Consequently it has been studied extensively. Both chemical (hydrolytic) and radiolytic reactions can decompose TBP. The degradation products from the radiolysis of TBP, wet or dry, include HDBP, H_2MBP, H_3PO_4, H_2, CH_4, C_2H_4, C_2H_6, C_4H_9OH, and other hydrocarbons. Of these, HDBP has the greatest product yield and has the largest adverse effect on separations. HDBP production is greater in anhydrous condition (G = 3) compared to the water-saturated condition (G = 1.8). The presence of degradation products such as HDBP has an adverse effect on the Purex separations because it reacts with the sought after products (U and Pu) and fission products preventing good separations.

Figure 4 shows the deleterious effects of both hydrolysis and radiolysis on plutonium extraction at 80°C expressed as the rate in grams of Pu complexation by degradation products. The presumption is that complexed plutonium will not be extracted into TBP and consequently will be lost to the waste stream.

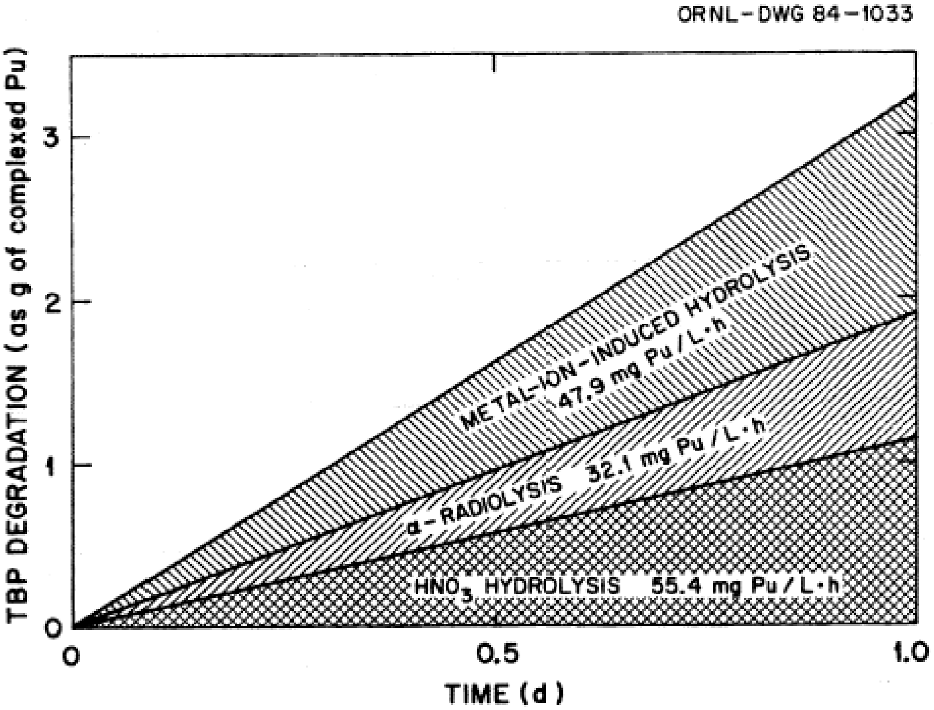


Figure 4. TBP degradation rates due to acid hydrolysis, alpha radiolysis, and metal-ion-induced hydrolysis at 80°C

Ion exchange resins

Organic ion exchange resins are used extensively in separations processes. Resins lose ion exchange capacity and may evolve gas when exposed to radiation. Doses of 10^5 to 10^6 Gy are significant to synthetic organic ion exchangers. Poly-condensation-type ion exchange resins are resistant to radiation damage, but the overall radiation-resistant properties of this type of ion exchange media are poor.

Polymers and steel

Both polymers and austenitic stainless steel are important materials for gaskets and valve seats and process equipment (tanks, valves, piping), respectively in separations processing equipment.

The irradiation effects in polymers that are important for seals in separations processing equipment include loss of sealing ability, gas evolution, and increased leachability of constituents or loss of chemical resistance of the polymer. Factors important to cause radiation effects in polymers are the total dose (in rads), the dose rate, and the presence of O_2. Most polymers are susceptible to degradation via oxidation of the resinous molecules.

Austenitic stainless steels are typically used as the materials of construction for piping and process vessels. These materials are subject to radiation hardening and embrittlement through formation of small “black spot” damage at low irradiation temperatures ($T_{irradiation} < 0.3\ T_{m.p.}$). The black spot damage, small extend defects in the crystalline structure of the stainless steel, consists of small dislocation loops, stacking fault tetrahedral or vacancy/interstitial clusters that are formed directly following the creation of displacement cascades by primary knock-on atoms (PKAs). The PKAs are themselves created by the incident particle (e.g., neutron). Only extremely low levels of displacement damage would be expected over the lifetime of process equipment. Radiation damage to process equipment is not considered significant to stainless steels subjected to attendant radiation in the separations processing.

Sorbent Synthesis and Column Separations

The paper by Tavlarides deals with two important aspects of nuclear separations: development of new separations materials and separations carried out in columns. It is important to continue to develop new materials that are more efficient and more economical than existing materials. The history of nuclear separations is replete with innovations in separations reagents and materials that have enabled progress to meet the ever more stringent separations demands.

Sol-gel processes are especially well suited for the preparation of “tailored” separations reagents. As noted earlier sol-gel processes have found application in preparing HTGR fuels. Many of the most important nuclear separations are carried out in columns so it is important to have at least a rudimentary understanding of how they work.

An often overlooked separations area is the separation of non-radioactive elements from process streams of various types. A very good example of this type of separation is removal of mercury from a variety of wastes and polluted aqueous systems. Very large amounts of mercury are present in such diverse places as HLW storage tanks at the weapons production plants and in pools of water where it has collected during lithium isotope separation at the Y-12 plant in Oak Ridge.

Sol-gel sorbents

The ability of many metallic elements to form oxy-hydroxide-hydrated bridges that connect the metals in an endless connected array is the basis of the formation of sols that that can subsequently be gelled by dehydration. Dehydration can be achieved by any of a number of means ranging from simple heating to extraction of water into a liquid that is immiscible with the sol. In some cases the gels themselves can be made from metals that have separations properties. In other cases various complexation and chelating agents chosen for separation of specific elements can be incorporated in the gels. In this way a large number of gels have been prepared for use in sequestering toxic elements such as mercury.

Column separations

Column separations are generally carried out in vertical tubes filled with liquids or solids that react when placed in contact with flowing liquids containing materials to isolate substances whose separation and purification is sought. The range in columns sizes may be very large, both in diameter and length. Law has discussed the use of pulse columns in separations processes. A common type of column is one filled with ion exchange resins such as is used in the purification of plutonium present as the anionic nitrate complex. There is a well developed literature on the theory of column operation. One of the most useful aspects of separations using columns is the presence of many separations stages in a single column. In the case of uranium isotope separation a one-meter long column may have as many as 1000 stages, each about one millimeter long. In this case it is necessary to fill the column with very small resin particles to reduce the time to reach equilibrium in a single stage to about one second.

Modeling and Simulation of Nuclear Fuel Recycling Systems

The paper by DePaoli discusses the status of computer codes for modeling nuclear systems, especially as they relate to sent fuel reprocessing. Use of such codes has the potential to greatly reduce the time and cost of developing reprocessing systems and improving proliferation resistance of fuel cycle plants.

Computing power has grown tremendously over the past several decades, as has the capability of scientific codes to simulate complex systems. This growth, coupled with increased interest in nuclear power, provides a great opportunity for the application of advanced modeling and simulation to aid in development of future nuclear energy systems.

Expected potential benefits of modeling and simulation of nuclear reprocessing systems include:

- Reduced cost of process development by guiding and minimizing the amount of laboratory experimental and pilot plant work
- Optimized system designs, with technically supported reduced design safety margins
- Development of improved or new chemical separations processes with lower cost and waste generation
- Reduced risk of material diversion by providing accurate predictions of materials streams

While it is understood that modeling and simulation will not supplant experimental testing, the value of modeling and simulation has long been recognized for in the development, design, and operation of reprocessing systems. The following potential uses are envisioned for a process simulator of a full reprocessing plant:

- Operator training
- Plant licensing
- Safeguards studies
- Process and/or chemical flowsheet design confirmation
- Safety studies
- Process diagnostics
- Process monitoring
- Sensitivity studies
- Modeling destination of minor streams having environmental impact
- Process instrumentation studies
- Surge capacity studies

Modeling an aqueous reprocessing plant to a sufficient level of realism to accomplish the tasks listed above is a significant undertaking.

There has been little relevant work in the United States over the past two decades in developing advanced modeling and simulation tools for reprocessing systems. There are only two simulation codes, SEPHIS and SOLVEX, with dynamic capability that are validated to any significant degree against actual operating data from fuel separation processes. Each of these codes has significant limitations.

Current reprocessing models provide only qualitative or semi-quantitative predictions of process performance. Empirical models of chemical behavior for major components are used to provide overall descriptions of various reprocessing strategies. Many species are not modeled well, or not at all. The models usually assume chemical equilibrium conditions are met instantly, and do not sufficiently incorporate mass transfer and reaction kinetics. Very few reaction rate constants are known, and where transient conditions are simulated, they are often assumed or selected heuristically. The current models are unable to answer many questions involving inter-phase transport and equilibria, such as precipitation from solution, micelle formation, third-phase formation, radiolysis, and do not address oxidation states where multiple possibilities exist. Hence, in order to support both detailed plant process design and safe operation, the improvement of reprocessing models requires improved chemistry modeling, including both equilibria and kinetics.

The development of new processes that can produce fuel and waste form materials meeting stringent specifications while also meeting environmental, safety, accountability, and cost constraints demands the development and use of modern, sophisticated modeling tools in concert with experimental development and testing for the design and optimization of reprocessing systems.

Molecular-level modeling has advanced to a point where it can provide valuable contributions to the development of separations systems. The simulation of molecular-level transport processes near interfaces is an example of an important area where progress in modeling may translate into practical understanding of the performance of separations processes.

Quantifying the Risk of Nuclear Fuel Recycling Facilities

This paper by Garrick and Gekler examines the status of nuclear facility safety analysis and how risk-informed safety analysis might be applied to nuclear fuel recycling facilities. Any decision to apply Quantitative Risk Assessment (QRA) to nuclear fuel recycling must be accompanied by the decision of which Quantitative risk assessment approach best serves the needs of the particular problem.

The primary advantages of a QRA are completeness, context, and realism; completeness, in the sense that all of the scenarios that can threaten the performance of the system are in principle considered, and context in the sense that the likelihood of the scenario, including its consequence, is part of the answer.

It may not be possible to manifest all of the scenarios that represent a threat to the system, but it is usually possible to account for the important ones. Similarly, it may not be possible to calculate absolute likelihoods (e.g., probabilities), but by embracing the concept of uncertainty in the “likelihood functions” the confidence in the likelihoods can be manifested.

The fundamentals of the QRA approach involve the following basic steps:

Step 1. Define the system being analyzed in terms of what constitutes normal operation to serve as a baseline reference point.

Step 2. Identify and characterize the sources of danger, that is, the hazards (e.g., stored energy, toxic substances, hazardous materials, acts of nature, sabotage, terrorism, equipment failure, combinations of each, etc.).

Step 3. Develop “what can go wrong” scenarios to establish levels of damage (consequences) while identifying points of vulnerability.

Step 4. Quantify the likelihoods of the different scenarios and their attendant levels of damage based on the totality of relevant evidence available.

Step 5. Assemble the scenarios according to damage levels, and cast the results into the appropriate risk curves and risk priorities.
Step 6. Interpret the results to guide the risk management process.

The general framework for QRA is the "set of triplets" definition of risk.

$$R = \{<S_i, L_i, X_i>\}_c,$$

In this format, the inner brackets enclose the triplet, the outer brackets denote "the set of", and the subscript c implies that the set is complete. The risk ("R") is a comprehensive answer to the following questions, which constitute the set of triplets:

- "*What can go wrong*?" This question is answered by describing a structured, organized, and complete set of possible damage scenarios ("S").
- "*What is the likelihood of each scenario*?" This question is answered by performing detailed analyses of each risk scenario, using the best available data and engineering knowledge of the relevant processes, and explicitly accounting for all sources of uncertainty that contribute to the scenario likelihood ("L").
- "*What are the consequences*?" This question is answered by systematically describing the possible end states, including the damage states, such as different radiation dose levels that may be received by a member of the public ("X").

The location and operating conditions are major factors in determining the threats to any facility. Some threats may cause a direct release of radioactive materials from the facility, while others may initiate a sequence of events that unless mitigated will result in such releases. Some threats may alter the site in ways that increase its vulnerability to other threats: e.g., loss of essential support services or events that could alter natural protective barriers of the site. Potential conditions that may affect the site are often grouped into two general categories.

- *Disruptive Events*. These are unexpected events that may cause an immediate change to the site or the facility. They are typically characterized by an event occurrence frequency and by directly measurable immediate consequences. Examples are severe storms, tornadoes, earthquakes, fires, and airplane crashes.
- *Nominal Events and Processes*. These are expected events and processes that evolve continuously over the life of the facility. They are typically characterized by a rate, which may be constant or changing over time. The potential consequences from these processes depend on the duration of the exposure period. Examples are the aging and degradation of engineered systems.

Given the events or conditions that could disturb any of the functions necessary for system success (usually labeled *initiating events or initial conditions*), what is the sequence of events to the final damage states of the individual scenarios? The damage states may take many forms from radiation release mechanisms to radiation dose and from physical damage to the plant and human injuries and fatalities. The total process is illustrated in Figure 5.

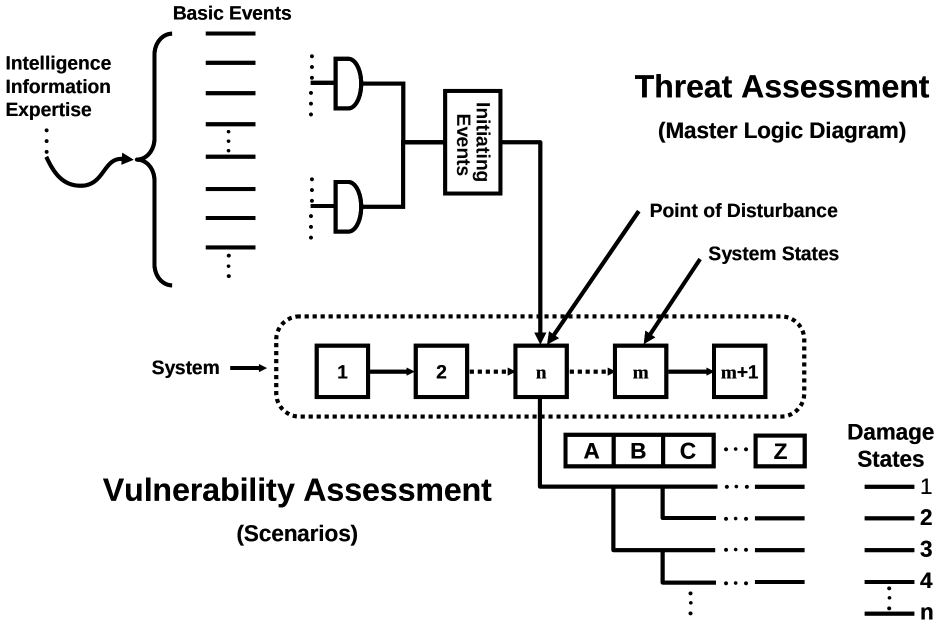


Figure 5. The Concept of Linking System Disturbances to System Damage States

A QRA of a complex system such as a nuclear fuel recycling plant may end up having hundreds, thousands, or possibly even millions of individual scenarios, each scenario represented by a probability of frequency curve.

The most important result from a QRA is full exposure of the contributors to the risk and their relative importance.

Environmental Transport

The paper by Higley addresses the transport of radioactive material through the environment. This is a very important issue and one that is as complex as the environment itself. Knowledge of transport processes, both in time and space, is vital to the licensing process for a facility containing radioactivity as well as to carrying out transport modeling studies.

Direct discharges of radioactivity are constrained by regulation; and indirect discharges are limited through the design of radioactive waste storage and disposal facilities. The radiation protection dose limits drive the design of both operating facilities and radioactive disposal sites. These protection limits compel us to understand how radionuclides are transported through the environment. We need this knowledge so that we can ensure our engineered systems are designed to control radioactive discharges. Figure 6 illustrates this concept.

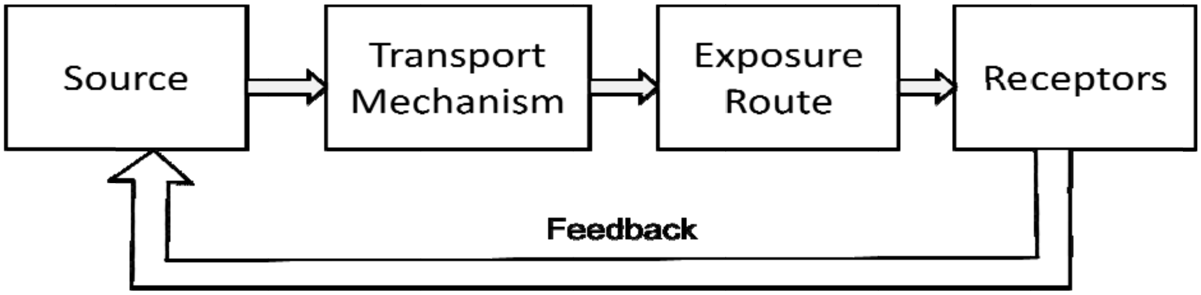


Figure 6. How environmental transport fits within the larger context of radiation protection

Transport processes can be this simple, or they can be extremely varied and complex. One approach that simplifies understanding environmental transport of radionuclides is to divide physical regions that contain the source into “near” and “far” field. These are arbitrary designations, but allow separating some important processes for consideration.
The near field is defined such that it encompasses the origin of the radioactive material (called the source or source term). We can also include in this region any engineered barrier system that is built surrounding or including the source.

The “far” field, includes the undisturbed environment surrounding the near field. It may, by design, include any naturally occurring barriers to transport. The “biosphere” (the near surface area of the earth that contains life) may be included for this particular instance. Depending on the transport scenario being considered, the definitions of near and far field may vary, and the biosphere may be a part of both zones.

One of the considerations for understanding how radioactive material moves through the environment is understanding the conditions of its release. In prospective analysis there are a number of options which can be considered. Is a catastrophic event responsible for quickly moving the material out of its initial condition? Is it a chronic release? How should degradation of the form of the material and its surroundings be addressed?

In retrospective analyses, presumably the release mechanism is known, although accurately describing it may be difficult. In some ongoing radioactivity discharges, the release mechanism may be specified by regulation (e.g., direct discharge through a stack or pipe discharge).

Barriers

Release and transport of radionuclides is often controlled through the use of barriers which are generally of two types: natural and engineered. Engineered barriers are designed to delay, direct, and generally control the release of radioactive materials such that they can be safely contained for some desired period of time. They can, for example be relatively simply systems, such as those that are designed to cover tailings piles in order to minimize radon gas release rates and to control erosion.

Natural barriers are a significant (and in some cases the primary) means of controlling radionuclide release. Features of the natural environment include the ability of the soil or rock to sorb radionuclide or chemical constituents. Clay soils are often used because of their low hydraulic conductivity and their affinity for some important radionuclides. Sites can be selected based on environmental considerations such as the absence of rainfall, type of native vegetative cover, and range of expected temperatures. The surface topography such as low slopes to minimize erosion may also be a factor. Depth to groundwater and distance to streams, rivers and lakes may also be an important factor.

Near field

Environmental transport in the near field can be the result of physical, chemical, and biotic processes. Water, either from surface infiltration or from subsurface systems is considered one of the principal means for mobilizing radionuclides. Issues that have to be considered include multiphase systems (gas, liquid, vapor), fractures in the host rock, porous rocks, chemical interactions with the host matrix, moisture flow as a consequence of heating from the waste forms, mechanical stresses, and radiation-induced physicol-chemical processes (such as gas evolution). Other issues that have to be dealt with include the water balance, and the depth of the unsaturated and saturated zones.

Far field

The far field is outside the engineered and altered natural environment which contains the source of radionuclides. Most of the processes contributing to near field transport also occur in the far field. Inhomogeneities in the far field can pose challenges equally to or more vexing than those presented in the near field. The structure of the receiving environment can be extremely complex, making the potential transport paths to the biosphere difficult to ascertain (or to model).

There may be multiple pathways of transport which may contribute to the exposure and dose of receptors (e.g., humans and other biota). A conceptual diagram that illustrates this process is shown below in Figure 7. It is incorrect to assume that the processes responsible for moving the radionuclide through the far-field are simpler than those operating in the near field.   While the underlying physico/chemical interactions are generally understood, data are lacking for specific nuclides for a number of the processes represented by the transfer arrows in the figure. As a consequence, predictions of transport are often based on the use of surrogates or the presumption of chemical behavior of the radionuclides.

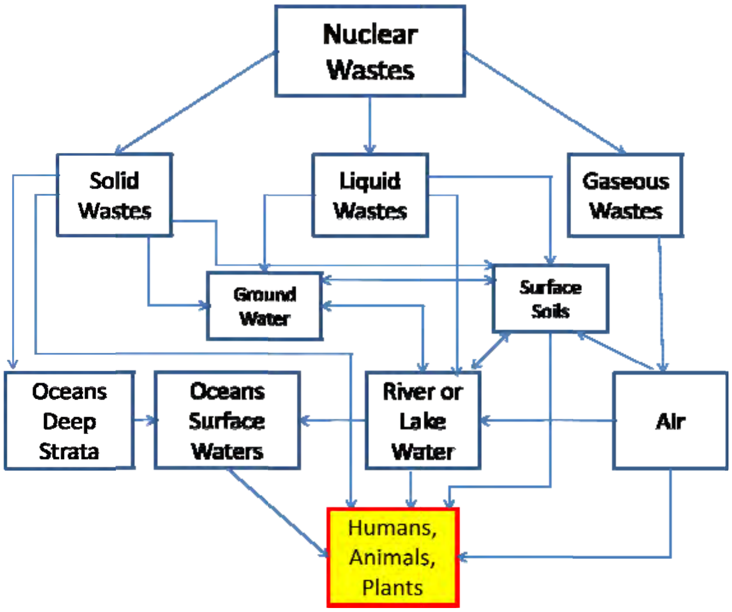


Figure 7. Simplified conceptual model of environmental transport pathways through the far field into the biosphere.

Nuclear Non-proliferation

The paper by Atkins-Duffin discusses non-proliferation and gives background on U.S. and international efforts to forestall or prevent proliferation of nuclear weapons made from highly enriched uranium or plutonium produced by reprocessing irradiated nuclear reactor fuel
Proliferation has been a concern from the beginning of the nuclear era and nuclear weapons proliferation has indeed taken place, although the world has not seen since World War II one nation or group use a nuclear weapon against another nation or group. This remarkable achievement is due in large measure to the leadership of the U.S. in aggressively pursuing and supporting non-proliferation initiatives worldwide.

In addition to the five "weapons states" (U.S., Russia, Great Britain, France and China) India, Pakistan, North Korea, and Israel are known to possess nuclear weapons and to have tested them, and several other nations have or probably soon will have them.

Most of the current non-proliferation efforts are directed at preventing non-weapons nations from obtaining the wherewithal to produce or obtain enriched uranium or plutonium, or from obtaining weapons already produced. Organizations established and actions taken to achieve this goal are discussed below.

IAEA (International Atomic Energy Agency)

The IAEA was created by the "Statute of the IAEA" in 1957 in response to Eisenhower's call for an international body to promote peaceful use of nuclear energy. The main functions of the IAEA are to:

- Encourage and assist research, development and practical application of atomic energy for peaceful uses throughout the world;
- Establish and administer safeguards designed to ensure that such activity assisted by the Agency is not used to further any military purpose;
- Apply safeguards to relevant activities at the request of Member States;
- Apply, under the Nuclear Non-Proliferation Treaty and other international treaties, mandatory comprehensive safeguards in non-nuclear weapon States Party to such treaties.

There are about 140 member states; the Secretariat is located in Vienna, Austria. The
IAEA is an independent international agency related to the United Nations (UN) and reports annually to the UN General Assembly and to its Security Council, as needed.

NPT (Nuclear Non-proliferation Treaty)

Then Nuclear Nonproliferation Treaty is a multilateral, indefinite-term treaty whose obligations are to see that the following restrictions are met:

- Nuclear weapon states (NWS) are not to transfer to any recipient whatsoever nuclear weapons or other nuclear explosive devices and not to assist, encourage, or induce any non-nuclear weapon states (NNWS) to manufacture or otherwise acquire them.
- NNWS are not to receive nuclear weapons or other nuclear explosive devices from any transferor, and not to manufacture or acquire them.

- NNWS must place all nuclear materials in all peaceful nuclear activities under IAEA safeguards.
- All Parties are obligated to facilitate and participate in the exchange of equipment, materials, and scientific and technological information for the peaceful uses of nuclear energy.
- All Parties must pursue negotiations in good faith on effective measures relating to the cessation of the nuclear arms race and to nuclear disarmament under strict and effective international control.

The NPT was signed on July 1, 1964 and entered into force on March 5, 1970. There are 189 parties to the Treaty. Three states with nuclear weapons, India, Israel, and Pakistan, have declined to sign the treaty and North Korea, who signed in 1985, withdrew from the treaty in 2003.

Zangger Committee

The Zangger Committee began work in 1971 to draft a list of items that would “trigger” IAEA safeguards if supplied by NPT parties to any non-nuclear weapons state. The list included:

- Source or special fissionable materials
- Equipment of materials especially designed or prepared for the processing, use, or production of special fissionable materials

and establishes three conditions of supply:

- A non-explosive use assurance
- An IAEA safeguards requirement
- A retransfer provision that requires the receiving state to apply the same conditions when re-exporting these items

The list was published in 1974 as IAEA INFCIRC/209. Since that time additional items have been added to the list:

- Heavy water production equipment
- Clarification on zirconium
- Isotope separation by the gas centrifuge process
- Clarification on reprocessing plants
- Clarification on isotope separation plant equipment from gaseous diffusion method

The Committee meets twice yearly.

Comprehensive Safeguards Agreements (CSA)

The Comprehensive Safeguard Agreements (INFCIRC/153) were established as “implementing instructions” to the NPT. They establish verification measures to assess the correctness and completeness of a State’s declared nuclear material and nuclear related activities. Permitted activities include on-site inspections, visits, and ongoing monitoring and evaluation. The principals involved are largely based on nuclear materials accountancy, complemented by containment and surveillance techniques, such as tamper-proof seals and cameras installed by the IAEA.

Additionally the confidentiality of the information obtained by the IAEA is established. The CSA requires the protection of commercial and industrial secrets and requires the IAEA to regime, including classification levels, markings, and physical protection.

Additional Protocol (AP)

Further implementing instructions are set out in the Additional Protocol (AP) (INFCIRC/540) which established new legal authority for strengthened IAEA inspection capabilities. This protocol grants the IAEA expanded rights (complementary access) to provide assurances about both declared and undeclared activities. Included in this additional information is declaration of exempted, terminated, and pre-safeguards material; all activities at sites of nuclear facilities; and nuclear fuel cycle infrastructure not involving nuclear material. Inspectors are granted broader access on nuclear sites and access to information about a wider range of about nuclear materials.

The US has recently signed the AP and the articles will be deposited in Vienna, Austria. As of January 1, 2009 the AP will be in force domestically. The US is currently in the process of making its first declaration under this Protocol.

The Nuclear Suppliers Group (NSG) intends to ensure that nuclear trade for peaceful purposes does not contribute to the proliferation of nuclear weapons or other nuclear explosive devices, while not hindering international trade and cooperation in the nuclear field. This is achieved by the implementation of two sets of guidelines (INFCIRC/254) for nuclear exports and nuclear-related exports. The first set of guidelines governs the export of items that are especially designed or prepared for nuclear use:

- Nuclear material
- Nuclear reactors and equipment
- Non-nuclear material for reactors
- Plant and equipment for the reprocessing, enrichment, and conversion of nuclear material and for fuel fabrication and heavy water production
- Technology associated with each of the above

The second set of guidelines governs the export of nuclear-related dual-use items and technologies, which could make a significant contribution to an unsafeguarded nuclear fuel cycle or nuclear explosive activity.

The NSG and the Zangger Committee differ in the content of their trigger lists, especially on items related to designed or prepared items and in the export conditions for the items on the lists. A major difference is the arrangement covering exports of dual-use items. Dual use items cannot be defined as especially designed or prepared items and therefore, are outside the scope of the Zangger Committee’s efforts but are an important part of the NSG guidance.

Proliferation Safety Initiative (PSI)

The Proliferation Security Initiative was announced by U.S. President Bush in May 2003. This initiative grew from the pursuit of new agreements on the search of planes and ships carrying suspect cargo and seizure of illegal weapons or missile technologies. The Initiative seeks to develop partnerships of states working together, employing their national capabilities to develop a broad range of legal, diplomatic, economic, military and other tools to interdict threatening shipments of Weapons of Mass Destruction (WMD) and missile-related equipment and technologies via air, land, and sea. The goal of PSI is pre-emptive interdiction, which includes detaining and searching ships and aircraft as soon as they enter PSI members' territorial waters or national airspace.

Mining, Milling, Conversion and Enrichment of Uranium Ores

Clarence J. Hardy
Immediate Past-President, Pacific Nuclear Council
Secretary, Australian Uranium Association
Managing Director, Nuclear Fuel Australia Ltd

Introduction to Uranium and the Nuclear Fuel Cycle

Uranium was discovered by Klaproth in Germany in 1789 and named after the newly discovered planet Uranus. Then in 1896, Professor Becquerel in Paris discovered radioactivity from a study of uranium minerals. After that, uranium and its daughter product radium quickly rose to fame especially through the pioneering work of Madame Curie in Paris. The main use for uranium for the next 40 years was as a source of radium for cancer therapy and in luminous paint.

Another important piece of history was that Frederick Soddy, a chemist working with Professor Rutherford in Cambridge, UK, proposed in 1910 that atoms with identical chemical properties but different atomic weights might exist. Three years later, Professor Thomson showed in experiments with neon, that Soddy's proposal was true at least for that one element and it was possibly true for all elements. Soddy then coined the name "isotope", from the Greek *isos*, "equal" and *topos* or "place". An increase of the proportion of an isotope of an element relative to other isotopes of that element later became known as "enrichment". The discovery of the neutron by Chadwick in Cambridge, UK, in 1932, enabled the structure of isotopes to be understood. Then Dempster in Chicago used a mass spectrometer in 1935 to show that uranium contained a small amount (0.7%) of a light isotope of mass 235 in addition to the major isotope of mass 238. Uranium-238 thus had 92 protons, 146 neutrons and 92 orbital electrons, while uranium-235 had 92 protons, 143 neutrons and 92 orbital electrons.

The next stage in the story of the applications of uranium was the discovery of fission of a uranium nucleus, attributed to Hahn and Strassman in Germany in 1939. They also proposed that not only did this fission produce a lot of energy, but it also released additional neutrons which could lead to a self-sustaining chain reaction in other uranium atoms. Thus the concept of the atomic bomb was developed and taken up in the Manhattan Project during the Second World War. The first major use of enrichment was in the production of enriched uranium-235 in that Project. The concept of producing useful energy in a controlled way, i.e. in a nuclear power station, was proposed during the war but not taken until long after the war finished. A review of all of the above historical events can be found in a book by the author (reference 1).

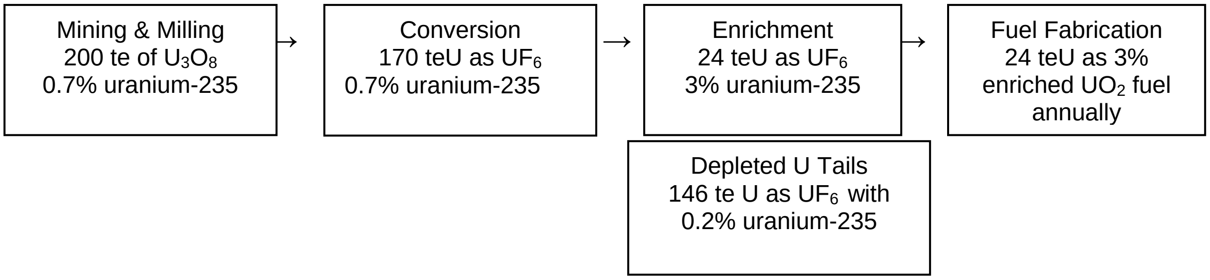
Unlike the use of coal in coal-fired power stations, uranium as mined cannot be fed directly into a nuclear power station. Uranium has to be taken through a number of stages to produce the fuel elements used in the nuclear power station. These stages are known as the "front- end" of the nuclear fuel cycle. The used fuel elements are taken out of the power station after 18 months to two years and also have to go through a number of stages before the contained uranium and plutonium can be recovered for re-use or disposed of safely. These stages are known as the "back-end" of the nuclear fuel cycle. This paper will only cover the front end of the nuclear fuel cycle.

The main stages of the front-end of the fuel cycle are: mining; ore processing (milling) to provide uranium oxide concentrate (yellowcake); conversion to uranium hexafluoride; enrichment of uranium hexafluoride; and fuel fabrication.

Both chemical and physical separation processes are used in the stages in the front end of the nuclear fuel cycle. The main objectives are to separate uranium from the many mineral and chemical impurities in the ore and from the radioactive daughter products of uranium. Then physical processes are used to enrich the uranium-235 from its mixture with uranium-238 to produce uranium with the optimum characteristics for use in nuclear power reactors.
The amounts of uranium in each of these stages are given in Figure 1 for the annual requirements for a 1000 MWe nuclear reactor.

Nuclear electricity supply utilities usually contract directly with mining companies for the supply of uranium concentrate (yellowcake) and then contract separately with the suppliers of conversion, enrichment and fuel fabrication services which may be in different countries. The utility also arranges for the transport between each supplier in the fuel cycle. There are transport and regulatory cost savings to the utility if several of the stages are in the same country.

Figure 1. The Front-end Stages in the Nuclear Fuel Cycle for Nuclear Power Reactors using Enriched Uranium (Reference 2, p.33)



Uranium Mining

World uranium resources

The world’s uranium resources are regularly assessed by the International Atomic Energy Agency (IAEA) and the OECD’s Nuclear Energy Agency (NEA) and reported every two years in a publication “Uranium Resources and Demand” known as “The Red Book”. The most recent was published in 2007 (Reference 3). The World Nuclear Association (WNA) also regularly reviews the world’s uranium resources and fuel cycle services and its last report “The Global Nuclear Fuel Market – Supply and Demand 2007-2030” was published in 2007 (Reference 4). A comparison of uranium resources in the major countries is given in Figure 2 based on the IAEA/NEA publication.

The world’s current 439 nuclear power reactors totalling 370 GWe require about 65,000 tonnes of uranium each year from mines or secondary sources. Thus, the presently known resources at less than US$130/kg U will be sufficient to last for over 80 years assuming the current practice of once-through use in most reactors. If, however, a greater amount of recycling of uranium and plutonium formed in the reactor fuel and reprocessed is practised in the future, then the resources will last for more than 80 years. Further exploration and higher prices will certainly lead to the discovery of more resources based on present geological knowledge.

Figure 2. Known Recoverable Resources of Uranium:
Reasonably Assured Resources plus Inferred Resources to US\$130/kg U, 2007

Country	Tonnes U	Percentage of World, %
Australia	1,243,000	23
Kazakhstan	817,000	15
Russia	546,000	10
South Africa	435,000	8
Canada	423,000	8
USA	342,000	6
Brazil	278,000	5
Nambia	275,000	5
Niger	274,000	5
Ukraine	200,000	4
Others	636,000	11
Total	**5,469,000**	**100**

World Uranium Production

The current world requirements for uranium for nuclear power are met partly by primary supply from new mine production (for example, only about 62% in 2006, WNA Reference 4) and partly by secondary resources which include the uranium product from the reprocessing of spent nuclear fuel, the re-enrichment of tails from enrichment plants (see later in section 4.2), depletion of utility stockpiles, and the re-use of highly enriched uranium from the decommissioning of nuclear weapons. World production of uranium from mines in several major countries is given in Figure 3 based on WNA estimates (Reference 4). Eight countries were responsible for 92% of world production.

The world spot price of uranium increased markedly from about US\$10/lb U_3O_8 in 2003 to over US\$135/lb in mid-2007, and then declined to its current level of about US\$50/lb in 2008. It should be noted that the spot market only accounts for less than 10% of trading in uranium with most purchases being made on long-term agreed contract prices.

Uranium Ore Types

The average concentration of uranium in the earth’s crust is 2-4 ppm. It is about 40 times more abundant than silver and more abundant than antimony, tin, cadmium, and mercury. It is found in hundreds of minerals, the best known ones being pitchblende, uraninite and autunite. It is also found in many phosphate rock deposits and monazite sands. The most important commercial deposits of uranium have been in veins in granitic rocks, adsorbed on sand grains in sandstone deposits and in porphyry deposits such as the large deposit at Olympic Dam in South Australia where it is associated with copper and gold.

Figure 3. World Production of Uranium in 2006

Country	Tonnes U	Percentage of World, %
Canada	9,862	25
Australia	7,593	19
Kazakhstan	5,279	13
Niger	3,434	9
Russia	3,262	8
Namibia	3,067	8
Uzbekistan	2,260	6
USA	1,672	4
Others	3,000	8
Total	**39,429**	**100**

Methods of Uranium Ore Mining

There are four basic methods of obtaining uranium from ores or other materials:

- Underground mining
- Open cut mining
- In-situ leaching
- Recovery from mining of other materials,
  e.g. phosphate rock, mineral sands, coal ash, etc

Underground mining usually employs vertical shafts down to the depth of the ore-body as found by exploratory drilling, or it may employ inclined access tunnels from the surface if the ore-body is not at a great depth. Open-cut (or open pit) mining involves excavation of a large amount of overburden to reach the ore-body found by exploratory drilling. An analysis of the depth of overburden, the depth of the ore-body or related ore bodies, the grade of the ore, the inclination of the ore bodies to the surface, and many other factors is required to decide which method (underground, open cut or in –situ leaching) is the most economic. Views of underground and open cut mines and processing plants in Australia are shown in Figures 4. 5 and 6 (reference 5).

Figure 4.
The Underground Mine and Copper, Gold and Uranium Processing Plants at Olympic Dam., South Australia

Aerial view Olympic Dam plant.

Aerial view of Ranger Mine and plant

Figure 5.
The Open Cut Mine and Uranium Processing Plant at Ranger in the Northern Territory, Australia

In-situ leaching has been used successfully in several countries in recent years, especially in Kazakhstan and Uzbekistan, and in one small operation in Australia. It requires a very special set of geological conditions to make it successful. There is a requirement that the ore body, which is usually in porous sandstone near the surface, is constrained between a lower impermeable layer, e.g. clay, and an upper impermeable layer. Then an acid or alkaline solution can be pumped into the ore body and pumped out again without leakage into strata below the lower impermeable layer or into aquifers above the upper impermeable layer. A detailed environmental assessment is usually required in the case of all types of mining methods, but especially so for in-situ leaching to ensure that acid or alkaline solutions containing uranium or other impurities do not enter aquifers used for human or animal consumption.

Figure 6.
The Uranium In-Situ Leaching Plant at Honeymoon, South Australia

In 2007, production was as follows: 62% from conventional underground and open cut mines, 29% from in-situ leaching (mainly in Kazakhstan and Uzbekistan) and 10% from by-product recovery operations (this latter considers the large Olympic Dam project as a by-product of copper mining, not as a separate underground mine). In 1999, only 33% was from underground mines, but the new production from high ore grades in deep underground mines in Canada raised it to 62% in 2007. Expansion of underground mining is expected in Canada and Australia in the next ten years while expansion of in-situ mining in Kazakhstan, Uzbekistan and Russia will probably maintain the percentages as indicated in 2007.

In the underground and open cut methods, the coarse primary ore is crushed in a primary crusher and then reduced in a secondary crusher to a fine powder suitable for the main leaching process. This leaching process can use dilute sulphuric acid or dilute sodium hydroxide or carbonate the choice depending on the chemistry of the uranium ore and the host rock. If for example, the host rock is somewhat acidic, then an acid leach would be used, but if the host rock is somewhat alkaline or contains substantial carbonate minerals, then an alkaline leach would be more economic. The primary objective is to extract the maximum amount of uranium at the minimum temperature and with minimum use of expensive acid or alkali. A problem arises if the uranium ore mineral (or minerals) are not easily dissolved in the leaching solution. In that case, extensive testing is carried out before even designing the plant to make the most economic use of reagents, temperature and time. Pitchblende, uraninite, autunite and similar minerals do not usually pose a problem whereas brannerite and some other uranium minerals have posed problems in some mines.

The main process solution is usually filtered or clarified to remove fine undissolved particles and the uranium is precipitated usually as ammonium diuranate. This is then dried and may be calcined to a moderate temperature, several hundred degrees Celsius, to provide the final product from the plant or mill. The product is usually called Uranium Ore Concentrate (UOC) or yellowcake and can have a yellow to dark brown colour. It is usually stored in standard 44 gallon/200 litre steel drums.

The solid undissolved material containing a small amount of undissolved uranium and a large proportion of radioactive daughter products of the uranium, is called “tailings” and sent for storage in a tailings pond near to the milling plant.

Transport of Uranium Ore Concentrate

The uranium ore concentrate packed in the standard 44 gallon/200 litre steel drums is usually packed in standard transport containers for shipment by truck or rail to the next stage in the cycle, either a conversion plant if it is for an enriched fuel reactor or a fuel fabrication plant if it is for a reactor using natural uranium fuel. The product is subject to strict accounting and national and international safeguards and security procedures to comply with the producing countries’` international agreements with the International Atomic Energy Agency and the customer countries.

Uranium Conversion

World demand and supply

Five major companies (Tenex, Russia; Areva, France; Cameco, Canada; Converdyn, USA, and Springfields Fuels Ltd, UK) supply over 90% of the world’s conversion services. The present nameplate capacity of conversion plants worldwide is about 68,000 te UF_6 per year which is sufficient
to satisfy estimated demand to between 2010 and 2015. However, such plants often do not operate at their nameplate capacity for a variety of reasons.

There has been no investment in new plants or in expansion of old plants for many years. However, Areva, France, has announced plans for a new conversion plant, Comhurex II, with facilities at Malvesi and Tricastin. The cost is estimated to be Euro 610M (about US$600M) for a plant of 15,000 teU/a capacity with full production available in 2014 (Source – Uranium Information Centre, Australia, May 2007: www.uic.com.au). The price of conversion services has nearly doubled in the last two years to approximately US$12/kg U as UF_6 (UMPNER Report, p.35, Reference. 2).

Uranium conversion methods

The conversion plant usually receives uranium ore concentrate from the min and milling plant in 44 gallon/200 litre steel drums. This material is a form of uranium oxide contaminated with a range of impurities which were not removed in the milling process, including a small amount of radioactive daughter products. The objective of the conversion plant is to produce very high purity uranium hexafluoride (UF6) for transfer to the next stage of uranium enrichment, or to produce pure natural uranium dioxide (UO2) for use in fuel for reactors not using enriched uranium.
There are two basic processes which have been used commercially for conversion of impure uranium ore concentrate to very pure uranium hexafluoride: the wet process and the dry process. Figures 7 and 8 show views of dry and wet process plants, respectively.

FIG. 14: ALLIED CHEMICALS CORPORATION URANIUM HEXAFLUORIDE PLANT (foreground)

Figure 7.
A Uranium Conversion Plant at Metropolis, Illinois, USA, which uses the dry process.

Figure 8.
A Uranium Conversion Plant at Springfields, UK, which uses the wet process.

Both processes receive uranium ore concentrates (UOC) from the uranium mines in standard steel drums in shipping containers.

In the wet process the UOC is dissolved in nitric acid and the resulting uranyl nitrate solution purified to a high degree by solvent extraction usually with a solvent such as tributylphosphate (TBP) dissolved in inert diluents such as odourless kerosene in mixer-settlers. The uranium is then washed out of the loaded solvent with water and precipitated with ammonia to produce a very pure form of ammonium diuranate, a yellow solid. This product is dried and calcined to form an intermediate product, uranium trioxide (UO_3). This is then reduced in a mixture of hydrogen and nitrogen to uranium dioxide (UO_2). If the customer wants this to go to a fuel fabrication plant as natural uranium dioxide, it is packaged into drums and transported to the fuel fabrication plant directly. If the customer wants the UO_2 product to go to an enrichment plant, then the conversion plants converts the UO_2 into uranium hexafluoride (UF_6).

The UO_2 is converted into UF_6 in a two-stage process in which the first stage is to convert it into uranium tetrafluoride (UF_4) with hydrofluoric acid. In the second stage, the UF_4 (known as green salt due to its green colour) is converted in UF_6 with fluorine gas. The product (UF_6) is a gas at the temperature of the fluorination vessel and is condensed out as a white solid into transport cylinders. The properties of UF_6 are that it can be a gas, liquid or solid depending upon the temperature and pressure. It has a triple point at which gas, liquid and solid are in equilibrium at 22 psia (1.5 times atmospheric pressure) and 64^oC (147^oF).It is a gas at above 57^oC (134^oF) and a solid below 52^oC (125^oF) at atmospheric pressure. Solid UF6 is a white crystalline material.

In the dry process, the solid UOC is treated to provide a suitable form for the first main stage which involves a fluidised bed. It is therefore pelletised, but if it contains more than an acceptable concentration of sodium which could cause problems in the bed, it may be pre-treated with an ammonium sulphate solution to remove the excess sodium. After any such pre-treatment the solid low-sodium UOC is dried and pelletised for feeding into the fluidised bed. In this bed, the UOC is reduced to UO_2 with a mixture of hydrogen and nitrogen, then hydro-fluorinated with HF in another fluidised bed to form UF_4 and finally converted to UF6 with fluorine gas in a third fluidised bed. The impurities derived from the UOC are contained in the UF_4 intermediate product. Those elements which have involatile fluorides (eg, calcium, sodium and some metals) are separated out in the third stage, since UF_6 is relatively volatile and many impurity fluorides are not. Any relatively volatile impurity fluorides are then separated from the UF_6 by fractional distillation in a final purification stage.

The main difference between the wet and dry processes is the way impurities are removed from the UOC. In the wet process they are removed in the second stage of solvent extraction, and only very pure UO_3, UO_2 and UF_4 are processed through the later stages. In the dry process, the impurities in the UOC are removed mainly in the final UF_4 fluorination stage and in a later purification stage if any volatile fluorides are analysed in the product of the fluorination stage. The final product in both processes is very pure UF_6 contained in cylinders suitable for storage or transport to the enrichment plant specified by the customer.

Enrichment of Isotopes

World demand and supply for uranium enrichment

There is general agreement between organisations estimating the world's supply/demand balance for enrichment services that there will be a surplus of capacity up to about 2010. However, between 2010 and about 2015 there will be a small deficit in supply compared with the reference scenarios of how nuclear power will expand. This change is due to the old large gaseous diffusion plants in France and the USA being closed down and the USA-Russian Highly Enriched Uranium (HEU) Agreement ending in 2013 (this Agreement is for conversion of HEU from decommissioned Russian nuclear weapons into low enriched uranium fuel for civil reactors). It will take several years, possibly until at least 2020, before the capacity of the existing and new centrifuge plants in Europe, Russia and the USA to bring supply and demand back into balance.

The supply of enrichment services from existing plants and new plants is estimated to be about 59,000 te SWU in 2010 compared with a demand of 53,000 te SWU, whereas the supply in

2015 is estimated to be about 53,000 te SWU compared with demand of 57,000 te SWU (a SWU or Separative Work Unit is a measure of the amount of energy required to produce one unit of enriched uranium at defined levels of product and tails enrichment) (reference 1).

Uranium Enrichment Methods

One of the first uranium enrichment methods used in the Manhattan Project was the calutron method, followed by enrichment by gaseous diffusion and gas centrifugation. Much later, methods of isotope enrichment using laser excitation and simple chemical exchange methods were developed. A brief review of these methods and their commercial importance is provided in the following sections.

Calutrons

A brief review of calutrons is provided for their historical importance as one of the first large scale machines used for enrichment of uranium isotopes. A calutron is a form of mass spectrometer which was itself a scientific instrument that had been developed by Dr F. W. Aston in the UK in 1919 to measure the atomic mass of elements with great precision (reference 1). When the US government agreed to undertake the Manhattan Project in the early 1940's, the electro-magnetic separation of uranium isotopes was highly favoured by Professor Lawrence of the University of California, who was one of the leading world authorities on cyclotrons and an advisor to the government. The alternatives of separation of uranium isotopes by thermal diffusion, gaseous diffusion and centrifugation were all considered and all studied experimentally in the USA and UK. Professor Lawrence was given the job of developing a large scale mass spectrometer based on his experience with cyclotrons with the objective of making kg amounts of the 0.7% abundant isotope uranium-235 from its mixture with the 99.3% abundant uranium-238. This machine was given the name calutron in recognition of the University of California (Cal U) and (tron) from cyclotron.

In a basic mass spectrometer or calutron, a small quantity of a uranium compound (specifically uranium tetrachloride) was bombarded with high energy electrons which caused positively charged ions of uranium-235 and uranium-238 to be formed in a high vacuum chamber. These were then accelerated and deflected in a circular trajectory in a powerful magnetic field and arrived at a collecting area at which the uranium-235 ions and uranium-238 ions could be collected. The mass difference was only 1.25% and great precision was required to control the magnetic field and the trajectories and even then the uranium-235 ions could not be collected at 100% efficiency. In the earliest form of the scaled up machine only about 15% enriched product could be obtained, thus requiring a second stage in which the 15% initial product was used as feed in a separate machine to obtain a product with greater than 90% uranium-235 as required for construction of an atomic weapon.

Lawrence had built a large scientific cyclotron at Berkeley with a radius of 37 inches (94 cm) and he modified this to demonstrate that uranium ions could be produced and separated in such a machine. He then designed the larger prototype calutron with a powerful 184 inch (467 cm) magnet with the uranium ions travelling in a semicircular trajectory to be collected in water-cooled receivers because of the large amount of heat deposited. Lawrence calculated that by the fall of 1942, ten calutrons each operating within the huge magnet and each with a 100 milliamp ion source could produce about 4 gm of enriched uranium each day. This design, the "alpha" calutron, was only capable of producing about 15% uranium-235.

A greatly improved design was then approved by the management of the Manhatten Project for installation in a large scale production plant (Y-12) located at Oak Ridge in 1943. The first production system required a huge magnet 24 times larger than before and the multiple calutron vacuum tanks were curved into an oval 122 feet (36 m) long, 77 feet (23 m) wide and 15 feet (4.5 m) high. The separate tanks were called “race tracks”. The shortage of copper in the war to use in the magnets led to a novel solution, the requisition of 14,700 tons of pure silver from the government’s stockpile. After a number of technical problems were overcome, a total of 200 g of uranium enriched to 12% uranium-235 was produced by the end of February 1944, only 20% of the goal of 1kg of enriched uranium per month.

At this stage it was realised that the product would have to be re-enriched in a second stage, the beta calutron, which was designed for recovery of the valuable product at the highest possible efficiency and recovery of feed material coating the vacuum tanks as its priority. The competing process of gaseous diffusion also operating at Oak Ridge had not met its design goals by late 1944, and therefore the management approved going ahead with a priority beta calutron program. It was reported that in the vital months of late 1944 and early 1945, about 22,000 persons including a large number of graduates and PhDs from Berkeley and thousands of process workers from the Tennessee Eastman company which was managing the secret Oak Ridge site, worked around the clock operating the old alpha calutrons and six beta calutrons containing 36 tanks each to produce the 50 kg of highly enriched uranium-235 needed. This material was sent to Los Alamos by special couriers to be fabricated into the precisely manufactured uranium-235 core of the atomic bomb. The first atomic weapon was dropped on Hiroshima on 6 August 1945.

Whilst most of the calutrons were decommissioned in the following years as the gaseous diffusion process overtook them, several were retained and produced a wide range of stable and radioactive isotopes of many elements for use in medicine and in research (see Figure 9).

Figure 9.

Overview of a Beta 3 Calutron preserved at the Y-12 National Security Complex, Oak Ridge, Tennessee, on view to the public in June 2005.

<u>Gaseous diffusion</u>

During 1940, two years before the USA commenced the Manhattan Project in 1942, Professor Peierls and his colleague, Dr Frisch, at Birmingham University, UK, carried out a detailed theoretical study of possible isotope separation processes both for laboratory and large scale use in enriching uranium for an atomic bomb. The method of thermal diffusion was shown to be unsuitable for scale up and the method of centrifuging gases at very high speed was not considered very promising. The method they recommended was gaseous diffusion in which gaseous uranium hexafluoride was allowed to diffuse through a porous barrier (Figure 10). The uranium-235 hexafluoride molecules pass through the fine pores faster than the uranium-238 hexafluoride molecules and a small degree of separation occurs. In order to achieve a high degree of separation the process must be repeated a large number of times.

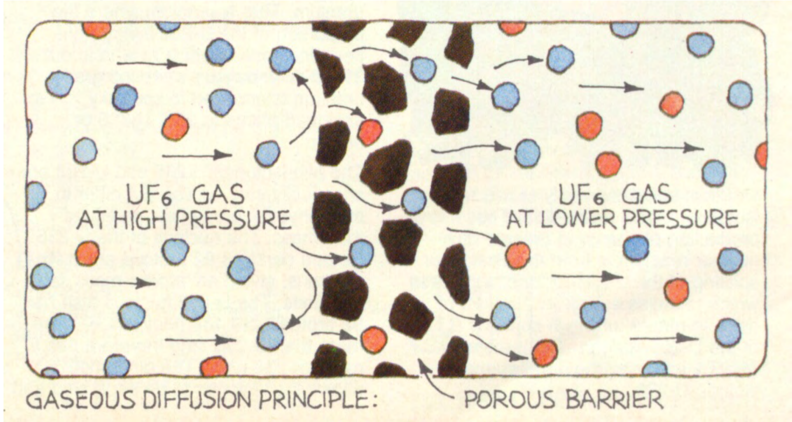


Figure 10. The Principle of Gaseous Diffusion Separation

Professor Symons of Oxford University provided a memo to the UK government in December 1940 on an “Estimate of the Size of an Actual Separation Plant”. The memo discussed the main features of a plant covering 40 acres (25 hectares), containing 70,000 m2 of porous membranes and requiring the large power consumption of 60MWe, to produce 1kg per day of 99% uranium-235 at a capital cost of £4 M and operating costs of £1.5M per year including the cost of 1,200 staff. This cost was stated to be equivalent to that for a large explosives factory or a modern battleship. All of this work and associated experimental work in the UK was kept secret.

The final outcome of UK studies in 1941 was that the production of an atomic bomb was technically possible but the large cost need for strategic materials and a large commitment of skilled and unskilled staff could not be justified at that time in the UK’s fight against Germany. These reports were made available to the US government in 1941 at the time the Japanese attack on Pearl Harbour brought the USA into the war. Research continued in both countries and there was initially very good scientific cooperation. The USA committed itself to the Manhattan Project in 1942 and commenced the huge investment in several parallel developments to obtain highly enriched uranium. One of these projects was the development of gaseous diffusion technology which led eventually to the construction of a huge secret K-25 plant at Oak Ridge (see www.wikipedia.org/K-25).

The K-25 plant was started in June 1943 and completed in early 1945 at a cost of $512M. The huge plant measured half a mile long (800 m) by 1,000 feet (300 m) wide and covered two million square feet (609,000 m^2), and was the largest building in the world at that time (see

Figure 11, references: www.smithdray1.net and www.lbl.gov). It was located eight miles northeast of the Y-12 calutron plant and construction started even before the design of the process was completed due to the urgency of the project. The nearby town of Oak Ridge, originally designed for 11,000 persons, grew to 50,000 persons by the summer of 1944, such was the demand to build and operate the K-25, Y-12 and other plants. A power plant was also built to produce the large amounts of electricity and steam for the plants. The technical difficulties in developing the technology on this scale were challenging and the plant did not achieve its target of kgs of highly enriched uranium by the deadline set for producing the first prototype atomic weapon by mid 1945. The plant did produce medium levels of enriched uranium similar to that produced in the alpha calutrons and thus provided essential feed material to the beta calutrons which could then produce over 90% enriched uranium by the deadline.

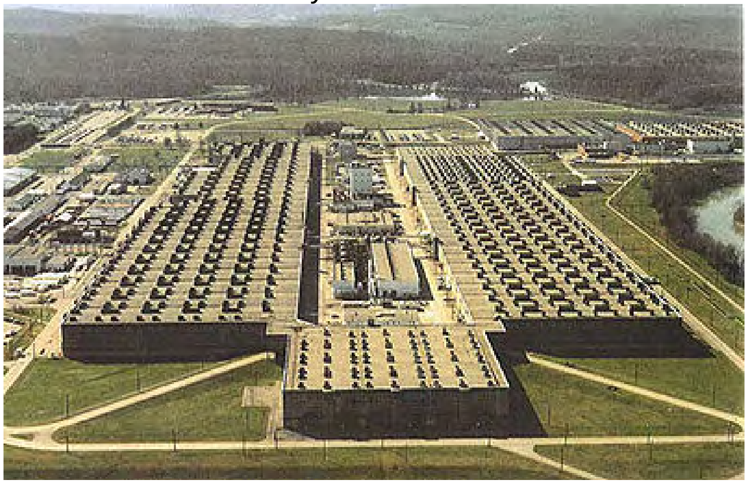


Figure 11. Overview of the K-25 Gaseous Diffusion Plant at Oak Ridge, Tennessee

The US went on to develop three large gaseous diffusion (GD) plants in the years after the Second World War. These were located at Oak Ridge (Tenn.), Portsmouth (Ohio) and Paducah (Kentucky) and their capacities were 6,000, 6,000 and 8,000 te SWU/year respectively. These plants provided both low enriched uranium (LEU) and high enriched uranium (HEU) for civil nuclear power and research programs worldwide as well as supplying these essential materials for the US defense program, both for nuclear weapons and for naval ships. In addition, the UK built a small GD plant at Capenhurst, UK , France built a small GD plant at Marcoule and a large GD plant of 10,800 te SWU per year at Tricastin (see Figures 12 and 13), and China and Russia built GD plants. By 1980, the USA had a total GD capacity of 20,000 te SWU/year out of the world total of 45,000 te SWU/year, and dominated the enrichment services market for civil nuclear power.

Figure 12.
The GD Plant at Tricastin, France (background) with four nuclear power plants (foreground)

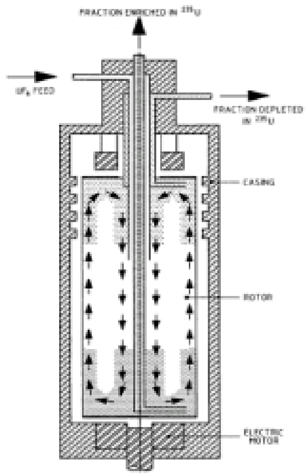
Figure 13.
The large size of the GD columns in the GD plant at Tricastin

The main reason why plants based on GD technology were replaced by plants based on gas centrifuge (GC) technology is that the GD technology has a very high specific power consumption., typically 2,500 KWh per SWU, compared with about 50 KWh/SWU for GC technology. In addition, GC plants can be built in small modules and expanded to meet the market demand whereas GD plants had to be built in large sizes to be economic in past decades. The last large GD plant was built by the French at Tricastin in 1984. Two of the three large US GD plants have been closed and are being decommissioned. The third plant at Paducah is still operating but is planned to be closed in about 2013 when a replacement GC plant being built at Portsmouth, Ohio, starts full operation.

Gas centrifugation

The method of gas centrifugation for separation of uranium isotopes was considered by the British team in their studies in 1940, but discarded as not promising. The US scientists in the early 1940's thought it was promising and allocated the study to Dr Murphree of the Standard Oil Development Company to follow up the pioneering work of Professor Beams (reference 1). However, once the US started to scale up effort in the Manhattan Project, gas centrifugation was dropped in favour of the calutron electromagnetic method, gaseous diffusion and thermal diffusion. The method of gas centrifugation was only taken up commercially in the 1960s by three European countries in parallel, the UK, Germany and the Netherlands, and by highly secretive work in Russia using the expertise of Dr Zippe from Germany. Later, in the 1970s, several other countries developed gas centrifuge technology, notably France, Japan and Australia.

The basic concept of gas centrifugation is that the uranium isotopes in uranium hexafluoride gas can be separated by centrifuging at very high speed (see Figure 14). The centrifuge shown diagrammatically is effectively spinning like a top on a bottom bearing with a non-contact top magnetic bearing. This is known as the basic Zippe design. The alternative design with contact bearings at both ends is known as the Beams design and is being used in the large advanced centrifuges in the new plant in the USA owned by the United States Enrichment Corporation (USEC). An illustration of advanced cascades of the spinning top design in the Urenco GC plant at Capenhurst, UK, is shown in Figure 15.



From USNRC Info Paper

Figure 14.
Diagram of a Zippe type centrifuge

Figure 15.
Cascade hall of advanced centrifuges at Urenco's Capenhurst Plant, UK (reference 2).

Three GC plants are currently being operated by Urenco in Germany, the Netherlands and the UK with a total capacity of 8,000 te SWU per year. New plants each of a capacity of about 3,000 te SWU per year are being constructed by Urenco at Eunice, NM, USA and by Areva near Idaho Falls, Idaho, USA. Areva is constructing a large GC plant of capacity 6,000 SWU per year at Tricastin, France, to replace the large GD plant shown in Figure 10. Russia has the largest operating capacity of GC plants in the world with a capacity estimated to be 25,000 te SWU per year. The total GC capacity in the world is currently about 34,000 te SWU per year compared with the current demand of 50,000 te SWU per year.

In a uranium enrichment plant, approximately 6kg U as UF_6 and 3.8 SWU (separative work units, a measure of the energy required) are required to produce 1kg U in the 3% enriched product assuming a 0.2% tails assay. If an enrichment plant is built with a capacity of 3,000te SWU/year, it will require about 4,500 teU feed material per year, and will provide enough fuel for about 30 x 1,000MWe nuclear reactors each year.

Laser methods

Two major types of laser enrichment were studied in the 1970s in several countries as alternatives to the established methods of gaseous diffusion and gas centrifugation. These laser processes used either atomic or molecular species of uranium irradiated with one or more lasers. Each of these two types and variants had advantages and disadvantages for possible scale up to commercial processes.

The basic concept of a laser method was that uranium-235 and uranium-238 had spectra in the infrared, visible or ultraviolet regions of the spectrum which were slightly different and that irradiation of a natural mixture of the two isotopes with lasers of selected frequencies could selectively excite either the uranium-235 or the uranium-238 atoms or molecules and enable them to be separated by chemical or physical processes. It was well known that the spectra of atoms of uranium-235 and uranium-238 were sufficiently different that if they could be irradiated at a selected wavelength, then one species could be excited preferentially. The problem was that no laser operating at the optimum wavelength was available in the early 1970s and therefore a suitable laser had to be developed. In contrast, the spectra of uranium compounds in the infrared, visible and uv wavelengths were only very slightly different although many lasers had been developed to work in these wavelengths, and some at high power suitable for scale up to an industrial process.

The two best known types of laser process in the 1970s and 1980s were the Atomic Vapour Laser Isotope Separation process, acronym AVLIS in the USA and SILVA in France, and the Molecular Laser Isotope Separation process, acronym MLIS. US government laboratories are reputed to have spent several billion dollars on R & D on AVLIS, with several European countries and Japan each spending millions of dollars, yet no country was able to develop the processes to a commercial scale.

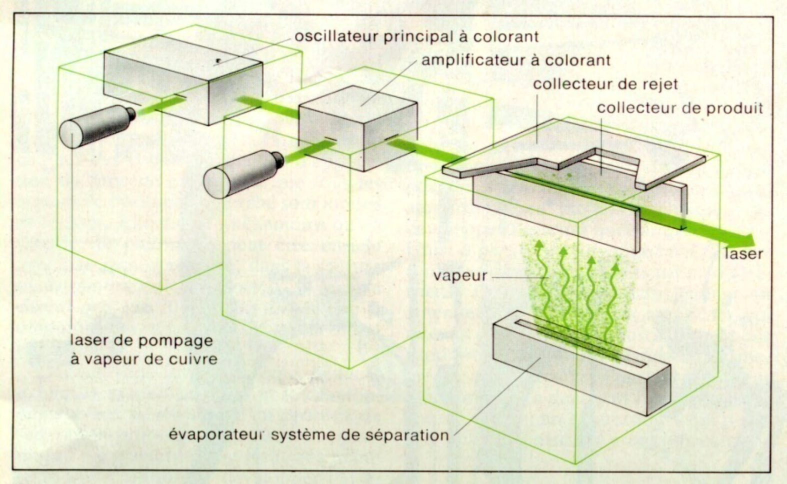


Figure 16. Schematic view of a SILVA process studied in France (reference 5)

The basic principle of AVLIS/SILVA is illustrated in Figure 16. Uranium metal was volatilised at high temperature in a vacuum chamber and a stream of uranium atoms was subjected to one or more laser beams tuned to frequencies which corresponded to the maximum absorption of the uranium-235 atoms. The laser irradiation caused the uranium-235 atoms to be selectively excited to a state in which they could be deflected by electrostatic or magnetic field to collectors. The uranium-238 atoms were less excited by the lasers and passed though to other collectors. The problems of this method were the high temperature needed to volatilise the uranium, the difficulty in obtaining collimated beams of uranium atoms to enter the laser beams, the need to develop completely new and powerful lasers in the optimum wavelengths, and the difficulty of collecting the separated uranium-235 product. Some of these problems had been encountered and solved in the historic development of the calutrons some 30 years before. The work proceeded to the pilot plant stage at US government laboratories at a cost of many billions of dollars, but no commercial process ever eventuated and the US government decided to terminate the program and concentrate on developing gas centrifugation. Similar conclusions were reached in several European countries, Japan and Russia.

The Molecular Laser Isotope Separation (MLIS) process used molecular uranium species not atomic species. The objective was to irradiate molecules such as uranium hexafluoride or organo-uranium compounds with lasers operating in the infrared or visible wavelengths. The advantages of these methods over the AVLIS method were that no high temperature and corrosive materials (such as high temperature molten uranium) were required, and that more readily available lasers could be used instead of developing new lasers. Australian research in the 1970s and 1980s used several volatile organo-uranium compounds and carbon dioxide infrared lasers, whereas research in other countries used uranium hexafluoride and visible wavelength lasers. Although uranium was enriched in laboratory scale work, no country developed the method to a commercial scale and most of the work was terminated in the 1990s. Details of laser enrichment studies in Australia are given in reference 1.

One company in Australia continued development work using uranium hexafluoride as the feed material and visible wavelength lasers and this process was named SILEX (Separation of Isotopes by Laser Excitation). SILEX received some support from the US Department of Energy in the early 2000s and the process was then licensed in 2006 to the US GE company which is developing it in pilot plant scale facilities operated by the Global Nuclear Fuel Co. at Wilmington, North Carolina. No details of the process have been published due to commercial and non-proliferation concerns.

Chemical methods

There were reports in the literature in the 1970s and 1980s that uranium isotopes could be separated by chemical methods using either solvent extraction or ion exchange even though the separation factors were very low, comparable to the gaseous diffusion separation factor of about 1.003 and far lower than that reported for gas centrifugation (at least 1.1). Considerable research and pilot scale development was carried out by the French Atomic Energy Commission on a solvent extraction process named Chemex and by the Asahi Chemical Company in Japan on an ion-exchange process, but neither was taken to a commercial scale.

Enrichment of other important isotopes

Deuterium/Heavy Water

Deuterium is an isotope of hydrogen with a nucleus containing a proton and a neutron with a mass of 2, and heavy water is the compound of deuterium and oxygen with the formula D_2O and is analogous to “light” water H_2O. Heavy water is of importance in nuclear reactors as it is a good moderator to slow down neutrons to fission uranium more efficiently. It is used in Heavy Water Reactors such as the CANDU type developed from the 1960s by Canada (CANDU standing for Canadian Deuterium Uranium Reactor which uses natural uranium not enriched uranium fuel). Some other countries have also developed commercial reactors using heavy water as well as research reactors.

Deuterium occurs naturally in all water and it is present predominantly as the HDO molecule with an abundance of 1 molecule in 3,200. The D_2O molecule only occurs naturally in water with an abundance of one molecule in 41 M. The HDO can be separated from normal water by distillation, by electrolysis and by various chemical exchange reactions. To produce pure heavy water (D_2O) requires a large cascade of distillation columns or electrolysis cells and a large amount of power. Norsk Hydro built the first commercial heavy water plant in Norway in 1934 with a capacity of 12 te per year, a great achievement in those days, considering that deuterium was only discovered by Urey in 1931.

Canada built a 6 te per year heavy water plant at Trail, British Columbia, in 1943 as part of its contribution to the Manhattan Project. In 1953, the USA began using heavy water in nuclear reactors for the production of plutonium and tritium for the US weapons program at the Savannah River site in South Carolina. The US developed a chemical exchange process known as the Girdler Sulphide (GS) Process which was first used in a plant in Indiana in 1945 and then in a plant at Savannah River in 1952.

When Canada decided to build a number of nuclear power plants using heavy water, it required large quantities of heavy water as the moderator and coolant. It built two plants on the east coast but these had serious problems and it then built a third plant in 1979, the Bruce Heavy Water Plant, at Douglas Point on Lake Huron in Ontario. This was the largest heavy water plant in the world with a capacity of 700 te per year and used the Girdler Sulphide Process. This plant required a huge amount of power which was supplied by four nuclear power plants and a large amount of water as 340,000 te water was required to produce one te of heavy water. There were also another four nuclear power plants on the site to produce electricity for Ontario. The Bruce plant proved to be more efficient than expected and this allowed the two other plants to be closed down in 1985. However, the Bruce plant was shut down in 1997 since enough heavy water was available for Canada's needs and it could be recycled.

The basic GS process in the Bruce Plant involved isotopic exchange between hydrogen sulphide (H_2S) gas and H_2O water in hot and cold towers. In the upper cold section (30-40^oC), deuterium in the hydrogen sulphide migrated into water, while in the lower hot section (120-140^oC) deuterium migrated preferentially from water into hydrogen sulphide. The columns were operated in complex cascades. In a first stage, the gas (H_2S) was enriched from 0.015% deuterium to about 0.07%. A second column enriched the 0.07% first stage product to 0.35% and a third column enriched from 0.35% to between 10 and 30%. This product was then vacuum distilled to produce 99.75% "reactor-grade" heavy water since distillation is more efficient at high concentrations. The cost of a kg of D_20 of high purity was about $700 in 2006, and the cost of the heavy water in a large heavy water nuclear power station can be as high as 20% of the capital cost of $2 billion (reference 6).

Another large scale use of heavy water today is in neutrino detectors such as that at the Sudbury Neutrino Observatory (SNO) in Sudbury, Ontario, which uses 1,000 te D_2O,in a tank 6,800 feet (2,000 m) underground.

Fuel fabrication

The providers of uranium ore concentrates, conversion services and enrichment services deliver relatively standardised products to customer's specifications, i.e. UOC (yellowcake) in standard drums, and pure uranium hexafluoride with natural uranium or enriched uranium in standard cylinders. Highly purified products of natural and enriched uranium hexafluoride do not need any further purification steps at the fuel fabrication plants. Nuclear fuel fabricators produce highly engineered fuel assemblies made especially to the specifications determined by the reactor's characteristics and the fuel cycle management strategy of the operator. There are 20 major fuel fabrication plants in the world, some producing natural uranium fuel elements, but the majority produces enriched uranium fuel in the range 3-5% uranium-235 enrichment. There is sufficient capacity in these plants to meet expected demand until at least 2020 (reference 5). Separation processes are not used in these fuel fabrication plants to any great extent.

Conclusions

The main stages of the front-end of the fuel cycle are: mining; ore processing (milling) to provide uranium oxide concentrate (yellowcake); conversion to uranium hexafluoride; enrichment of uranium hexafluoride; and fuel fabrication.

Both chemical and physical separation processes are used in the stages in the front end of the nuclear fuel cycle. The main objectives in mining and milling uranium ores are to separate uranium from the many mineral and chemical impurities in the ore and from the radioactive daughter products of uranium.

Physical processes are then used to enrich the uranium-235 from its mixture with uranium-238 to produce uranium with the optimum characteristics for use in nuclear power reactors. The three major large scale processes that have been used to enrich uranium are electromagnetic separation (calutrons), gaseous diffusion and gas centrifugation. A great deal of research has been carried out on laser processes for uranium enrichment but no process has been taken to a commercial stage up to the present.

Physical and chemical isotope separation processes are also used in the production of heavy water for use in some types of nuclear power stations.

References

1. “Enriching Experiences: Uranium Enrichment in Australia, 1963-2008,” Clarence Hardy, Glen Haven Publishing, PO Box 85, Peakhurst, NSW 2210, Australia, Second Edition, 2008, ISBN 978 1 74018 437 3. Also presentation on “Status of International Enrichment,” by Clarence Hardy to Engineers Australia, Sydney, 1 September 2004.
2. “The Uranium Mining, Processing and Nuclear Energy Review (UMPNER),” publishing by the Australian Government, Canberra, 2006, ISBN 0-9803115-0-0978-0-9803-115-0-1.
3. “Uranium Supply and Demand”, published by the OECD Nuclear Energy Agency, Paris, 2007, for the NEA and IAEA.
4. “The Global Nuclear Fuel Market – Supply and Demand 2007-2030”, World Nuclear Association, London, 2007.
5. “The Case for Uranium Enrichment in Australia”, published by Nuclear Fuel Australia Ltd, 2007, Suite 1005, Cliveden, 4 Bridge St, Sydney, NSW 2000, Australia.
6. “An Early History of Heavy Water”, Chris Waltham, 2002, Dept. of Physics and Astronomy, Univ. of British Columbia (see also article on Heavy Water in www.wikipedia.org).

Nuclear Radiation

Robert L. Sindelar
Savannah River National Laboratory

Introduction

Fundamental to safe and efficient operations, the effects of radiation must be considered in the design of a nuclear materials separations facility in terms of:

- personnel exposure;
- adverse effects on the chemical processes; and
- degradation of the materials of construction.

The first major facility for conducting separations processes for spent nuclear fuel in the United States was the T Plant, a Chemical Separations Building at the Hanford site that began operation December 26, 1944 for the U.S. defense mission. The early separations buildings were massive concrete canyon-like structures, and provided for remote operations for dissolving spent fuel in high acid solutions and processing the highly radioactive solutions in multiple stainless steel tanks (Figure 1). Management of radiation effects have improved since this early era of processing from increased understanding through investigations, and technology development.

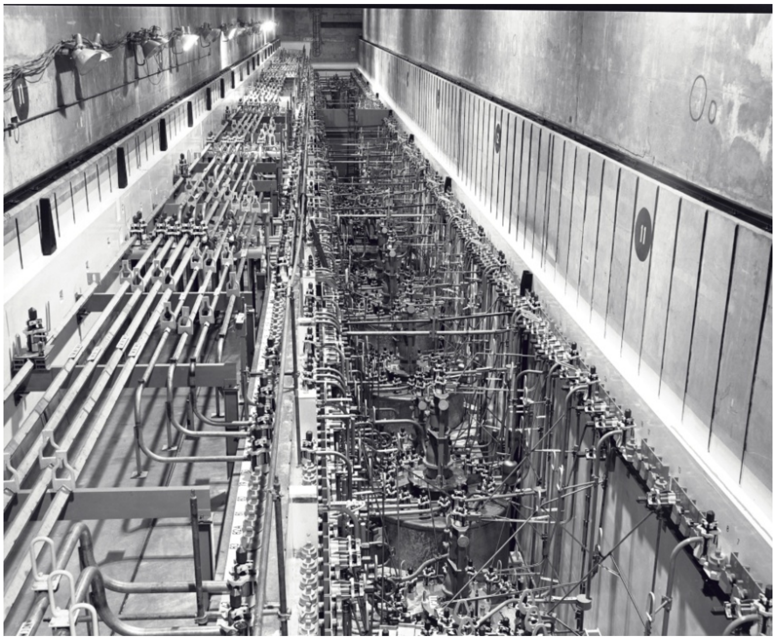


Figure 1. Photograph of the Savannah River Site F-Canyon, Hot Side, Pre-Operation (circa 1955)

A brief overview of radiation effects on materials and systems relevant to nuclear fuel cycle separations is presented in this chapter with an emphasis on the methodologies used to evaluate and/or mitigate the effects. Key references are provided for additional details on the topics.

Radiation Shielding

Shielding against ionizing radiation must be provided in separations facilities for spent nuclear fuel due to the attendant radiation from radioisotopes produced via fission or capture reactions during irradiation of the fuel.

Ionizing radiation in the form of energetic subatomic particles or high energy electromagnetic radiation from unstable or radioactive atoms is radiation that can cause electron removal from atoms or molecules [1]. The primary particles from radioactive decay are the alpha particle, the beta particle, and the neutron. Gamma ray radiation is the term for the high energy electromagnetic radiation from radioactive atoms. A description of the various modes of decay of radioactive atoms is provided in reference 2.

Examples of nuclear fuel that are used in research reactors are shown in Figure 2. The fuels shown in Figure 2 are aluminum-clad, uranium-aluminum alloy fuel in plates that are joined by side plates into a box-like assembly.

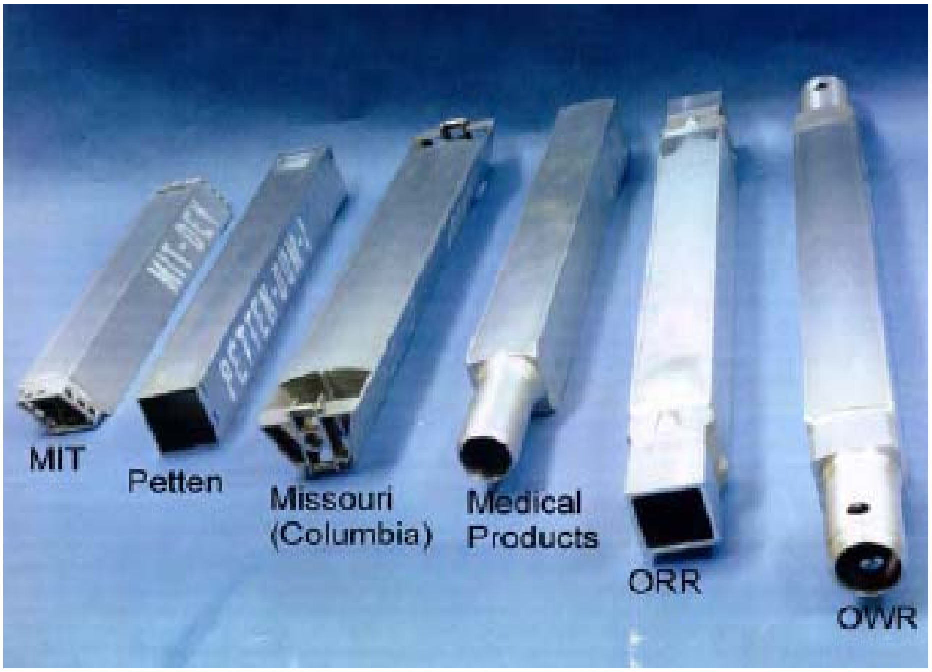


Figure 2. Photograph of Materials Test Reactor Design Nuclear Fuel Assemblies used in Foreign and Domestic Research Reactors including the Massachusetts Institute of Technology Reactor (5 MW); the High Flux Reactor at Petten (50 MW); the Missouri University Research Reactor (10MW); the Oak Ridge Research Reactor (30 MW); and the Omega West Reactor (8 MW)

Spent nuclear fuel contains a suite of radioisotopes. As an example of the radioisotopes generated in nuclear fuel during reactor operation, an analysis is performed on assembly #F1369 irradiated in the Petten High Flux Reactor. This fuel assembly initially contained 484 grams of uranium, enriched to 93% uranium-235. The fuel was irradiated for 158 days in the reactor at 50 MW power with 211 MWD/assembly or 58% burn-up. A 28-day cycle with 24.7 days on and 3.3 days off was used in the 158-day irradiation. Figure 3 shows the activity levels with time from the radioisotopes from fission products, and from actinides in the fuel assembly. The burnup simulation of the fuel assembly was modeled with the ORIGEN-S module of SCALE 4.4a. ORIGEN-S [3] computes time-dependent concentrations and source terms of a large number of isotopes, which are simultaneously generated or depleted through neutronic transmutation, fission, radioactive decay, input feed rates, and physical or chemical removal rates. A 28-day cycle with 24.7 days on and 3.3 days off was used to model the 158-day irradiation.

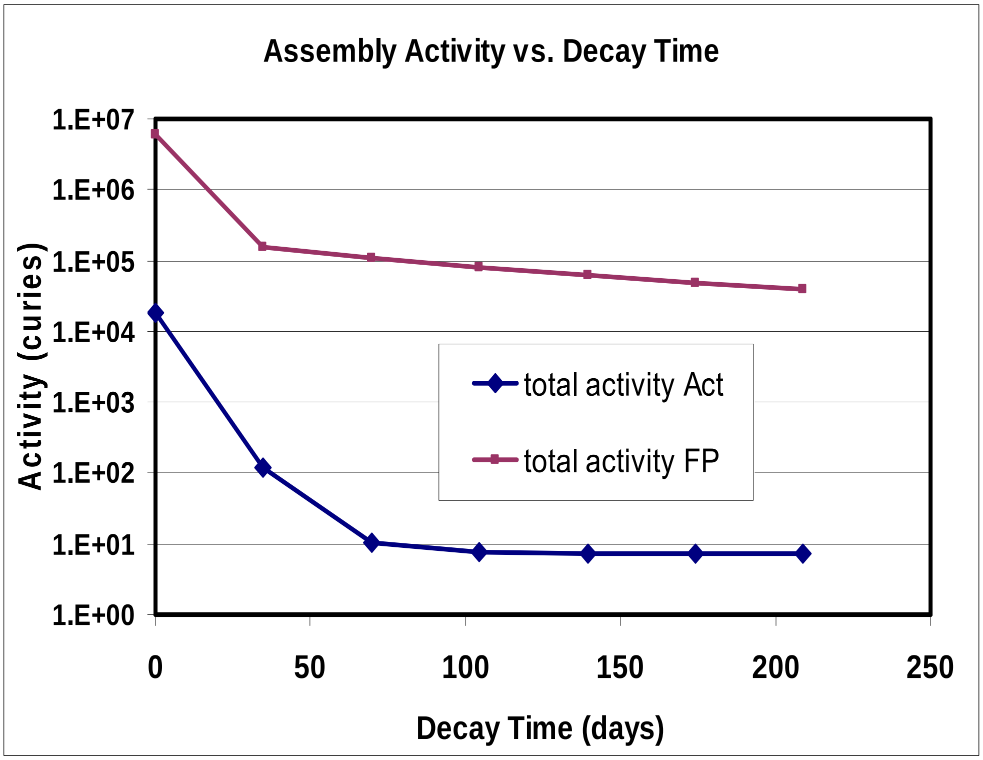


Figure 3. Total Activity from Fission Products (FP) and Actinides (Act) from a Research Reactor Fuel Assembly with 58% Burn-up from158 Day Irradiation or 211 MWD/assembly in the HFR Petten Reactor at 50 MW

Table 1A and 1B show the specific high activity actinides and fission product radioisotopes, respectively at the 209-day cool down time. It is noted that the radioisotopes include alpha, beta, and gamma emitters,[1] but also spontaneous fission occurs with the emission of neutrons in isotopes such as Cf-252, Am-243, Pu-240, and U-238. In addition, secondary reactions,

---

[1] There are few pure alpha or beta emitters, gamma emission is typically concomitant

namely an (α, n) reaction such as Be-9(α, n)C-12, would produce a source of neutrons that would need to be considered in shielding for personnel.

Simplified shielding approaches for ionizing radiation are given in Table 2. Table 2 indicates that, without shielding, gamma and neutron radiation travel hundreds of feet in air.

Table 1A. Actinides with activity > 10-4 Ci from the HFR Petten assembly #F1369 following 209 days cool-down

Actinide	Curies
th231	3.95E-04
pa233	6.34E-04
u235	3.95E-04
u236	2.69E-03
u237	1.34E-04
np237	6.34E-04
np239	1.06E-04
pu236	1.36E-04
pu238	1.57E+00
pu239	3.25E-02
pu240	3.49E-02
pu241	5.54E+00
am241	7.32E-03
am243	1.06E-04
cm242	1.42E-01
cm244	2.80E-03
total	**7.34E+00**

Table 1B. Fission product radioisotopes with activity > 102 Ci from the HFR Petten assembly #F1369 following 209 days cool-down

Fission Product	Curies
sr89	1.21E+03
sr90	6.84E+02
y90	6.84E+02
y91	2.25E+03
zr95	3.09E+03
nb95	6.28E+03
ru103	3.33E+02
rh103m	3.33E+02
ru106	6.81E+02
rh106	6.81E+02
cs134	3.35E+02
cs137	6.91E+02
ba137m	6.53E+02
ce141	2.86E+02
ce144	9.59E+03
pr144	9.59E+03
pr144m	1.34E+02
pm147	1.83E+03
total	**3.96E+04**

Table 2. Range in air and shielding for various ionizing radiation sources

Type of Ionizing Radiation	Characteristics	Range in Air	Shield	Hazards	Source
Alpha	**Large mass, +2 charge**	**Very short, 1- 2 inches**	**Paper, skin**	**Internal**	**Pu, U**
Beta	**Small mass, -1 charge**	**Short, 10 feet**	**Plastic, glass, metal**	**Internal, external skin & eyes**	**Fission & activation products**
Gamma/x-ray	**No mass or charge, photon**	**Several 100 feet**	**Lead, steel, concrete**	**Whole Body internal or external**	**Fission & activation products**
Neutron	**Mass, no charge**	**Several 100 feet**	**Water, concrete, plastic**	**Whole Body internal or external**	**Cf, neutron sources**

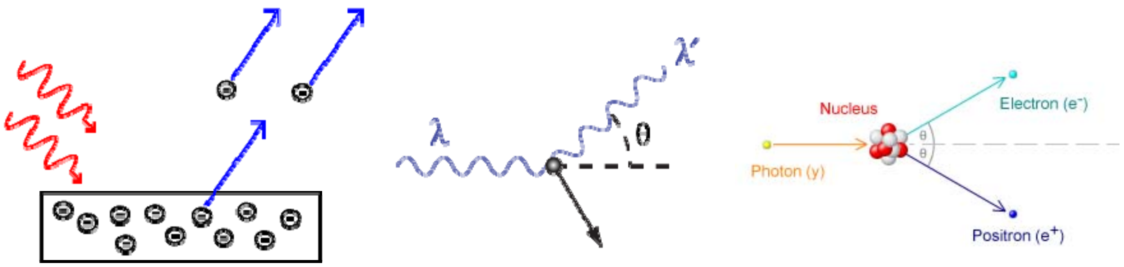


Figure 4a, b, c. The interaction of gamma radiation with matter. Figure 4a depicts the photoelectric effect in which the gamma ray interacts with atom and the initial gamma ray is consumed. Figure 4b depicts the Compton effect or Compton scattering in which an incident photon is scattered through an angle theta and loses energy with a recoil electron. Figure 4c depicts pair-production in which an incident photon is lost in the creation of an electron and positron following an interaction with the atomic nucleus.

An initial understanding of shielding processes can be obtained by considering the three primary interactions of gamma radiation with matter. Reference 2 provides a good description of these interaction processes described herein. Figures 4a – 4c are sketches of the three processes: the photoelectric effect; the Compton effect; and pair-production, respectively. In the photoelectric effect, a photon of energy hf where h is Planck's constant and f is the frequency of the incident gamma ray, is consumed by the binding energy of the electron to the atom, and the kinetic energy of the ejected electron in the following relation:

$$hf = \phi + E_{k_{\max}} \tag{1}$$

In Compton scattering, the photon is scattered and loses energy. The energy loss by the photon is transferred to an electron with conservation of energy and momentum. The following relation can be derived for the change in wavelength of the gamma ray after a Compton scattering event where m_e is the rest-mass of the electron:

$$\lambda' - \lambda = \frac{h}{m_e c}(1 - \cos\theta) \tag{2}$$

In the pair-production process, the photon is consumed, and an electron pair consisting of a positron and electron are created. A threshold energy for the incident photon energy is needed to create the electron pair as identified in the following:

$$hf \geq 2m_e c^2 = 1.02\,MeV \tag{3}$$

Figure 5 shows, in effect, the probability for photoelectric, Compton, and pair-production processes for a gamma ray interaction with lead, that is equivalent to the mass attenuation coefficients, and given as a function of gamma ray energy. The attenuation coefficients for material are dependent on the atomic number of the nucleus [2].

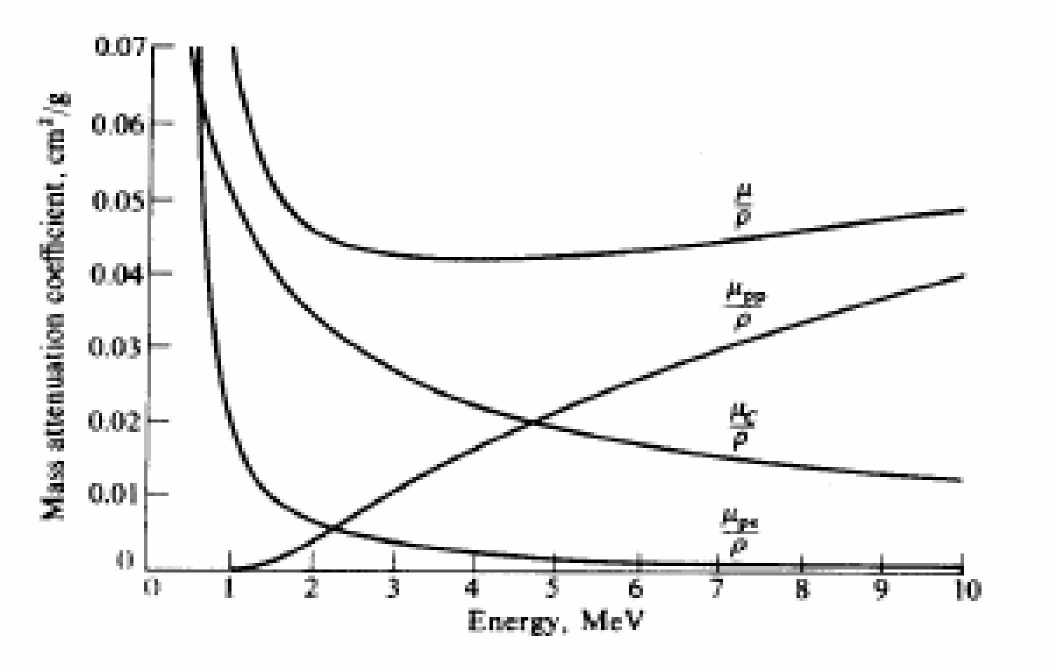


Figure 5. The mass attenuation coefficients of lead as a function of gamma ray energy. The total mass attenuation coefficient and the contributions from the photoelectric effect, Compton effect, and pair-production are shown. [from reference 2]

An engineering approach to evaluate gamma radiation shielding is summarized from the description given in Chapter 10 of reference 2. Consideration is first given to a monodirectional beam of monoenergetic gamma rays with initial energy E_0 in air with a mass absorption coefficient of $(\mu_a / \rho)_{\text{air}}$ and intensity or incident flux of ϕ_0 gamma rays/cm^{2}sec. The equation for the exposure rate, in units of milliRoentgens per hour (mR/hr), is given by:

Exposure Rate with No Shield: $\dot{X}_0 = 0.0659 E_0 (\mu_a / \rho)_{\text{air}} \phi_0$ (4)

The presence of a shield will reduce the exposure rate, and the introduction of the concept of "buildup flux," ϕ_b, in replacement of the incident flux is used to obtain:

Exposure Rate with Shield: $\dot{X} = 0.0659 E_0 (\mu_a / \rho)_{\text{air}} \phi_b$ (5)

The concept of buildup flux is based on the phenomenon that a monoenergetic beam of gamma rays will actually become a distribution of gamma rays emergent from the shield as pictured in Figure 6A and 6B. This reduction in intensity of the gamma rays at the initial energy with a buildup in lower energy gamma rays is due to gamma rays from Compton scattering, and Bremsstrahlung (radiation from deceleration of electrons from the photoelectric effect, Compton scattering, and pair-production processes).

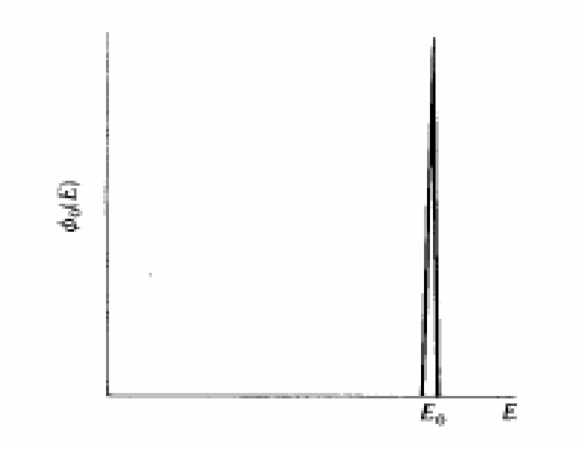


Figure 6A. Energy spectrum of incident monoenergetic gamma rays on a shield [from reference 2]

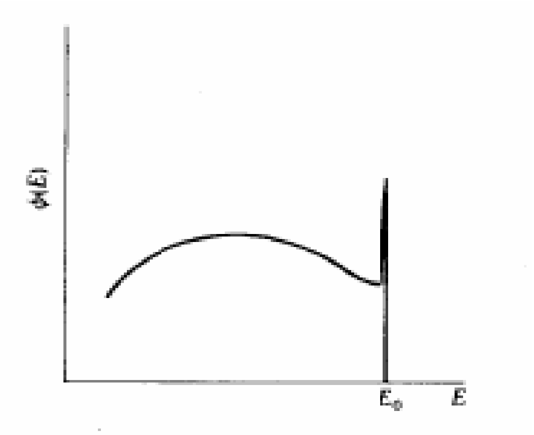


Figure 6B. Energy spectrum of gamma rays emergent from a shield [from reference 2]

As an example, the buildup flux, for a point source of intensity S at a distance R from the source travelling through a shield material is given by:

$$\phi_b = \phi_0 \times Buildup = \frac{S e^{-\mu R} B_p(\mu R)}{4\pi R^2} \qquad (6)$$

where the term $B_p(\mu R)$ is the buildup factor for the point source, and the balance of the terms on the right hand side constitute the uncollided flux or flux of gamma rays at the incident energy at distance R from the point source. The buildup factor can be determined by involved deterministic transport theory or Monte Carlo calculations. For simple engineering analysis, the build up factors can be expressed in a mathematical function with tabulated values for the parameters in the function. As an example, the buildup factor for the point source in the Taylor Form is written as [2]:

$$B_p(\mu r) = A e^{-\alpha_1 \mu r} + (1 - A) e^{-\alpha_2 \mu r} \qquad (7)$$

where A and α_1 and α_2 are the parameters that are functions of the initial energy.

The considerations in neutron shielding are similar to that for gamma shielding described above, except for the dose from secondary photons from inelastic neutron scattering, and from radiative capture. Due to the potential for radiative capture from isotopes of the shield material, isotopic rather than elemental composition of the shield medium must be considered. Shine or indirect streaming for shielding neutrons must also be considered.

The expressions for radiation exposure from a point source can be used in point kernel methods for a distributed source by deconvolution of the distributed source, and then summation of the exposure results from each element to obtain total exposure due to the distributed source. Several computer codes are available to perform this method of analysis including MicroShield, QAD, QAD-CG, QADMOD, and G3. More accurate and robust, but more complicated engineering analyses can be performed for shielding including deterministic transport theory, and Monte Carlo methods. A good review on the history of shielding and an overview of shielding analysis methods is provided in reference 4.

The radioactivity or the strength of the radioactive source is measured in units of becquerels (Bq) where 1 Bq = 1 decay per second. A common unit for measuring radioactivity is the curie (Ci) where 1 Ci = 3.7 x 10^{10} decays per second. Radioactivity can lead to exposure and absorbed dose that are described below.

Table 3. Radiation units in conventional and SI units

Radiation Unit	**Measures**	**Effect On**	**Type of Radiation**	**Relates to**	**Conversion**
Roentgen (R) **C/kg**	**Exposure**	**Air**	**Gamma and x-ray**		**1 R = 1000 milliroentgen (mR)** **1 C/kg = 3,876 R**
rad (Radiation Absorbed Dose); **Gray (Gy)**	**Dose**	**Any Material**	**All Types**	**Energy Deposited into the Material**	**1 Gy = 100 rad =1 J/kg** **10 µGy = 1 mrad** **1 Wh/l ≅ 360,000 rad**
rem (Roentgen Equivalent Man); **Sievert (Sv)**	**Dose Equivalence** **(Dose Equivalence = Dose x Quality Factor)**	**Man**	**All Types**	**Accounts for Difference in Dose and Damage**	**1 Sv = 100 rem** **10 µGy = 1 mrad**

Several terms are defined to characterize the exposure from radioactive sources as listed in Table 3. The characteristic of a radiation beam that is typically measured is exposure. This quantity expresses how much ionization the beam causes in the air through which it travels. The exposure relates to the electric charge produced in air. The SI unit of radiation exposure is the coulomb per kilogram. It is defined as the quantity of X- or gamma-rays such that the associated electrons emitted per kilogram of air at standard temperature and pressure (STP) produce ions carrying 1 coulomb of electric charge. The Roentgen is defined as the quantity of X- or gamma-rays such that the associated electrons emitted per kilogram of air at STP produce ions carrying 2.58 x 10^{-4} coulombs of electric charge. Note that this unit is confined to radiation beams consisting of X-rays or gamma-rays.

Energy is deposited in the absorber when radiation interacts with it. The quantity that is measured is called the absorbed dose. The SI unit of absorbed dose is called the gray. The gray, Gy, is defined as the absorption of 1 joule of radiation energy per kilogram of material. The traditional unit of absorbed dose is called the rad (radiation absorbed dose). It is defined as the absorption of 10^{-2} joules of radiation energy per kilogram of material.

The biological effects of absorbed dose are expressed by the effective dose that is equal to a quality factor or weighting factor times the absorbed dose. The effective dose is measured in derived SI units called sieverts (Sv).

Additional details on the units for radiation can be found in references 5 and 6. The limits for a radiation worker as dictated in U.S. Code of Federal Regulations [7] is assigned as limits to radiation workers, including those at Department of Energy sites, and members of the public[2]. Other agencies and commissions, such as the International Commission on Radiation Protection, and the U.S. Environmental Protection Agency develop specify limits for radiation exposure. Chapter 9 of reference 2 provides a discussion of the history of the international and U.S. bodies that have developed standards for radiation protection.

Table 4. Dose limits for radiation workers at a DOE facility

	DOE Limit (rem/yr)	**DOE Admin Control (rem/yr)**	**SRS Admin Control, Rad Workers (rem/yr)**
Whole Body	**5**	**2**	**1.0**
Extremity	**50**	**n/a**	**n/a**
Skin/Other Organs	**50**	**n/a**	**n/a**
Lens of Eye	**15**	**n/a**	**n/a**
Visitors/Public	**0.100**	**n/a**	**n/a**
Pregnant Worker	**0.5 during gestation**		

Administrative limits can be instituted at a site or facility to provide a margin below the legal limits as prescribed in reference 7. Table 4 lists limits for radiation workers at a U.S. DOE facility. Another important construct to control radiation exposure for a worker is the limit for airborne radioisotopes. The permissible limit for inhalation of a radionuclide is the corresponding Annual Limit on Intake expressed as a radioactivity unit that would limit the committed effective dose to 5 rem. Because it is easier to measure and control the concentration of radioactivity in air than to measure or control the intake, the Derived Air Concentration for a radionuclide is defined as radioactivity of a radioisotope per volume such that if the personnel worked the entire year and breathed the air activity, the ALI would not be exceeded. The equation for DAC for a specific radioisotope is:

---

[2] The dose limit to a member of the public is 100 mrem/year

$$\begin{aligned} \mathrm{DAC} &= \mathrm{ALI\,(in\ \mu Ci)/(2000\ hours\ worked\ per\ year\ x\ 60\ min/hr\ x\ 2\ x\ 10^{4}\ ml\ per\ minute\ breathing\ rate)} \\ &= \mathrm{ALI/(2.4\ x\ 10^{9})\ \ \mu Ci/ml} \end{aligned} \qquad (8)$$

For multiple radioisotopes, the sum of the air concentration, C_i for each radioisotope, divided by its DAC_i must be less than 1.

Additional legal limits including those for lifetime exposures for radiation workers are contained in reference 7. It is emphasized that time, distance, and shielding are all practical methods for using engineering and administrative controls to reduce personnel exposure and ensure radiation workers are well within the legal limits.

Radiolysis

Radiolysis, the molecular breakdown of a material as a result of radiation absorbed dose, can strongly affect chemical processes. The radiolytic production rate of species is characterized by the G-value that is the number of molecules of the species produced per 100 eV of absorbed energy. The G-value is typically dependent on the radiation type - that is, particles that deposits their energy in a small linear of material is referred as high Linear Energy Transfer (LET) radiation whereas particles, or gamma rays, that deposit their energy in along a greater length in a material are low LET radiation. Figures 7A and 7B depict low and high LET production of radiolytic products, respectively.

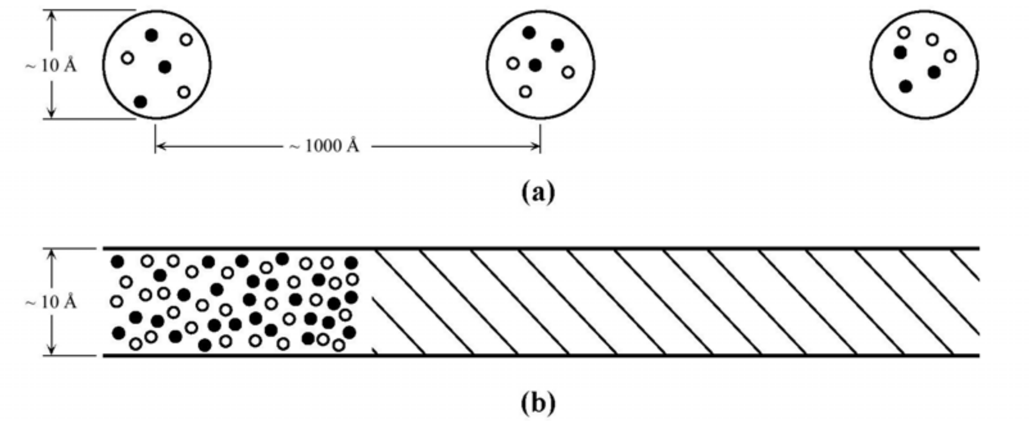


Figure 7A. Low Linear Energy Transfer results in radiolysis product (e.g. molecular products and free radicals) regions being created at widely spaced regions. Figure 7B – High Linear Energy Transfer radiation results in a high concentration of radiolysis products.

Another concept in radiolysis is that concept of forward (radiolytic process driven) and back reactions. The net effect is best evaluated by benchmarked experiments in irradiators, especially when addressing the effects of impurity species in the reactions. Even a simple system such as pure water has several potential forward and back reactions that are listed as follows:

Forward Reactions: $H_2O \xrightarrow{incident\ \ radiation} H_2O^+_{aq},\ OH,\ e^-_{aq},\ H,\ H_2O_2,\ H_2$ (9)

Back Reactions:

$$\begin{aligned} &H + H_2O_2 \rightarrow OH + H_2O \\ &OH + H_2 \rightarrow H + H_2O \\ &H_2 + H_2O_2 \rightarrow 2H_2O \end{aligned} \qquad (10)$$

A strong forward reaction processes make reaction products that themselves interact in back reactions. Impurities in the water may act as catalysts to drive the forward or back reactions in a chemical system [8].

Three key separations processes and effects of radiolysis on these processes are highlighted as some examples for separations processes. A proposed separations process should be thoroughly reviewed, and any new process should be checked for radiolysis issues prior to full operations to ensure process conditions are as expected and manageable.

Tri-*n*-butyl Phosphate (TBP) is an ester used in solvent extraction in the PUREX and HM processes as discussed in other chapters of this book. Both chemical (hydrolytic) and radiolytic reactions can decompose TBP in the following breakdown sequence [9]:

TBP + H_2O → Dibutyl Phosphoric Acid (HDBP) + Butyl Alcohol
Dibutyl Phosphoric Acid (HDBP) + H_2O → Monobutyl Phosphoric Acid (H_2MBP) + Butyl Alcohol
Monobutyl Phosphoric Acid (H_2MBP) + H_2O → Phosphoric Acid (H_3PO_4) + Butyl Alcohol

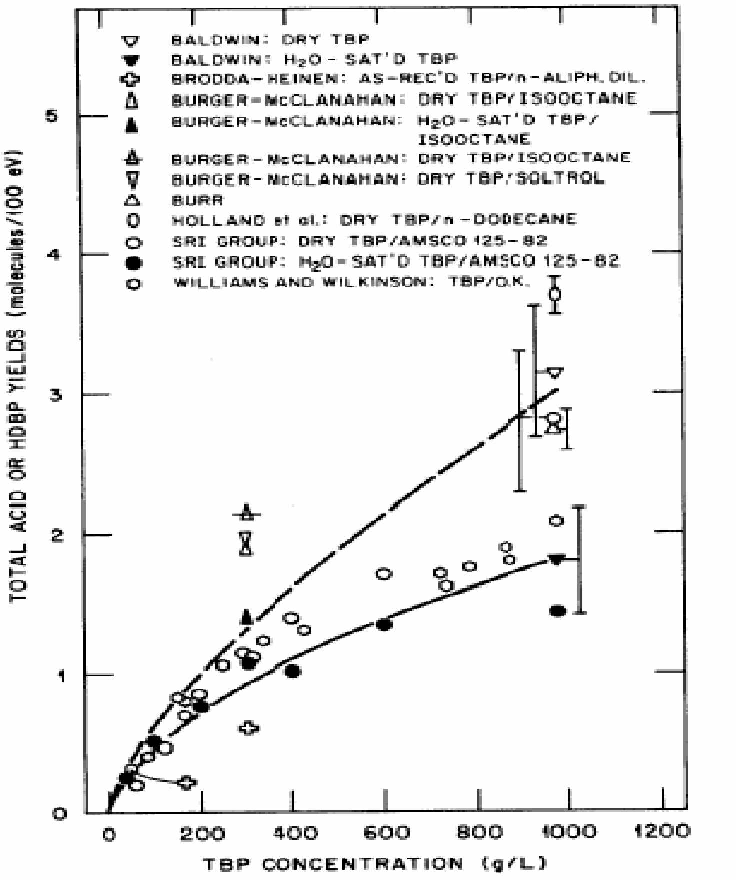


Figure 8 – Correlation of published data for yields (G-values) of total acid and HDBP from irradiation of TBP aliphatic diluent solutions [from reference 9].

Reference 9 is a key reference providing a comprehensive set of basic data concerning the products of radiolysis of pure TBP, of various hydrocarbon diluents, and of solutions of TBP in these diluents. In some experiments these materials were anhydrous whereas in others they were saturated with water. The degradation products from the radiolysis of TBP, wet or dry, include HDBP, H_2MBP, H_3PO_4, H_2, CH_4, C_2H_4, C_2H_6, C_4H_9OH, and other hydrocarbons. Of these, the greatest product yield is HDBP. The results also show a greater yield of HDBP in anhydrous condition (G = 3 acid molecules/100 eV) compared to the water-saturated condition (G = 1.8 acid molecules/100 eV) (see Figure 9).

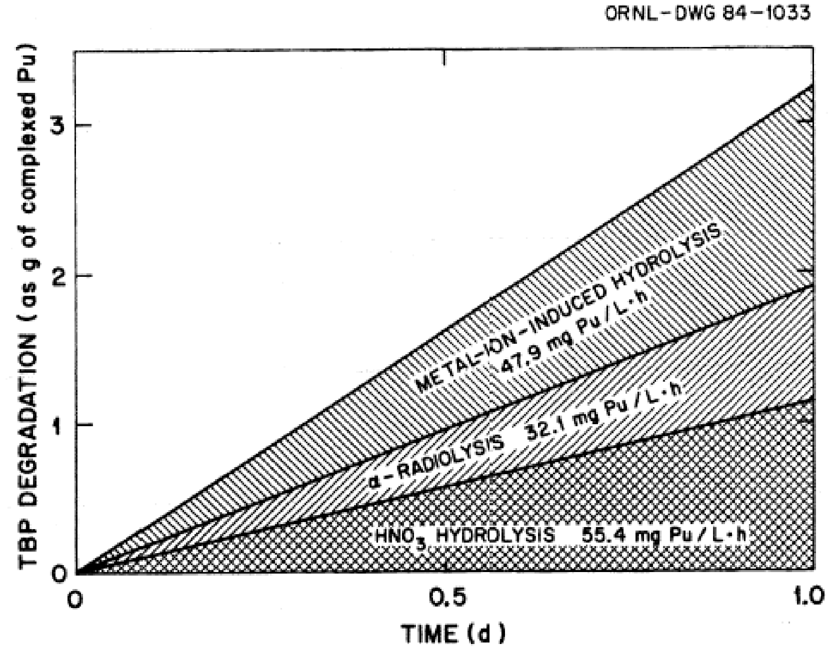


Figure 9. TBP degradation rates due to acid hydrolysis, alpha radiolysis, and metal-ion-induced hydrolysis at 80°C (shown a mg of plutonium complexed by degradation products for each factor) [from reference 10].

Figure 10 from reference 10 show the partition in breakdown rate of TBP at 80°C due to acid hydrolysis, alpha radiolysis, and metal-ion-induced hydrolysis. Reference 10 shows a strong effect of temperature on the breakdown rate for both hydrolysis and radiolysis of TBP.

Ferrous sulfamate is an important reductant in which Fe(II) is used to reduce Np(V) to Np(IV) and Pu(IV) to Pu(III) for subsequent solvent extraction or ion exchange of the Np and Pu from irradiated uranium fuels. The sulfamate specie, $(NH_2SO_3^-)_2$, acts to prevent NO_3-caused oxidation of Fe(II). Reference 11 describes the experimentation and results in which actual fuel solutions were used in a test and gamma irradiation was used as a radiation source to investigate to radiolytic-induced oxidation of Fe(II) and destruction of sulfamic acid (SA).

Figures 10A and 10B shows the results from tests with actual process solutions that if Fe(II) is not present, there is almost immediate reversion of Np(IV) to Np(V) and Pu(III) to Pu(IV). These results in reference 10 show that a high dose rate process solution can cause rapid depletion of

Fe(II). Additional results validate gamma irradiation testing to investigate the breakdown of Fe(II) (see Figure 11).

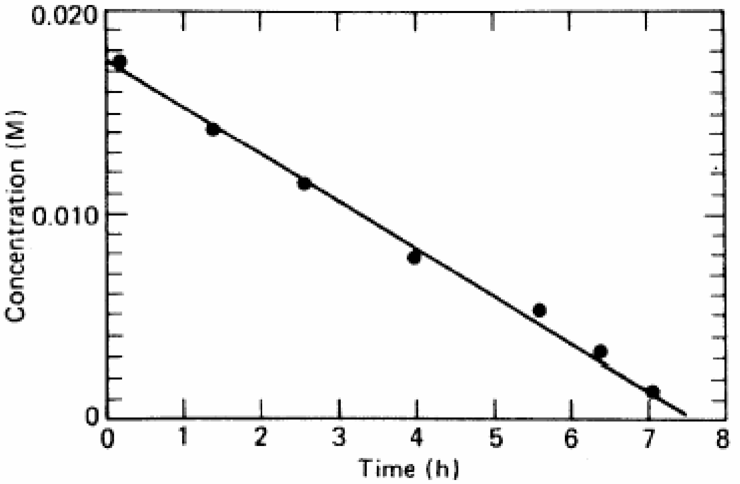


Fig. 2. Depletion of Fe(II) from radiolysis by dissolved fission products of ^{235}U in actual process solution. Dose rate = 1.5 X 10^5 rad/h, T = ~25°C.

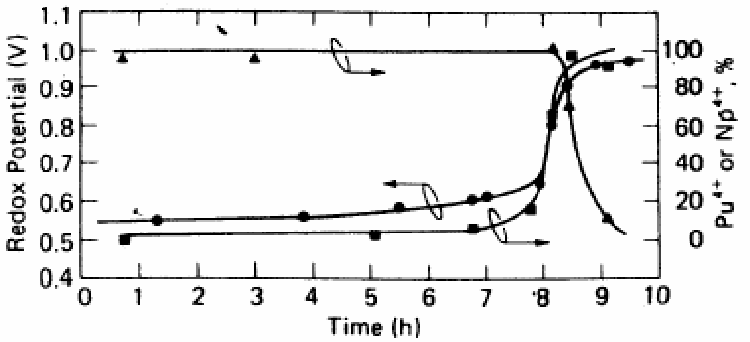


Fig. 3. Dependence of the redox potential and fraction of ^{237}Np or ^{238}Pu in the 4+ state on radiolysis by dissolved fission products of ^{235}U in an actual process solution. Dose rate = 1.5 X 10^5 rad/h, T = ~25°C, ● = redox potential, ■ = percent Pu(IV), and ▲ = percent Np(IV).

Figure 10A. Shows the depletion of the ferrous (Fe(II)) ion from radiolysis by dissolved fission product of U-235 [from reference 11]. Figure 10B shows the dramatic change to cause oxidation of of Pu (III) to Pu (IV) and indirectly the oxidation of Np (IV) to Np (V) as its Figures 10A and 10B taken together show the dramatic change when the Fe (II) ion is reduced below a certain level by radiolysis.

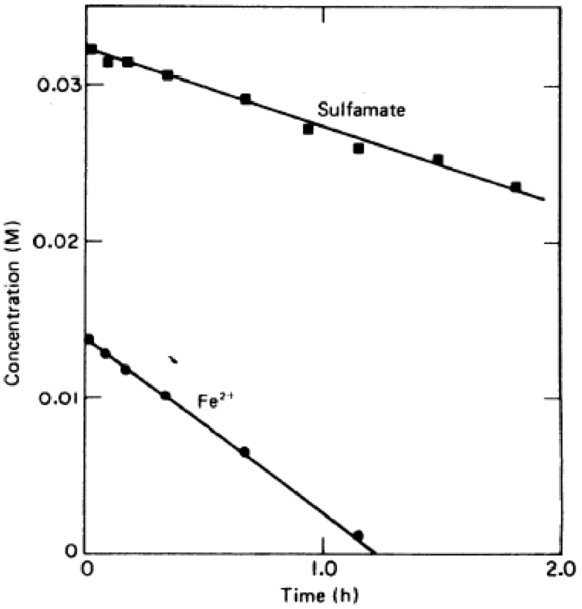


Fig. 1. Depletion of Fe(II) and sulfamate from ^{60}Co gamma radiolysis of simulated process solutions. Dose rate = 6.09 × 10^5 rad/h, T = 30 to 37°C, ● = Fe(II), and ■ = sulfamate.

Figure 11. This figure shows the depletion of the ferrous (Fe(II)) ion from radiolysis by Co-60 gamma irradiation used to investigate radiolysis effects in process solutions [from reference 11].

Ion exchange media are used extensively in separations processes. A review of radiolysis effects on ion exchange materials [12] shows resins lose ion exchange capability and may evolve gas when exposed to radiation. Doses of 10^5 to 10^6 Gy are significant to synthetic organic ion exchangers. Polycondensation-type ion exchanger media are resistant to radiation damage, but the overall properties of this type of ion exchange media is poor. Figure 12 shows significant loss of ion exchange capacity in several 4% cross-linked styrene-DVB sulfonic acid resins.

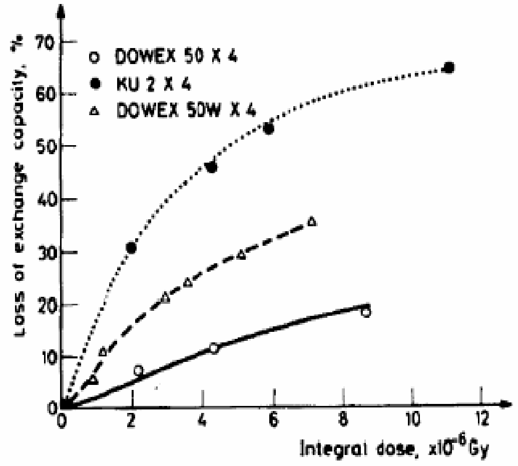


Fig. 1. A comparison of the change in total exchange capacity of 4% cross-linked styrene-DVB sulfonic acid resins (from References 31, 35, and 38)

Figure 12. Reduction in the ion exchange capacity of several 4% cross-linked styrene-DVB sulfonic acid resins [from reference 12]

Radiation Effects on Materials

Both polymers and austenitic stainless steel are important materials for gaskets and valve seats; and process equipment (tanks, valves, piping), respectively in separations processing equipment. Polymer selection is often principally dictated by chemical resistance rather than strictly radiation resistance, and therefore the use of polymers should be limited to the extent practical and/or designed for replacement.

Effects on Polymers

Polymers are complex molecules that are formed by chains of duplicated groups of atoms that themselves are typically linked by covalent bonds along a “backbone” of carbon or silicon atoms. The irradiation effects in polymers important to seals in separations processing equipment include loss of sealing ability, gas evolution, and increased leachability of constituents or loss of chemical resistance of the polymer. Factors important to cause radiation effects in polymers are the total dose (in rads), the dose rate, and the presence of O_2; most polymers are susceptible to degradation via oxidation of the resinous molecules.

The primary types of degragation mechanisms are: 1) Scission – molecular bonds are ruptured with an effective reduction in molecular weight and strength, and gas evolution; and 2) Cross-linking - polymer molecules are linked to form large 3D molecular networks which causes hardening and embrittlement; and 3) enhanced oxidation of the resinous molecules that cause severe loss of strength.

Typically, one degradation mechanism is dominant; however it is not always easy to predict the effect. For carbon-carbon chains (backbones), cross-linking will occur is H is attached to the carbon. In contrast, scission will occur at tetra-substituted carbon [13]. Polymers with aromatic molecules are more resistant to radiation damage than aliphatics. Polystyrenes and polyamides are aromatics with good radiation stability. Tables 5 and 6 from reference 13 describe the radiation resistance of a listing of polymeric materials.

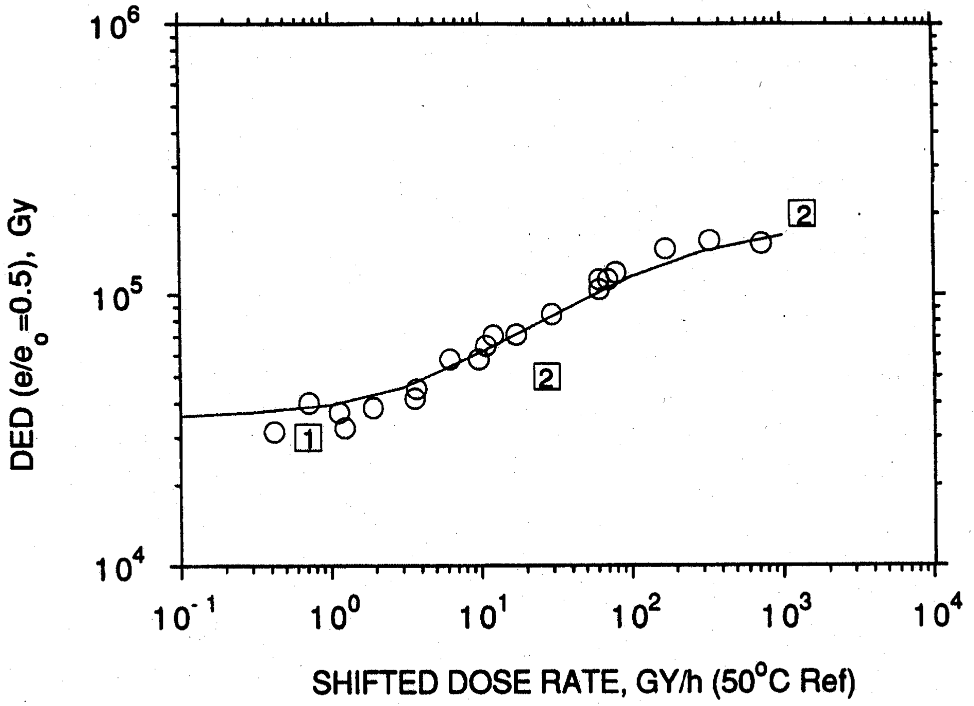


Figure 13. Dose to 50% elongation loss in PVC cable insulation (data shifted by superposition to a reference temperature of 50°C) [from reference 14]

An important note of caution in the use of polymers in radiation service is the effects of dose rate in which a high dose rate exposure may not be indicative of aging experience in a low dose environment for material irradiated to a common dose. That is, materials “qualified” in short-term exposures for a 40-year service life may fail sooner. Figure 13 shows this effect on a PVC cable insulation polymer. It is suspected that low dose rate irradiation may exacerbate the oxidation degradation mechanism that causes the dose rate effect.

For separations service, strong acid chemical resistance is needed. The following are fluoropolymers that have been reviewed and/or used for service at the Savannah River Site for chemical-resistance service:

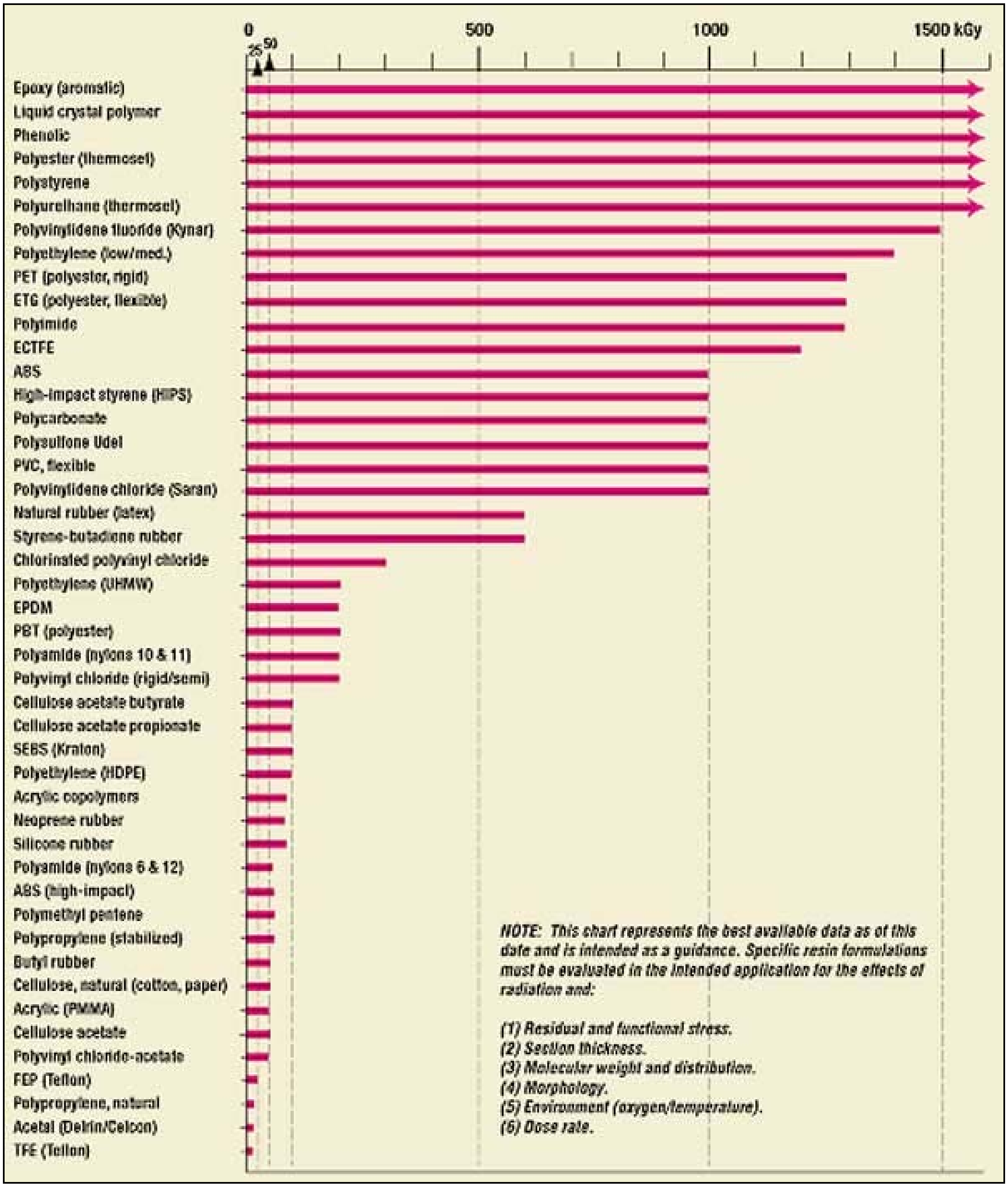
- Teflon –initial damage at 1-5E4 rad, severe damage at 1-10 Mrad
- Jumper Gaskets: Teflon-asbestos (functional to 100-1000 Mrad)
- Viton® B – FKM fluoroelastomer, older formulations with lead oxide, not suitable for TBP solutions
- Kalrez® FFKM perfluoroelastomer – expensive, resistant to acids at high temp
- Halar®/ECTFE – low permeability, possible chloride release
- Tefzel®/ETFE copolymer – used in HLW transfer lines, ball valves
- Kynar®/PVDF – most resistant fluoropolymer, less resistant to strong nitric acid or NaOH solutions (stress-cracking).

Table 5. General guide to radiation stability of polymer materials [from reference 13]

Material	Radiation Stability	Comments
Polystyrene	Excellent	
Polyethylene, various densities	Good/Excellent	High-density grades not as stable as medium- or low-density grades.
Polyamides (nylon)	Good	Nylons 10, 11, 12, 6-6 are more stable than 6. Film and fiber are less resistant.
Polyimides	Excellent	
Polysulfone	Excellent	Natural material is yellow.
Polyphenylene sulfide	Excellent	
Polyvinyl chloride (PVC)	Good	Yellows. Antioxidants and stabilizers prevent yellowing. High-molecular-weight organotin stabilizers improve radiation stability; color-corrected radiation formulations are available.
Polyvinyl chloride/Polyvinyl acetate	Good	Less resistant than PVC.
Polyvinylidene dichloride (Saran)	Good	Less resistant than PVC.
Styrene/acrylonitrile (SAN)	Good/Excellent	
Polycarbonate	Good/Excellent	Yellows. Mechanical properties not greatly affected; color-corrected radiation formulations are available.
Polypropylene, natural Polypropylene, stabilized	Poor/Fair	Physical properties greatly reduced when irradiated. Radiation-stabilized grades, utilizing high molecular weights and copolymerized and alloyed with polyethylene, should be used in most radiation applications. High-dose-rate E-beam processing may reduce oxidative degradation.
Fluoropolymers:		When irradiated, PTFE and PFA are significantly damaged. The others show better stability. Some are excellent.
Polytetrafluoroethylene (PTFE)	Poor	
Perfluoro alkoxy (PFA)	Poor	
Polychlorotrifluoroethylene (PCTFE)	Good/Excellent	
Polyinyl fluoride (PVF)	Good/Excellent	
Polyvinylidene fluoride (PVDF)	Good/Excellent	
Ethylene-tetrafluoroethylene (ETFE)	Good	
Fluorinated ethylene propylene (FEP)	Fair	
Cellulosics:		Esters degrade less than cellulose does.
Esters	Fair	
Cellulose acetate propionate	Fair	
Cellulose acetate butyrate	Fair/Good	
Cellulose, paper, cardboard	Fair/Good	
Polyacetals	Poor	Irradiation causes embrittlement. Color changes have been noted (yellow to green).
ABS	Good	High-impact grades are not as radiation resistant as standard-impact grades.
Acrylics (PMMA)	Fair/Good	
Polyurethane	Good/Excellent	Aromatic discolors; polyesters more stable than esters. Retains physical properties.
Liquid crystal polymer (LCP)	Excellent	Commercial LCPs excellent; natural LCPs not stable.
Polyesters	Good/Excellent	PBT not as radiation stable as PET.
Thermosets:		
Phenolics	Excellent	Includes the addition of mineral fillers.
Epoxies	Excellent	All curing systems.
Polyesters	Excellent	Includes the addition of mineral or glass fibers.
Allyl diglycol carbonate (polyester)	Excellent	Maintains excellent optical properties after irradiation.
Polyurethanes:		
Aliphatic	Excellent	
Aromatic	Good/Excellent	Darkening can occur. Possible breakdown products could be derived.
Elastomers:		
Urethane	Excellent	
EPDM	Excellent	
Natural rubber	Good/Excellent	
Nitrile	Good/Excellent	Discolors.
Polychloroprene (neoprene)	Good	Discolors. The addition of aromatic plasticizers renders the material more stable to irradiation.
Silicone	Good	Phenyl-methyl silicones are more stable than are methyl silicones. Platinum cure is superior to peroxide cure; full cure during manufacture can eliminate most postirradiation effects.
Styrene-butadiene	Good	
Polyacrylic	Poor	
Chlorosulfonated polyethylene	Poor	
Butyl	Poor	Friable, sheds particulates.

Table I. General guide to radiation stability of polymer materials.[2]

Table 6. Dose limits for radiation applications for various polymer materials [from reference 13]



NOTE: This chart represents the best available data as of this date and is intended as a guidance. Specific resin formulations must be evaluated in the intended application for the effects of radiation and:

(1) Residual and functional stress.
(2) Section thickness.
(3) Molecular weight and distribution.
(4) Morphology.
(5) Environment (oxygen/temperature).
(6) Dose rate.

Effects on Metals

Austenitic stainless steels are typically used as the materials of construction for piping and process vessels. These materials are subject to radiation hardening and embrittlement through formation of small “black spot” damage at low irradiation temperatures ($T_{irradiation} < 0.3\ T_{m.p.}$). The black spot damage, that is small extend defects in the crystalline structure of the stainless steel, consists of small dislocation loops, stacking fault tetrahedral, or vacancy/interstitial clusters that are formed directly following the creation of displacement cascades by primary knock-on atoms (PKAs). The PKAs are themselves created by the incident particle (e.g. neutron) as shown schematically in Figure 14. A review of the fundamental aspect of radiation effects in irradiated metals and alloys is given in reference 15.

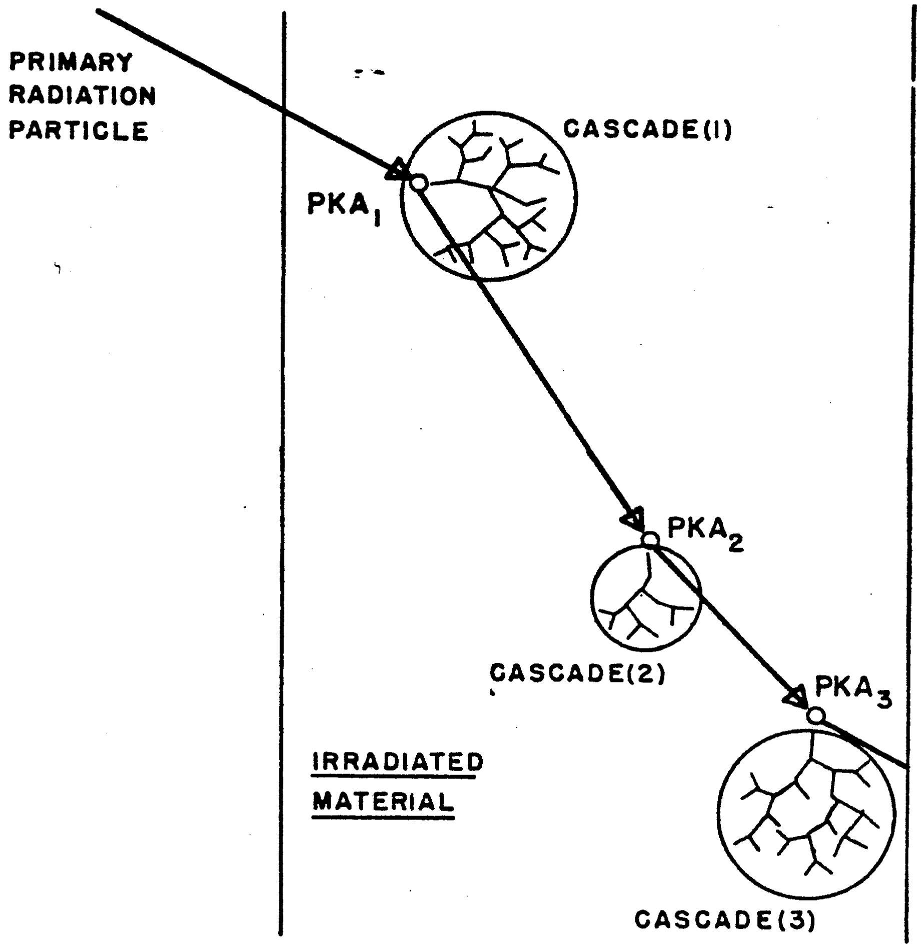


Figure 14. Basic concept of the damage process in which the incident radiation particle creates Primary Knock-on Atoms in the material which themselves create damage cascades with much local displacements

Displacements per atom (dpa) is the parameter used to characterize the dose a metal or ceramic material receives during irradiation. A material that has received a dose of 1 dpa means that on average, each atom in the material has been displaced from its lattice position one time during the irradiation. The dpa is a calculated quantity, and the model for $\mathrm{dpa_{NRT}}$ (Norgett, Robinson, Torrens in Nuc. Engr. Design, 53 50 (1975) used in the nuclear industry is:

$$K\left(\frac{\mathrm{dpa}}{\sec}\right) = N \int_{0}^{E_{max}} \Phi(E)dE \int_{E_d}^{\Lambda E} \nu(T) \frac{d\sigma(E,T)}{dT} dT \tag{11}$$

where E_d is the threshold energy for displacement of a lattice atom and $\Lambda E = [4Mm/(M+m)^2]E$ is the maximum energy that can be transferred from a incident particle of mass m (e.g. a neutron) to the lattice atom of mass M in a hard sphere model. E_d is strongly dependent on crystallographic orientation. An average energy of E_d = 40 eV is used and for iron, chromium, and nickel alloys.

N is the atomic density of the metal, $\Phi(E)$ is the energy-dependent flux of radiation, and $\sigma(E,T)$ is the microscopic cross section for transfer of energy T to a primary knock-on atom. The term $\nu(T)$ is the number of displacements caused by a PKA itself that has received energy T.

The energy transfer to the lattice atom must exceed $2E_d$ for the PKA and lattice atom to both remain displaced from original lattice atom site. The factor of 0.8 is a deviation from a hard sphere model and compensates for forward scattering in the displacement cascade. That is,

$\nu(T) = 0$ displacements for $T<E_d$
$\nu(T) = 1$ for $E_d < T < 2E_d$
$\nu(T) = 0.8T/(2E_d)$ for $T>2E_d$

Even gamma rays, if at sufficient energy, can cause displacements via initial creation of Compton or pair-production electrons. Figure 15 gives the displacement cross section for gamma rays incident on iron.

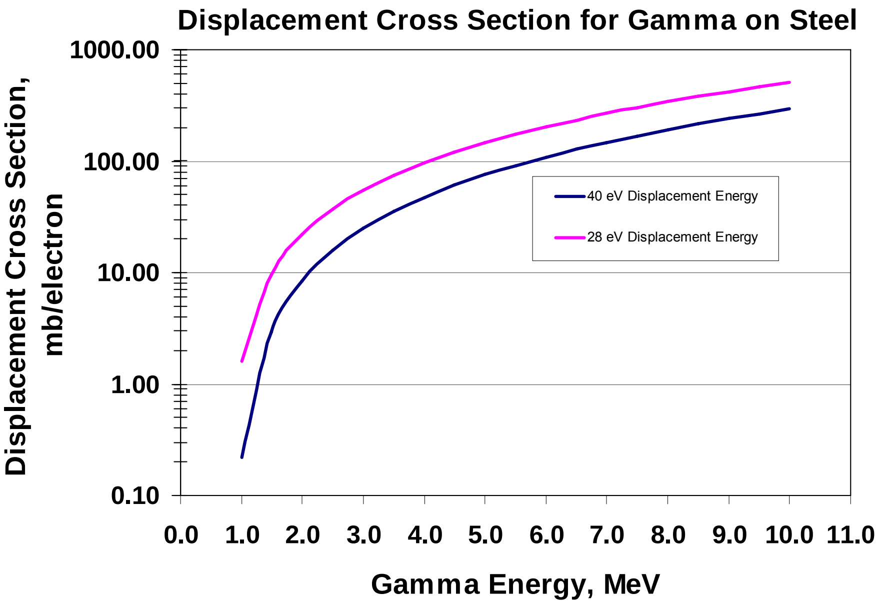


Figure 15. Displacement cross section for gamma radiation on iron

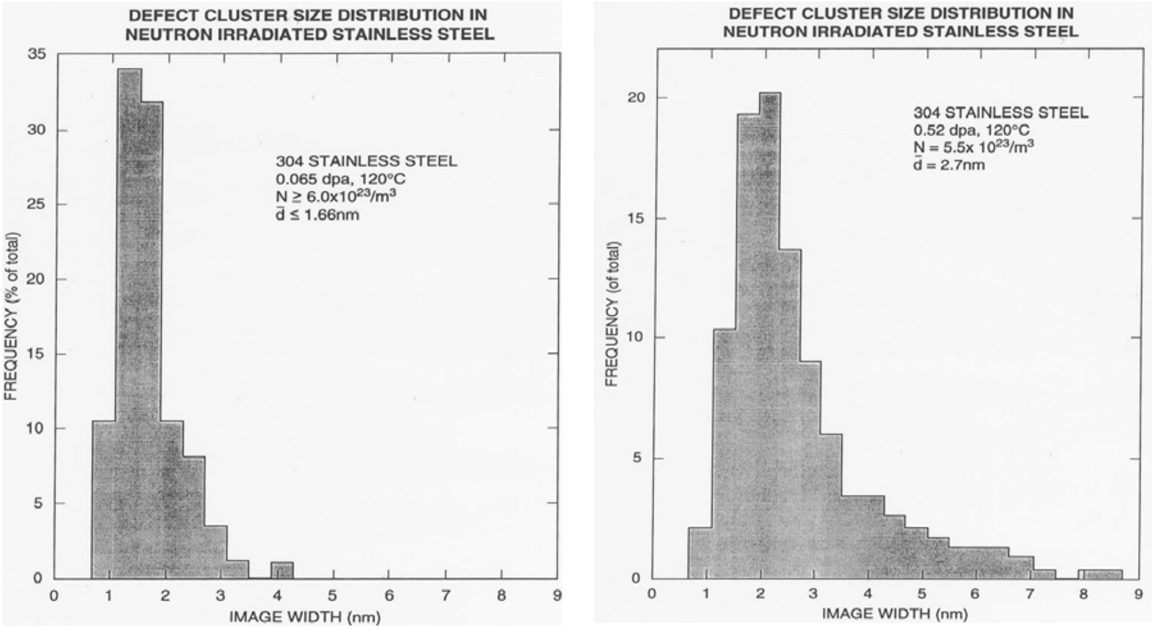


Figure 16. Low temperature Defect microstructure created during low temperature (120°C) irradiation of Type 304 stainless steel irradiated to low doses [from reference 16]

Only extremely low levels of displacement damage would be expected over the lifetime of process equipment. A fair representation of the damage microstructure that could be formed in process equipment is given in Figure 16. The mechanical response from this damaged microstructure would be slight radiation hardening. That is, radiation damage to process equipment is not considered significant to stainless steels subjected to attendant radiation in the separations processing.

Acknowledgments

This document was prepared in under the sponsorship of the U. S. Department of Energy, Office of Environmental Management. The support of Mark Gilbertson is gratefully acknowledged. The technical contributions from Ned Bibler, Dennis Vinson, and Eric Skidmore of the staff of the Savannah River National Laboratory were of paramount value to the production of this document.

References

1. http://en.wikipedia.org/wiki/Ionizing_radiation
2. John R. Lamarsh and Anthony J. Baratta, Introduction to Nuclear Engineering, 3rd edition, Addison-Wesley Series in Nuclear Science and Engineering, 2001, ISBN-10: 0201824981
3. O.W. Herman, and R.M. Westfall, "ORIGEN-S: SCALE System Module to Calculate Fuel Depletion, Actinide Transmutation, Fission Product Buildup and Decay, and Assocated Radiation Source Terms," NUREG/CR-0200, Revision 6, Volume 2, Section F7 (September 1998).
4. J. Kenneth Shultis and Richard E. Faw, "Radiation Shielding Technology," Health Physics, April 2005, Volume 88, Number 4.
5. DOE. Radiological Control Manual. DOE/EH-0256T, Rev. 1. April 1994.
6. Canadian Centre for Occupational Health & Safety; http://www.ccohs.ca/oshanswers/phys_agents/ionizing.html
7. NRC Regulations (10 CFR) PART 20--STANDARDS FOR PROTECTION AGAINST RADIATION.
8. D.W. Vinson, R.W. Deible, and R.L. Sindelar, "Evaluation of Hydrogen Generation from Radiolysis from Breached Spent Nuclear Fuel," in proceedings of American Nuclear Society Fifth Topical Meeting - DOE Spent Nuclear Fuel and Fissile Materials Management, September 23-27, 2002, Charleston, SC
9. Chapter 7, "RADIOLYTIC BEHAVIOR," in Science and Technology of Tributyl Phosphate, Volume I, Wallace W. Schulz and James D. Navratil, eds., CRC Press, Inc., 1984
10. M.H. Lloyd and R.L. Fellows, "Alpha Radiolysis and Other Factors Affecting Hydrolysis of Tributyl Phosphate," ORNL/TM-9565, June 1985
11. N.E. Bibler, "Radiolytic Instability of Ferrous Sulfamate in Nuclear Process Solutions," Nuclear Technology, Volume 34, August 1977
12. K.K.S. Pillay, "A Review of the Radiation Stability of Ion Exchange Materials," Journal of Radioanalytical and Nuclear Chemisry, Articles, Vol. 102, No. 1 (1986) 247-268.
13. K.J. Hemmerich, "RADIATION STERILIZATION, Polymer Materials Selection for Radiation-Sterilized Products," Medical Device & Diagnostic Industry, Feb 2000, p. 78

14. NUREG/CR-2877, SAND81-2613, “Investigation of Cable Deterioration in the Containment Building of the Savannah River Nuclear Reactor,” K.T. Gillen, R.L. Clough, L.H. Jones, August 1982.
15. S.J. Zinkle, “Microstructure Evolution in Irradiated Metals and Alloys: Fundamental Aspects," NATO Advanced Study Institute, Course on Radiation Effects in Solids, Erice, Sicily, Italy, July 17-29, 2004.
16. Chapter 9, “Physics of Radiation Damage in Metals,” in Nuclear Materials, Volume 10B, B.R.T. Frost, ed., Materials Science and Technology Series, VCH Verlagsgesellschaft mbH and VCH Publishers,Inc., 1994.
17. M.J. Norgett, M.T. Robinson, and I.M. Torrens,1975, Nucl. Eng. Des., 33, p. 50
18. S.J. Zinkle and R.L. Sindelar, "Defect Microstructures in Neutron-Irradiated Copper and Stainless Steel," J. Nucl. Mat. 155-157 (1988) p. 1196.

Reactors and Fuels

Allan G. Croff
Oak Ridge National Laboratory, Retired
United States Nuclear Regulatory Commission

INTRODUCTION

In the case of the nuclear fuel cycle, one of the primary materials that may be separated is the fuel for nuclear reactors. This paper focuses on the characteristics of fresh (unirradiated) and used (irradiated) fuels as a foundation for later discussion of the separation of the used fuel into its constituent parts: nuclear fuel reprocessing. In particular, this paper focuses on fuels for existing and possible future U.S. civilian nuclear power reactors that could constitute the material fed to a fuel reprocessing plant. This paper also has some discussion of the characteristics of the reactors in which the fuel is irradiated. This paper presupposes the availability of raw materials from earlier separations such as enriched uranium, thorium, and structural metals such as zirconium and stainless steel.

The first category of fuels discussed will be those in which the fuel material is encased in a metal tube called cladding. Such fuels are used in nearly all U.S. reactors that have or are operating, and are planned for most advanced nuclear reactors. Fuels for the following types of reactors will be described:

- Light water reactors (LWRs): These are reactors in which the core containing the fuel is cooled with water. The hydrogen in the water also slows (moderates) the fission neutrons produced by the nuclear reactor which allows it to operate using fuel having fissile material concentrations less than 10%. All U.S. power reactors are LWRs of which there are two variants:
    - Pressurized-water reactors (PWRs) in which the water in the reactor vessel is under sufficiently high pressure so that it does not boil. Steam is generated in a heat exchanger and routed to the turbine generator.
    - Boiling-water reactors (BWRs) in which the water in the reactor vessel is allowed to boil and the resulting steam is routed direction to the turbine generator.
- Fast reactors: These are reactors in which the core is cooled with a molten metal such as Na, Na/K, Bi, or Pb, or by helium gas. Because these elements are relatively heavy (or, in the case of He, having a low density) fission neutrons are not significantly slowed and these are known as “fast” reactors. Such reactors require fissile material concentrations around 20%. Relatively few of these reactors have operated but they are being developed for future use in the U.S. and elsewhere.

The paper will then turn to a second category of fuels: graphite-based fuels where the major constituent is the graphite form of carbon. Most of these reactors are cooled by He but some designs have considered molten salt coolants such as mixtures of light-element fluorides.

Finally, changes in the fuel resulting from neutron irradiation and the characteristics of the fuel after irradiation will be described.

METAL-CLAD FUELS

Light Water Reactors (LWRs)

PWRs

A PWR fuel assembly[1] is composed of square array of circular fuel elements (or pins or rods). A fuel element is a long, thin tube made of Zircaloy that contains a stack of right circular uranium dioxide fuel pellets each of which is a few centimeters long. The stack of fuel pellets is about 0.3m shorter than the tube to allow space for fission gases to collect to avoid over-pressurizing the fuel element. The array of fuel elements is held in place laterally by several Zircaloy grid spacers. Instead of containing a fuel element some of the positions in the grid contain a guide thimble assembly. The guide thimble (tie rod) serves multiple purposes:

- Its threaded ends extend through the top and bottom nozzle and serve to hold the assembly together in the axial direction
- It provides a guide for neutron-absorbing control rods that are used to control the chain reaction. The control rods are similar in shape to a fuel element but contain a neutron poison such as gadolinia instead of fuel.
- It provides access for instrumentation and small neutron sources used to initiate a stable chain reaction.

Traditional PWR fuels contained uranium enriched to 3-3.5%. However, in efforts to get more energy per dollar invested, fuel burnup and, as a consequence, fuel enrichments have steadily increased and are now approaching 5%. PWR fuel assemblies also can include burnable poison rods containing boron or gadolinium to offset the initially high reactivity of fuel assemblies containing the higher enrichments.

The core of a large reactor contains 200-250 fuel assemblies. At each refueling a quarter to a third of the highest burnup fuel assemblies are replaced with fresh fuel and the assemblies that were removed are placed in racks in large storage pools. The fuel assemblies are lifted from the top using crane and normally remain in the vertical position.

BWRs

BWR fuel elements and assemblies are conceptually similar to the PWR. However, there are a number of noteworthy differences:

- BWR assemblies are about 40% of the size of PWR assemblies and there are proportionately more assemblies in the reactor core
- BWR fuel assemblies are surrounded by a Zircaloy channel (or shroud) to control the steam formed in the upper portion of the assembly
- BWR fuel elements have a larger diameter than PWR elements
- On average, BWR fuel tends to have lower enrichments and burnup than PWR fuel

---

[1] Nomenclature concerning nuclear reactor fuel is not consistent. Some documents call the array of fuel rods a sub-assembly and others call it a fuel element.

- BWRs have traditionally had a more complex fuel design that included burnable poisons mixed with the fuel matrix and variable axial enrichment.
- BWRs control the chain reaction with boron carbide control rods in the shape of a cross (cruciform) inserted between four fuel assemblies.

PWR and BWR Variants: LWR vendors continue to evolve their fuel designs to be more reliable, cost-effectively increase burnup, and anticipate advanced fuel cycles. Some of the key trends are as follows:

- Developing and deploying advanced cladding to allow higher fuel burnup to be reliably achieved. This generally involves modifications to the composition of Zircaloy.
- Moving to fuel assemblies containing more fuel elements having a smaller diameter: up to 10x10 for BWRs, 18x18 for PWRs.
- Recycling transuranic actinides. Recycle of Pu in LWR fuels is established practice overseas and the U.S. has test assemblies in U.S. reactors to disposition plutonium from nuclear weapons. Technology to recycle of other actinides is being developed. Fuel containing U-Np-Pu is a modest extension of established technology for U-Pu fuels. Fuels or targets[2] containing Am and/or Cm require further development.
- PWR fuel designs are moving in the direction of having enrichment gradation and burnable poisons in the fuel matrix
- Use of thoria-based LWR fuels has been investigated because the Th-^{233}U fuel cycle is more efficient in thermal reactors, which leads to the potential for very high burnups (subject to cladding capabilities).

Fast Reactors (FRs)

FR fuel assemblies are conceptually similar to the BWR, including the channel. However, there are a number of noteworthy differences:

- The cladding and other fuel assembly structural material for a FR fuel assembly is made of stainless steel, not Zircaloy
- FR fuel assemblies are hexagonal
- The radial dimensions of a FR fuel assembly are similar to those of a BWR and significantly smaller than those of a PWR
- Fuel elements have a smaller diameter than for LWRs.
- The stack of fuel pellets in the FR is shorter (~2m) than in the BWR (~3.5m). About 2/3 of the FR stack is driver fuel to sustain the chain reaction and the rest is a depleted uranium oxide axial blanket to produce plutonium.
- Driver fuel is composed of 15-30% plutonia with the remainder being urania.
- In the radial direction the driver assemblies are surrounded by blanket fuel assemblies composed of fuel elements containing larger-diameter depleted uranium dioxide fuel pellets to produce plutonium.

---

[2] A target contains nuclear material that cannot sustain a chain reaction but which absorbs neutrons to yield beneficial products.

- Fuel elements are typically separated by a spiral wire wrap on the surface of each element instead of grid spacers.

FR Fuel Variants

Large fast reactors have been built and operated but mainly as demonstration facilities. The design of the reactor per se and the fuel assemblies continues to evolve. In particular, the fuel assembly and element length, fuel enrichment, and the number of elements per assembly continue to evolve.

The FR design described above is designed so that the used fuel and blankets contain 10-20% more Pu than was present in the fuel inserted into the reactor. Doing so was believed to be desirable in the 1970s and 1980s to sustain rapid expansion of nuclear power production. However, with the growth of nuclear power having been much slower than projected and the accumulation of Pu and other transuranic elements in the U.S. used fuel inventory, enhancing Pu production rates is not a desirable goal for the foreseeable future. Instead, the U.S. is now developing technology to recover the transuranic elements from used fuel and transmute (fission) it to produce shorter-lived and less-toxic fission products. This has resulted in efforts to change FR fuel designs in two respects:

- The axial blankets above and below the driver fuel and the radial blanket assemblies outside the driver fuel region are being replaced by materials that do not produce Pu but which reflect neutrons back into the core such as yttria, zirconia, or stainless steel.
- The uranium dioxide in the driver fuel is being replaced by inert materials such as ZrO_2 that do not produce Pu.

R&D is also underway to develop fuels that may be better than the oxide fuels described above. In particular, efforts are underway to develop fuel pellets composed of actinide carbides, nitrides, or metals with the largest U.S. efforts being on the latter. All of these offer the advantage of higher thermal conductivity but such fuels have not been fabricated in substantial quantities. Additionally, carbides and nitrides produce substantial amounts of ^{14}C that must be managed.

METAL-CLAD FUEL FABRICATION

Conventional Uranium Dioxide Fuel Conversion and Fabrication

Conventional nuclear fuel fabrication

Conventional nuclear fuel fabrication involves converting enriched uranium to uranium dioxide powder and then going through a number of steps to produce pellets, elements, and assemblies. This is called the “powder-to-pellet” process.

Conversion:

The feed material to uranium dioxide fuel fabrication is enriched uranium hexafluoride. The first step is to process the uranium hexafluoride by reducing it with a mixture of hydrogen and steam to yield uranium dioxide and hydrofluoric acid (HF) to yield uranium dioxide powder. Along with this new fuel material, uranium dioxide scrap from the fuel fabrication plant is recycled by converting it to powder.

Pelletization: Uranium dioxide powder is mixed with additives, converted to the proper particle size, aggregated into larger particles, and pressed into green pellets. The green pellets are then sintered at high temperature to form the initial fuel pellet which is then ground to yield a fuel pellet suitable for constituting nuclear fuel (subject to inspection which yields scrap for recycle).

Fuel Element (Rod) Assembly: A Zircaloy cladding tube is loaded with fuel pellets by sliding them into the tube by force and/or gravity. Helium is injected into the tube, the top end spring is inserted, and the end plugs are welded. Then QC procedures are performed.

Machining Fuel Assembly Components: In separate facilities, the key structural components of the fuel assembly, such as the end pieces/nozzles, are fabricated.

Construct Fuel Assembly: A “cage,” composed of the grid spacers and guide thimbles (tie rods), is constructed on a horizontal table. The fuel elements are then pushed into the cage. The end pieces/nozzles are then attached. The resulting assembly is inspected and loaded into special carriers for transportation to the reactor.

Conventional Mixed-Oxide Fuel Fabrication

For the most part, conventional fabrication of fuels containing mixed oxides (MOX) of actinide elements proceeds in essentially the same way as that for uranium dioxide fuels with one important exception: blending. In particular, it is necessary to blend the various actinide oxides to achieve a very homogenous powder having precise proportions of the various actinide elements to achieve an acceptable and desirable power profile from the fuel as function of burnup. Historically, such blending has been achieved by combining pure uranium and plutonium oxides containing a higher proportion of plutonium oxide than what is needed for the fuel and mixing the oxides for extended times in tumbling vessels to yield a “master blend.” Additional uranium dioxide is then combined with small batches of the master blend and other additives and again thoroughly mixed to yield the final proportions needed for a particular amount of fuel pellets.

An alternative method for homogenizing the actinides is to dissolve them in nitric acid which readily yields a homogenous mixture. The actinides are then precipitated by neutralizing the acid with chemicals such as ammonia or oxalic acid to yield ammonium compounds of the actinides or actinide oxalates, respectively. The precipitate is then calcined to yield the actinide oxides which are reduced to the dioxide with hydrogen.

Essentially all MOX fuels made and used to-date have been composed oxides of uranium and plutonium. Such fuels have been irradiated in LWRs and fast reactors, primarily in Europe and Japan. The U.S. is building a plant at Savannah River that will use plutonium from dismantled nuclear weapons to make fuel for U.S. LWRs. Test assemblies are presently being irradiated in U.S. LWRs. More advanced fuel cycles may add Np, Am, and/or Cm to the U-Pu oxides. Manufacture of such fuels is challenging because they can be highly radioactive and Am oxide has significant volatility at fuel sintering temperatures.

Sol-Gel/Sphere-Pac Fuel Fabrication

Sol-gel approaches to fuel fabrication are liquid-based and, as a consequence, do not involve blending powders. Instead, the process yields small spheres having a diameter of tens to a thousand microns. This process involves the precipitation of gelatinous hydrated uranium or plutonium oxides from the mixture of an acidic solution of U and/or Pu and a gelation agent such as hexamethlyenetetramine and/or urea using a compound containing ammonia. The gel passes through a vertical nozzle to yield gelatinous spheres. There are two processes for producing such spheres (internal and external gelation) where the essential difference is the order in which the ingredients are added. The spheres are washed to remove process chemicals, aged, and dried.

Once the dry spheres are available they can be calcined to yield hard, dense actinide oxide spheres which can then be made into a pellet fuel using the rest of the conventional fabrication process described earlier (called DIPRES). However, this has many of the same disadvantages as the conventional processes such as generated considerable amounts of dust during grinding. An alternative to DIPRES is the Sphere-Pac process in which calcined spheres are sintered and made in three different sizes designed to achieve maximum packing density. The spheres are simply mixed and poured into cladding tubes where smear densities of about 85% can be achieved. Sphere-Pac fabrication may be particularly useful in the manufacture of fuels containing high-activity actinides but it still does not solve the Am volatility problem.

Fabrication of Non-Oxide Matrix Fuels

Advanced metal-clad fuels in which the fuel matrix is composed of actinide carbide, nitrides, and metals are being developed. Fabrication of carbides and nitrides is similar to that for oxide fuels with the exception that these fuels are very sensitive to the presence of oxygen and humidity and so they must be fabricated under carefully controlled inert atmospheres. Development efforts are in their early stages.

Fabrication of metal matrix fuels is entirely different from other fuels. The starting point for such fuels is a molten mixture of actinide metals which might contain significant amounts of some fission products and possibly inert alloying elements. The source of this material would likely be from reprocessing used fuel using electrochemical technology which will be described in a later presentation. For metal matrix fuels the equivalent of a fuel pellet is a metal fuel rod ~0.5m long. This rod is formed by first making a mold composed of quartz tubes having the desired internal diameter and one open end. The tube is inserted into a furnace containing molten fuel matrix. The furnace is sealed and evacuated to vacuum conditions. The open end of the mold is lowered into the metal bath and the pressure in the furnace is increased which forces the metal into the quartz tubes. The tubes are raised from the melt and allowed to cool after which the tubes are destroyed to yield the metal rods. The rods are then inserted in cladding tubes much like oxide fuel pellets.

Metal matrix fuels have been made for decades and irradiated in demonstration reactors such as EBR-I and II at Idaho National laboratory.

Fabrication Scrap Recycle

Although not shown in most drawings of fuel fabrication processes, all such processes must include provisions to recycle fuel pellets or rods that do not meet specifications. For oxide fuels this involves dissolving the fuel in nitric acid and recovering the actinides in pure form using solvent extraction or possibly ion exchange for some minor actinides. For metal fuels the matrix would be routed back to the melt furnace or the electrorefiner.

GRAPHITE FUELS

In reactors using graphite fuels the graphite serves as both a structural material that partially substitutes for metal cladding as well as being a neutron moderator. Two types of graphite-based fuels are under development: prismatic fuel assemblies for the high-temperature gas-cooled reactor (HTGR) and spherical fuel assemblies for a pebble-bed modular reactor (PBMR).

The equivalent of a fuel pellet in graphite fuels begins with the sintered U/Pu/Th oxide (possibly plus other actinides in advanced fuel cycles) kernel prepared using the sol-gel process described earlier. This is coated with layers of graphite and pyrolytic carbon to yield a tristructural-isotropic (TRISO) fuel particle 350 to 500 microns in diameter for the HTGR and about 900 microns for the PBMR.

HTGR Prismatic Fuel

For HTGR fuel the particles containing 8-20% enriched uranium are made into “compacts” (process described later) having a diameter of about 1.3 cm and a length of 5-6 cm. The compacts are inserted into about half of the ~200 axial holes a hexagonal prismatic machined graphite block that is about 0.8m tall and 0.36m across the flats. Each hole contains 14 to 15 compacts. The holes that do not contain fuel provide passage for the helium coolant. Additionally, some assemblies contain a few larger holes for control rods.

The completed fuel block is the equivalent of a fuel assembly for the HTGR. Each block weighs about 135 kg and contains 5-7 kg U and 4 kg SiC with the remainder being carbon. A three-dimensional stack of the blocks constitutes the core of an HTGR which requires about 1000 blocks to produce 600 MW(t).

PBMR Fuel

For PBMR fuel ~15,000 TRISO particles containing 7-10% enriched uranium are made into a spherical “pebble” (process described later). The diameter of a pebble is about 6 cm and it weighs about 210 g of which about 9g is uranium and 6 g is SiC with the remainder being carbon.

The pebble is the equivalent of a fuel assembly for this reactor. The core of the PBMR is simply a random bed of pebbles where pebbles are inserted at the top, drop downward by gravity, and are removed at the bottom. A PBMR producing 400 MW(t) would require about 360,000 pebbles.

GRAPHITE FUEL FABRICATION

Fabrication of both HTGR and PBMR fuels begins with sintered fuel kernels from the sol-gel process. In a series of operations conducted at elevated temperatures in fluidized beds the following layers are deposited:

- Porous carbon from a ethane-argon atmosphere
- Pyrolytic carbon from a propane-argon atmosphere
- SiC (to retain fission products) from an atmosphere of methltrichlorosilane, hydrogen, and argon
- Pyrolytic carbon from a propane-argon atmosphere

to yield a coated kernel otherwise known as a TRISO fuel particle.

For HTGR fuels the particles are mixed with graphite and other additives and cold pressed to form a green compact. The compact is carbonized at ~800 C in an inert atmosphere and then sintered at ~1800 C in a vacuum.

For PBMR fuels the particles first coated with graphite and additives. The coated particles are mixed with more graphite and other additives and cold pressed at relatively low pressure to form a green pebble core. A graphite shell is then molded around the core using higher pressure and the shell is machined to achieve the desired dimensions. The green pebble is carbonized at ~800 C in an inert atmosphere and then sintered at ~1800 C in a vacuum.

USED FUEL CHARACTERISTICS

Neutron irradiation causes many changes in the fuel. Some of the most important changes are:

- Fissioning actinides to produce energy and fission products: About a net 1% of the actinides are destroyed by fission for each 10 GWd/MTHM of burnup and essentially the same mass of fission products is produced. Fuel burnup for PWRs and BWRs are now approaching 50 GWd/MTHM and 45 GWd/MTHM, respectively.

- Capturing neutrons to produce a variety of radionuclides
    - Other actinide isotopes:$^{232,\,236}$U,^{237}Np, $^{238\text{-}242}$Pu, $^{241\text{-}243}$Am, ^{244}Cm (U-Pu fuel cycle) and ^{232,233}U (U-Th fuel cycle)
    - Radionuclides from activation of hardware
      - Main constituents: ^{60}Co (stainless steel and Inconel), ^{93}Zr (Zircaloy), ^{14}C (graphite)
      - Trace constituents: transuranics from U, ^{3}H from lithium, ^{14}C from nitrogen

- Physical changes: The fuel matrix swells and cracks, the cladding is embrittled and contains a layer of ‘crud’ on the outside, and fission gases are released to the plenum of metal clad fuel elements.

Key implications of the foregoing to separations are as follows:

- Essentially the entire periodic table of elements is contained in the used fuel and must be considered in separations.

- The radioactivity of most fuels has increased by orders of magnitude because of the fission products, activation products, and short-lived actinides, which leads to large amounts of photons (gamma rays and x-rays), neutrons (spontaneous fission and alpha,n), alpha particles, and beta particles. The impacts of the radiation are:
    - Penetrating radiation leads to the need for thick radiation shielding
    - Radiation, especially from alpha particles, leads to degradation of materials in general and organic materials in particular.
    - The amount of decay heat is sufficient so that active provisions for heat removal are required for years and passive provisions for much longer times.

References

1. AREVA, Seminar titled “AREVA's Fuel business and its strategic and financial significance”given by Claude Jaouen at “AREVA Technical Days” (December 15-16, 2003) available at http://www.areva.com/servlet/BlobProvider?blobcol=urluploadedfile&blobheader=application%2Fpdf&blobkey=id&blobtable=Downloads&blobwhere=1073577265770&filename=Combust_vA2.pdf
2. Atomic Energy of Canada Limited, http://www.nuclearfaq.ca/cnf_sectionA.htm
3. Ayer J.E. et al, “Nuclear Fuel Cycle Facility Accident Analysis Handbook,” NUREG-1320 (May 1988).
4. Benedict, M. et al “Nuclear Chemical Engineering,” 2nd Edition, McGraw-Hill (1981)
5. Charollais F. et al, “Latest Achievements of CEA & AREVA NP on HTR Fuel Fabrication,” 3rdInternational Topical Meeting on High Temperature Reactor Technology, Johannasburg, South Africa (October 2006).
6. Croff A.G. et al, “Revised Uranium-Plutonium Cycle PWR and BWR Models for the ORIGEN Computer Code,” ORNL/TM-6051 (September 1978).
7. Croff A.G. and C.W. Alexander, “Decay Characteristics of Once-Through LWR and LMFBR Spent Fuels, High-Level Wastes, and Fuel-Assembly Structural Material Wastes,” ORNL/TM-7431 (November 1980).
8. Croff A.G. et al, “Graphical and Tabular Summaries of Decay Characteristics for Once-Through PWR, LMFBR, and FFTF Fuel Cycle Materials,” ORNL/TM-8061.
9. Croff A.G. and M.A. Bjerke, “An ORIGEN2 Model and Results for the Clinch River Breeder Reactor,” NUREG/CR-2762 (ORNL-5884) (July 1982)
10. Croff A.G. et al, “Background, Status, and Issues Releated to the Regulation of Advanced Spent Nuclear Fuel Recycle Facilities,” White Paper of the U.S. Nuclear Regulatory Commission’s Advisory Committee on Nuclear Waste and Materials, NUREG-1909 (May 2008).
11. Del Cul G.D. et al, “TRISO-Coated Fuel Processing to Support High-Temperature Gas-Cooled Reactors,” ORNL/TM-2002/156 (Sept 2002)
12. Forsberg C.W. et al, “Practical Aspects of Liquid-Salt-Cooled Fast-Neutron Reactors,” presentation at the International Congress on Advances in Nuclear Power Plants Seoul, Korea May 15–19, 2005
13. Forsberg C.W., “Refueling Options and Considerations for Liquid-Salt- Cooled Very High-Temperature Reactors,” ORNL/TM-2006/92 (June 2006)
14. Gee D., “The Pebble Bed Modular Reactor,” reference Gee (2002) [RM194] in the U.S. Department of Energy, “Draft Global Nuclear Energy Partnership Programmatic Environmental Impact Statement,” DOE/EIS-0396, published October 2008 (March 16, 2002)
15. Hilton B.A. et al, “Metallic Fuels for Actinide Transmutation,” unpublished presentation at the: 9th OECD/NEA Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation Nîmes, France (September 25-29, 2006).
16. IAEA, “Fuel Performance and Fission Product Behaviour in Gas-Cooled Reactors,” IAEA-TECDOC-978 (November 1997).
17. IAEA, “Current Status and Future Development of Modular High-Temperature Gas Cooled Reactor Technology,” IAEA-TECDOC-1198 (Feb 2001)

18. IAEA, “Status and Advances in MOX Fuel Technology,” Technical Report Series (TRS) No. 415 (May 2003)
19. IAEA Fast Reactor Data Base at http://www.iaea.org/inisnkm/nkm/aws/frdb/index.html
20. Kitamura N. et al, “PRESENT STATUS OF INITIAL CORE FUEL FABRICATION FOR THE HTTR,” High temperature gas cooled reactor technology development, Proceedings of a Technical Committee meeting held in Johannesburg, South Africa, IAEA-TECDOC-988 (13-15 November 1996)
21. Lee Y.W., “Development of HTGR Coated Particle Fuel Technology in Korea,” 3rdInternational Topical Meeting on High Temperature Reactor Technology, Johannasburg, South Africa (October 2006).
22. Lerch R.E. and R.E. Norman, “Nuclear Fuel Conversion and Fabrication Chemistry,” Radiochimica Acta 36, 75-88 (1984).
23. Long J.T., “Engineering for Nuclear Fuel Reprocessing,” Gordon and Breach (1967).
24. Pasamehmetoglu K. et al, The Global Nuclear Energy Partnership: Transmutation Fuels Campaign: FY’08 Accomplishments and FY’09 Plans, GNEP Annual Meeting, Idaho Falls, Idaho (October 8, 2008).
25. PMBR Web Site at https://www.pbmr.co.za/
26. Sterbentz J.W., “Reactor Physics Parametric and Depletion Studies in Support of TRISO Particle Fuel Specification for the Next Generation Nuclear Plant,” INEEL/EXT-04-02331, (Sept 2004)
27. Tang C., “Irradiation Testing of Matrix Material for Spherical HTR-10 Fuel Elements,” 3rdInternational Topical Meeting on High Temperature Reactor Technology, Johannasburg, South Africa (October 2006) [lower left]
28. U.S. Department of Energy, “Characteristics of Potential Repository Wastes,” DOE/RW-0184-R1, vol 2 (July 1992)
29. U.S. Department of Energy, “A Technology Roadmap for Generation IV Nuclear Energy Systems,” GIF-002-00 (December 2002)
30. U.S. Department of Energy, “Yucca Mountain License Application,” DOE/RW-0573 (June 2008).
31. U.S. Department of Energy, “Draft Global Nuclear Energy Partnership Programmatic Environmental Impact Statement,” DOE/EIS-0396, Fig. A.4.1.4-1 (October 2008)
32. U.S. Nuclear Regulatory Commission, http://www.nrc.gov/reactors
33. Wigeland R.A., “Criteria Derived for Geologic Disposal Concepts,” unpublished presentation at the: 9th OECD/NEA Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation Nîmes, France (September 25-29, 2006)
34. Wymer R.G. et al, “Light Water Reactor Nuclear Fuel Cycle,” CRC Press Inc. (1981).

Spent Fuel Reprocessing

Robert Jubin
Oak Ridge National Laboratory

Reprocessing of used nuclear fuel is undertaken for several reasons. These include (1) recovery of the valuable fissile constituents (primarily ^{235}U and plutonium) for subsequent reuse in recycle fuel; (2) reduction in the volume of high-level waste (HLW) that must be placed in a geologic repository; and (3) recovery of special isotopes. There are two broad approaches to reprocessing: aqueous and electrochemical. This portion of the course will only address the aqueous methods.

Aqueous reprocessing involves the application of mechanical and chemical processing steps to separate, recover, purify, and convert the constituents in the used fuel for subsequent use or disposal. Other major support systems include chemical recycle and waste handling (solid, HLW, low-level liquid waste (LLLW), and gaseous waste). The primary steps are shown in Figure 1.

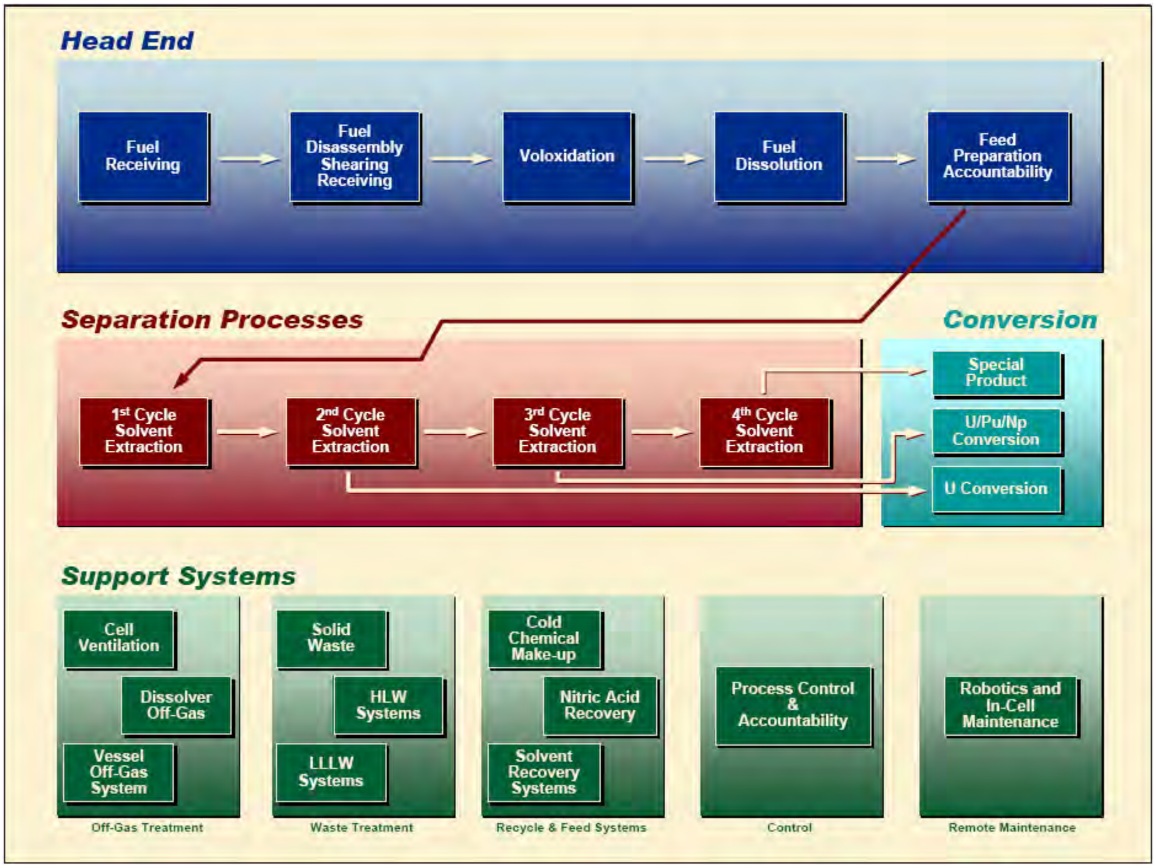


Figure 1. Aqueous Reprocessing Block Diagram.

Head-End Processes

Mechanical Preparations

The head end of a reprocessing plant is mechanically intensive. Fuel assemblies weighing ~0.5 MT must be moved from a storage facility, may undergo some degree of disassembly, and then be sheared or chopped and/or de-clad. The typical head-end process is shown in Figure 2. In the case of light water reactor (LWR) fuel assemblies, the end sections are removed and disposed of as waste. The fuel bundle containing the individual fuel pins can be further disassembled or sheared whole into segments that are suitable for subsequent processing. During shearing, some fraction of the radioactive gases and non-radioactive decay product gases will be released into the off-gas systems, which are designed to recover these and other emissions to meet regulatory release limits.

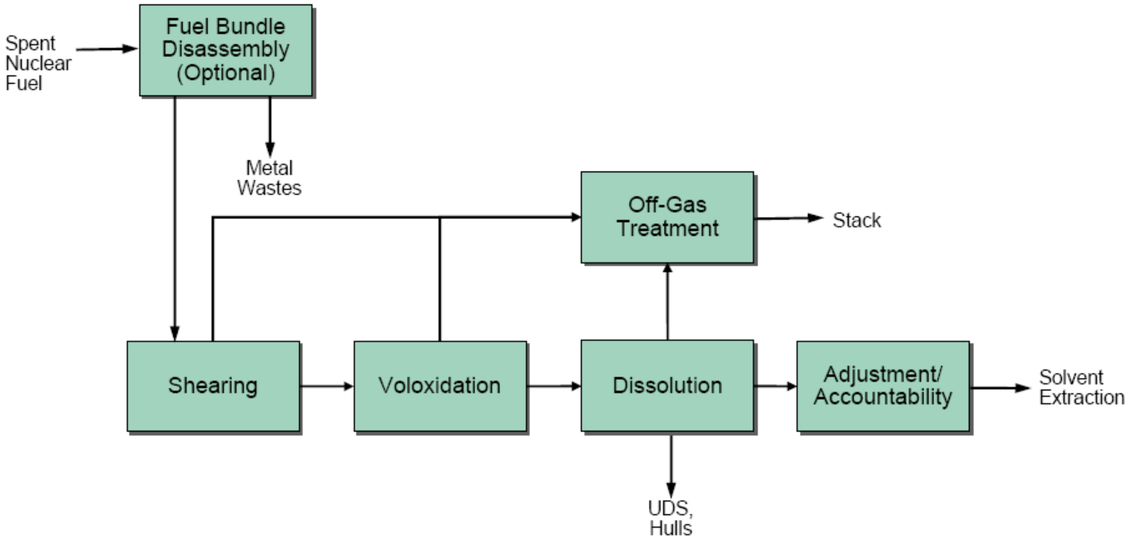


Figure 2. Block Flow Diagram for Aqueous Head-End Processing.

Fast reactor fuel is treated in a similar manner with a few additional complications. These include the need to (1) address any residual sodium coolant adhering to the fuel bundle and (2) potentially remove the metal shroud from the fuel bundle.

The fuel is typically cut into segments that are 1 to 2 inches in length using a hydraulically activated shear. Key aspects of any shear design include remote maintenance considerations, control of particulates, off-gas capture, and ensuring that the shearing action does not result in crimping of the segments which would prevent the fuel “meat” from being fully exposed to the reactive gases in voloxidation or the nitric acid in dissolution/leaching process steps. To address this latter point, a number of blade designs have been evaluated. Figure 3 shows one such shear blade design with a zigzag blade similar to a pinking shear.

Figure 3. Typical Fuel Shear Blade Design (Croff, 1997).

Voloxidation

Voloxidation is a dry head-end process that has been proposed for oxidation of spent fuel oxide and the removal of tritium from fuel prior to aqueous processing (Spencer, 2006). If effective, this process would avoid introducing tritium into the aqueous systems where it would accumulate and greatly complicate the separation, recovery, and packaging of tritium, should this be required to meet regulatory emission requirements.

Spent LWR fuel consists of about 94% UO_2, with the remainder composed of fission product oxides, transmutation (or transuranium) products, and activation product oxides. Thus, oxidation behavior is almost entirely determined by the uranium component. During voloxidation, the UO_2 reacts with oxygen via reaction (1) to form U_3O_8, causing an expansion of the crystalline structure and resulting in the formation of a relatively fine powder:

$$3UO_2 + O_2 \rightarrow U_3O_8 \ . \tag{1}$$

The voloxidation process usually takes place at 450°C to 650°C. Higher temperatures increase the reaction rate. The rate of reaction at 480°C is such that >99.9% of the tritium is released in about 3 to 4 h (Goode and Stacy, 1978; Goode et al., 1980). Over 99% of the fuel particles are typically reduced to <44 µm.

Tritium is released from the fuel matrix and diffuses to the surface of the particles where it reacts with oxygen to form tritiated water, which then enters the off-gas stream. Off-gases from the voloxidizer usually flow through a “catalytic combiner” to ensure that all released tritium is converted to tritiated water (Spencer, 2006). In the standard process, minor but radiologically significant fractions of other volatile radionuclides are released. This includes ~ 50% of the carbon (^{14}C); 1% of the iodine (^{129}I); and 5% of the krypton (^{85}Kr). (Note: the isotopes shown in parentheses are the isotopes of primary concern for fuel cooled greater than 5 years.) It is known that iodine is chemically bonded with cesium and oxides of uranium and is the reason it is not completely released in standard voloxidation. The evolution of semivolatiles at 480°C includes less than about 0.2% of the ^{106}Ru, ^{125}Sb, and $^{134–137}Cs$. Trace amounts of tellurium and selenium would also be expected to volatilize. Higher temperatures increase the fraction of volatiles and semivolatiles evolved (Spencer, 2006)

The reduction in particle size by voloxidation greatly accelerates the rate of the subsequent dissolution process. The higher oxidation state of the uranium reduces the nitric acid requirement and reduces the amount of NO_x evolved. Standard voloxidation at 480°C generally increases the insolubility of Ru, Rh, Pd, Mo, and Tc, while the solubility of PuO_2 is generally unchanged (Spencer, 2006; Goode, et al., 1980). However, higher voloxidation temperatures can cause sintering of the plutonium and slightly increase the insoluble fraction, which may only be significant for mixed oxide (MOX) fuels.

Advanced voloxidation methods are under development using higher operating temperatures and oxidants other than oxygen to remove other fission products (Del Cul et al., 2006; Del Cul, Spencer, and Collins, 2006). Repeated cycling between UO_2 and U_3O_8 using air at ~500°C and H_2 at ~800°C enhances the release of fission products [e.g., the Oxidation Reduction Oxidation (OREOX) process under development in Korea] by breaking the particles. Tests at ORNL show that black U_3O_8 (prepared by voloxidation of UO_2 at 500°C) readily reacts with ozone to form a red-colored monoclinic UO_3 at temperatures below 200°C that decomposes back to U_3O_8 at temperatures above 300°C (Del Cul, 2008).

Dissolution

The primary purpose of dissolution in an aqueous process is to convert the solid fuel “meat” into an aqueous chemical form suitable for subsequent separation steps. During the dissolution operation, which can either be a batch or continuous process, the fuel is typically reacted with nitric acid to solubilize the uranium, plutonium, minor actinides, and most of the fission products. This completes the separation of the fuel from the cladding and results in the release of certain fission products to the off-gas system. Depending on the fuel burn-up and previous head-end processing, some fraction of the fuel remains as undissolved solids. The key reactions are shown as follows.

For uranium metal:

$$U + 5.5HNO_3 \rightarrow UO_2\,(NO_3)_2 + 2.25NO_2 + 1.25NO + 2.75H_2O. \qquad (2)$$

The addition of O_2 to the dissolver leads to what is referred to as “fumeless dissolution” (Long, 1967), which avoids the formation of NO_x gases:

$$U + 2HNO_3 + 1.5O_2 \rightarrow UO_2\,(NO_3)_2 + H_2O. \qquad (3)$$

Similar reactions can be written for the direct dissolution of the uranium oxide fuel pellets (not showing the dissolution of the remaining actinides and fission products):

$$3UO_2 + 8HNO_3 \rightarrow 3UO_2\,(NO_3)_2 + 2NO + 4H_2O \qquad (4)$$

and

$$UO_2 + 4HNO_3 \rightarrow UO_2\,(NO_3)_2 + 2NO_2 + 2H_2O. \qquad (5)$$

While both reactions (4) and (5) occur, reaction (4) tends to dominate when the nitric acid concentration is below 10 M (Benedict, Pigford, and Levi, 1981).

In like manner to that of the dissolution of metal [reaction (3)], the addition of O_2 during the dissolution of the oxide limits the formation of nitric oxides:

$$2UO_2 + 4HNO_3 + O_2 \rightarrow 2UO_2(NO_3)_2 + 2H_2O. \qquad (6)$$

If the fuel has undergone “standard” voloxidation and the uranium is oxidized to U_3O_8, then the dissolution reactions are approximated by adding reaction (4) + reaction (5) + eight times reaction (9) to yield (Lewis, 2008)

$$U_3O_8 + 7HNO_3 \rightarrow 3UO_2(NO_3)_2 + 0.5NO_2 + 0.5NO + 3.5H_2O \qquad (7)$$

or by the approximate equation

$$U_3O_8 + 7.35HNO_3 \rightarrow 3UO_2(NO_3)_2 + NO_2 + 0.35NO + 3.65H_2O. \qquad (8)$$

And if the uranium source is fully oxidized uranium from advanced voloxidation, one again has a “fumeless dissolution” reaction:

$$UO_3 + 2HNO_3 \rightarrow UO_2(NO_3)_2 + H_2O. \qquad (9)$$

In batch dissolution, the sheared fuel is placed in a perforated metal basket that is immersed in hot nitric acid to dissolve about 99% of the fuel meat (Croff, 1997). At the end of the dissolution period, only the hulls segments will remain in the basket. A small portion of the fuel that is insoluble (e.g., noble metals such as palladium) will typically fall to the bottom of the dissolver vessel where it is either recovered for subsequent treatment or disposed of as a waste.

While most operating reprocessing plants use batch dissolution, there has been and continues to be considerable interest in continuous dissolution. Several designs have been developed and deployed.

In a “ferris wheel” design, the fuel segments are placed in baskets located around a large wheel. As the wheel is rotated, the baskets are submerged in heated nitric acid. The rotation rate is set to provide sufficient immersion time for the fuel meat to dissolve. As the wheel continues its rotation, the empty hulls are dumped into a collection hopper for metal waste. The basket is then loaded with more fuel segments to repeat the process (Croff, 1997). The most recent installation of such a dissolver is at the Rokkasho Reprocessing Plant in Japan.

A horizontal dissolver design has been developed and cold tested at ORNL. In this design, the fuel segments are fed into one end of a rotating, nearly horizontal cylinder and forced along its length by its internal structure (e.g., a helix). The rotating actions are of two types; the first is an action that moves the fuel from one stage or segment of the dissolver to the next, and the second is a rocking action to aid the dissolution. Nitric acid enters the other end and moves countercurrent to the fuel/cladding. During this countercurrent movement, the acid contacts and dissolves the fuel material. The countercurrent movement of the acid and cladding also ensures that the more difficult fuel particles see the strongest acid and provides a degree of washing of the hulls in fresh acid.

In all cases the dissolver must be designed to prevent criticality (typically by virtue of its geometry) and operate while in contact with highly corrosive reagents.

Separation Processes

There are two primary separation processes used in aqueous fuel reprocessing: solvent extraction and ion exchange.

Solvent Extraction

Solvent extraction (SX) is the workhorse for industrial-scale separations in fuel reprocessing. Solvent extraction is a very flexible process that is easily adapted to multistage operations. This is highly desirable when very high purification is needed or when the properties of materials to be recovered are so similar that single-stage precipitation or crystallization would not result in acceptable separations (Benedict et al., 1981). Ion exchange, which will be discussed later, can also be used to achieve high degrees of separation but is generally most suited for situations where small quantities or low concentrations are involved.

Solvent extraction involves bringing two immiscible phases into intimate contact, typically an aqueous phase and an organic phase. When this occurs, the extractable components will distribute between the two phases. Assuming sufficient contact time, equilibrium will be established between the two phases. The ratio of the concentration in the resulting phases is referred to as the distribution coefficient, D.

$$D_i = y_i / x_i \quad , \qquad (10)$$

where y_i = concentration of *i* in the organic phase and
x_i = concentration of *i* in the aqueous phase .

Figure 4 shows a single stage (stage N) of a multistage series SX unit. For the sake of simplicity, this is shown as a mixer/settler system. Typically solute-free flow rates or molal units are used to eliminate the necessity of recalculating volume changes resulting from changes in composition.

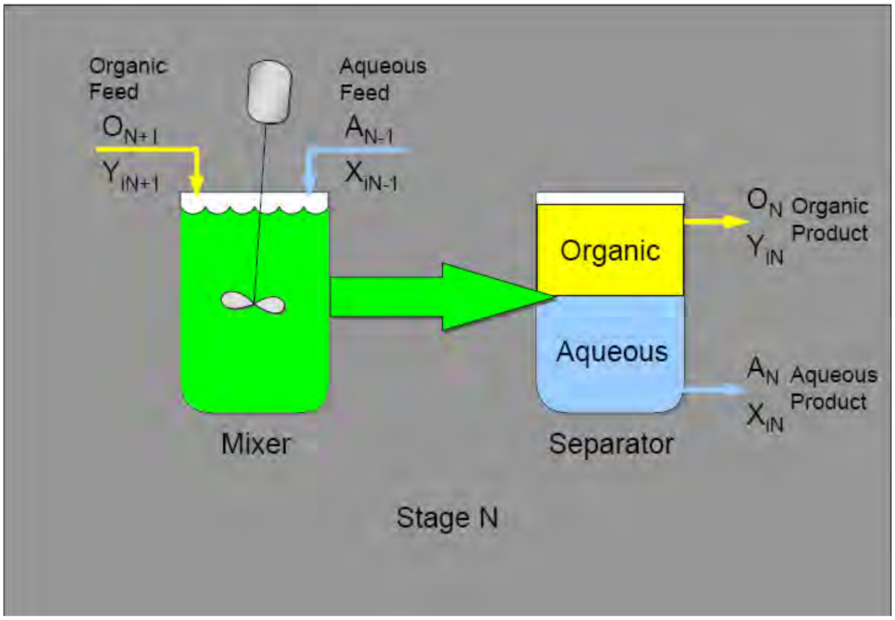


Figure 4.
Mixer Settler – Stage N.

For a simple one-stage batch extraction based on Figure 4, one can write the following material balance assuming that the extractable component is initially only in the aqueous feed:

$$O(y_{n+1}) + A(x_{n-1}) = O(y_n) + A(x_n) \ , \qquad (11)$$

where O = organic volume and
A = aqueous volume.

Assuming $y_{n+1} = 0$ and $D = y_n/x_n$ yields the following:

$$y_n = D(x_{n-1}) / (OD/A + 1). \qquad (12)$$

The fraction extracted is

$$O(y_n) / A(x_{n-1}) = (OD/A) / (1 + OD/A). \qquad (13)$$

This equation clearly shows the obvious conclusion that the greater the distribution coefficient or the higher the O/A ratio, the greater the fraction of the extractable component that will be removed from the aqueous phase.

Solvent extraction provides a number of “knobs” to allow the process engineer to design the desired separation. First is the selection of the extractant itself; its physical properties control the resulting distribution coefficients. Second, as already shown, there is the phase ratio (i.e., relative flow rates), which can be varied. Then for a typical extractant, the distribution coefficient is also a function of temperature. Figure 5 shows distribution coefficients for various solutes in 30% tributyl phosphate (TBP).

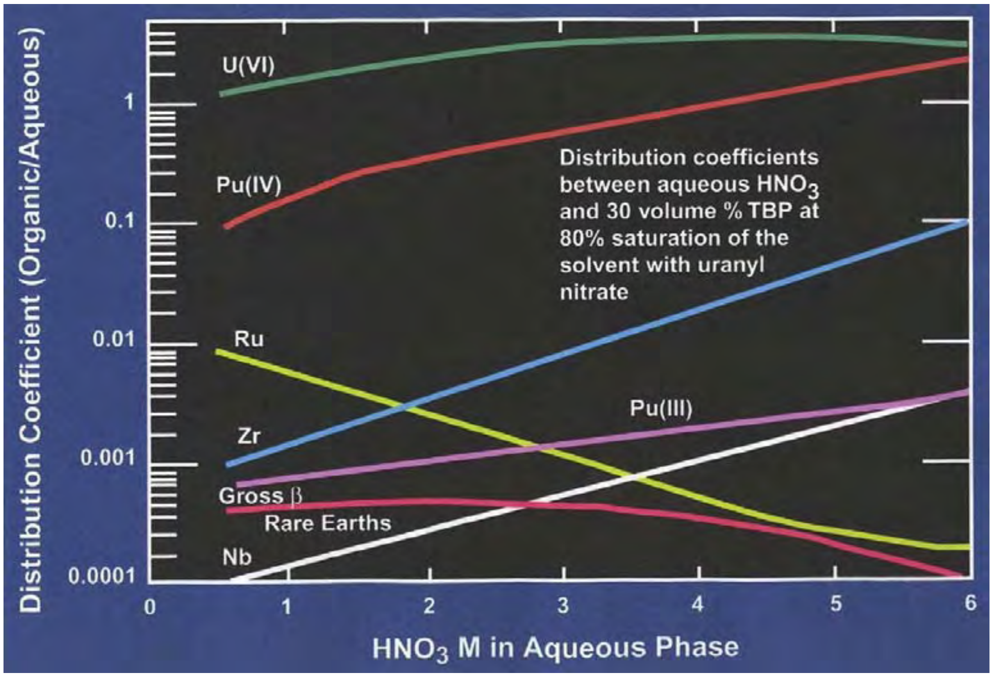


Figure 5. Distribution Coefficients for 30% TBP.

Note the strong impact of nitric acid concentration on the various distribution coefficients in Figure 5. This figure also shows the significant impact that valence state has on the extractability of metals such as plutonium. While Pu^{4+} is highly extractable at high acid conditions, Pu^{3+} is virtually impossible to extract. What is not shown clearly in this figure is that the distribution coefficients are also impacted by the interaction of the solutes present as well as the impact that temperature has on the distribution coefficients.

Solvent extraction in most fuel cycle applications is performed in multiple stages to effect the desired separations. This is accomplished by coupling multiple contactors in series or banks such that the aqueous and organic flows are countercurrent (Figure 6).

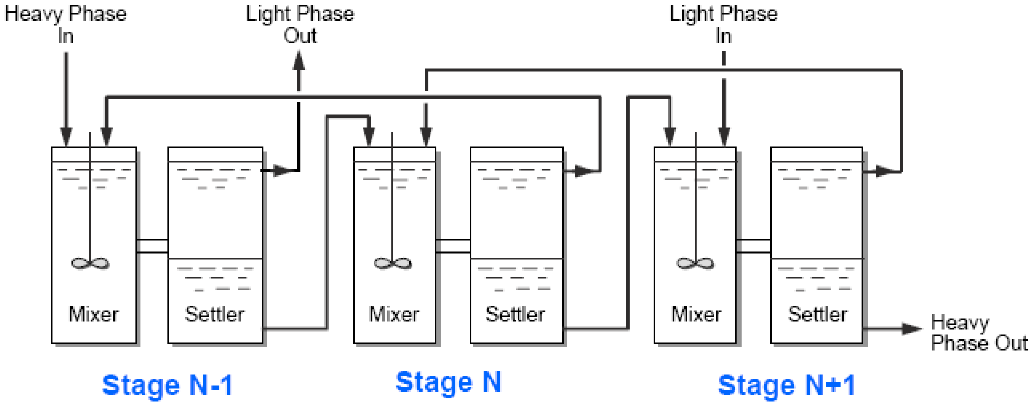


Figure 6. Multistage Countercurrent SX Bank.

One of the most widely used solvent extraction processes in fuel reprocessing is the PUREX (**Pl**utonium - **UR**anium **EX**traction) process. The PUREX process dates back to 1949 when it was discovered that tetravalent cerium nitrate could be separated from trivalent rare earths using TBP (Benedict et al., 1981). Based on this discovery, process development and demonstration work was conducted at Knolls Atomic Power Laboratory and ORNL prior to deployment in the plutonium production plant at the Savannah River Site in 1954 and then at the Hanford site in Washington State. Since that time it has been used in all commercial reprocessing plants.

The SX cycle is defined for the PUREX process as “those operations in which separations are achieved by transferring the U and/or Pu from the aqueous phase to the organic phase and then recovering the U and/or Pu by back-extraction into an aqueous phase” (Wymer and Vondra, 1981).

In the PUREX process, the aqueous phase is the adjusted dissolver product and the organic extractant is typically a 30% TBP in a purified kerosene or n-dodecane diluent. Under highly acidic conditions, the uranium and plutonium are extracted into the organic phase. The loaded organic phase is then contacted with dilute acid to strip the uranium and plutonium back into the aqueous phase. Most other constituents of spent fuel prefer the aqueous phase under both conditions. Ordinarily, the plutonium is in the +4 valence state and tends to be extracted with the uranium. If a separation of uranium and plutonium is desired, the Pu^{4+} can be reduced to the +3 valence state by using suitable chemicals; when in this state, it has a very low distribution coefficient and prefers the aqueous phase. This process is most often conducted in a bank of mixer/settler contactors or in a pulsed column, both of which are configured to provide countercurrent flow of the two phases and a sufficient number of theoretical stages to effect the desired separation.

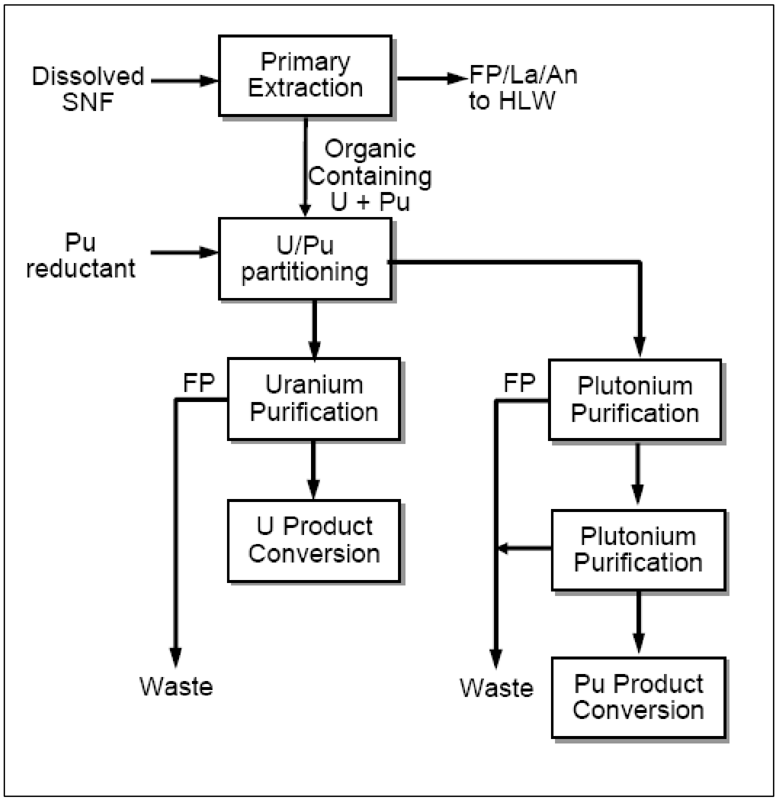


Figure 7. Block Flow Diagram for PUREX Process

In the “normal” PUREX flowsheet the U/Pu loaded organic phase is contacted with an aqueous phase containing nitric acid and a reductant (see Figure 7). This results in the Pu^{3+} transferring to the aqueous phase while the uranium remains in the organic phase. The separated aqueous phase, containing the plutonium, then advances to the plutonium purification cycles where any residual uranium is removed resulting in a pure plutonium stream. For the Barnwell Nuclear Fuel Plant (BNFP) in South Carolina, specifications for the plutonium product were < 100 ppm uranium, less than 40µCi/g Pu total gamma, and <5 µCi/g Pu zirconium-niobium activity. The uranium is then back-extracted as part of the uranium/plutonium partitioning cycle into a clean aqueous phase using dilute nitric acid (Benedict et al., 1981). The resulting uranium stream is further separated from residual fission products in the uranium purification cycle. Multiple cycles can be used to improve product purity. One PUREX cycle typically has an upper limit on its decontamination factor or its ability to decontaminate the uranium or plutonium from the fission products and transplutonium elements of about 1000 (Wymer and Vondra, 1981).

Research and development efforts under the DOE Advance Fuel Cycle Initiative (AFCI) have examined a number of SX options that allow a variety of processing options and product stream combinations. Figures 8 and 9 show schematically two sample flow sheets for the separation of uranium, plutonium, and other fuel components. These are of varying complexity but show how combining various SX processes and produce very different products.

The goal in the flow sheet shown in Figure 8 is to recover “pure” uranium, americium, and curium streams while never producing pure plutonium. The initial step uses a TBP-based SX process to separate uranium and technetium from the dissolved fuel solution while not extracting the plutonium. The technetium would be recovered from the uranium/technetium stream using an ion exchange process. The raffinate from the uranium extraction cycle contains the transuranium actinides, rare earth/lanthanides, and other fission products. To remove the bulk of the heat-generating fission products, a process called Fission Product Extraction (FPEX) is employed. This cycle extracts the cesium, strontium, and decay daughters barium and rubidium using an extraction solvent consisting of, 4,4',(5')-di-(t-butyldicyclo-hexano)-18-crown-6 (DtBuCH18C6), calix[4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6), and 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (Cs-7SB modifier) in a branched aliphatic kerosene (Isopar® L). Following the FPEX process, the TBP-based Neptunium / Plutonium Extraction (NPEX) process is used to separate plutonium/neptunium. The raffinate or aqueous “waste” from NPEX contains the rare earths/lanthanides, other fission products, and transuranium actinides americium and curium. The transuranic elements extraction (TRUEX) process is then used to separate the rare-earth lanthanides and transuranium actinides from the remaining fission products. The TRUEX process uses an extractant containing TBP and N, N di-isobutyl octylphenyl carbamoylmethyl-phosphine oxide (CMPO) in a n-dodecane diluent. The Trivalent Actinide-Lanthanide Separations by Phosphorous reagent Extraction from Aqueous Komplexes (sic) (TALSPEAK) process separates the actinides from the lanthanides. TALSPEAK uses HDEHP (di-2-ethylhexyl phosphoric acid) in n-dodecane as the extractant. The resulting americium/curium stream might be further separated using processes that are still in development. While this scheme provides extensive partitioning of the fuel constituents, it also requires a significant amount of primary process equipment and support processes to manage the large number of individual extractants required.

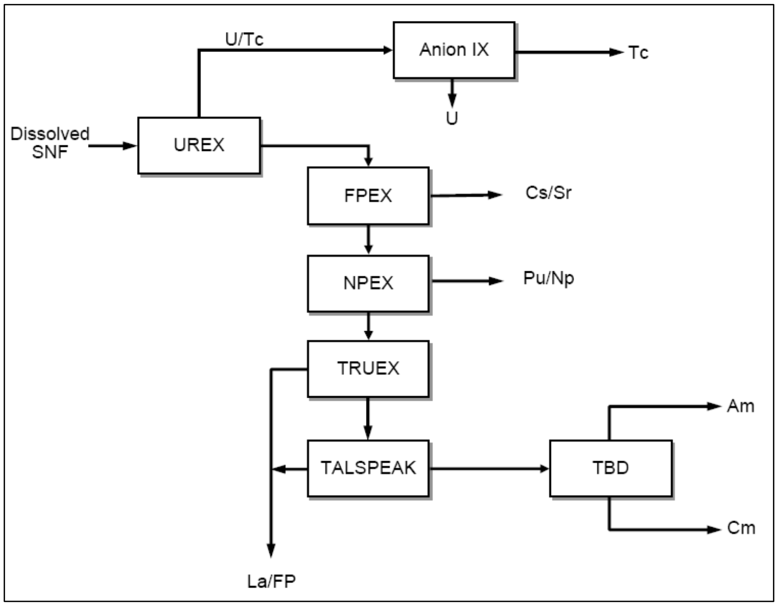


Figure 8. Block Flow Diagram for a Flow Sheet Option Producing Separated Americium and Curium Streams.

The flow sheet represented by Figure 9 was recently demonstrated. This flow sheet utilizes a TBP-based co-extraction–partial partitioning first cycle which results in three streams: (1) a U/Tc product, (2) a U/Pu/Np/Tc product, and (3) a raffinate stream that contains the fission products, the lanthanides, and the remaining actinides. Both of the first-cycle product streams could be further purified to remove the technetium (in the recent demo, only the technetium from the uranium stream was recovered.) The first-cycle raffinate was then fed to the TRUEX process that recovered the Am/Cm/Ln product from the “other fission product” stream. This “other fission product” stream was then further separated using FPEX to recover the high-heat cesium/strontium fission products. The Am/Cm/Ln product from the TRUEX process was separated into the Am/Cm product and a lanthanide (Ln) waste stream using the TALSPEAK process.

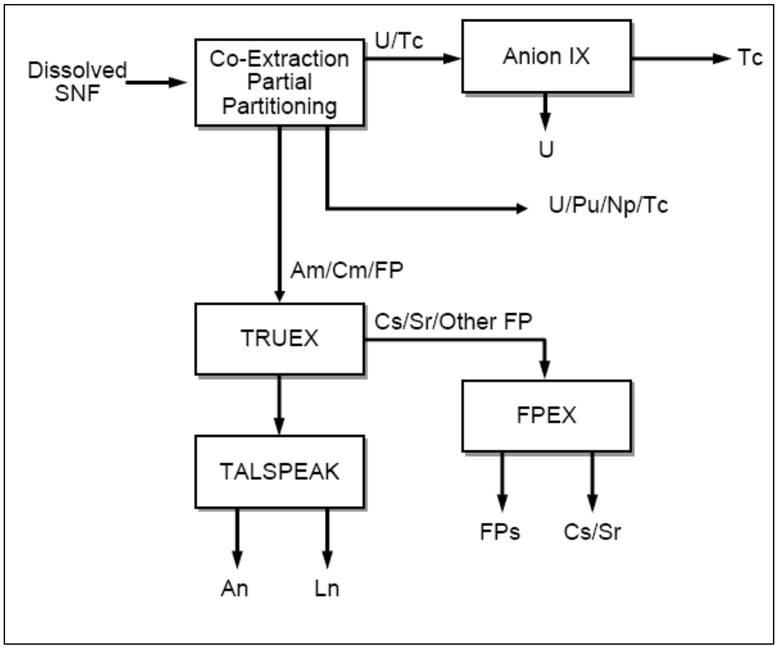


Figure 9. Block Flow Diagram for Recent AFCI SX Demonstration.

Product Specifications

To be suitable for reuse as reactor fuel, the resulting products must meet certain product specifications for impurities among other requirements. ASTM provides such specifications for UO_2, PuO_2 powder, mixed UO_2/PuO_2 powder, and sintered UO_2 pellets. The impurity specifications for these fuel forms are discussed below.

ASTM specifications for sinterable uranium dioxide powder is provided in ASTM C753 (2004) as containing ≤ 1500 µg/g U total impurities. This standard also provides specific maximum impurities for individual elements. For example the iron and molybdenum impurities are limited to ≤ 250 µg/g U each, nitrogen to ≤ 200 µg/g U, but thorium impurities are limited to ≤ 10 µg/g U. A recent IAEA (2007) document discusses the management of reprocessed uranium and provides some typical impurity analysis data for recovered UO_3 powder.

Separate specifications are also spelled out for the sintered uranium dioxide pellets in ASTM C776-06 (2006b). As with the powder, the maximum total impurities are to be ≤ 1500 µg/g U. This standard also provides specific maximum impurities for individual elements. For example the iron impurities rise to ≤ 500 µg/g U, nitrogen is limited to ≤ 75 µg/g U, and thorium impurities remain limited at ≤ 10 µg/g U.

ASTM specifications for sinterable plutonium dioxide powder are provided in ASTM C757 (2006a) as containing ≤ 6000 µg/g U total impurities excluding americium. The uranium is not specified, and americium content is to be agreed upon between the parties involved. This standard also provides a somewhat shorter list of specific maximum impurities for individual elements. For example, the iron impurities are limited to ≤ 300 µg/g U and thorium impurities are limited to ≤ 200 µg/g U.

Under the current AFCI thinking where there will be no pure plutonium stream produced, ASTM C1008 (2008) is applicable for fast reactor fuel. This standard provides the impurity specification for sintered MOX pellets. Total impurities are to be ≤ 5000 µg/g (U+Pu) total impurities excluding americium and thorium. Test specifications for LWR MOX pellets were developed as part of the Fissile Materials Disposition Program (Cowell, 1997) and are significantly tighter than the ASTM MOX specification.

Ion Exchange – Organic/Inorganic

Ion exchange (IX) is often used to either "polish" the uranium and plutonium product that has been initially separated via SX or for the recovery of specific elements from dilute streams. Hence one is either (1) trying to retain undesired constituents (polishing) on the IX media and the "product" is what passes through the bed or (2) capturing a target constituent on the IX media and later recovering product from the media. There are several variations available to the process designer. The IX material is chosen based on its selectivity for specific constituents. The media are typically solid organic resins, but inorganic materials are also used.

For the purposes of illustration, one of the most common uses of IX is that of softening water. This is accomplished using a bed of polymeric beads in which large organic anions are incorporated. The organic anions are paired with sodium cations. As the "hard" water flows through the bed, the calcium and magnesium ions are exchanged from the solution for sodium ions from the bed by the following reactions (King, 1971):

$$\mathrm{Ca^{++} + 2Na^{+}\ resin^{-} \rightarrow Ca^{++}\ (resin)2^{--} + 2Na^{+}},\ \text{and} \tag{13}$$

$$\mathrm{Mg^{++} + 2Na^{+}\ resin^{-} \rightarrow Mg^{++}\ (resin)2^{--} + 2Na^{+}}. \tag{14}$$

Other constituents in the solution for which the IX resin is not selective will remain in the aqueous solution and pass through the IX bed.

The capacity of IX material is finite and can be defined by the equilibrium constant (K) (King, 1971):

$$K_{\mathrm{Ca++\text{-}Na+}} = (\mathrm{Ca^{++}})_{\mathrm{resin}}(\mathrm{Na^{+}})^{2}_{\ \mathrm{aqueous}}\ /(\mathrm{Ca^{++}})_{\mathrm{aqueous}}(\mathrm{Na^{+}})^{2}_{\ \mathrm{resin}}. \tag{15}$$

Once the K value is exceeded, the bed will cease to remove the constituent of interest. After the material is loaded with the desired product, the IX bed must be regenerated. The inflow of the product-bearing solution is stopped, and a new, clean aqueous stream (called the eluant) is passed through the ion exchange bed. The properties in the eluent are typically opposite those of the initial stream. In the water softening example, the eluent stream is high in sodium and drives the IX reaction in reverse.

In fuel reprocessing applications, the product stream from solvent extraction may still contain a level of contaminants such that subsequent use in recycle fuel will be out of specification. This stream may be polished by IX. In the case of the PUREX process, the plutonium product stream from the second plutonium cycle is removed from the aqueous stream by the IX bed while the contaminants remain in the highly acidic aqueous solution. The plutonium is recovered from the IX bed using an eluant stream that will be only slightly acidic. A second example is from the AFCI work is the recovery of the technetium from the uranium stream from the <u>Ur</u>anium <u>Ex</u>traction (UREX) cycle. Here the very small amount (mass-wise) of technetium present in the aqueous uranium product stream is recovered from the much larger quantity of uranium using IX.

Product Conversion

The product(s) that are recovered from the spent fuel via the SX/purification cycles are typically converted from the nitrate solutions to an oxide form. This can be accomplished by various approaches including direct thermal denitration, Modified Direct Denitration (MDD), or by resin loading/calcination.

Supporting Operations (Separations)

Distillation

While distillation is the dominate separation process of the petrochemical industry, it plays a secondary role in fuel reprocessing. While this role does not get the attention that the SX processes do, it is critical to the overall plant operation. The fuel comes into the facility as a solid and the products and waste leave the facility as solids, yet all of the separation steps involve liquids, mainly containing nitric acid. Looking back to reactions (4)–(6), one will observe that nitric acid is consumed at the rate of two to four moles per mole of uranium processed. For a 800 MT/yr plant, the quantity of nitric acid required would approach 1,000,000 liters per year. If the acid is not recycled, this amount would require disposal or destruction. Acid vapors are recovered primarily from the dissolver off-gas, product conversion (a denitration process), and waste solidification. Other sources include condensates from evaporation operations to concentrate inter-cycle or intra-cycle streams and product streams. Conventional distillation technology can be used noting remote maintenance requirements as fission products will tend to accumulate in the bottoms or reboiler.

Steam Stripping

A little context is needed here that will become apparent shortly. An explosive compound can be formed when an organic material (e.g., TBP) comes in contact with concentrated nitric acid at temperature above 120°C (NRC, 2008). If formed, red oil can explosively decompose if the temperature goes above 130°C. Such explosions have occurred in the United States, Canada, and Russia.

Steam stripping can be used to remove trace organics from an aqueous stream. This process uses a steam stream to effect a transfer of organic compounds from the heated aqueous phase to the vapor phase. The process takes place at a temperature close to the boiling point of water. One interesting feature of steam stripping is that typically no off-gas treatment is required. The only waste stream is the recovered concentrated organics. Steam stripping has also been considered for the recovery/separation of the organic diluent for use in “diluent” washing of the aqueous product from the SX cycles.

Both approaches (steam stripping directly or diluent washing) address the same problem: eliminate the potential for accumulation of nitrated polymeric material that arises from the carryover of TBP into a plant evaporator. Any aqueous stream that leaves a bank of SX equipment will contain some level of organic material. This includes both the dissolved TBP and some entrained organic phase. The quantity is determined by the physical properties of the materials and by the operating conditions of the equipment. Steam stripping can be used directly to recover the organics from the aqueous phase, but this is a fairly energy-intensive process. A second approach involves the addition of several solvent extraction stages in which the aqueous phase is contacted with a small stream of the organic phase diluent to recover the dissolved and entrained TBP.

Off-Gas Treatment

Off-gas treatment in a fuel reprocessing plant must address three main gaseous streams. The first is the off-gas from the head end which includes the shear, optional voloxidizer, and the dissolver. This collectively is sometime called the Dissolver Off-Gas (DOG). The second is the "vessel off-gas" (VOG), which collects in-leakage to all of the process equipment and the instrument air used in bubblers, air sparge discharge, etc. The third is the cell ventilation, which provides confinement to the process cell. Each of these has unique characteristics and processing challenges.

Regulatory Requirements/Drivers

There are several key regulatory drivers that impact volatile gas emissions from a nuclear fuel recycle facility. The United States Environmental Protection Agency (EPA) has established annual individual dose limits for specific organs and for the whole body resulting from nuclear fuel cycle facilities in the commercial sector through 40 CFR 190. Radionuclide-specific release limits in terms of curies released per unit of power produced is also defined in 40 CFR 190.10 (CFR, 2007a). These limits are as follows:

> (a) The annual dose equivalent does not exceed 25 millirems to the whole body, 75 millirems to the thyroid, and 25 millirems to any other organ of any member of the public as the result of exposures to planned discharges of radioactive materials, radon and its daughters excepted, to the general environment from uranium fuel cycle operations and to radiation from these operations
>
> (b) The total quantity of radioactive materials entering the general environment from the entire uranium fuel cycle, **per gigawatt-year of electrical energy produced by the fuel cycle, contains less than 50,000 curies of ^{85}Kr, 5 millicuries of ^{129}I**, and 0.5 millicuries combined of ^{239}Pu and other alpha-emitting transuranic radionuclides with half-lives greater than 1 year.

While DOE is not subject to the EPA requirements, future commercial reprocessing facilities will be. Table 1 shows the 10 CFR 20 dose limits to both workers and to the individual members of the public. Section 20.1302 (CFR, 2007b) also provides release limits at the site boundaries for both gaseous and liquid effluents.

Table 1. 10 CFR 20 Site Boundary Release Limits

10 CFR 20	Air (Ci/m^3) at site boundary	Water (Ci/m^3)
Tritium	1.0×10^{-7}	1.0×10^{-3}
Carbon-14 (as CO_2)	3.0×10^{-5}	---
Krypton-85	7.0×10^{-7}	**N/A**
Iodine-129	4.0×10^{-11}	2.0×10^{-7}

40 CFR 61 sets limits for the dose equivalent to the public to10 mrem/yr.

Off-Gas Recovery Processes

Tritium

Tritium may be removed from the off-gas stream with desiccants or molecular sieves. Anhydrous $CaSO_4$ has been reported as a possible desiccant (Benedict et al., 1981). Molecular sieves exhibit high water capacities—10 to 20% based on the dry weigh of the sorbent (Brown, 1983). Type 3A desiccants have been shown to also sorb carbon dioxide at temperatures significantly below room temperature (Rivera et al., 2003).

Iodine

Numerous technologies have been developed for the recovery of airborne ^{129}I based on scrubbing with caustic or acidic solutions and chemisorption on silver-coated or impregnated adsorbents. However, to achieve the high decontamination factors (DFs) required to meet the regulatory requirement (> 500), a critical step is to ensure that the iodine is volatilized into as concentrated a gas stream as possible. The distribution of ^{129}I in gas and liquid process streams has been measured at the Karlsruhe reprocessing plant (WAK) (Herrmann et al., 1993) and predicted for the BNFP (Hebel and Cottone, 1982). These evaluations indicate that about 94% to 99% of the ^{129}I reports to the DOG and the remaining is distributed among the aqueous high-, medium-, and low-level waste. While the primary recovery technology is applied to the DOG, the VOG may also require treatment to recover ^{129}I arising from other processing steps and vessels.

<u>Silver-Exchanged Solid Sorbents</u>

Various types of adsorbents for iodine have been studied and developed over the years. Natural or artificial porous material like zeolite, mordenite, alumina, and silica gels have been loaded with metals (such as Ag, Cd, Pb) and/or the metal nitrate ($AgNO_3$), and used in performance studies. Commercially available inorganic sorbent materials include silver-exchanged zeolites [i.e., faujasite (AgX) and modenite (AgZ)] and silver-impregnated silicic acid (AC-6120).

The development of silver-exchanged AgX and AgZ was conducted primarily in the United States and has not advanced beyond laboratory tests for ^{129}I recovery. Published literature surveyed by Thomas et al. (1977) indicate iodine loadings ranging from 80 to 200 mg of iodine per gram of AgX or AgZ while maintaining DFs in the range of 100 to 10,000 for elemental iodine. While effective in removing iodine from gas streams, the AgX substrate decomposes in the presence of NO_x and water vapor. Therefore a more acid-resistant substrate was desirable for use in the DOG application.

The AgZ sorbent has been developed specifically for application in DOG streams because of its high acid resistance. Elemental iodine loadings of 170 mg I_2 per gram of AgZ (Staples et al., 1977; Thomas et al., 1978) and typical methyl iodide loadings of 140 to 180 mg CH_3I per gram of substrate (Jubin, 1983; Scheele et al., 1983) have been obtained for tests on simulated DOG streams.

Liquid Scrubbing

Caustic scrubbing for ^{129}I recovery has been applied at the Windscale, Thorp, UP1, UP2, and PNC fuel reprocessing plants (FRPs) (Hebel and Cottone, 1982; IAEA, 1987). The Windscale FRP reports a DF of 50 while the other DFs are not reported. The organic iodides pass through the solution essentially unreacted, and CO_2 and NO_x deplete the scrubbing solution by forming carbonate and nitrates. The operating experience at the Tokai FRP indicated that while the caustic scrubber in the DOG provides sufficient removal efficiency, that of the VOG scrubber was lower than expected. This was attributed to the formation of iodine-organic compounds in the VOG stream (IAEA, 1987). The THORP plant utilizes a caustic scrubber to achieve an iodine DF of 100. This same caustic scrubber is used to scrub NO_x, ruthenium (gas), and ^{14}C with DFs of 100, 100, and 70, respectively.

The IODOX (IODine Oxidation) technology was developed for application to liquid-metal fast breeder reactor (LMFBR) fuel reprocessing where the spent fuel would have been processed within 180 days of leaving the reactor and would have required high DFs to control ^{131}I releases ($>10^4$). Decontamination factors up to 10^6 have been obtained in cold engineering tests. The process uses 20–22 M HNO_3 in a bubble cap column to recover the iodine as HI_3O_8 (ERDA, 1976).

The Mercurex process was also developed for the treatment of the dissolver off-gas evolved during the processing of very short cooled fuels where very high DFs are required ($>10^5$). The process uses a mercuric nitrate – nitric acid solution in a packed or bubble cap column to recover the iodine as HgI_2, which is subsequently oxidized to the iodate ($Hg(IO_3)_2$. In the Mercurex process, airborne iodine is absorbed in a $Hg(NO_3)_2$ – HNO_3 solution to form mercury iodate and iodide complexes. Decontamination factors for elemental iodine and methyl iodide of 1000 to 5000 and 100, respectively, have been obtained at temperatures of 50°C. Mecurex has been applied at an industrial scale at the Dounreay and Nuclear Fuel Services FRPs with reported DFs of 150 and 32, respectively (Hebel and Cottone, 1982). Two scrubbers in series were installed in the BNFP. The claimed DFs were 10–75 (IAEA, 1987).

Krypton

Most of the ^{85}Kr (>99%) remains in the spent fuel until it is sheared and dissolved. The ^{85}Kr would be primarily released to the DOG in the range of hundreds of parts per million. Recovery processes are based on physical separation from the off-gas since krypton is chemically inert. The primary technologies for ^{85}Kr control are cryogenic distillation, fluorocarbon adsorption, and sorption on molecular sieves or charcoal. Xenon is also recovered by these processes. The xenon is present at about 10 times the krypton concentration in the gas stream.

Cryogenic distillation is a technology to recover rare gases that has been used commercially for many years. The cryogenic distillation process has been successfully used at the Idaho Chemical Processing Plant (ICPP) to recover krypton. This is commercial technology but was not optimized for high krypton recovery DFs. Further development work has been done in Belgium, France, Germany, and Japan on the cryogenic process. Decontamination factors of 100 to 1000 have been reported (Goossens et al., 1991).

Fluorocarbon absorption technology has been developed at the Oak Ridge Gaseous Diffusion Plant and at the Karlsruhe, Germany (Little et a1., 1983; IAEA, 1980a; Henrich et al., 1985; Hebel and Cottone, 1983). This process uses an organic solvent (CCl_2F_2 called R-12) to selectively absorb noble gases from air or DOG streams; the noble gases are then stripped from the solvent by boiling. The basis for this recovery process is the solubility difference that exists between the various gas compounds in the solvent chosen for the process. Krypton recoveries greater than 99% have been demonstrated with concentration factors ranging from 1000 to 10,000.

Both activated carbon and zeolites have been studied to recover krypton from the DOG stream. One possible system uses a bed of synthetic silver mordenite (AgZ) at ambient temperatures to recover xenon. The “xenon-free” gas is then chilled and passed onto a second hydrogen mordenite (HZ) operated at ~80°C that absorbs the krypton. Laboratory tests have shown DFs of 400 for krypton and 4000 for xenon (Pence, 1981).

Carbon-14

The bulk of the ^{14}C found in the irradiated nuclear fuel is assumed to be evolved as CO_2 into the DOG during fuel dissolution. If standard voloxidation is used, then approximately 50% of the ^{14}C will be released in the voloxidizer.

There are a number of technologies that have been developed for CO_2 removal. These include caustic scrubbing, molecular sieve adsorption, adsorbent bed fixation, and co-absorbtion/concentration in conjunction with ^{85}Kr recovery followed by fixation.

Adsorption of CO_2 utilizing a caustic solution in a packed column to form carbonates is a common industrial process (Trevorrow et al., 1983). While the process has never been applied specifically for ^{14}C recovery in the nuclear fuel cycle, the EPA indicated in 1977 that it would be the most probable candidate for application at that time (Brown et al., 1983).

The adsorption of CO_2 by packed adsorbent beds is also a common industrial process. The 4A molecular sieve has been demonstrated at laboratory scale to removed the CO_2 down to the level of detection (10 ppm) from a >90% CO_2 stream. The bed is regenerated by heating to 200°C.

Pilot-scale studies have been conducted by researchers at Ontario Hydro on a gas solid reaction process to remove ^{14}C using beds of either $Ca(OH)_2$ or $Ba(OH)_2 \cdot 8H_2O$.

Recovery of Semi-Volatile Components and Particulates

The head-end portion of the fuel reprocessing plant and the waste processing portion presents additional challenges in terms of the composition of the off-gas streams to be treated. In addition to the gaseous species already discussed, a number of "semi-volatile" species are released to the off-gas stream. These include oxides of Ru, Cs, Tc, Te, and Sb. Of these, the most studied are ruthenium and cesium, which also typically require the highest recovery factors. The amount released is highly dependent on the processing conditions. For example, under normal voloxidation conditions only very limited fractions of krypton, ^{14}C, and iodine are released. Work in the United States and Korea has recently shown that under high temperatures and O_2 or O_3 oxidizing conditions, virtually all of the ^{3}H, ^{14}C, ^{85}Kr, ^{129}I, ^{99}Tc, Ru, and Cs are released to the off-gas and significant fractions of the Te, Rh, and Mo are also volatilized.

Ruthenium is present in the gas phase as RuO_4. Sakurai et al. (1985) report that RuO_4 may be deposited on metal surfaces at low temperatures. It is hypothesized that the deposition forms weak Ru-O-O-Ru bonds on the metal surfaces. The deposit is easily removed with a 1 N NaOH solution containing 1.5 wt% $K_2S_2O_8$. If this deposit is heated above 500°C, a large portion is volatilized, but a portion is reduced to elemental ruthenium. At high temperatures ruthenium can also plate out on metal surfaces and is difficult to remove even with strong acids. This results in lower oxides and even the ruthenium metal being formed via an autocatalytic reaction. This can cause line plugging and localized high radiation fields (Goossens, 1991). Volatile ruthenium is easily trapped by physical absorption on silica gel or molecular sieves at low temperatures or on iron oxides at temperatures between 300 and 500°C.

Cesium is only volatilized at high temperatures above about 800°C. Data presented by Goossens (1991) shows ~0.8% of cesium is released in 6 hours from borosilicate glass at 800°C. This increases to ~25% at 1000°C. Upon cooling, submicron particles are formed.

In addition, the head-end processes may result in the production of very fine particulates which must also be removed prior to the release of the gas stream to the facility stack. Particulate filtration is for the most part a well-established technology [see Goossens (1991) and DOE (2003)]. Typical pleated paper HEPA filters recover 99.99% of 0.3 µm particles and operate at temperature less than 120°C. It is possible to recover 99.99% of particles down to 0.1–0.3 µm range with modest penalty in filter resistance. Specially designed filters can operate at temperatures above 500°C.

References

1. ASTM, “Standard Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder,” ASTM C753-04, West Conshohocken, PA (2004).
2. ASTM, “Standard Specification for Nuclear-Grade, Plutonium Dioxide Powder, Sinterable,” ASTM C757-06, West Conshohocken, PA (2006a).
3. ASTM, “Standard Specification for Sintered Uranium Dioxide Pellets,” ASTM C776-06, West Conshohocken, PA (2006b).
4. ASTM, “Standard Specification for Sintered (Uranium-Plutonium) Dioxide Pellets – Fast Reactor Fuel,” ASTM C1008-08, West Conshohocken, PA (2008).
5. Benedict, M., Pigford, T., and Levi, H., Nuclear Chemical Engineering, 2nd ed., McGraw-Hill, New York, 1981.
6. Brown, R. A., et al., *Airborne Radionuclide Waste Management Reference Document*, ENICO-1133, 1983.
7. CFR, 2007a, http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&sid=db67e95c3d4a927808b6ddb9678033ff&rgn=div5&view=text&node=40:24.0.1.1.1&idno=40
8. CFR, 2007b, http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&sid=53b98591404efa3237001e957af84570&rgn=div6&view=text&node=10:1.0.1.1.16.4&idno=10
9. Cowell, B. S., “Technical Specification: Mixed-Oxide Pellets for the Light-Water Reactor Irradiation Demonstration Test,” ORNL/MD/LTR-75, Lockheed Martin Energy Research Corp., Oak Ridge National Laboratory, June 1997.
10. Croff, A. G., *Reprocessing*, Lockheed Martin Energy Systems, K/NSP/Part 23/R2, May 1997.
11. Del Cul, G. D., Hunt, R. D., Spencer, B. B., Collins, E. D., Westphal, B. R., and Howden, K. L., “Advanced Head-End Processing of Spent Fuel: A Progress Report on a Pyrochemical Front-End,” Transactions of the American Nuclear Society Annual Meeting, Reno, Nevada, June 4–8, 2006, Vol. 94, pp. 101–102.
12. Del Cul, G. D., Spencer, B. B., and Collins, E. D., “Advanced Head-End Alternatives for the Processing of US Spent Fuel,” The Ninth Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Nuclear Science Committee of the OECD-NEA, Nimes, France, September 25–29, 2006, Programme and Abstracts.
13. Del Cul, G. D., Oak Ridge National Laboratory, personal communication with author, 2008.
14. DOE Handbook, *Nuclear Air Cleaning Handbook*, DOE-HDBK-1169-2003, Nov 2003.
15. ERDA (U.S. Energy Research and Development Administration), “Alternatives for Managing Wastes from Reactors and Post-Fission Operations of the LWR Fuel Cycle,” Vol. 2 of 5, ERDA-76-43, Chaps. 13 and 14, 1976.
16. Goode, J. H., and Stacy, R. G., *Head-end Reprocessing Studies with H. B. Robinson-2 Fuel*, ORNL/TM-6037, Oak Ridge National Laboratory, June 1978.
17. Goode, J. H., Stacy, R. G., and Vaughen, V. C. A., *Comparison Studies of Head-End Processing Using Three LWR Fuels*, ORNL/TM-7103, Oak Ridge National Laboratory, Oak Ridge, TN, June 1980.
18. Goossens, W. R. A., Eichholz, G. G., and Tedder, D. W., editors, “Treatment of Gaseous Effluents at Nuclear Facilities,” *Radioactive Waste Management Handbook*, Volume 2, Harwood Academic Publishers, Chur, 1991.
19. Hebel, W. and Cottone, G., editors, McKay, H. A. C. , et al., *Management Modes for Iodine-129*, proceedings of a meeting organized by the Commission of the European Communities and held in Brussels on September 25, 1981 (February 1982).

20. Hebel, W. and Cottone, G., editors, Leudet, A., et al., *Methods of Krypton-85 Management*, proceedings of a meeting organized by the Commission of the European Communities and held in Brussels, 29 June 1982 (February 1983).
21. Henrich, E., et al., “Selective Absorption of Noble Gases in Freon-12 at Low Temperatures and Atmospheric Pressure,” in *Proceedings of the 18th DOE Nuclear Air Cleaning Conference*, CONF-820833, pp. 959–981, 1985.
22. Herrmann, F. J., et al., “Minimizing of Iodine-129 Release at the Karlsruhe Reprocessing Plant WAK,” in *Proceedings of the 22nd DOE/NRC Nuclear Air Cleaning Conference*, August 24–27, 1992, Vol. 1, CONF-9020823, pp. 75–90, July 1993.
23. IAEA, *Separation, Storage and Disposal of Krypton-85*, Technical Report Series No. 199, International Atomic Energy Agency, Vienna, 1980a.
24. IAEA, *Treatment, Conditioning and Disposal of Iodine-129*, IAEA Technical Report Series No. 276, 1987.
25. IAEA, *Management of Reprocessed Uranium, Current Status and Future Prospects*, IAEA TECDOC-1529, 2007.
26. Jubin, R. T., “Organic Iodine Removal from Simulated Dissolver Off-Gas Systems Using Partially Exchanged Silver Mordenite,” in *Proceedings of the 17th DOE Nuclear Air Cleaning Conference*, CONF-820833, pp. 183–197, 1983.
27. King, C. J., *Separation Processes*, McGraw-Hill Book Company, New York, N.Y., 1971.
28. Lewis Jr., B. E., Oak Ridge National Laboratory, personal communications with author, 2008.
29. Little, D. K., et a1., “Noble Gas Removal and Concentration by Combining Fluorocarbon Absorption and Adsorption Techniques,” in Proceedings of the 17th DOE Nuclear Air Cleaning Conference, CONF-820833, pp. 694–717, 1983.
30. Long, J., *Engineering for Nuclear Fuel Reprocessing*, Gordon and Breach Science Publishers, Inc., New York, N.Y., 1967.
31. Nuclear Regulatory Commission (U.S. NRC), *Background, Status, and Issues Related to the Regulation of Advanced Spent Nuclear Fuel Recycle Facilities*, NUREG-1909 (June 2008).
32. Pence, D. T., “Critical Review of Noble Gas Recovery and Treatment Systems,” *Nucl. Saf*. **22**(6) (November–December 1981).
33. Rivera, D. A., Alam, M. K., Martin, L., and Brown, J. R., *Characterization of Water and* CO_2 *Adsorption by Stores 3A Desiccant Samples Using Thermal Gravimetric Analysis and Fourier Transform Infrared Spectroscopy*, SAND2003-0398, Sandia National Laboratories, February 2003.
34. Sakurai, T, et al., “Adsorption of Ruthenium Tetroxide on Metal Surfaces,” *J. Phys. Chem*. **89**, 1892–1896 (1985).
35. Scheele, R. D., Burger, L. L., and Matsuzaki, C. L., *Methyl Iodide Sorption by Reduced Silver Mordenite*, PNL-4489 (July 1983).
36. Spencer, B. B., Oak Ridge National Laboratory, personal communications with author, 2006.
37. Staples, B. A., et al., “Airborne Elemental Iodine Loading Capacities of Metal Zeolites and a Dry Method for Recycling Silver Zeolite,” *Proceedings of 14th ERDA Air Cleaning Conference*, Vol. 1, CONF-760822, p. 363, 1977.
38. Thomas, T. R., et a1., *Airborne Elemental Iodine Loading Capacities of Metal Zeolites and a Method for Recycling Silver Zeolite*, ICP-1119, 1977.
39. Thomas, T. R., et al., “The Development of Ag°Z for Bulk ^{129}I Removal from Nuclear Fuel Reprocessing Plants and PbX for ^{129}I Storage,” in *Proceedings of the 15th DOE Nuclear Air Cleaning Conference*, Vol. 1, CONF-780819, p. 394, 1978.

40. Trevorrow, L. E., et al., *Compatibility of Technologies with Regulations in the Waste Management of H-3, I-129, C-14, and Kr-85. Part I. Initial Information Base*, ANL-83-57 Part I, August 1983.
41. Wymer, R. G, and Vondra, B. L, *Light Water Reactor Nuclear Fuel Cycle*, CRC Press, Inc., Boca Raton, FL, 1981.

Non-Aqueous Processes

Mike Goff
Idaho National Laboratory

Introduction

Non-aqueous separation technologies have been used for treatment of spent nuclear fuel since the 1960s, and they are still being developed and demonstrated in many countries including the United States, Russia, Japan, Korea, France, United Kingdom, China, and India. In the United States, work on non-aqueous technologies is being pursued as part of the Global Nuclear Energy Partnership/Advanced Fuel Cycle Initiative.

A variety of definitions exist for the various types of non-aqueous technologies that have been considered for treatment of spent nuclear fuel. A good definition is found on the website for IGCAR (http://www.igcar.ernet.in/lis/nl46/igc-29-1(4p).htm). It is as follows: "Pyrochemical reprocessing methods use high temperature oxidation –reduction reactions in non-aqueous media to separate the actinides, U and Pu from the fission products. These methods exploit the differences in the volatilities or thermodynamic stabilities of the compounds of actinides and fission products to achieve the separation. Pyrochemical separations can be achieved by using electrochemical methods instead of chemical equilibrations."

Non-aqueous technologies offer potential advantages compared to traditional aqueous separation technologies like PUREX. The solvents used in non-aqueous technologies typically are not subject to radiation damage. Larger quantities of fissile material can be handled, since a water moderator is not present. These technologies are potentially more compact than aqueous technologies, so the option exists to co-deploy separations facilities with reactor complexes to lessen shipment of spent nuclear fuel and special nuclear material. Non-aqueous technologies have typically resulted with incomplete separation of fissile material from fission products and transuranic elements. Early in the development of nuclear technology this was considered a disadvantage, since incomplete separation meant that the recovered materials still had to be processed in shielded hot cells. The recycled spent fuel would have to be remotely fabricated instead of either hands-on or glovebox fabrication. With the increased focus on non-proliferation, this feature is now considered a significant benefit. Because of this inherent characteristic of incomplete separations, there are now more than 40 years of experience with remote fabrication of fuel from materials recovered from non-aqueous technologies.

The benefits of non-aqueous technologies have made them ideal candidates to recycle fast reactor fuels, which generally have higher radiation fields due to increased burnups and have much higher fissile material concentrations. In general they are not suitable as separation technologies for recycle of fuel to thermal reactors because they do not remove enough of the fission products that act as neutron poisons in a thermal spectrum. These fission products are not neutron poisons in a fast neutron spectrum. Because of the focus on fast reactors, the technology has been assessed or used for many of the fuel types considered for advanced reactor technologies including metals, nitrides, and oxides. Flowsheets have been developed for many other exotic fuel types as well.

Classes of Non-Aqueous Technologies

A number of technologies and flowsheets have been examined using non-aqueous systems. At present, most work is directed on an electrochemical technology, which will be the focus of much of this paper. A few of the other technologies will first be noted.

One class of non-aqueous technology is volatilization. Volatilization takes advantage of the different vapor pressures of the elements or compounds in spent nuclear fuel. In general, the fuel can be heated to release gaseous fission products, and if taken to even higher temperatures, some of the more volatile fission products like cesium and technetium can also be removed. In some applications, spent oxide fuel can be converted from UO_2 to U_3O_8 that is less dense. As the fuel is converted, the structure of the oxide pellets is destroyed, and the resulting material is powder. This operation facilitates removal of volatile fission products. It removes only gaseous or volatile fission products, while leaving most fission products and transuranic elements in the spent fuel. Therefore application of this technology has focused in two areas: a head-end operation for another separation process or a recycle option to specialized reactors like the CANDU design. For the CANDU option, pressurized or boiling water reactor fuel can be treated by voloxidation to remove a fraction of the fission products. The resulting powder material can then be converted remotely into new fuel for a CANDU reactor that can operate with the enrichment values of uranium in spent fuel from either pressurized or boiling water reactors.

Halide volatility is another class of non-aqueous separation technology. Halides (fluorides or chlorides) can form volatile compounds of the actinides, most notably UF_6. By converting spent fuel into halides, the actinide halides can be separated from the bulk of the fission products as gases. Because of the challenge to convert some of the transuranic elements to halides, this technology works best in systems that are primarily uranium based.

One of the first non-aqueous technologies deployed was a partial oxidation process called melt refining or skull refining. In this process a portion of the fission products are again separated from the spent fuel. The fission products are chemically oxidized to separate them from the actinides in the spent fuel. Melt refining was used to recycle fuel from the Experimental Breeder Reactor II (EBR-II) from 1964 through 1969. In this process, the fuel was a metallic alloy of uranium. The spent fuel was placed into a Zr_2O crucible and melted. Chemically reactive fission products reacted with the crucible to form oxides. The uranium and noble metals remained in the metallic state. Injection casting was used to remote fabricate metallic fuel for recycle into EBR-II, a fast reactor. Limitations to this recycle technology eventually led to the development of a non-aqueous electrochemical separation technology that is the topic of the remainder of this paper.

Electrochemical Technology

(Material on electrochemical technology is taken from the following paper: K. M. Goff and M. F. Simpson, "Treatment of Spent Nuclear Fuel with Molten Salts," *Proceedings of the 2008 Joint Symposium on Molten Salts*, Kobe, Japan, October 19-23, 2008.)

Electrochemical Technology Background

In the mid-1980s, the U.S. Department of Energy's Office of Nuclear Energy, Science and Technology started working on electrochemical processes employing molten salts and liquid metals for treatment of spent nuclear fuel. Potential benefits of this technology compared to traditional aqueous separations technologies include: capability to produce low purity products for non-proliferation benefits, potential compactness of the technology so process treatment facilities can be co-located with reactors, resistance of molten salt solvent to radiation effects so short-cooled spent fuel can be processed, and criticality control benefits since water moderators are not used.

This work was initiated at Argonne National Laboratory (ANL) and is now performed at both Idaho National Laboratory (INL) and ANL. Development of the technology includes work with simulates, transuranics, and actual spent nuclear fuel. Integral to this work are research and development activities focused on developing and implementing process improvements, qualifying resulting high-level waste forms, and demonstrating the overall electrochemical fuel cycle for treating spent nuclear fuel.

Much of the development work associated with electrochemical technology is focused on treatment of fuel from fast-spectrum nuclear reactors, like the Experimental Breeder Reactor II (EBR-II) in Idaho. EBR-II used a metallic alloy of uranium, uranium-plutonium, or uranium-transuranics as fuel. Such reactor systems are focuses of both the Global Nuclear Energy Partnership (GNEP) and the Generation IV Nuclear Energy Systems, two international nuclear programs.

The flowsheet for treatment of metallic spent fuel starts with chopping. The stainless-steel cladded fuel pins are chopped into 0.6 to 1.3 cm segments that are loaded into steel baskets. The steel baskets are transferred into an electorefiner where they serve as an anode. The electrorefiner contains a solution of LiCl-KCl eutectic molten and dissolved actinide chlorides, such as UCl_3 and $PuCl_3$. The electrorefiners are typically operated at 500°C.

In the electrorefiners, spent fuel is electrochemically dissolved from anode baskets, and an equivalent amount of uranium is deposited on a steel cathode. The uranium is separated from the bulk of the fission products and transuranics. Most of the fission products (alkali, alkaline earth, rare earth, and halides) and transuranics accumulate in the salt. The electrorefiners operate in a batch mode. When cathodes are removed from the heated electrorefiner, adhering salt freezes to the surface of the recovered uranium. This salt is separated from the uranium in a distillation operation, and the uranium is processed into an ingot. The distillate salt, pictured in Figure 1, is recycled back to the electrorefiners. It is purple due to the presence of UCl_3.

Figure1. Molten salt distillate separated from recovered uranium metal.

Electrochemical treatment of spent nuclear fuel results in two high-level waste (HLW) forms, the ceramic waste form and the metal waste form. The ceramic waste form, which stabilizes electrorefiner salts, is a glass-bonded sodalite produced from thermal conversion of zeolite A. Salts are occluded into the zeolite structure in a heated V-mixer. After the salt is occluded in the

V-mixer, the salt–loaded zeolite is mixed with 25% glass frit. This mixture is loaded into a canister and then consolidated into a monolithic waste form in a furnace at 915ºC.

The metal waste form consists of metallic ingots that are used to stabilize noble metal fission products, the non-actinide fuel matrix, and cladding materials. Zirconium metal is added to improve performance properties and to produce a lower melting point alloy. The typical composition is stainless steel and 15 weight percent zirconium. It is produced in a casting operation at 1600ºC.

Fuel Treatment Process Development

Electrochemical technology development makes use of EBR-II spent fuel. This work is performed in the Fuel Conditioning Facility (FCF) at INL. This facility consists of two shielded hot cells for handling highly radioactive material like spent nuclear fuel. Process testing is performed in a hot cell filled with argon gas. An inert gas is needed because of the hygroscopic nature of the molten salts and the pyrophoric and reactive characteristics of the actinide metals.

Two electrorefiners are employed in FCF. The first was installed in 1994 and the second in 1998. Both electrorefiners are 1 m in diameter. They contain between 420 and 650 kg of molten salt. Between 29 and 35 kg of this mixture are actinides as actinide tri-chlorides to facilitate electrotransport of spent fuel. The base salt is high purity LiCl-KCl. After treating spent nuclear fuel, the salt also contains chlorides of fission products that are more stable than actinide chlorides. This includes CsCl, $SrCl_2$, $LaCl_3$, $NdCl_3$, etc. The salt also contains an increasing concentration of NaCl that forms from the reaction of sodium metal which is loaded into individual fuel elements as a thermal bond. The electrorefiners now contain between 9 and 13 kg of sodium as NaCl.

In 1996, spent fuel was first processed in FCF. For development testing and demonstration operations, more than 3.5 metric tons of heavy metal (MTHM) have been processed in these systems. Because of the resistance of these salts to radiolysis effects, the same salt solvent has been used throughout these operations, and it will not require change out during treatment of all EBR-II spent fuel, more than 25 MTHM.

In the electrochemical process, stainless steel fuel clad is not dissolved. More noble fission products like technetium, rhodium, ruthenium, and molybdenum are also not oxidized. They remain with the clad in elemental form.

Electrorefining process improvements are a major focus of technology development. Three electrorefiners are remotely operated in hot cells at INL. The first, the Hot Fuel Dissolution Apparatus (HFDA), is a laboratory-scale device used to demonstrate feasibility of the technology through tests with spent fuel. From this first device to units FCF, the current capacities were increased from 3.5 to 2400 amps, and potential throughputs were increased by three orders of magnitude.

Figure 2. Electrorefiner operational in the hot cells of the Fuel Conditioning Facility

The two FCF electrorefiners are identical in size. They differ in anode-cathode configuration. Both electrorefiners have four ports in which electrodes are inserted into the molten salt. In the first of these electrorefiners, an individual anode or cathode is placed into each port, so two anode-cathode configurations can be operated simultaneously with two power supplies. For the second electrorefiner, the anode and cathode are combined into a concentric module. Four anode-cathode modules can be operated simultaneously in the second electrorefiner. The capacity of the modules is twice that of the initial anode configuration for the first electrorefiner. Additionally, the current capacity of this design is approximately a factor of six higher. In total, the throughput increase between the first FCF electrorefiner and the later design is a factor of 20 in an identical size vessel.

Establishing performance data is also a focus of electrorefining work with spent fuel. One key performance aspect is dissolution of spent fuel, specifically the actinides. Tests have been performed on laboratory scale with uranium-plutonium fuels and in FCF with uranium fuels. The results of both tests indicated the ability to dissolve at least 99.7% of the actinides [1]. High dissolution of actinides results in significant positive benefits for geological disposal of resulting high-level wastes.

Electrochemical technology with molten salts is also being assessed for treatment of fuel types other than metallic. Most commercial spent nuclear fuel is oxide. Laboratory-scale tests with oxide fuels have been performed. To treat these fuel types, the oxides are first electrochemically reduced from oxides to metals. Oxygen gas is evolved in the process. The reduced metal is then processed using the flowsheet discussed earlier. Reduction occurs in separate vessel from the uranium electrorefiners. The base salt for oxide reduction is LiCl with 1 wt% Li_2O, and the operating temperature is 650°C.

Laboratory-scale tests with spent oxide fuels have been performed. These laboratory-scale tests were completed with 50-gram loadings of irradiated oxide fuel. Reduction values as high as 99.7% have been obtained [2]. Electrorefining of the reduced metal in a standard LiCl-KCl electrorefiner was also demonstrated.

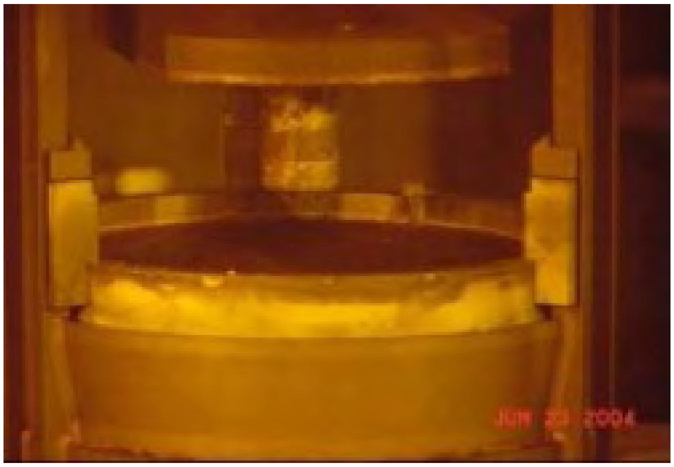


Figure 3. Liquid-cadmium cathode for group recovery of actinides in FCF

Development of electrochemical treatment of spent fuel is focused on recovery of transuranics as a group. Because of the chemical similarity of the rare earth fission products with the transuranics, a portion of these and some uranium are also recovered with the transuranics. This transuranic product will have a significant radiation field associated with it so that fabrication of fuel for recycle will have to be performed remotely in a hot cell. This aspect of the technology provides a potential nonproliferation benefit. A group recovery technology using a cathode of liquid cadmium was demonstrated in both HFDA and in a FCF electrorefiner [3]. Separation factor data obtained indicate that the transuranics including plutonium are recovered together along with some of the lanthanide fission products. The amount of fission products that remain are still at levels that are not expected to affect fuel performance in fast reactors. Transuranic recoveries at the kilogram scale were demonstrated.

Electrochemical High-Level Waste Qualification and Production

Demonstration and qualification of the two high-level wastes from electrochemical treatment were performed in parallel with development of the electrorefining processes. The waste forms were tailored to the process. Activities are underway to support both qualification of waste forms and qualification of production processes. Extensive characterization activities were performed on both waste forms, and degradation models were developed to simulate performance in a geological repository.

Figure 4. Furnace for production of the metal high-level waste installed in the hot cells of the Hot Fuel Examination Facility.

High-level waste operations for electrochemical treatment of spent nuclear fuel are performed in the Hot Fuel Examination Facility (HFEF) at INL. Like FCF, HFEF is a hot cell facility. The furnace for metal waste form production is pictured in Figure 4. This vacuum furnace is used to separate adhering salt from spent fuel cladding by distillation and then to melt the remaining metals into an ingot for disposal.

A consolidation furnace for the production of full-scale ceramic waste was procured, installed, and is ready for operation and process testing out of cell. Process testing will first be performed with waste form surrogates before installation in a hot cell. This furnace is capable of producing 400-kg waste forms. Other equipment used for the production of the ceramic waste form, including a large heated V-mixer and a mill/classifier, are already installed and operational in HFEF

Conclusions

Electrochemical treatment of spent nuclear fuel using molten-salt systems has progressed significantly over the last 20 years. Development testing and demonstration operations for aspects of the flowsheet have been performed with spent fuel. During this period, electrorefining testing employing LiCl-KCl were scaled by three orders of magnitude in remote hot cells. Critical process goals like high fuel dissolution were achieved. Work is currently underway to demonstrate additional key aspects of the technology including both group recovery of transuranics and application of the technology to commercial oxide fuels. In parallel with work on fuel treatment processes, HLW production processes are being designed, tested, and implemented. This technology may provide benefits over conventional aqueous options for treating spent nuclear fuel and may enable the deployment of the next generation of nuclear power systems.

Acknowledgements

Global Nuclear Energy Partnership within the Department of Energy's Office of Nuclear Energy, Science and Technology is funding the work on electrochemical processing. Prior to formation of INL in February 2005, these activities were part of work scope at Argonne National Laboratory-West and were performed in collaboration with ANL in Illinois.

References

1. S. X. Li, T. A. Johnson, B. R. Westphal, K. M. Goff, and R. W. Benedict, “Electrorefining Experience for Pyrochemical Reprocessing of Spent EBR-II Fuel,” Proceedings of GLOBAL 2005, Tsukuba, Japan, October, (2005).
2. S. D. Hermann, S. X. Li, M. F. Simpson, S. Phongikaroon, “Electrolytic Reduction of Spent Nuclear Oxide Fuel as Part of an Integral Process to Separate and Recover Actinides from Fission Products,” Separations Science and Technology, 41: 1965-1983, 2006.
3. D. Vaden, S. X. Li, B. R. Westphal, K. B. Davies, T. A. Johnson, and D. M. Pace, “Engineering Scale Liquid Cadmium Cathode Experiments,” Journal of Nuclear Technology, Vol. 162, No. 2, pp. 124 (2008)

Additional General References

1. Benedict, Pigford, and Levi. *Nuclear Chemical Engineering* (New York: McGraw-Hill Book Company, 1981).
2. Nuclear Wastes: Technologies for Separations and Transmutation (National Academy Press: Washington, DC, 1996).
3. J. J. Laidler, J. E. Battles, W. E. Miller, J. P. Ackerman, and E. L Carls, “Development of Pyroprocessing Technology” *Progress in Nuclear Energy*, 31:1/2 (1997).
4. R. W. Benedict and H. F. McFarlane, “EBR-II Spent Fuel Treatment Demonstration Project Status,” *Radwaste Magazine*, 5:4, 23 (July 1998).
5. National Research Council, “Electrometallurgical Techniques for DOE Spent Fuel Treatment: Final Report,” National Academy Press, Washington, DC (2000).
6. K. M. Goff, R. W. Benedict, K. L. Howden, G. M. Teske, And T. A. Johnson, “Pyrochemical Treatment of Spent Nuclear Fuel,” *Proc. Of Global 2005*, Tsukuba, Japan, Oct. 9-13, 2005, (2005).
7. Y. I. Chang, “The Integral Fast Reactor,” *Nuclear Technology*, Vol. 88, p.129 (1989).
8. K. M. Goff, R. W. Benedict, S. G. Johnson, R. D. Mariani, M. F. Simpson, and B. R. Westphal, “Electrometallurgical Treatment Demonstration at ANL-West,” *Proceedings of the ANS Embedded Topical Meeting DOE Spent Nuclear Fuel and Fissile Material Management*, (June 4-8, 2000).
9. S. Li, T. Johnson, B. Westphal, K. Goff, and R. Benedict, "Electrorefining Experience for Pyrochemical Reprocessing of Spent EBR-II Driver Fuel," *Proc. Of Global 2005, Tsukuba*, Japan, Oct. 9-13, 2005, (2005).
10. S. Herrmann, S. Li, M. Simpson, "Electrolytic Reduction of Spent Oxide Fuel – Bench-Scale Test Results," *Proc. Of Global 2005*, Tsukuba, Japan, Oct. 9-13, 2005, (2005).
11. J. E. Battles, W. E. Miller, and E. C. Gay, “Pyrometallurgical Processing of Integral Fast Reactor Metal Fuels,” *Proc. 3rd Int. Conf. Nucl. Fuel Reprocessing and Waste Management*, Sendai, Japan, April 14-18, 1991, Atomic Energy Society of Japan (1991).

Precipitation and Crystallization Processes

Gordon Jarvenin
Los Alamos National Laboratory

Introduction

Precipitation and crystallization refer to unit operations that generate a solid from a supersaturated solution. The non-equilibrium supersaturated condition can be induced in a variety of ways such as removal of solvent by evaporation, addition of another solvent, changes of temperature or pressure, addition of other solutes, oxidation-reduction reactions, or even combinations of these.

The distinction between precipitation and crystallization is quite often based on the speed of the process and the size of the solid particles produced. The term precipitation commonly refers to a process which results in rapid solid formation that can give small crystals that may not appear crystalline to the eye, but still may give very distinct x-ray diffraction peaks. Amorphous solids (at least as indicated by x-ray diffraction) may also be produced. The term precipitation also tends to be applied to a relatively irreversible reaction between an added reagent and other species in solution whereas crystallization products can usually be redissolved using simple means such as heating or dilution. Precipitation processes usually begin at high supersaturation where rapid nucleation and growth of solid phases occur. In both precipitation and crystallization processes the same basic steps occur: supersaturation, nucleation and growth. Nucleation does not necessarily begin immediately on reaching a supersaturated condition, except at very high supersaturation, and there may be an induction period before detection of the first crystals or solid particles. Nucleation can occur by both homogeneous and heterogeneous processes. In general, homogeneous nucleation is difficult to achieve because of the presence of heteronuclei from colloids, dust, or other foreign material in the solution. This is especially true in industrial practice. The walls of the solution container may also be a source of nucleation sites. After nucleation the growth phase begins and agglomeration and aging are terms used to describe features of the changes in the solid particles.

Agglomeration describes the tendency of small particles in a liquid suspension to coalesce into larger aggregates. Other terms used in the literature include aggregation, coagulation, and flocculation. The term aging refers to a variety of other processes that change a precipitate after it forms. For example, Ostwald ripening refers to the tendency of larger crystals to grow at the expense of smaller crystals when the crystals formed after nucleation are smaller than ~1 micron. Another important process is initial nucleation of a metastable solid phase that transforms with aging, e.g., amorphous solid particles that crystallize with time or a hydrated crystalline solid that converts to a more stable material. Agglomeration and crystal growth can also be influenced substantially by the presence of impurities in the solution.

The details of performing the precipitation or crystallization process can be very important to produce a pure product and one that separates well from the liquid phase. Thus, the degree of supersaturation, the order and speed of reagent addition, the temperature, and the aging time before filtration or centrifugation are used to recover the solid, and the presence of "active" impurities can all be important parameters in a precipitation or crystallization process. Usually aging results in larger particle sizes and may be referred to with terms such as digestion or ripening of the precipitate.

The references "Crystallization, 4th Edition" [Mullin, 2001] and "Handbook of Industrial Crystallization, 2nd Edition [Myerson, 2002] provide extensive information on the theory and practice of industrial precipitation and crystallization processes. This includes the great variety of applications from crystallizing drugs and proteins for medical applications, to preparing silicon materials for electronics, to waste water treatment with metal hydroxide precipitates. These references also describe some of the vast array of equipment used to perform industrial precipitation and crystallization processes including batch and continuous operation.

Many industrial precipitations of metal species are batch processes that involve the rapid mixing of two aqueous solutions to generate supersaturation and after subsequent nucleation and growth of the solid; the solid is collected by filtration or centrifugation. This is certainly a common method for precipitating actinide metal ions from aqueous solutions. For precipitating plutonium and other fissile actinides, there is an advantage to using batch processing to simplify criticality safety operations. One can use a batch size well below the level of criticality concern and clean and inspect the solution containment vessels between batches to prevent build-up of fissile solids.

Mullin briefly summarizes (p. 323-324) some guidelines for using the strong influence of supersaturation to determine the mean particle size of a precipitate based on the Weimarn "laws" of precipitation:

1. As the concentration of reacting substances in solution is increased, i.e., as the initial supersaturation is increased, the mean size of the precipitate particles (measured at a given time after mixing the reactants) increases to a maximum and then decreases. As the time at which the measurement is made is increased, the maximum is displaced toward lower initial supersaturation and higher mean sizes.

2. For a completed precipitation, the precipitate mean size decreases as the initial supersaturation is increased.
   In addition to confirming the well-known beneficial effect of using reasonably dilute reactants to produce coarse precipitates, the laws demonstrate that excessive dilution can be detrimental, a fact that is not always fully appreciated. Experimental evidence for the Weimarn laws has been provided by Mullin and Ang (1977) for the precipitation of nickel ammonium sulfate.
   Some measure of control over nucleation and growth, and hence of precipitation, may also be exercised by the addition of substances, such as surfactants and polyelectrolytes. Impurities in the system, whether deliberately added or already present, can have a powerful influence on the morphology of the final precipitated particles.

For the actinide metal ion precipitations to be reviewed briefly below, limiting the amount of added precipitating agent such as oxalic acid (e.g., to form $Pu_2(oxalate)_3$) is used to both control the initial supersaturation to get larger particle sizes that are readily filtered and to limit the formation of soluble anionic complexes of the actinide that reduce the yield of the product. The optimal "recipes" for accomplishing this balance were generally developed empirically with knowledge of the solubility of the limiting metal ion compound (K_{sp}), guidance from general principles such as the Weimarn laws for precipitation, and, in some cases, knowledge of the stability constants for the metal species in solution.

Coprecipitation refers to the variety of ways that other solutes in a multicomponent solution or impurities may associate with a precipitate or crystal. This includes surface adsorption, incorporation of other anions or cations in the lattice of a growing crystal as part of a stable solid solution or by entrapment, and even physical inclusion of pockets of mother liquor. Coprecipitation is a very important method for recovering small amounts of a solute that may be far below its solubility limit in the precipitate of a major component (sometimes refered to as the carrier). Coprecipitation has been a crucial separation process to isolate traces of radionuclides and investigate their chemical behavior since the discovery of radioactivity.

Precipitation, Coprecipitation, and Crystallization Methods for Actinide Processing

The different oxidation states of the early actinide ions (particularly U, Np, and Pu) in aqueous solution show large differences in coordination chemistry that facilitate separation by a variety of methods. Table 1 lists the qualitative solubility behavior of the actinides in oxidation states III-VI with some common anions. These precipitations are very useful for separating mixtures of the actinides and for recovery of solid products from an aqueous stream usually after using another separation process such as ion exchange or solvent extraction. They are generally not selective enough to be used as the primary process for separation of plutonium or other actinides from all the fission products in irradiated fuel or targets. This is illustrated by a study (Winchester and Maraman, 1958) that used precipitation of Pu(III) oxalate, Pu(IV) oxalate, Pu(III) fluoride and Pu(IV) peroxide to recover plutonium directly from an irradiated plutonium-rich alloy dissolved in nitric acid. The decontamination factors reported in Table 2 indicate that none of the precipitation processes used achieved high enough fission product or corrosion product (Fe and Co) removal for use as a primary separation process. However, as will be described below, a series of coprecipitations with other metal ion species such as bismuth phosphate were used in the first large-scale separations of plutonium from irradiated uranium. These processes were replaced in time by more efficient solvent extraction processes.

The examples of actinide precipitations and coprecipitations discussed below are excerpted from the chapter on plutonium from the Chemistry of the Actinide and Transactinide Elements 3rd Edition, 2006. The behavior of other actinide metal ions in the same oxidation state is similar. The choice of plutonium examples was made because they illustrate many of the important features that go into choosing a particular separation approach. In addition, plutonium is a crucial component of nuclear fuel recycle and has been separated on a larger scale than any other synthetic element.

Table 1. Precipitation reactions characteristic of various actinide oxidation states (aqueous solution 1 M H+).a

Anion	*M*$^{3+}$	*M*$^{4+}$	*MO*$_2^+$	*MO*$_2^{2+}$
OH^-	I	I	I	I
F^-	I	I	I[b]	S
IO_3^-	I	I	S	S
O_2^{2-}	-	I	-	I[h]
$C_2O_4^{2-}$	I	I	I	I
CO_3^{2-}	(I)[c]	I[c]	I[d]	S
$CH_3CO_2^-$	S	S	S	I[e]
PO_4^{3-}	I	I	I[f]	I[g]
$Fe(CN)_6^{4-}$	I	I	S	I

I=insoluble, S=soluble.

[a] The OH^- and CO_3^{2-} precipitations occur in alkaline solution.

[b] At pH=6, $RbPuO_2F_2$ and $NH_4PuO_2F_2$ may be precipitated by addition of RbF or NH_4F, respectively.

[c] Complex carbonates are formed.

[d] Solid $KPuO_2CO_3$ precipitates on addition of K_2CO_3 to Pu(V) solution.

[e] From solution of Pu(VI) in CH_3CO_2H, $NaPuO_2(CH_3CO_2)_3$ precipitates on addition of Na^+.

[f] Addition of $(NH_4)_2HPO_4$ to Pu(V) solution yields $(NH_4)HPuO_2PO_4$ with Pu(V).

[g] On addition of H_3PO_4, $HPuO_2PO_4 \cdot xH_2O$ precipitates.

[h] At higher pH (2-4), $UO_4 \bullet 2H_2O$ precipitates; Np(V), Pu(V), Np(VI), Pu(VI) reduced by H_2O_2.

Table 2. Decontamination factors for plutonium precipitated from an irradiated plutonium alloy dissolved in nitric acid

Element	*Pu(III) oxalate*	*Pu(IV) oxalate*	*Pu(IV) peroxide*	*Pu(III) fluoride*
Fe	33	10	50	1.4
Co	47	> 95	30	8.6
Zr	3.5	> 44	1	1.1
Mo	> 13	> 15	> 140	1.1
Ru	> 38	33	> 14	36
Ce	1	1	6	1.1

Coprecipitation methods

Coprecipitation processes were the first to be used for the recovery of plutonium and to examine its chemical properties. The tiny amounts of plutonium present in the first preparations were too small to be precipitated directly, so coprecipitation or "carrier" precipitations were used to purify, and deduce the chemical properties of plutonium and many other radioactive elements. Coprecipitation separation methods are a common feature of many analytical procedures for radionuclides. In general, an actinide metal ion will coprecipitate if the anion contained in the bulk precipitate forms an insoluble salt with the actinide metal ion in the same oxidation state or states present in the solution. Coprecipitation methods have been used to purify plutonium in microgram amounts and for recovery on a production scale. Useful precipitation methods for uranium and plutonium have been reviewed (Sorantin, 1975). A very large and useful set of separation procedures compiled by element for most of the periodic table are contained in the Nuclear Science Series: Monographs on Radiochemistry and Radiochemical Techniques published by the National Academy of Science – National Research Council from 1959 to 1977. This series is out of print, but can be found online (http://lib-www.lanl.gov/radiochemistry/elements.htm). A useful collection of radioanalytical procedures that use many coprecipitation steps is found in the report: Collected Radiochemical and Geochemical Procedures 5th Edition, LA-1721, May 1990, compiled and edited by J. Kleinberg.

Lanthanum fluoride

Precipitation of lanthanum fluoride or other lanthanide fluorides from acid solutions carries trivalent and tetravalent actinides, but not the pentavalent and hexavalent ions. The lanthanide and yttrium fission products coprecipitate, but most of the other fission products remain in solution. The behavior of neptunium and plutonium in the lanthanum fluoride precipitation was used to establish the existence of two oxidation states of these elements before weighable quantities were available (Seaborg and Wahl, 1948). The lanthanum fluoride carrier precipitation was also a key step in the first isolation of a weighable quantity of plutonium compound described briefly below.

Cunningham and Werner isolated PuO_2 and weighed 2.77 micrograms, the first weighable quantity of any synthetic element, on September 10, 1942 at the Metallurgical Laboratory of the University of Chicago (Cunningham and Werner, 1949). The plutonium had been separated from about 90 kilograms of uranyl nitrate hexahydrate that had been irradiated for one to two months with neutrons produced by bombarding a beryllium target with deuterons at the cyclotron facility at Washington University in St. Louis. The separation of plutonium was accomplished through oxidation state adjustments and a series of LaF_3 precipitations that carried Pu(IV) and Np(IV) but not Pu(VI) or Np(VI). The brief overview that follows provides an example of a coprecipitation separation method and also illustrates the painstaking effort required in these first explorations of plutonium chemistry.

The 90 kg of irradiated $UO_2(NO_3)_2 \bullet 6H_2O$ was mixed with 100 liters of diethyl ether to yield about 120 liters of ether solution containing uranyl nitrate solvate, $UO_2(NO_3)_2[O(CH_2CH_3)_2]_2$, and a small amount of fission products and 8 liters of an aqueous phase that consisted of about 50 wt% uranyl nitrate hydrate with most of the fission products and transuranic elements, principally neptunium and plutonium. This was essentially a solvent extraction step that partitioned most of the U(VI) to the ether phase along with a small amount of the fission products.

The aqueous phase was diluted to 20 liters and made 2 M in nitric acid and 0.014 M in La(III) and then HF was added to give a solution 4 M in HF. The 40 g of LaF_3 precipitate contained the transuranium elements and about 25% of the original fission product activity (mostly the lanthanide and yttrium fission products). The separated LaF_3 precipitate was heated in concentrated sulfuric acid to distill HF and then dissolved in and diluted to 5 liters with 2 M nitric acid. The Pu(IV) was oxidized to Pu(VI) by using $K_2S_2O_8$ and Ag(I) as a catalyst. The solution was then made 4 M in HF and the LaF_3 precipitate separated by filtration. The ~40 g of LaF_3 contained most of the remaining fission product activity, while the solution contained the Pu(VI) and Np(VI). The addition of a 6% SO_2 solution to the filtrate and washings reduced the Pu and Np and the excess peroxydisulfate. Addition of 2 g of $La(NO_3)_3$ in solution, precipitated LaF_3 that carried the tetravalent Pu and Np. Repeated cycles of precipitation with progressively smaller amounts of LaF_3 were used to further decontaminate the Pu and Np. For two of the LaF_3 precipitation cycles, $KBrO_3$ was employed as the oxidizer to selectively oxidize Np, but not Pu. This allowed the separation of the Np into the filtrate solutions while Pu was carried with the LaF_3. These additional cycles of smaller precipitations eventually yielded a 120 microliter solution of 1.7 M HNO_3 and 5 M HF that was fumed in a platinum crucible and treated with 10 M ammonium hydroxide. The washed precipitate of plutonium hydroxide contained about 40 micrograms of Pu. The microliter-scale solution manipulations were performed in a specially designed glass apparatus viewed with a microscope. Additional purification steps yielded a 50 microliter solution of Pu in nitric acid. Ten microliters of this solution were placed on a platinum weighing pan, dried, and heated to give the oxide. This sample provided the first weighable quantity of plutonium that is now displayed in the Seaborg Museum at the University of California, Berkeley.

Bismuth phosphate process

The bismuth phosphate process was used for the first large-scale purification of plutonium from neutron-irradiated uranium at the Hanford site during the Manhattan Project and after the war until the 1950's when it was displaced by solvent extraction processes. The precipitation of $BiPO_4$ from acid solutions carries the trivalent tetravalent actinides and especially Pu(IV), but not the pentavalent and hexavalent ions. Bismuth phosphate is quite insoluble in moderately concentrated nitric and sulfuric acids. This is an important property because addition of sulfuric acid to a nitric acid solution of neutron-irradiated uranium could be used to keep the relatively large quantity of U(VI) in solution as a sulfate complex while bismuth phosphate was precipitated and carried the plutonium. The $BiPO_4$ solid carried only small amounts of the fission products. The $BiPO_4$ could be redissolved in concentrated nitric acid; this simplified the process relative to using a lanthanum fluoride carrier that is difficult to redissolve. A series of oxidation state adjustments and precipitations of $BiPO_4$ from solutions of neutron-irradiated uranium in nitric acid separated the plutonium from the uranium, neptunium and fission products in a scheme that resembles the lanthanum fluoride process described above. In fact, cycles of lanthanum fluoride precipitation from nitric acid were incorporated into the bismuth phosphate process to concentrate and further purify the plutonium.

Thompson and Seaborg first developed the bismuth phosphate process (Thompson and Seaborg, 1956). The scale-up of the process from the laboratory to an operating plant by a factor of 10^8 in a short time is a remarkable story (Hill and Cooper, 1958). An overall decontamination factor from the fission products of 10^7 was obtained at Hanford for the plutonium product. The disadvantages of the process included discarding the uranium with the fission products, generation of large volumes of high salt wastes, and batch operation. Continuous solvent extraction processes based on extraction of uranium and plutonium from nitric acid solutions of dissolved fuel displaced the bismuth phosphate process.

Precipitation and crystallization methods for conversion chemistry of plutonium

Solvent extraction processes have displaced the original bismuth phosphate co-precipitation method for production scale plutonium separation from neutron-irradiated uranium fuels and targets, but precipitation and crystallization from aqueous solutions have always been important for preparing and purifying solid compounds for the various applications of plutonium. The major products are plutonium metal for irradiation targets and fuels, weapons components, or storage and PuO_2 for mixed oxide fuels, heat sources (when the ^{238}Pu content is high), and storage.

The bulk of the aqueous processing of plutonium takes place in nitric or hydrochloric acid solutions and most plutonium solids are precipitated from these solutions (Cleveland, 1980; Christensen, Bowersox *et al.*, 1988). The most common precipitations are oxalate, peroxide, hydroxide, and fluoride. The typical reasons for using these precipitations are:

- Good recovery of the plutonium can be obtained in the solid in a form suitable for preparing metal or oxide.
- Relatively concentrated plutonium nitrate or chloride solutions can be largely or partially purified from many cationic impurities.
- Precipitation from relatively dilute solutions provides a very quick and convenient method for concentrating plutonium.
- Calcination at 500-800 °C readily converts properly precipitated Pu(III) and Pu(IV) oxalates to PuO_2 which is suitable for direct oxide reduction with calcium to the metal or hydrofluorination to PuF_4 that is then reduced to metal.
- Precipitation of plutonium or americium hydroxides from waste solutions such as oxalate or peroxide filtrates generally provides an effective method to recycle the plutonium and americium in the separated precipitate and to disposition the alkaline filtrate to low-level waste treatment operations.

This group of common precipitation methods will be briefly reviewed. The detailed procedures used at different facilities have varied quite widely because of the many facility-specific factors that enter into the process design. Both batch and continuous processes have been developed for these precipitations.

Plutonium(III) oxalate precipitation

Since the time of the Manhattan project, workers have found it useful to precipitate the easily filterable turquoise-blue $Pu_2(C_2O_4)_3 \bullet 10H_20$ by reducing plutonium to the trivalent state in low acid solution and carefully adding an oxalic acid solution. Directly adding solid oxalic acid will produce a crystalline precipitate with a smaller average particle size (Christensen, Bowersox *et al.,* 1988). The solubility of $Pu_2(C_2O_4)_3 \bullet 10H_20$ can be approximated by the expression $[Pu\ (mg\ L^{-1})] = 3.24[H^+]^3[H_2C_2O_4]^{-3/2}$ (Harmon and Reas, 1957). However, the typical filtrate from a production run will have somewhat higher concentrations of plutonium (0.1-0.5 g L^{-1}) left in solution than that calculated from this equation. The precipitation is useful over a wide range of conditions when the Pu(III) concentration is more than 1 g L^{-1} and with less than 4 M acid. The Pu(III) oxalate precipitation gives good decontamination factors from such impurities as Al(III), Fe(III), and U(VI). There is less decontamination from sodium, potassium and calcium and none from Am(III). Plutonium(III and IV) can be scavenged from very dilute solutions using Ca(II) or Pb(II) oxalates as carriers (Maraman, Beaumont *et al.*, 1954; Akatsu, 1982; Akatsu, Moriyama *et al.*, 1983).

Plutonium(IV) oxalate precipitation

Plutonium(IV) precipitates as the tan solid $Pu(C_2O_4)_2•6H_20$ from low acid solutions upon addition of oxalic acid, but is usually a very fine solid and tacky at room temperature (Christensen, Bowersox *et al.,* 1988). Precipitation at elevated temperatures can greatly improve the filterability of the solid. Typical losses of plutonium to the filtrate in practical operations are 0.2-0.5 g L^{-1}. The precipitation is used over a wide range of conditions with Pu(IV) concentrations greater than 1 g L-1 and acid concentrations between 1-5 M. The decontamination factors for impurities such as Al(III), Fe(III) and U(VI) are typically higher than for the Pu(III) oxalate method. There is no decontamination from Am(III).

The French process used to make MOX fuel in the MELOX plant uses a PuO_2 powder derived from carefully controlled precipitation of Pu(IV). The Pu(IV) oxalate provides a crystal morphology that gives the required characteristics in the oxide powder for mixing and grinding with uranium oxide to prepare the MOX pellets. However, the MOX material does not have U and Pu oxides in a true solid solution and the Pu oxide domains can be difficult to dissolve in nitric acid at higher burn-ups. Recently the CEA has been studying the coprecipitation of U(IV) and Pu(III) with oxalic acid. Pu/(U+Pu) ratios as high as 29% and 45%were used and the mixed solution of U(IV) and Pu(III) in nitric acid was mixed with a concentrated solution of oxalic acid. The solid was converted into oxide at 700 °C under Ar flow. X-ray diffraction and SEM analysis demonstrated the formation of a solid solution of $(U,Pu)O_2$ with a controlled oxygen stoichiometry and well-define particle morphology that resembles that of the oxalate precusor solid (Arab-Chapelet et al. 2008).

Plutonium(IV) peroxide precipitation

Plutonium peroxide is an olive-green solid formed by the addition of hydrogen peroxide solutions to acid solutions of Pu(IV). The typical range of acid concentration is 2.5-5.5 M. The solutions are often cooled to 10-15 °C to reduce the decomposition of hydrogen peroxide. High levels of iron, copper, manganese or nickel catalyze the decomposition of the H_2O_2 and interfere with the precipitation. At higher acid concentrations and with careful H_2O_2 addition, a very filterable hexagonal form of plutonium peroxide precipitates. At lower acidities a gelatinous cubic form precipitates that is difficult to filter. Plutonium peroxide is not a stoichiometric compound and its O:Pu ration may approach 3.5 (Cleveland, 1979; Cleveland, 1980), but does not reach 4.0 as is suggested by the formula $Pu(O_2)_2$. Anions such as nitrate, chloride and sulfate, if present in the solution, are incorporated into the solid. Indeed, sulfate is added in some processes at a concentration of 0.1-0.3 M to nitric acid solutions to improve the filterability of the peroxide precipitate.

The Pu(IV) peroxide precipitation is a powerful method for purification of plutonium from many impurity elements except those such as Th, Np, and U that form similar peroxides under these conditions. Unlike the oxalate precipitations, Am(III) is removed to a high degree. The excellent decontamination factors obtained for many elements and the use of one reagent that is easily decomposed to water and oxygen in subsequent operations are the major advantages of using this process. The disadvantages are greater losses of plutonium in the filtrate (typically 0.1 to 0.5%) and violent decomposition that can occur during precipitations in the presence of high concentrations of iron and other metal ion catalysts for the decomposition reaction.

Plutonium(III) fluoride precipitation

Addition of aqueous HF to a solution of Pu(III) in nitric or hydrochloric acid precipitates blue-violet $PuF_3 \bullet xH_2O$ (x ~ 0.75) (Christensen, Bowersox *et al.,* 1988). The Pu(IV) concentration should be kept low because the hydrated PuF_4 precipitate is very gelatinous and much more soluble than the trifluoride. Significant Pu(IV) content will thus increase filtering time and plutonium losses to the filtrate. Reducing agents such as hydroxylamine, sulfamic acid or ascorbic acid are commonly used. With careful oxidation state control losses of plutonium to the filtrate are very low (0.05-0.1%). A disadvantage of preparing any fluorine-containing compound of plutonium is increased production of neutrons from alpha-n reactions relative to the oxygen, carbon, and nitrogen-based precipitants. The trifluoride precipitation does not give decontamination factors from cationic impurities that are as high as the oxalate or especially the peroxide precipitations. It gives moderate decontamination from many impurities including iron, but not from aluminum, zirconium, and uranium. Dried PuF_3 can be roasted in oxygen to produce a mixture of PuF_4 and PuO_2 that can be directly reduced with calcium metal to give 95-97% yields of plutonium metal.

Plutonium hydroxide precipitation

Hydroxide precipitation is quite useful to produce a filtrate with very low levels of plutonium. Sodium or potassium hydroxide solutions are commonly added to precipitate the gelatinous green Pu(IV) hydroxide (Christensen, Bowersox *et al.,* 1988). If Pu(III) is present, it will slowly oxidize to Pu(IV). Many other metal ions will precipitate as hydroxides as well or be carried by the plutonium hydroxide so that this is not a useful purification procedure. The hydroxide is generally difficult to filter. If large amounts of magnesium or calcium are present, the voluminous hydroxide precipitates of these metal ions make filtration especially difficult, unless they are avoided by carefully controlling the pH. The dried hydroxide cake can be recycled for plutonium recovery by dissolving it in acid. The formation of the Pu(IV) oxy-hydroxide polymer should be avoided because this material behaves quite differently from the hydroxide precipitate and can be quite difficult to redissolve in acid.

Miscellaneous precipitations

Other precipitations have been tested for plutonium processing operations, but have not been deployed or as widely used as those reviewed above. These include $CaPuF_6$ and Cs_2PuCl_6 from acid solutions for metal production operations (Christensen, Bowersox *et al.*, 1988; Muscatello and Killion, 1990) and $(NH_4)_4PuO_2(CO_3)_3$ or mixed $(NH_4)_4(Pu,U)O_2(CO_3)_3$ from alkaline solution for the preparation of mixed oxide fuels (Roepenack, Schneider *et al.,* 1984).

Examples of Precipitation, Coprecipitation, and Sorption Separation Methods for Fission Products or Other Metal Species

Cesium and strontium recovery at Hanford

A variety of precipitation and coprecipitation processes were used at various stages to recover Cs and Sr from the waste tanks at Hanford. The Cs-137 and Sr-90 were recovered for use as irradiation sources and thermoelectric generators, to reduce heat load in the waste tanks, and to explore methods for removal of Cs and Sr in advanced nuclear power cycles. Some selected examples are briefly outlined, but much more detail is available on the operation of the processes (Gasper, www.if.uidaho.edu/~beitgeor/hlwfiles/Cs%20and%20Sr%20Recovery%20and%20Encapsulation.pdf).

The first 30,000 curies of Cs-137 was recovered from the tank wastes using a nickel ferrocyanide precipitation process. The feed was the acid raffinate from PUREX operations that was concentrated by evaporation and partially denitrated (CAW for Current Acid Waste). The CAW feed was neutralized with NaOH and ammonia gas to precipitate the bulk of the fission products and Fe, Al, Cr, and Ni. The filtered supernatent containing the Cs was acidified, boiled to remove CO_2 and the pH adjusted to 4. Soluble nickel and ferrocyanide salt solutions were added simultaneously to precipitate $Ni_2Fe(CN)_6$ which ion exchanges some of the Ni for Cs. The loaded nickel ferrocyanide was metastasized with Ag_2CO_3 to generate Cs_2CO_2 and silver loaded nickel ferrocyanide. The Cs recovery was greater than 99%. The ferrocyanide precipitation process was eventually replaced by a phosphotungstic acid (PTA) precipitation of Cs directly from the CAW feed. The PTA precipitation process was used to recover over 18 megacuries of Cs-137.

The first megacurie of Sr-90 was produced at Hanford using a lead sulfate coprecipitation process. Sodium sulfate and tartaric acid (used to hold iron in solution) were added to the acidic waste stream from PUREX operations. Then $Pb(NO_3)_2$ and sodium hydroxide were added to precipitate $PbSO_4$. The $PbSO_4$ was separated by centrifugation. Sodium hydroxide and sodium carbonate were added to convert the sulfate to the carbonate. The $PbCO_3$ was dissolved in nitric acid and oxalic acid added to precipitate lead, cerium, and the other rare earths leaving the Sr in solution. This method was later replaced with a solvent extraction process using di-2-ethylhexylphosphoric acid to recover strontium.

Additonal examples of cesium precipitants or ion exchangers

A review by Todd et al. (2004) covers a broad range of cesium and strontium separation processes and some selected examples of cesium precipitants/ion-exchangers are noted here. The use of phosphotungstic acid to precipitate Cs from acidic solution was noted above. The compound ammonium molybdophosphate has also been used to selectively recover Cs from acidic tank wastes. It has usually been deployed as a solid powder that is added to the solution and ion exchanges Cs for ammonium, but the compound has also been bound in a polymer binder, polyacrylonitrile (PAN), and used in a column.

Many types of metal ferrocyanides have been studied for Cs removal from acidic to basic solutions. These materials are finely divided solids that are typically added to the Cs-containing solution and recovered by centrifugation or filtration. Some granular solid forms and PAN-bound materials have been used in column mode. The removal of Cs involves both ion exchange for the metal ions, protons, or ammonium cations not bound in the cubic $Fe(CN)_6$-M(II,III) framework and more complex incorporation of cesium into new phases that form in the solid material.

Sodium tetraphenylborate has been used as a selective precipitant for Cs from alkaline solutions. It was proposed for in-tank precipitation of Cs for processing of high-level waste supernatants at the Savannah River site. Problems with rather rapid catalytic decomposition of tetraphenylborate to give benzene from metal species in the complex tank mixtures resulted in the adoption of the Caustic-Side Solvent Extraction process based on calixarene-crown type compounds as the primary method to remove Cs from the alkaline tank solutions.

Examples of Sorbents for Radionuclides

Many solid materials have been used as sorbents for radionuclides and are used in radioanalytical procedures. Activated charcoal, silica, alumina, clays, and iron hydroxides are among the many materials used to sorb ions from solutions. The negatively charged surfaces of oxide materials can sorb cations from solution sometimes with seemingly surprising selectivity. For example, in a radioanalytical procedure for sodium it is noted that in concentrated HCl only sodium and tantalum, among 60 elements tested, were retained on hydrated antimony(V) oxide, $Sb_2O_5 \bullet xH_2O$ (Kleinberg, 1990). Careful preparation of the sorbent material is often required. For example, a large literature exists to prepare silica and alumina materials for applications in chromatographic columns. Sorbents have been deployed as finely divided solids or used in columns. The compendia of radioanalytical procedures noted above contain other examples of the use of sorbents.

Sorbents are commonly used for wastewater treatment in industry and that is also true for nuclear processing applications. Sand filters that are used for particulate removal in wastewater treatment can also function as sorbents for low-levels of some radionuclides. Silica has been used to remove radioactive zirconium-niobium from solutions of uranyl nitrate produced in PUREX operations (Karraker, 1957). Iron hydroxides are used as sorbents, but more often as a carrier in precipitations and soluble salts of both Fe(II) and Fe(III) are used in the initial precipitation reaction. Iron hydroxide precipitations have been used to remove low-level activity from plutonium and americium from actinide processing facility wastewaters at Los Alamos to very low levels before discharge to the environment. More recently ultrafiltration and reverse osmosis steps have replaced the iron hydroxide precipitation to reduce overall solid waste volumes (Moss et al., 1998).

References

1. Akatsu, J. (1982). *Sep. Sci. Technol.* 17(12): 1433-1442.
2. Akatsu, J., Moriyama, N., Dojiri, S., Matsuzuru, H. and Kobayashi, Y. (1983). *Sep. Sci. Technol.* 18(2): 177-186.
3. Arab-Chapelet, B., De Bruycker, F., Picart, S., Leturcq, G. and Grandjean, S. (2008) Proceedings of ATALANTE 2008 Conference, Montpellier, France, May 19-22, 2008, P3 02.
4. Christensen, D. C., Bowersox, D. F., McKerley, B. J. and Nance, R. L. (1988). *Wastes from plutonium conversion and scrap recovery operations*, Los Alamos National Laboratory,Los Alamos, NM, Report LA-11069-MS, 96 pp.
5. Cleveland, J. M. (1979). *The chemistry of plutonium*. La Grange Park, IL, American Nuclear Society, 680 pp.
6. Cleveland, J. M. (1980). *Section IV - Chemical processing*. Plutonium handbook: a guide to the technology. O. J. Wick, Eds. LaGrange Park, IL, American Nuclear Society. 2**:** 966 pp.
7. Cunningham, B. B. and Werner, L. B. (1949). *The first isolation of a synthetic element* $^{94}Pu^{239}$. The transuranium elements. G. T. Seaborg, J. J. Katz and W. M. Manning, Eds. New York, McGraw-Hill**:** 1733 pp.
8. Harmon, K. M. and Reas, W. H. (1957). *Conversion chemistry of plutonium nitrate*, Report HW-49597 A, 15 pp.
9. Hill, O. F. and Cooper, V. R. (1958). *Ind. Eng. Chem.* 50(4): 599-602.
10. Karraker, D. G. and Parker, S. G. (1957). *Adsorption of zirconium-niobium on silica gel*, USAEC Report DP-228, E. I. du Pont de Nemours & Co., Inc., July 1957.
11. Kleinberg, J. (1990). *Collected Radiochemical and Geochemical Procedures 5th Edition*, Los Alamos National Laboratory Report, LA-1721, May 1990.
12. Maraman, W. J., Beaumont, A. J., Christensen, E. I., Henrickson, A. V., Hermann, J. A., Johnson, K. W. R., Mullins, L. J. and Winchester, R. S. (1954). *Calcium oxalate carrier precipitation of plutonium*, Los Alamos Scientific Laboratory, Report LA-1692, 10 pp.
13. Mullin, J. W. (2001). *Crystallization*, 4th Edition, Boston, MA, Butterworth-Heinemann (ISBN 0-7506-4833-3).
14. Mullin, J. W. and Ang, H-M. (1977). *Supersaturation and crystal size distribution changes during precipitation of nickel ammonium sulfate hexahydrate*, Kristall and Technik. 12, 105-115.
15. Muscatello, A. C. and Killion, M. E. (1990). *Chloride anion exchange coprocessing for recovery of plutonium from pyrochemical residues and* Cs_2PuCl_6 *filtrate*, EG and G Rocky Flats, Inc, Report RFP--4325, 19 pp.
16. Moss, D., Williams, N., Hall, D., Hargis, K., Saladen, M. Sanders, M., Voit, S., Worland, P. and Yarbro, S. (1998). *Elimination of liquid discharge to the environment from the TA-50 Radioactive Liquid Waste Treatment Facility*, Los Alamos National Laboratory Report, LA-13452-MS, June 1998.
17. Myerson, A. S. (2002). *Handbook of Industrial Crystallization*, 2nd Edition, Boston, MA, Butterworth-Heinemann (ISBN 978-0-7506-7012-8).
18. Roepenack, H., Schneider, V. W. and Druckenbrodt, W. G. (1984). *Am. Ceram. Soc. Bull.* 63(8): 1051-1053.
19. Seaborg, G. T. and Wahl, A. C. (1948). *J. Am. Chem. Soc.* 70(3): 1128-1134.
20. Sorantin, H. (1975). *Determination of uranium and plutonium in nuclear fuels*. Weinheim, Germany, Verlag Chemie, 285 pp.
21. Thompson, S. G. and Seaborg, G. T. (1956). *First use of bismuth phosphate for separating plutonium from uranium and fission products*. Progress in nuclear energy-Series 3: Process chemistry. F. R. Bruce, J. M. Fletcher, H. H. Hyman and J. J. Katz**:** 163-171.

22. Todd, T. A., Batcheller, T. A., Law, J. D. and Herbst, R. S. (2004). *Cesium and strontium separation technologies literature review*, INEEL/EXT-04-01895, March 2004.
23. Winchester, R. S. and Maraman, W. J. (1958). *Proc. U.N. Intern. Conf. Peaceful Uses At. Energy, 2nd, Geneva, 1958* 17: 168-171.

Complexation Reactions
In Nuclear Separations

Raymond G. Wymer
Vanderbilt University

Nuclear separations are a mainstay of the nuclear industry, and complexation reactions play a major role in nuclear separations. This paper concentrates not only on those separations that are both of primary importance to spent nuclear fuel reprocessing and waste management and the complexation reactions that make those separations possible, but also on some of the most unusual aspects of the chemistry involved.

Nuclear separations find applications in all parts of the nuclear fuel cycle from mining and milling of ores, to purification of nuclear materials, to uranium enrichment, to reactor fuel fabrication, to reactor spent fuel reprocessing, and to radioactive waste management. Separations in these areas rely to a very large extent on reactions with chemical complexation species that form chemical complexes with a relatively small number of radioactive elements. The chemistries of some of the elements of greatest importance in the nuclear fuel cycle are quite remarkable and make possible many of the separations processes that are fundamental to the nuclear industry.

Significant Elements in Separations and Complexation Reactions

Isotopes of a relatively small number of radioactive elements have special significance in the context of the nuclear fuel cycle. Their complexation reactions are illustrative of the important role played by complexes. The elements selected for attention here are: technetium (Tc), uranium (U), neptunium (Np), plutonium (Pu), americium (Am), and curium (Cm). Some radioisotopes of these elements that are especially important in the nuclear fuel cycle are given in Table 1.

Table 1. Some Radioisotopes of Importance in the Nuclear Fuel Cycle

Element	**Isotopes of Interest**	**Half life**
Technetium	^{99}Tc	2.111E+05 yr
Uranium	^{232}U, ^{233}U, ^{234}U, ^{235}U, ^{238}U	Various
Neptunium	^{237}Np	2.144E+06 yr
Plutonium	^{238}Pu, ^{239}Pu, ^{240}Pu, ^{242}Pu	Various
Americium	^{241}Am	432.2 yr
Curium	^{242}Cm, ^{244}Cm	162.8 days, 10.1 yr

These elements and their isotopes have importance for a variety of reasons which are discussed below. Some of the reasons for importance in separations of specific isotopes of the six elements listed in Table 1 are given in Table 2.

Table 2. Some Reasons for Importance in Separations of Specific Radioisotope

Radioisotope	Reason for Importance
^{232}U	Present with ^{233}U; Hazardous gamma emitter in its daughter chain
^{233}U	Potential reactor fuel; weapons usable
^{234}U	High specific activity alpha emitter; naturally occuring
^{235}U	Reactor fuel; weapons usable
^{238}U	Fertile isotope for ^{239}Pu production; good radiation shield
^{99}Tc	Dose limiting isotope in geologic repository release path
^{237}Np	Dose limiting isotope in repository release path; precursor to ^{238}Pu
^{238}Pu	Producer of heat for thermoelectricity production in space
^{239}Pu	Potential reactor fuel; long-term heat producing isotope in repository
^{240}Pu	Heat producing isotope in repository
^{241}Am	Important intermediate-term heat producing isotope in repository
^{244}Cm	Heat producer in repository; high specific activity alpha biohazard

Complexation reactions of elements are very strongly dependent on the valence states of the elements. Changing the valence of an element dramatically changes its chemistry and consequently changes its complexation reactions and separations chemistry. Table 3 lists common valence states of the elements of interest here as well as some of the important features of them. The most common valence states are in bold face.

Table 3. Important features of Some Common Valence States

Element	Valences	Features
Tc	**+4**, *+5, +6*, **+7**	Environmentally mobile as TcO_4^-; Tc_2O_7 is volatile at relatively low temperatures
U	*+3*, **+4**, +5, **+6**	UO_2^{2+} forms extractable species; U^{+4} is used in oxide fuels; UF_6 is volatile
Np	*+3, +4*, **+5**, *+6, +7*	NpO_2^-: Environmentally mobile; extractable in organic solvents
Pu	*+3*, **+4**, **+5**, **+6**, *+7*	Mobile as Pu^{+4} colloid; Pu^{+4} is extractable in organic solvents; Pu^{+4} is used in oxide fuels
Am	**+3**, *+4,+5, +6*	Am^{+3} is very stable in aqueous media; Am^{6+} is potentially useful in separations from other actinides
Cm	**+3**, *+4*	Cm^{+3} is the only common valence state in aqueous solution; it behaves much like rare earths

Uranium

Uranium is at the heart of commercial nuclear power and is vital to the entire nuclear enterprise. Its presence and use worldwide has resulted in a vast literature, not only on uranium complexation and separations reactions, but also on all aspects of the uranium fuel cycle: mining and, milling; isotope enrichment; reactor fuel manufacturing; spent reactor fuel reprocessing; and weapons production. Only a small fraction of that literature is covered in this discussion of complexation reactions used in nuclear separations.

The chemistry of uranium is very unusual, and although it cannot be said to be unique, it certainly can be said to be remarkable. The number of valence states of uranium that are easily obtainable under ordinary conditions make possible a wealth of compounds and complexation reactions that present almost unparalleled opportunities for separations processes, both of uranium from contaminants and of uranium isotopes. Trivalent uranium as a chloride complex in water is used in a quite unusual example of uranium isotope separations chemistry. The trivalent chloride is thermodynamically unstable in aqueous media in the presence of metallic ions that catalyze its reaction with water to form hydrogen and U^{+4}, but when catalytic ions are absent it is stable indefinitely. This unusual meta-stability has been used in a practical uranium isotope separation process called the Chemex process.

Table 4 lists common aqueous ionic uranium chemical species and some chemical properties of interest in separations processes.

Table 4. Common Aqueous Ionic Uranium Chemical Species

Aqueous Species	Chemical Properties
U^{+3}	Thermodynamically unstable in aqueous media but kinetically stable
U^{+4}	Forms complexes with Cl^-, SO_4^{2-}, F^-, CNS^-, et al.; hydrolyzes easily
UO_2^+	Transient existence; disproportionates to U^{+4} and UO_2^{2+}
UO_2^{+2}	Predominant aqueous species; some salts are stable to 300° C

Uranium in the tetravalent state forms colloids and gels that are easily formed into different shapes, e.g., small spheres that find application in preparing certain types of reactor fuels. The colloidal dispersions (sols) of uranium hydroxide are gelled by precipitation with a chemical base or by removal of water as a step in the preparation of UO_2 for use in uranium dioxide reactor fuel. Because it is highly charged the U^{+4} ion easily forms a wide variety of complex ions. It is also readily oxidized or reduced by a variety of redox reagents. It precipitates as the fluoride which is the chemical form used to produce uranium metal by thermochemical reduction with alkali metals.

The uranyl ion (UO_2^{2+}) is the most common uranium ion in aqueous media. The oxygen atoms in the uranyl ion are bound extremely tightly and do not detach readily in chemical reactions. Thus UO_2^{2+} behaves much as a divalent monatomic cation. Reduction reactions of (UO_2^{2+}) to produce U^{+4} are slow due to the stability of the uranyl ion. Uranyl salts and complexes are formed with most common anions such as NO_3^-, Cl^-, SO_4^{-2}, F^- and PO_4^{3+}. These anions may react with the uranyl ion to form anionic complexes that are useful in carrying out separations using anion exchange resins. Uranyl phosphate is found in phosphate deposits and may be economically recovered as a byproduct in fertilizer manufacture. Uranyl ion complexes extract readily into organic solvents. This is the basis of the widely used Purex Process for reprocessing spent nuclear reactor fuel. Uranyl nitrate in nitric acid reacts with tributyl phosphate when contacted with a TBP phase to form $UO_2(NO_3)_2{\cdot}2TBP$ which is highly soluble in a TBP (tributly phosphate) solvent formed by mixing TBP with a hydrocarbon diluent such as dodecane or kerosene. Most fission products and some actinides do not extract in that solvent except under conditions of considerably more concentrated TBP than is use in the Purex Process (see the discussion of curium below). Whether or not other actinides extract depends strongly on the valence state of the actinides. Uranyl salts are often exceptionally stable at temperatures well above the boiling point of water, e.g., 300° C. This property found application in the aqueous homogeneous reactor which employed a solution of UO_2SO_4 at temperatures well above the boiling point of water at atmospheric pressure. $UO_2(NO_3)_2$ has been proposed for use in an aqueous homogeneous reactor for the production ^{99}Mo which is a high-yield fission product and is the parent of ^{99m}Tc, a widely used isotope in medical diagnostics.

Addition of chemical bases such as NH_4OH and NaOH to solutions of uranyl salts precipitate uranium as a diuranate, for example as $(NH_4)_2U_2O_7$, a rather ill-defined but useful compound called ammonium diuranate that finds use in uranium milling and in reactor fuel manufacture. The uranyl ion reacts in mildly acidic solutions of hydrogen peroxide to form the insoluble complex peroxide salt $UO_4{\cdot}2H_2O$. This reaction, although not unique to uranium, is unusual and may be used to purify uranium. A complexation reaction of uranyl ion with sodium and zinc acetates forms the unique precipitate $NaZn[UO_2(CH_3O_2)_3]_3$ that may be used for the quantitative determination of sodium.

The very unusual and highly volatile compound UF_6 is at the heart of commercial uranium isotope separations, both by gaseous diffusion and by gas centrifugation. Because it can be distilled UF_6 finds use in uranium purification.

A very useful and extraordinarily stable uranyl tricarbonate complex anion, $UO_2(CO_3)_3^{-4}$, forms with carbonate anions. This extraordinary anionic uranyl tricarbonate complex finds use in uranium solution mining, in fuel fabrication, and in separations from a host of cations that do not form such anionic complexes.

The capacity of uranium to form slightly non-stoichiometric uranium dioxide makes possible adjustments to its composition to optimize its behavior as fuel in nuclear reactors.

Indeed, nature has provided the chemist and chemical engineer with a uranium complexation and separations cornucopia that is rich in its variety, versatility, and complexity.

Plutonium

Plutonium finds its greatest importance from two of its isotopes: ^{238}Pu (formed from ^{237}Np) which is used as a heat source for thermoelectric power generation for space applications and ^{239}Pu (formed from the abundant ^{238}U isotope) which is fissionable and thus affords a way to extend the period of production of nuclear power from the uranium fuel cycle. The high specific radioactivity of ^{238}Pu complicates studies of its aqueous chemistry both because of its radiotoxity and tendency of its solid compounds to migrate and because of its radiolytic reaction with water to form chemically reactive radicals and oxidizing species such as hydrogen peroxide. At high concentrations of ^{238}Pu the water may effervesce. Plutonium has the unique property of existing in significant amounts in four valence states simultaneously in aqueous solutions. It is, however, possible to stabilize it in each of its valence states. The variety of valence states of plutonium presents ample opportunities for it to engage in complexation reactions and for a range of separations processes. Its proclivity to form very strong complexes with fluoride ion provides a method for the dissolution of the very refractory plutonium dioxide as well as a chemical form useful in the formation of plutonium metal.

Plutonium chemistry has been found to be almost equal to uranium in its diversity and complexity. Pu^{+4} in particular forms a wide variety of complexes, as do all of the tetravalent actinide elements. In high nitrate concentrations anionic nitrate complexes of Pu^{+4} are formed. These complexes are readily sorbed on organic anion exchange resins. This reaction is capitalized on as a means of separating plutonium from other actinides that do not form anionic complexes with nitrate ion. Care must be taken to not let the anion exchange resins go to dryness when the nitrate complex is on them. Serious explosions have occurred due to the oxidative reaction of the concentrated nitrate ion with the organic resin. Tetravalent plutonium as the nitrate complex has the unusual property of extracting easily into organic liquids, e.g., TBP, much as uranyl nitrate does. This property is used in spent nuclear reactor fuel reprocessing.

Plutonium colloid is an important chemical species that forms by the hydrolytic reaction of tetravalent plutonium with water even at relatively low pH. Once formed the colloid is very stable. Over time the colloid becomes very refractory and is difficult to dissolve, often requiring the addition of fluoride ion to aid in dissolution in acids. The colloid moves easily through the environment and is a potentially important contributor to radiation dose in the neighborhood of nuclear weapons test sites, at the site boundary of a geologic repository, and in the vicinity of nuclear incident sites such as the Mayak site in Russia, where there was a catastrophic nuclear waste explosion that spread radioactivity over a large area. The colloid may also be used beneficially in the preparation of nuclear fuels by sol-gel processes as note above for uranium.

Technetium

Technetium has the distinction of being a radioactive element that has a lower atomic number than uranium in the periodic table of the elements, but not occurring naturally. This fact by itself makes technetium of interest to chemists. However, because of its radioactivity it is difficult for a chemist who does not have a radiochemistry laboratory to work with technetium. Fortuitously much of the chemical behavior of technetium is very similar to that of rhenium. Consequently, to avoid the complications inherent in carrying out studies with radioactive materials rhenium is often used as a surrogate for technetium to study its behavior in separations and compexation reactions. Of course rhenium is not a perfect analog, and eventually technetium itself must use for confirmatory studies of its chemical reactions under the conditions of interest.

Technetium has a complex and rich chemistry. There are many ways to effect its separation from other elements including several solvent extraction methods. Very few of these ways have been employed in separations used in the nuclear fuel cycle.

In acidic media such as nitric acid technetium is in the +7 oxidation state and exists as the pertechnetate anion, TcO_4^-, which is a moderately strong oxidizing acid. The pertechnetate ion is readily and strongly sorbed on cation exchange resins. Because technetium moves easily from one valence state to another during processing of spent nuclear fuel it may be found in several reprocessing streams, including in dissolver sludges that are made up primarily of noble metals, e.g., Rh, Ru, Pd, Mo and Tc. The best way to avoid these complications is to maintain an oxidizing condition in solution to keep the technetium in the +7 valence state. In this valence state the chemical behavior is more predictable than in the other valence states. Reduction reactions to lower valence states are often kinetically slow. Allowance should be made for this when preparing lower valence states.

One of the most interesting technetium complexation reactions, and one of considerable importance in nuclear separations, is the ability of the pertechnetate anion to form a complex with zirconium that extracts readily into tributly phosphate (TBP). In the presence of the uranyl nitrate/TBP complex the zirconium in the zirconium complex is replaced by the uranyl ion. This complexation reaction provides a basis for essentially complete separation of technetium from other fission products and has the potential to provide a means of controlling the path of technetium in separations processes using TBP. This is of special importance because it is desirable to keep technetium out of a waste repository where upon its release from the waste form it could become a long-term dose-limiting isotope in the repository radionuclide release path.

Heptavalent technetium is readily converted to volatile Tc_2O_7 upon evaporating acidic pertechnetate solutions to dryness. This transformation may occur during many operations involving heating Tc^{+7}. For example, it could happen during waste vitrification. If it happens during vitrification of wastes containing TcO_4^- the technetium pentoxide enters the vitrifier off-gas system and can be distributed throughout the off-gas system unless steps are taken to isolate and trap it.

Technetium in the +4 oxidation state is much less environmentally mobile than the +7 oxidation state. It is sorbed on environmental materials and is not readily transported by ground water, so is less likely to be a dose-limiting radioisotope in a waste repository. Tc^{4+} is sorbed quite efficiently by UO_2. Sorption in this way has the potential to limit its transport through the environment. However, as noted Tc^{+4} is fairly easily oxidized to Tc^{+7}. Waste form studies are under way to prepare materials that maintain reducing conditions in the waste and in this way limit oxidation to the more labile TcO_4^- ion.

Neptunium

The principal beneficial use of neptunium is for the production by neutron capture of the heat-producing isotope ^{238}Pu as noted above in the discussion of plutonium. A major problem with neptunium is that the long-lived ^{237}Np isotope readily forms $^{237}NpO_2^+$ that behaves much like an alkali metal, forming few complexes and moving easily with water through the environment. Its low charge results in very little sorption on common minerals that tend to sorb many of the fission products, most notably cesium which is sorbed by clays. Thus $^{237}NpO_2^+$ becomes a potential major contributor to the long-term radiation dose at the site boundary of a geologic HLW repository. Of all the actinide elements neptunium is the one most prone to form a stable monovalent actinyl ion, and with the possible exception of plutonium colloid is the most mobile actinide in the environment.

The similarity in the chemistries of neptunium and plutonium complicates their separation from each other in the Purex process. However, it has been found that by careful control of redox conditions it is possible to maintain inextractable NpO^{2+} in the presence of extractable Pu^{4+} and thus to effect their separation. By careful manipulation of redox conditions it is also possible to co-extract uranium, neptunium and plutonium into TBP and in this way to produce an actinide stream that is both proliferation resistant and also useful for recycle into reactors.

Despite the relatively small tendency of Np^{+5} to form complexes, it does form chloride complexes in brines through a strong ionic interaction with the chloride ion. This behavior has implications for storage of neptunium in a salt geologic repository where brines may be expected to exist. Although Np^{+5} solubility is low in brines ($1x10^{-5}$ to $3x10^{-6}$ molal, depending on the brine concentration), it is high enough to effect neptunium solubility and consequently its availability for environmental transport.

Americium

Americium is present in significant amounts in high burnup spent nuclear fuel. For this reason americium is important in separations and in waste management, mostly because the isotope ^{241}Am has a relatively short half life and would be a major intermediate-term heat producer in a geologic repository. The decay heat could contribute to limiting the density of packing of high-level waste packages and thus limit the repository capacity to hold waste. Consequently it is important to keep americium out of wastes destined for geologic repositories.

The high volatility of americium metal at relatively low temperatures is an unusual property, and one that is different from those of other actinides. The volatility must be taken into account if alloys containing americium are to be fabricated for burnup in future fast flux reactors.

Americium is the first of the actinide elements in which the trivalent state is the most stable ion in solution. It is very difficult to oxidize it above the +3 oxidation state in aqueous solution. In this respect it differs significantly from uranium, neptunium and plutonium. In addition, it does not readily form the typical actinyl dioxide (americyl) $AmO_2^{(+5, +6)}$ core. This is fortuitous from the point of view of waste management because the americyl ion could complex with the ubiquitous carbonate and hydroxide ions as well as other moieties (NO_2^-, NO_3^-, and SO_4^{-2}) to form charged complexes which tend to be readily mobile with low tendencies for attachment to soil. Like the other actinides (except curium) the AmO_2^{2+} ion forms carbonate complexes and insoluble hydroxy-carbonate species that may find application in its separation.

Americium +3, like the trivalent lanthanides, has insoluble fluorides, hydroxides, phosphates, oxalates, iodates, etc. However because precipitates with these anions are common with many multivalent cations, the americium compounds are not generally useful for separation of americium.

Americium forms a stable and soluble anionic thiocyanate complex that has been used in the quantitative anion exchange separation and purification of gram quantities of americium from rare earths. Rare earths are a major contaminant of actinides because of the strong analogies in the chemistries of the lanthanide and actinide series of elements. Consequently group separation of the actinides from lanthanides is difficult. Formation of the anionic thiocyanate complex is quite unusual and useful, especially because it is also soluble enough to be useful in practical separations of americium from lanthanides, a property not found with most americium complexants, for example citrate ion, that have been used in americium separations.

In its most common valence state of +3 americium forms the usual suite of complexes with most common acid anions and also with some organic acid anions that have found use in separations.

Curium

Curium, like americium, is present in significant amounts in high burnup spent nuclear fuels. Because curium's most common isotopes are heat producers, and therefore undesirable in a geologic repository, there is incentive to separate it from lanthanides and other fission products so it can be fissioned in nuclear reactors.

Curium, like americium, forms characteristic Cm^{+3} ions in aqueous solutions, and is even more difficult than americium to oxidize to higher valence states. The +3 valence state forms complexes with common acid anions. Precipitates form with fluoride, hydroxide, oxalate, et al. The extreme radioactivity of ^{242}Cm makes its separations in aqueous systems in all but tracer amounts very difficult because of vigorous radiolytic alpha- particle-induced decomposition of the water. ^{244}Cm, with its longer half life is more tractable.

Ion exchange is the most commonly used method for curium separations. Like americium, curium forms an exceptionally stable anionic complex with thiocyanate ion and through its sorption on anion exchange resins it may be efficiently separated from lanthanide fission products. Curium has been separated from americium using ion complexation reactions with citrate, tartrate, lactate and α-hydroxyisobutyrate ions in combination with ion exchange.

Solvent extraction with undiluted TBP separates curium from lanthanide solutions salted with acidified, concentrated sodium nitrate.

References

1. *The Radiochemistry of Technetium*, NAS-NS-3021, Edward Anders, 1960.
2. *Chemistry in Nuclear Technology*, by S. Peterson and R. G. Wymer, Addison-Wesley Publishing Company, Inc., 1963.
3. *Radiochemistry and Nuclear Chemistry*, by Gregory Choppin, Jan Rydberg and Jan-Olov Liljenzin, Butterworth-Heinemann, 3rd edition, 2001.
4. *The Chemical Interactions of Actinides in the Environment*, by Wolfgang Runde, Los Alamos Science Number 26, 2000, LA-UR-00-4100, 2000
5. *The Chemical Complexities of Plutonium*, by David L. Clarke, Los Alamos Science Number 26, 2000, LA-UR-00-4100, 2000.
6. "Sol-Gel microsphere pelletization process for fabrication of (U,P)O_2, (U,Pu)C and (U,Pu)N fuel pellets for the prototype fast breeder reactor in India," *Journal of Sol-Gel Science and Technology*, Vol. 9, No. 3, pp. 285-295, 1997.*The Elements beyond Uranium,* by G. T. Seaborg and W. D. Loveland, New York: Wiley-Interscience, 1990.
7. "Purification of Gram Amounts of Americium," D. E. Armstrong et al., LA-1975, May, 1956.
8. *Americium and Curium Chemistry and Technology*, N. M. Adelstein, J. Navratil and W. W. Schulz, eds., D. Reidel Publishing Company, 2007.

Liquid-Liquid Extraction Equipment

Jack D. Law and Terry A. Todd
Idaho National Laboratory

Liquid-liquid extraction (also called solvent extraction) was initially utilized in the petroleum industry beginning in the 1930's. It has since been utilized in numerous applications including petroleum, hydrometallurgical, pharmaceutical, and nuclear industries. Liquid-liquid extraction describes a method for separating components of a solution by utilizing an unequal distribution of the components between two immiscible liquid phases. In most cases, this process is carried out by intimately mixing the two immiscible phases, allowing for the selective transfer of solute(s) from one phase to the other, then allowing the two phases to separate. Typically, one phase will be an aqueous solution, usually containing the components to be separated, and the other phase will be an organic solvent, which has a high affinity for some specific components of the solution. The process is reversible by contacting the solvent loaded with solute(s) with another immiscible phase that has a higher affinity for the solute than the organic phase. The transfer of solute from one phase into the solvent phase is referred to as extraction and the transfer of the solute from the solvent back to the second (aqueous) phase is referred to as back-extraction or stripping. The two immiscible fluids must be capable of rapidly separating after being mixed together, and this is primarily a function of the difference in densities between the two phases.

While limited mass transfer can be completed in a single, batch equilibrium contact of the two phases, one of the primary advantages of liquid-liquid extraction processes is the ability to operate in a continuous, multistage countercurrent mode. This allows for very high separation factors while operating at high processing rates. Countercurrent operation is achieved by repeating single-stage contacts, with the aqueous and organic streams moving in opposite directions as shown in Figure 1.

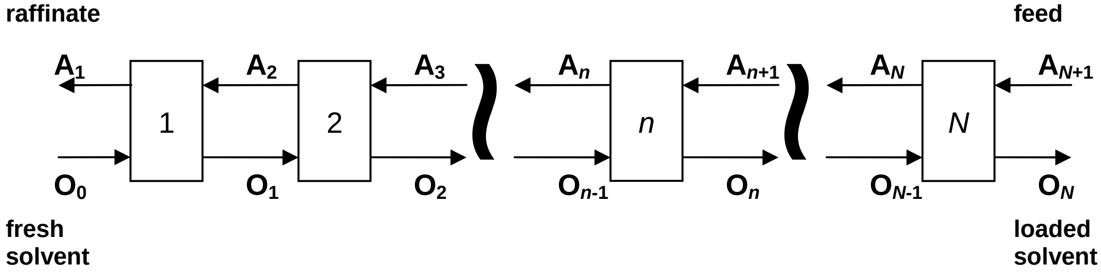


Figure 1. Countercurrent – multistage extraction process flow diagram

In this flow diagram, the aqueous feed stream containing the solute(s) to be extracted enters at one end of the process (A_{N+1}), and the fresh solvent (organic) stream enters at the other end (O_0). The aqueous and organic steams flow countercurrently from stage to stage, and the final products are the solvent loaded with the solute(s), O_N, leaving stage N and the aqueous raffinate, depleted in solute(s), leaving stage 1. In this manner, the concentration gradient in the process remains relatively constant. The organic at stage O_0 contains no solute(s), while the raffinate stream is depleted of solute(s). Streams A_n and O_{n-1} contain intermediate concentrations of the solute(s) and finally, streams A_{N+1} and O_N contain the highest concentration of the solute(s). The concentration of the solutes in a countercurrent process is shown graphically in Figure 2, where the orange color shows the relative concentration of the solute(s) in the process.

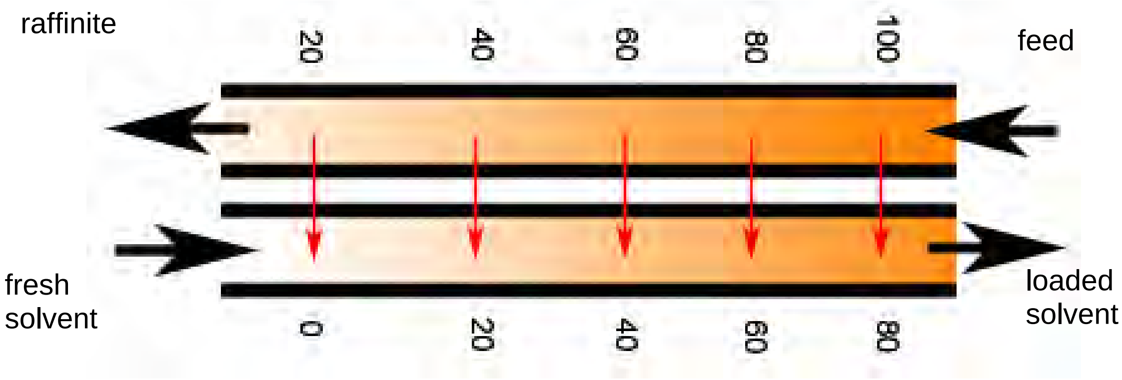


Figure 2. Countercurrent process concentration profiles

For the process to be economical, the solvent must be recycled. In order to recycle the solvent, the solute is subsequently stripped from the solvent, and the solvent is then recycled back to the countercurrent extraction process. This allows the solvent to be recycled indefinitely, until it has degraded (due to acid hydrolysis or radiolytic degradation) or the solvent composition has changed due to solubility in the aqueous phase.

While countercurrent processes could be performed in laboratory glassware, their primary advantage is to enable continuous processing at high throughputs. In order to achieve continuous processing, specific equipment is needed that can efficiently mix and separate the two phases continuously. In the nuclear industry, specific constraints, such as remote operation and maintenance must be considered, since the solutions processed are highly radioactive. There are three basic types of equipment used in industrial-scale nuclear solvent extraction processes: mixer-settlers, columns and centrifugal contactors. In selecting the type of equipment, a number of process parameters must be considered. These include:

- Process foot print and building size/height
- Operational flexibility (continuous long-term operation or frequent start-stop operation)
- Solvent inventory and in-process volume holdup
- Degradation of solvents due to radiolysis/hydrolysis
- Time required to reach steady-state operation
- Potential to operate complex multi-cycle processes linked together
- Tolerance to cross-phase entrainment
- Tolerance to solids in process solutions
- Tolerance to process upsets
- Process chemistry (e.g. kinetics of valance adjustment)
- Mass transfer kinetics
- Remote maintenance capabilities
- Criticality constraints

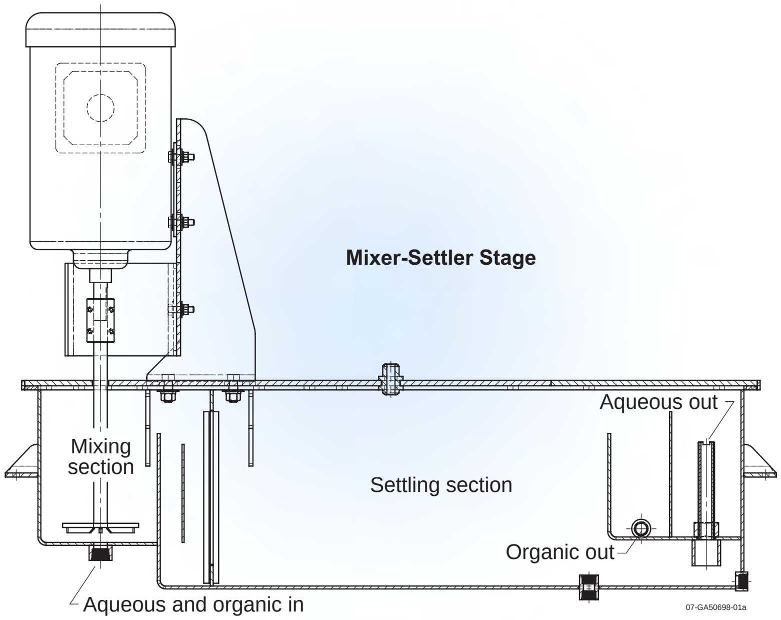
A detailed description and comparison of the three types of equipment is provided to further elucidate applicability of each of these equipment types.

Mixer-Settlers

This device consists of a small mixing chamber followed by a larger gravity settling chamber as shown in Figure 3.

Each mixer-settler unit provides a single stage of extraction. The two phases enter the mixing section where they are mixed using an impeller. The two-phase solution flows into the settling section where they are allowed to separate by gravity due to their density differences. Typical mixer settlers have mixing times on the order of a few minutes and settling times of several minutes. The separate phases exit the settling section by flowing over a weir (organic solution) or through an underflow then over a weir (aqueous phase). The separation interface is controlled by the height of the weirs on the outlets of the settler section. Only minimal instrumentation is required and mechanical maintenance is limited to occasional mixing motor replacement. In a countercurrent process, multiple mixer settlers are installed with mixing and settling chambers located at alternating ends for each stage (since the outlet of the settling sections feed the inlets of the adjacent stage's mixing sections). Mixer-settlers are used when a process requires longer residence times and when the solutions are easily separated by gravity. They require a large facility footprint, but do not require much headspace, and need limited remote maintenance capability for occasional replacement of mixing motors. (Colven, 1956; Davidson, 1957)

Figure 3. Diagram of a mixer-settler



Columns

There are two basic types of columns employed industrially, packed columns and pulse columns with plates or trays.

Packed columns are filled with some type of packing material, such as Raschig Rings, to create a tortuous path for the two solutions as they flow through the column (typically aqueous feed downward and solvent upward), ensuring that the two phases are in constant contact. Packed columns have no moving parts and are relatively simple to operate, but they are not very efficient. Since columns do not have discrete stages, such as mixer-settlers or centrifugal contactors, the number of stages is determined by the height of a theoretical stage. For most packed columns, this height to achieve one theoretical stage of extraction is usually several feet, meaning that a countercurrent process utilizing several stages to effect a given separation factor, would require very tall columns.

To reduce the height of a theoretical stage in the column, other packing (trays or perforated plates) are used and mechanical energy is applied to force the dispersed phase into smaller droplets, improving mass transfer. The most common type of column used, particularly in the nuclear industry, is the pulse column.

In a pulse column, liquids are continuously fed to the column and flow counter-currently, as is done with a packed column, but mechanical energy is applied to pulse the liquids in the column up and down. This is normally done by injecting pressurized air into a pulse leg that pushes liquid into the column, then venting the pulse leg to fill the pulse leg with solution from the column. The pulse action lifts and lowers the solution in the column, usually only a few inches. The column is filled with perforated plates or other plates to promote droplet formation as the dispersed phase is pushed through the plates. This pulsing action reduces droplet size of the dispersed phase and improves mass transfer. A perforated plate pulse column is shown in Figure 4. There are a number of plate designs used. Early pulse columns used sieve plates, which are flat plates with holes drilled into them. A more effective plate is the nozzle plate, which has different contours on the top and bottom of the plate (making it directional, in that it must be configured according to the continuous phase in the column). The French and Japanese pulse columns employ a “disk and donut” configuration, where the plates are solid (no openings) but the alternating plates enable effective contacting of the phases.

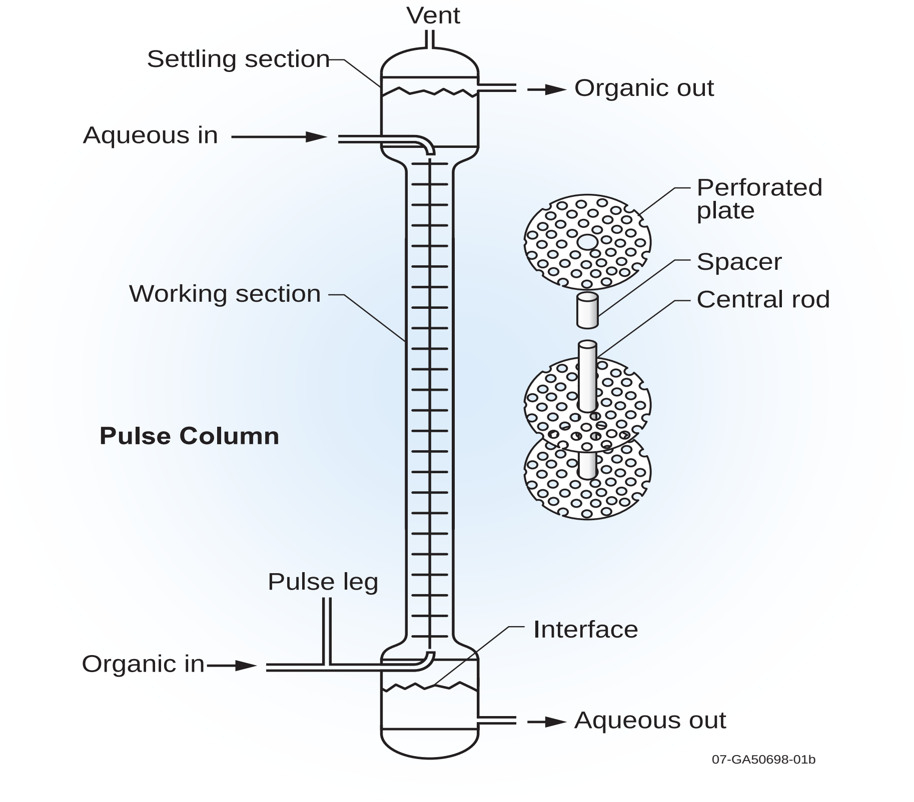


Figure 4. Pulse Column with perforated plates

The separation interface is controlled during column operation using bubble probes in the disengaging section. The probes are interfaced to a controller that drains heavy phase from the bottom of the column. The bubble probes allow operators to monitor the "weight" of the column, which gives them a good indication of column performance, by determining the ratio of heavy and light phases in the column. In addition, pulsing devices and pulse speed controllers are required as pulse frequency and amplitude must be controlled during operation. Periodic maintenance is required only for the pulsing equipment, which is located out of cell, above the columns. Pulse columns are used when a process requires intermediate residence times, as residence time is easily varied by adjusting flowrate. They require a small facility footprint, but do require much headspace (typically 40-50 feet). Pulse columns do not need remote maintenance capability, as all moving parts (pulser equipment) are located outside the shielded cell. Extensive literature has been published on pulse columns (Sege, 1954; Geier, 1954; Richardson, 1961)

Centrifugal Contactors

Centrifugal contactors, like mixer-settlers, are discrete-stage units, providing one stage of extraction per unit and are readily linked together as each rotor pumps separated fluids to the next stage inlet in each direction. The primary difference between a centrifugal contactor and a mixer-setter is the separation of the two-phase mixture. Centrifugal contactors employ a spinning rotor that 1) intensely mixes the two phases and 2) separates the two phases inside the rotor where the centrifugal forces can be as high as 300 g, resulting in efficient and fast phase separation. The separated phases exit the contactor by overflow and underflow weirs, similar to a mixer-settler. A cutaway view of an operating centrifugal contactor is shown in Figure 5.

Centrifugal contactors have high single stage efficiency (routinely greater than 95% of theoretical for chemical processes with rapid kinetics). Process flow interruptions cause no loss of process concentration profiles if centrifugal contactor rotors are kept spinning. Thus centrifugal contactor based processes can be "paused" for a period of time sufficient to re-establish flow or even replace a motor without significant loss of product or rework. Centrifugal contactors require a minimum of instrumentation for process operation. Computer control via commercial software allows monitoring of motor amperage, rotor rpm, inlet flow rates, temperatures and many other process parameters. Centrifugal contactors are used when a process requires short residence times, on the order of several seconds. They require a small facility footprint, and minimal headspace, but do require remote maintenance capability, for periodic removal of the motor and/or rotor.

Centrifugal contactors have been the subject of much recent development work, over the past 40 years, while the designs of pulse column and mixer-settlers has changed little over the same time period (Leonard, 1988; Jubin 1988; Meikrantz, 2001). Early designs included a paddle-wheel to mix the phases below the spinning rotor (Watts, 1977). This precluded removal of the rotor assembly, and so the annular centrifugal contactor was developed, which allowed the motor and rotor assembly to be easily removed (Bernstein, 1973). Other designs included multistage units, units for low-mix applications (higher phase separation), and clean-in-place units that have an array of internal spray nozzles to facilitate solids removal, if necessary. (Drain, 2003; Meikrantz,1996; Macaluso, 1999)

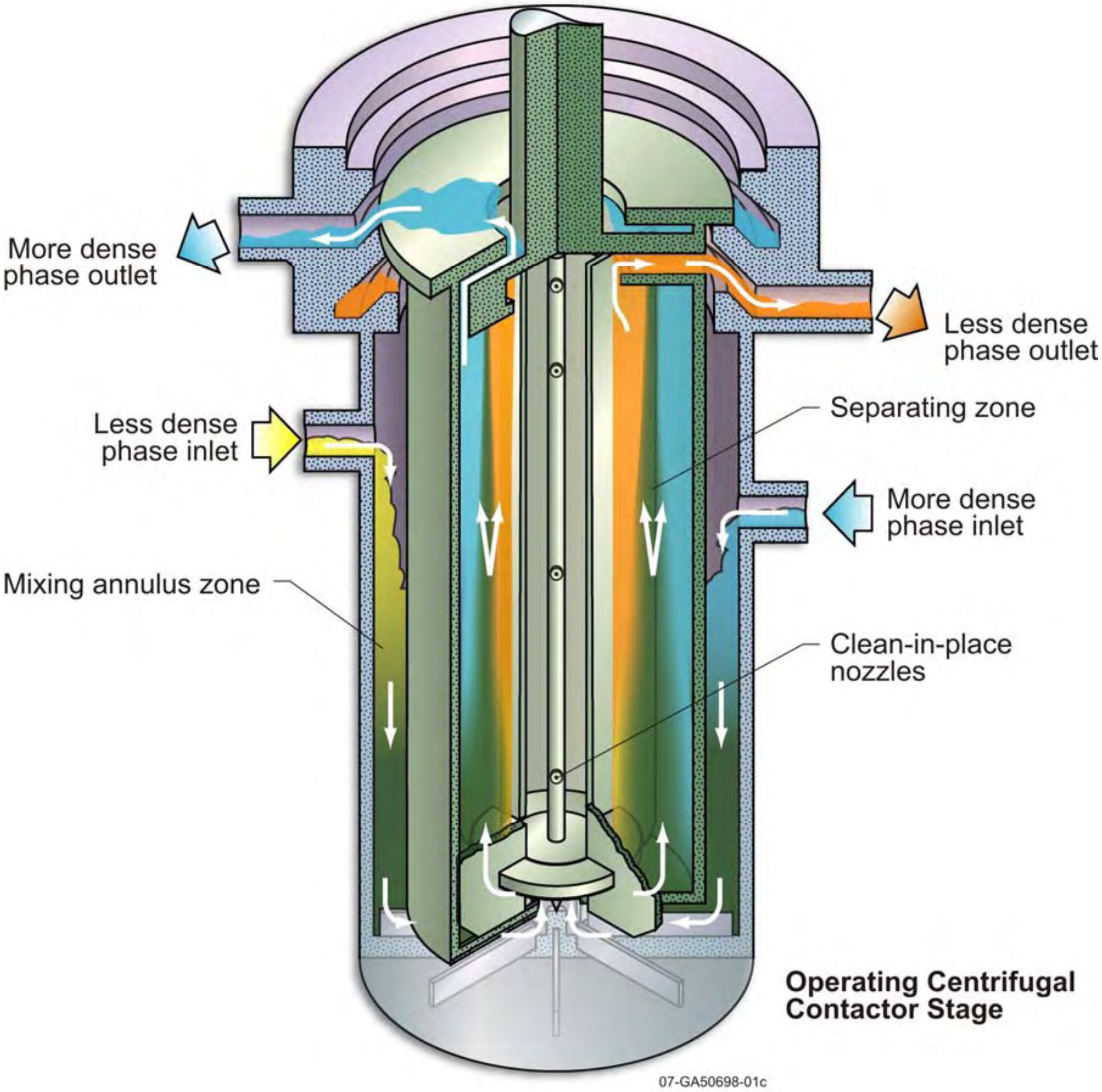


Figure 5. Cutaway view of an operating centrifugal contactor

Comparison of Contactors

Solvent extraction contacting equipment has been extensively studied and employed for the past 50 years. Each type of equipment has been proven over many years of operation and has inherent advantages and disadvantages (Cooley, 1962). The type chosen for a particular process application should be based on several factors *vide supra*. These include: criticality constraints, process (holdup) volume, process complexity (operability), reliability, maintenance philosophy, throughput, costs and performance issues such as solvent exposure (contact time), solids tolerance, flow rate turndown, equilibrium upset resistance, and process kinetics. An in-depth review and comparison of packed columns, pulse columns, mixer-settlers and centrifugal contactors for the Hanford PUREX plant was performed (Jealous, 1951). Later another comprehensive review was performed at Pacific Northwest Laboratories (Geier, 1977) and another review performed as part of the DOE Plutonium Technical Exchange Committee (Todd, 1998). A summary of the comparisons from this committee is shown in Table 1.

Table 1. Comparison of Mixer-Settler, Pulse Column and Centrifugal Contactors

Criteria	Ratings[a]			
	Mixer-settler	**Pulse Column**	**Centrifugal Contactor**	**Comments**
Long residence time[b]	5	4	1	
Short residence time[c]	1	2	5	
Building headroom	5	1	5	
Floor space required	1	5	3	May be small percentage of total floor area.
Instrumentation/control	5	4	5	
Ease of scale-up	3	3	5	
Low hold-up volume	2	3	5	
Equipment reliability	4	5	3	
Equipment capital cost	4	5	4	May be insignificant in relation to building cost.
Process flexibility[d]	4	3	5	
High throughput	2	5	5	Based on criticality safe by geometry equipment.
Ability to tolerate solids	2	5	2	
Reach steady state quickly	2	3	5	
Rapid restart	5	2	5	After temporary shutdown.

a. 5 = superior, 4 = good, 3 = average, 2 = below average, 1 = poor.

b. Considered an advantage when process chemistry requires long residence time.

c. Considered an advantage when solvent degradation is a concern.

d. Process flexibility includes such factors as the range of O/A flow ratio, the turndown in flowrate, and the ease with which the location of feed and product streams can be changed.

Industrial Reprocessing Experience

United States

Four industrial-scale nuclear reprocessing facilities were built in the United States, for defense purposes, that employed the PUREX process to separate and recover uranium and/or plutonium. These facilities were the H-canyon and F-canyon at Savannah River Site, The PUREX plant at Hanford, and the Idaho Chemical Processing Plant in Idaho.

Savannah River H and F-Canyon facilities

The Savannah River H-Canyon began operations in 1953 and was used to recover high-enriched uranium and neptunium from spent aluminum-clad reactor fuel. It utilized large mixer-settler banks for the PUREX process. The H-canyon is the only industrial-scale reprocessing facility still operational in the United States, as of 2008.

The Savannah River F-Canyon was originally meant to be a redundant facility to H-canyon, but was used to recovery plutonium from reactor targets. It began operation in 1954 and like H-Canyon, used large mixer-settlers. In the mid 1960's a bank of 25-cm centrifugal contactors were installed in the first-cycle extraction process to minimize solvent damage from radiolysis. The F-Canyon extraction operations were terminated in 2002, after nearly 50 years of operation. (Watts, 1977; Fernandez, 2000; www.globalsecurity.org)

Hanford PUREX plant

The Hanford PUREX plant operated from 1956 to 1986 to separate uranium, plutonium and neptunium from Hanford reactors. It replaced the Hanford REDOX facility, which utilized packed columns and required a "penthouse" extension to the facility to accommodate the height of the columns. The use of pulse columns in the PUREX plant resulted in a 50% reduction in height to achieve the same level of separations efficiency as the REDOX facility. An extensive research and development program of over 50 man-years of effort was undertaken from 1950-1953 to develop pulse column technology for the PUREX plant. (Courtney, 1954; Gerber 1993)

Idaho Chemical Processing Plant

The Idaho Chemical Processing Plant began operation in 1953 and used packed columns with methyl isobutyl ketone (hexone) as the solvent. In 1957, a new first cycle was added which utilized pulse columns and tributylphosphate in dodecane as the solvent. The packed columns utilizing hexone became the second and third cycle extraction processes. The first cycle solvent wash operations were performed in a series of mixer-settlers. Extraction operations were performed on numerous fuel types including zirconium, aluminum, stainless steel and graphite. During ROVER graphite fuel processing, the graphite was burned, the ash dissolved in nitric and hydrofluoric acid and the solution processed contained significant solids loading. No operational problems with first cycle pulse column operation were observed. A new fuel reprocessing facility was under construction in 1991, when fuel reprocessing in Idaho was terminated by the DOE. This facility included three cycles of TBP extraction using pulse columns. (Wagner, 1999)

Three commercial nuclear reprocessing facilities were built in the U.S., however, only one ever operated with spent nuclear fuel. These facilities were the West Valley Nuclear Fuel Services plant, the GE- Midwest Fuel Recovery Plant (Morris, Il), and the Allied General Nuclear Services Barnwell facility.

West Valley

The West Valley Nuclear Fuel Services plant utilized pulse columns for solvent extraction processing. The plant operated from 1966 until 1972 and was the only commercial reprocessing facility that operated in the U.S. (Sinclair)

Midwest Fuel Recovery Plant

The Midwest Fuel Recovery Plant built by General Electric in Morris, Illinois, utilized one cycle of solvent extraction in pulse columns, and then used a fluoride volatility process to convert UO_3 to UF_6 and further purify it from impurities. The plant was completed in 1968 and GE withdrew the license application to the NRC in 1972. The plant never operated due to close coupled unit operations and problems associated with handling solid uranium in the feed to the volatility process. (Zentner, 2005)

AGNS Barnwell Facility

The Barnwell facility was designed have a 1500 MTHM/yr throughput capacity, larger than any nuclear fuel reprocessing plant in the world. It utilized a multi-stage centrifugal contactor to make the initial separation of plutonium and uranium from fission products, and then used pulse columns to partition uranium from plutonium and for separate uranium and plutonium purification cycles. The Barnwell facility was shutdown in the late 1970's and permanently closed in the early 1980's without ever processing spent nuclear fuel. (Benedict, 1982)

International

France

The LaHague reprocessing facililty in France has been reprocessing commercial fuel since 1976 in the UP-2 plant (originally 400 MT/yr, then throughput was increased to 800 MT/yr), and added another plant (UP-3) in 1990. Each plant has a throughput of 800 MTHM/yr and use combinations of pulse columns, mixer-settlers and/or centrifugal contactors. A summary of the equipment types used in both facilities is given in Table 2. (Drain, 2003)

Table 2. Liquid-liquid extraction equipment in the La Hague reprocessing plants

Plant	Process Section	Process Equipment
UP-3/ UP-2 800	1st extraction cycle: highly active section	Annular pulse columns
UP-3	1st extraction cycle –U/Pu separation	Mixer-settler bank
UP-2 800	1st extraction cycle – U/Pu separation	Annular pulse columns
UP-3/ UP-2 800	1st extraction cycle – U stripping	Mixer-settler bank
UP-3/ UP-2 800	Uranium purification	Mixer-settler bank
UP-3	Plutonium purification	Pulse columns
UP-2 800	Plutonium purification	Centrifugal contactors
UP-3/ UP-2 800	Solvent regeneration	Mixer-settler bank

Japan

The Tokai reprocessing plant has been in operation since 1975 and includes three cycles of solvent extraction using only mixer-settlers. The Rokkasho reprocessing plant is undergoing final checkout testing with spent fuel, expecting to start full commercial operations in 2009. This plant is designed by AREVA and is very similar to the UP-3 plant design at LaHague. The Rokkasho plant utililzes annular pulse columns for first cycle extraction and plutonium partitioning. Mixer-settlers are used for the uranium and plutonium purification cycles as well as solvent washing.

United Kingdom

The Thermal Oxide Reprocessing Plant (THORP) was commissioned in 1994 and was designed for a throughput of 7 MT/yr in the headend processing section and 5 MT/yr in the separations portion of the plant. The THORP plant utilizes pulse columns in the first cycle HA process and in the plutonium purification cycle. Mixer-settlers are used in the first-cycle solvent wash and the uranium purification cycle. (Phillips, 1999)

Summary

Solvent extraction processing has demonstrated the ability to achieve high decontamination factors for uranium and plutonium while operating at high throughputs. Historical application of solvent extraction contacting equipment implies that for the HA cycle (primary separation of uranium and plutonium from fission products) the equipment of choice is pulse columns. This is likely due to relatively short residence times (as compared to mixer-settlers) and the ability of the columns to tolerate solids in the feed. Savannah River successfully operated the F-Canyon with centrifugal contactors in the HA cycle (which have shorter residence times than columns).

All three contactors have been successfully deployed in uranium and plutonium purification cycles. Over the past 20 years, there has been significant development of centrifugal contactor designs and they have become very common for research and development applications. New reprocessing plants are being planned in Russia and China and the United States has done preliminary design studies on future reprocessing plants. The choice of contactors for all of these facilities is yet to be determined.

References

1. Benedict, M., Pigford, T. H., and Levi, W. H., Nuclear Chemical Engineering, 2nd Ed., McGraw-Hill, New York, 1982.
2. Bernstein, G. L., et al., “A High-Capacity Annular Centrifugal Contactor” *Nuclear Technology,* 20, 1973.
3. Colven, T. J. Jr., “Mixer-Settler Development-Operating Characteristics of a Large-Scale Mixer-Seller,” Savannah River Laboratory, DP-140, 1956.
4. Cooley, C. R., “Liquid-Liquid Solvent Extraction Contactors- A Literature Survey,” HW-74532, 1962.
5. Courtney, J. J., and Clark, B. E. Jr., “An Introduction to the PUREX Plant, Hanford Atomic Projects Operations, HW-32413, 1954.
6. Davidson, J. K., et al., “Application of Mixer-Settlers to the PUREX Process,” TID-7534, Book 1, 1957.
7. Drain, F., et al., “Forty years of Experience with Liquid-Liquid Extraction Equipment in the Nuclear Industry,” Waste Management Conference 2003, Tucson, AZ, 2003.
8. Fernandez, L. P., “Savannah River Site Canyons – Nimble Behemoths of the Atomic Age,” Westinghouse Savannah River Company, WSRC-MS-2000-00061, 2000.
9. Geier, R. G., “Application of the Pulse Column to the PUREX Process, USACC, Report TID-7534, 1954.
10. Geier, R. G., “Solvent Extraction Equipment Evaluation Study – Part 1,” Battelle Northwest Laboratory, BNWL-2186 Pt. 1, 1977.
11. Gerber, M. S., “A Brief History of the PUREX and UO_3 Facilities,” Westinghouse Hanford Company, WHC-MR-0437, 1993.
12. http://www.globalsecurity.org/wmd/library/report/enviro/eis-0219/eis0219_a.html
13. Jealous, A. C. and Stewart, E. C., “A Review of the Relative Merits of Packed Columns, Pulse Columns, Mixer-Settler Mechanism, and Centrifugal Contactors,” Oak Ridge National Laboratory, CF-51-1-10, 1951.
14. Jubin, R. T., et al., “Developments in Centrifugal Contactor Technology, Oak Ridge National Laboratory, ORNL/TM-10768, 1988.
15. Leonard, R. A., “Recent Advances in Centrifugal Contactor Design,” *Separation Science and Technology,* 23(12&13), 1988.
16. Meikrantz, D. H., et al., “Annular Centrifugal Contactors for Multiple Stage Extraction Processes,” *Chem. Eng. Comm.,* Vol 188, 2001.
17. Meikrantz, D. H., et al., “Rotor Sleeve for a Centrifugal Separator,” U.S. Patent # 5,571,070, 1996.
18. Macaluso, L. L., and Meikrantz, D. H., “Self-cleaning Rotor for a Centrifugal Separator,” U.S. Patent # 5,908,376, 1999.
19. Phillips, C., “The Thermal Oxide Reprocessing Plant at Sellafield: Four Years of Successful Treatment of Irradiated Nuclear Fuel,” Waste Management Conference 1999, Tucson, AZ, 1999.
20. Richardson, G. L. and Platt, A. M., *Progress in Nuclear Energy, Series IV, Technology Engineering and Safety,* Vol. 4, Pergammon Press, New York, 1961.
21. Sege, G, and Woodfield, F. W., *Chemical Engineering Progress,* 50(8), 1954.
22. Sinclair, E. E., et al., “Existing and Projected Plants and Processes for Thermal Reactor Fuel Recovery: Experience and Plans,” OSTI, Conf-710901-12, date unknown.
23. Todd, T. A., et al., “Waste, Nuclear, Reprocessing and Treatment Technologies, Encyclopedia of Chemical Processing and Design, John J. McKetta editor, Marcell Dekker Inc., NY, Vol. 65, 1998.
24. Wagner, E. P., “Process Description and Operating History for the CPP-601/-640/-627 Fuel Reprocessing Complex at the Idaho National Engineering and Environmental Laboratory,

INEEL/EXT-99-00400, 1999.

25. Watts, C., “Solvent Extraction Equipment Evaluation Study – Part 2,” Battelle Northwest Laboratory, BNWL-2186 Pt. 2, 1977.
26. Zentner, M. D., et al., “Nuclear Proliferation Technology Trends Analysis,” Pacific Northwest National Laboratory, PNNL-14480, 2005.

Waste Forms for an Advanced Fuel Cycle

John D. Vienna
Pacific Northwest National Laboratory

Waste Classification and Disposal

Classification

In the U.S., radioactive wastes are classified into categories of HLW, low-level waste (LLW), and mixed waste. The definitions of these wastes are briefly discussed below to clarify the discussion of waste disposal environments, requirements, and standards.

High-level radioactive waste is defined in 10CFR60.2 as:

> *"(1) Irradiated reactor fuel, (2) liquid wastes resulting from the operation of the first cycle solvent extraction system, or equivalent, and the concentrated wastes from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated reactor fuel, and (3) solids into which such liquid wastes have been converted."*

while the Nuclear Waste Policy Act (NWPA) defines HLW as:

> *"…(A) the highly radioactive material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations; and (B) other highly radioactive material that the Commission, consistent with existing law, determines by rule requires permanent isolation."*

Despite slight differences in the definitions, it is clear that HLW is defined from the source of waste rather than the radioactivity. The source includes the waste resulting from the first cycle raffinate of spent nuclear fuel (SNF) reprocessing. According to the NWPA it also includes other highly radioactive materials derived from SNF reprocessing as determined through the Nuclear Regulatory Commission (NRC) rule making process.

Low-level radioactive waste is defined by the NRC in 10CFR61.55 as class A, B, C, and "other":

> *(i) Class A waste is waste that is usually segregated from other waste classes at the disposal site. The physical form and characteristics of Class A waste must meet the minimum requirements set forth in § 61.56(a). If Class A waste also meets the stability requirements set forth in §61.56(b), it is not necessary to segregate the waste for disposal.*
> *(ii) Class B waste is waste that must meet more rigorous requirements on waste form to ensure stability after disposal. The physical form and characteristics of Class B waste must meet both the minimum and stability requirements set forth in §61.56.*
> *(iii) Class C waste is waste that not only must meet more rigorous requirements on waste form to ensure stability but also requires additional measures at the disposal facility to protect against inadvertent intrusion. The physical form and characteristics of Class C waste must meet both the minimum and stability requirements set forth in §61.56.*
> *(iv) Waste that is not generally acceptable for near-surface disposal is waste for which form and disposal methods must be different, and in general more stringent, than those specified for Class C waste. In the absence of specific requirements in this part, such waste must be disposed of in a geologic repository as defined in part 60 or 63 of this chapter unless proposals for disposal of such waste in a disposal site licensed pursuant to this part are approved by the Commission.*

Classification of LLW is given by a comparison of radionuclide concentrations with Tables 1 and 2 from 10CFR61.55. The sum of fractions of radionuclides listed in each of the following tables must be below one for a given classification.

Table 1. Long-lived Isotopes, 10CFR61.55

Radionuclide	***A***	***C***
C-14	*0.8*	*8 Ci/m^3*
C-14 in activated metal	*8*	*80 Ci/m^3*
Ni-59 in activated metal	*22*	*220 Ci/m^3*
Nb-94 in activated metal	*0.02*	*0.2 Ci/m^3*
Tc-99	*0.3*	*3 Ci/m^3*
I-129	*0.008*	*0.08 Ci/m^3*
TRU (α >5yr)	*10*	*100 nCi/g*
Pu-241	*350*	*3,500 nCi/g*
Cm-242	*2,000*	*20,000 nCi/g*

Table 2. Short-lived Isotopes, 10CFR61.55

Radionuclide	***Ci/m^3***		
	A	***B***	***C***
Total > 5 yr half-life	*700*		
H-3	*40*		
Co-60	*700*		
Ni-63	*3.5*	*70*	*700*
Ni-63 in activated metal	*35*	*700*	*7,000*
Sr-90	*0.04*	*150*	*7,000*
Cs-137	*1*	*44*	*4,600*

Those materials that exceed Class C activity levels, but do not meet the source definition for HLW, are known as greater-than-class C wastes (GTCC). The final category of radioactive wastes is mixed wastes – defined in 40CFR261 as "…any hazardous waste containing radioactive waste."

Nuclear Waste Disposal Facilities and their Capacity

There are currently three disposal facilities operating in the U.S. for commercial Class-A, -B and/or -C LLW (see below). Each of these sites are privately owned and are subject to different requirements for waste acceptance based on state and federal regulations, legal decisions, and corporate preference. The criteria and capacity of each of these sites is given below along with a site in Texas, which has recently applied for a license. Estimates for closure are nominally extrapolations of recent annual disposal quantities. Ongoing efforts to reduce LLW volumes by compaction and voluntary waste reduction campaigns have been increasingly successful, and further reductions may extend the lifetime of some facilities.

Operator: Energy Solutions Barnwell Operations
Location: Barnwell, SC
Waste Accepted: Class A, B, and C
States Accepted: Atlantic Interstate Compact (Connecticut, New Jersey, and South Carolina)
Capacity: 30,000,000 ft^3 (27,000,000 ft^3 used as of 2007)
Estimated Closure: 2050

Note: There is significant concern that the recent (June, 2008) limitation on acceptance of waste to the Atlantic Interstate Compact will make the Barnwell facility uneconomical.

Operator: United States Ecology
Location: Richland, WA
Waste Accepted: Class A, B, and C
States Accepted: Northwest Compact (AK, HI, WA, OR, ID, UT, WY, MT) and Rocky Mountain Compact (NV, CO, NM)
Capacity: 35,000,000 ft^3 (13,900,000 ft^3 used as of 2003)
Estimated Closure: 2056
Note: The lease between the state and US Ecology for the land the commercial LLW site occupies expires on September 9, 2063. At that time or before, permanent closure of the site is planned. The US Department of Health has proposed the year 2056 as the latest possible year for disposal operations to cease and closure to begin.

Operator: Energy Solutions Clive Operations
Location: Clive, UT
Waste Accepted: Class A, Mixed Waste, NORM
States Accepted: All
Capacity: ~165,000,000 ft^3 remaining
Estimated Closure: Estimated to fill to capacity in 2041 by extrapolation of 2008 fill rate

Operator: Waste Control Specialists LLC
Location: Andrews, TX
Waste Accepted: Class A, B, or C; (Mixed A/B/C for Federal Generators ONLY)
States Accepted: Texas Compact (Texas and Vermont)
Capacity: 59,400,000 ft^3
Estimated Closure: Unknown volume disposal rate
Note: A draft license was issued by the Texas Commission on Environmental Quality on August 12, 2008. A twelve-month public hearing period is required before full licensing can occur, followed by a further 10 months for construction. Operations are scheduled to begin 12/15/2010.

There is currently one planned geologic repository -- the Yucca Mountain Facility (YMF). The NWPA limits the capacity of the YMF to 70,000 metric tons of initial heavy metal (MTIHM) until a second repository is in operation:

> *The Commission decision approving the first such application shall prohibit the emplacement in the first repository of a quantity of spent fuel containing in excess of 70,000 metric tons of heavy metal or a quantity of solidified high-level radioactive waste resulting from the reprocessing of such a quantity of spent fuel until such time as a second repository is in operation. In the event that a monitored retrievable storage facility, approved pursuant to subtitle C of this Act, shall be located, or is planned to be located, within 50 miles of the first repository, then the Commission decision approving the first such application shall prohibit the emplacement of a quantity of spent fuel containing in excess of 70,000 metric tons of heavy metal or a quantity of solidified high-level radioactive waste resulting from the reprocessing of spent fuel in both the repository and monitored retrievable storage facility until such time as a second repository is in operation.*

Through various policy agreements, this limit has been divided in allotments of 63,000 MTIHM for commercial SNF and HLW and 7,000 MTIHM for DOE HLW and SNF (*Civilian Radioactive*

Waste Management System Requirements Document, Section 3.2.1.D). The U.S. Department of Energy (DOE) license application to the NRC in June of 2008 was consistent with that limit. Based on commercial inventories of SNF, that limit is expected to be exceeded sometime in 2010, well in advance of the scheduled repository opening date. The DOE is also required to submit a second repository report on the heels of the license application. That report is scheduled to be submitted in November, 2008. Of the alternatives presented in that report, DOE is expected to recommend to the Congress and the President that the 70,000 limit at YMF should be raised to at least 119,000 MTIHM.

In addition to the commercial LLW disposal facilities and the YMF there are a number of DOE operated disposal facilities for disposal of LLW (for example the Solid Waste Disposal Facility at Hanford). These facilities are not regulated by the NRC and may dispose of some wastes that would be classified by 10CFR61.55 as GTCC as long as the facility complies with DOE Order 435.1, *Radioactive Waste Management*, (DOE 1999). As these are used specifically for DOE LLW they won't be specifically discussed.

The Waste Isolation Pilot Plant (WIPP) located outside of Carlsbad, New Mexico was listened by the U.S. Environmental Protection Agency (EPA) in 1998 to receive transuranic waste (TRU) from DOE. The WIPP land withdrawl act of 1992 gives the EPA responsibility to ensure that the federal radioactive waste disposal regulations are followed by the WIPP. This act also limits the waste to be disposed of in the WIPP including prohibits disposal of HLW and SNF. In 1999 WIPP began receiving contact handled (CH) TRU from DOE sites and in 2007 WIPP began the receipt of remote handled (RH) TRU.

Currently there are no commercial disposal sites or repositories for commercially generated GTCC.

Disposal Paths for Current Nuclear Wastes

The current U.S. nuclear waste strategy is to dispose of commercial SNF in the repository. Defense HLW at the Hanford Site (Richland, Washington) and the Savannah River Site (Aiken, South Carolina) are to be vitrified into borosilicate glass and disposed of in the repository. Commercial HLW at West Valley (New York) was vitrified into borosilicate glass for disposal in the repository. Defense HLW at the Idaho National Laboratory (Idaho Falls, Idaho) was calcined into a granular mineralized waste form for disposal in the repository potentially with further treatment. Defense TRU are being disposed of in the WIPP and DOE LLW's are being disposed of in DOE regulated disposal facilities at DOE sites. Commercial LLW's are disposed of in the three disposal facilities listed above.

Commercially generated GTCC, for which there is currently no disposal facility, are being managed by the DOE. Section 3(b)(1)(D) of the *Low-Level Radioactive Waste Policy Act, Amended* (LLRWPAA PL99-240) reads:

> *The Federal Government shall be responsible for the disposal of any other low-level radioactive waste with concentrations of radionuclides that exceed the limit established by the Commission for Class C Waste, as defined by Section 61.55 of Title 10, Code of Federal Regulations, as in effect on January 26, 1983.*

The DOE has embarked upon an Environmental Impact Statement (EIS) and Record of Decision process to establish a disposition pathway for GTCC by the end of 2010. However, this EIS is written for a very limited inventory of GTCC and does not include any GTCC to be produced from commercial SNF recycling.

High-level Waste Vitrification

Vitrification into borosilicate glass is the current baseline technology for HLW treatment in the U.S. This process/form was selected based on the following features (DOE 1982, DOE 1990 for examples):

- continuous, high-throughput, operation of glass melters
- high solubility of waste components in the glass
- tolerance to variation in waste composition
- low raw materials costs
- highly durable waste form
- technology based on extensive commercial application of glass fabrication
- high resistance to damage from radiation and radioactive decay

The vitrification of HLW from SNF reprocessing began on an industrial scale in 1978 in Marcoule, France, and continues today throughout the world (Vienna 2005). Virtually every nuclear fuel reprocessing nation has adopted vitrification as the process of choice for HLW immobilization. In Russia, vitrification is performed at the Mayak facility, but, the waste form is an alumino-phosphate glass as opposed to the borosilicate glass used in the rest of the world (Odel 1992).

The international use of vitrification is based on the wastes generated from the plutonium-uranium extraction (PUREX) process where virtually all of the highly radioactive components of the fuel – transuranics (TRU) and fission products (FP) – are consolidated into a single raffinate stream. Advanced separations technologies are able to partition waste components into individual streams of chemically similar components. An unprecedented level of waste processing control can be achieved enabling the immobilization of each stream separately or combined with others. The waste forms can be selected to match waste and disposal environment chemistry. Therefore, an evaluation of waste management strategy is warranted.

Reference Separations Strategy

A reference separations process is assumed in this document to add context for waste management opportunities. The family of aqueous processes based on the uranium extraction (UREX) plus one described in the *Draft Global Nuclear Energy Partnership Programmatic Environmental Impact Statement* (DOE 2008) are assumed for light water reactor (LWR) fuel processing. A molten salt electrochemical process also described in DOE 2008 is assumed for metal fast reactor (FR) fuel. Those aspects of the processes important to waste treatment are described briefly here.

UREX+1 Process

Under the assumed aqueous process, SNF is sheared (or chopped) into pieces that are fed through a rotary calciner for voloxidation (Volox). The spacers, end pieces and other fuel assembly hardware are segregated for later combination with fuel cladding hulls. Volox is primarily aimed at removal of tritium from the fuel before if first contacts the aqueous media. Without prior separation, tritium would contaminate most of the aqueous and organic streams generated by the plant. The oxidized fuel is then dissolved in a nitric acid solution. The hulls are returned to be disposed of with the hardware and off-gasses from volox and the dissolver are treated. A series of solvent extraction (SX) steps are performed on dissolved fuel as shown in Figure 1. Uranium and Tc are recovered by UREX. These elements are then separated by pertechnetate ion exchange (IX). The UREX raffinate is treated by fission product extraction (FPEX) to remove the alkali and alkaline earth components (Cs/Sr). FPEX raffinate is separated into transition metal fission products (TMFP) and lanthanides and actinides by the transuranics extraction (TRUEX) process. The actinides (TRU) are separated from the lanthanides (LNFP) using trivalent actinide lanthanide separations by phosphorus-reagent extraction from aqueous complexes (TALSPEAK).

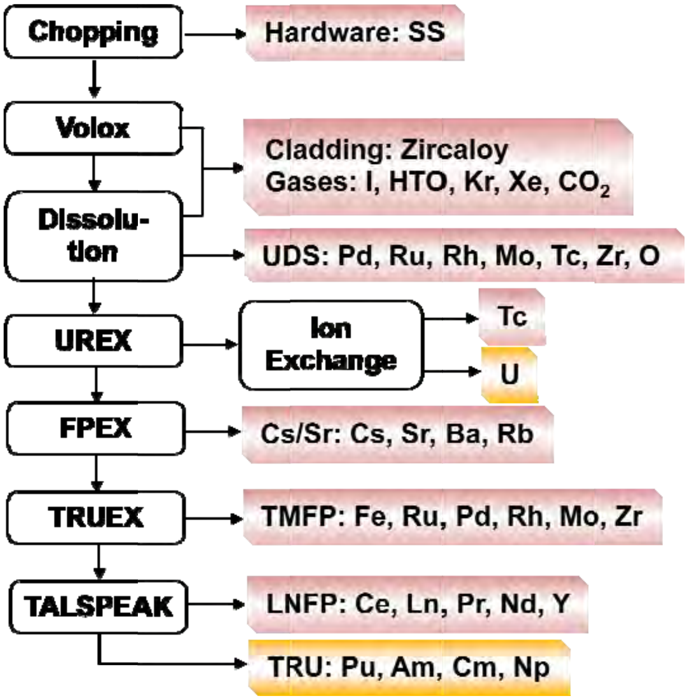


Figure 1. Schematic of UREX+1 Aqueous Process with Waste and Product Streams

Highly radioactive gasses from volox and dissolution will be treated according to a process similar to that shown in Figure 2. Voloxidizer off-gas is filtered by a high efficiency particulate air (HEPA) filter and then flows through a trap to precipitate Ru and Rh on a metal surface before being combined with the dissolver off-gas (DOG). The DOG passes through a condenser and nitrogen oxide (NOx) absorber. Water and nitric acid are recycled to the dissolver. The combined DOG and volox off-gas are sent through a silver mordenite (AgZ) bed to capture iodine then a caustic scrubber for CO_2 removal. The off-gas is then dried and sent through an AgZ bed for Xe capture followed by a hydrogen mordenite (HZ) bed for Kr capture. The resulting gasses are passed through a HEPA and combined with the vessel off-gas stream (VOG).

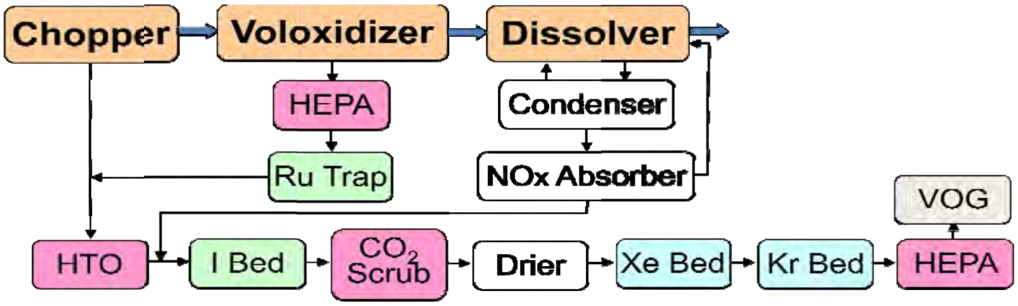


Figure 2. Potential Process for Treatment of Aqueous Head-end Off-gasses

Key wastes from this aqueous process include:

- hulls and hardware (HH) comprised of 1) zircaloy fuel hulls with activation products, embedded TRU (from recoil and activation), and tritium; and 2) stainless steel hardware pieces containing activation products and contaminated from reactor coolant
- undissolved solids (UDS) from incomplete dissolution of the fuel or reprecipitation in the dissolver. UDS are comprised of noble metals (NM) such as Pd, Ru, and Rh; Mo, Zr, Tc, and some oxygen
- technetium (Tc) is captured on an anion exchange column as nearly pure pertechnetate
- alkali and alkaline earth fission products (Cs/Sr) contain dilute concentrations of Cs, Sr, Ba, and Rb in the nitric acid FPEX strip solution
- transition metal fission products (TMFP) is the TRUEX raffinate containing NM, Mo, Zr, corrosion products (Fe, Ni, Cr), and many trace impurities in a dilute nitric acid solution
- lanthanide fission products (LNFP) contain the lanthanide elements (e.g., Nd, Ce, La, Pr, etc.) plus Y and trace TRU contaminants in a lactic acid solution
- tritiated water (HTO) is captured on a 3A molecular sieve and release as a gas for condensation
- iodine (I) is capture on a silver mordenite (AgZ) media
- carbon-14 dioxide ($^{14}CO_2$) is captured in a caustic scrub
- krypton (Kr) is partitioned between an AgZ and HZ bed with the largest fraction on the HZ; it is extracted from the bed as a gas (either with or without Xe)

In addition to these primary waste streams, there are a number of secondary low-level waste (LLW) streams that must be disposed of. The LLW streams include spent solvents, personal protective equipment, rags, bags, tags, laboratory returns, evaporator bottoms, HEPA filters, and maintenance wastes.

Electrochemical Separations

The assumed molten salt electrochemical process is described in DOE 2008. The metal FR fuel is sheared (or chopped) into pieces that are dissolved in a molten alkali chloride bath. The spacers, end pieces and other fuel assembly hardware are segregated for later combination with undissolved fuel components. A fraction of the fuel and cladding remains undissolved in the salt. A majority of the uranium is deposited on a cathode for recycling. The salt is then contacted with molten Cd for partitioning of TRU with the remaining U. Finally, the fission product laden salt is occluded on a zeolite for immobilization. These processes are shown schematically in Figure 3.

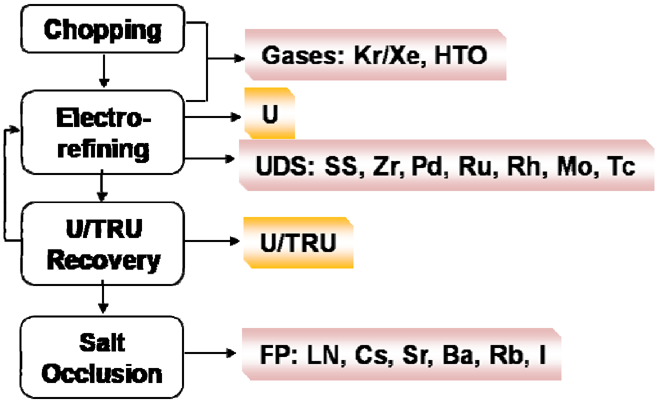


Figure 3. Schematic of Electrochemical Processes with Waste and Product Streams

Key wastes from this aqueous process include:

- fission gasses include Kr and Xe and a portion of the tritium. These gasses are treated in much the same manner as those from aqueous dissolution.
- undissolved solids (UDS) from incomplete dissolution of the fuel containing metals more noble than uranium such as Pd, Ru, Rh, Mo, Zr, Tc, Fe, Ni, and Cr. The UDS is captured in an anode basket. The adherent salt is drained and vacuum distilled.
- fission products including lanthanides, alkalis, alkaline earths, and iodine plus trace TRU impurities are left in the K, Li, Na chloride salt

In addition to these primary waste streams, there are a number of secondary low-level waste (LLW) streams that must be disposed of. The LLW streams include spent solvents, personal protective equipment, rags, bags, tags, laboratory returns, evaporator bottoms, HEPA filters, and maintenance wastes.

An Opportunity for Waste Management

The advanced separations scheme highlighted in Section 0 should allow for an optimized waste management system. By separating the wastes in to chemically similar components, they can be immobilized in forms specifically tailored to match their chemistry and perform well in their target disposal environment. For example, the alkali and alkaline earth wastes will generate a high does and high heat for the first few centuries due to decay of ^{134}Cs, ^{137}Cs, and ^{90}Sr. After the decay of these isotopes, only ^{135}Cs remains with a half-life of 2.3×10^{6} years. The waste form for this material should be tolerant to high β-γ fields and high temperature; but, won't required chemical durability sufficient to last for millennia.

Gombert (2008) performed an evaluation of waste management opportunities for an advanced closed fuel cycle in the U.S. They recommend that the waste management system be modified to address the unique opportunities afforded by advanced separations of commercial SNF. Figure 4 demonstrates the general philosophy proposed to evaluate waste management.

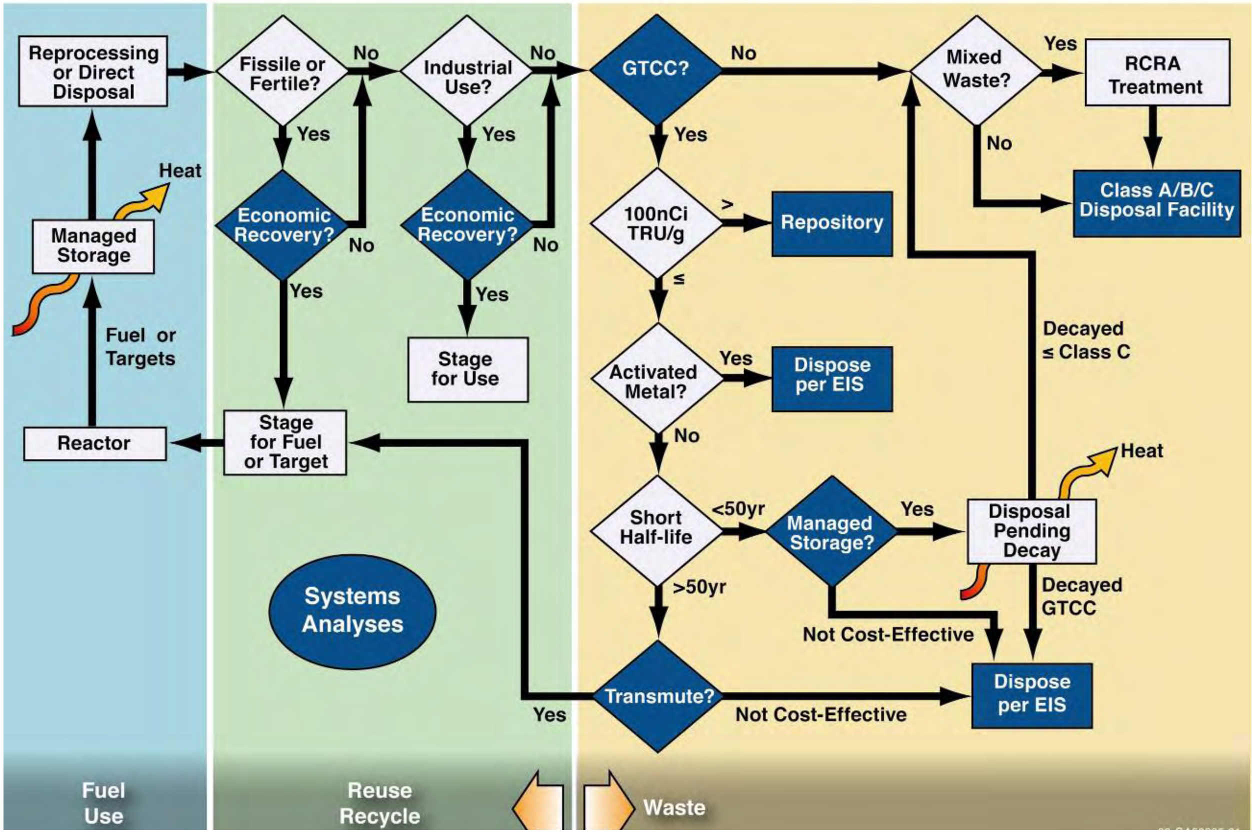


Figure 4. Integrated Waste Management Strategy Logic Diagram (From Gombert 2008)

The general strategy is three fold: 1) promote the reuse of materials if economically viable (considering waste management costs as part of the economic evaluation), 2) classify wastes on a risk basis, for example by extending the categories considered by 10CFR61.55, 3) develop disposal systems for classes of waste containing radioactive risk factors described by the classification and allowing all wastes within a risk factor to be disposed in facilities designed to protect against those risks.

Waste Form Options for Key Waste Streams

This section gives a brief overview of some of the waste process/form options for key waste streams. The options described are by no means the only options for a given stream nor has a final decision been made on the methods to treat, immobilize, and dispose of any of the streams coming from an advanced closed fuel cycle in the U.S.

HTO and $^{14}CO_2$

The NRC regulation 10CFR20 requires that ^{3}H decontamination factor (DF) of roughly 1000 from an 800 MTIHM/y plant processing 20 year old fuel. That translates to roughly 99.9% capture of the HTO. ^{14}C on the other hand may be released depending on the total β-γ released at the site boundary. However, CO_2 must be removed prior to Xe/Kr capture and depending on the capture selectivity. It is generally assumed that HTO and $^{14}CO_2$ would be combined and immobilized and disposed as LLW. Cementation is considered to be the most cost effective method for immobilizing this waste and should be sufficient to protect the environment from their hazard. Tritium with a half-life of 12.3 years will decay by the time it is released from cement and ^{14}C has a 5730 y half-life but has a soft beta decay that poses a relatively small hazard if released due to dilution with ^{12}C in nature.

Cementation for HTO and CO_2 is best performed using a low-water cement to reduce the volatilization of the waste components during mixing and curing. In-container cementing has been developed and used for a number of nuclear applications (K-basin sludge at Hanford or PM-2A waste at INL for example) and would likely be implemented in a fuel recycling plant for HTO and CO_2 immobilization. In this process Portland cement, fly-ash, and sand are mixed with the liquid waste in a drum. A sacrificial paddle mixes the raw materials inside the drum. The paddle is disconnected and a lid is placed over the drum.

Cemented wastes should comply with the requirements of the NRC position paper on cemented LLW, including constraints on (NRC 1991):

- compression strength
- thermal cycling
- irradiation stability
- biodegradation
- leach resistance
- immersion stability
- free liquids

In addition, the waste form must meet disposal site specific requirements.

Portand cement (a mixture of calcium silicates, calcium aluminate, and gypsum ($CaSO_4 \circ 2H_2O$)) is mixed with silica sand, fly ash (a glassy silica based material generated from coal firing), and water to form grout. The calcium silicate bonding gives the structural strength to the grout. Waste components are either chemically bound or encapsulated in the waste form.

Grouted waste forms are somewhat permeable and allow diffusion of water through the waste form. Contaminants that remain soluble in the high pH pore pour water (e.g. nitrate/nitrite and Tc) can diffuse to the surface of the waste form where they can be leached by infiltrating water released to the environment while contaminants that form precipitates inside the grout are controlled by both solubility and the physical attributes of the grout, thus their diffusional release is lower and they are retained. The release rates for individual contaminants from grout are generally expressed as a diffusion coefficient in the grout waste form that can then be used to assess waste form performance. Contaminant specific diffusion coefficients in grout have been traditionally determined using the ANSI/ANS 16.1 leach test.

Grouts are structurally strong and avoid degradation and subsidence in a disposal site. If property formulated and fabricated they can withstand freeze-thaw cycles over hundreds of years and keep their mechanical strength for millennia (as evidenced by ancient cements).

Iodine

The iodine stream contains ^{129}I with a 1.57×10^{7} y half-life that must be immobilized for a long time (e.g., hundreds of thousands of years). The EPA regulation 40CRF190 requires an ^{129}I capture DF of roughly 200 (more than 99% captured and immobilized). This stream is captured from the DOG on AgZ. The silver is meant to reside in the cages of the mordenite structure (Figure 5) where it remains reduced until it reacts with iodine to form AgI within the mordenite cage.

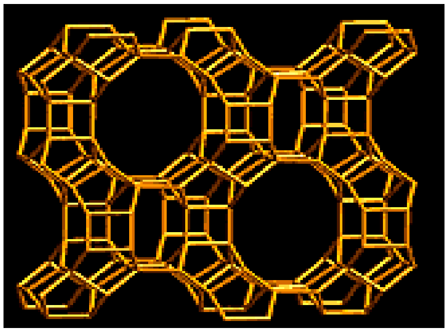


Figure 5. Ideal Mordenite Structure (From Nenoff et al. 2008)

Potential waste forms for the ^{129}I include: 1) AgZ encapsulated in low melting glass, 2) AgZ encapsulated in cement, 3) AgZ encapsulated in silico-geopolymer, 4) apatite-like minerals, 5) low-melting glass, and 6) Bi-containing ceramics. The first three are based on encapsulating the iodine loaded AgZ in a matrix media designed to generate a monolith and improve the retention of iodine. Options four through six require the removal of iodine from the AgZ and subsequent processing to generate a waste form.

These are all viable options, however, focus will be given to the forms and processes currently under development in the U.S. – 1 and 2. Option 1 is under development by Nenoff et al. (2008) where a low-temperature melting bismuth-zinc-borate glass is mixed with the I-loaded AgZ and the mixture is heated in the disposal can at a temperature below the onset of I_2 volitilization (≤ 500°C). This process partially dissolves the AgZ into the glass and retains the I better than the other two encapsulation techniques.

Option 2 is under development by Scheele et al. (2002) where AgZ is encapsulated by a cement that contains CaI_2 to decrease the solubility of radioiodine in the pour water. This was found to have a far superior performance that the grouted AgZ alone. This process was adopted as a baseline for the Hanford Tank Waste Treatment and Immobilization Plant (WTP) and is less expensive than option 1. However, one option for iodine disposal is in the geologic repository which will not accept cement waste forms due to the impact of cement on canister and spent fuel corrosion and neptunium solubility.

Options 4-6 are likely to generate more durable waste forms, but, will be more expensive to operate.

Krypton

According to EPA regulation 40CFR190 ^{85}Kr release must be below 50 kCi/GWye which translates to a capture requirement between zero for 30 y cooled fuel to 80% for 5 year cooled

fuel. Once captured, the ^{85}Kr must be stored until sufficiently decayed to release. With a 10.76 y half-life, this may only take 10 to 30 years.
Kr is captured by HZ at low temperature, it is then released from the HZ upon heating. With the need to store the Kr for less than 100 y, the favored waste management strategy is to store the Kr in compressed gas cylinders. However, two additional waste forms have been proposed 1) a molecular sieve with cages designed for the size of Kr and 2) sputtering of Kr into a metal surface (e.g., Cu).

Cost appears to scale with quality of the waste form. The cheapest being compressed gas which is the least immobile form while the most expensive is sputtering into Cu which would be the most durable of the waste forms.

Hulls and Hardware (aqueous)

Hulls and hardware are comprised of zircaloy from LWR hulls and stainless steel fuel bundle hardware. The hulls contain TRU from nucleus recoil and activation of U impurities in the zirconium. The hardware contains activation products and coolant contamination. These wastes are GTCC due to > 100nCi TRU/g. The cost of nuclear grade Zr makes the hulls an ideal candidate for recycling of this material. Activities are underway to compare the costs and benefits of zircaloy recycling into new fuel hulls, but, no conclusive results are yet available.

Four waste forms have been proposed for immobilization of these wastes: 1) compacted metal, 2) low melting alloy, 3) high melting alloy, and 4) zirconia rich ceramic (e.g., zircon). Once again, the waste form robustness increases with immobilization cost from one through four. The compacted metal waste form/process is used at LaHauge reprocessing plant. In this process the hulls and hardware are compressed under high pressure. Roughly 65% of the metal density is achieved. Slugs of compacted metal will be loaded into a disposal container (see Figure 6 for example).

Figure 6. Photograph Compacted Hulls and Hardware Metal Slug (Courtesy of Areva)

The hulls and hardware are mixed with iron and or copper to reduce the melting temperature to below roughly 1600°C which will lower the processing complexity. The material is melted under a reducing atmosphere in a batch process. The metal slug (see Figure 7 for example) is then placed in a canister.

The high-temperature alloy is Zr rich, essentially, the hulls and hardware without additives which requires a melting temperature in excess of 1600°C as shown in Figure 8. There is actually a continuum of compositions that can be formed between Fe and Zr rich. Targeting a eutectic composition yields an alloy of the microstructure shown in Figure 9.

Figure 7. Photograph of Low-temperature (85% SS, 15% Zr) Alloy Slug (Courtesy of INL)

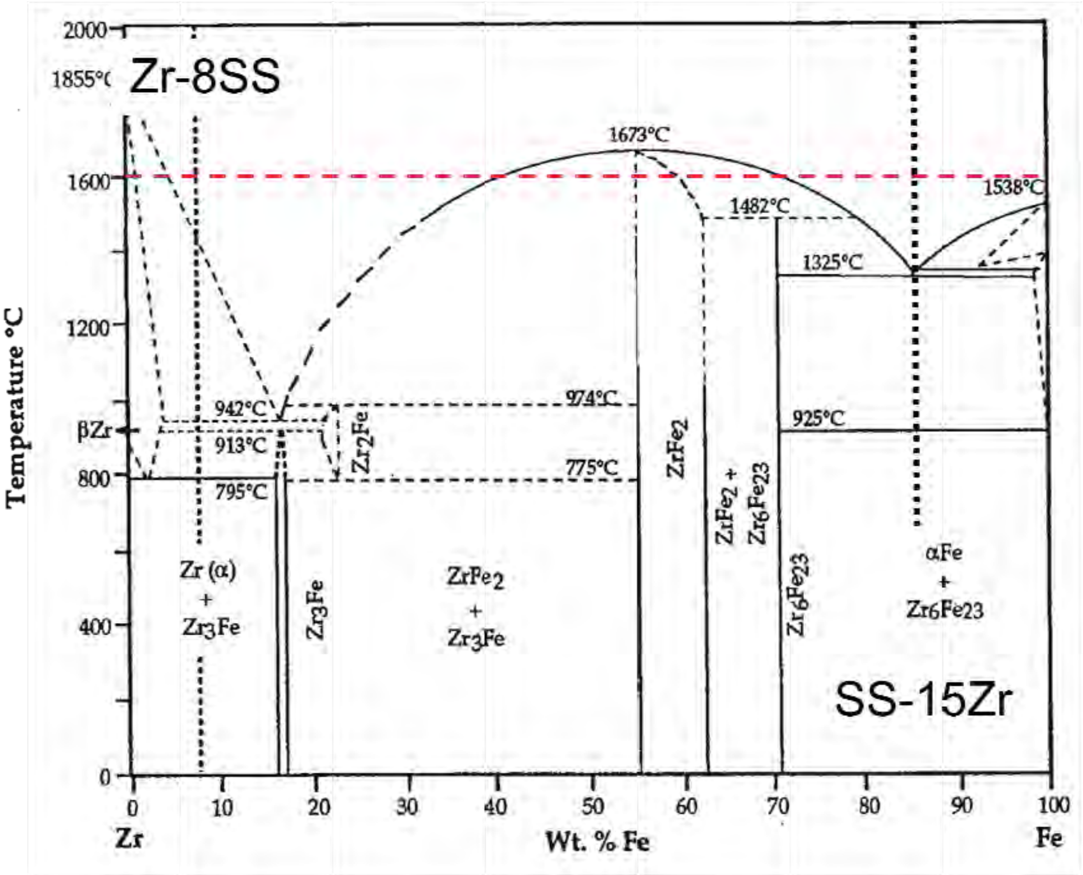


Figure 8. Zr-Fe Binary Phase Diagrams

Figure 9. Microsturcture of Fe – 15% Zr Alloy (from Ebert 2005)

The corrosion rate of the Fe-15% Zr alloy shown in Figure 9 is given by (Ebert 2005):

$$r = \frac{a_{\max} \times \ln\left(1 + \frac{b \times a_{\max}}{a_{\max}} T_e\right)}{T_e}$$

where r is the corrosion rate in g/(m^2·d), Te is the time for which the passivation layer is effectively slowing the rate and b and $a_{\max}$ are given by:

$$\ln a_{\max} = 7.98 + (2.39 \times 10^{-4} \times [Cl^-]) - 1.23 \times pH$$

$$\ln (b \times a_{\max}) = -0.10 + (0.015 + 5.82 \times 10^{-6} \times [Cl^-]) \times T - 0.698 \times pH$$

where $[Cl^-]$ is the concentration of chloride ion in moles per liter and T is temperature. The passivation effect strongly reduces the corrosion rate. However, there is not a mechanistic model for its action. Only an empirical relationship has yet been developed. This model doesn't include Eh or other parameters known to impact metal corrosion.

The final waste form is a zirconia rich ceramic such as zircon ($ZrSiO_4$), baddeleyite (ZrO_2), pyrochlore ($Zr_2Ln_2O_7$), etc. These ceramics have high durability controlled by solubility. The metals must first be oxidized, then mixed with sufficient quantity of additives, pressed into pucks (or loaded into a hot-press) and sintered. This process requires a significant amount of mechanical handling, may generate fines, and is relatively expensive to operate.

Undissolved Solids (aqueous) and Tc

Aqueous UDS are comprised of Ru, Rh, Pd, Mo, Zr, Tc, and some oxygen. The primary radionuclide to immobilize is ^{99}Tc. The Tc waste stream is comprised of relatively pure pertechnetate ion on an ion exchange resin. With a half-life of 2.1×10^5 y this waste must be immobilized for a long time (hundreds of thousands of years). If Tc is oxidized, it is highly soluble as pertechnetate and is therefore mobile. As both the Tc and UDS are meant to immobilize Tc, it is assumed that these waste streams will be immobilized together. One potential exception would be the definition of HLW based on the NWPA includes the Tc, but, not necessarily the UDS.

Four waste forms have been proposed for the combined UDS-Tc waste stream: 1) Fe or Zr rich alloy, 2) glass with noble metal inclusions, and 3) pyrochlore ceramic -- $[Tc,Zr,Mo,Ru,Rh,Pd]_2[Ln,An]_2O_7$. To fabricate a metal alloy waste form as described in Section 0, the Tc must be reduced. Several processes have been demonstrated to perform the reduction including elution from the resin followed by electrochemical reduction on Fe or precipitation and steam reforming of the pertechnetate to metal. The metal waste form would be virtually the same as that describe above in Section 0. This form has the distinct advantages of generating the lowest volume of the three options, maintaining the Tc in a reduced state, and relatively inexpensive process (compared to pyrochlore).

Incorporation of UDS-Tc into a glass would cause for an increase in glass volume since the noble metals Ru, Rh, and Pd are virtually insoluble. The amount of NM tolerated in the glass is dependent on the melter technology and operating conditions. The allowable concentration typically ranges from roughly 0.15 wt% for large ceramic-lined, Joule-heated (JHCM) melters such as that at the Defense Waste Processing Facility (DWPF) at the Savannah River Site and WTP to roughly 3 wt% for cold-crucible induction melters (CCIM) used at SAI Radon in Moscow and to be implemented in LaHauge. In a glass melter, Tc will be oxidized to TcO_2 which, disproportionate to Tc_2O_7 and Tc^0 at roughly 1100°C (Darab and Smith 1996). As Tc_2O_7 has a boiling point of 311°C, it will volatilize from the melter and require capture and recycle. Although this disproportionation would generate a gas from 2/3 of the Tc, in practical experience, less than 25% of the Tc is actually lost to the off-gas. For Tc to be released from glass, the glass must corrode. The corrosion of glass is determined by solution pH and chemistry, temperature, and saturation of orthosilicic acid according to (McGrail et al. 2000 for example):

$$r = k_0 \cdot pH^{\pm\eta} \exp\left[\frac{-E_a}{RT}\right]\left(1-\frac{Q}{K_g}\right)^{\sigma}$$

where r is the corrosion rate in g/(m^2·d), k_0 is the forward rate constant, η is the pH coefficient, E_a is the apparent activation energy, Q is the concentration of “glass” (practically the concentration of orthosilicic acid) in solution, K_g is the concentration of orthosilicic acid in equilibrium with the glass (a pseudo equilibrium must be assumed), and σ is the Temkin coefficient (effectively 1). Glass is a non-equilibrium state and so will continue to corrode even after silicic acid saturation. It is not as durable as the pyrochlore waste form but is based on a well practiced and understood process and should give sufficient durability (e.g., orders of magnitude better than SNF).

Finally, the pyrochlore mineral is highly durable. As a stable phase its durability is controlled by both kinetics and solubility. Many processes are can be used to form the pyrochlore, all of which are relatively expensive compared to the vitrification process. See Section 0 for more detail.

Alkali and Alkaline Earth Fission Products

The Cs/Sr waste contains over 80% of the radioactivity of SNF at the time of processing. This material will decay in a relatively short time (<300 y) leaving only ^{135}Cs and trace impurities. The waste is classified by the NWPA as HLW, but, with policy changes, may be disposable as LLW after decay storage. Key requirements for the waste forms include tolerance to the high temperature, high ionizing radiation field, and decay from $Cs^+ \rightarrow Ba^{2+}$ and $Sr^{2+} \rightarrow Zr^{4+}$.

The potential waste forms include: 1) titanate and niobate ceramics, 2) aluminosilicate ceramics, 3) silicate glass, 4) fluorides and chlorides, and 5) carbonates. The chemical durability of the waste forms decreases from the titanates and niobates which are highly durable to the carbonates that are at least partially water soluble. However, as mentioned earlier, durability may not be the most significant criteria for this waste form. Table 3 shows the ranking of these waste forms for some of the key criteria.

Table 3. Comparison of Cs/Sr Waste Form against Key Criteria

Form	***Titanate/ Niobate***	***Alumino-silicate***	***Glass***	***Fluoride/ Chloride***	***Carbonate***
durability	very high	high	high	low	low
temp resistance	very high	high	med	low	low
dose resistance	very high	unknown	high	high	unknown
decay tolerance	unknown	unknown	high	unknown	unknown
cost	very high	high	med	low	low

This comparison brings into sharp contrast the question "… how good is good enough?" If this waste form is to be disposed of in a repository, the ^{135}Cs remaining after decay storage will be nearly completely immobile; suggesting that lower durability may be appropriate. However, the material must be stored for a number of years (50 to 300 y) prior to disposal.

Transition Metal Fission Products

The TRUEX raffinate or TMFP contain trace impurities plus Mo, Zr, Pd, Ru, Rh, Fe, Ni, and Cr. These metals are in a nitric acid solution. The key waste forms considered for this waste include: 1) iron based alloys, 2) glass, and 3) pyrochlore minerals. These are the same waste forms considered for UDS-Tc (Section 0) only in this case there should be very little Tc to immobilize. By the NWPA, this waste stream is considered HLW and would be disposed of in the repository. However, preliminary testing suggests that the radionuclide concentrations in solution may be low enough to entertain other disposal options if policy were to change.

Lanthanide Fission Products

This waste stream contains the lanthanides and yttrium in a lactic acid solution. There will be trace TRU contamination in this stream. The potential waste forms include: 1) glass, 2) pyrochlore ceramic, and 3) monazite like phosphate ceramics. High lanthanide glasses were developed for Am-Cm immobilization at the Savannah River Site (Peeler et al. 2000 and 2000b, and Vienna et al. 1999 and 1999b). This glass can contain a combined lanthanide and actinide concentration of over 50 wt% while demonstrating chemical durability far in excess of typical HLW glasses. This glass would be processed in a hot-walled induction melter (HWIM) at approximately 1350°C.

Pyrochlore ceramics were described in Sections 0 and 0 so won't be repeated here.

The monazite (Ce,La,Nd,Y)PO_4 cyrstals can be formed at relatively low temperatures (~1200°C) and have durability to rival the pyrochlore ceramics. In addition they contain phosphate that will limit the solubility of actinides in a repository environment.

Undissolved Solids (electrochemical)

The UDS from electrochemical treatment are nearly a waste form of their self. After salt distillation these materials can be melted at ~1600°C to for a durable metal waste form of the type described in Sections 0, 0, and 0. Ebert (2005) describes this waste form in detail. Figure 10 shows a sample of the metal waste form produced in the INL hot cells.

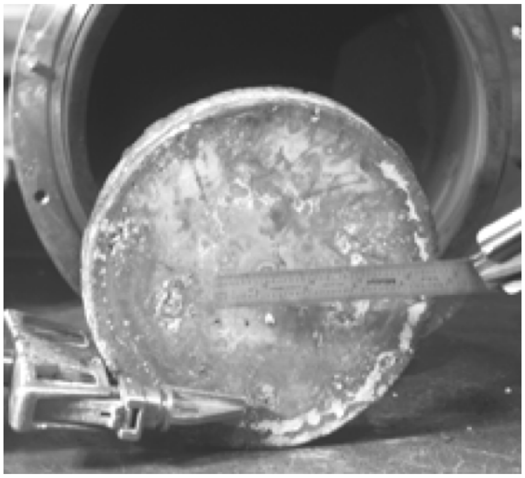


Figure 10. Metal Slug from Electrochemical Processing of EBR-II Fuel (Courtesy of INL)

Fission Products (electrochemical)

With the high chloride and alkali in the electrochemical waste, there are not many options for waste forms. Further processing of the waste to remove the halides and some of the alkali will allow for waste forms described in Sections 0, 0, 0, and 0. However, an evaluation of the options for the waste as is yielded the conclusion that glass bonded sodalite is the preferred option as describe in Ebert 2005.

This waste process includes the occlusion of salt waste onto zeolite 4A the zeolite is then mixed with a binder glass in a 3:1 ratio of zeolite:glass. The material is heated to 915°C for four hours and results in a monolith that can be loaded into waste disposal canisters (as shown in Figure 11). The reactions between the salt, zeolite, and silica from the glass convert the waste form into a sodalite and pollucite form encapsulated by the glass matrix according to:

$$\underset{\textbf{zeolite 4A}}{4\ Na_{12}(AlSiO_4)_{12}} + \underset{\textbf{salt}}{12\ CsCl} + \underset{\textbf{glass?}}{12\ SiO_2} \rightarrow \underset{\textbf{sodalite}}{6\ Na_8(AlSiO_4)_6Cl_2} + \underset{\textbf{Cs-pollucite}}{12\ CsAlSi_2O_6}$$

The loading of waste in the glass bonded sodalite waste form is determined by the stoichiometry of Cl in the sodalite and the soda required to obtain that amount of sodalite. This loading tends to be on the 2 to 10 wt% of fission products in the final waste form. The lathanides convert to Ln_2O_3 and are encapsulated in the glass phase along with the sodalite and pollucite. The iodine dissolves in the glass. This process was developed for the salt waste from EBR-II processing at INL and will be implemented in waste treatment in 2009.

Figure 11. Simulated Glass Bonded Ceramic Waste Form (Courtesy of INL)

Mixed Waste Streams

It's clear from the above discussion that waste forms such as glass, pyrochlore, and metal can be used to immobilize many of the streams. Reducing the number of waste processes and forms may significantly reduce the cost and complexity of waste management. Gombert et al. 2008 performed a study to evaluate the cost of combining certain aqueous streams into glass and metal waste forms. The streams evaluated include UDS, Tc, TMFP, Cs/Sr, and LNFP from the UREX+1a process. Table 4 shows the three options considered.

Table 4. Summary of Options Considered in Mixed Waste Stream Trade Study

Case	**UDS**	**Tc**	**TMFP**	**LNFP**	**Cs/Sr**
Base	Fe-alloy	Zr-alloy	ABS glass	LaBS glass	ABS glass
Opt 1	Fe-alloy		ABS glass		
Opt 2	Fe-Alloy			LaBS glass	

The baseline option generates five waste forms using five processes out of the five waste streams. Options one and two each generate only two waste processes and two waste forms from the same five waste streams. The difference is the treatment of TMFP. In option one, they are incorporated into the glass while in option two they are reduced to metal and incorporated into the alloy form.

Figure 12 shows the impact of the two options on waste form volume. Option one shows only a minor reduction in waste form volume relative to the baseline while option two reduces waste form volume to less than a third of the baseline value. However, it should be noted that the waste form volume does not necessarily determine the repository impact. In particular, the Cs/Sr stream generates sufficient heat to limit the amount that can be placed in a waste package. This yields almost the same amount of Cs/Sr packages with or without the other streams contained in the same glass. Figure 13 demonstrates this point by showing the waste packages generated by each of the three options. Both options generate roughly half of the waste packages relative to the baseline.

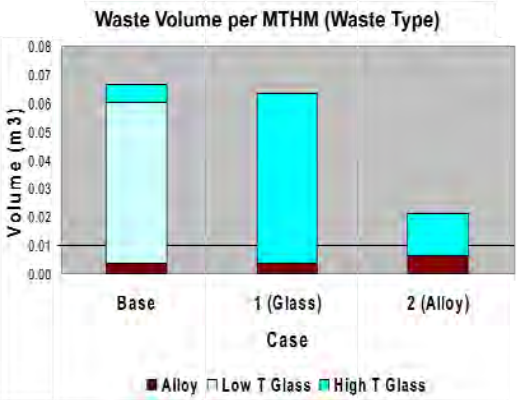


Figure 12. Volume of Waste Forms Evaluated (From Gombert et al. 2008)

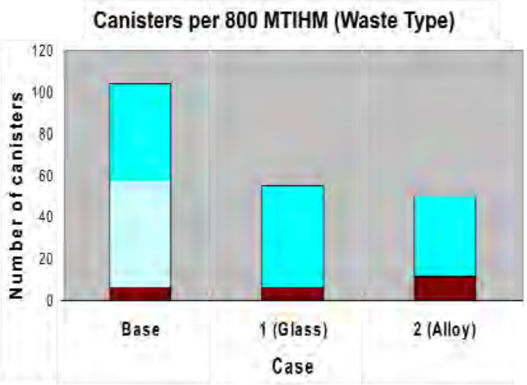


Figure 13. Waste Canisters Generated per 800 MTIHM of Fuel Processed (From Gombert et al. 2008)

Preliminary cost estimates were performed to further evaluate these options. As shown in Figure 14, the capital cost of option one is well below that of the baseline while the capital cost of option two is above the baseline. This difference in capital costs is due to the changes in the flowsheet. In option one, the Cs/Sr is combined with TMFP so the FPEX process is not required. This change along with the reduction in the number of waste processes creates a lower plant footprint, capital cost, and operating cost. For option two the FPEX is still required and an additional process to reduce the TMFP to the metal form is also required. This reduction step generates secondary waste streams and requires a significant plant footprint. These differences in cost, both capital and operating, suggest that the more economical waste treatment option is option one which combines the UDS and Tc into a single alloy waste form and combines the Cs/Sr, TMFP, and LNFP into a single glass waste form. This conclusion was tested by varying all of the most significant cost components in a sensitivity study. Although the relative cost changed, the ranking of the three options did not.

Also recently evaluated was the option to combing the Tc and UDS into the glass waste form. No differences in capital cost between option one and this option. A slight reduction in operating costs occurred after roughly 13 years of operation.

This study did not address waste form quality, environmental impacts, or other decision criteria. Rather only the cost impacts of these options were evaluated.

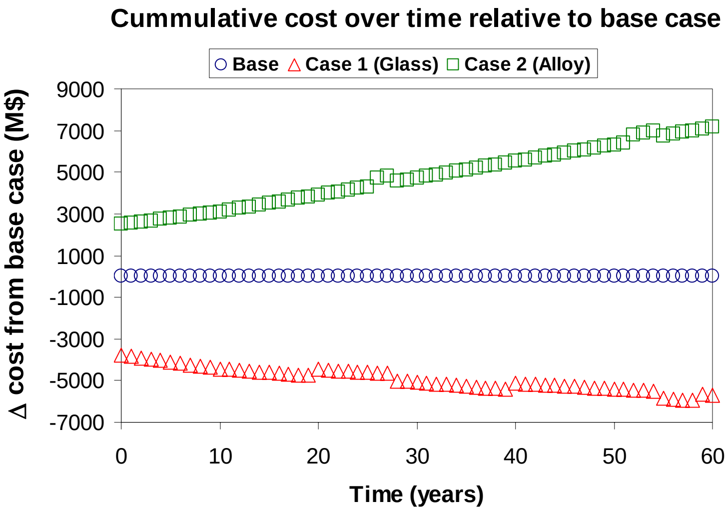


Figure 14. Estimated Cost Difference from the Baseline for Options 1 and 2 (Gombert et al. 2008)

Concluding Remarks

The advanced separations being developed for a closed U.S. nuclear fuel cycle will yield and unprecedented level of control over waste management not afforded by the PUREX process previously employed. The waste forms can be tailored for specific waste chemistry and disposal environments. Development work on these advanced waste management and waste form options is ongoing. Preliminary results suggest that the combination of waste streams into a metal waste form and a glass waste form would be the most economical path. However, this conclusion does not take into account performance of the waste forms or other criteria that would be used in an official decision process.

References

1. 10 CFR 61.55, *Licensing Requirements for Land Disposal of Radioactive Waste, Waste Classification*. Code of Federal Regulations, as amended.
2. Advocat, T., et al. 2001. "Long-Term Alteration Mechanisms in Water for SON68 Radioactive Borosilicate Glass." *Journal of Nuclear Materials* 298:55-62.
3. Amerine, D.B. 1995. *Defense Waste Processing Facility Waste Qualification Report (U)*, WSRC-IM-91-116, Westinghouse Savannah River Company, Aiken, SC.
4. ASME. 2008. *Quality Assurance Requirements for Nuclear Facility Applications*, ASME NQA-1–2008, the American Society of Mechanical Engineers, New York, NY.
5. ASTM. 1997. “Standard Practice for Prediction of the Long-Term Behavior of Waste Package Materials Including Waste Forms Used in Geologic Disposal of High-Level Nuclear Waste,” Standard C-1174 *Annual Book of ASTM Standards* Vol. 12.01, American Society for Testing and Materials, West Conshohocken, PA.
6. ASTM. 2008. “Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT),” Standard C-1285, *Annual Book of ASTM Standards* Vol. 12.01, American Society for Testing and Materials, West Conshohocken, PA.
7. ASTM. 2008b. “Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste ,” ASTM Standard C-1220, *Annual Book of ASTM Standards*, Vol. 12.01, American Society for Testing and Materials, West Conshohocken, PA.
8. Barnes, S.M. 1996. *WVDP Waste Form Qualification Report*, WVDP-186, Rev. 3, West Valley Nuclear Services, West Valley, NY.
9. Barnes, J.L. 2003. *DWPF Waste Form Compliance Plan (U)*, WSRC-IM-91-116, Rev. 7, Westinghouse Savannah River Company, Aiken, SC.
10. Damerow, F., A. Arakali, C.A. Musick, J.M. Perez, and R. Peterson. 2003. *Research and Technology Plan*, 24590-WTP-PL-RT-01-002, Rev. 2, River Protection Project, Waste Treatment Plant, Richland, WA.
11. Darab, J.G., and P.A. Smith. 1996. “Chemistry of Technetium and Rhenium Species during
12. Low-Level Radioactive Waste Vitrification,” in *Chemistry of Materials*, **8**:1004-1021.
13. DOE. 1982. *The Evaluation and Selection of Candidate High-Level Waste Forms*, DOE/TIC 11611, U.S. Department of Energy, Savannah River Office, Aiken, SC.
14. DOE. 1990. *Evaluation and Selection of Borosilicate Glass as the Waste Form for Hanford High-Level Radioactive Waste*, DOE/RL-90-27, U.S. Department of Energy, Richland Office, Richland, WA.
15. DOE. 1999. *Radioactive Waste Management,* DOE O 435.1,*U.S. Department of Energy*, Washington, D.C.
16. DOE. 2000. *Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant*, Contract DE-AC27-01RV14136, as amended, U.S. Department of Energy, Office of River Protection, Richland, WA.
17. DOE. 2007. *Civilian Radioactive Waste Management System Requirements Document*, DOE/RW-0406, Rev. 08., U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Washington, D.C.
18. DOE. 2007b. *Quality Assurance Requirements and Description*, DOE/RW-0333P, Rev.19, U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Washington, D. C.
19. DOE. 2008. *Draft Global Nuclear Energy Partnership Programmatic Environmental Impact Statement*, DOE/EIS-0396, U.S. Department of Energy, Office of Nuclear Energy, Washington, D.C.

20. DOE. 2008b. *Civilian Radioactive Waste Management System, Waste Acceptance System Requirements Document*, DOE/RW-0351, Rev. 5, ICN-01, U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Washington, D.C.
21. Ebert, W.L. 2005. *Testing to Evaluate the Suitability of Waste Forms Developed for Electrometallurgically-Treated Spent Sodium-Bonded Nuclear Fuel for Disposal In The Yucca Mountain Repository*, ANL-05/43, Argonne National Laboratory, Argonne, IL.
22. Ebert, W.L. 2008. *Testing Protocols to Support Waste Form Development, Production, and Acceptance*, GNEP-WAST-WAST-AI-RT-2008-000302, U.S. Department of Energy, Office of Nuclear Energy, Washington, D.C.
23. EPA. 2008. *Waste Management System; Testing and Monitoring Activities; Final Rule: Methods Innovation Rule and SW-846*, Update IVB, Environmental Protection Agency, Washington, D.C.
24. Gombert, D. 2008. *Global Nuclear Energy Partnership Integrated Waste Management Strategy*, GNEP-WAST-WAST-AI-RT-2008-000214, U.S. Department of Energy, Office of Nuclear Energy, Washington, D.C.
25. Gombert, D., S. Piet, T. Trickel, J. Carter, J.D. Vienna, and W.L. Ebert. 2008. *Combined Waste Form Cost Trade Study*, GNEP-SYSA-PMO-MI-DV-2009-000003, U.S. Department of Energy, Office of Nuclear Energy, Washington, D.C.
26. Grambow, B., and R. Müller. 2001. "First-Order Dissolution Rate Law and the Role of Surface Layers in Glass Performance Assessment." *Journal of Nuclear Materials* 298:112-24.
27. McGrail, BP, et al. 2000, *A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford*, PNNL-11834 Rev. 1, Pacific Northwest National Laboratory, Richland, WA.
28. McGrail, BP, et al. 2001. "Near-Field Performance Assessment for a Low-Activity Waste Glass Disposal System: Laboratory Testing to Modeling Results." *Journal of Nuclear Materials* 298:95-111.
29. McGrail, B.P., et al. 2001b. "The Structure of Na_2O-Al_2O_3-SiO_2 Glass: Impact on Sodium Ion Exchange in H_2O and D_2O." *Journal of Non-Crystalline Solids* 296:10-26.
30. Nelson, J.L., and J.D. Vienna. 2008. *IHLW Waste Form Compliance Plan for the Hanford Tank Waste Treatment and Immobilization Plant*, 24590-HLW-PL-RT-07-0001, Rev. 2, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, WA.
31. Nenoff, T.M., J.L. Krumhansl, T. Garino, N.W. Ockwig, and K. Holt-Larese. 2008. *Waste Form Development and Testing for* I_2, GNEP-WAST-PMO-MI-DV-2008-000149, U.S. Department of Energy, Office of Nuclear Energy, Washington, D.C.
32. NRC. 1991. *Waste Form Technical Position, Revision 1*, U.S. Nuclear Regulatory Commission, Rockville, MD.
33. Odell, M. 1992. "Vitrification - World Review," in *Nuclear Engineering International*, p. 52
34. Palmer, R.A. 2002. *Waste Form Compliance Plan for the West Valley Demonstration Project High-Level Waste Form*, WVDP-185, Rev. 14, West Valley Nuclear Services, West Valley, NY.
35. Peeler, D.K., T.B. Edwards, I.A. Reamer, J.D. Vienna, D.E. Smith, M.J. Schweiger, B.J. Riley, and J.V. Crum. 2000. "Composition / Property Relationships for the Phase 1 Am/Cm Glass Variability Study," in *Ceramic Transactions*, 107, pp. 427-439, American Ceramic Society, Westerville, OH.
36. Peeler, D.K., J.E. Marra, I.A. Reamer, J.D. Vienna, and H. Li. 2000b. "Development of the Am/Cm Batch Vitrification Process," in *Ceramic Transactions*, 107, pp. 397-406, American Ceramic Society, Westerville, OH.
37. Peterson, P.F. 2003. "Will the United States Need a Second Geologic Repository?" in *The Bridge*, National Academy of Engineering, Volume 33, Number 3.

38. Piepel, G.F., B.G. Amidan, A. Heredia-Langner, D.R. Weier, and S.K. Cooley. 2005. *Statistical Methods and Results for WTP IHLW and ILAW Compliance*, PNWD-3568 (WTP-RPT-072, Rev 1), Rev. 0, Battelle-Pacific Northwest Division, Richland, WA.
39. Strachan, D.M. 2004. *Defense HLW Glass Degradation Model*, ANL-EBS-MD-000016, Rev. 2, Bechtel SAIC Company, Las Vegas, NV
40. Strachan, D.M. 2003, *Ancient Glass Studies: Potential Archaeological Sites Relevant to Low-Activity Waste Disposal at Hanford*, PNNL-14232, Pacific Northwest National Laboratory, Richland, WA.
41. Van Iseghem, P., et al. 2007. *GLAMOR, A Critical Evaluation of the Dissolution Mechanisms of High Level Waste Glasses in Conditions of Relevance for Geological Disposal*, FINAL REPORT 2001-11-01 to 2004-10-31, SCK-CEN, Mol, Belgium.
42. Verney-Carron, A, S Gin, and G Libourel. 2008, "A Fractured Roman Glass Block Altered for 1800 Years in Seawater: Analogy with Nuclear Waste Glass in a Deep Geological Repository," *Geochimica et Cosmochimica Acta* 72:5372-85.
43. Vienna, J.D. 2005. “Nuclear Waste Glasses,” in *Properties of Glass Forming Melts*, eds. L.D. Pye, I. Joseph, and A. Montenaro, CRC Press, Boca Raton, FL.
44. Vienna, J.D., and D.S. Kim. 2008. *Preliminary IHLW Formulation Algorithm Description*, 24590-HLW-RPT-RT-05-001, Rev. 0, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, WA.
45. Vienna, J.D., B.J. Riley, M.J. Schweiger, D.E. Smith, D.K. Peeler, and I.A. Reamer. 1999. *Property Data for Simulated Americium/Curium Glasses,* PNNL-13009, Pacific Northwest National Laboratory, Richland, WA.
46. Vienna, J.D., D.K. Peeler, J.G. Darab, J.R. Zamecnik, H. Li, and J.E. Marra. 1999b. “Chemistry of Rare Earth Oxalate Vitrification,” in *Scientific Basis for Nuclear Waste Management XXII*, pp. 321-328, Materials Research Society, Warrendale, PA.

Environmental Transport

Kathryn Higley
Department of Nuclear Engineering & Radiation Health Physics
Oregon State University

Abstract

An overview is provided of processes contributing to the environmental transport of radionuclides released from activities in the fuel cycle. Concepts reviewed include source term, release scenario, waste characteristics, engineered barriers, natural barriers, biotic transport and exposure. The methodologies used in predicting transport are discussed. Challenges that remain are presented.

Introduction

“Environmental transport” is a very vague and nebulous term. In the context of radiological assessment, it generally refers to the movement of radioactive contaminants from one location (often referred to as the source) to another (the receptor(s)). At the end of transport, exposure and dose to the receptor occurs. The transport may be rapid or slow and the receptor may be adjacent to the source or thousands of kilometers distant. The dose may be large, or not. The transport may have occurred in the past, be ongoing, or have the potential to occur in the future. This all depends on the source, the environment, and the receptor. The purpose of this paper is to very briefly explore the processes that can move a radioactive material from point to point in the environment. It will also, as briefly, consider how someone might choose to conceptualize this transport, so as to make an assessment of radiological impact.

Environmental Transport – A Complex Subject

The emphasis of this paper is on radionuclides released through the nuclear fuel cycle. The nuclear fuel cycle encompasses those activities necessary to the generation of power from nuclear plants, and includes excavation of uranium ore, processing the ore, creating fuel, using the fuel in nuclear reactors, recycling portions of the fuel and disposing of the waste. An image of the nuclear fuel cycle is shown in Figure 1 (modified from that of the U.S. Nuclear Regulatory Commission). The issue of environmental transport of radionuclides is therefore relevant to every step, from mining through disposal. This paper focuses on ***radionuclide*** transport, but it is important to note that the processes and systems can largely apply to stable chemical contaminants as well. The reader is directed to several excellent review papers and textbooks which can provide a comprehensive discussion of many of the issues introduced in this paper.

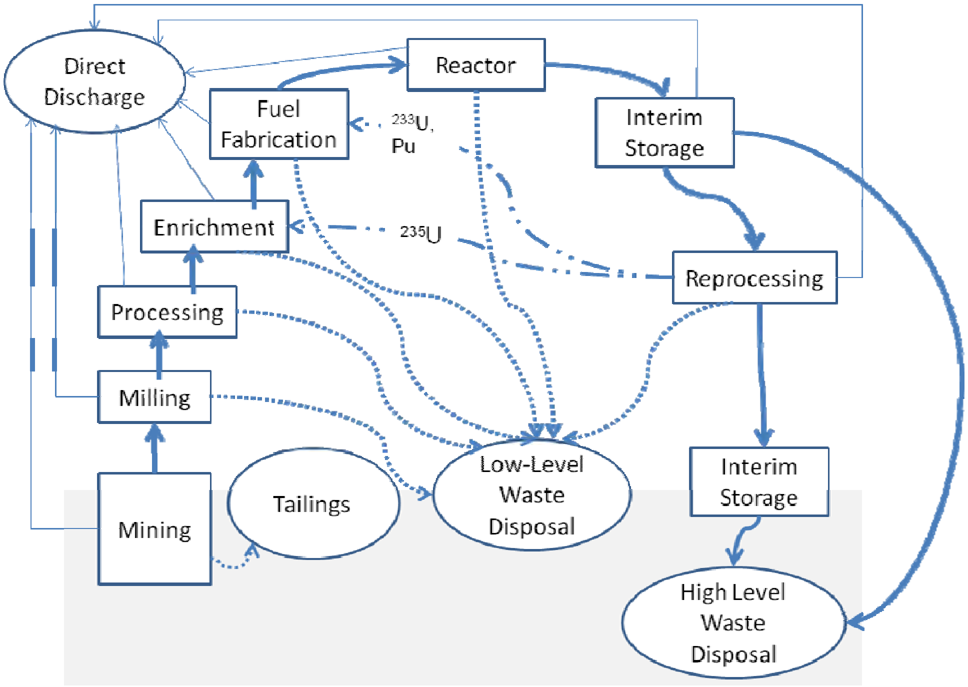


Figure 1. The nuclear fuel cycle including radioactive waste streams and discharges; modified from http://www.nrc.gov/materials/fuel-cycle-fac/stages-fuel-cycle.html

Environmental Transport: One Part of a Larger Question

While release of radioactive materials into the environment can occur at any stage in the nuclear fuel cycle, the resultant radiation dose to the public is much less than that received from natural background sources. Direct discharges are constrained by regulation, and indirect discharges are limited through the design of radioactive waste storage and disposal facilities. The radiation protection dose limits drive the design of both operating facilities and radioactive disposal sites. These protection limits compel us to understand how radionuclides are transported through the environment. We need this knowledge to that we can ensure our engineered systems are designed to control radioactive discharges. Figure 2 illustrates this concept.

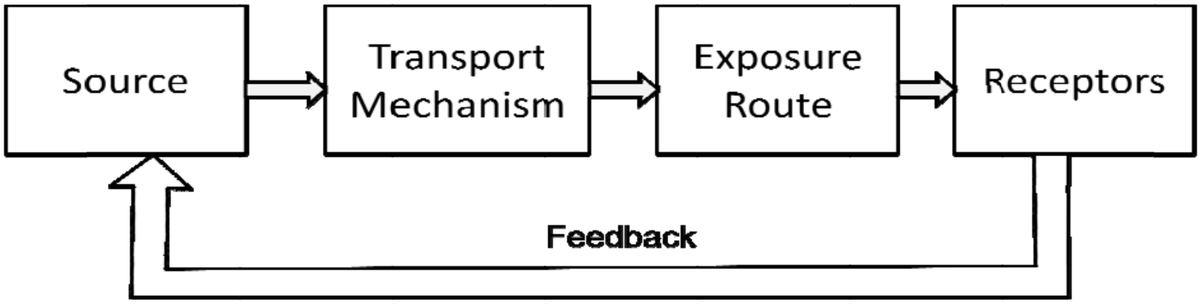


Figure 2. How environmental transport fits within the larger context of radiation protection

An example of how this process works is as follows. Consider a facility that will discharge small amounts of radionuclides into a receiving stream (such discharges are permitted under U.S. law). In order to know if they are going to meet radiation protection standards, the facility operator must know the source of the radionuclide (how much and what kind). This is identified in Figure 2 as the box marked “Source”. Once the source is known, the principal mechanisms responsible for moving the radioactive material must be identified. This is the box marked “Transport Mechanism”. The transport mechanisms for this scenario would include diffusion and mixing (advection) as the waste is discharged into the stream. The next box, “exposure route”, is used to identify significant pathways where one might come in contact with the effluent. Examples could include drinking of the water, swimming in it, or using it for growing crops. The last box, “receptors” would be individuals located downstream from the discharge point that are considered likely to be exposed to the release. All of this information, source, transport, exposure, and receptors are combined to produce and estimate of radiation dose. The magnitude of the radiation dose received by the individual would be determined by the amount of activity discharged into the stream, how much dilution and mixing occurred in the stream, how much water was consumed by the individual, and ultimately, the type of radiations emitted by the radionuclide(s) and their biological behavior in the individual.

Transport processes can be this simple, or they can be incredibly varied and complex, as discussed in the next few sections. The principle objective of this review is to focus on mechanisms responsible for transport of radionuclides through the environment; the types of mechanisms, where they operate, how they are determined, where work needs to be done, and most significantly, how they fit within the overall framework of assessing impact from the release.

Conceptual Zones for Environmental Transport

One approach to understanding environmental transport of radionuclides is to divide physical regions that contain the source into “near” and “far” field (Figure 2). These are arbitrary designations, but allow us to separate some important processes for consideration. The near field is defined such that it encompasses the origin of the radioactive material (called the source or source term). We can also include in this region any engineered barrier system that is built surrounding or including the source. One example would be the encapsulated fission product ^{137}Cs (as described on page 53 of reference). We can also consider any other construction/disturbances in the immediate vicinity of our waste that have disturbed the properties of the natural environment as belonging to the near field.

The second zone, called the “far” field, includes the undisturbed environment surrounding the near field. It may, by design, include any naturally occurring barriers to transport (more on this later). We can also distinguish the “biosphere” for this particular instance – the near surface area of the earth that contains life. Depending on the transport scenario being considered, the definitions of near and far field may vary, and the biosphere may be a part of both zones. Again, these are artificial constructs used for convenience.

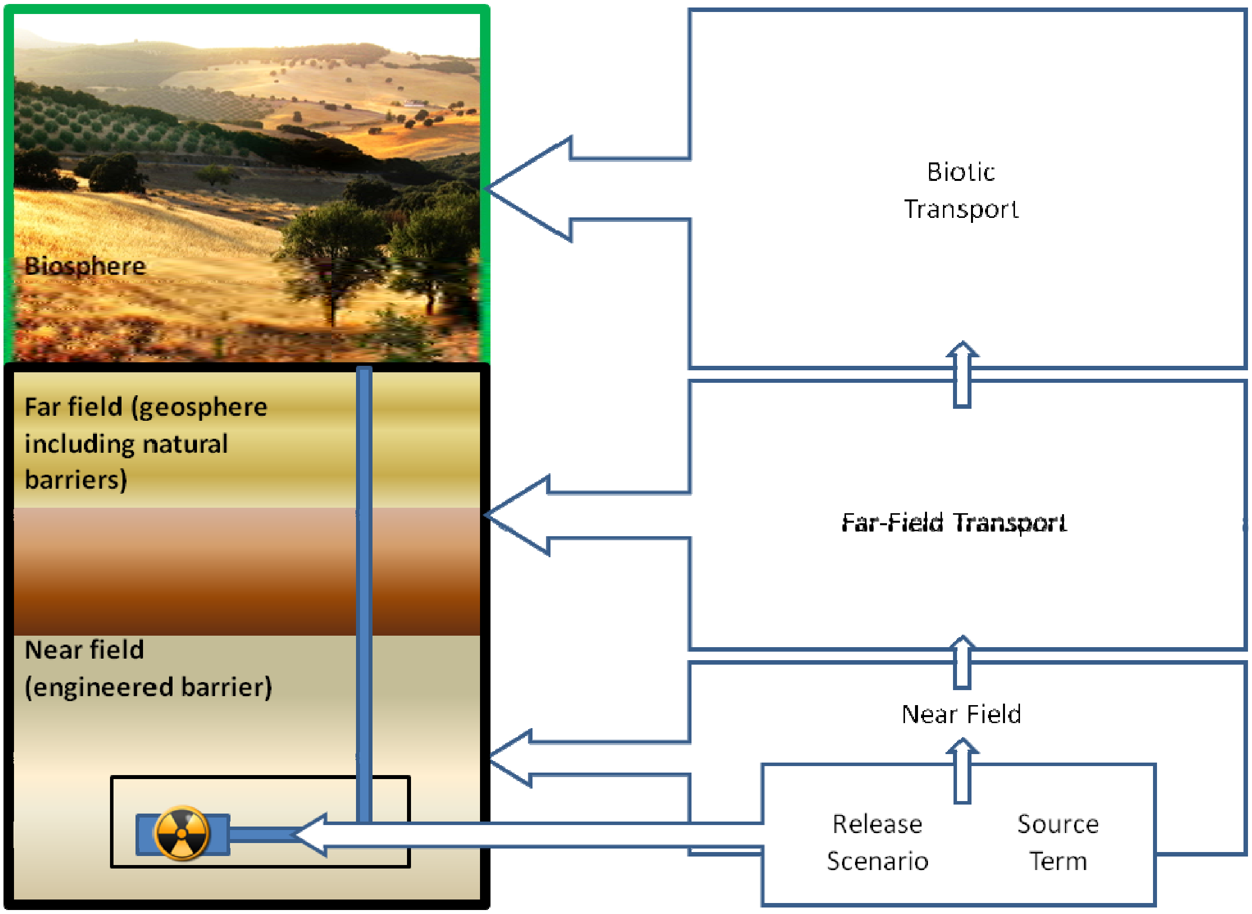


Figure 3. Conceptual zones used for simplifying discussions on environmental transport. This example is based on consideration of the design for a geologic repository. It is adapted from an illustration of work undertaken at the Grimsel Test Site. The original can be found at http://www.grimsel.com/general/bg_ebs.htm

Release Scenario Determination and Source Term Quantification

"Source Term" is a phrase that is used to describe the radioactive material which is the object of calculations. As shown in Figure 2, it is represents the first step in assessing impacts. Source term descriptions caninclude the quantity of the radionuclides being evaluated (in Bq, kg, or some other unit), by nuclide (e.g., ^{137}Cs) or by other identifiers (i.e., gross alpha, beta-emitters). However in addition to the source term, there is other information which is necessary to undertaking an assessment. This is called the "release scenario". One of the considerations in getting the radioactive material to move through the environment is knowing how it is/was/will be released. In prospective analysis there are a number of options which can be considered. Is a catastrophic event responsible for quickly moving the material out of its initial condition? Is it a chronic release? How should degradation of the form of the material and its surround be addressed? In retrospective analyses, presumably, the release mechanism is known, although accurately describing it may be difficult. In some ongoing discharges, the release mechanism will be specified by regulation (e.g, direct discharge through a stack or pipe discharge).

There is also the issue of the time frame over which the release occurs. It may happen very quickly – in the event of an energetic release scenario (e.g., a criticality, an earthquake, a chemical explosion), or it make transpire over very long periods of time as the material slowly diffuses out of its initial location. The type and quantify of radioactive material, as well as the physical (solid, liquid, gaseous?) and chemical form (reactive or corrosive?) can also influence how rapidly the release occurs. Past instances with nuclear waste have shown that radiolysis can evolve gases such as hydrogen to create explosive conditions in waste forms.

The source term and the attendant mechanism of release represent a critical starting point for an assessment effort.

Engineered & Natural Barriers

Engineered barriers are designed to delay, direct, and generally control the release of radioactive material such that they can be safely contained for some desired period of time. They are not solely the province of deep geologic repositories. They can, for example be relatively simply systems, such as those that are designed to cover tailings piles in order to minimize radon gas exhalation rate and control erosion. Engineered barriers also can include sophisticated designs, such as those being constructed for modern low-level waste repositories. In the U.S., engineered barriers utilized for radioactive waste disposal facilities are defined by the U.S. NRC in 10CFR61.2.

Natural barriers also play a significant (and in some cases the primary) means of controlling radionuclide release. Features of the natural environment include the ability of the soil or rock to sorb radionuclide or chemical constituents. Clay soils may be used because of their low hydraulic conductivity. Sites can be selected based on environmental considerations such as the absence of rainfall, type of native vegetative cover, range of expected temperatures. The surface topography may also be a factor –such as low slopes to minimize erosion. Depth to groundwater and distance to streams, rivers and lakes may also be a determining factor.

Three types of systems designed for the containment of radioactive waste arising from the nuclear fuel cycle will be briefly discussed. This is by no means an exhaustive list, but is used to highlight different approaches to minimizing environmental transport.

Low-level waste sites

Low level waste burial sites have undergone considerable evolution since they were originally created. Early waste disposal sites were not much more than a shallow excavation in the soil where radioactive wastes were haphazardly discarded and then covered over with soil. Instances of flooding of waste sites (with subsequent “floating” of buried drums); or human, animal and plant intrusion into sites (with redistribution of radioactive materials) led to greater emphasis on site selection and control as well as trench and cover design. Figure 4 is an example of potential failure mechanisms for a poorly designed low-level waste site.

Today, low-level waste sites are intended to contain moderately radioactive materials which do not pose a long term hazard. They are built to guard against accidental intrusion by humans and other biota (i.e., plants and animals), preclude the infiltration of water, and contain the radioactive constituents until they have undergone sufficient radiological decay as to no longer be considered a threat. The designs of facilities are varied, but they are generally include a subsurface trench (which may be lined or not), with a layered cover. Newer approaches have considered how natural features can be utilized to optimize waste site design to preclude failure and prolong the integrity and lifespan of the site. These designs can vary based on the environment in which they are located. In some instances shallow rooted vegetation is encouraged as a means to help minimize erosion and to control water infiltration. For an example of one design used outside the U.S., see that used at the Radium Hill site in South Australia.

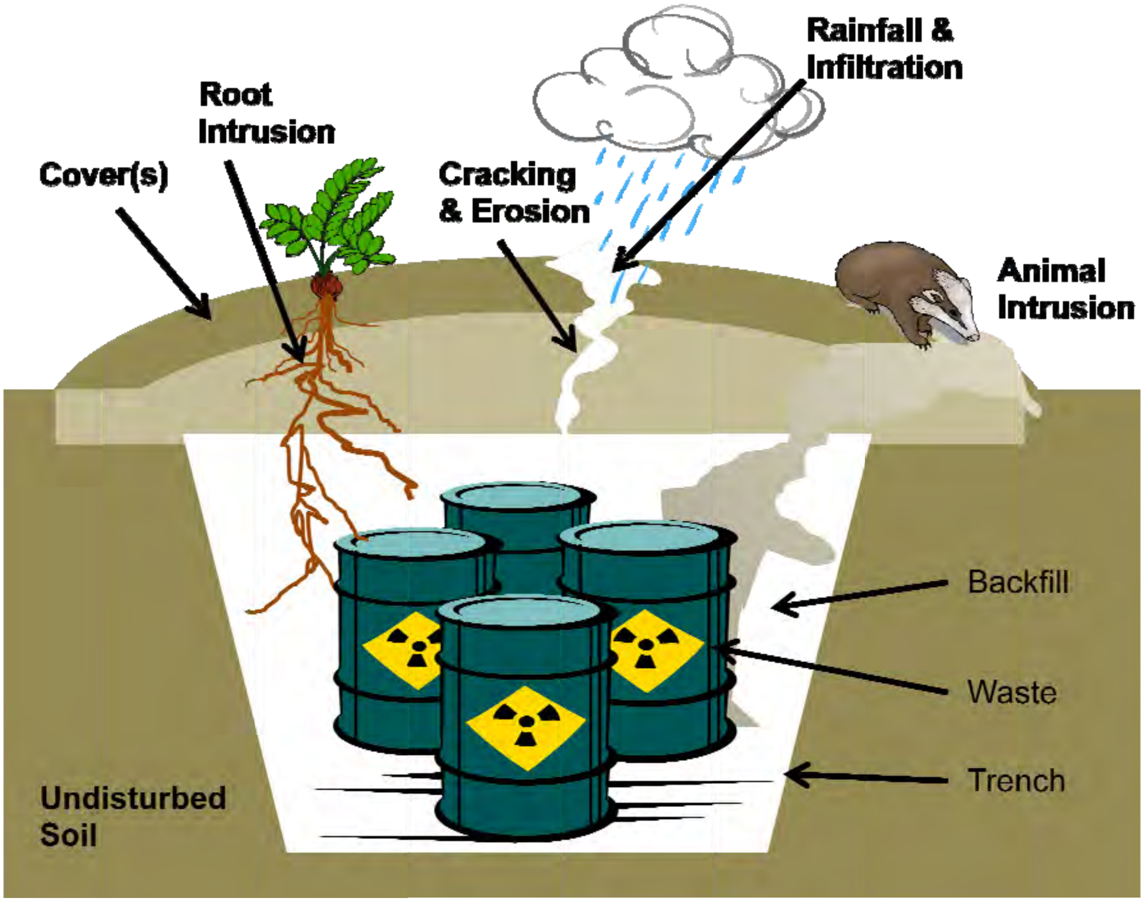


Figure 4. Example of seepage, intrusion, and runoff transport pathways that have lead to cover failure and migration of wastes from past practices at surface disposal sites. Such failures have led to substantial revision in the design of such facilities. After Hakonson.

<u>Liquid Waste Storage Facilities</u>

Reprocessing of nuclear fuel, particularly during the cold war, led to the creation of highly radioactive waste products. This waste included residues of dissolved fuel, cladding, organic solvents used in the separations process as well as acids, metals and a host of other chemicals. For the nuclear weapons production program it was important to extract and purify as much plutonium as possible for creation of warheads. Consequently, large volumes of this “chemically aggressive waste fluids” were produced. They were stored in enormous (ML) tanks, such as the one depicted in Figure 5 from the Hanford Site. Because of their propensity to leak after decades of storage, most of the tanks were dewatered, leaving an intensely radioactive sludge.

The tanks were typically constructed on a gravel and concrete pad, with a tank liner of steel overlain with concrete, and the entire system backfilled with gravel and soil. Several access ports were installed in the tank, allowing for the introduction and removal of waste, as well as to provide for sampling and analysis. These systems were not intended for final disposal of waste, but provided a means to contain the material during processing activities.

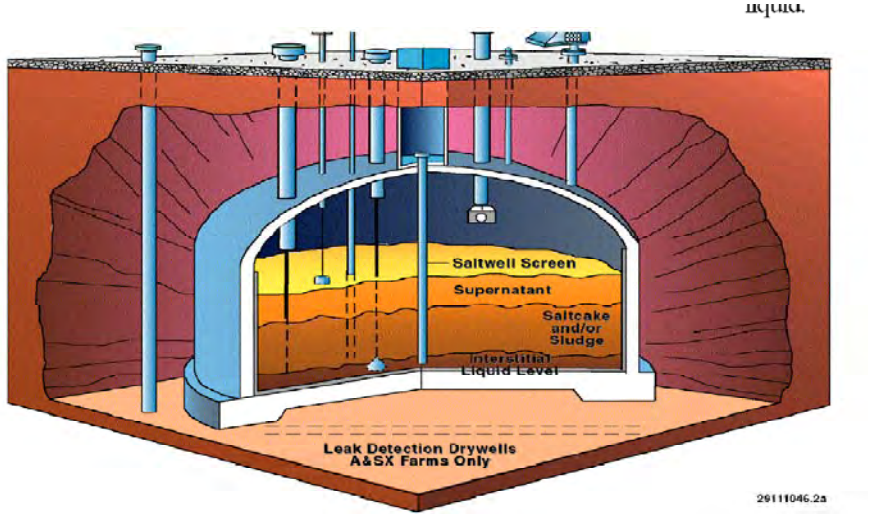


Figure 5. Waste tank used for interim storage of high level radioactive waste at the Hanford site. Such tanks are destined for closure. From http://www.hanford.gov/hanford/files/TPA_HUSummer2007.pdf

<u>Geologic repositories</u>

Geologic repositories are intended to contain long-lived radioactive wastes, such as transuranics (for example the isotopes of plutonium) or spent nuclear fuel (which includes short and long-lived fission products as well as the neutron-activated components of the fuel cladding). In the early years of nuclear era a number of alternative disposal options for this waste were considered. These included placement beneath ice-sheets, deep-ocean disposal, and launching rockets to the sun. The option recommended for disposal of these wastes in the U.S. is deep geologic disposal. It is not the intention of this paper to explore the basis for the selection of the current repository sites. However, transuranic wastes are currently being disposed of in the bedded salt near Carlsbad, New Mexico. Yucca Mountain in Nevada is undergoing characterization for purposes of disposing high-level wastes. Both sites have been selected because of the geologic stability of the sites, the minimal moisture content, and the low population density near the sites.

The proposed design for the Yucca Mountain site is shown in Figure 6. The system under consideration utilizes a combination of engineered and natural barriers to retard the movement of radionuclides from the waste and into the biosphere.

The U.S. is not the only country that is in the process of identifying and characterizing sites for nuclear waste disposal. Substantial work is underway in several countries. The Grimsel Test Site (which is not a repository), is being used to study and identify key characteristics for waste emplacement. Figure 7 illustrates one of the waste-emplacement designs being assessed.

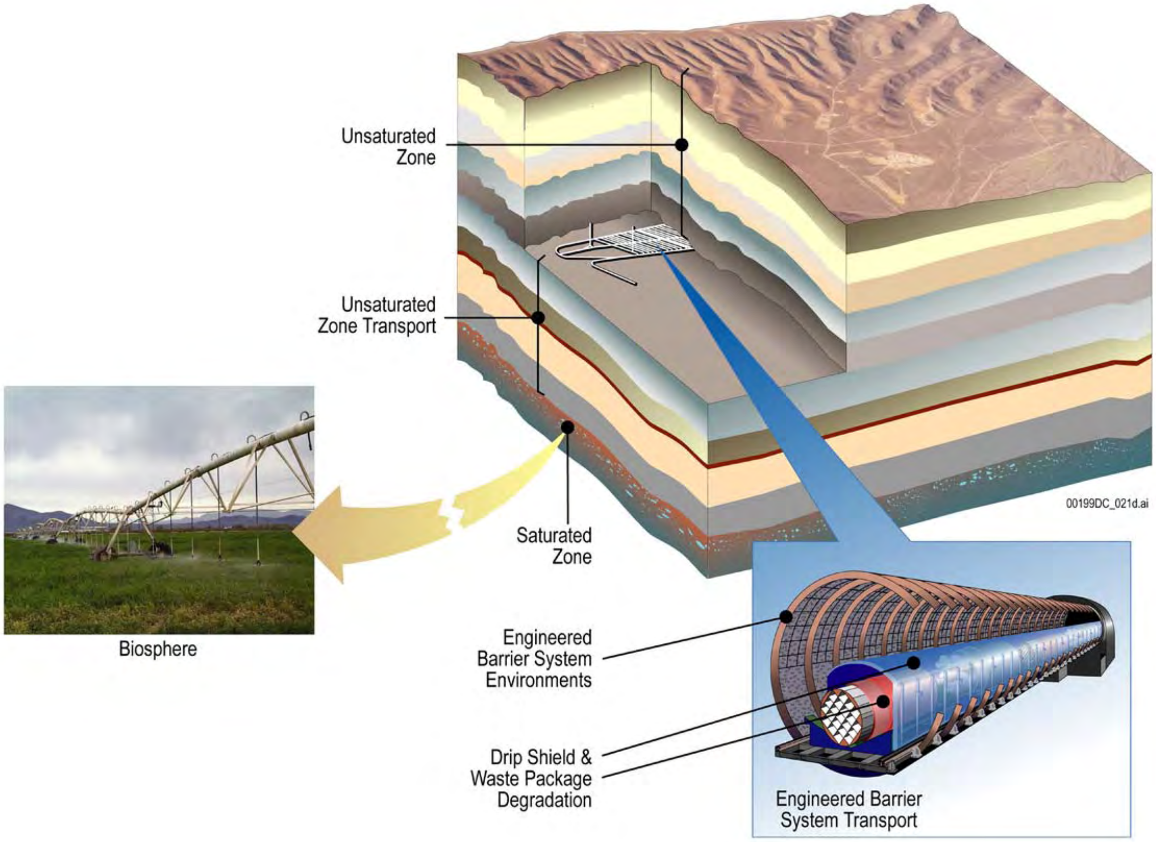


Figure 6. An example of an engineered barrier. This particular design is proposed for waste disposed at the Yucca Mountain Repository and illustrates both engineered and natural barriers to transport. Image from http://ocrwm.doe.gov/info_library/newsroom/photos/photos_graphics.shtml

The illustration in Figure 7 is similar to that for Yucca Mountain, but is being assessed by the European Commission Joint Research Centre Institute for Transuranium Elements (see http://itu.jrc.ec.europa.eu/index.php?id=169). Nuclear waste in corrosion resistant containers will be emplaced in impermeable rock and backfilled with concrete. Studies are currently ongoing to determine parameters that control the rate of release from this system.

Figure 7. Example of an engineered and natural barrier designed to complement. After a design considered by the European Commission. See: http://itu.jrc.ec.europa.eu/index.php?id=169

Considerations for Transport in the Near Field

As previously noted, environmental transport in the near field can be the result of physical, chemical, and biotic processes. In Section A an example was given where radioactive liquid was discharged from a facility into a receiving body of water. In this example the dominant physical factors that dictate the initial transport include the flow rate of liquid from the discharge pipe and the volume and velocity of the receiving body of water. These can determine if turbulent mixing is likely to occur. Another physical parameters that could impact the mixing (and ultimately dilution) of the waste stream is the temperature of both systems. A substantial temperature elevation of the waste stream may cause it to remained buoyant and constrain initial mixing. Chemical speciation of the waste, and the turbidity of the stream (a combination of physical and chemical aspects of the environment), determine if the radionuclides sorb to suspended particulates in the water or remain in solution. The acidity or alkalinity of the either the discharge or receiving water can also play a role in keeping radionuclides in solution and facilitating downstream transport rather than having them precipitate out of the water column. If the waste stream contains particulates (such as specks of activated fuel cladding or failed fuel), then settling from the water column can occur as it is transported downstream. Finally, the presence of biota, such as algae, can result in concentration and retention of radionuclides in aquatic environments.

Unlike liquid wastes, solid wastes must escape from their containment and then diffuse or be mobilized in some fashion. Water, either from surface infiltration or from subsurface systems is considered one of the principal means for mobilizing radionuclides from a waste package. However wastes can be volatilized if heat from radioactive decay (or other means) is sufficiently high. One example of such an occurrence is at the 200-Area tank farm at the Hanford Site.

Sludges generated as waste byproducts of the plutonium production effort were stored in million gallon tanks (e.g., Figure 5). These wastes, which included extraordinarily high levels of radioactive fission and activation products were mixed in with chemically reactive constituents. Characteristics of this waste included very high temperatures (in some cases the waste tanks were boiling) and being quite corrosive and reactive. This combination resulted in degradation of the waste tank walls (steel and concrete) and leakage of the waste into the surrounding unsaturated soils. The elevated temperatures of the tanks caused precipitation of solids near the tank, and dehydration of areas in the vicinity of the tank. This combination resulted in a complex situation of multiphase fluid flow and heat transfer.

A somewhat similar challenge faces the scientists and engineers modeling high-level waste repositories. For these systems one needs to accurately model large-scale coupled processes in systems that are not homogeneous, Figure 8. The sheer enormity of the problem, requiring analysis of systems in three dimensions with very large time scales requires considerable computational power. Issues that have to be considered for this environment include multiphase systems (gas, liquid, vapor), fractures in the host rock, porous rocks, chemical interactions with the host matrix, moisture flow as a consequence of heating from the waste forms, mechanical stresses, and radiation-induced physical-chemical processes (such as gas evolution). Other issues that have to be dealt with include the extent of water infiltration, water balance, and the depth of the unsaturated and saturated zones (see Figure 6 for an example).

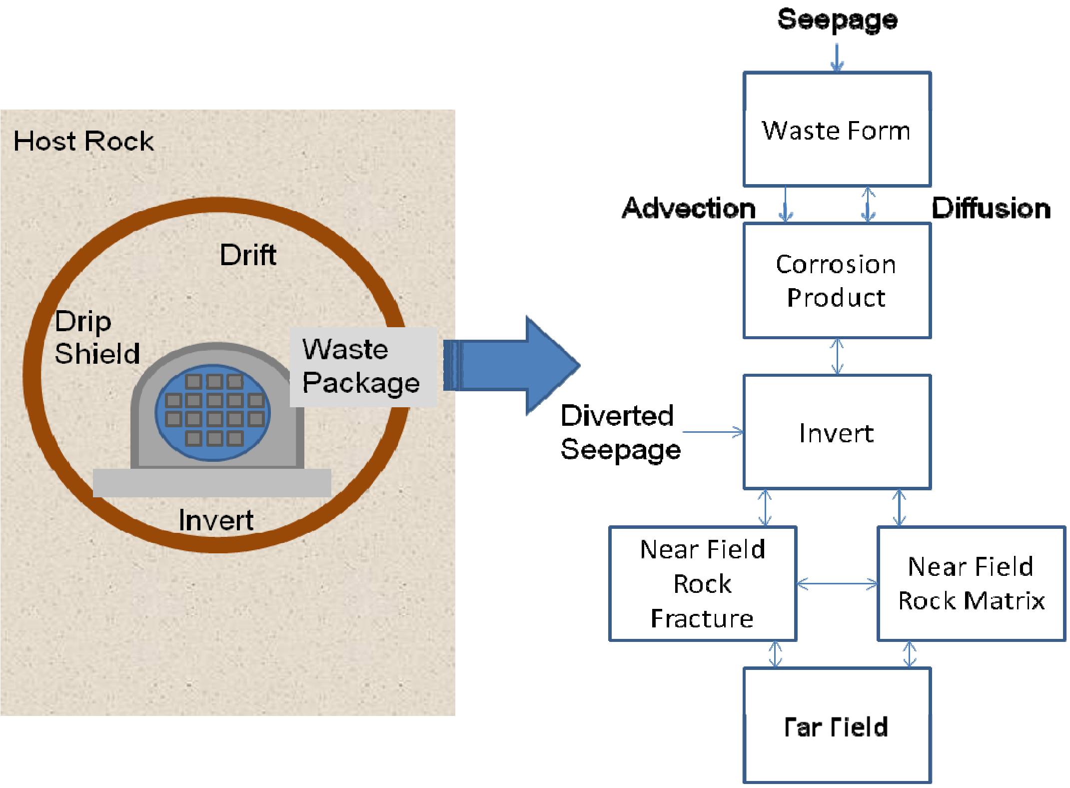


Figure 8. An example of processes that must be modeled in the waste package and near field to predict the release and migration of radionuclides in a geologic repository. This example is from studies ongoing at Yucca mountain. After the illustration at http://monitorsci.com/software/index.html

Maintaining the integrity of the waste form is critical to slow the migration of radionuclides from waste. Waste package degradation has been extensively studied for Yucca and many other proposed sites. Figure 8 graphically illustrates some factors that scientists are modeling in their efforts to determine the durability of waste packages proposed for Yucca Mountain (definition of terms such as durability can be found at [29]). Work ongoing at Yucca Mountain has also examined the significance of corrosion in the near field.

In summary, movement of radionuclides in the near field (including the waste form) is dictated by a host of processes, including physical, chemical, and biotic mechanisms. A by no means complete list includes how:

- heat flow and changes in temperature in the surroundings due to radioactive decay can act as a driving force ;
- stress and strain in the waste package can result in package failure;
- the properties of host-rock and the interface with the engineered barrier influence transport;
- inhomogeneity in the host material can facilitate, or retard transport;
- fractures in the host rock can provide preferential flow paths;
- movement of fluids in and adjacent to the waste can dissolve the waste form, corrode the waste package and mobilize the contents;
- sorption of radionuclides to rocks and engineered components can retard migration;
- facilitated transport of nuclides can occur by large molecules such as humic acids and colloids; and,
- alteration of chemical phases in the vicinity of waste canister can expedite transport.

Considerations for the far-field

The far field is outside the engineered and altered natural environment which contains the waste. Excluding issues surrounding degradation of the waste form, and temperature effects attributable to the waste, most of the processes contributing to near field transport also occur in the far field. Inhomogeneities in the far field can pose challenges equally vexing as those presented in the near field. The structure of the receiving environment can be extremely complex, making the potential transport paths to the biosphere difficult to ascertain (or to model). One example is the fractured nature of Karst topography featured at the Oak Ridge site, and the difficulties it causes in modeling groundwater transport. The reader is directed to the work of Thiessen et al, which discusses some of the issues related to the use of models in radionuclide distribution and transport assessments.

There may be multiple pathways of transport which may contribute to the exposure and dose of receptors (e.g., humans and other biota). A conceptual diagram that illustrates this process is shown below in Figure 9. It is incorrect to assume that the processes responsible for moving the radionuclide through the far-field are simpler than those operating in the near field. While the underlying physic/chemical interactions are generally understood, data are lacking for specific nuclides for a number of the processes represented by the transfer arrows in Figure 9. As a consequence, predictions of transport are often based on the use of surrogates or the presumption of chemical behavior of the radionuclides.

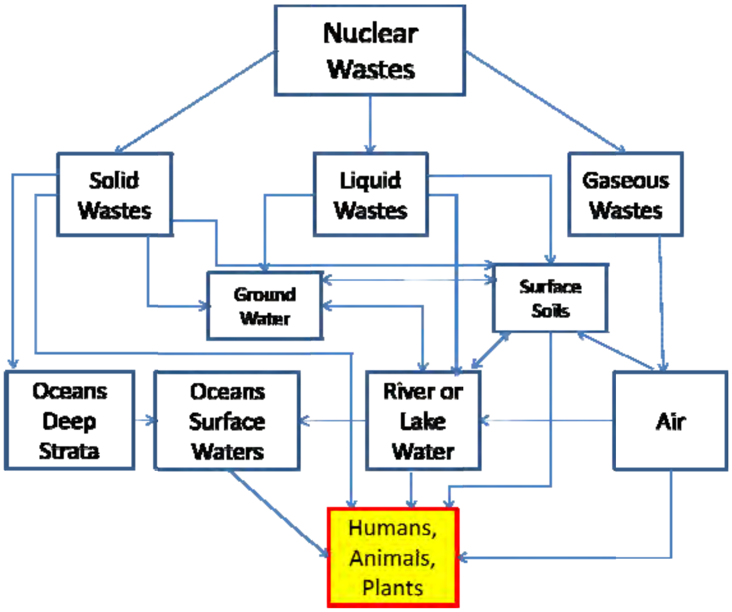


Figure 9. A simplified conceptual model of environmental transport pathways through the far field into the biosphere. After the drawing of Peterson in Till and Meyer, Ch 5[4].

In radiological risk assessments there also is often a “disconnect” between the transport calculations and the exposure assessment (see Figure 2 for a depiction of the process). Typically the near and far field modeling is based on fundamental physico/chemical processes. However, in the exposure portion of a radiological assessment, the extent of contact with the contaminants is frequently scenario-based.

Not shown in Figure 9 are the biotic processes which ultimately lead to exposure and dose of individuals. One example of these is shown in Figure 10 for exposure of humans to the direct discharge of radionuclides to the air and water. Figure 10 minimizes the complexity of the transport pathways and focuses on the complexity of the exposure and uptake pathways. Uptake of radionuclides into plants and animals is done using empirically-obtained transfer coefficients. The transfer coefficients relate concentration of a contaminant in an environmental compartment (e.g., soil) to biota (e.g., corn). Implicit in the exposure analysis is that the transfer of radionuclides through all of these compartments is known for all nuclides under consideration. The reality is that assumptions are often made for uptake, based on comparison to chemically similar species.

The exposure scenarios are crafted based on consideration of standard/routine behaviors likely to result in contact with the radioactive material. This may be behavioral in origin (from specific studies) or may utilize standardized, and generally accepted, exposure scenarios such as “resident-farmer”, “office-worker”, or “recreational visitor”. Estimates of contact extent (e.g., consumption rates, showering rates, indoor/outdoor residence time) may be drawn from surveys such as the National food consumption survey.

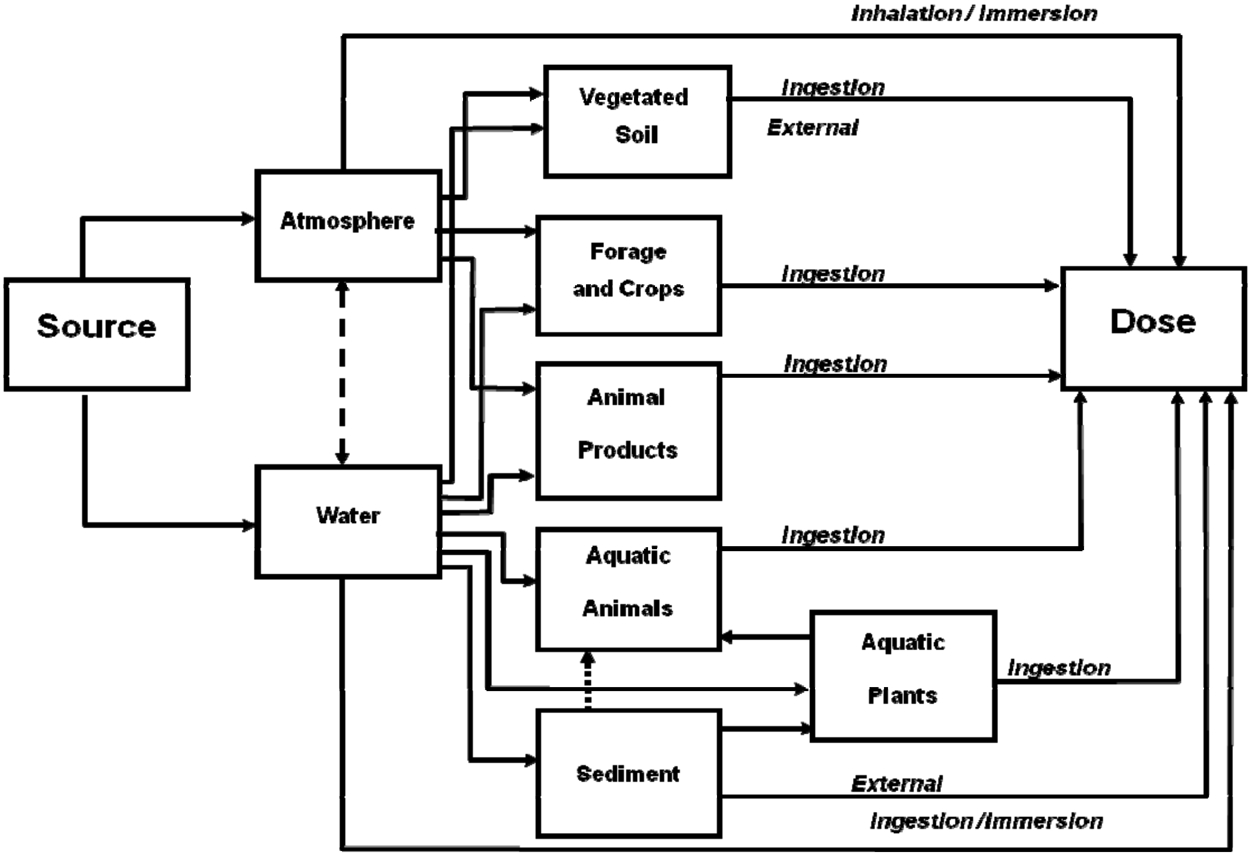


Figure 10. A simplified model of radiation exposure and uptake pathways for humans

Because of the use of scenarios and transfer coefficients, there is some degree of subjectivity in the determination of exposure and dose. Several studies have looked at this issue and have proposed approaches to limit variability.

Separate from human exposure assessment is an area that is still evolving: radiological dose assessment for nonhuman biota. Until recently dose calculation to species other than humans were regarded as unnecessary in radiological assessments. Transport and exposure pathways were evaluated predominantly for biota present in the human food chain. Changes in philosophy regarding protection of the environment, as well as the need to be more comprehensive in assessing impact have resulted in a revisiting of this approach.

Results obtained to date suggest that doses to non human biota arising from modern fuel cycle activities are likely to be low. However, the effort is in its infancy, and made more difficult because of the complex nature of food webs in nature. The requirement to make predictions of radionuclide transfer at many trophic levels in an ecosystem in order to fully assess uptake and exposure of a particular species is formidable. An example of biotic compartments that might be considered in the assessment of dose from a release to an aquatic environment is shown in Figure 11, below. As can be seen from this illustration, dose assessment for a fish-eating bird necessitates prediction of radionuclide concentration in all its food sources and their precursors. Dose assessment of non human biota is still evolving, and the tools are still be developed and debated. The U.S. currently has one standard in place for radiological protection of the environment.

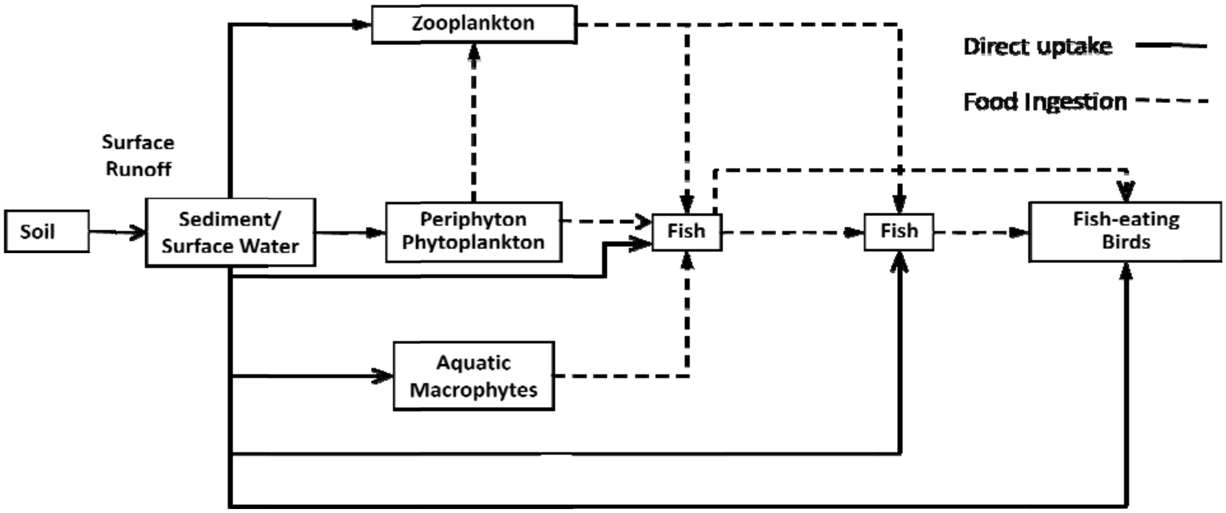


Figure 9. An example of some of the exposure routes in which would need to be considered in a radiological dose assessment for biota in an aquatic environment.

Summary

The objective of this paper was to review factors which contribute to environmental transport of radionuclides from releases throughout the fuel cycle. An approach to conceptualizing the significant processes was provided, and major constituents of each were discussed. Traditional approaches to understanding and predicting transport (and fate) were presented, along with areas where more research might be needed. Above all, the reader is encouraged to delve in to the scientific literature, both peer-reviewed and gray, where it is abundantly clear that there is still room for improvement and research!

References

1. Till, J.E.a.G., H.A. , *Radiological Risk Assessment and Environmental Analysis*. 2008, Oxford, New York: Oxford University Press.
2. Eisenbud, M.a.G., T., *Environmental Radioactiviy, From Natural, Industrial, and Military Sources*. 1997, San Diego: Academic Press.
3. Whicker, F.W.a.S., V., *Radioecology: Nuclear Energy and the Environment*. Vol. 2 volumes. 1982, Boca Raton, FL: CRC Press.
4. Till, J.E.a.M., H. R., *Radiological assessment. A textbook on environmental dose analysis*. 1983. p. Size: Pages: 882.
5. Whicker, F.W., et al., *Radioactive contamination: state of the science and its application to predictive models.* Environmental Pollution, 1999. 100(1-3): p. 133-149.
6. MacKenzie, A.B., *Environmental radioactivity: experience from the 20th century -- trends and issues for the 21st century.* The Science of The Total Environment, 2000. 249(1-3): p. 313-329.
7. Measurements, N.C.o.R.P.a., *Public Radiation Exposure from Nuclear Power Generation in the United States*. 1987: National Council on Radiation Protection and Measurements.
8. Radiation', U.N.S.C.o.t.E.o.A., *Sources and Effects of Ionizing Radiation: United Nations Scientific Committee on the Effects of Atomic Radiation : UNSCEAR 2000 Report to the General Assembly, with Scientific Annexes*. 2000, United Nations Publications.
9. Agency, E.P., *40 CFR Part 191: Environmental radiation protection standards for the management and disposal of spent nuclear fuel, high-level and transuranic radioactive wastes; final rule*. 1993, Federal Register.
10. Commission, U.S.N.R., *10 CFR 20 Standards for Protection Against Radiation*, Federal Register.
11. Committee on Improving the Scientific Basis for Managing Nuclear Materials and Spent Nuclear Fuel through the Environmental Management Science Program, N.R.C., *Improving the Scientific Basis for Managing DOE's Excess Nuclear Materials and Spent Nuclear Fuel*. 2003: The National Acadamies Press.
12. Schwartz, A.J., et al., *Characterization and modelling of helium bubbles in self-irradiated plutonium alloys.* Philosophical Magazine, 2005. 85: p. 479-488.
13. NAS, *End Points for Spent Nuclear Fuel and High-Level Radioactive Waste in Russia and the United States*. 2003, The National Acadamies Press.
14. NRC, U.S., *Part 60--Disposal of High-Level Radioactive Wastes in Geologic Repositories*, in *10*, U.S.N.R. Commission, Editor.
15. DOE, U.S., *Directions in low-level radioactive waste management: A brief history of commercial low-level radioactive waste disposal*. 1990. p. Size: Pages: (93 p).
16. Hakonson, T.E., et al. *Some interactive factors affecting trench-cover integrity on low-level waste sites. [Shallow land burial]*. 1982. United States.
17. Kyong Won Han, J.H., and Arnold Bonne, *Special Report: Radioactive waste disposal: Global experience and challenges*, in *IAEA Bulletin*. 1997, International Atomic Energy Agency.
18. Bedinger, M.S., *Geohydrologic aspects for siting and design of low-level radioactive-waste disposal*. 1991, United States: Denver, CO (US) ;Geological Survey. Pages: (36 p).
19. James H. Clarke, M.M.M.E.D.S.R.J.D.W.J.W., *Engineered Containment and Control Systems: Nurturing Nature.* Risk Analysis, 2004. 24(3): p. 771-779.
20. Mcleary, M., *Radium Hill Uranium Mine and Low Level Radioactive Waste Repository, Management Plan, Phase I Preliminary Investigation, 2004*, D.o.P.I.a.R. South Australia, Editor. 2004.
21. Gephart, R.E., *Hanford: a conversation about nuclear waste and cleanup*. 2003: Battelle Press.

22. Pruess, K., et al., *Fluid Flow, Heat Transfer, and Solute Transport at Nuclear Waste Storage Tanks in the Hanford Vadose Zone.* Vadose Zone J, 2002. 1(1): p. 68-88.
23. NAS, *Disposition of High-Level Waste and Spent Nuclear Fuel: The Continuing Societal and Technical Challenges*. 2001: The National Acadamies Press.
24. Bluumlmling, P., *Borehole Sealing Project at the Grimsel Test Site.* Geotechnical and Geological Engineering, 2005. 23: p. 843-858.
25. Wu, Y.-S., C. Haukwa, and G.S. Bodvarsson, *A site-scale model for fluid and heat flow in the unsaturated zone of Yucca Mountain, Nevada.* Journal of Contaminant Hydrology, 1999. 38(1-3): p. 185-215.
26. Mohanty, S., et al., *An approach to the assessment of high-level radioactive waste containment -- II: radionuclide releases from an engineered barrier system.* Nuclear Engineering and Design, 2000. 201(2-3): p. 307-325.
27. Malekifarsani, A. and M.A. Skachek, *Effect of precipitation, sorption and stable of isotope on maximum release rates of radionuclides from engineered barrier system (EBS) in deep repository.* Journal of Environmental Radioactivity. In Press, Corrected Proof.
28. Forsberg, C.W., *Repository criticality control with depleted uranium dioxide cermet waste packages*, in *Embedded Topical Meeting on Practical Implementation of Nuclear Criticality Safety, American Nuclear Society, November 11–15, 2001*. 2001: Reno, Nevada.
29. T. H. Fanning, T.H., Bauer, E.E., Morris, and R.A. Wigeland, *A generalized definition for waste form durability*, in *American Nuclear Society Fifth Topical Meeting - DOE Spent Nuclear Fuel and Fissile Material Management*. 2002: Charleston, South Carolina.
30. Hua, F., et al., *Some Materials Degradation Issues in the U.S. High-Level Nuclear Waste Repository Study (The Yucca Mountain Project)*, in *Other Information: PBD: 19 Sep 2005*. 2005. p. Size: 46 pages.
31. Gens, A., Guimaraes, L. do N. Garcia-Molina, A. Alonso, E. E., *Factors controlling rock-clay buffer interaction in a radioactive waste repository.* Engineering Geology, 2002. 64(2-3): p. 297-308.
32. Möri, A., et al., *The colloid and radionuclide retardation experiment at the Grimsel Test Site: influence of bentonite colloids on radionuclide migration in a fractured rock.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2003. 217(1-3): p. 33-47.
33. Shevenell, L. and J.F. McCarthy, *Effects of precipitation events on colloids in a karst aquifer.* Journal of Hydrology, 2002. 255(1-4): p. 50-68.
34. Thiessen, K.M., et al., *Modelling radionuclide distribution and transport in the environment.* Environmental Pollution, 1999. 100(1-3): p. 151-177.
35. Amiro, B., *Frontiers of environmental radioactivity.* Journal of Radioanalytical and Nuclear Chemistry, 1999. 239(1): p. 45-52.
36. U.S. Dept. of Agriculture, H.N.I.S., Consumer Nutrition Center, *Nationwide Food Consumption Survey 1977-78*, C.N.C. (U.S.), Editor. 1978, U.S. Dept. of Agriculture, Human Nutrition Information Service, Consumer Nutrition Center.
37. Igor Linkov, D.B., *Model Uncertainty and Choices Made by Modelers: Lessons Learned from the International Atomic Energy Agency Model Intercomparisons&#x2020.* Risk Analysis, 2003. 23(6): p. 1297-1308.
38. Davis, P.A., et al., *BIOMOVS II: An international test of the performance of environmental transfer models.* Journal of Environmental Radioactivity, 1998. 42(2-3): p. 117-130.
39. Morris, R.C., *Applying DOE's Graded Approach for assessing radiation impacts to non-human biota at the INL.* Journal of Environmental Radioactivity, 2006. 87(1): p. 77-100.
40. Higley, K.A., S.L. Domotor, and E.J. Antonio, *A probabilistic approach to obtaining limiting estimates of radionuclide concentration in biota.* Journal of Environmental Radioactivity, 2003. 66(1-2): p. 75-87.
41. DOE, U.S., *A Graded Approach for Evaluating Radiation Doses to Aquatic and Terrestrial Biota*, U.S.D.o. Energy, Editor. 2002: Washington, D.C.

42. Pentreath, R.J. and D.S. Woodhead, *A system for protecting the environment from ionising radiation: selecting reference fauna and flora, and the possible dose models and environmental geometries that could be applied to them.* The Science of The Total Environment, 2001. 277(1-3): p. 33-43.
43. Beresford, N.A., et al., *Estimating radionuclide transfer to wild species—data requirements and availability for terrestrial ecosystems.* Journal of Radiological Protection, 2004. 24(4A): p. A89-A103.
44. K. John Holmes, J.A.G.T.M.C.W., *Regulatory Models and the Environment: Practice, Pitfalls, and Prospects.* Risk Analysis, 2009. 9999(9999).
45. Beck, M., et al., *On the problem of model validation for predictive exposure assessments.* Stochastic Environmental Research and Risk Assessment, 1997. 11(3): p. 229-254.

Modeling and Simulation of Nuclear Fuel Recycling Systems

David DePaoli
Oak Ridge National Laboratory

The effective utilization of nuclear power through the use of a sustainable fuel cycle will require the development of efficient systems that address issues of cost, safety, waste, and proliferation. Computing power has grown tremendously over the past several decades, as has the capability of scientific codes to simulate complex systems. This growth, coupled with increased interest in an expected resurgence of nuclear power, provides great opportunity for the application of advanced modeling and simulation for responsible development of future nuclear energy systems.

Expected potential benefits of modeling and simulation of nuclear reprocessing systems include the following:

- Reduced cost of process development by guiding and minimizing the amount of experimental and piloting work required
- Optimized system designs, with technically supported reduced design margins
- Development of new chemical processes with lower cost and waste generation
- Reduced risk of material diversion by providing accurate predictions of materials streams

This article provides a brief overview of the application of modeling and simulation for separations processes relevant to nuclear fuel recycling. This is a subset of the applications for modeling and simulation of the nuclear fuel cycle; the reader is directed to references of systems analysis fuels, waste forms and near-field repositories for discussion of those areas.
The references in this article consist of open-literature publications; therefore, discussion of developments and application of nuclear process model technology is limited to that which is publicly available. The reader is also directed to reports of recent workshops which provide more detailed information on the current state of understanding and opportunities for the future.

Background

The panel report on predictive modeling and simulation from the recent Basic Energy Sciences Workshop on Basic Research Needs for Advanced Nuclear Energy provides a concise description of modeling and simulation and its applicability to nuclear energy systems:

> Modeling and simulation is now considered to be the third branch of science, bridging experiment and analytical theory. Through modeling one incorporates the most relevant theories and concepts developed by the full range of scientific and engineering disciplines. Through simulation one exploits leading-edge computational methods, algorithms, and platforms to obtain results unattainable by any other means. Together modeling and simulation enhance understanding of known systems, provide qualitative/quantitative insights and guidance for experimental work, and produce quantitative results that replace difficult, dangerous, or expensive experiments. These advantages are well suited to basic research for (Advanced Nuclear Energy Systems) because of the experimental difficulties posed by radioactive materials and harsh environments.

While it is understood that modeling and simulation will not supplant experimental testing, the value of modeling and simulation has long been recognized for multiple tasks in the development, design, and operation of reprocessing systems. For example, a 1979 paper on the SEPHIS code for transient simulation of countercurrent solvent extraction indicated it could be used to “(1) guide flowsheet optimization studies and thus minimize the amount of experimentation required to establish a particular set of operating conditions; (2) aid in a nuclear criticality analysis of the solvent extraction plant; (3) analyze the transient response to startup or shutdown operations and optimize methods of control; (4) study the effects of a process upset caused by component failure, process solution error, or change in feed characteristics, and the return of the process to normal operation on correction of the problem; (5) aid in maintaining an exact inventory of security-sensitive materials for nuclear safeguards purposes; (6) help maintain process control in an automated solvent extraction plant."

A memorandum from 1990 lists the following potential uses envisioned for a process simulator of a full reprocessing plant:

- Operator training
- Plant licensing
- Safeguards studies
- Process and/or chemical flowsheet design confirmation
- Safety studies
- Process diagnostics
- Process monitoring
- Sensitivity studies
- Modeling destination of minor streams having environmental impact
- Process instrumentation studies
- Surge capacity studies

Modeling an aqueous reprocessing plant to a sufficient level of realism to accomplish the tasks listed above is a significant undertaking. As detailed elsewhere in this course, the overall process involves many interconnected steps, each of which entails complex physical and chemical phenomena. Fuel disassembly involves mechanical processes (chopping, clad removal, filtration), chemical dissolution in strong acid, and feed clarification. The fuel solution is then passed through several stages of solvent extraction in order to separate several fission product and actinide streams. Multiple solvent extraction processes are required to accomplish this separation, each using different additives and components in the organic phase, as well as different acid concentrations in the aqueous phase. The separated streams containing the isolated species are further processed and solidified to produce materials meeting specifications for fuel and waste forms. Supporting systems, including those for solvent recovery and off-gas treatment, are also integral parts of a complete plant. Safety and environmental considerations require (1) monitoring of volatile fission product and organic gaseous releases, (2) careful evaluation of component inventories throughout the system, (3) strict attention to nuclear criticality safety in actinide solutions with widely varying component inventories, and (4) control systems that are based on realistic models of processes.

Previous Work

Development of models of aqueous reprocessing systems has historically focused primarily on the solvent extraction steps, which constitute the main separations in the process. The goal is to predict the performance of countercurrent extraction processes, in which the constituents of dissolved spent nuclear fuel are separated by selectively transferring metal ions between aqueous solutions and organic solvents containing complexing agents in a series of fluid-contacting devices. The separations performance is governed by a complicated interplay between reaction kinetics, interfacial mass transport, fluid dynamics, and thermodynamics in highly nonideal, multicomponent, multiphase chemical systems.

Starting in the 1960's, computer models were developed to convert equilibrium distribution data and material balance equations into stagewise calculations for predicting steady-state concentration profiles in solvent extraction processes. A significant amount of effort was subsequently spent during the following two decades to improve the predictive capability of several different model families, including SEPHIS, PUMA, SOLVEX, and AMUSE. Development of these codes has been primarily focused on the partitioning of uranium and plutonium in PUREX systems; however, other systems have been addressed to some extent. AMUSE, initially developed for the TRUEX flowsheet, has been modified to provide predictions of PUREX, UREX, SREX, and, with input of appropriate experimental data, flowsheets for other processes, including CSSX, CCD-PEG, and TALSPEAK. SEPHIS modules have been written for THOREX, BUTEX, and a process for co-extraction of plutonium and neptunium; in addition, preliminary blocks have been added to calculate extraction coefficients or provide coefficient data bases for UREX, TRUEX, FPEX, and TALSPEAK. The models have been of significant value in advancing the development of nuclear separations technologies, guiding experimental development work, and serving as the basis for safety analyses and for accountability in safeguards development. While significant efforts have been aimed at improving predictions through adding features to account for issues such as oxidation reaction kinetics, partitioning variation with ionic strength and temperature, solvent degradation, non-ideal fluid contacting, etc., the existing models are still limited in capability. These models, which are based on equilibrium predictions from correlations to experimental data, do not predict the partitioning of a wide range of trace or non-key species and are not highly accurate under conditions (temperature, concentration, etc.) outside the data ranges for which the correlations were developed. New models for prediction of equilibrium partitioning in solvent extraction continue to be developed.

Little information exists in the published literature regarding the development of full plant simulations. During the 1980's, under the Consolidated Fuel Reprocessing Program, Oak Ridge National Laboratory prepared a complete plant simulation to run in the Advanced System for Process Engineering (ASPEN) simulator. The model tracked up to 52 components throughout a preconceptual plant design containing 32 systems and approximately 700 streams, including fuel cleaning and storage; disassembly and shearing; dissolution and feed preparation; hulls drying; feed clarification; feed preparation and accountability; solvent extraction (codecontamination, partitioning, uranium purification, plutonium purification); solvent extraction ancillary systems (concentration, backcycle, storage, high-activity waste concentration, solvent recovery); process support (acid and water recovery and recycle, process steam, and sump); product conversion; cell atmosphere cooling and purification; process off-gas (vessel off-gas, dissolver off-gas iodine recovery and noble gas recovery); and vitrification and vitrification off-gas treatment. The large size of the simulation relative to the computers of the time required that it be broken down into three segments that were executed separately to achieve a steady-state material balance for the complete plant. This comprehensive model provides an outline of the types of processes involved in a reprocessing plant and a view of the complexity needed in code development for realistic simulations. Recently, Savannah River National Laboratory and Argonne National Laboratory have collaborated on efforts toward reestablishing plant-level plant modeling, coupling current versions of ASPEN with AMUSE.

Significant advances have been made in molecular-level modeling and simulation. An area where this has impacted the development of nuclear separations technology is in the computer-aided selection of sequestering agents for design of extraction solvents. Identification of optimal ligands through experimental development involving synthesis and testing is time-consuming. Computer screening of candidate molecules through electronic structure and force field models has been validated by experiment and can significantly reduce the experimental effort needed.

Recent progress has been made toward computer-generated design of molecules, in which fragment libraries, structure-generating algorithms, and binding affinity evaluation are combined to yield improved candidate ligands. This approach has considerable value in the near to mid term for application to the persistent issue of Am/Cm separations.

Current Status

The status of codes for modeling and simulation of nuclear reprocessing systems in the United States reflects the relative lack of activity in the area over the past two decades. Currently available computer codes that have been developed by the U.S. Department of Energy for dynamic modeling of countercurrent solvent extraction processes specific to nuclear fuel reprocessing efforts are summarized in a recent report. The authors conclude there has been little relevant work in the United States over the past two decades in developing advanced modeling and simulation tools for reprocessing systems. That analysis indicates there are only two simulation codes – SEPHIS and SOLVEX – with dynamic capability and validated to any significant degree against actual data from operating fuel separation processes. The authors also recognize the merit of the steady-state tool AMUSE and its current use among flowsheet developers. As discussed by the authors of the review, each of these codes has significant limitations.

In addition to those established models, a recent effort to develop a Safeguards Performance Model is worth noting. This model, developed using Simulink (a simulation software package that runs under MATLAB), enables the transient analysis of material flow in a reprocessing plant for evaluation of accountancy systems. The current model includes simple descriptions of processes in five submodels – the front end and four solvent extraction processes – and was used to demonstrate the capability of alternative instrumentation approaches to improve materials accountability. This modeling effort indicates the flexibility of newer computational tools, which are expected to provide opportunity for expansion in simulation capability.

In summary, current reprocessing models provide only qualitative predictions of process performance. Empirical models of chemical behavior for major components are used to provide overall descriptions of various reprocessing strategies. Many species are not modeled well, or not at all. The models usually assume chemical equilibrium conditions are met instantly, and do not sufficiently incorporate mass transfer and reaction kinetics. Very few reaction rate constants are known, and where transient conditions are simulated, they are often assumed or selected heuristically. The current models are unable to answer many questions involving interphase transport and equilibria, such as precipitation from solution of micellization, third-phase formation, radiolysis, or determining oxidation states, where multiple possibilities exist. Hence, in order to support both detailed design and safe operation, the improvement of reprocessing models requires improved chemistry modeling, including both equilibria and kinetics. The development of new processes that can produce fuel and waste form materials meeting stringent specifications while also meeting environmental, safety, accountability, and cost constraints demands the development and use of modern, sophisticated modeling tools in concert with experimental development and testing for the design and optimization of reprocessing systems.

Looking Forward — Opportunity to Employ Advanced Modeling and Simulation

Recent workshops and studies have evaluated the research and development needs for advanced nuclear energy systems. These studies point to several key areas where advanced modeling and simulation can play an important role in enabling understanding and providing useful tools for practical implementation.

The workshop on Basic Research Needs for Advanced Nuclear Energy Systems, sponsored by the Department of Energy's Office of Science in 2006, identified several key topical areas for advancement of understanding related to reprocessing systems. It is recognized that modeling and simulation conducted in concert with fundamental experiments will be needed to develop understanding in these areas. The reader is directed to the workshop report, which provides detailed discussion on the following areas:

- Scientific Grand Challenges
    - Resolving the f-electron challenge to master the chemistry and physics of actinides and actinide-bearing materials
    - Developing a first-principles, multiscale description of material properties in complex materials under extreme conditions
    - Understanding and designing new molecular systems to gain unprecedented control of chemical selectivity during processing
- Priority Research Directions
    - Physics and chemistry of actinide-bearing materials and the f-electron challenge
    - Microstructure and property stability under extreme conditions
    - Mastering actinide and fission product chemistry under all chemical conditions
    - Exploiting organization to achieve selectivity at multiple length scales
    - Adaptive material-environment interfaces for extreme chemical conditions
    - Fundamental effects of radiation and radiolysis in chemical processes
    - Predictive multiscale modeling of materials and chemical phenomena in multi-component systems under extreme conditions
- Crosscutting Research Themes
    - Tailored nanostructures for radiation-resistant functional and structural materials
    - Solution and solid-state chemistry of 4f and 5f electron systems
    - Physics and chemistry at interfaces and in confined environments
    - Physical and chemical complexity in multi-component systems

A 2006 workshop co-sponsored by the Offices of Nuclear Energy and Advanced Scientific Computing Research of the U.S. Department of Energy focused on modeling and simulation related to advanced nuclear energy systems. The reader is directed to the workshop report, which identifies several key challenges and discusses potential issues and approaches for developing and implementing modeling and simulation tools useful for advancing nuclear technologies. The modeling and simulation challenges related to separations processes include the following:

- Plant-scale simulation
    - integrated toolset 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, 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
- 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 nm–1 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
  - provide sufficient computer resources and access
  - export control issues

The Advisory Committee on Nuclear Waste and Materials of the Nuclear Regulatory Commission has 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”

Figure 1 provides a vision toward the possible hierarchy and integration of future development efforts in modeling and simulation to advance technologies and capabilities in nuclear separations and accompanying safeguards to address the challenges listed above. This figure presents four planes—a top plane that represents the physical reality of the interacting unit operations of an integrated recycling plant and three planes that represent different levels of modeling. A primary goal is the development of a plant model that allows dynamic simulations of the separations plant operations under various configurations and conditions, and integration of relevant analysis modules for specific tasks. Future codes will be developed on modern, expandable architecture with flexibility to explore and evaluate a wide range of process options. While the top-level models will initially incorporate relatively simple models for each process, the codes will be developed with the capability for bridging to subscale models to provide required fidelity in chemical and physical processes.

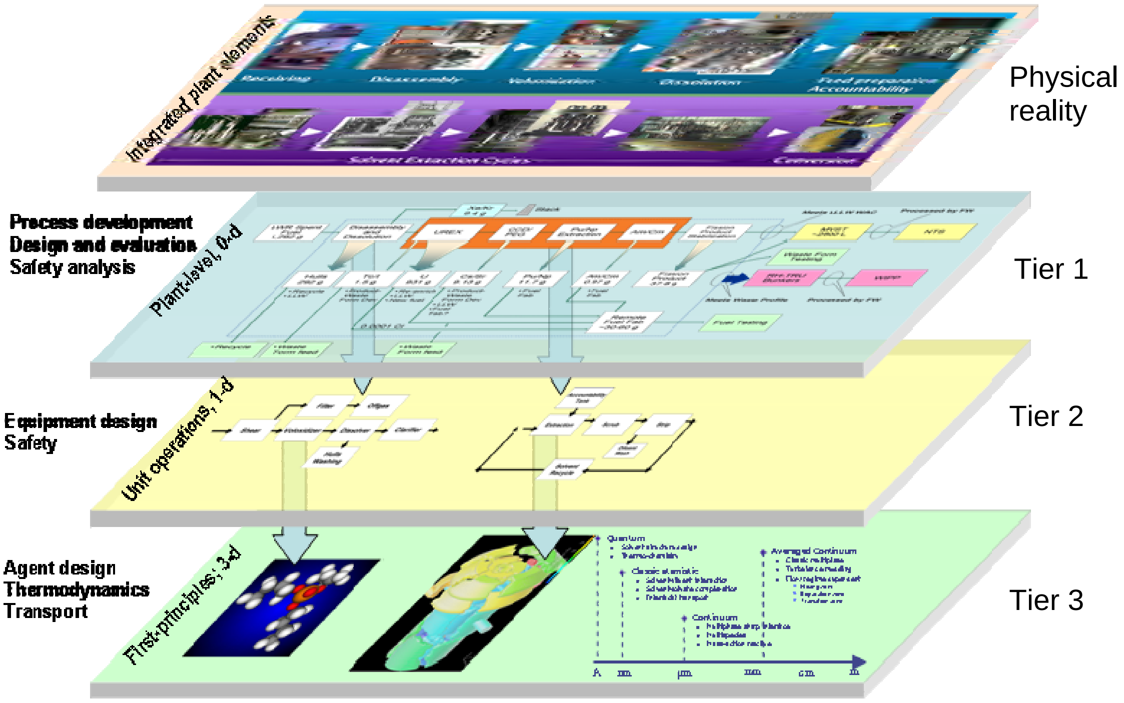


Figure 1. Vision of the hierarchy and integration of modeling and simulation efforts for separations and safeguards.

The top level of modeling in Figure 1 (Tier 1) is a network of units represented by discrete events providing throughput analysis, scheduling impacts, and output chemical compositions. Models at this level generally summarize significant sections of the separations plant lumped together or connected as individual units. These high-level models (i.e., zero-dimensional models for which elapsed time is the principal independent variable) interact through a simulation environment and are calibrated by a combination of experimental data and simulations at other levels of finer detail. Plant-level modeling and simulation is a key practical tool for designing, operating, and safeguarding a separations plant and should be able to follow thousands of streams and chemical species. The computational power requirements for this effort are relatively modest; a dedicated cluster of commodity workstations (e.g., hundreds of processors) is probably sufficient for keeping a live plant simulator running in real time.

The safeguards performance model described previously is an example of current work at the plant level. That work has shown that the process modeling tools currently available provide the capability for a user to define a system that constitutes all or part of a plant, perform simulations under a wide variety of operating conditions, track a large number of variables, and visualize the transient response of any variable in the process (see example in Figure 2). The current tools provide the flexibility to readily change the operations included in the process and their connectivity. The models used for each unit operation can be created with the desired level of sophistication; in addition, it is possible to link to other codes. With further development of transient process models for unit operations, powerful tools will be accessible for analysis of recycling plant design and operation.

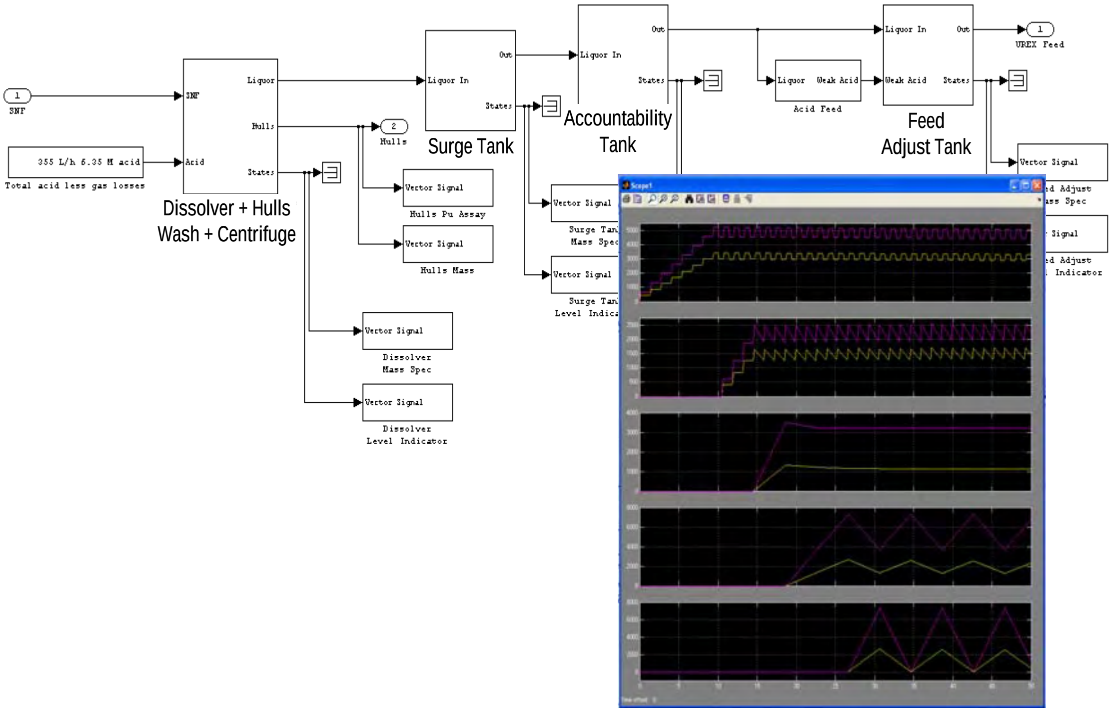


Figure 2. Example of dynamic process modeling made possible with easily adaptable current tools. This figure30 shows a portion of process and instrumentation connections for a model of the head-end section of a plant and sample visualization of transient response in the inventories of multiple tanks through a series of operational cycles.

In view of stringent specifications for the output of a separations plant, the calibration of the plant-level models needs to be improved. This prompts the development of a second hierarchical modeling and simulation level that focuses on any of the top-level units for which a more accurate model is needed. Models at this level (Tier 2 in Figure 1) are modular and may consist of several interchangeable models for the same separations plant section at varying levels of detail. This level includes accurate models of multi-phase flows, high-temperature chemistry, hydraulics, phase transformation, and/or transport, which must be developed for the design and optimization of many required plant operations. These models are necessary to simulate the performance of units under expected plant conditions and to ensure greater reliability in designs before they are physically installed and operated, addressing issues related to process scale-up. The models that currently exist for many unit operations can be further refined; however, for several key operations, even basic models do not currently exist. Unit operations where models can provide substantial immediate benefit to the design of a full-scale plant include voloxidation, solidification, and solvent extraction. In addition to the process chemistry, criticality, and radiation effects must be factored into rigorous designs for optimal operation. Efforts in model and code development must be combined with concurrent experimentation at the benchtop and engineering-scale testing for validation and verification. The computational power required for each of the models at this level is estimated as up to several dozen dedicated processors. Therefore it is envisioned that simulations at this level can take place in parallel to the plant-scale level on an on-demand basis, which could bring the estimate of computing power for both levels together to several hundreds of processors.

An example of current work at this level is fluid dynamics modeling of centrifugal contactors for solvent extraction. Recent efforts have illustrated the capability of continuum modeling to help provide better understanding of the complex flows within these devices. Figure 3 shows examples of simulations of the flow of a single liquid phase in the annular mixing zone of a contactor. These simulations have provided significant insight into system performance and may enable further advancements in design and operation of these units. Further expansion of this capability to provide realistic description of turbulent flows of multiple liquid phases in contactors will require model development and experimental validation; fruitful research in these areas is ongoing.

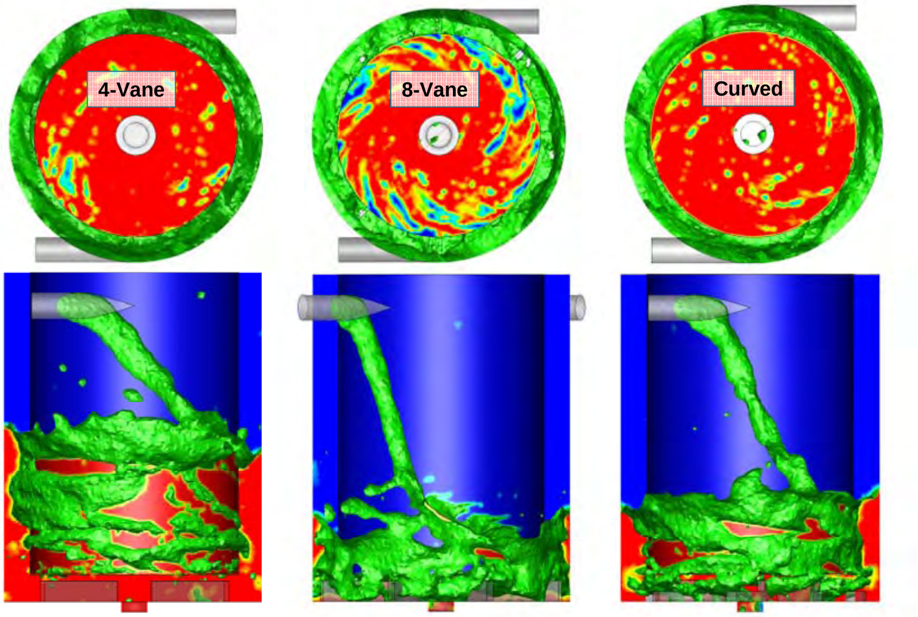


Figure 3. Example of fluid dynamics modeling of the complex free-surface flows in centrifugal contactors used for solvent extraction33. This figure compares the flows of a single liquid phase under identical conditions except for the configuration of the vanes at the bottom of the vessel. Surfaces are color-coded blue for gas-solid, red for liquid-solid, and green for liquid-gas.

At the most fundamental level are key topics for which greater complexity is warranted to deliver accurate predictions, including chemical thermodynamics, interfacial phenomena, reaction kinetics and equilibria, radiolytic and hydrolytic degradation, design of new separating agents, and multicomponent transport in three-dimensional, turbulent multiphase flows. At this root level (Tier 3 of Figure 1) of the modeling and simulation hierarchy resides the most computer-intensive calculations needed to accurately describe time-dependent, three-dimensional (or higher-dimensional) systems. For example, these models could include specific fluid-phase equilibrium and heat and mass transfer calculations, microstructured computational fluid flow, specialized data retrieval, detailed adsorption models, and could even include detail as fine as molecular dynamics, computational chemistry, and radiative transport, if it is necessary, to adequately model the system of interest. Computing power requirement at this level could be the highest available—to hundreds of thousands of processors. These fundamental modeling efforts will calibrate simpler models at the higher level and will form the basis for future advancements in long-term research and development. Fundamental model development projects at this level will necessarily be conducted in close connection with experiments for validation. The fundamental nature of the work will actively engage academic research, providing educational opportunities, and will enable international cooperation.

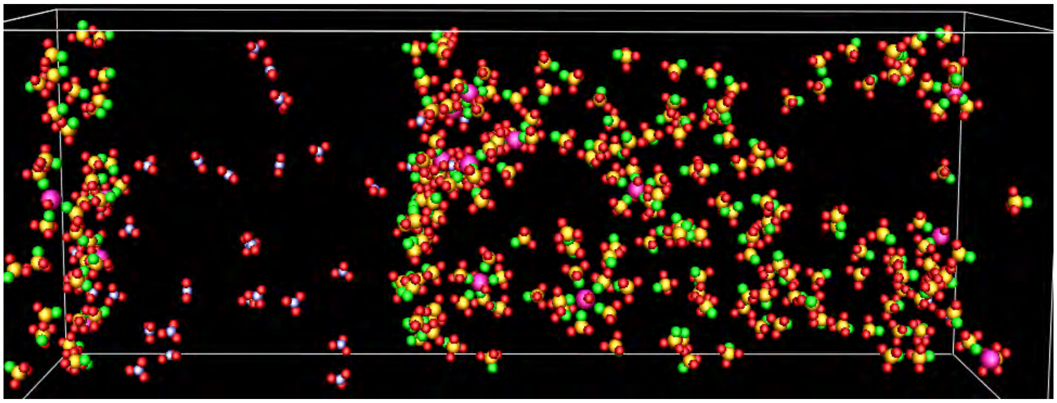


Figure 4. Snapshot of a molecular dynamics simulation of interfacial transport of uranyl nitrate extracted by tri-butyl phosphate (TBP) diluted in dodecane34. In this image, the water and dodecane molecules and the hydrocarbon tails of the TBP molecules are not shown. The uranium atoms of uranyl ions are depicted by magenta spheres, the nitrogen atoms of nitrate ions by blue spheres, the phosphorous atoms of TBP molecules by yellow spheres, and the electro-active oxygen of the TBP phosphoryl groups by green spheres. The complexation of uranyl by TBP is readily visualized by the clustering of green spheres around a magenta center.

Molecular-level modeling has advanced to a point where it can provide valuable contributions toward the development of separations systems. In addition to the agent-design example discussed above, the simulation of molecular-level transport processes near interfaces is an example of an important area where progress in modeling may translate into practical understanding on the performance of separations processes. An example of current work at this fundamental level is shown in Figure 4, a snapshot of a molecular dynamics simulation of uranyl nitrate extraction from an acidic aqueous phase into a tri-butyl phosphate/dodecane solvent. Recent simulations, which include a large number of atoms (>18,000), long-chain hydrocarbon diluents, and flexible molecules, have provided significant insight into the nature of interfacial transport. For example, surfactant behavior of TBP was exhibited, with a resultant heterogeneous distribution of diluent near the interface. This suggests a bridging mechanism for transporting complexed ions into the bulk phase of the solvent. These simulations indicate potential value in further experimental and computational study of molecular aggregation and transport at interfaces. For molecular-level simulations to provide useful data on transport processes for use in higher level models, further work is needed to improve force fields for description of molecules, including systematic experimental calibration.

The NEAMS Program

Motivated by the challenges and needs in nuclear energy systems that can be addressed by modeling and simulation, the Office of Nuclear Energy of the U.S. Department of Energy has articulated a vision for a Nuclear Energy Advanced Modeling and Simulation (NEAMS) program. The NEAMS vision is “To rapidly create, and deploy next generation, verified and validated nuclear energy modeling and simulation capabilities for the design, implementation, and operation of future nuclear energy systems to improve the U.S. energy security future.”

NEAMS is aimed toward building on the success of recent programs in advanced scientific computing, namely, ASCI and SciDAC, with a focus on very different challenges. These challenges include the need for nuclear energy systems to be licensed by regulators and moving advanced technologies out of the research environment and into the hands of the engineers who will design, build, and operate the new nuclear energy systems. NEAMS will provide a comprehensive solution and is organized into the following five elements:

- Integrated Performance and Safety Codes—End-to-end codes to understand the detailed, integrated performance of new nuclear systems including the following:
    - Nuclear Fuels
    - Reactor Core & Safety
    - Separations and Safeguards
    - Waste Forms and Near-Field Repositories
- Fundamental Methods and Models
- Verification, Validation, and Uncertainty Quantification
- Capability Transfer Enabling Computational Technologies

Summary

Modeling and simulation have provided useful input to the development of fuel cycle separations over the past several decades. With significant scientific advancements and vast increases in computational power, modeling and simulation can play an increasing role in solving the complex challenges to be overcome in developing advanced nuclear energy systems. In conjunction with experimental efforts, concurrent development of tools at three levels of detail—plant, unit operations, and fundamental—is needed to enable fruitful progress in the near, mid, and long term.

References

1. Massachusetts Institute of Technology, 2003. *The Future of Nuclear Power – An Interdisciplinary MIT Study*, J. Deutch and E. J. Moniz, co-chairs. Available at http://web.mit.edu/nuclearpower/
2. Jacobson, J. J., L. Malczynski, V. Tidwell, 2008. "Very Large System Dynamics Models – Lessons Learned," Proc. 2008 Intl. Conf. System Dynamics Soc., July 20–24, Athens, Greece. Available at http://www.systemdynamics.org/conferences/2008/proceed/papers/MALCZ214.pdf.
3. Schweitzer, T. M., 2008. Improved Building Methodology and Analysis of Delay Scenarios of Advanced Nuclear Fuel Cycles with the Verifiable Fuel Cycle Simulation Model (VISION), Master's thesis, North Carolina State University. Available at http://www.lib.ncsu.edu/theses/available/etd-05022008-161622/
4. Yacout, A.M., J.J. Jacobson, G.E. Matthern, S.J. Piet, D.E. Shropshire, C. Laws, 2006. "VISION – Verifiable Fuel Cycle Simulation of Nuclear Fuel Cycle Dynamics," Waste Management Symposium 2006, February 2006.
5. Stan, M., 2005. Materials Models and Simulations in Support of Nuclear Fuels Development, Los Alamos National Laboratory report LA-UR-05-5652, June. Available at http://public.lanl.gov/mastan/MMSNF/Models%20and%20Simulations%20report.pdf
6. Peters, M. T., R. C. Ewing, and C. I. Steefel, 2008. *GNEP Waste Form Campaign Science & Technology and Modeling & Simulation Program: Roadmap with Rationale & Recommendations*, report GNEP-M50-3040-303 prepared for U.S. Department of Energy Global Nuclear Energy Partnership Waste Form Campaign, March 14. Available at http://www.energetics.com/meetings/univworkshopaug08/pdfs/presentations/02%20AFCI%20Separations%20&%20Waste%20Forms/FY09%20NE%20Univ%20Prog%20Workshop%20Program%20Recommendations%20.pdf
7. Office of Science, U.S. Department of Energy, 2006. *Basic Research Needs for Advanced Nuclear Energy Systems,* J. B. Roberto and T. Diaz de la Rubia, co-chairs. available at http://www.sc.doe.gov/bes/reports/abstracts.html#ANES
8. Office of Science, U.S. Department of Energy, 2005. *The Path to Sustainable Nuclear Energy – Basic and Applied Research Opportunities for Advanced Fuel Cycles*, P. Finck and N. Edelstein, co-chairs. Available at http://www.er.doe.gov/bes/reports/files/PSNE_rpt.pdf.
9. Offices of Nuclear Energy and Advanced Scientific Computing Research, U.S. Department of Energy, 2006. *Workshop on Simulation and Modeling for Advanced Nuclear Energy Systems,* P. Finck, D. Keyes, and R. Stevens, co-chairs. Available at http://www-fp.mcs.anl.gov/anes/SMANES/gnep06-final.pdf.
10. Groenier, W. S., R. H. Rainey, and S. B. Watson, 1979. "An analysis of the transient and steady-state operation of a countercurrent liquid-liquid solvent extractions process," *Ind. Eng. Chem. Process Des. Dev.* 18 (3), 385-39.
11. B. B. Spencer, personal communication, "Minutes of May 14, 1990, Planning Meeting for Process Simulator Project."
12. Ryon, A. D., 1961*. McCabe-Thiele Graphical Solution of Uranium-Thorium Partitioning from 30% TBP-AMSCO Solvent*, Oak Ridge National Laboratory report ORNL-3045. Available at http://www.ornl.gov/info/reports/1961/3445603642217.pdf.
13. Burton, W. R., and A. L. Mills, 1963. "Computer calculation of flowsheets for reprocessing nuclear fuels," *Nucl. Eng.* 8, 248–252.
14. Mills, A. L., 1965. *A Review of Computer Programmes for Solvent Extraction Calculations*, United Kingdom Atomic Energy Authority TRG report 902 (D).

15. Rainey, R. H., and S. B. Watson, 1975. *Modification of the SEPHIS Computer Code for Calculating the PUREX Solvent Extraction System*, Oak Ridge National Laboratory Report ORNL-TM-5123. Available at http://www.osti.gov/energycitations/servlets/purl/4167160-Ke5fTt/4167160.PDF
16. Bendixsen, C. L., 1982. *ICPSEF: A User's Manual for the Computer Mathematical Model of the ICPP PUREX Solvent Extraction System*, Exxon Nuclear Idaho Company report ENICO-1124. Available through NTIS.
17. Geldard, J. F., A. L. Beyerlein, and H.-L. Chiu, 1986. "PUMA - a new mathematical model for the rapid calculation of steady-state concentration profiles in mixer-settler extraction, partitioning, and stripping contactors using the Purex process" *Nucl. Technol*. 75 (2), 160–167.
18. Scotten, W. C., 1975. *SOLVEX – A Computer Program for Simulation of Solvent Extraction Processes*, E. I. Du Pont de Nemours & Co., Savannah River Laboratory, report DP-122. Available through NTIS.
19. Leonard, R. A., and M. C. Regalbuto, 1994. "A spreadsheet algorithm for stagewise solvent extraction," *Solvent Extr. Ion Exch.* 12 (5), 909–930.
20. Regalbuto, M. C., J. M. Copple, R. Leonard, C. Pereira, and G. F. Vandegrift, 2004. "Solvent Extraction Process Development for Partitioning and Transmutation of Spent Fuel," *OECD Nuclear Energy Agency (NEA), Actinide and Fission Product Partitioning & Transmutation, Eighth Information Exchange Meeting, Session II: Partitioning and Waste Management*, Las Vegas, Nevada, USA November 2004. Available at http://www.nea.fr/html/pt/iempt8/abstracts/Abstracts/Regalbuto_8thP&T.doc
21. Kyser, E. A., 1998. *Validation of the SEPHIS Program for the Modeling of the HM Process*, Westinghouse Savannah River Company report WSRC-TR-98-O0376. Available at http://www.osti.gov/bridge/servlets/purl/4836-DH2Tqp/webviewable/4836.PDF.
22. Morrison, G. W., and E. D. Blakeman, 1979. *Real Time Material Accountability in a Chemical Reprocessing Unit*, Oak Ridge National Laboratory report CONF-790707-17. Available at http://www.osti.gov/energycitations/servlets/purl/5954925-twmsd4/.
23. G. J. Lumetta, B. K. McNamara, and B. M. Rapko, 1999. *The SX Solver: A New Computer Program for Analyzing Solvent-Extraction Equilibria,* Pacific Northwest National Laboratory report PNNL-12085. Available at http://www.pnl.gov/main/publications/external/technical_reports/PNNL-12085.PDF.
24. Baes Jr., C. F., 2001. "Modeling solvent extraction systems with SXFIT," *Solvent Extr. Ion Exch.* 19 (2), 193–213.
25. Jubin, R. T., personal communication, "ASPEN Material Balance Simulation of an Advanced Reprocessing Plant, Preliminary Design - DRAFT"
26. Lumetta, G. J., B. M. Rapko, B. P. Hay, R. D. Gilbertson, T. J. R. Weakly, J. E. Hutchison, *J. Am. Chem. Soc.* 2002, *124*, 5644.
27. Hay, B. P., and T. K. Firman, 2002. "HostDesigner: a program for the de novo structure-based design of molecular receptors with binding sites that complement metal ion guests," *Inorg. Chem*. 41, 5502–5512.
28. Hay, B. P., A. A. Oliferenko, J. Uddin, C. Zhang, and T. K. Firman, 2005. "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, 17043–17053.
29. Tranter, T. J., and D. R. Haefner, 2008. *Survey of Dynamic Simulation Programs for Nuclear Fuel Reprocessing*, Idaho National Laboratory report INL/EXT-08-14476. Available at http://www.inl.gov/technicalpublications/Documents/4027525.pdf.
30. Cipiti, B. B., and N. L. Ricker, 2008. *Advancing the State of the Art in Materials Accountancy through Safeguards Performance Modeling*, Sandia National Laboratories

report SAND2008-5100. Available at http://www.prod.sandia.gov/cgi-bin/techlib/access-control.pl/2008/085100.pdf.

31. Croff, A. G., R. G. Wymer, L. L. Tavlarides, J. H. Flack, and H. G. Larson, 2008. “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. Available at http://www.nrc.gov/reading-rm/doc-collections/nuregs/staff/sr1909/index.html
32. de Almeida, V. F. et al., 2006. Nuclear Fuel Reprocessing Plant Simulation – GNEP Modeling and Simulation White Paper, Oak Ridge National Laboratory report ORNL/TM-2007/113, September.
33. Wardle, K. E., T. R. Allen, M. H. Anderson, and R. E. Swaney, 2007. “Free surface flow in the mixing zone of an annular centrifugal contactor,” *AIChE J*. 54, 74–85.
34. Cui, S., V. F. de Almeida, B. Khomami, 2008. “Atomistic simulation of water/TBP-dodecane interface: molecular processes of uranyl extraction,” *Proc. International Solvent Extraction Conference*, ISEC2008, Tucson, AZ, September 17.
35. Multiple overview presentations on NEAMS available on the web, including http://www.ccs.ornl.gov/workshops/FallCreek08/presentations/a_larzerele.pdf, and http://computing.ornl.gov/workshops/neams/program_intro.shtml

Sol-Gel Synthesized Sorbent Development and Analysis for Column Separations

Lawrence L. Tavlarides
Department of Biomedical and Chemical Engineering
Syracuse University

Outline

The scope of the presentation includes an introduction, synthesis methods of adsorbents, application examined: mercury removal, noble metal separation, and germanium separation, analysis of adsorption in batch and column systems, and conclusions.

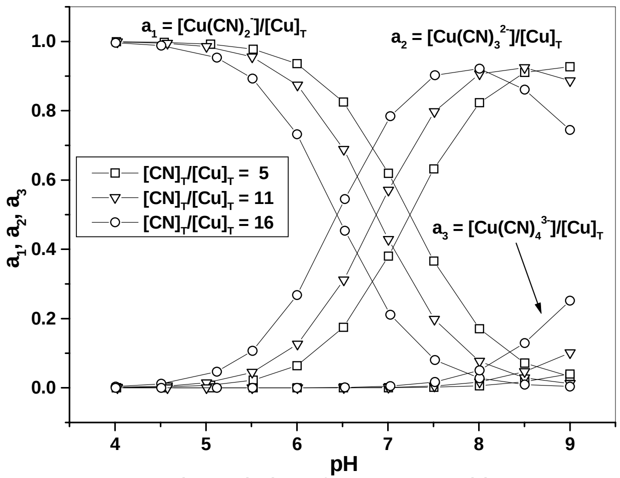
Introduction

There are numerous potential uses of adsorbents for gaseous and metal separations in nuclear fuel cycle processing. These include radioactive gas capture (^{85}Kr, ^{129}I and ^{14}C as $^{14}CO_2$) prior to and during dissolution of spent nuclear fuels, technicium separation in the UREX stage of the UREX+1a Process, mercury separation in INEEL/DOE SBR waste and EPA Scrubber solutions, amongst other. The Team at Syracuse University has been engaged in development of new adsorbents for metal ion separations for nuclear, industrial, environmental, and bio-separations.[1-6] These developments employ organic – ceramic synthesis methods to design sorbents at the nano-scale with desirable selectivity, capacity, mechanical properties and stability. We demonstrate the sorbent capabilities through column studies and analysis. This approach can be used for pilot plant column design and studies which can lead to full scale process implementation, and is directly applicable to separations in the nuclear fuel cycle.

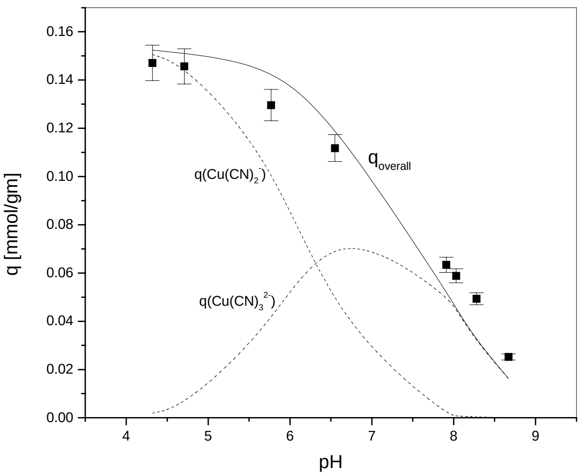
- Examples of sorbent separations in the fuel cycle and nuclear waste process:
    - ^{85}Kr, ^{129}I and ^{14}C as $^{14}CO_2$ gas capture from spent fuel dissolution.
    - ^{99}Tc as pertechnetate anion (TcO_4^-) removal from dissolved spent fuel in the UREX process (modified PUREX)
    - Mercury ion separation from nuclear waste solutions.
- New robust sorbents of high selectivity, capacity and stability and stable mechanical properties are required.
- The Team at Syracuse University develops such sorbents using sol-gel methods and demonstrates sorbent usefulness in column applications.

Aqueous Phase Equilibrium of Copper Cyanide Complexes in Cyanide Solutions

The next figure shows why it is important to design a sorbent with the appropriate ligand to match the chemistry of the ions we seek to separate. The figure on the left[1] shows the three different complex forms that copper (I) exists in cyanide solution, such as $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$ depending on the pH and cyanide solution composition. A silica gel immobilized with tetraethylenepenta-amine modified with propyl groups was used to remove copper cyanide from these solutions. The figure on the right[7] shows that the total amount of adsorbed copper cyanide is the sum of the two complexes adsorbed on the surface. Therefore a chelating agent must be selected that can chelate with the metal ion at the expected conditions of extraction. Alternatively, we can alter the solution pH to have favorable binding conditions.



Computed Speciation of Copper Cyanide Complexes in Cyanide Solutions with Respect to the Solution pH
(L. L. Tavlarides et al. CRC Press, 2008. With permission)

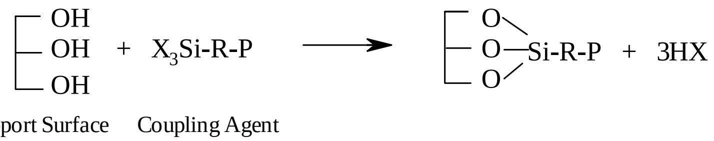


pH Isotherm of Copper Cyanide : [Cu(I)]ini = 200 mg/L; [CN]T/[Cu]T = 16; Experimenal Data, —— : Computed overall copper(I) uptake; – – – – : Computed individual copper(I) complex uptake (J. S. Lee MS Thesis, Syracuse University, 1997.)

Covalent Attachment to Support by Method A

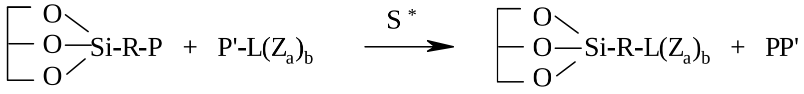
Two basic sorbent network systems are Polymeric Network Systems and Inorganic Network Systems. Polymeric systems have been developed and applied for metal separations from aqueous solutions such as noble metal separations, nuclear waste treatment, and electroplating waste clean-up. Inorganic solid extractants made of functional liqands and inorganic supports attract much attention because of their mechanical strength, thermal stability, wide range of particle size, and well defined pore structure. The latter can be adjusted for rapid intraparticle metal ion diffusion characteristics. We will focus on the inorganic network systems and describe two synthesis approaches. The first involves covalent attachment of the organic ligand to the inorgnanic silica gel by two methods. The first attachment method[1] is shown in this figure. In step 1, a coupling agent (3-chloropropyltrimethoxysilane) is immobilized on the silica gel support. Step 2 attaches the ligand (5-methyl-8-hydroxy-quinoline) by reacting it with the bonded coupling agent.

Step 1: Immobilization of Coupling Agent



X: Halide, Alkoxy, Acetoxy, and/or Hydroxy
R: Substituted or Unsubstituted Alkyl/Aryl
P: Appropriate Reactive Group

Step 2: Ligand Attachment



P': Appropriate Reactive Group
Za: Donor Atom of Type 'a'
    a = 1 - 8 (upto eight) types
b: Number of each Donor Atom per Ligand
*: Different Reaction Schemes to Attach Ligand

Covalent attachment to support by Method B

The second attachment method[1] is shown on the next figure. In the first step here the functional precursor silane (5-methyl-8-hydroxy-quinoline) and the coupling agent (3-chloropropyltrimethoxysilane) are independently hydrolyzed and condensed. This product is then immobilized on the silica gel.

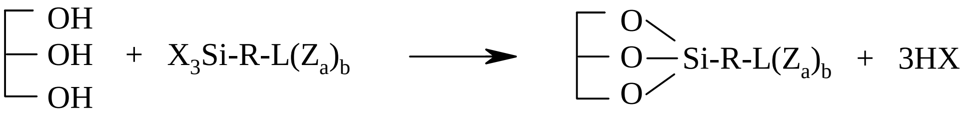
Step 1: Ligand Attachment to Coupling Agent

$$X_3Si\text{-}R\text{-}P \;+\; P'\text{-}L(Z_a)_b \xrightarrow{S^*} X_3Si\text{-}R\text{-}L(Z_a)_b$$

Coupling Agent — Ligand/Ligand Derivative — Ligand-Coupling Agent Derivative

*: Different Reaction Schemes to Attach Ligand

Step 2: Immobilization of Ligand Coupling Agent Derivative



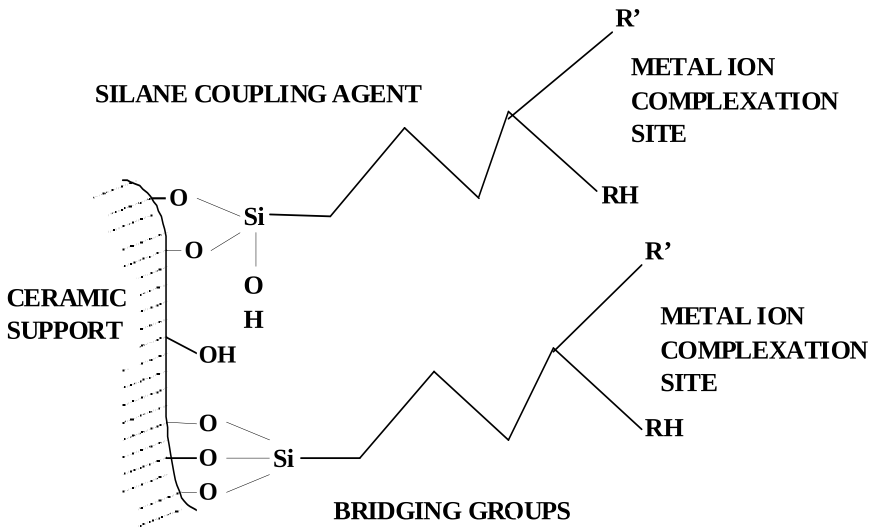
$$[\text{OH})_3 + X_3Si\text{-}R\text{-}L(Z_a)_b \longrightarrow [\text{O})_3Si\text{-}R\text{-}L(Z_a)_b + 3HX$$

Choice of Ligand Attachment Scheme:

1. **Depends on Reactive Groups and Conditions**
2. **Desire to Achieve Ligand with Specific Donor Atoms and Preferred Geometry**
3. **Desire to Achieve High Ligand Density on the Support Surface**

Adsorbent Prepared by Covalent Bonding Using Silane-coupling Agent

The resulting structure by either method is shown on the following slide. The functional portion of the attached ligand is free in the silica pores to complex the metal ion.



Examples of Adsorbents Developed by Covalent Attachment Technique

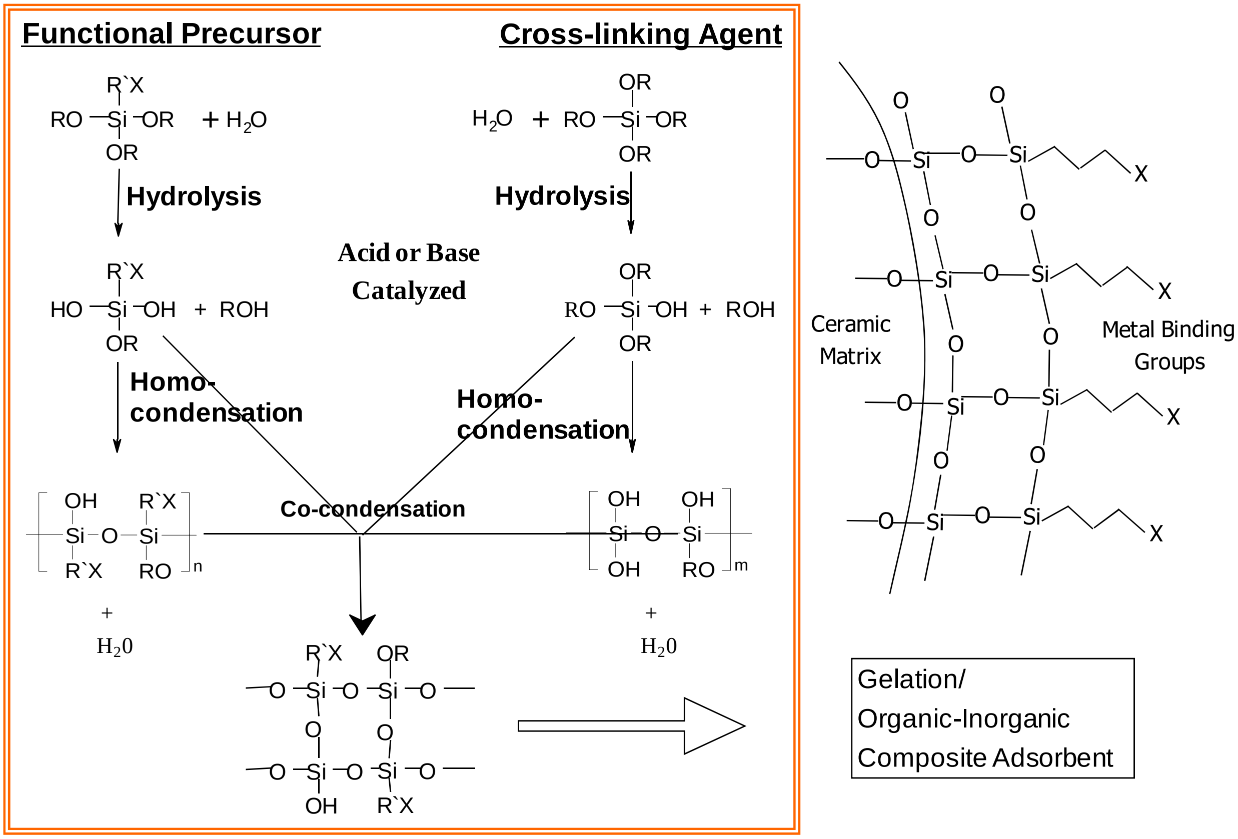
The next figure shows adsorbents developed by the covalent attachment technique using either or both methods described in the previous sections. These sorbents are applied to a variety of metal ion separations as shown.[2]

Support	Functional Group	Method/Coupling Agent	Metal Ions
Silica gel	5-methyl-8-hydroxy-quinoline	Organic functional silane derivatives in solutions and surface	Pb(II), Cu(II), Ni(II), Cd(II)
Silica gel	Thio Sulfide acid	Organic functional silane in solution	Cd(II), Hg(II), Zn(II), Pb(II)
Silica gel	Primary secondary and tertiary amines, and diazole	Organic functional silane on surface	Cu(II), Ni(II), anionic cyanide complexes, $Cr_2O_7^{2-}$, CrO_4^{2-}
Silica gel	Pyrogallol	Derivatization on surface modified with organo-functional silane	Antimony(III) Al(III), Cu(II)

Recent Work on Organo-ceramic Adsorbents

A second approach to synthesis of organo-ceramic adsorbents led to a series of adsorbents called SOL-AD.[3,5] In this approach a functional precursor is co-condensed with a hydrolyzed cross-linking agent. Advantages of these materials are high ligand densities, homogeneous distributions of the functional moiety throughout the matrix, and controlled pore characteristics.

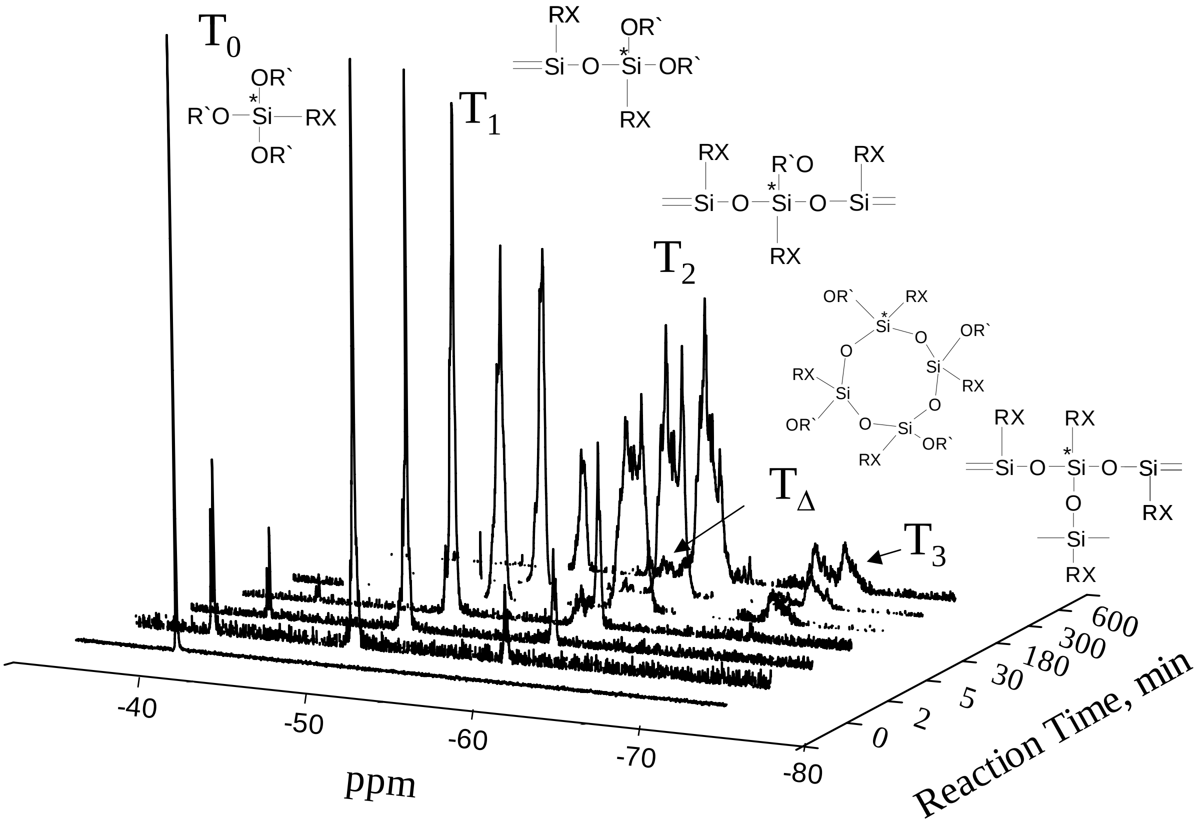
As an example the functional precursor containing an active group, such as 3-mercapto-propyltrimethoxysilane is hydrolyzed and undergoes self-condensation. Likewise, a cross-linking agent, such as tetra-ethoxy silane is hydrolyzed and undergoes self-condensation. The two reaction systems can be combined at a certain time to maximize the density of ligand in the matrix and properties of the matrix.



Functional Group Clustering

The evolution of the polymers of the hydrolysis-condensation reaction of the precursor, 3-mercaptopropyltrimethoxysilane (MPS) is shown via the ^{29}Si-NMR spectra on this figure.[3] Oligomers composed mostly of the T2 silicons are the most favorable for the formation of functional clusters.

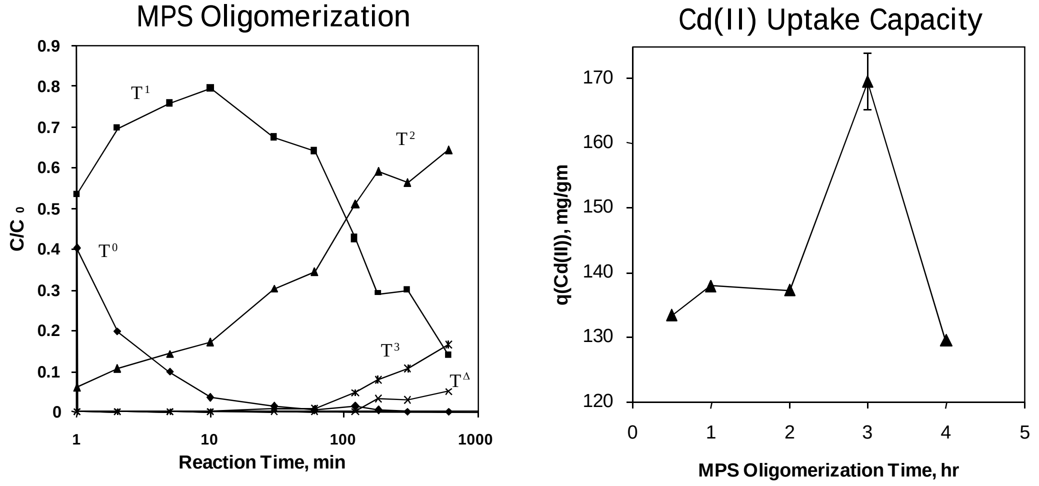
^{29}Si-NMR Spectra: Oligomerization vs. time
3-mercaptopropyl-trimethoxysilane (MPS)



Oligomerization of MPS and Cd(II) Uptake Capacity

This figure[3] shows that the uptake capacity of Cd (II) is maximized when the MPS oligomerization reaction time is chosen to maximize the concentration of the T2 oligomer.

SOL-AD-IV: Thiol Functionalized Adsorbent



Importance of Molar Ratio to Adsorbent Properties

This next figure shows the importance of the ratio of the CS/FPS on adsorbent.[3]
Here q_a and q_t are the actual capacity and theoretical capacity of SOL-AD-IV with the molar ratio of CS to FPS. For a q_a ratio less than 2 we see that the actual capacity decreases below the theoretical capacity due to (a) poor pore accessibility, (b) strong hydrophobicity, and (c) poor structural integrity. Also, Dp increases and SA decreases. As the CS to FPS ratio increases above 2, q_a follows the theoretical capacity, and the SA increases while the pore diameter stabilizes to a constant value as a greater portion of the pores are made up with the CS.

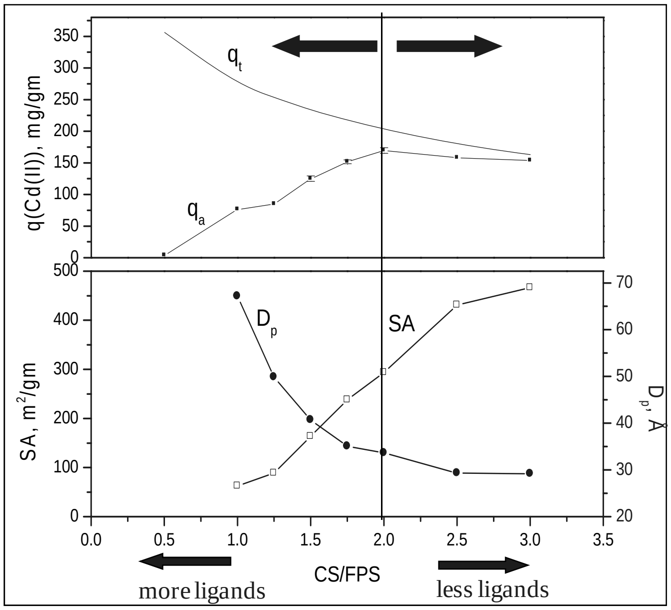
SOL-AD-IV

q_a decreases:

- poor pore accessibility
- strong hydrophobicity
- poor structural integrity

Dp increases and SA decreases:

- coagulation and entanglement of precursor oligomers



q_a follows :

- theoretical capacity

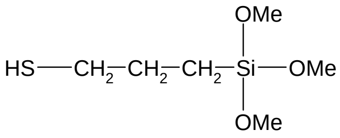
SA increases and Dp stays constant

- greater portion of pores made up with CS

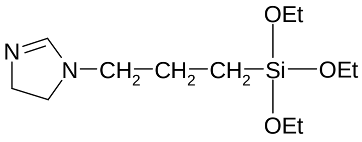
Adsorbents Developed by Sol-Gel Processing

The next figures show some of the adsorbents we developed by sol-gel processing. They include (a) Thiol system (SOL-AD-IV)[3,5], (b) Imidazole system (SOL-IPS)[8,9], (c) Kelex-100 system (SOL-KELEX)[10], and (d) Pyrazole System (SOL-PzPs)[6].

- Thiol System (SOL-AD-IV)
    - Precursor : 3-(mercaptopropyl)-trimethoxysilane
    - Target Ions: Cadmium, Lead, Mercury, and Copper


$HS-CH_2-CH_2-CH_2-Si(OMe)_3$

- Imidazole System (SOL-IPS)
    - Precursor : 1-(triethoxysilylpropyl)-imidazoline
    - Target Ions: Platinum, Palladium, Gold, and Rhodium



Synthesis Conditions of Sol-Gel Adsorbents

These figures show the conditions of the synthesis reactions to produce the four sol-gel adsorbents shown on the previous four figures. Note how the FPS and CS condensation time vary for each sorbent.[3, 5, 6, 8-10]

SOL-AD-IV
- Chemical Compositions
    - MPS : TEOS = 1 : 2
    - MPS : EtOH : H_2O : HCl : NaCl =
      1 : 3 : 3 : 0.01 : 0.01
    - TEOS : EtOH : H_2O : HCl : NaCl =
      1 : 4 : 4 : 0.006 : 0.01
- Reaction Time
    - MPS condensation : 3 hrs
    - TEOS condensation : 30 mins
    - Co-condensation : 5 mins

SOL-PzPs-BD-5
- Chemical Compositions
    - PzPs : TEOS = 1 : 2
    - PzPs : EtOH : H_2O : HCl : NaF =
      1 : 3 : 3 : 0.01 : 0.01
    - TEOS : EtOH : H_2O : HCl : NaF =
      1 : 4 : 4 : 0.01 : 0.01
- Reaction Time
    - PzPs condensation : 2 hrs
    - TEOS condensation : 15 mins
    - Co-condensation : 5 mins

SOL-KELEX
- Chemical Compositions
    - APS : TEOS = 1 : 3
    - APS : EtOH : H_2O : HCl =
      1 : 4 : 1 : 10^{-5}
    - TEOS : EtOH : H_2O : HCl =
      1 : 3 : 1 : $3x10^{-5}$
- Reaction Time
    - MPS condensation : 15 mins
    - TEOS condensation : 15 mins
    - Co-condensation : 5 mins

SOL-IPS
- Chemical Compositions
    - IPS : TEOS = 1 : 2
    - IPS : EtOH : H_2O : HCl =
      1 : 3 : 2 : $4.5x10^{-3}$
    - TEOS : EtOH : H_2O : NaF =
      1 : 4 : 1 : $0.67x10^{-3}$
- Reaction Time
    - IPS condensation : 30 mins
    - TEOS condensation : 30 mins
    - Co-condensation : 5 mins

Comparison of Sol-Gel Adsorbents with Other Types of Adsorbents

These figures compare the sol-gel adsorbents we prepared with others available in the literature.[2, 4, 12-19] For example; our SOL-AD-IV sorbent has a greater capacity for mercury than available sorbents. In most comparisons the sol-gel sorbents have a greater capacity.

Palladium Separation

Adsorbent	Capacity	BET Analysis		Functional Group	Reference
		D (Å)	SA (m^2/g)		
Chelating resin	65.4			DEHTPA / impregnated polymer resin	Rovira et al., Sol. Extr. & Ion Exch., 17, 1999
Doulite Ge-73 resin	28.5			Thiol / polymer resin	Iglesias, Anal. Chim. Acta, 381, 1999
SOL-IPS	162.3			Imidazole/ sol-gel processing	This study
SOL-PzPs	150.8	37	437	Pyrazole / sol-gel processing	This study

Mercury Separation

Chelating resin	562	107	41	Thiazole and thiazolin / polymer resin	Sugii A. et. al., Talanta. 27, 1998
Functionalized silica	505	55	900	Thiol / covalent attachment on SAMMS	Feng X. et. al., Science, 276, 1997
SOL-AD-IV	1280	82	640	Thiol / sol-gel processing	This study

Germanium Separation

Adsorbent	Capacity	BET Analysis		Functional Group	Reference
		D (Å)	SA (m^2/g)		
Activated Carbon	10.1			$H_3PO_4^-$ activated carbon,	J.P. Marco-Lozar
Cellulose	115.2			di(2-hydroxyethyl)amine / polymer	Y. Inukai
Goethite	4.3			$FeSO_4$ / oxidative hydrolysis	O.S. Pokrovsky
SOL-KELEX	23.8	72	421	Kelex-100 / sol-gel processing	This study

Cadmium Separation

ISPE-302	19.7			Cyanex-302 / solvent deposion on silica	Deorkar et al., Emerging Separation Technology II, 1996
ICAA-S	71.1			Thiol / covalent bond on silica	Deorkar et al., Ind. Eng. Chem. Res., 36, 1997
Chelating resin	146.0			Mercaptoacetamide / polymer resin	Colella et. al., Anal. Chem., 52, 1980
SOL-AD-IV	222.3	82	640	Thiol / sol-gel processing	This study

Applications Studied

We now turn to several applications of these sol-gel materials to important metal ion separation processes. We will outline our results for (a) mercury removal including Scubber solution and DOE acidic nuclear waste solutions, (b) noble metal separation, and (c) germanium separation.

SOL-AD-IV for Mercury Separations

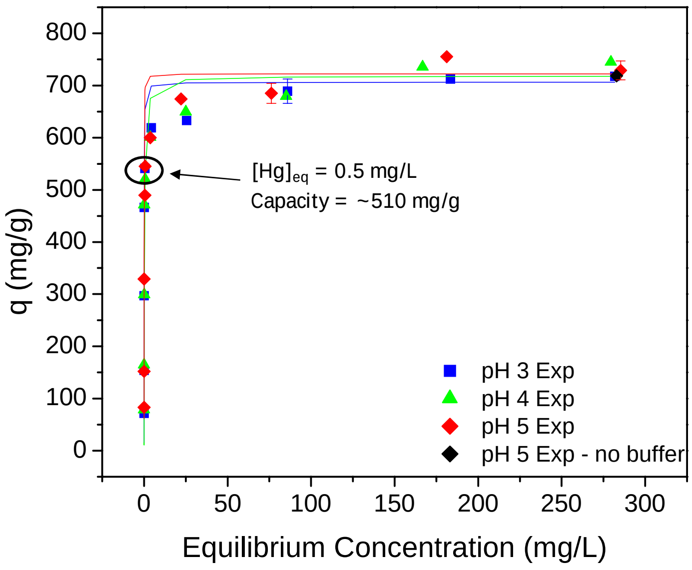
The mercury separation problem was motivated by the presence of mercury in INEEL/DOE sodium bearing waste solutions and in EPA scrubber solutions and the need for separation. This chart shows the composition of these solutions. The EPA scrubber solution shown is used in these studies except that mercury concentrations are adjusted as needed.

	Compositions (molar)	
Species	**INEEL/DOE**	**EPA**
	SBW Solution	**Scrubber Solution**
Al^{3+}	0.6	-
Ca^{2+}	-	0.00873
Cl^-	-	0.03102
F^-	0.1	-
K^+	0.18	-
H^+	***2***	***pH 5***
Hg^{2+}	***0.00758*** **(1500ppm)**	***$2.5x10^{-6}$*** **(0.5ppm)**
Mg^{2+}	-	0.00206
Na^+	-	0.03104
NH_4^+	-	0.01144
NO_3^-	3.8	0.02158
SO_4^{2-}	-	0.00572
Zn^{2+}	-	0.00046

Equilibrium Isotherms

Equilibrium isotherms are used to show the uptake capacity of adsorbents over a range of pH values and concentration of the solute in solution. The adsorption equilibrium behavior of SOL-AD-IV shown on this slide shows a high mercury uptake capacity of ~510mg/g at 0.5mg Hg/L, which is the scrubber water concentration.[5] Capacities as high as ~750-800 mg/g are obtained at 200 mg/L solution concentrations. We also developed a two species equilibrium model when acetate ion is present in the system. In this case, mercury chloride complexes with the ligand in reaction 1 and mercury acetate complexes with the ligand in reaction 2. The equilibrium model is shown below. When no acetate is present the model reduces to a simpler form. This model was used to predict the isotherms.

EPA Scrubber Matrix Solution



$[Hg]_{eq}$ = 0.5 mg/L
Capacity = ~510 mg/g

Batch Contactor Mode

Adsorbent: 0.2g of SOL-AD-IV
Solution:
100 ml of simulated solution
Total Mercury = 300 – 1800 mg/L
Buffered = 0.2M Sodium Acetate
Contact time: 24 hrs

$$\overline{RSH} + HgCl_2 \overset{1}{\Leftrightarrow} \overline{RS \cdot HgCl} + H^+ + Cl^-$$

$$\overline{RSH} + HgAc_4^{-2} \overset{2}{\Leftrightarrow} \overline{RS \cdot HgAc} + H^+ + 3Ac^-$$

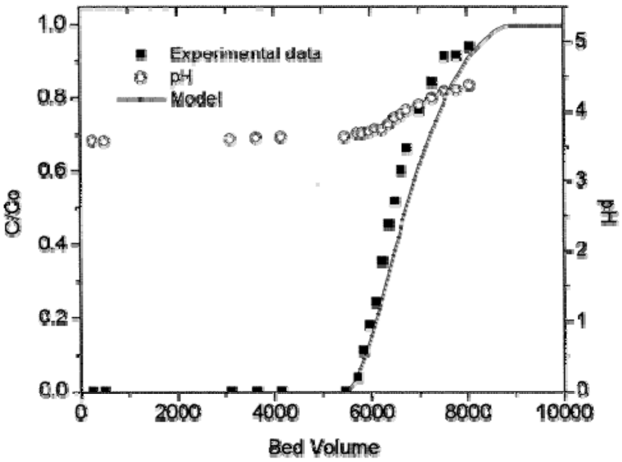
$$q = \frac{S_T K'_{eq1}[HgCl_2] + S_T K'_{eq2}[HgAc_4^{-2}]}{1 + K'_{eq1}[HgCl_2] + K'_{eq2}[HgAc_4^{-2}]}$$

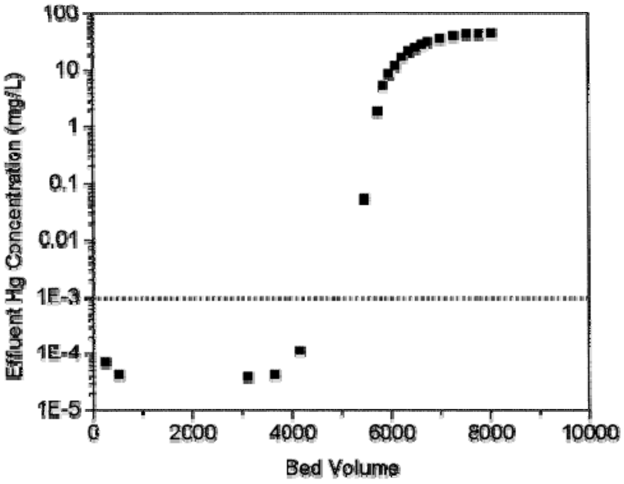
Breakthrough Curve Study

To evaluate the performance of the adsorbent we did column studies to determine the breakthrough curve and provide a check on the uptake capacity. The results of these experiments are shown on this slide. The figure on the left shows little breakthrough up to 5500 bed volumes of flow.[5] At bed saturation the column capacity was 391mg/g. Further, the effluent concentration is less than 1ppb up to approximately 5000 bed volumes.

EPA Scrubber Matrix Solution

Column: 0.7 cm ID
SOL-AD-IV = 0.175 g
Solution: Simulated scrubber solution
C_0 = 0.564 mg/L, pH = 5.0

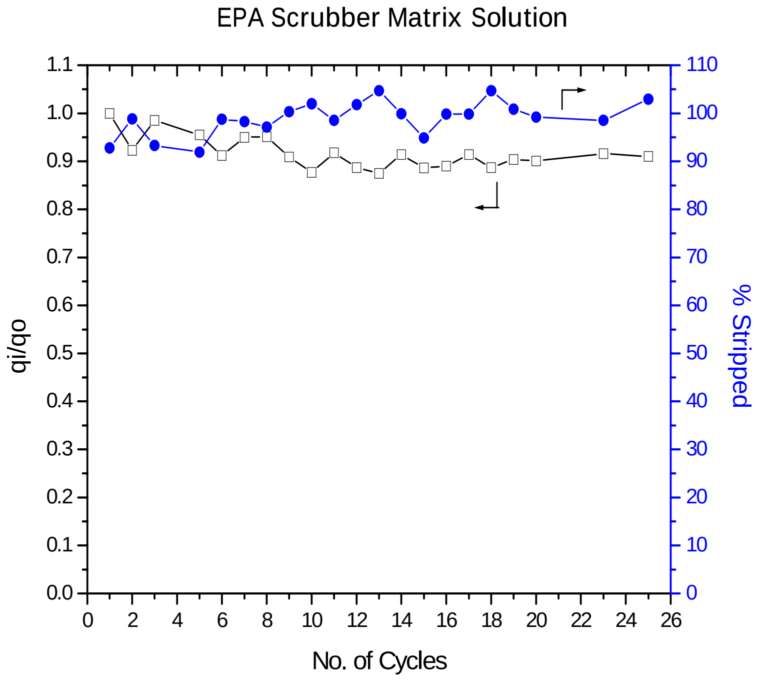




Flow rate: 6 ml/min

Stability of SOL-AD-IV for Multiple Adsorption/Desorption Cycles

An important factor is the operational stability of sorbents after multiple adsorption/desorption cycles. This slide shows such behavior of SOL-AD-IV. The conditions of the experiments are shown on the right of the slide. Here q_i is the mercury uptake after the ith cycle and q_o is the uptake capacity after the first cycle. The adsorption capacity gradually decreases through the 10 th cycle and then retains approximately 90% of the original capacity through 25 cycles.[5] This thiol adsorbent is chemically stable in 12 M HCl stripping solutions.



Column Operation Mode

m = 0.2g SOL-AD-IV
Flow rate = 0.8ml/min
Loading:
1 Liter of 300mg/L Hg @ pH 5
Stripping:
25ml of 12.1M HCl
Washing:
10ml of DI water before and after stripping

q_0 = 760 mg/g
Capacity loss after 25 cycles = ~ 10%

Noble Metal Separation

The second adsorption system we will evaluate is SOL-PzPs (the pyrazole functional adsorbent) which we demonstrate can separate noble metals of palladium, platinum and gold.[6] The chemistry of adsorption is shown here.

- SOL-PzPs: Pyrazole Functionalized Adsorbent
- Extraction and Separation of Pd(II), Pt(IV), and Au(III) from 2.0 M HCl Solutions
    - Protonation of Functional Ligand $$H^{+} + \overline{R} \Leftrightarrow \overline{RH^{+}}$$
    - Adsorption of Chlorocomplexes $$M^{X-} + X\,\overline{RH^{+}} \Leftrightarrow \overline{M(HR)_{X}}$$

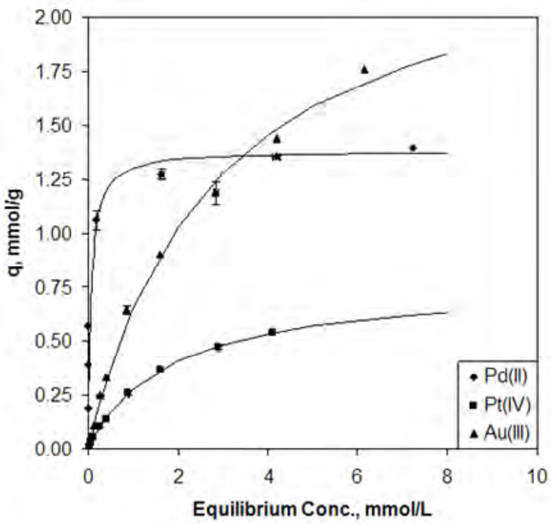
M^{X-} is $PdCl_4^{2-}$, $PtCl_6^{2-}$, and $AuCl_4^{-}$

$\overline{R}$ is Functional Ligand

$\overline{RH^{+}}$ is Protonated Ligand

Adsorption Isotherm

The adsorption isotherms were constructed as mentioned previously and we see that the palladium isotherm is the Langmuir form. Further in the practical range of concentration of <0.2 mmol/L, complete palladium separation from platinum and gold can be achieved.[6]



- Affinity order:
- Pd(II) >> Au(III) > Pt(IV)
- In practical conc. Range (<0.2 mmol/L):
  Complete Pd(II) separation

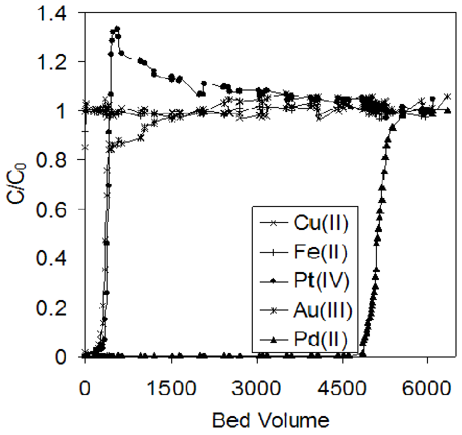
$$q_{PdCl_4^{2-}} = \frac{q_m K[PdCl_4^{2-}]}{1+K[PdCl_4^{2-}]}$$

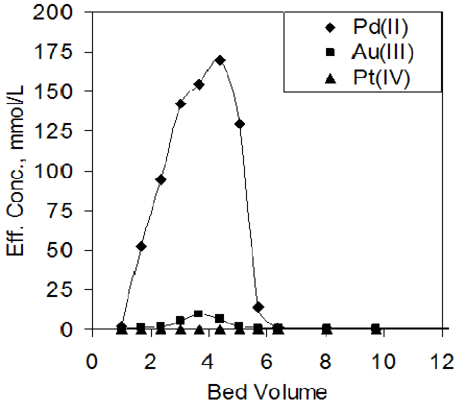
q_m = 1.284 mmol/g
K = 182 L/mmol

Breakthrough in Packed Column

Again we have to test the adsorbent in column operation with a typical feed composition one expects from noble metal leachate solutions. The figure on the left shows that copper and iron do not adsorb and that the platinum and gold are effectively displaced by palladium due to competitive adsorption. Appropriate stripping solutions are evaluated and thiourea solution in HCl removes 100% of the Pd and 91% of the Au from the solution.[6]

- Mixed Metal Feed Solution





- **Feed Solution**
  - **0.1 mmol/L each of Pd, Pt, and Au**
  - **2.5 mmol/L each of Cu(II) and Fe(II)**
- **Column Bed Volume = 2.98 ml**

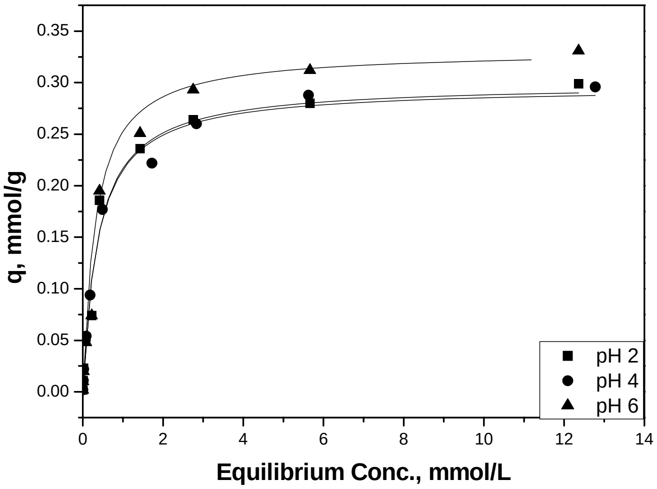
- 0.5 mol/L thiourea in 0.1 mol/L HCl
- Stripping Efficiency (Pd : 100 %, Au : 91 %)
- 12 liters into 0.021 liters

Adsorption Mechanism and Isotherm

The third system we present in that for germanium separation from zinc leachate ores. This system is interesting because of the high value of germanium due to the use in semi conductors. ($ 1700/ kg) The adsorption isotherms here show a Langmuir type behavior, although the detailed chemistry gives the complicated isotherm model shown on the right.[10] We note that at the pH range studied essentially only $Ge(OH)_4$ is present.

- Adsorption Mechanism (SOL-KELEX)

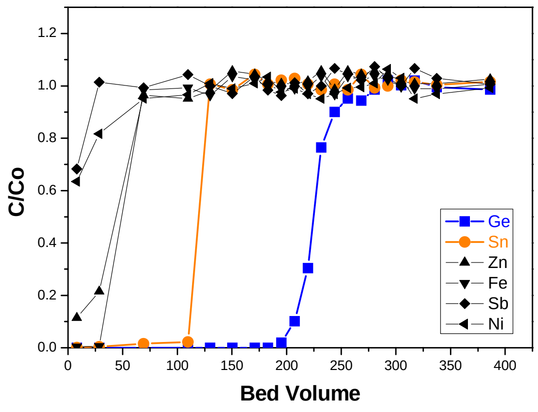
$$Ge(OH)_4 + 2\overline{HR} \leftrightarrow \overline{GeR_2(OH)_2} + 2H_2O \qquad q = \frac{4K_{eq}[Ge(OH)_4][\overline{HR}]_T{}^2}{(1+\sqrt{1+8K_{eq}[Ge(OH)_4][\overline{HR}]_T})^2}$$

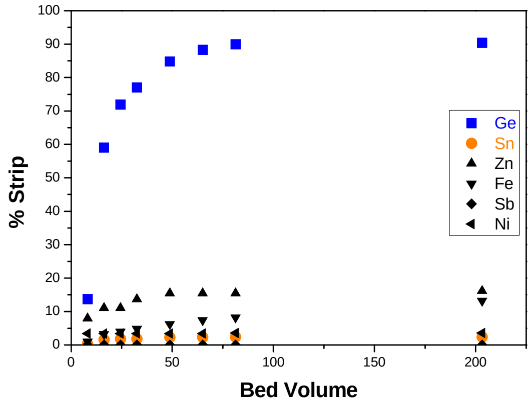


- ini Conc. = 1 ~ 1000ppm
- pHe = 2, 4, 6
- Adsorbent = 0.1 g
- Solution volume = 15 ml
- Batch Exp for 24hrs
- Buffer = 0.05M NaAc
- q_{max} = 21.5mg/g
- (0.33mmol/g)
- K_{eq} (L/mmol^2) = 2.65

Column selectivity (17 metals)

A major problem with germanium separation from zinc leachate solutions is the presence of numerous metals. Accordingly a selective ligand is required to yield a relatively pure germanium product. This figure shows the selectivity of SOL-KELEX for germanium in a column extraction from a simulated leachate solution. Germanium has the lowest concentration. The selectivity is about 91% germanium, 4% tin, and 5% combined of the four other metals shown.[10] Thus, multiple column adsorption/ stripping would yield an acceptable product.





Simulated solution composition

- **Zn: 2.28 ppm**
- **Ni: 2.08 ppm**
- **Fe: 2.21 ppm**
- **Sb: 1.39 ppm**
- **Sn: 1.37 ppm**
- **Ge: 0.59 ppm**
- As: 0.59 ppm
- Mg: 1.97 ppm
- Cu: 1.98 ppm
- Ca: 2.21 ppm
- Na: 1.28 ppm
- Pb: 2.41 ppm
- Al: 2.65 ppm
- Co: 2.23 ppm
- Cd: 2.04 ppm
- Mn: 1.34 ppm
- In: 2.06 ppm

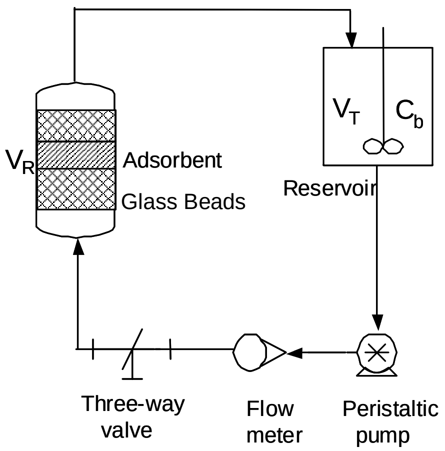
Modeling of $\mathbf{HgAc_4^{2-}}$ Adsorption Kinetics in Batch and Packed Column

It is necessary to develop models to describe the adsorption kinetics of the systems and permit analysis of fixed bed columns. These models can then be employed to design adsorption columns and process analysis can be executed. To outline the method, we will describe two laboratory experimental equipment, the analysis employed and results obtained for the SOL-AD-IV (thiol) adsorbent used in mercury separations. The equipment used are shown in this slide.

For the batch differential recycle reactor (BDRR), feed solution is circulated by a pump from a reservoir to a differential reactor containing a layer of the adsorbent between glass beads. A sample of the reservoir solution is taken at time intervals for mercury concentration analysis. The conditions are specified.

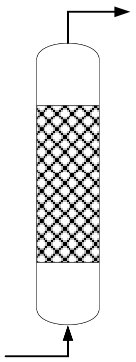
For the packed column the adsorbent is placed in the column of the geometry specified and flow of the mercury solution is started. Samples are taken at time intervals from the column exit flow and analyzed for mercury concentration. The conditions are specified. Different particle size ranges can be used but the 125-180 um range provides rapid adsorption with acceptable pressure drop.

Batch Differential Recycle Reactor



SOL-AD-IV (Thiol) = 0.2 gm (125 – 180 μm)
1.0 cm ID column
Vol. of solution = ~ 500 ml
Flow rate = ~ 40 ml/min

Packed Column



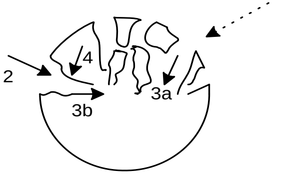
SOL-AD-IV (Thiol) = 2.0 gm (125 – 180 μm)
0.7 cm ID column
Solution = 0.5-50mg/L Hg, pH 5, 0.1M Ac
Flow rate = ~1.0 ml/min

Mass Transfer in Adsorption Processes

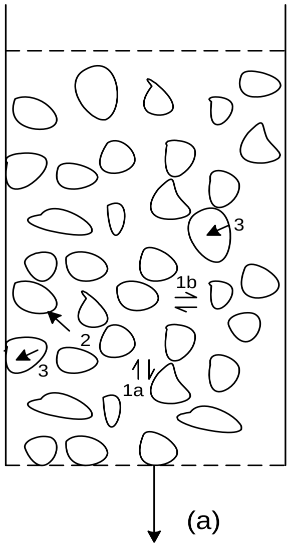
The details of mass transfer in adsorption processes are described in this slide.[11] For interpellet / intrapellet mass transfer the solute can undergo the three steps described. These include interphase mass transfer (2), intrapellet mass transfer by pore diffusion or/and surface diffusion (3a, b), and surface adsorption (4). In fixed beds the solute flows down (up) through the bed due to convection motion and can undergo axial dispersion (1a) and radial dispersion (1b).

a. Fixed Beds
b. Intrapellet mass transfer

1a	Axial dispersion
1b	Radial dispersion
2	Interphase mass transfer
3	Intrapellet mass transfer
3a	Pore diffusion
3b	Surface diffusion
4	Adsorption



(b)



(a)

Kinetic Modeling of Adsorption

There are several approaches to model the adsorption of solutes in particles. The first of two we have employed assumes that the kinetics of surface adsorption controls; the chemical reaction model. This case is likely for small particle size ranges where intrapellet diffusional resistances are small and high flow rates are employed through the bed.

For mercury adsorption on SOL-AD-IV, the adsorption stoichiometric equation, the corresponding rate expression, the design equation for the BDRR and the solution is presented. A statistical method is employed to obtain the best value for the forward reaction rate coefficient k_2 and the reverse coefficient is obtained from $K_{eq,2}$. The model can be used to describe adsorption kinetics.

- Case 1: Chemical Reaction Model: Kinetics of Surface Adsorption Controls. Hg adsorption on SOL-AD-IV (pH ≥ 5; acetate buffered chloride solution):

$$\overline{RSH} + HgAc_4{}^{2-} \underset{k_{-2}}{\overset{k_2}{\longleftrightarrow}} \overline{RS \cdot HgAc} + H^+ + 3Ac^- \qquad K_{eq} = k_2 / k_{-2}$$

$$rate = -\frac{d[HgAc_4{}^{2-}]}{dt} = k_2[\overline{RSH}][HgAc_4{}^{2-}] - k_{-2}[\overline{RS \cdot HgAc}][H^+]\{Ac^-\}^3$$

Design Equation for Batch Differential Recycle Reactor:

$$-rate = \left(\frac{V_R + V_T}{V_R}\right)\frac{dC_T}{dt}$$

Solving above two equations (linear regression method of Levenberg-Marquardt)

$$C(t) = \frac{De^{Ak_2} - EB}{2B - 2e^{Ak_2}} \qquad A,B,D,E = \text{constants} = f(C_{B0}, S_T, M, V, [H^+], \{Ac^-\})$$

Solve for k_2 : k_{-2} obtained from $K_{eq,2}$

The second approach employed is when we assume that the rate of adsorption is controlled by solute transport through the film and particle pores. The chemical rate of adsorption is assumed instantaneous. This case is likely for larger particle size ranges and small pore diameters.
A macroscopic balance is made for the BDRR where the average mass of mercury adsorbed per unit mass of adsorbent, q, is calculated for average particle size with appropriate initial and boundary conditions.

The pore diffusion equations are solved to calculate the rate of mercury acetate adsorbed into an average particle with time during the BDRR experiment. These equations can also be employed to describe adsorption kinetics.

- Case 2: Film-Pore Model: Solute Transport Through Film and Pore Adsorption Controls (Spherical Particle):

Macroscopic Balance for Batch Differential Reactor:

$$V\,(C_{b_o} - C_b) = M\,\bar{q}$$

$$\bar{q} = \frac{3}{R_p{}^3}\int_0^R q\, r^2 dr$$

$$q = [\overline{RS \cdot Hg \cdot Ac}] = \frac{S_T K_{eq2}[HgAc_4{}^{2-}]}{[H^+][Ac^-]^3 \gamma_{Ac}{}^3 + K_{eq2}[HgAc_4{}^{2-}]}$$

Pore Diffusion Equation:

$$\left[\varepsilon_p + \rho_{\mathrm{p}} \frac{\partial q}{\partial c}\right]\frac{\partial c}{\partial t} = \frac{D_p}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right)$$

$$c = 0, \qquad t \leq 0 \qquad 0 \leq r \leq R$$

$$\frac{\partial c}{\partial r} = 0, \qquad r = 0$$

$$D_p \frac{\partial c}{\partial r} = k_f\ (c_b - c), \qquad r = R$$

The last set of equations we will discuss are those used to model the performance of the adsorption column. These are shown on the next figure and include the column mass balance and the same set of pore diffusion equations for intraparticle mass transfer we used in previous slide.

- Modeling Column Adsorption (Film-Pore Resistance Controls Adsorption)

Column Mass Balance

$$u_s \frac{\partial c_b}{\partial z} + \varepsilon \frac{\partial c_b}{\partial \theta} + \rho_b \frac{\partial \overline{q}}{\partial \theta} = 0$$

$$c_b = 0, \qquad z \geq 0 \quad and \quad t \leq 0$$

$$c_b = c_{b0}, \qquad z = 0 \quad and \quad t > 0$$

where

$$\rho_b = (1 - \varepsilon_b)\rho_p, \ \theta = t - z\varepsilon / u_s$$

Pore Diffusion Equation:

$$\left[\varepsilon_p + \rho_{\mathrm{p}} \frac{\partial q}{\partial c}\right]\frac{\partial c}{\partial t} = \frac{D_p}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right)$$

$$c = 0, \qquad t \leq 0 \qquad 0 \leq r \leq R$$

$$\frac{\partial c}{\partial r} = 0, \qquad r = 0$$

$$D_p \frac{\partial c}{\partial r} = k_f\ (c_b - c), \qquad r = R$$

Solution of Case 2 BDRR Adsorption and Column Adsorption Equations

The solution method used is beyond the scope of this presentation. To summarize we used the numerical method of lines and transformed the PDE's to a set of ODE's and solved the set of ODE's simultaneously. The parameters were estimated from the classical correlations shown and D_m and t are determined as fitting parameters.

Numerical Method

- Method of Lines
  - Transform PDEs to set of ODEs
  - Solve the set of ODEs simultaneously
  - Parameter Estimation

$$D_p = \frac{\varepsilon_p \, \mathrm{D_M}}{\tau} \qquad k_f = J_D \, \frac{u_s}{Sc^{2/3}}$$

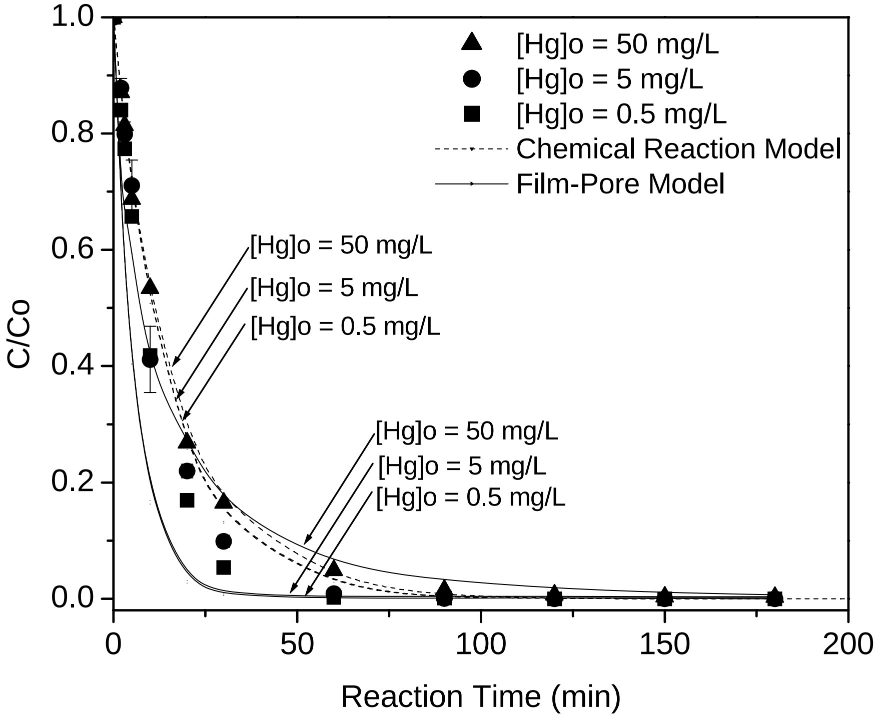
$$\mathrm{Re} = \frac{\rho_f \, u_s \, d_p}{\mu_f} \qquad Sc = \frac{\mu_f}{\rho_f \, D_M}$$

- D_M and t are determined as fitting parameters

Adsorption Kinetics for Mercury

The adsorption kinetics for mercury acetate adsorbed on SOL-AD-IV(Thiol) using the BDRR are shown on this slide.[5] The two curves for [Hg] of 5 and 0.5 mg/L for both the chemical reaction and film-pore models essentially overlap.

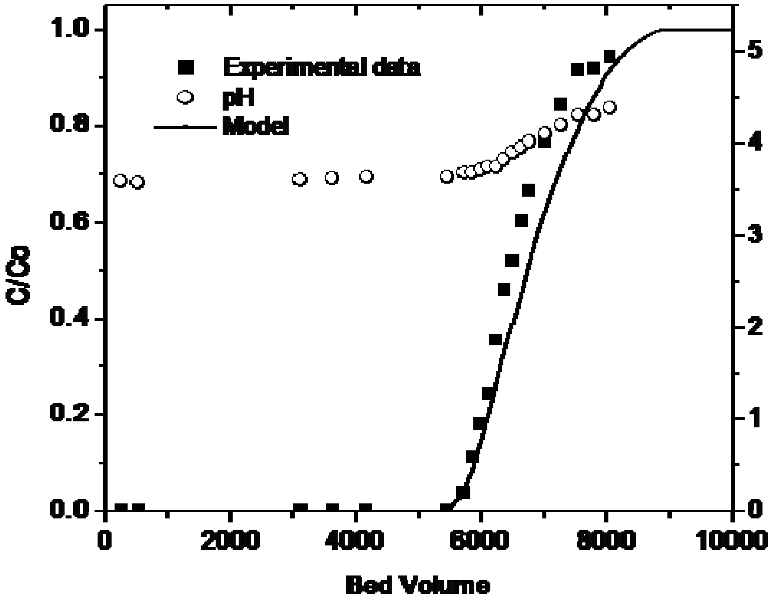
An average particle diameter of 152 um for the range 125-180 um is used in the calculations. Quantitative evaluation of the two models can be made and the error analysis suggests that the film-pore model better predicts the data.



Model	Overall AARD*	D_p (cm^2/s)	k_2 (L/mmol·s)	
Film-Pore	0.35	1.72×10^{-6}	-	**τ = 2**
Chemical Reaction	0.50	-	0.399	

Breakthrough for Mercury

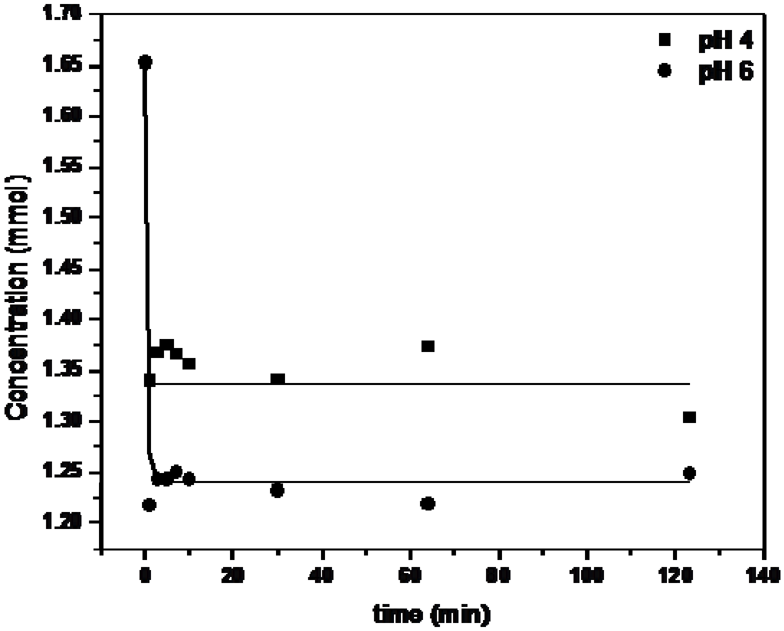
The high mercury concentration [Hg]= 50mg/L breakthrough curve for the experiment and the predicted film-pore differ model is shown in this slide.[5] A good agreement is seen in the comparison.



Loading Condition
0.25 mmol/L Hg at pH 5
12 liters into 0.021 liters
0.2 g in 0.7 cm ID column;
Flow rate = 1 ml/min

Adsorption Kinetics for Germanium

Similar adsorption studies in the BDRR are shown in slide 36 to demonstrate utility of this approach for other systems, this case being the adsorption kinetics of germanium. The concentration change of germanium is modeled well at two pH experiments using the film-pore model for the controlling resistance for the adsorption of germanium.[10] The values of the parameters employed and calculations are provided.

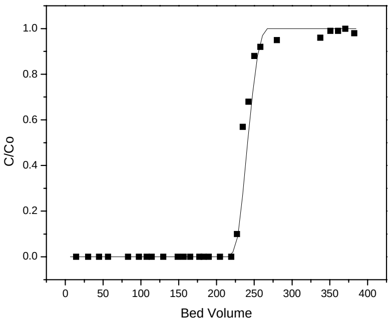


- ini Conc. = 100ppm
- pHe = 4, 6
- Adsorbent = 0.5 g
- Solution volume = 100 ml
- $D_M = 3.8 \times 10^{-6}$ cm^2/s
- $k_f = 1.983 \times 10^{-1}$ cm/s
- $\tau = 0.5$
- $D_p = 2.97 \times 10^{-10}$ m^2/s

Breakthrough for Germanium

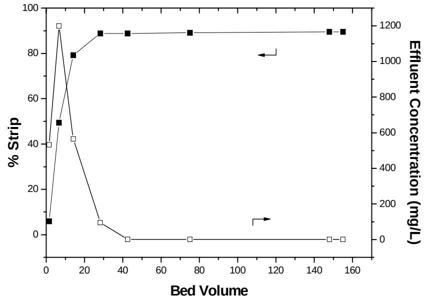
Similarly, column breakthrough experiments are modeled using the film-pore model. A good fit of the experimental data is shown in this study as well. The parameters of the experiment are presented and the values for τ and D_p shown in the previous slide were employed.

Also shown is the subsequent stripping experiment. Approximately 90% of the adsorbed germanium can be recovered using the stripping conditions shown.[10]



- Loading Condition

- 0.5 g in 0.7 cm ID Column
- $[Ge]_{in}$ = 51.3ppm
- pH_{in} = 6.11
- Flow rate = 0.86 mL/min
- Capacity = 0.21 mmol/g



- Stripping Condition

- Strip Conc. = 1M HCl
- Flow rate = 1.08 mL/min
- Stripping Efficiency = 92%

Conclusions

- Examined methods to develop adsorbents through covalent attachment of ligands using sol-gel synthesis techniques.
- Described methods to characterize these adsorbents including ^{29}Si-NMR spectra; uptake capacity studies; BET measurement of pore diameters, porosity and surface area.
- Results show sol-gel adsorbents have metal selectivity, good physical/chemical stability, and capacities comparable to highest polymer resins.
- Three applications were shown for mercury removal, noble metal separations and germanium recovery from zinc leachate solutions. The results are promising.
- Mathematical modeling of batch adsorption was outlined to evaluate the rate determining steps of adsorption when either chemical reaction rate or film-pore diffusion controls.
- Mathematical modeling of fixed bed absorbers was outlined to evaluate breakthrough curves of adsorption columns for the specific separations and sol-gel adsorbents developed.
- The sol-gel systems have potential for application to nuclear fuel separations and the modeling approaches can be employed to design column and evaluate unit operation performance.

Notations

c = metal concentration in the pore, mmol/L
c_b = metal concentration in the bulk, mmol/L
c_{bo} = initial metal concentration in the bulk, mmol/L
c_s = metal concentration at the pellet surface, mmol/L
c_T = total concentration of each metal, mmol/L
D_p = pore diffusion coefficient, cm^2/s
D_M = molecular diffusion coefficient, cm^2/s
K_{eq} = equilibrium constant, $L \cdot g/mmol^2$, L/mmol
k_f = film coefficient, cm/s
q = local concentration in the pellet, mmol of metal/g of adsorbent
= average concentration in the pellet, mmol of metal/g of adsorbent
r = radial direction of the pellet, cm
R_p = radius of pellet, cm
q_{max} = max capacity of the adsorbent, mmol/g
t = time, min
u_s =superficial velocity, cm/s
V = volume of solution, L
V_R = volume of reactor, L
V_T = volume of tank, L
z = axial direction in the column, cm
τ= particle tortuosity
ε_p = pellet porosity
ε_b = bed porosity
ρ_p = pellet density, g/cm^3
ρ_b = bed density, g/cm^3
ρ_s = solid density of the adsorbent, g/cm^3
θ = corrected time in column calculations, $t\text{-}z\varepsilon/\ u_s$; min, s
k_2 = forward reaction rate constant
k_{-2} = reverse reaction rate constant
M = weight of adsorbent, g
γ = activity coefficient
μ = liquid viscosity, cP

References

1. L. L. Tavlarides; J.S. Lee. New Materials in Solvent Extraction. In Solvent Extraction and Liquid Membranes: Fundamentals and Applications in New Materials (Ion Exchange and Solvent Extraction); Aguilar, M.; Cortina, J. L., Eds.; CRC Press, Florida, 2008; 225-260.
2. N.V. Deorkar; L. L. Tavlarides. Emerging Separation Technologies for Metals II, The Minerals, Metals & Materials Society, Warrendale, Pennsylvania, USA, 1996, 107 – 118.
3. S. S. Gomez; L.L. Tavlarides. Synthesis of thiol functionalized organo-ceramic adsorbent by sol-gel technology, Reactive and Functional Polymers 2001, 49, 159-172.
4. N. V. Deorkar; L. L. Tavlarides. Zinc, Cadmium, and Lead Separation from Aqueous Streams Using Solid-Phase Extractants, Ind. Eng. Chem. Res., 1997, 36, 399-406.
5. K. H. Nam; S. S. Gomez; L. L. Tavlarides. Mercury(II) Adsorption from Wastewaters Using a Thiol Functional Adsorbent, Ind. Eng. Chem. Res. 2003, 42(9), 1955-1964.
6. J. S. Lee; L. L. Tavlarides. Pyrazole Functionalized Organo-Ceramic Hybrids for Noble Metal Separations, AIChE, 2005, 51, 2702-2711.
7. J. S. Lee. MS Thesis, Syracuse University, Syracuse, NY 1997.

8. J. S. Lee; L. L. Tavlarides. Application of Organo-Ceramic Adsorbents Functionalized with Imidazole for Noble Metal Separations, *Solvent Extr. Ion Exch*., 2002, 20(3), 407-427.
9. H. J. Park; L. L. Tavlarides.Adsorption of Chromium (VI) from Aqueous Solution Using an Imidazole Functionalized Adsorbent, *Ind. Eng. Chem. Res*., 2008, 47, 3401-3409.
10. H. J. Park; L. L. Tavlarides. Germanium (IV) Adsorption from Aqueous Solution Using a Kelex-100 Functional Adsorbent, *Ind. Eng. Chem. Res*., 2009, submitted.
11. C. Tien. Adsorption Calculations and Modeling, Butterworth-Heinemann Series in Chemical Engineering, Butterworth Heinemann, Boston, USA, 1994
12. Rovira; J. L. Crotina; J. Arnaldos; A. M. Sastre. Impregnated Resins Containing Di-(2-ethylhexyl) Thiophosphoric Acid for the Extraction of Palladium (II). II. Selective Palladium (II) Recovery from Hydrochloric Acid Solutions, Solvent Extraction and Ion Exchange, 1999, 17, 351-366.
13. M. Iglesias; E. Antico; V. Salvado. Recovery of Palladium (II) and Gold (III) from Dilute Liquors using the Resin Duolite GT-73, Analytica Chimica Acta, 1999, 381, 67-67.
14. A. Sugii; N.. Ogawa; H. Hashizume. Preparation and Properties of Macroreticular Resins Containing Thiazole and Thiazoline Groups, Talanta, 1980, 27, 627-631.
15. X. Feng; G. E. Fryxell; L. Q. Wang; A. Y. Kim; J. Liu; K. M. Kemner. Functionalized Monolayers on Ordered Mesoporous Supports, Science, 1997, 276, 923-926.
16. J. P. Marco; D. Cazorla; S. A. Linares. A New Strategy for Germanium Adsorption on Activated Carbon by Complex Formation. Carbon. 2007, 45(13), 2519-2528.
17. Y. Inukai; Y. Tanaka; Y. Shiraishi; T. Matsuda;, N. Mihara;, K. Yamada; N. Nambu; O. Itho; T. Doi;, Y. Kaida; S. Yasuda. Selective Separation of Germanium (IV) by Di-(2-hydroxyethyl) Amine-Type Cellulose Derivative. Analytical Sciences. 2001, 1, 1117-1120.
18. O. S. Pokrovsky; G.S. Pokrovski; J. Schott; A. Galy. Experimental Study of Germanium Adsorption on Goethite and Germanium Coprecipitation with Iron Hydroxide: X-ray Absorption Fine Structure and Macroscopic Characterization. Geochimica et Cosmochimica Acta. 2006, 70, 3325-3341.
19. M. B. Colella; S. Siggia; R.M. Barnes. Synthesis and characterization of a poly(acrylamidoxime) metal chelating resin. *Anal. Chem.* 1980, 52, 967-9722.

Quantifying the Risk of Nuclear Fuel Recycling Facilities

B. John Garrick
Willard C. Gekler
U.S. Nuclear Waste Technical Review Board

Introduction

Quantitative risk assessment (QRA) as a method of safety analysis of nuclear facilities is most strongly identified with probabilistic risk assessment (PRA) of nuclear power plants. The last safety analysis (Nuclear Fuel Services, 1962) of a commercial U.S. nuclear fuel recycling plant that actually went into operation was performed in 1962 to support the license application of the West Valley Spent Fuel Processing Plant under Title 10, Part 50, "Domestic Licensing of Production and Utilization Facilities," of the *Code of Federal Regulations* (10 CFR Part 50). This, of course, was some 13 years before the publication of the famous Reactor Safety Study (USNRC, 1975). Meanwhile, QRA (QRA and PRA have the same meaning in this paper) has become the foundational approach for comprehensively implementing the concept of risk-informed safety analysis. This does not mean that QRA has been universally accepted in the safety analysis world, although it pretty much has when it comes to such high profile facilities as nuclear power plants and nuclear waste repositories. As renewed interest develops in the U.S. for recycling nuclear fuel, it is prudent to examine the progress that has been made in nuclear facility safety analysis and how risk-informed safety analysis might be applied to nuclear fuel recycling facilities. Thus, it is the purpose of this paper to consider how QRA might be applied to a nuclear fuel recycling plant.

Any decision to apply QRA to nuclear fuel recycling must be accompanied with the decision of which QRA approach best serves the needs of the particular problem. In this case we adopt what is referred to in the literature (Garrick, et al., 2008) as the scenario approach to risk assessment based on the triplet definition of risk discussed later. In the absence of an actual QRA of a nuclear fuel recycling plant, the approach will be to highlight the methodology and illustrate how selected QRA algorithms might be applied, including the type and form of the results.

Why Quantitative Risk Assessment

The primary advantages of a QRA are completeness, context, and realism; completeness, in the sense that all of the scenarios that can threaten the performance of the system are in principle considered, and context in the sense that the likelihood of the scenario, including its consequence, is part of the answer. Of course, it may not be possible to manifest all of the scenarios that represent a threat to the system, but it is usually possible to account for the important ones. Similarly, it may not be possible to calculate absolute likelihoods (e.g., probabilities), but by embracing the concept of uncertainty in the likelihood functions the confidence in the likelihoods can be manifested. The concept of likelihoods and scenarios allows for the systematic importance ranking of the contributors to risk and a scientific basis for effective risk management. It also allows for the aggregation of the risk of individual scenarios into the total risk of the system. Finally, one of the important drivers for QRA was to have a method of safety analysis that targeted realistic results, as opposed to bounding analyses, that tend to leave the reader wondering what the experts believe is the real risk.

Fundamentals of Quantitative Risk Assessment

The fundamentals of the QRA approach that are advocated here involve the following basic steps:

Step 1. Define the system being analyzed in terms of what constitutes normal operation to serve as a baseline reference point.

Step 2. Identify and characterize the sources of danger, that is, the hazards (e.g., stored energy, toxic substances, hazardous materials, acts of nature, sabotage, terrorism, equipment failure, combinations of each, etc.).

Step 3. Develop “what can go wrong” scenarios to establish levels of damage (consequences) while identifying points of vulnerability.

Step 4. Quantify the likelihoods of the different scenarios and their attendant levels of damage based on the totality of relevant evidence available.

Step 5. Assemble the scenarios according to damage levels, and cast the results into the appropriate risk curves and risk priorities.

Step 6. Interpret the results to guide the risk management process.

Steps 1 through 4 are founded on five basic principles and conditions, (1) the triplet definition of risk, (2) scenarios linking threats to consequences, (3) the quantification of uncertainties, (4) the *credibility* definition of probability, and (5) Bayesian inferential reasoning.

Definition of Risk

The general framework for QRA is the "set of triplets" definition of risk.

$$R = \{<S_i, L_i, X_i>\}_c,$$

In this format, the inner brackets enclose the triplet, the outer brackets denote "the set of", and the subscript c implies that the set is complete. The risk ("R") is a comprehensive answer to the following questions:

- "What can go wrong?" This question is answered by describing a structured, organized, and complete set of possible damage scenarios ("S").

- "What is the likelihood of each scenario?" This question is answered by performing detailed analyses of each risk scenario, using the best available data and engineering knowledge of the relevant processes, and explicitly accounting for all sources of uncertainty that contribute to the scenario likelihood ("L").

- "What are the consequences?" This question is answered by systematically describing the possible end states, including the damage states, such as different radiation dose levels that may be received by a member of the public ("X").

Structuring the Scenarios

The process of structuring “what can go wrong” scenarios involves three major activities. The first is the development of the so called success scenario for the system being analyzed. The success scenario usually involves linearizing the system to the extent possible into different stages, phases or functions that must perform in sequence in order for the total system to perform its intended function. The success scenario must be structured such that any significant threat to the system can be represented as a disturbance to one or more of the function boxes in the success scenario. This suggests the second activity and that is the performance of a threat assessment. The threat assessment is the process of analyzing each function in the success scenario in terms of the types of events that could disturb the function. In many respects the threat analysis is the most important and creative part of risk modeling because it is the key to the completeness of the process. The location and operating conditions are major factors in determining the threats to any facility. Some threats may cause a direct release of radioactive materials from the facility, while others may initiate a sequence of events that unless mitigated will result in such releases. Some threats may alter the site in ways that increase its vulnerability to other threats: e.g., loss of essential support services or events that could alter natural protective barriers of the site. Potential conditions that may affect the site are often grouped into two general categories.

- **Disruptive Events**. These are unexpected events that may cause an immediate change to the site or the facility. They are typically characterized by an event occurrence frequency and by directly measurable immediate consequences. Examples are severe storms, tornadoes, earthquakes, fires, and airplane crashes.

- **Nominal Events and Processes**. These are expected events and processes that evolve continuously over the life of the facility. They are typically characterized by a rate, which may be constant or changing over time. The potential consequences from these processes depend on the duration of the exposure period. Examples are the aging and degradation of engineered systems.

The scope of potential threats should be as complete as reasonably possible and include a broad range of natural phenomena and processes, equipment degradation, and human-caused events. Generally, risk assessments do not include intentional acts of destruction, war, terrorism, or sabotage, although the QRA methodology can be effectively applied to such threats (Garrick, et al., 2004). For security reasons, it is prudent to do such QRAs separately. Threats can be screened out when there is evidence that they do not compete with the threats driving the risk. In the table below are examples of the types of threats that might be considered for a nuclear fuel recycling plant.

Internal Threats: Fires, Explosions, Equipment Failure including Safety Equipment, Operator Error, Instrument Malfunction, Criticality Events, Process Malfunctions, Power Disruptions, Building Failure, Deliberate Human Acts, Failure to Follow Procedures or Believe Instrument Readings

External Threats: Fires, Loss of External Power Supplies, Loss of Other Utilities, Severe Storms, Sitewide Pipeline and Utility Accidents, Seismic Events, Hurricanes, Tornadoes, Nearby Facility Accidents, Site Intrusions, Toxic Gas Releases, Transportation Accidents, Volcanoes, Surface Geology, Lightning, Flooding Events

Each threat must be considered and its disposition determined in order to decide how much analysis it deserves.

Finally, the third activity of structuring scenarios is given the events or conditions that could disturb any of the functions necessary for system success (usually labeled *initiating events or initial conditions*), what is the sequence of events to the final damage states of the individual scenarios, another very creative part of risk assessment. The damage states may take many forms from radiation release mechanisms to radiation dose and from physical damage to the plant to human injuries and fatalities. The total process is illustrated in Figure 1.

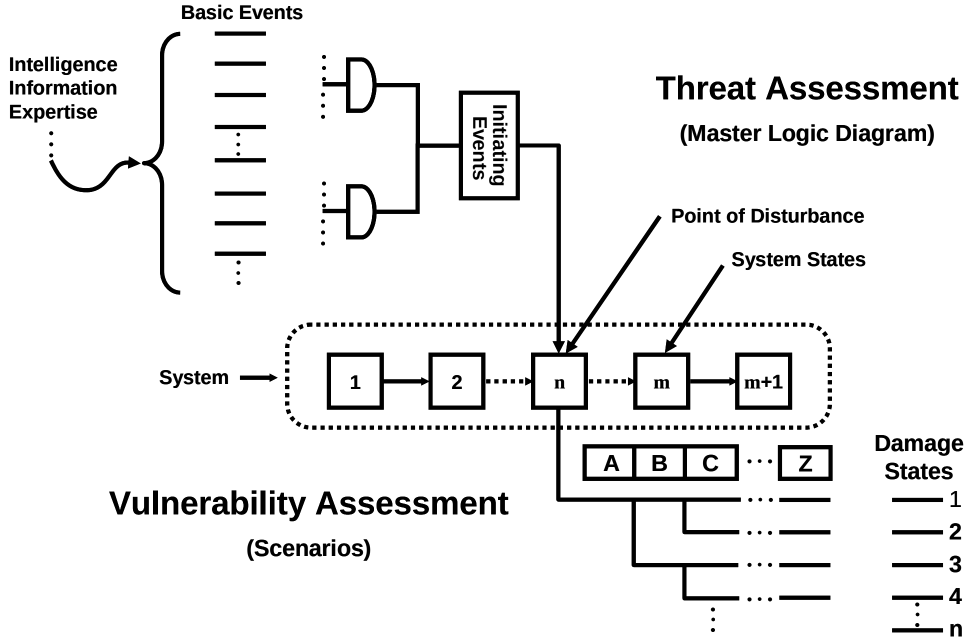


Figure 1. The Concept of Linking System Disturbances to System Damage States

Quantification, Probability, and Bayes Theorem

Given that we know what the scenarios are, the question now is, how do we go about quantifying their consequences and converting the results into a statement of risk. The answer lies in the parameter chosen to measure risk, the manner in which uncertainties are quantified, and the interpretation given to *probability*. The parameter chosen to measure risk is the frequency of occurrence of different states of damage (consequences). Quantification is recognizing that the damage state frequencies are uncertain and must be quantified. Frequency uncertainty is communicated by a probability distribution (probability of frequency concept). Two types of uncertainty that dominate the quantification process are information uncertainty and modeling uncertainty. Both have to be addressed.

We define probability as synonymous with *credibility*, as in the credibility of a hypothesis based on all the available evidence. It is a positive number ranging from zero to one that obeys Bayes theorem. The probability curves for the frequency of different damage states are inferred from all of the available evidence, using the fundamental mathematical principle of logical inference, known as Bayes theorem. In particular, Bayes theorem answers the question, how does the probability of a given hypothesis change with new information.

The actual quantification process is done with the aid of an event tree, a decision type diagram first used in the nuclear field in the Reactor Safety Study. The event tree traces the sequence of events following any abnormal disturbance of the system and is illustrated in Figure 2.

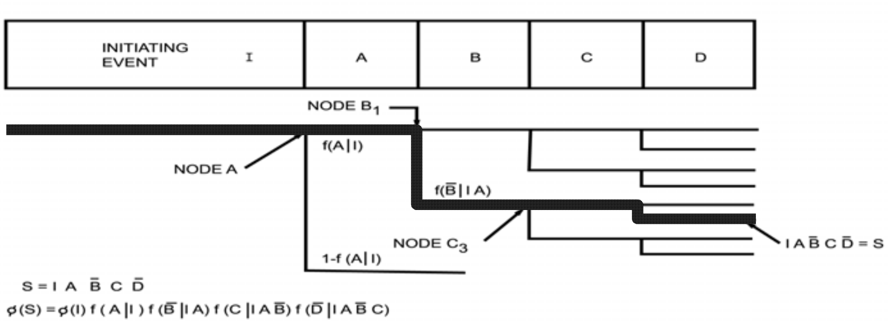


Figure 2. Quantification of a Scenario Using an Event Tree

The boxes A, B, C, and D represent intervening events, such as a backup system, that can alter the course of the scenario. The likelihood of a scenario depends on the quantification of the split fractions at the branch points in the scenario. All branch points that are logically relevant are considered. Each scenario is represented by a Boolean equation combining branch point events. The form of each term in the Boolean equation is a probability density function and the risk of a scenario is the convolution of the various terms in equations of the type shown in Figure 2. The convolution process is illustrated for the highlighted scenario in Figure 3.

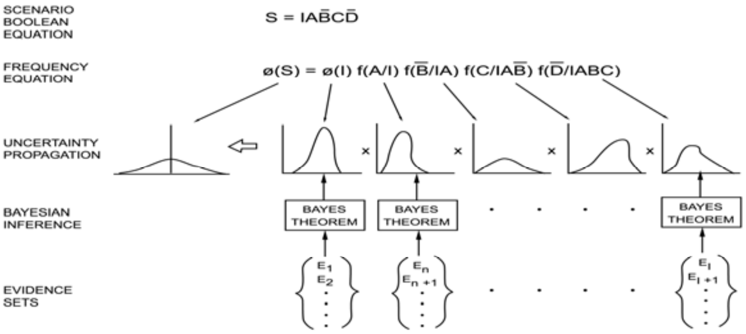


Figure 3. Bayes Theorem Used to Process Parameters

Assembling the Scenarios

A QRA of a complex system such as a nuclear fuel recycling plant may end up having hundreds, thousands, or possibly even millions of individual scenarios, each scenario represented by a probability of frequency curve of the form of Figure 4.

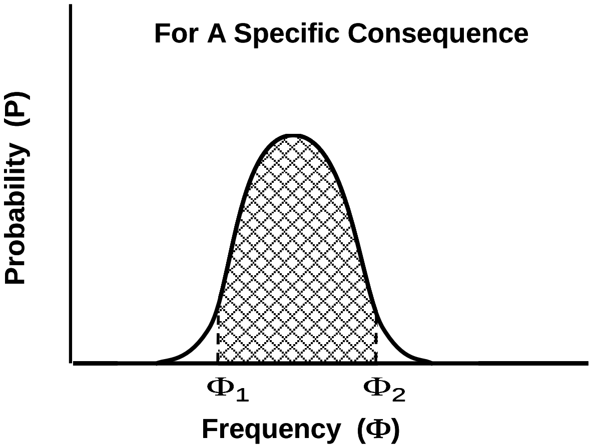


Figure 4. Probability of Frequency Curve

Figure 4 is a very convenient form for representing the risk of an individual scenario. Suppose the shaded area is 90% of the total area under the curve. What this curve tells us is that we are 90% confident that the frequency range of this consequence is between φ_1 and φ_2.

The question is: how do we assemble the individual scenarios into a form that represents the risk of the total system? The most common form of such a representation is to construct from the individual scenarios, using probability arithmetic, frequency-of-exceedance curves, also known as complementary-cumulative-distribution-functions. In particular, such curves are obtained by ordering the scenarios by increasing levels of damage and cumulating the probabilities from the bottom up in the ordered set against the different damage levels and plotting the results in a log-log format. The result is a curve of the form of Figure 5.

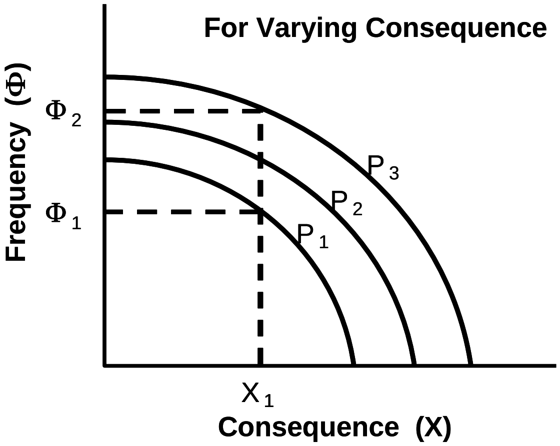


Figure 5. Risk Curves for Varying Consequences

Suppose in Figure 5 that P_1 and P_3 are the 5^{th} and 95^{th} percentile curves. The total risk of the system under consideration would be described in the following manner: we are 90% confident that the frequency of occurrence of X_1 level of damage, or greater, is in the range of φ_1 to φ_2.

Interpreting the Results

While it is a major achievement to obtain results of the above forms, the most important result from a QRA is full exposure of the contributors to the risk and their relative importance. The above method of assembling the results provides the information necessary to deconstruct the results into different types of contributors and their relative importance. This is the information that is most valuable in making decisions for controlling the risk, the primary reason for doing a QRA.

Safety Experience of Nuclear Fuel Recycling Plants

As a preamble to how the above methodology might be applied to a nuclear fuel recycling plant, it is appropriate to make a few observations on what the safety experience has been with such plants. Currently there are no operating nuclear fuel recycling plants in the U.S. The major recycling plants operating worldwide are in France, the United Kingdom, Japan, and Russia. India has three plants, but little is known about their safety experience.

The past U.S. experience includes large Government-owned plants located in Richland, Washington, and Savannah River, South Carolina, for plutonium production and a plant in Idaho to recover spent naval reactor and other highly enriched fuels (USNRC, 2008). The only commercial nuclear fuel recycling plant to operate in the U.S. was the Nuclear Fuel Services' West Valley plant, which is now shutdown and being decommissioned. The West Valley plant differed from the government facilities in that it processed high burnup oxide fuels. It was a multi-purpose plant designed to reprocess a wide range of fuel types. Its product was uranyl nitrate and plutonium nitrate in the form of concentrated aqueous solutions.

There have been no known accidents in recycling plants that involved large numbers of fatalities. There have been criticality accidents that resulted in deaths and major radiation exposure injuries at Tomsk in Russia (fuel reprocessing plant) and Tokaimura in Japan (nuclear fuel plant). In both cases, plant operators were performing manual transfers that had not been properly reviewed and moved nuclear material into geometrically unsafe (for criticality control) vessels. Such experiences have been used to design fuel reprocessing and fuel fabrication facilities so that nuclear criticality is prevented by physical controls that cannot be bypassed except after a safety review.

Over the several decades of operation of the U.S. government plants there were incidents of fires, leaks and spills, chemical and resin explosions, and temporary failures of offgas treatment systems. The most high profile events have been the so called "red oil incidents" that have occurred in government plants in the U.S., Russia and Canada (USNRC, 2008). Red oil is formed when tributyl phosphate (TBP) comes in contact with concentrated nitric acid at temperatures above 130°C. Under these conditions the TBP undergoes decomposition and nitration reactions causing formation of nitrated organic compounds that give the organic phase an amber color, hence the name "red oil". If the temperature is above 130°C the red oil can undergo rapid decomposition generating gases and overpressure. These gases can also detonate or decompose explosively. Studies of red oil explosions recommend a maximum process temperature of 120^{o} C to provide a safety margin where TBP may be present.

Red oil incidents have occurred in the Hanford reprocessing plant in 1953 and at the Savannah River plant in 1953 and 1957. There were no major personnel injuries associated with any of these incidents. Red oil explosions have also occurred in reprocessing plants in Russia and Canada. The exact nature of the damage or injuries outside of the U.S. from reprocessing plant accidents is not known, but is not believed to have been extensive, especially with respect to radiological consequences. It should be noted that in each red oil incident a major cost consequence was the downtime to evaluate the incident and define requirements for safely resuming operation. The French plant has not experienced the red oil phenomenon.

As to the safety experience of the West Valley commercial plant which operated from 1966 to 1972 by Nuclear Fuel Services, Inc., there were no accidents where the radiological consequences resulted in any fatalities. However, there were several incidents involving the release of radioactivity (Mellon, 2008). While the number of leaks and spills was quite high for such a short operating period, most were inconsequential from a worker and public safety standpoint because of the design of the process cells to accommodate limited leaks and spills. Two incidents are noted that did go beyond the ability of the design to provide full containment. One occurred in 1967 and involved a leak of about 200 gallons of recovered nitric acid from one of the lines in the offgas operating aisle. The leak traveled from the breached line down the walls of the offgas cell and the adjacent southwest stairwell below and under the Main Process Building through a floor expansion joint. This turned out to be the dominant contributor to what was later identified as the North Plateau groundwater plume. ^{90}Sr and its decay product ^{90}Y are the principal radionuclides of health concern in this plume.

The second incident of some radiological consequence was an uncontrolled airborne release in 1968. This leak occurred when a high-efficiency particulate air filter in the main ventilation system failed and part of the filter media was drawn into the blower, cut into pieces, and discharged out the main stack. While no excessive doses of radiation were received by members of the public, this event did have offsite radiological consequences.

During the operating period of the plant there were numerous leaks, spills, small fires, and operating errors involving radioactive liquids (E.R. Johnson, 1980). While the safety risk was generally limited, some of the events had serious operational risk consequences. For example, there was a leak of high activity waste from a line rupture between the general purpose evaporator and the high-level waste tank that required operations to be halted for some 2 months to decontaminate the affected area and replace equipment.

The U.S. experience with nuclear fuel recycling while limited is still sufficient to support meaningful risk analysis and management. In combination with the international experience, there exists a reasonably robust data and information base on the safety of operations to support very meaningful quantitative risk assessments providing the uncertainties become part of the results of the assessment.

Structuring a QRA Model for Recycling Facilities

As previously indicated, a QRA was not available to the authors to illustrate the six-step QRA process noted earlier. We will discuss how each step might be implemented for a recycling plant and in some cases illustrate the QRA modeling algorithms.

Step 1. Define the system being analyzed in terms of what constitutes normal operation

For a fuel recycling facility the sequence processing steps needed for successful operation can be derived from the process flow diagram. For example, Figure 6 is a simplified process flow diagram or block flow diagram showing the major processing steps in a typical nuclear fuel recycling plant based on the PUREX technology.

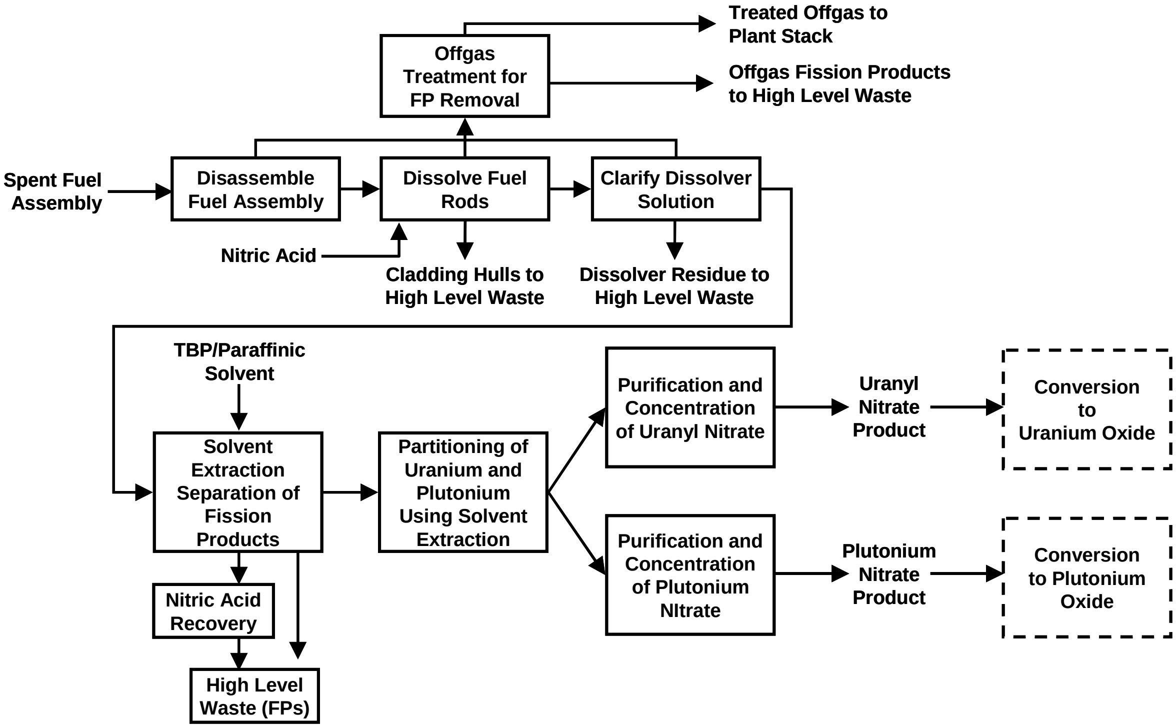


Figure 6. Simplified PUREX Process Flow Chart

For any given plant it may be different depending on the operating objectives of that plant; e.g., whether that plant will supply both plutonium and uranium products for use in fuel fabrication and the form of the products required by the fuel fabrication operation. A brief description of the generic PUREX process follows.

Spent fuel from nuclear reactors used in power plants is shipped to the PUREX facility in spent fuel casks. The fuel casks are placed in a spent fuel pool which provides shielding from radiation associated with the spent fuel. The casks are then opened and the spent fuel assemblies are placed in criticality safe racks. When scheduled for processing the spent fuel assemblies are removed from the rack and transferred to a shielded head end processing unit where the inlet nozzle is cut off the fuel assembly. The head end facility and downstream processes are remotely operated in shielded cells until the fission products have been separated from the spent fuel.

After removal of the inlet nozzle from the fuel assembly the fuel rods, consisting of cylindrical oxide pellets inside a long stainless steel or zircalloy tube, are pushed out of the assembly from the bottom end into a fuel chopping system. In the chopping system the tubes or cladding containing the spent fuel pellets are chopped into short lengths and collected in criticality safe baskets. Fission product gases released during chopping are sent to the offgas treatment system for removal of radioiodine and subsequent monitoring and dilution for release to the facility stack. While this is current practice, future plants in the U.S. will be required to remove additional radioactive fission product gases such as ^{85}Kr and tritium.

The baskets are then transferred into a dissolver vessel where they are placed in rack positions in the dissolver. Nitric acid is added to the dissolver at a controlled rate to dissolve the fuel pellets and the temperature is increased to 90^{o}C at a rate that keeps offgas generation within the operating range of the offgas treatment system. Temperature control is provided for the dissolver by return of cool offgas condensate and by steam to the dissolver steam jacket. Fission product gases in the fuel pellet matrix are released from the matrix as the pellets dissolve. The offgases are directed from the top of the dissolver to the offgas treatment system for removal of radioiodine and subsequent release to the stack. The dissolver offgas stream is the primary source of radioactive offgases in the process. After the dissolution of spent fuel pellets is complete, the nitric acid solution is drained from the dissolver to an accountability and feed adjustment tank where the solution is analyzed and the concentration of dissolved elements and acidity of the solution is adjusted. The adjusted mixture is then pumped to a feed tank for the partitioning process step. The baskets containing undissolved tube fragments or cladding hulls are transferred to an unloading facility where the hulls are collected and prepared for disposal. The empty baskets are returned to the head end facility for reuse.

This feed solution for the partitioning cycle contains dissolved fission products and nitrates of uranium, plutonium and other transuranic elements. The separation of fission products from the U and Pu is accomplished by feeding the solution to a solvent extraction system, typically a pulse column, where the aqueous feed stream flows countercurrent to an organic mixture of about 30% tributyl phosphate (TBP) and kerosene. As the aqueous and organic solutions mix, the nitrates of uranium and plutonium are selectively extracted into the organic solution and flow out of the extraction system with the TBP-kerosene solution. The aqueous solution containing over 99.9% of the fission products flows into a feed tank for the nitric acid recovery system to reduce liquid waste volume and minimize the need for additional acid.

The aqueous phase/organic phase extraction technology is at the heart of the PUREX process. The aqueous phase is an acidic solution and the organic phase is a TBP-kerosene mixture. Chemicals are added to the aqueous phase to selectively reduce or oxidize the plutonium and allow its transfer between the aqueous and organic phases. The PUREX process has been used since the 1940’s and the chemistry is well known. Proper control of the chemistry and the solution temperatures and extraction system operation in the extraction steps is key to achieving very high separation efficiencies and guaranteeing that contaminants do not accumulate in unplanned locations or amounts in the various process steps.

After removing the fission products, the U-Pu nitrate mixture is sent to the Pu separation unit feed tank and mixer where the Pu chemistry is adjusted to cause the Pu nitrate to selectively enter the aqueous phase in a solvent extraction system. The U nitrates remain in the organic phase. The Pu chemistry is again adjusted to selectively transfer the Pu nitrate into the organic phase. The U and Pu nitrates are then sent to respective second stage product purification units that also use solvent extraction for removal of essentially all of the remaining fission products.

From the second stage cleanup cycle the separate U and Pu nitrate streams are then sent to respective evaporation units to concentrate the nitrate solutions. The concentrated solutions are then passed through ion exchangers to remove trace amounts of zirconium and niobium fission products. The product nitrate solutions are then transferred to a fuel fabrication process where the solutions are fed to a calciner or denitrator where the nitrate cation is decomposed causing release of NO_x gases and the uranium and plutonium is converted to a dry oxide powder for use in fuel fabrication.

There are numerous support systems associated with the above operating steps. Examples are (1) offgas treatment systems, (2) waste treatment systems, (3) acid and solvent recovery, cleanup and recycle systems, and (4) essential process/instrument air, water, steam and electrical power systems. For purposes of illustrating the QRA process only the main process steps are considered. In particular, based on the process flow chart, a top level success diagram for the process takes the form of Figure 7. It is assumed that the evaporation and purification is the last step of the process and denitration or calcining the uranium and plutonium to an oxide is part of the fuel fabrication process which may or may not be at the same site.

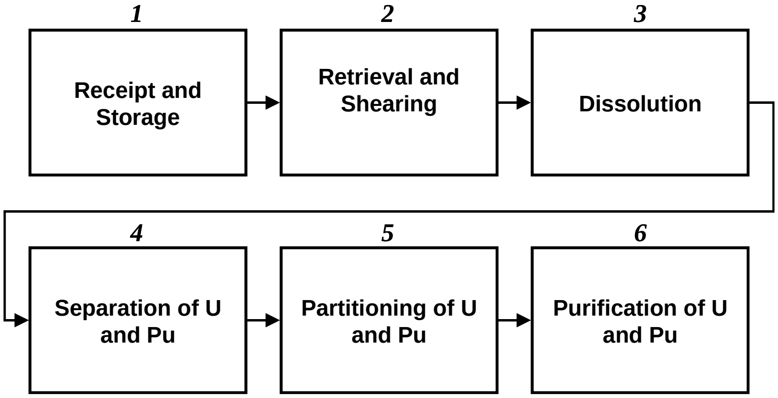


Figure 7. Top Level Success Diagram for a PUREX-Type Fuel Reprocessing Plant (Definition of the Success Scenario)

To keep the illustration simple and interesting, only one block of the diagram in Figure 7 will be considered. In particular, Block 6 is assessed in terms of a possible red oil explosion (DNFSB, 2003). In a fuel reprocessing plant opportunities for red oil generation and potential red oil incidents exist in the evaporators provided for concentrating nitrates of uranium and plutonium and in the acid recovery unit where recovered nitric acid is purified. The uranium and plutonium evaporators are of particular interest. The nitric acid concentrators or evaporators are located in a non-radioactive process area and are not part of Block 6. Thus, the success diagram for Block 6 becomes the basis for our example.

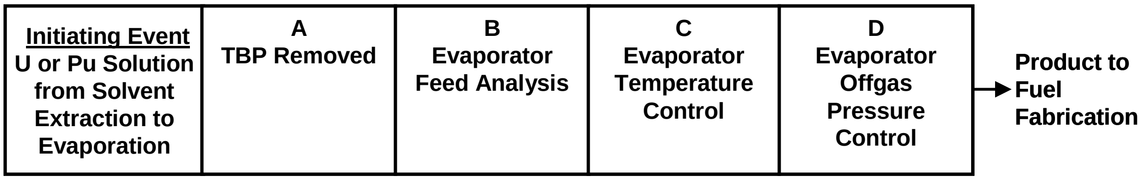


Figure 8. Success Diagram for Product Evaporation

Step 2. Identify and characterize the hazards

The overarching hazard of concern is ionizing radiation. Of course, other hazardous materials are involved and the same methodology could be applied to address them. For our example, we go only so far as a precursor event that could possibly lead to the spread of alpha contamination, namely the risk of a red oil explosion.

Step 3. Develop “what can go wrong” scenarios to establish levels of damage

As indicated earlier, the process of developing initiating events and the subsequent event sequences is the creative part of the risk model. This part of the risk assessment must involve experts on the process, the plant design, and operations. Once the initiating events are developed, the course of the subsequent events is best characterized in the form of an event tree of the type of Figure 2 shown earlier. Given a specific threat or initiating event, it is a matter of determining how the scenario is affected by the functions, A, B, C, and D of the success diagram, Figure 8. An event tree, Figure 9, identifies all possible combinations of success and failure for the process steps.

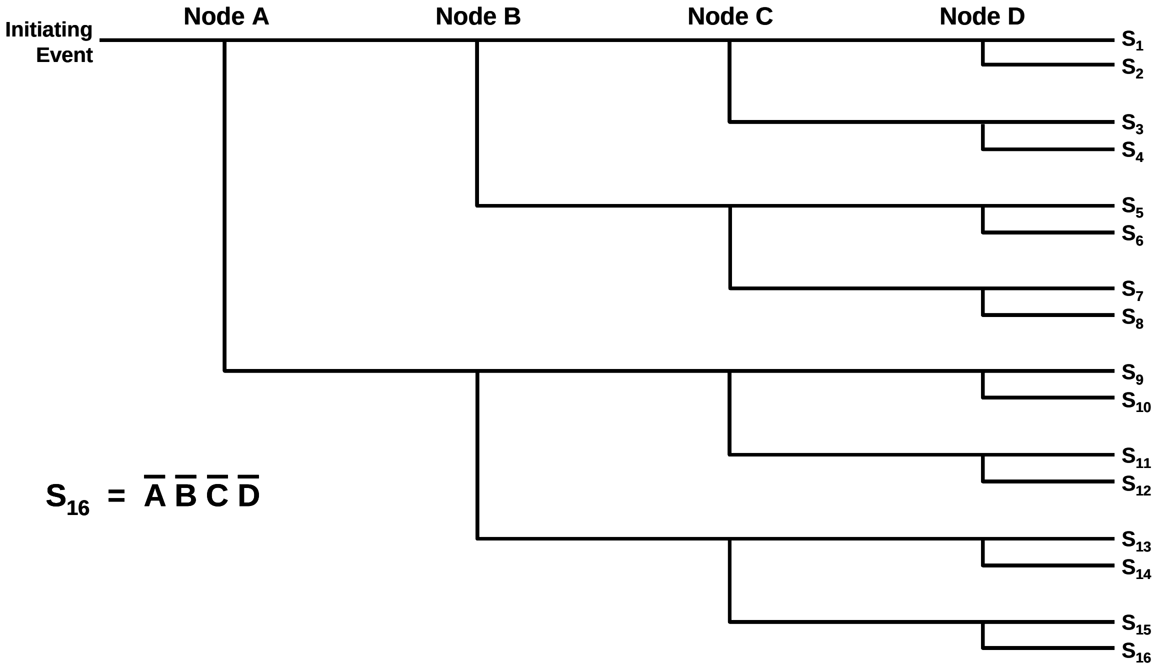


Figure 9. Event Tree for Red Oil Explosion Risk

Each path through the event tree is a scenario or event sequence and can be represented by a Boolean equation. For example, the expression for scenario 16 (S_{16}) is

$$S_{16} = \overline{A}\ \overline{B}\ \overline{C}\ \overline{D}$$

Table 1 is a summary of the 16 scenarios characterized by the event tree of Figure 9. Each scenario in the table is characterized by the success or failure of each step or node identified in the top level diagram for Block 6. Failures to properly complete each step are called the split fraction for that step. The combinations of successes and failures in the process steps are then used to define the consequence for each scenario.

Table 1. Summary of Scenarios and Consequences

Scenario	Description	Consequence or Outcome
S_1	Evaporator systems operate as designed.	Product conforming to specification.
S_2	All systems work except offgas system pressure fails high or low.	Off spec product.
S_3	Evaporator temperature control fails high increasing heat input to evaporator; pressure control compensates for increased heat input.	Off spec product.
S_4	Temperature control fails high; pressure control does not compensate.	Off spec product; possible nitrate precipitation in evaporate and shut down for repair.
S_5	Evaporator feed analysis fails. All other systems function.	Possible off spec product.
S_6	Evaporator feed analysis fails; evaporator pressure control fails.	Off spec product.
S_7	Evaporator feed analysis fails; temperature control fails high; pressure control works.	Off spec product.
S_8	Evaporator feed analysis fails; evaporator temperature control fails high; evaporator pressure control fails.	Off spec product; possible nitrate precipitation in evaporate and shut down for repair.
S_9	Excess TBP in feed tank; feed analysis detects TBP.	Rework of evaporator feed required.
S_{10}	Excess TBP in feed tank: feed analysis detects TBP; temperature control works; pressure control fails high or low.	Rework of evaporator feed required.
S_{11}	Excess TBP in feed tank: feed analysis detects TBP; temperature control fails high; pressure control works.	Rework of evaporator feed required.
S_{12}	Excess TBP in feed tank: feed analysis detects TBP; temperature control works; pressure control fails high or low.	Rework of evaporator feed required.
S_{13}	Excess TBP in feed tank: feed analysis fails to detect TBP; temperature control works; pressure control works.	Off spec product; possible fire in fuel fabrication denitrator from TBP in product.
S_{14}	Excess TBP in feed tank: feed analysis fails to detect TBP; temperature control works; pressure control fails high or low.	Off spec product; possible fire in fuel fabrication denitrator from TBP in product.
S_{15}	Excess TBP in feed tank: feed analysis fails to detect TBP; temperature control fails; pressure control works.	Off spec product; possible fire in fuel fabrication denitrator from TBP in product.
S_{16}	Excess TBP in feed tank: feed analysis fails to detect TBP; temperature control fails; pressure control fails high.	Red oil formation and possible overpressure or red oil explosion.

Step 4. Quantify the likelihoods of the different scenarios and damage states

This step requires quantification of the various split fractions of the event tree, the development of their probability density functions and convoluting them in the manner of Figure 3. For this example the steps are treated as independent and the split fractions are not conditional upon prior failures or successes. The development of the probability distributions for the split fractions start with the examination of the details of all of the red oil events that have occurred and a detailed assessment of the specific plant systems involved. Accounting for the uncertainties allows the use of all supporting evidence. The reliability data base developed by the Center for Process Safety of the American Institute of Chemical Engineers (AIChE, 1989) provides a good starting point for data. It can be augmented by data generated in additional studies such as the SRS H-Canyon fault tree analysis performed by Christensen and Vail (Christensen and Vail, 1995).

For each split fraction, the likelihood of failure is quantified from data that is judged applicable to the equipment failure(s) being considered. In some cases quantification may require development of fault trees with the split fraction failure as the top event and the tree development carried to a point at which basic data can be determined for input to the identified failure events. Examples of fault trees that might be associated with the feed analysis failure and evaporator overtemperature are given in Figures 10 and 11.

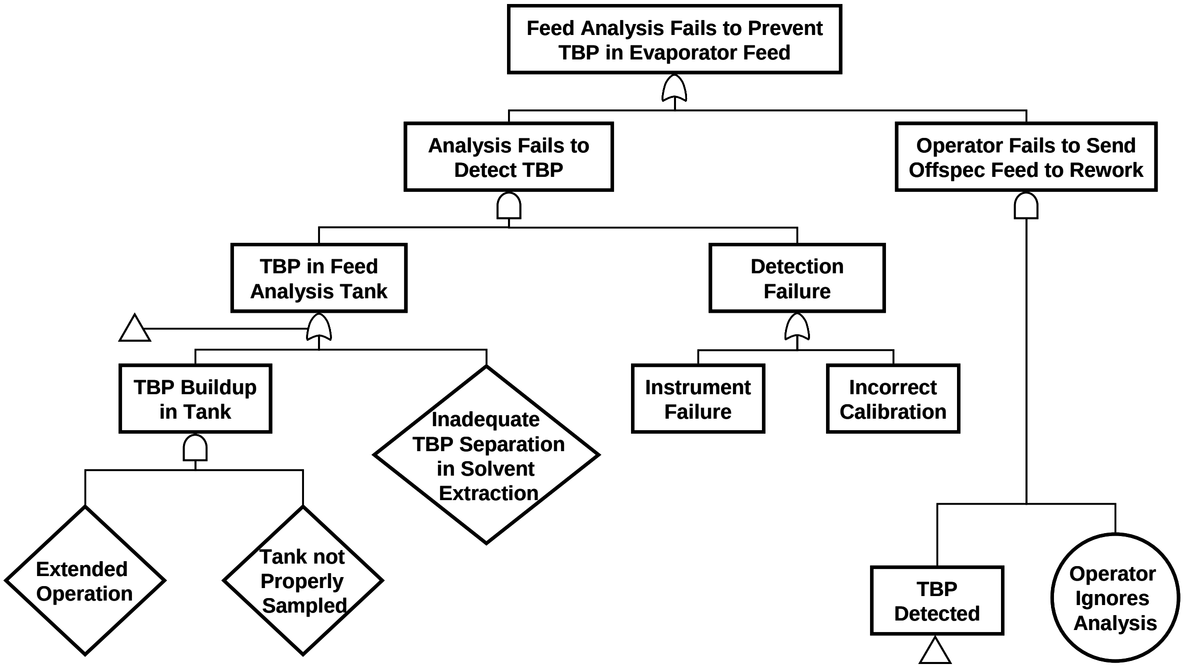


Figure 10. Fault Tree: Evaporator Feed Analysis Failure

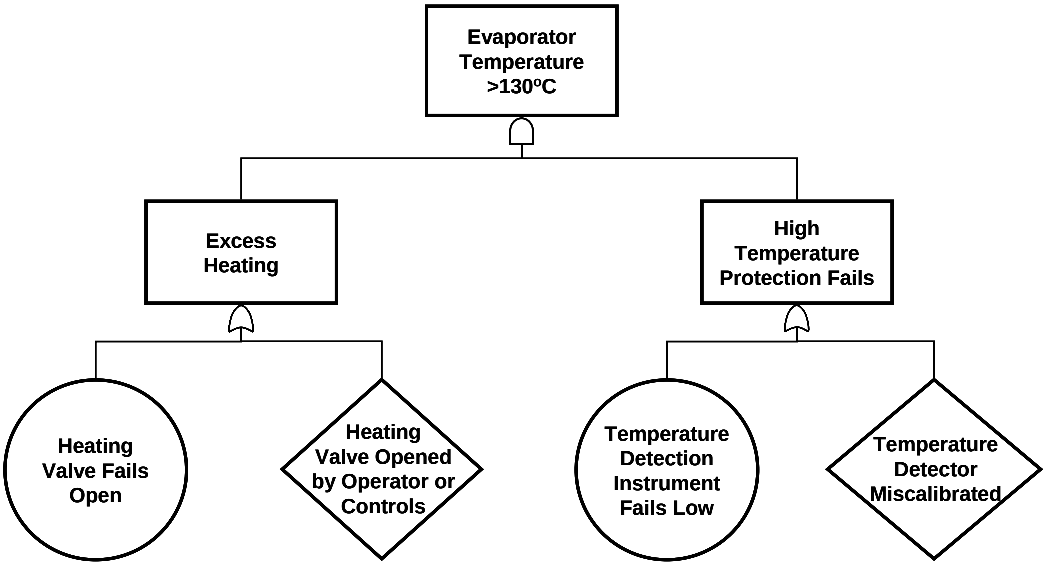


Figure 11. Fault Tree: Evaporator Temperature Control Failure

This is as far as the example is taken in terms of implementing the six QRA steps. The above steps are believed sufficient to have confidence that such analyses are feasible not only for recycling plants but any kind of natural or engineered system.

Steps 5 and 6. Assemble and interpret the results

As noted, our example was taken only far enough to illustrate some of the most creative aspects of a QRA. For example, we have illustrated for a subsystem of a nuclear fuel recycling plant the concept of the success diagram, the manner in which threats to successful operation are treated, the structuring of scenarios that could lead to different damage states, and some features of the quantification of the scenarios. What remains is the actual numerical quantification of the scenarios and the assembly of the scenario results into total risk curves of the form of Figure 5. These are all straightforward applications of probability arithmetic, which are highlighted in Figures 1 to 3 and the associated discussions.

On the matter of interpreting the results to support the risk management of a chemical operation, one very good example of where this was actually done is the U.S. Army's risk assessment work to support their program to destroy chemical weapons (National Research Council, 2002). QRAs were developed in parallel with the design of chemical agent disposal systems to provide feedback on design specifications and planned operating procedures to assure that the level of risk was being appropriately managed. As noted in the National Research Council report, "The QRAs, and an understanding of their results, provide a framework for managing the risk …" These and other applications of QRA provide considerable evidence of the value of such comprehensive assessments.

Conclusion

The advances that have been made in the theory and practice of quantitative risk assessment set the stage for a new era of safety analysis of nuclear fuel recycling plants. The principles of QRA that have been developed and applied to other segments of the nuclear industry such as nuclear power plants and nuclear waste repositories equally apply to other segments of the nuclear fuel cycle. The result is not only a much more complete representation of the risk of such plants, but a detailed blueprint for managing that risk.

References

1. AIChE (American Institute of Chemical Engineers). 1989. Guidelines for Process Equipment Reliability Data, with Data Tables. Center for Chemical Process Safety (CCPS).
2. ISBN-13:9780816904228, Wiley, February 15.
3. Christensen, L.W., and R.E. Vail. 1995. Fault Tree Analysis of Red Oil Reactions in the H-Canyon Evaporators. Westinghouse Savannah River Company. S-CLC-H-00227,
4. February 24.
5. E.R. Johnson Associates, Inc. 1980. Review of the Operating History of the Nuclear Fuel Service, Inc., West Valley, New York Irradiated Fuel Processing Plant, December 26.
6. DNFSB (Defense Nuclear Facilities Safety Board). 2003. Control of Red Oil Explosions in Defense Nuclear Facilities.
7. Garrick, B.J., et al. 2004. Confronting the Risks of Terrorism: Making the Right Decision, *Reliab. Eng. Syst. Saf.* V. 86, No. 2, November.
8. Garrick, B.J., et al. 2008. Quantifying and Controlling Catastrophic Risks. ISBN: 978-0-12-374601-6, Elsevier Inc./Academic Press.
9. Mellon, A. Verbal communication. 2008. New York State Energy Research and Development Authority.
10. National Research Council. 2002. Evaluation of Chemical Events at Army Chemical Agent Disposal Facilities. Board on Army Science and Technology, National Academy Press.
11. Nuclear Fuel Services, Inc. 1962. Safety Analysis, Fuel Processing Plant. Three Volumes.
12. USNRC (U.S. Nuclear Regulatory Commission). 1975. Reactor Safety Study: An Assessment of Accident Risks in Commercial Nuclear Power Plants. WASH-1400 (NUREG-75/014).
13. USNRC (U.S. Nuclear Regulatory Commission). 2008. Background, Status, and Issues Related to the Regulation of Advanced Spent Nuclear Fuel Recycle Facilities. ACNW&M White Paper. NUREG-1909.

Nuclear Nonproliferation

Cynthia E. Atkins-Duffin
Lawrence Livermore National Laboratory

The Nuclear Dilemma

With an explosion equivalent of about 20kT of TNT, the Trinity test was the first demonstration of a nuclear weapon. Conducted on July 16, 1945, in Alamogordo, New Mexico, this site is now a Registered national Historic Landmark.

The concept and applicability of nuclear power was demonstrated on December 20, 1951, with the Experimental Breeder Reactor Number One (EBR-1) lit four light bulbs. This reactor is now a Registered National Historic Landmark, located near Arco, ID.

From that moment forward it had been clearly demonstrated that nuclear energy has both peaceful and military applications and that the civilian and military fuel cycles can overlap. For the more than fifty years since the Atoms for Peace program, a key objective of nuclear policy has been to enable the wider peaceful use of nuclear energy while preventing the spread of nuclear weapons.

Volumes have been written on the impact of these two actions on the world by advocates and critics; pundits and practitioners; politicians and technologists. The nations of the world have woven together a delicate balance of treaties, agreements, frameworks, and handshakes that are representative of the timeframe in which they were constructed and how they have evolved in time. Collectively these vehicles attempt to keep political will, nuclear materials, and technology in check. This paper captures only the briefest abstract of the more significant aspects on the Nonproliferation Regime.

Of particular relevance to this discussion is the special nonproliferation sensitivity associated with the uranium isotope separation and spent fuel reprocessing aspects of the nuclear fuel cycle.

Evolution of the Nonproliferation Regime

Atoms for Peace

http://www.eisenhower.archives.gov/All_About_Ike/Speeches/Atoms_for_Peace.pdf

In a speech commonly known as the “Atoms for Peace” address, U.S. President Dwight Eisenhower addressed the General Assembly of the United Nations on the Peaceful Uses of Atomic Energy on December 8, 1953. In this address, Eisenhower sought to address “the fearful atomic dilemma” by directing “the miraculous inventiveness of man” on peaceful uses of atomic energy.

In this talk, Eisenhower proposed:

> An international body where “the Governments principally involved… make contributions from their stockpiles of normal uranium and fissionable materials to an international Atomic Energy Agency… under the aegis of the United Nations… [This] Atomic Energy Agency could be made responsible for the impounding, storage, and protection of the contributed fissionable and other materials. The ingenuity of our scientists will provide special safe conditions under which such a bank of fissionable material can be made essentially immune to surprise seizure.”

Eisenhower challenged Congress to:

> "First, encourage world-wide investigation into the most effective peace time uses of fissionable material, and with certainty that they had all the material needed for the conduct of all experiments that were appropriate;
>
> "Second, begin to diminish the potential destructive power of the world's atomic stockpiles;
>
> "Third, allow all people of all nations to see that, in this enlightened age, the great powers of the earth, both of the East and of the West, are interested in human aspirations first, rather than in building up the armaments of war;
>
> "Fourth, open up a new channel for peaceful discussion, and initiate at least a new approach to the many difficult problems that must be solved in both private and public conversations, if the world is to shake off the inertia imposed by fear, and is to make positive progress toward peace."

International Atomic Energy Agency (IAEA)

http://www.iaea.org/About/index.html

The IAEA was created by the "Statue of the IAEA" in 1957 in response to Eisenhower's call for an international body to promote peaceful use of nuclear energy. The main functions of the IAEA are to:

- Encourage and assist research, development, and practical application of atomic energy for peaceful uses throughout the world
- Establish and administer safeguards designed to ensure that such activity assisted by the Agency is not used to further any military purpose
- Apply safeguards to relevant activities at the request of Member States;
- Apply, under the Nuclear Non-Proliferation Treaty and other international treaties, mandatory comprehensive safeguards in non-nuclear weapon States party to such treaties.

There are about 140 member states and the Secretariat is located in Vienna, Austria. The IAEA is an independent international agency related to the United Nations (UN) and reports annually to the UN General Assembly and to its Security Council, as needed.

Nuclear Non-Proliferation Treaty (NPT)

http://www.un.org/Depts/dda/WMD/treaty/

The Non-proliferation Treaty is a multilateral, indefinite term-treaty whose obligations are:

- Nuclear weapon states (NWS) are not to transfer to any recipient whatsoever nuclear weapons or other nuclear explosive devices and not to assist, encourage, or induce any non-nuclear weapon states (NNWS) to manufacture or otherwise acquire them.

- NNWS are not to receive nuclear weapons or other nuclear explosive devices from any transferor, and not to manufacture or acquire them.
- NNWS must place all nuclear materials in all peaceful nuclear activities under IAEA safeguards.
- All Parties are obligated to facilitate and participate in the exchange of equipment, materials, and scientific and technological information for the peaceful uses of nuclear energy.
- All Parties must pursue negotiations in good faith on effective measures relating to the cessation of the nuclear arms race and to nuclear disarmament under strict and effective international control.

The NPR was signed on July 1, 1964, and entered into force on March 5, 1970. There are 189 parties to the Treaty. Three states – India, Israel, and Pakistan – have declined to sign the treaty, and North Korea, who signed in 1985, withdrew from the treaty in 2003.

Zangger Committee

http://www.zanggercommittee.org/Zangger/default.htm

The Zangger Committee began work in 1971 to draft a list of items that would "trigger" IAEA safeguards if supplied by NPT parties to any non-nuclear weapons state. The list included:

- Source or special fissionable materials
- Equipment of materials especially designed or prepared for the processing, use, or production of special fissionable materials

It establishes three conditions of supply:

- A non-explosive use assurance
- An IAEA safeguards requirement
- A retransfer provision that requires the receiving state to apply the same conditions when re-exporting these items

The list was published in 1974 as IAEA INFCIRC/209. Since that time additional items have been added to the list:

- Heavy water production equipment
- Clarification on zirconium
- Isotope separation by the gas centrifuge process
- Clarification on reprocessing plants
- Clarification on isotope separation plant equipment from gaseous diffusion method

The Committee meets twice yearly.

Comprehensive Safeguards Agreement (CSA)

http://www.iaea.org/Publications/Factsheets/English/sg_overview.html

The Comprehensive Safeguard Agreements (INFCIRC/153) were established as "implementing instructions" to the NPT. They establish verification measures to assess the correctness and completeness of a State’s declared nuclear material and nuclear-related activities. Permitted activities include on-site inspections, visits, and ongoing monitoring and evaluation. The principals involved are largely based on nuclear materials accountancy, complemented by containment and surveillance techniques, such as tamper=proof seals and camerals installed by the IAEA.

Additionally, the confidentiality of the information obtained by the IAEA is established. The CSA requires the protection of commercial and industrial secrets and requires the IAEA to regime, including classification levels, markings, and physical protection.

Additional Protocols (AP)

http://www.iaea.org/Publications/Factsheets/English/sg_overview.html

Further implementing instructions are set out in the Additional Protocol (AP) (INFCIRC/540) which established new legal authority for strengthened IAEA inspection capabilities. This protocol grants the IAEA expanded rights (complementary access) to provide assurances about both declared and undeclared activities. Included in this additional information is declaration of exempted, terminated, and pre-safeguards material; all activities at sites of nuclear facilities; and nuclear fuel cycle infrastructure not involving nuclear material. Inspectors are granted broader access on nuclear sites and access to information about a wider range of nuclear materials.

The US has recently signed the AP and the articles will be deposited in Vienna. As of January 1, 2009, the AP will be in force domestically. The US is currently in the process of making its first declaration under this Protocol.

Nuclear Suppliers Group (NSG)

http://www.nsg-online.org

The Nuclear Supplier Group (NSG) intends to ensure that nuclear trade for peaceful purposes does not contribute to the proliferation of nuclear weapons or other nuclear explosive devices, while not hindering international trade and cooperation in the nuclear field. This is achieved by the implementation of two sets of guidelines (INFCIRC/254) for nuclear exports and nuclear-related exports. The first set of guidelines governs the export of items that are especially designed or prepared for nuclear use:

- Nuclear material
- Nuclear reactors and equipment
- Non-nuclear material for reactors
- Plant and equipment for the reprocessing, enrichment, and conversion of nuclear material and for fuel fabrication and heavy water production
- Technology associated with each of the above

The second set of guidelines governs the export of nuclear-related dual-use items and technologies, which could make a significant contribution to an unsafeguarded nuclear fuel cycle or nuclear explosive activity.

The NSG and the Zangger Committee differ in the content of their trigger lists, especially related to designed or prepared items and in the export conditions for the items on the lists. A major difference is the arrangement covering exports of dual-use items. Dual-use items cannot be defined as especially designed or prepared items and therefore, are outside the scope of the Zangger Committee's efforts but are an important part of the NSG guidance.

United Nations Security Council Resolution 1540

http://www.un.org/sc/1540

Following the 9/11 terrorist attacks, the United Nations Security Council unanimously passed UNSCR 1540 in 2004. The resolution contained (among others) the following provisions:

"… Decides that all States shall refrain from providing any form of support to non-State actors that attempt to develop, acquire, manufacture, possess, transport, transfer or use nuclear, chemical or biological weapons and their means of delivery…"

"… Decides also that all States, in accordance with their national procedures, shall adopt and enforce appropriate effective laws which prohibit any non-State actor to manufacture, acquire, possess, develop, transport, transfer or use nuclear, chemical or biological weapons and their means of delivery, in particular for terrorist purposes…"

It calls upon States to:

"… Renew and fulfill their commitment to multilateral cooperation, in particular within the framework of the International Atomic Energy Agency, … as important means of pursuing and achieving their common objectives in the area of non-proliferation and of promoting internation cooperation for peaceful purposes…"

These activities have been extended in 2006 by UNSCR 1673 and in 2008 by UNSCR 1810.

Proliferation Security Initiative

http://www.state.gov/t/isn/rls/fs/105217.htm

The Proliferation Security Initiative was announced by U.S. President Bush in May 2003. This initiative grew from the pursuit of new agreements on the search of planes and ships carrying suspect cargo and to seize illegal weapons or missile technologies.

The Initiative seeks to develop partnerships of states working together, employing their national capabilities to develop a broad range of legal, diplomatic, economic, military, and other tools to interdict threatening shipments of WMD and missile-related equipment and technologies via air, land, and sea.

The goal of PSI is pre-emptive interdiction, which includes detaining and searching ships and aircraft as soon as their enter PSI members' territorial waters or national airspace.

Non-Compliance

http://www.iaea.org/NewsCenter/Focus/IaeaIran/index.shtml
http://www.iaea.org/NewsCenter/Focus/IaeaDprk/index.shtml

http://www.iaea.org/NewsCenter/Focus/IaeaIraq/index.shtml
http://www/iaea.org/NewsCenter/Focus/IaeaLibya/index.shtml

Challenges Ahead

Next Generation Safeguards Initiative

http://nnsa.energy.gov/news/2119.htm

NNSA/NA-20 Priorities

http://nnsa.energy.gov/nuclear_nonproliferation/index.htm

Conclusion

Hopefully this paper has provided the reader with a brief insight into the scope, complexity, and nuance of the Nonproliferation Regime. The Regime has its own life, with each aspect responding to daily changes in domestic and international political relationships; advances in technology; and the value, availability, and uses of nuclear materials. The reader is guided to the vast depth and breadth of available literature to understand the concepts[1] resented here and many others.

---

[1] Auspices Statement: This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.