

# Nuclear Fuel Reprocessing

Michael F. Simpson  
Jack D. Law

February 2010



The INL is a U.S. Department of Energy National Laboratory  
operated by Battelle Energy Alliance

**INL/EXT-10-17753**

**Nuclear Fuel Reprocessing**

**Michael F. Simpson  
Jack D. Law**

**February 2010**

**Idaho National Laboratory  
Idaho Falls, Idaho 83415**

**<http://www.inl.gov>**

**Prepared for the  
U.S. Department of Energy  
Office of Nuclear Energy  
Under DOE Idaho Operations Office  
Contract DE-AC07-05ID14517**

# Nuclear Fuel Reprocessing

Michael F. Simpson and Jack D. Law  
Fuel Cycle Science and Technology Division  
Idaho National Laboratory  
Idaho Falls, ID 83415

## Outline

1. Glossary
2. Introduction
3. Reprocessing Technology
  - 3.1 Aqueous Reprocessing
    - General Description
    - History of Aqueous Separation Technology
    - PUREX Process Technology
    - PUREX Process Waste Technology
    - Advanced Aqueous Separations Process Technology
    - Advanced Aqueous Reprocessing Strategies
    - Advanced Versions of PUREX
    - Aqueous Reprocessing Equipment
  - 3.2 Pyroprocessing
    - General Description
    - Process Technology
4. Future Direction
5. Bibliography

### 1. Glossary

*Actinides* – The series of elements that include and lie between actinium and lawrencium in the periodic table. In spent fuel, the major actinides of interest are uranium, plutonium, neptunium, americium, and curium.

*Cathode Processor* – A high temperature vacuum distillation furnace used to separate salt from metallic actinides deposited on an electrorefiner cathode.

*Centrifugal contactors* – Liquid-liquid extraction equipment used for aqueous solvent extraction that consists of a spinning rotor to intensely mix the different phases.

*Ceramic Waste* – The glass-bonded sodalite matrix used to encapsulate waste salt from electrorefiner operation.

*COEX™*-- French process for co-extracting uranium and plutonium using extraction methods similar to PUREX.

*Electrorefiner* – An electrochemical system used to separate actinides from spent fuel using a molten salt electrolyte.

*Experimental Breeder Reactor-II* – A sodium-cooled, fast test reactor operational at Argonne National Laboratory-West from 1963 to 1994.

*Geologic repository* – A permanent nuclear waste disposal site located deep within a geological formation.

*Metal Waste* – The stainless steel-zirconium matrix used to encapsulate cladding hulls and noble metals left in anode baskets after U electrorefining is completed.

*Mixer-Settler* – Liquid-liquid extraction equipment used for aqueous solvent extraction requiring a relatively large footprint.

*Noble Metals* – Elements found in spent nuclear fuel that have chloride forms that are thermodynamically less stable than uranium chloride.

*Pulsed Columns* – Liquid-liquid extraction equipment used for aqueous solvent extraction involving a single column consisting of trays of perforated plates to promote interphase mass transport.

*Pyroprocessing* – Nuclear fuel treatment technology that uses electrochemical reactors with molten salt electrolytes to separate actinides from fission products.

*PUREX* – Nuclear reprocessing technology that separates actinides from the spent fuel via liquid-liquid extraction involving acidic aqueous and organic liquid phases.

*Spent fuel* – Nuclear fuel that has gone through at least one irradiation cycle in a nuclear reactor. It contains a mixture of actinides and fission product waste.

*Solvent extraction* – A separations method for extracting species from a liquid phase. In this article, it refers to a process for removing uranium from spent fuel that utilizes dissolution in acid followed by liquid-liquid extraction between aqueous and organic liquid phases.

*UREX* – A variant of the PUREX process that separates uranium from spent fuel without recovering pure plutonium

*V-blender* – A v-shaped vessel that is designed to efficiently blend two or more different kinds of powders with or without applied heat.

## 2. Introduction

Nuclear reprocessing is the chemical treatment of spent fuel involving separation of its various constituents. Principally, it is used to recover useful actinides from the spent fuel. Radioactive waste that cannot be re-used is separated into streams for consolidation into waste forms. The first known application of nuclear reprocessing was within the Manhattan Project to recover material for nuclear weapons. Currently, reprocessing has a peaceful application in the nuclear fuel cycle. A variety of chemical methods have been proposed and demonstrated for reprocessing of nuclear fuel. The two most widely investigated and implemented methods are generally referred to as aqueous reprocessing and pyroprocessing. Each of these technologies is described in detail in Section 3 with numerous references to published articles.

Reprocessing of nuclear fuel as part of a fuel cycle can be used both to recover fissionable actinides and to stabilize radioactive fission products into durable waste forms. It can also be used as part of a breeder reactor fuel cycle that could result in a 14-fold or higher increase in energy utilization per

unit of natural uranium. Reprocessing can also impact the need for geologic repositories for spent fuel. The volume of waste that needs to be sent to such a repository can be reduced by first subjecting the spent fuel to reprocessing. The extent to which volume reduction can occur is currently under study by the United States Department of Energy via research at various national laboratories and universities. Reprocessing can also separate fissile and non-fissile radioactive elements for transmutation.

The current known reserves of uranium that can be economically harvested is 5.5 metric tons U. At the current usage rate of 65,000 metric tons U/year, the known uranium resources will last for about 85 years<sup>1</sup>. However, nuclear power expansion in India, China, and other countries will soon lead to a substantial increase in the global usage rate for uranium. Increased investment in uranium exploration will undoubtedly reveal additional recoverable resources. And the inevitable increase in cost of uranium will lead to a higher fraction of economically-recoverable resources. Reprocessing of spent fuel can also serve to improve efficiency of uranium resource utilization. Estimates range from about 10 to 30% for reduction of natural uranium usage as a result of reprocessing spent fuel based upon non-breeder reactor technology.

### 3. Reprocessing Technology

#### 3.1 Aqueous Reprocessing

##### *General Description*

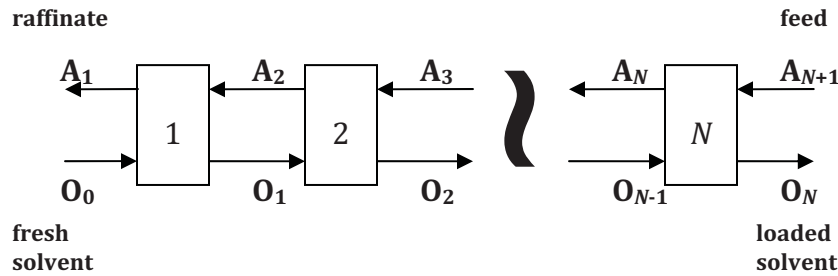
With this technology, nuclear fuel is dissolved into an acidic solution. The resulting solution is then chemically processed to separate the metals of interest, typically uranium and/or plutonium. Minor actinides as well as other fission products may also be separated using advanced aqueous processes. Specific unit operations utilized in the past primarily consist of precipitation and liquid-liquid extraction. Precipitation was the primary method used in the defense industry initially for the production of

plutonium. Liquid-liquid extraction was later developed as an improved method for reprocessing in the defense industry and also became the primary method of reprocessing of commercial nuclear fuel internationally. Since the vast majority of aqueous reprocessing applications continue to utilize liquid-liquid extraction, this will be the primary focus of discussion in this article.

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 exploiting an unequal distribution of the component(s) 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 component(s) 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 streams 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,  $A_1$ , depleted in solute(s) and 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  $A_{N+1}$  and  $O_N$  contain the highest concentration of the solute(s).

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 and/or evaporation.



### *History of Aqueous Separation Technology*

Aqueous separations processes for nuclear reprocessing evolved from early United States defense programs for the separation of Pu for weapons manufacture. The bismuth phosphate process began operation at the Hanford Nuclear Reservation in 1944 for the separation of Pu from irradiated slugs from the B reactor.<sup>2</sup> The first continuous solvent extraction reprocessing plant replaced the bismuth phosphate process at Hanford in 1952. This facility used the reduction oxidation (REDOX) process to separate Pu. The REDOX process utilized methyl isobutyl ketone as an extractant. In the REDOX process, uranium and plutonium nitrate is preferentially extracted from the fission products in a high salting strength aqueous solution.<sup>3,4</sup> The uranium and plutonium are then selectively stripped from the solvent by adjusting the valence state of the Pu to back-extract it and use a low salting strength strip solution to back-extract U. Additional cycles of extraction were used to decontaminate the products. General Electric's Knolls Atomic Power Laboratory developed the PUREX process in the 1950's. PUREX-based operations at Savannah River F Canyon began in 1954 and replaced the REDOX process at Hanford in 1956.<sup>2</sup> The PUREX process became the standard method of reprocessing used nuclear fuel throughout the world.

### *PUREX Process Technology*

PUREX-based used fuel reprocessing consists of leaching the used fuel from the cladding using a nitric acid solution, chemical adjustment and filtration of the resulting feed solution, several cycles of solvent extraction to separate and purify the uranium and plutonium, solidification of the resulting uranium and/or plutonium product, as well as the waste solutions. The plutonium oxide product, with or without uranium, is then recycled as mixed oxide (MOX) fuel. This resulting MOX fuel can be used as an alternative to low enriched uranium in light water reactors. MOX fuel is widely used in Europe, and there are plans for use in Japan. About 40 reactors in Europe (Belgium,

Switzerland, Germany and France) are licensed to use MOX fuel.<sup>5</sup> Existing aqueous commercial reprocessing facilities throughout the world primarily utilize the PUREX solvent extraction process or a variant of this process to accomplish the separation of U and Pu.

The front end of the PUREX process involves chopping of the used nuclear fuel assemblies followed by leaching of the used fuel in a nitric acid solution. The chopped pieces of the pins, as well as spacers and other fittings, must then be separated from the leached fuel solution. This has been performed through the use of perforated baskets that hold the hardware, such as in the batch operations performed at the THORP facility in the United Kingdom, or through the use of a continuous dissolver, such as the wheel dissolver at the UP2 and UP3 plants in France which holds the hardware in buckets formed in sections of the wheel as the wheel rotates through the nitric acid solution.<sup>6</sup> The dissolver solution, after further clarification and feed adjustment, is then processed through the use of the PUREX technology to separate and purify the uranium and plutonium from the dissolver product solution.

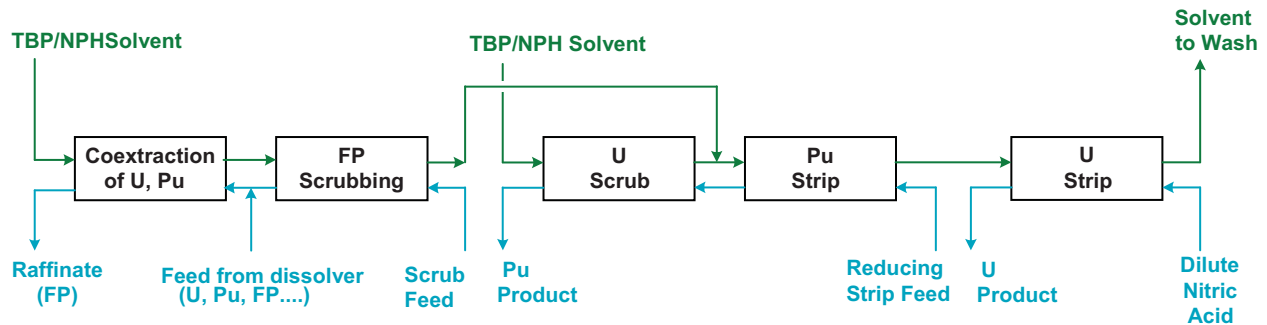
The PUREX process utilizes 20 to 40 vol% tributyl phosphate in a hydrocarbon diluent to extract uranium and plutonium from the acidic solution resulting from the dissolution of used nuclear fuel. In general, metals in the +4 and +6 oxidation state are extracted in the PUREX process. The chemical equilibria for U (VI) in a nitrate media is



The chemical equilibria for the actinides in the +4 oxidation state is



Plutonium maintained in the +4 oxidation state is, therefore, co-extracted with the U. Pu (III) and other actinides and lanthanides in the +3 or lower oxidation state are not extracted in the PUREX Process. Neptunium, if maintained in the +6 oxidation state, can be co-extracted with the U and Pu. The strong extraction of the +4 and +6 oxidation states, along with the weak extraction of the other oxidation states, results in the effective use of the PUREX process for separation of uranium and plutonium from nearly all of the other metals present in the used nuclear fuel.



**Figure 2.** Typical PUREX first cycle flowsheet

A typical PUREX process first extraction cycle is provided in Figure 2. The solution resulting from the dissolution of the used nuclear fuel is the feed to the co-extraction section of the flowsheet. The aqueous feed flows countercurrent to the PUREX solvent, and the U and Pu are extracted by the TBP into the normal paraffin hydrocarbon (NPH) organic phase. The loaded organic phase enters the fission product (FP) scrub section in which a nitric acid scrub solution (approx. 2 M  $\text{HNO}_3$ ) is used to remove co-extracted fission products, such as Zr and Ru, from the solvent. The scrub solution containing the Zr and Ru combines with the feed solution entering the extraction section. The solvent then enters a Pu strip section in which the Pu is back-extracted from the organic phase. This is accomplished by reducing the Pu from the extractable +4 oxidation state to the inextractable +3 state. A

strip solution containing a reductant, such as hydroxylamine nitrate, U (IV), or ferrous sulfamate, is typically used.<sup>7</sup>

Reduction and back extraction of the Pu also results in back extraction of a portion of the uranium. The strip product from the Pu strip section therefore enters a uranium scrub section in which the Pu strip solution is contacted with a fresh solvent feed to re-extract this uranium into the organic phase. The organic phase containing the re-extracted U combines with the loaded solvent from the extraction section which enters the Pu strip section. Once the Pu has been back extracted from the PUREX solvent, the solvent enters the uranium strip section, which utilizes dilute nitric acid (typically 0.01 M HNO<sub>3</sub>) at elevated temperature to back extract the U into the aqueous phase.

The resulting solutions from the first cycle PUREX extraction process include a solvent solution that is washed with a carbonate or hydroxide solution to remove degradation products and recycled back to the extraction section, a raffinate stream which is depleted of the U and Pu and disposed of as waste, and the Pu and U product streams. The U and Pu product streams are typically further processed with additional PUREX cycles to purify these streams.<sup>8</sup>

#### *PUREX Process Waste Treatment*

The separation of the Pu and U from used nuclear fuel results in a high-level waste requiring immobilization and storage. The immobilization technology currently in use in the United Kingdom, France and Japan is vitrification of the waste to form a stable borosilicate glass waste form suitable for long term storage.<sup>9</sup> The glass waste produced is poured into canisters and are stored until long-term geological storage is available. Appropriate geological repositories are currently being pursued in these countries. Low and

intermediate-level wastes are also generated from aqueous reprocessing and require treatment and disposal.

#### *Advanced Aqueous Separations Process Technology*

Advanced aqueous separations processes are being developed throughout the world including the United States, France, United Kingdom, Japan, Russia, and China. The goals of the development of advanced aqueous processes include closing the nuclear fuel cycle and reducing the proliferation risk of the technologies. Reduction in proliferation risk is being addressed through development of modified PUREX processes which do not separate pure plutonium. In addition, advanced separation processes are being developed to separate the actinides for reactor recycle to close the fuel cycle.

#### *Advanced Aqueous Reprocessing Strategies*

Numerous strategies are being developed internationally for advanced aqueous reprocessing processes. The goals of these processes typically are to accomplish separations beyond the Pu and U that is separated with the PUREX process in order to reduce the volume, radiotoxicity and heat generation of the used nuclear fuel. The components targeted include the minor actinides as a group, the short-lived fission products (Cs and Sr), and/or individual actinides, such as Am. The minor actinides or Am separated from the used fuel would be recycled for burning in a fast reactor. If separated, the Cs and Sr could be placed into decay storage.

A wide variety of advanced processes are currently being developed to accomplish these advanced separations. Major research efforts on advanced processing are ongoing in France, Japan, United Kingdom, United States, China and Russia<sup>10-16</sup>. These technologies are at various stages of maturity, and none have been implemented into full-scale reprocessing facilities to date.

Advanced aqueous processing has the potential to significantly reduce the volume, heat load (long and short-term) and radiotoxicity of HLW requiring disposal in a geological repository.<sup>17</sup> These processes, however, will result in the generation of a significant quantity of low-level waste requiring treatment and disposal. These wastes include spent solvent, solvent treatment solutions, and decontamination solutions, among others. Additionally, solid waste is generated from facility operations (e.g., gloves, shoe covers, cleaning supplies, filters) and will require treatment and disposal.

#### *Advanced Versions of PUREX*

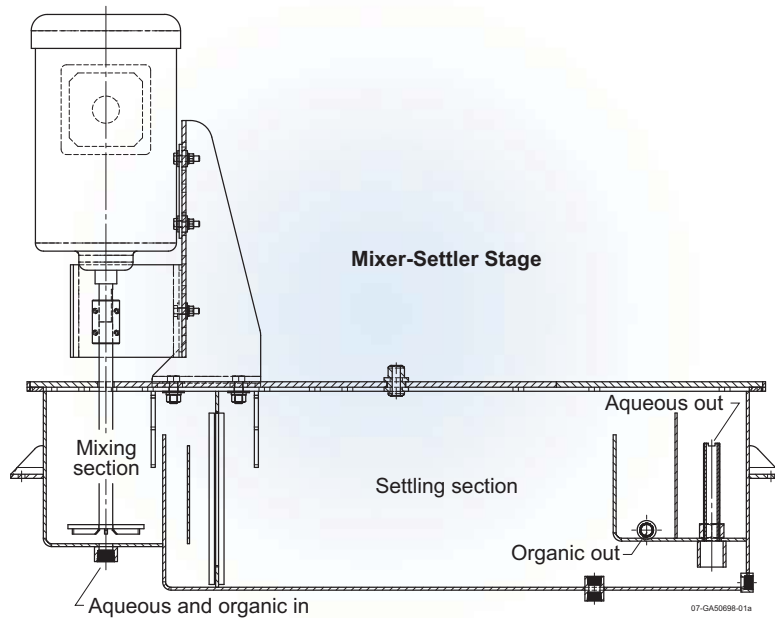
The primary focus of recent development of advanced PUREX processes is to prevent the separation of pure Pu, thus reducing proliferation risk, as well as controlling Np and Tc chemistry to allow for the extraction of these metals. In France, the COEX™ process is being developed which coextracts the U and Pu and producing a Pu/U product instead of a pure Pu product.<sup>18</sup> This is accomplished by adjusting the chemistry of the PUREX process to allow some U to be back-extracted from the solvent with the Pu. The process also uses a co-conversion process to produce a (Pu, U) oxide product. Co-extraction of Np is also being evaluated with the COEX™ process to produce a (Pu, U, Np) oxide product.<sup>18</sup> The Rokkasho reprocessing plant in Japan, which has been constructed and is currently undergoing operational testing, also uses a PUREX process that has been modified to combine uranium with the separated plutonium in a 50/50 mix prior to denitration.<sup>19</sup> In the United States, the uranium extraction (UREX) process has been developed which separates the uranium from used nuclear fuel. The UREX process is a modification of the PUREX process in which the Pu is prevented from extracting with the U by adding acetohydroxamic acid as a reductant/complexant.<sup>20,21</sup>

#### *Aqueous Reprocessing Equipment*

The solvent extraction equipment utilized for industrial-scale aqueous reprocessing must enable continuous processing at high throughputs while efficiently mixing and separating the two phases. 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. A detailed description of the three types of equipment follows.

*Mixer-Settlers.* This equipment 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 the phases 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 (less dense phase – typically organic) or through an underflow then over a weir (more dense phase – typically aqueous). 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 best suited for use 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.<sup>22,23</sup>

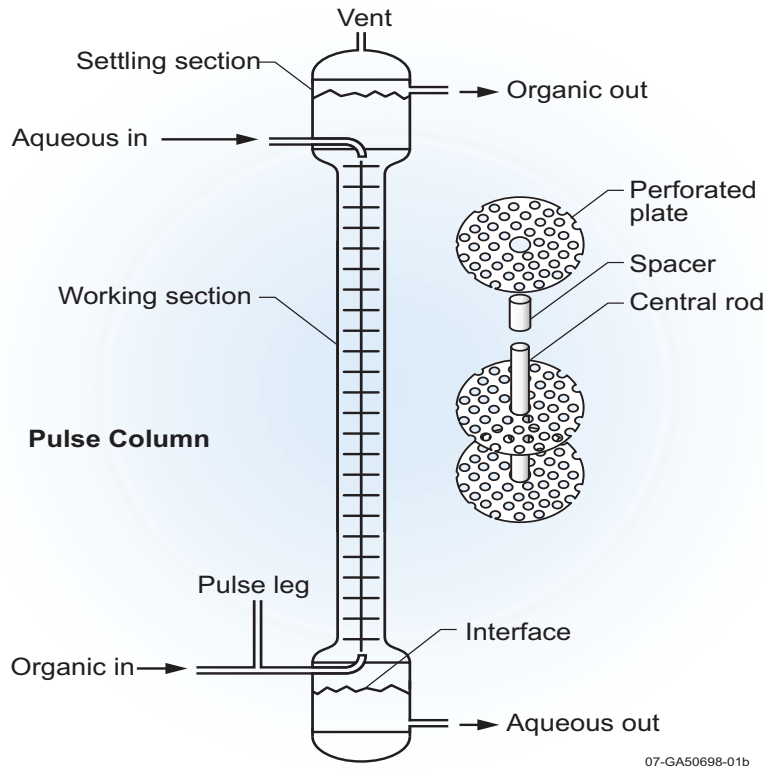


**Figure 3.** Diagram of a mixer-settler

*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 equivalent of a theoretical stage (HETS).<sup>24</sup> For most packed columns, this HETS 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) is used and mechanical energy is applied to force the dispersed phase into smaller droplets, improving mass transfer.



The most common type of column used today, particularly in the nuclear industry, is the pulse column.



**Figure 4.** Pulse Column with perforated plates

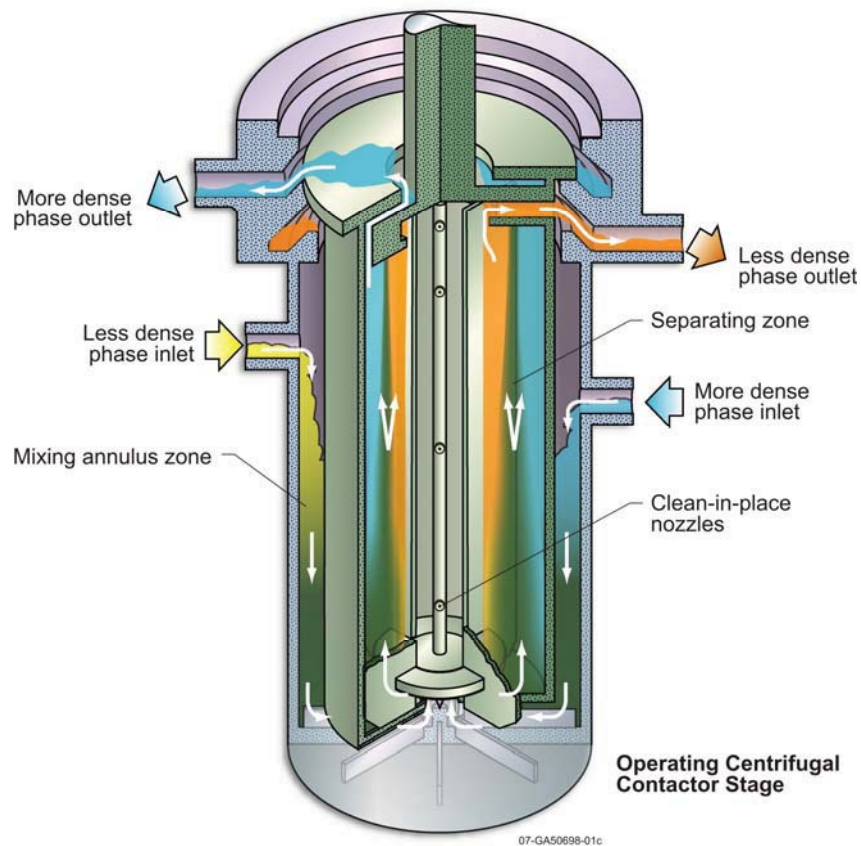
In a pulse column, liquids are continuously fed to the column and flow counter-currently, as is done with a packed column, but mechanical energy is applied to pulse the liquids in the column up and down. This is normally done by injecting pressurized air into a pulse leg that pushes liquid into the column, 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 doughnut configuration, where the plates are solid (no openings) but the alternating plates enable effective contacting of the phases.<sup>25</sup>

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 adjusting flow rate easily varies residence time. 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.<sup>8,26-28</sup> Pulse columns are the primary type of aqueous separation equipment utilized in the nuclear industry today.

*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-settler is the separation of the two-phase mixture. Centrifugal contactors employ a spinning rotor that intensely mixes the two

phases and separates the two phases inside the rotor where the centrifugal forces can be as high as 300 g. This results 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.



**Figure 5.** Cutaway view of an operating centrifugal contactor

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 minimal 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 they 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.<sup>29-31</sup> Early designs included a paddle-wheel to mix the phases below the spinning rotor.<sup>32</sup> This precluded removal of the rotor assembly. The annular centrifugal contactor was subsequently developed, which allowed the motor and rotor assembly to be easily removed.<sup>33</sup> 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 as necessary.<sup>34-36</sup> Design of remote operation and maintenance capabilities has also continued, resulting in more efficient remote handling.<sup>37,38</sup>

## 3.2 Pyroprocessing

### *General Description*

Pyroprocessing is currently considered an alternative reprocessing technology to the more commonly used aqueous processing technology that accomplishes separations by way of high-temperature electrorefining. It has yet to be implemented on a large scale, limited to date to laboratory-scale and engineering-scale experimentation and demonstration. Much of the

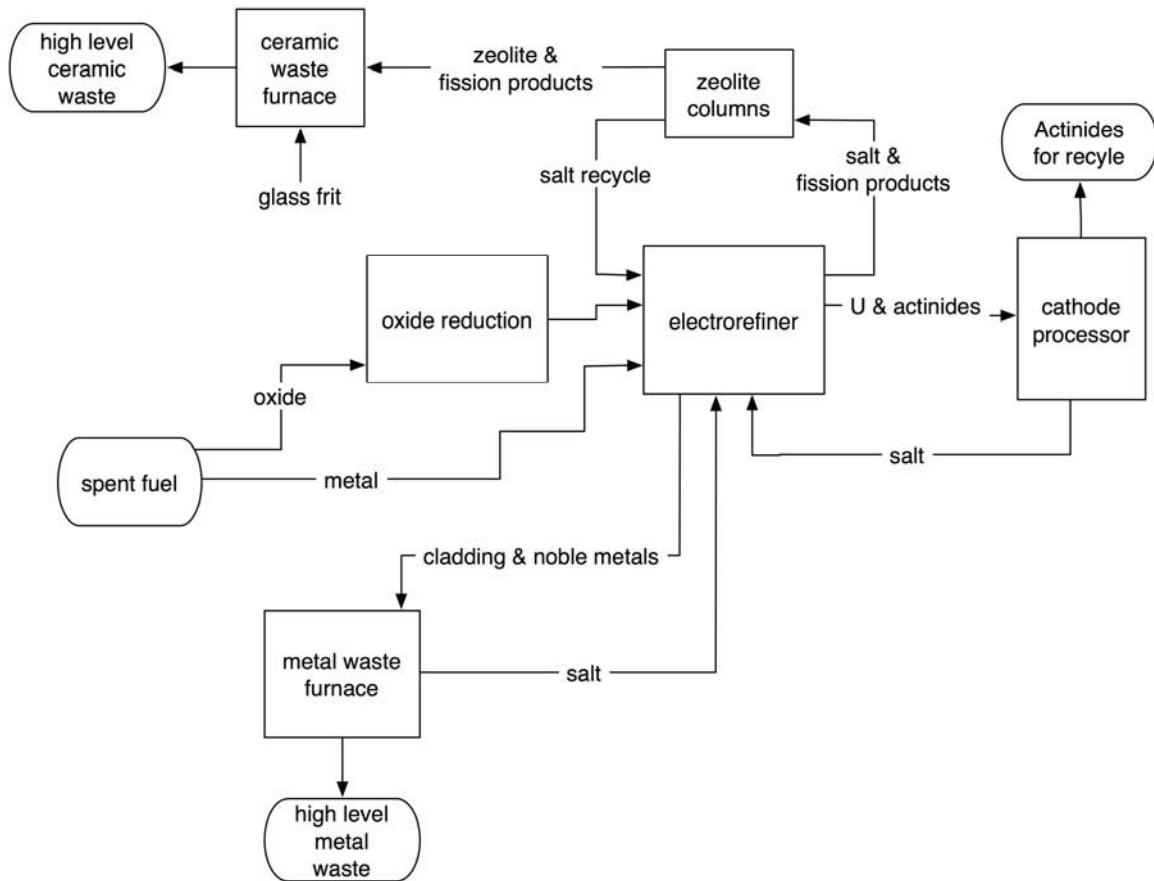
current state of the art for pyroprocessing was developed during the Integral Fast Reactor (IFR) program, which was carried out at Argonne National Laboratory from about 1984 to 1995<sup>39,40</sup>. With the shutdown of Experimental Breeder Reactor-II in 1995, the IFR program was converted into a spent fuel treatment program to safely treat the 25 MT of heavy metal from that reactor<sup>41</sup>. Pyroprocessing utilizes molten salt electrolytes as the media rather than acidic aqueous solutions and organic solvents<sup>42</sup>. These electrolytes are principally used to support electrochemical separations such as uranium electrorefining and electrolytic reduction of oxide fuel. The process includes vacuum furnaces that accomplish salt/metal separations and melt metal deposits into ingots for either waste disposal or fuel fabrication. Ceramic and metal waste streams are generated that immobilize fission products and, optionally, plutonium and minor actinides into high level waste forms. For eventual commercial implementation, it is expected that plutonium and minor actinides will be recycled and used for fast reactor fuel fabrication. While this technology has yet to reach the commercialization stage, it has been the subject of extensive, government-funded research and development worldwide in addition to the EBR-II spent fuel treatment work in the U.S. For example, the Republic of Korea is currently pursuing a strategy of developing pyroprocessing technology for treatment of spent fuel from their commercial light water reactors to minimize volume of high-level waste and possibly extract fissile actinides for eventual fabrication of fast reactor fuel<sup>43-44</sup>. Russia has already demonstrated production of MOX based on pyroprocessing and plans to develop a closed fuel cycle using the technology by 2020.

While PUREX and related aqueous reprocessing technology has superior maturity, pyroprocessing does have unique benefits that make it a credible alternative and in some cases a preferred alternative. This includes use of process liquids that are more stable than organics in the presence of high radiation fields, improved criticality safety due to the lack of neutron

moderators in the process, and waste processing that is integrated with the separations flowsheet.

### *Process Technology*

There are many variants of the pyroprocessing flowsheet, but the IFR scheme shown in Figure 6 can be used as a reference, as it contains all of the key unit operations.



**Figure 6.** Fuel Processing Flowsheet for the Integral Fast Reactor Program

The electrorefiner is at the center of the flowsheet and is used to perform the primary separation of actinides from fission products<sup>45-46</sup>. It contains a molten salt electrolyte—typically LiCl-KCl-UCl<sub>3</sub> maintained at 450-500°C. The eutectic composition of LiCl-KCl (44.2 wt% LiCl, 55.8 wt% KCl) is

maintained to keep the melting point at approximately 350°C. The  $\text{UCl}_3$  content varies depending on desired operating conditions from about 0.5 to 10 wt%. It is used as a charge carrier for electrotransport through the electrolyte. After the spent fuel is chopped into segments, it is loaded into anode baskets, and the baskets are lowered into the electrorefiner. As current is passed between the anode and cathode, U metal is oxidized to  $\text{U}^{3+}$  at the anode and reduced back to metallic form at the cathode. The deposit contains high purity uranium and is typically dendritic. An example of a U cathode deposit is shown in Figure 7.



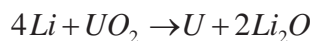
**Figure 7.** Dendritic uranium deposit on electrorefiner cathode.

Transuranic (TRU) elements and active metal fission products are oxidized electrochemically or via reaction with uranium chloride in the salt and enter the electrolyte. Under normal conditions, Pu and minor actinides cannot deposit at the cathode, because their back-reaction with  $\text{UCl}_3$  is thermodynamically spontaneous. However, co-deposition of U and TRU can be achieved via a combination of elevating the TRU to U ratio in the salt and utilizing a liquid cadmium cathode (LCC). In the molten cadmium phase, TRU elements have a very low activity coefficient compared to U. This allows for TRU metals to be present in quantities comparable to that of uranium in the

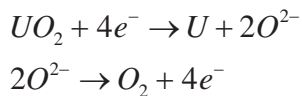
cadmium. Alternative methods are currently being investigated to co-recover U and TRU without the need for an LCC.

Fission product elements segregate between the anode basket and the molten salt during the electrorefining process. Noble metals such as Tc, Ru, and Rh remain with the cladding hulls in the anode basket. Active metals that typically include Group I and II elements in addition to lanthanides are oxidized to chloride form and accumulate in the salt. If sodium metal is used as a bonding agent, as in the case of EBR-II fuel, this sodium is oxidized to sodium chloride, which accumulates in the ER electrolyte.

Note in Figure 6 that both metal fuel and oxide fuel can be treated via pyroprocessing. Treatment of metallic fuel is relatively straightforward due to the fact that it is already in a state compatible with the ER. Oxide fuel must first be converted to metallic form. This can be accomplished in an oxide reduction step. Various methods have been investigated for reducing spent oxide fuel. Early efforts were focused on chemical reduction via lithium. Similar to electrorefining, a molten salt is used for carrying out this reaction. In this case, it is LiCl saturated with lithium metal at 650°C. The lithium reduction reaction is as follows.<sup>47</sup>



More recently, a similar process based on electrochemical reactions has been favored for development. It also uses a vessel containing molten LiCl at 650°C, but it contains lithium oxide in the salt rather than lithium metal. The reactions for the electrolytic process are shown below<sup>48</sup>.





The generated oxygen bubbles out of the salt as a gas and can be sent to an off-gas treatment system to remove any entrained or volatile contaminants. The advantages of the electrolytic method based on the above reactions are that lithium oxide concentration in the molten salt can be kept low (~1 wt%), and there is no need for a separate vessel to regenerate lithium metal from lithium oxide.

U or U/TRU product deposited on the cathode in the electrorefiner is transferred to a cathode processor, which is essentially a vacuum distillation furnace. The salt is separated from the metals and recycled to the electrorefiner. The purified metals can be fed into a process for fabricating metallic fuel for fast reactors. For the case of the EBR-II Spent Fuel Treatment process, the cathode processor operates at a temperature up to 1200°C and achieves pressures less than 1 torr.

After an electrorefining run, the anode basket contains the cladding hulls, undissolved actinides, inert fuel matrix material such as zirconium, adhering salt, and noble metal fission products such as Tc, Mo, Rh, and Ru. All of this material is removed from the anode baskets and loaded into an inductively heated vacuum distillation furnace that is used to distill adhering salt and consolidate the metals into an ingot. The metal ingot becomes a waste form that has been tested and shown to be suitable for disposal in a high level waste repository<sup>49-50</sup>.

Electrorefiner salt becomes progressively more contaminated with fission product chlorides as well as sodium chloride in the process of treating fuel. Once the contamination level has exceeded a pre-determined limit, the salt must be removed from the electrorefiner and either disposed or processed through a purification step and returned to the electrorefiner. The basis for that limit can be fission product decay heat, salt melting point, or criticality

limits. Another potential limiting factor is contamination of the metallic actinide products recovered in the cathode processor. High concentrations of rare earth fission products in the salt, for example, have been shown to lead to high rare earth contamination levels in the actinide product. The process flow sheet shown in Figure 6 includes zeolite ion exchange columns for achieving this salt purification. Zeolite-A has been shown to exhibit selectivity for the fission product ions when in contact with molten chloride salt<sup>51-54</sup>. Other alternatives that have been considered for treating the salt to remove fission products and other contaminants include selective precipitation, zone freeze refining, and adsorption by non-zeolitic materials<sup>55</sup>.

The current baseline technology for dealing with the salt waste from electrorefining EBR-II spent fuel is to non-selectively immobilize the salt into a ceramic waste form consisting of glass-bonded sodalite<sup>56,57</sup>. In this process, salt is removed from the electrorefiner, sized via crushing and milling to a fine particulate, and absorbed into zeolite-4A in a high temperature blending operation. A V-blender capable of heating and mixing particulate material to 500°C is used for this absorption step. Prior to being loaded into the V-blender, it is necessary to dry the zeolite to less than 1 wt% water. This drying is used to maximize salt absorption in the zeolite while minimizing evolution of water vapor in a high temperature, corrosive environment. Drying the zeolite should also minimize pores in the final ceramic waste form. Zeolite drying is accomplished via mechanically fluidizing the zeolite under vacuum at temperatures up to 550°C<sup>56,57</sup>. Heating the zeolite-4A to temperatures of 600°C or higher has been determined to cause structural damage that inhibits its ability to absorb salt<sup>58</sup>. Final consolidation into the ceramic waste form occurs after borosilicate glass binder has been mixed with the salt-loaded zeolite, loaded into a steel canister, and heated to a maximum temperature of 915-950°C. During the process of consolidation, the zeolite-A phase converts to sodalite. In the glass-bonded sodalite waste

form, the fission products are distributed between the glass and sodalite phases<sup>59</sup>.

If an ion exchange process with zeolite-A has been used to selectively remove fission products from the salt, the resulting fission product loaded zeolite-A can be similarly converted into a glass-bonded sodalite ceramic waste form. Zeolite-A used for ion exchange is typically in pelletized form and must be milled to a fine particulate prior to blending with additional dried zeolite-4A and borosilicate glass. The flowsheet shown in Figure 6 includes zeolite ion exchange followed by conversion of this zeolite into the ceramic waste form.

#### 4. Future Directions

In the United States, the current focus is on research and development into both aqueous reprocessing and pyroprocessing technology to support a future decision on closing the fuel cycle. The U.S. Department of Energy under President Obama has established the Fuel Cycle Research and Development program for carrying out this research in national laboratories and universities. At this time, there are no large-scale demonstration projects planned. Meanwhile, plans to open a geologic repository for spent nuclear fuel and waste in Nevada's Yucca Mountain have been suspended. The government has commissioned a study to evaluate alternative options for disposal of the spent fuel and waste.

In Japan, the main option for reprocessing spent nuclear fuel is based on aqueous process technology. The Rokkasho plant based on such technology is currently operational with a design capacity of 800 tons of spent light water reactor fuel per year, extracting up to 8 tons of plutonium per year for MOX fuel production. Pyroprocessing is considered an option for fast reactors once they have been included in the Japanese energy fleet. A

commercial fast reactor is not planned for completion in Japan until about 2050.

In France, advanced aqueous processing technologies are being developed and assessed to support future recycling of Am and Cm or the minor actinides together with U and Pu to fast reactors. Pilot-scale demonstration is planned within the next decade with a goal of industrial deployment to support the deployment of Generation IV fast reactors. France is also in the process of selecting a site for a geological repository for disposal of high-level waste with a goal to open the repository in 2025. Research related to the study of geological formations and the capacity as a deep geological repository for HLW is being conducted at the Meuse/Haute Marne Underground Research Laboratory located in Bure, France.

Russia is currently processing used fuel from civilian power reactors as well as spent HEU fuel from naval and other reactors at Mayak's RT-1 aqueous reprocessing plant. The Experimental-Demonstration Center (EDC), which will be a 100 MT/yr pilot facility for evaluation of the fuel cycle based on modified PUREX extraction technology, is currently being designed. This facility will also be used to develop other advanced processing technologies for processing used fuel from thermal reactors. The current goal is to support completion of a new aqueous reprocessing facility around 2025. Research is also actively being performed relative to pyroprocessing technologies for the processing of spent fuel from future fast reactors. To this end, the Multipurpose Pyroprocessing Complex (MPC) is being designed at the Research Institute of Atomic Reactors (RIAR) to support molten salt processing development at a capacity of up to 2,500 kg fast reactor used fuel per year.

In South Korea (Republic of Korea), on-site wet storage capacity for spent nuclear fuel at its twenty operating nuclear power plants is rapidly approaching current limits. In December 2008, Atomic Energy Commission of

South Korea decided to develop a closed fuel cycle associated with pyroprocessing and SFR with metallic fuels. A demonstration SFR is planned to operate from 2030 initially with U-Zr metal fuels and later with recycled U/TRU/Zr metal fuels produced from PWR SNF in a pyroprocessing facility that is planned to be operated from 2025. Pyroprocessing technology research and development continues at Korea Atomic Energy Research Institute with plans to build an engineering scale facility by 2016. Aqueous reprocessing technology is currently not being actively studied and is not considered a candidate for commercialization in the Republic of Korea. The lack of a high-level waste repository is another problem faced by the country due to severely limited land resources. Waste minimization is, thus, a major objective with pyroprocessing technology research and development in South Korea.

## 5. Bibliography

1. OECD and IAEA, *Uranium 2007: Resources, Production, and Demand*; Nuclear Energy Agency, June 2008.
2. Gray LW (1999) From separations to reconstitution – A short history of plutonium in the US and Russia. Lawrence Livermore National Laboratory, UCRL-JC-133802
3. Evans TF and Tomlinson RE (1954) Hot semiworks REDOX studies, Hanford Atomic Products Operations, HW-31767
4. (1951) REDOX technical manual, Hanford Works, HW-18700.
5. Hore-Lacy I (2009) Mixed oxide fuel (MOX). World Nuclear Association (Content Partner); Cutler J. Cleveland (Topic Editor). In: *Encyclopedia of Earth*. Eds. Cutler J. Cleveland (Washington, D.C.: Environmental Information Coalition, National Council for Science and the Environment).
6. Denniss IS and Jeapes AP (2001) Reprocessing irradiated fuel In: Wilson PD (ed) *The nuclear fuel cycle: from ore to wastes*, Oxford University Press, Oxford, UK, p. 120
7. Poczynajlo A (1988) Studies on reductive back extraction of plutonium in PUREX process. *J. Radioanal. Nucl. Chem.*, vol 125 no.2, p 445-465
8. Long, JT (1967), *Engineering for Nuclear Fuel Reprocessing*, Gordon Breach Sci. Publ., N.Y.

9. Petitjean V, Fillet C, Boen R, Veyer C, Flament T (2002) Development of Vitrification Process and Glass Formulation for Nuclear Waste Conditioning, *Proceedings of Waste Management 2002, Tucson, AZ USA*.
10. Spent Fuel Reprocessing Options. International Atomic Energy Administrations, IAEA-TECDOC-1587, Vienna, Austria 2008.
11. Boullis, B (2008) Future nuclear fuel cycles: prospects and challenges. In Solvent Extraction: Fundamentals to Industrial Applications, *Proceedings of ISEC 2008 International Solvent Extraction Conference*, Bruce Moyer editor, Vol. 1, pp 29-42.
12. Nash K (2008) Key features of the TALSPEAK and similar trivalent actinide-lanthanide partitioning processes. In Solvent Extraction: Fundamentals to Industrial Applications, *Proceedings of ISEC 2008 International Solvent Extraction Conference*, Bruce Moyer editor, Vol. 1, pp 511-519.
13. Laidler J (2008) An overview of spent-fuel processing in the Global Nuclear Energy Partnership. In Solvent Extraction: Fundamentals to Industrial Applications, *Proceedings of ISEC 2008 International Solvent Extraction Conference*, Bruce Moyer editor, Vol. 1, pp 695-701.
14. Riddle C, Baker J, Law J, McGrath C, Meikrantz D, Mincher B, Peterman D, and Todd T (2005) Development of a novel solvent for the simultaneous separation of strontium and cesium from acidic solutions. *Solvent. Extr. Ion Exch.*, Vol. 23, No. 3, pp. 449-461.
15. Christiansen B, Apostolidis C, Carlos R, Courson O, Glatz JP, Malmbeck R, Pagliosa G, Römer K and Serrano-Purroy D (2004) Advanced aqueous reprocessing in P&T strategies: Process demonstrations on genuine fuels and targets. *Radiochim. Acta* Vol 92, 475–480.
16. Miguiditchian M, Chareyre L, Hérés X, Hill C, Baron P, Masson M (2007) GANEX : adaptation of the DIAMEX-SANEX process for the group actinide separation, *Proceedings of GLOBAL 2007 Advanced Nuclear Fuel Cycles and Systems*, Bosie, Idaho, USA.
17. Wigeland R, Bauer T, Fanning T, Morris E (2006) Separations and Transmutation Criteria to Improve Utilization of a Geologic Repository. *Nuclear Technology*, Vol. 154, No. 1, p.95-106.
18. Drain F, Emin JL, Vinoche R and Baron P (2008) COEX process: cross-breeding between innovation and industrial experience. *Proceedings from Waste Management 2008*, Tucson, AZ, USA.
19. Katsuta T, Suzuki, T (2009) Japan's spent fuel and plutonium management challenge. *Energy Policy*, In press.
20. Pereira C, Vandegrift G, Regalbuto M, Bakel A, Bowers D, Gelis A, Hebden A, Maggos L (2007) Lab-scale demonstration of the UREX+1a process using spent fuel. *Proceedings from Waste Management 2007*, Tucson, AZ, USA.
21. Nuñez L and Vandegrift G (2000) Evaluation of hydroxamic acid in uranium extraction process: literature review, Argonne National Laboratory, ANL00/35.

22. Colven, TJ Jr, (1956) Mixer-Settler Development-Operating Characteristics of a Large-Scale Mixer-Seller. Savannah River Laboratory, DP-140
23. Davidson J K, Shafer AC, and Haas WO (1957) Application of Mixer-Settlers to the PUREX Process. In: The symposium on the reprocessing of irradiated fuels, Book 1 United State Atomic Energy Commission, TID-7534.
24. Benedict M, Pigford TH and Levi HW (1981) *Nuclear Chemical Engineering*, McGraw-Hill, N. Y.p 210
25. Milot JF, Duhamet J, Gourdon C, Casamatta G (1990) Simulation of a pneumatically pulsed liquid-liquid extraction column. *Chem. Eng. J.* 45:111-122.
26. Sege G, and Woodfield FW, (1954) *Chemical Engineering Progress*, 50(8).
27. Geier RG (1954) Application of the Pulse Column to the PUREX Process. USACC, Report TID-7534.
28. Richardson GL and Platt AM (1961) *Progress in Nuclear Energy, Series IV, Technology Engineering and Safety*, Vol. 4, Pergammon Press, New York.
29. Leonard RA (1988)Recent Advances in Centrifugal Contactor Design. *Separation Science and Technology*, 23(12&13).
30. Jubin RT et al. (1988) Developments in Centrifugal Contactor Technology. Oak Ridge National Laboratory, ORNL/TM-10768.
31. Meikrantz DH, et al. (2001) Annular Centrifugal Contactors for Multiple Stage Extraction Processes. *Chem. Eng. Comm.*, Vol 188.
32. Watts C. (1977) Solvent Extraction Equipment Evaluation Study – Part 2. Battelle Northwest Laboratory, BNWL-2186 Pt. 2.
33. Bernstein GL, et al. (1973) A High-Capacity Annular Centrifugal Contactor. *Nuclear Technology*, 20.
34. Drain F., et al. (2003) “Forty years of Experience with Liquid-Liquid Extraction Equipment in the Nuclear Industry,” Proceedings from Waste Management Conference 2003, Tucson, AZ.
35. Meikrantz DH et al. (1996) Rotor Sleeve for a Centrifugal Separator. U.S. Patent # 5,571,070.
36. Macaluso LL and Meikrantz DH (1999) Self-cleaning Rotor for a Centrifugal Separator. U.S. Patent # 5,908,376.
37. Garn, TG, Meikrantz DH and Law JD (2008) Remote Evaluation of a Three-Stage 5 Cm Annular Centrifugal Contactor Remote Module at the INL. Idaho National Laboratory, INL/EXT-08-13670.
38. Meikrantz DH, Garn TG, Law JD and Macaluso LL (2009) Evaluation of a New Remote Handling Design for High Throughput Annular Centrifugal Contactors. Idaho National Laboratory INL/EXT-09-16824
39. Chang, Y.I.; “The Integral Fast Reactor;” *Nuclear Technology*, vol. 188, n.2, pp. 129-138 (1989).
40. Till, C.E., Chang, Y.I. and Hannum, W.H., “The Integral Fast Reactor – An Overview,” *Progress in Nuclear Energy*, 31, 1-2, 3 (1997)



41. Benedict, R.W.; "EBR-II Spent Fuel Treatment Demonstration Project;" *Transactions of the American Nuclear Society*, vol. 77, pp. 75-76 (1997).
42. Ackerman, J.P.; "Chemical Basis for Pyrochemical Reprocessing of Nuclear Fuel;" *Industrial and Engineering Chemistry Research*, vol. 30, N. 1, pp. 141-145 (1991).
43. Lee S.Y. et al. (2007) A Preliminary Study on the Safeguardability of a Korean Advanced Pyroprocessing Facility (KAPF). *Proceedings of Global 2007*, Boise, Idaho.
44. Lee H.S., Hur J.M., Ahn D.H., Kim I.T., and Lee J.H. (2009) Development of Pyroprocessing Technology at KAERI. *Proceedings of Global 2009*, Paris, France.
45. Willit J.L., Miller W.E., and Battles J.E. "Electrorefining of Uranium and Plutonium – A Literature Review." *Journal of Nuclear Materials*, vol. 195, No. 3, 1992, pp. 229-249.
46. Goff K.M. and Benedict R.W. "Electrorefining Experience for Pyrochemical Reprocessing of Spent EBR-II Fuel." *Proceedings of Global 2005*, Tsukuba, Ibaraki (Japan).
47. Karell E.J., Gourishankar K.V., Smith J.L., Chow L.S., and Redey L. "Separation of Actinides from LWR Fuel Using Molten-Salt-Based Electrochemical Processes." *Nuclear Technology*, vol. 136, December 2001, 342-353.
48. Gourishankar K., Redey L., and Williamson M. "Electrochemical Reduction of Metal Oxides in Molten Salts." *Light Metals 2002*, TMS.
49. Westphal B.R., Keiser D.D., Rigg R.H., and Laug D.V. "Production of Metal Waste Forms from Spent Fuel Treatment," *Proceedings of the DOE Spent Nuclear Fuel Meeting: Challenges and Initiatives*, Salt Lake City, Utah; December 13-16, 1994.
50. Abraham D.P., McDeavitt S.M., and Park J. "Metal Waste Forms from the Electrometallurgical Treatment of Spent Nuclear Fuel." *Proceedings of the Embedded Topical Meeting on DOE Spent Nuclear Fuel and Fissile Material Management*, Reno, Nevada, June 16-20, 1996.
51. Pereira C., Hash M.C., Lewis M.A., Richmann M.K., and Basco J. *Materials Research Society Symposium Proceedings* 556 (1999), 115.
52. Ahluwalia R.K., Geyer H.K., Pereira C., and Ackerman J.P. *Ind. Eng. Chem. Res.* 1998, 37, 145.
53. Lexa D. and Johnson I. Occlusion and Ion Exchange in the Molten (Lithium Chloride-Potassium Chloride-Alkali Chloride) Salt + Zeolite 4A System with Alkali Metal Chlorides of Sodium, Rubidium, and Cesium. *Metallurgical and Materials Transactions* 2001, 32B, 429.
54. Phongikaroon S. and Simpson, M.F. "Two Site Equilibrium Model for Ion Exchange Between Multivalent Cations and Zeolite-A in a Molten Salt;" *AIChE Journal*, Vol. 52, No. 5, pp. 1736-1743, May 2006.
55. Kim E.H., Park G.I., Cho Y.Z., and Yang H.C. "A New Approach to Minimize Pyroprocessing Waste Salts Through a Series of Fission Product Removal Process." *Nuclear Technology*, vol. 162, No. 2, 2008, pp. 208-218.



56. Simpson M.F. and Sachdev P. "Development of Electrefiner Waste Salt Disposal Process for the EBR-II Spent Fuel Treatment Project;" *Nuclear Engineering and Technology*, vol. 40, No. 3, April 2008.
57. Simpson M.F., Goff K.M., Johnson S.G., Bateman K.J., Battisti T.J., Toews K.L., Frank S.M., Moschetti T.L., and O'Holleran T.P. "A Description of the Ceramic Waste Form Production Process from the Demonstration Phase of the Electrometallurgical Treatment of EBR-II Spent Fuel," *Nuclear Technology*, vol.134, pp. 263-277 (2001).
58. Thomas J.L.,Mange M., and Eyraud C. *Molecular Sieve Zeolites-I*, R.F. Gould, Ed., *Amer. Chem. Soc.* (1971).
59. Ebert W.E. "Testing to evaluate the suitability of waste forms developed for electrometallurgically treated spent sodium-bonded nuclear fuel for disposal in the Yucca Mountain repository." Argonne National Laboratory, ANL-05/43, September 2005.