

Aqueous Reprocessing of Used Nuclear Fuel

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Chapter 1

Aqueous Reprocessing of Used Nuclear Fuel

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Aqueous reprocessing of used nuclear fuel has a long history of successful operation worldwide. The history of aqueous reprocessing and a description of current and past operating aqueous reprocessing facilities are provided and the main types of solvent extraction equipment utilized in the nuclear industry are described. While the PUREX process is well established for separating U and Pu from used nuclear fuel, numerous variants to the PUREX process are being developed and are described. Finally, advanced separation processes in which minor actinides are separated from the used nuclear fuel are a key research focus worldwide. These processes and the current state of development are discussed.

1. Introduction

Aqueous technologies for used nuclear fuel reprocessing have historically been utilized to recover uranium and plutonium from irradiated nuclear reactor fuel for recycle. The purpose for reprocessing used fuel has been to recover unused plutonium and uranium in the used fuel elements. This results in gaining more energy from the original uranium and contributes to the national energy security of the country reprocessing their fuel. Also, reprocessing results in a reduction in volume of high-level waste for disposal and the radiotoxicity is lower and reduces more rapidly than with used nuclear fuel.

With aqueous technologies, the used nuclear fuel is typically mechanically chopped into small pieces and leached into an acidic

solution. The resulting dissolver product is chemically processed to separate actinides for recycle to a reactor. The remaining metals and fission products are treated for disposal as a high-level waste. The primary aqueous separation method utilized to accomplish the required separation is solvent extraction, although precipitation has been used initially in the US defense industry for the recovery of Pu for weapons.

The Plutonium Uranium Reduction Extraction (PUREX) process is the most common solvent extraction technology utilized in the US and internationally for the separation of U and Pu from used nuclear fuel. Variations on the PUREX process are being developed and implemented to prevent the separation of pure plutonium. Additionally, advanced aqueous separation technologies are being developed in the US and internationally for the separation and recycle/transmutation of minor actinides.

2. Solvent Extraction

Solvent extraction is the primary technology utilized in aqueous used nuclear fuel reprocessing. First, used nuclear fuel from a reactor, after some amount of decay storage, is leached with an acidic solution. The resulting aqueous solution is separated from the remaining fuel cladding and then chemically processed via solvent extraction to separate the components of interest, typically uranium and/or plutonium.

Solvent extraction within used nuclear fuel reprocessing utilizes an organic phase containing an extractant, in contact with the aqueous dissolver product via mixing, to extract the components of interest into the organic phase. Typically, 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. The component of interest is subsequently removed from the organic phase to an aqueous phase via back-extraction. In order for effective processing, the two phases must be immiscible, have enough of a density difference to allow rapid disengagement, be of an appropriate viscosity to be transported through process equipment, limited solubility of the organic phase in the aqueous phase to maintain the extractant

concentration over long-term use, and the organic phase must have sufficient hydrolytic and radiolytic stability to allow for long-term reuse to minimize organic waste volumes.

One of the primary advantages of solvent extraction processes is the ability to operate in a continuous, countercurrent manner with multiple contacting/separating stages to achieve the desired removal efficiency of the components being extracted. This allows for continuous operation instead of batch operation. Countercurrent operation is shown graphically for an extraction section of a U/Pu separation flowsheet in Figure 1.

In this flow diagram, the aqueous dissolver product feed stream containing the components to be extracted enters at one end of the process (A_{N+1}), and the fresh solvent (organic) stream enters the other end (O_0). The aqueous and organic streams flow countercurrently from stage to stage where they are intimately mixed and separated, and the final products are the solvent loaded with the desired components (e.g. U and Pu), O_N , leaving stage N and the aqueous raffinate, A_1 , depleted in U and Pu leaving stage 1.

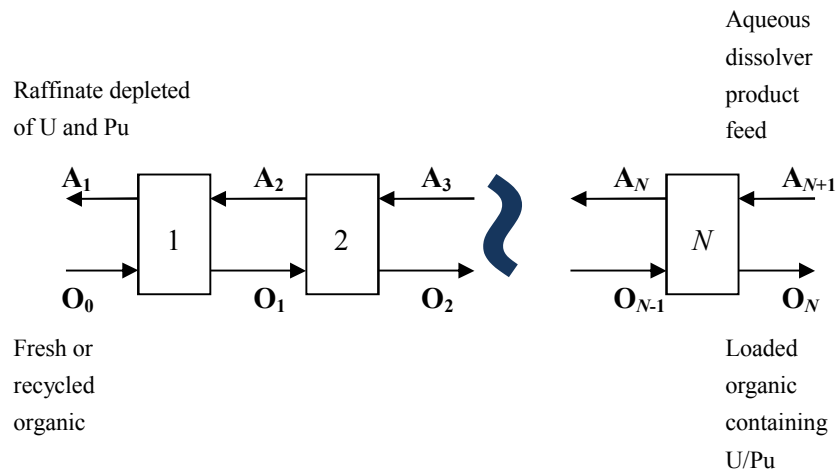


Fig. 1. Countercurrent – multistage extraction process flow diagram.

Following an extraction section, scrub, strip and solvent wash sections are typically employed. The purpose of the scrub section is to back extract (scrub) to the extraction section any metals/fission products (e.g. Zr) that may have co-extracted along with the desired components. The strip section is utilized to back-extract the desired components (e.g. U and Pu) into an aqueous phase where they will ultimately be re-enriched and converted into an oxide form for recycle to a reactor, typically as MO_x fuel. The solvent wash section is utilized to remove any hydrolytic or radiolytic degradation products from the solvent and prepare the solvent for recycle to the extraction section, thus minimizing organic waste volumes.

3. Solvent Extraction Equipment

Solvent extraction equipment has been utilized in the nuclear industry since the implementation of the PUREX process for the separation of plutonium and uranium from fission products for weapons production in the 1950's.¹ This technology was later implemented for the reprocessing of used nuclear fuel from commercial power reactors. PUREX based solvent extraction processing has been and continues to be utilized worldwide including France, Japan, Russia, the United Kingdom and the United States. Additionally, considerable research in the development of advanced separation processes is ongoing, requiring the use of solvent extraction equipment. In these efforts, solvent extraction equipment is utilized to efficiently mix and separate the aqueous and organic phases to facilitate separation of the species of interest. The solvent extraction equipment is designed for countercurrent flow to facilitate high separation efficiencies and continuous operation.

To support operation in a radioactive environment, solvent extraction equipment must be remotely operable and maintainable, resistant to high radiation fields, capable of continuous countercurrent operation, and be critically safe for certain applications. In addition, desirable attributes include the ability to accommodate solids, a small process footprint, and operational flexibility (continuous long-term operation or frequent start-stop operation). The three main types of solvent extraction equipment

used in industrial-scale reprocessing facilities and in fuel cycle research laboratories include 1) columns, 2) mixer-settlers, and 3) centrifugal contactors. A brief description of each type of equipment follows. More detailed descriptions of these types of equipment can be found in literature.^{2,3}

3.1. Columns

Packed columns and pulse columns with sieve plates or trays are the typical type of solvent extraction column utilized in the nuclear industry. Packed columns contain packing material (e.g. Raschig Rings) to create mixing of the two phases as they flow counter currently. The phases disengage at either the top or the bottom of the column depending upon whether the column is operated in an aqueous or organic continuous mode. Pulsed columns with trays or plates were developed to increase the mixing intensity of the phases and, thus, decrease the height requirement of the column. The mechanical energy applied to the column via pulsing with air facilitates the formation of small droplets for mass transfer. A photograph of an operating pulsed column used to support laboratory testing is shown in Figure 2.

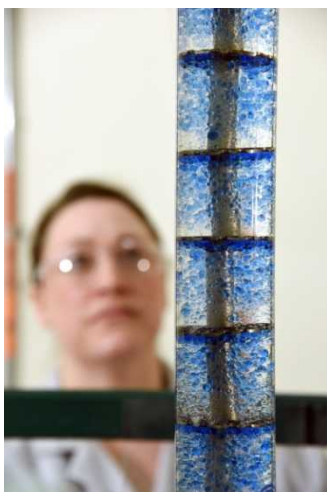


Fig. 2. Operating lab-scale pulsed column at Idaho National Laboratory.

3.2. Mixer-Settlers

A mixer-settler contains a small mixing chamber and a larger settling chamber. The two immiscible phases enter the mixing chamber containing an impeller. This dispersion that forms flows into the settling chamber where the two phases separate by gravity. A system of weirs allow for the light phase to flow over the higher weir and the heavy phase to flow under the lower weir. Multiple mixer-settlers are configured for countercurrent flow to achieve high separation efficiency. A photo of several mixer-settlers is shown in Figure 3.



Fig. 3. Industrial and lab-scale mixer-settlers.

3.3. Centrifugal Contactors

Centrifugal contactors consist of a hollow rotor that rotates within a cylindrical housing utilizing a motor mounted above the housing. The aqueous and organic feed solutions enter a stage near the top of the housing and are mixed as they flow downward. For annular centrifugal contactors, the shear forces between the spinning rotor and the stationary housing mix the two phases. Other contactor designs utilize alternative methods of mixing such as mixing pins attached to the bottom of the spinning rotor. When the mixture enters the spinning rotor through an

opening at its base, the spinning rotor acts as a centrifuge with the heavy phase going to the rotor wall. A series of weirs allow the separated heavy and light phases to flow out of the contactors as separate streams. Multiple centrifugal contactors are configured for countercurrent flow to achieve high separation efficiency. An operating centrifugal contactor is shown in Figure 4.



Fig. 4. Operating 5-cm centrifugal contactor with plastic housing.

4. Reprocessing History

Aqueous reprocessing technologies were first utilized at the Hanford Site during the Manhattan Project for the recovery of Pu-239 using a bismuthate phosphate precipitation process.¹ Recovery transitioned to solvent extraction processes that allowed for continuous instead of batch operation, as well as the concurrent recovery of U and Pu. Also, the purpose of the reprocessing of used fuel transitioned from defense purposes to commercial use for the recycle of U and Pu.

The first solvent extraction process implemented was the reduction oxidation (REDOX) process.¹ The process was developed and tested at Argonne National Laboratory and Oak Ridge National, and the first REDOX plant operated at Hanford. The REDOX process utilizes Methyl

isobutyl ketone (hexone) to extract uranyl nitrate and plutonium nitrate. U (VI) and Pu(IV) are co-extracted then the Pu is reduced to Pu(III) using ferrous sulfamate and selectively stripped from the uranium. One disadvantage of this process is the required addition of aluminum nitrate to increase the nitrate concentration. Also, hexone is a flammable and volatile solvent.

The BUTEX process was developed by British scientists at Chalk River Laboratory.⁴ This process utilized dibutyl carbitol as the extractant and used nitric acid as a salting agent instead of aluminum nitrate, thus reducing the problem of larger waste volumes due to the addition of $\text{Al}(\text{NO}_3)_3$. This process was implemented at the Windscale plant at the Sellafield Site in the United Kingdom for the reprocessing of used fuel.

Aqueous reprocessing transitioned to the PUREX process in the 1950's.¹ The PUREX process was developed by Knolls Atomic Power Laboratory and tested at ORNL. A modified PUREX production-scale plant was used in Idaho at the Idaho Chemical Processing Plant beginning in 1953. This process utilized hexone as an extractant in the first cycle and PUREX second and third cycles. The PUREX process was utilized on a production scale at Savannah River in the F-Canyon in 1954.⁵ It has been used at the Savannah River Site since 1955 in the H-Canyon facility.⁵ It replaced the REDOX process at Hanford in 1956. From here, the use of the PUREX process expanded within the US and internationally.

5. PUREX Process

The PUREX process has historically been the primary aqueous separation process utilized world-wide for the reprocessing of used nuclear fuel. Table 1 lists historical, current, and in-construction reprocessing facilities utilizing the PUREX process or a variant.

The front-end of the PUREX-based reprocessing consists of chopping the used fuel into small pieces, leaching the used fuel from the cladding using a nitric acid solution, separation of the fuel cladding pieces, spacers and other fittings, chemical adjustment and filtration of this dissolver product. This dissolver product is then fed to a first cycle of

Table 1. Historical PUREX reprocessing facilities.

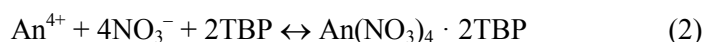
Facility	Country	Operation	Capacity (MTHM/yr)	Comments
Savannah River F, H-Canyon ⁵	USA	1955 - present	5 – 10 MT/yr	Recovered Pu, U and Np from weapon production reactors
Hanford ⁶	USA	1956-1972, 1983-1988	8.3 MT/day design up to 20 actual	Recovered Pu, U and Np from Hanford production reactors
UP1 Magnox- Marcoule ⁷	France	1958-1997	960 MT/yr	Fuel from Pu production reactors- later, power reactors
B20 - Sellafield Trombay ^{8,9}	UK India	1964-present 1964-73, 1983-present	1500MT/yr 60 Mt/yr	Magnox Fuel[6] research reactor fuel[10]
West Valley ^{8,10}	USA	1966-1972	300 MT/yr	First plant in US to process commercial fuel
Morris, IL ^{8,10}	USA	NA	300 MT/yr	Construction halted prior to ops. F volatility polishing
Barnwell, SC ^{8,10}	USA	NA	1500 MT/yr	Shutdown during startup testing -US reprocessing policy change
UP2 Magnox- LaHague ⁷	France	1966-1976	800 MT/yr	Magnox fuel then later converted to oxide fuel
Tokai ⁸	Japan	1975 - 2014	210 MT/yr design, 100 actual	BWR and PWR fuel, Adv. Thermal Reactor Fuel
UP2 Oxide- LaHague ⁵	France	1976 - present	800 MT/yr design, 400 actual	Commercial LWR fuel
RT1 Mayak ⁸	Russia	1976- present	400 MT/yr	VVER-440 fuel, preparing to expand to VVER-1000 fuel
UP3 Oxide- LaHague ⁷	France	1989 - present	800 MT/yr	Commercial LWR fuel for foreign countries
Thorp ⁸	UK	1994 - present	1200 MT/yr	Foreign and domestic fuel. Planned shutdown in 2018
KARP- Kalpakkam ⁹	India	1996 - present	100 MT/yr	Reprocesses oxide fuels from PHWRs
Jiuquan ¹¹	China	2010-present	50 MT/yr	Pilot scale facility
PREFRE-2 Tarapur ⁹	India	2011-present	100 MT/yr	Oxide fuels from PHWRs
Rokkasho ⁶	Japan	2018	800 MT/yr	Planned startup in 2018.
New ¹²	China	2025-2030	800 MT/yr	PUREX process variant AREVA contract to design, 2030 target

solvent extraction where the U and Pu are separated from the dissolver product and subsequently separated from each other. Several additional cycles of solvent extraction are used to further purify the uranium and plutonium. The resulting uranium and/or plutonium product is converted to an oxide form. In commercial fuel reprocessing, the plutonium oxide product, with or without uranium, is recycled to a reactor as mixed oxide (MOX) fuel in light water reactors. About 50 reactors in Europe and Japan are licensed to use MOX fuel with around 30 actually doing so.

The PUREX process utilizes 20 to 40 vol% tributyl phosphate in a hydrocarbon diluent (typically kerosene or n-dodecane) to extract uranium and plutonium from the dissolver product. The PUREX process is effective in extracting actinides in the +4 and +6 oxidation state. Uranium, as U(VI) is extracted as follows:



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



In the PUREX process, Pu is present as Pu(IV) and is co-extracted with the U. Other actinides and lanthanides present in the +3 or lower oxidation state are not extracted with the PUREX Process, thus allowing for an efficient separation. Neptunium is another actinide that can be maintained as Np(VI), if desired, and co-extracted with the U and Pu.

6. PUREX Process Variants

Numerous modifications to the standard PUREX process have been or are currently being developed. The primary purpose of these variations is to prevent the production of a pure plutonium stream due to concerns with proliferation. With the standard PUREX process, a pure uranium stream and a pure plutonium stream are produced. Theft or diversion of the reactor-grade Pu for weapons use has been a concern under these conditions. While no separations process can be made proliferation-proof, modifications to the PUREX process can effectively reduce the

proliferation risk. Table 2 lists several PUREX process variants that have been or are currently being developed.

Table 2. PUREX process variants

Technology	Country	Variation
COEX TM	CEA/AREVA France	No separation of pure Pu
UREX	DOE, USA	Single cycle U and Tc separation, lower acidity
Co-decontamination	DOE, USA	No separation of pure Pu
NUEX	Energy Solutions	No separation of pure Pu
NNL Advanced Process	National Nuclear Laboratory, UK	Single cycle, no separation of pure Pu
NEXT Process	JAEA, Japan	Combines crystallization with PUREX process, no separation of pure Pu
Simplified PUREX	Russia	Thermochemical decladding of the used fuel assemblies instead of chopping. Operated at lower acidity
PARC Process	India	Tc and Np are extracted by TBP along with the U and Pu. Single cycle

6.1. COEXTM Process

The Co-extraction (COEXTM) process, developed in France by AREVA, utilizes variants of the PUREX process chemistry to allow some of the extracted uranium to follow the plutonium, resulting in three streams; a U/Pu product, a U product and a raffinate waste solution containing fission products and minor actinides.¹³ This is accomplished using a reducing agent, such as U(IV) nitrate or hydroxylamine nitrate to reduce the Pu(IV) to Pu(III) and back-extract this Pu while only partially reducing and back-extracting the U(VI). Additionally, this multi-cycle process includes the use of a co-conversion process to produce a uranium/plutonium oxide product. At no point during the process is pure plutonium separated.

6.2. UREX

The Uranium Extraction (UREX) process is a variant of the PUREX process that was developed by the US Department of Energy as a method to separate uranium, without co-extracting Pu.^{14,15} Co-extraction of Pu and Np is prevented by introduction of a complexant/reductant, such as acetohydroxamic acid in the scrub feed. The complexation of Pu and Np are enhanced in the UREX process through the use of low acidity feed and scrub solutions, as well as to enhance the extractability of technetium. Development of the UREX process has progressed to the point of demonstrations with actual used nuclear fuel using 2-cm centrifugal contactors, with good results.¹⁴

6.3. Co-Decontamination Process

The Co-decontamination process is a variant of the PUREX process that is being developed by the US Department of Energy as a method of co-extracting U and Pu, with no separation of pure Pu.¹⁶ There are several variants of this process with similar goals that utilize various reductants. Previously, a co-decontamination process has been demonstrated with actual used nuclear fuel at the laboratory scale. With these tests, it has been demonstrated that a U-Pu-Np product can be produced which contains approximately 10% Pu-Np and, in a second test, which contains approximately 30% Pu-Np.¹⁵ Recent focus of development of the Co-decontamination process is being pursued through a multi-year experimental study to evaluate the technological capability to control the preparation of U/Pu product.¹⁸ To this end, the process being developed, after co-extraction of U and Pu via standard PUREX process chemistry, uses hydrazine-stabilized U(IV) as a Pu reductant. An excess of the reductant will produce a U/Pu nitrate solution at a flexible range of U/Pu ratios, dependent upon process goals. This ratio is determined by adjusting the flowrate in the back-extraction section, the purpose of which is to remove excess uranium in the solvent and produce the desired product ratio. The co-decontamination process is under active development by the US DOE, with flowsheet testing planned in the 2018 timeframe.¹⁸

6.4. NUEX Process

The New Uranium Extraction (NUEX) process is a PUREX process variant that was designed by EnergySolutions as a potential near-term reprocessing flowsheet for application in the USA for used LWR fuel.^{17,19} This process modifies the PUREX process flowsheet utilized in the Thorp reprocessing facility at the Sellafield Site in the UK to produce a U/Pu/Np product and prevent the production of a pure Pu stream. This is accomplished through modifications to the three cycle PUREX process by replace the U(IV)/N₂H₄ reductant from the THORP flowsheet with acetohydroxamic acid (AHA). This would result in partitioning U from U/Pu by complexation rather than reduction, resulting in U and U/Pu/Np products. Technetium is also separated and recovered with this process.

6.5.>NNL Advanced Process

The National Nuclear Laboratory in the United Kingdom is developing a simplified flowsheet variant of the PUREX process for the reprocessing of GenIV fuel.¹⁷ The process consists of a single cycle flowsheet that utilizes a hydroxamic acid complexant, much like the NUEX process described previously. Research and development to date have indicated that the use of AHA 1) results in a high decontamination factor for Pu in the U product stream, 2) the uranium DF in the Pu product stream can be maintained low enough to result in a U/Pu product instead of pure Pu, 3) Np is separated with the U/Pu product stream, 4) Tc mostly follows the uranium but more R&D is needed, 5) process kinetics allow the use of centrifugal contactors as the separation equipment, and 6) AHA degradation to acetic acid is an issue relative to recycle of nitric acid within a facility.

6.6. NEXT Process

The New Extraction System for TRU Recovery (NEXT) is being developed by the Japan Atomic Energy Agency (JAEA) for the reprocessing of fast reactor fuel.^{20,21} The process combines PUREX process chemistry with crystallization. First, U is partially recovered

(approximately 70%) by crystallization of uranyl nitrate hexahydrate from the used fast reactor fuel dissolver product accomplished by lowering the temperature. The resulting uranyl nitrate hexahydrate crystals are washed with nitric acid to further decontaminate them from TRU elements and fission products. The crystals can then be further treated in a crystal purification step.²¹ U/PU/Np is recovered from the mother liquor via PUREX process chemistry without the need for multiple cycles of purification. Further recovery of Am and Cm is obtained through the use of extraction chromatography. The PUREX solvent extraction portion of this process has been demonstrated with actual fast reactor (JOYO) irradiated MOx fuel dissolved in nitric acid using laboratory-scale centrifugal contactors. With this test, it was shown that Np is recovered with the U and Pu.²⁰

6.7. Simplified PUREX Process

The Simplified PUREX process is being developed in Russia as a next generation of reprocessing with the goal of reducing the volume of low-level waste generated.²² The Simplified PUREX process, as compared to classical PUREX, implements thermo-chemical (dry) operations in the head-end of the process. This is accomplished through thermochemical decladding of the used fuel assemblies instead of chopping. Low temperature voloxidation of the fuel is performed to release volatile fission products prior to dissolution and to generate a more quickly dissolvable U_3O_8 form. The end result is a more concentrated dissolver product, relative to U concentration in a lower nitric acid concentration feed, resulting the generation of less liquid waste. One variant of the Simplified PUREX process dissolves the SNF, after voloxidation, with a $TBP \cdot nHNO_3$ adduct in a supercritical fluid for extraction.²²

6.8. PARC Process

The Partitioning Conundrum Key (PARC) process is a PUREX process variant being developed by JAEA.²³ With this process, Tc and Np are extracted by TBP along with the U and Pu in a co-extraction step. Extracted Np and Tc are separated from the U/Pu stream via selective

reduction of Np(VI) to Np(V) using normal-butyraldehyde in the presence of U(VI) and Pu(IV) and high acid scrubbing of technetium. The U and Pu can then be separated from each other resulting in four product streams – Tc, Np, Pu, and U products. Second and third cycles of PUREX purification are not required. Further processing of the raffinate to separate Am and Cm can then be performed using adsorption techniques with TODGA and alkyl-BTP solvents.²³

7. Advanced Reprocessing Technologies

Reprocessing technologies for the separation of minor actinides from lanthanides are expected to be an important part of future advanced reprocessing for used nuclear fuel. The recovery and transmutation, in a fast reactor or potentially LWR or BWR's²⁴, of long-lived minor actinides to short-lived fission products would reduce the long-term heat load and radiotoxicity of used fuel or high-level waste resulting from reprocessing. Transmutation is accomplished by irradiation in an intense neutron field to form short-lived fission products. The main focus for minor actinide recycle is the separation of Am and Cm from used fuel. There are two main approaches, homogenous and heterogeneous recycle. With homogeneous recycle, the minor actinides are combined with the U and Pu in fast reactor nuclear fuel. With heterogeneous recycle, the minor actinides, are manufactured into targets which are subsequently transmuted in the reactor. Minor actinide separation has become a key R&D area worldwide in the development of advanced reprocessing technologies. Many, but not all, of the areas of development are presented below.

7.1. TRUEX/TALSPEAK Process

The TRUEX/TALSPEAK process is a two cycle solvent extraction process in which the trivalent actinides and lanthanides are first co-extracted from the high acidity raffinate of a PUREX-based U/Pu separation process raffinate using the Transuranic Extraction (TRUEX) process. The actinide/lanthanide product stream from the TRUEX

process is then treated using the TALSPEAK process to separate the actinides from the lanthanides.

The TRUEX Process was developed by Argonne National Laboratory²⁵ and consists of an octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) extractant in an aliphatic diluent. The CMPO extracts the trivalent actinides and lanthanides from the acidic raffinate of the upfront U/Pu separation process. TBP is added as a solvent modifier to prevent third phase formation. The TRUEX solvent typically consists of 0.2 mol/L CMPO and 1.4 mol/L TBP in n-dodecane. With the TRUEX process, trivalent actinides and lanthanides are co-extracted from the PUREX raffinate. Once extracted, the actinides and lanthanides are effectively stripped using low acidity nitric acid. Alternatively, an aqueous solution consisting of diethylenetriaminepentaacetic acid (DTPA) in a lactate buffer at pH 5 is used to facilitate separation in the subsequent TALSPEAK process. This actinide/lanthanide strip product can then be fed directly into the TALSPEAK process with only minor adjustments.

The TALSPEAK process was developed at Oak Ridge National Laboratory (ORNL).²⁶ This process functions based on the higher affinity of polyaminocarboxylate ligands for trivalent actinides as compared to the trivalent lanthanides. DTPA is added to the aqueous phase, resulting in selective complexation of the actinides, holding them in the aqueous phase while the lanthanides are extracted into the organic phase using bis-(2-ethylhexyl)phosphoric acid (HDEHP). The aqueous phase is buffered with lactic acid to control the pH and also to improve the extraction kinetics.²⁷ The TRUEX/TALSPEAK process has been demonstrated at the laboratory-scale using actual used nuclear fuel. In these tests, the TRUEX and TALSPEAK testing followed an upfront UREX process.²⁸ Results from these tests indicated >99.99% recovery of Pu, Np, and Cm and 99.97% recovery of Am.²⁸

7.2. TRUEX/Advanced TALSPEAK

The TALSPEAK process is very sensitive to aqueous solution pH. In order to reduce the dependence of the process performance on the pH, and thereby obtain more predictable extraction behavior, and,

additionally, to obtain more rapid extraction kinetics, the Advanced TALSPEAK process is currently being developed in the USA by the Department of Energy. For the Advanced TALSPEAK process, some adjustments are made to the TRUEX process. Primarily, the DTPA/lactate stripping solution is replaced with a (HEDTA)/citric acid stripping solution which is compatible with the Advanced TALPSEAK process. The Advanced TALSPEAK flowsheet is a modified version to the TALSPEAK flowsheet that utilizes a 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester acid (HEH[EHP]) extractant instead of HDEHP and utilizes an aqueous feed composition of HEDTA)/citric acid instead of DTPA/lactate.²⁹

Recently, as a collaboration between the US Department of Energy and Forschungszentrum (FZ) Jülich in Germany, an Advanced TALSPEAK flowsheet test was performed at Jülich facilities using a radiotraced feed simulant and 24 stages of 1-cm annular centrifugal contactor manufactured by the Institute of Nuclear Energy Technology (INET) in Beijing, China. Results of these recent tests are yet to be published but separation goals were met.

7.3. ALSEP Process

The most recent focus in the USA for development of a minor actinide separation process center on simplification to a single process as opposed the two process TRUEX/TALSPEAK system. The primary simplified process being developed is the Actinide-Lanthanide Separation (ALSEP) concept which consists of N,N,N',N'-tetraoctyldiglycolamide (TODGA) or N,N,N',N'-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) as extractants combined with (mono-2-ethylhexyl ester [2-ethylhexylphosphonic acid] (HEH[EHP])) for the co-extraction of trivalent actinides and lanthanides.³⁰ Scrub sections with nitric acid and citrate are used to back-extract Mo. A citrate buffered DTPA solution in the pH range of 2.5 to 4 is used to selectively strip the actinides from the solvent and a solution of tetraethyldiglycolamide (TEDGA) in nitric acid is used to strip the lanthanides from the solvent.

Proof-of-principle testing of the ALSEP concept has been completed using radio-traced feed streams.³⁰ These tests have resulted in separation

factors of the minor actinides from the lanthanides in the range of 20 to 40. ALSEP development continues with the development of stripping agents (i.e. modified polyaminocarboxylate chelates) that exhibit enhanced kinetics³¹ with a near-term goal of laboratory-scale flowsheet testing in centrifugal contactor equipment using radio-traced simulant leading to a laboratory-scale demonstration with actual dissolved used nuclear fuel.

7.4. *Am(VI) Extraction*

Another approach being developed in the USA by the DOE-NE Sigma Team for Advanced Actinide Recycle (STAAR) is through the exploitation of higher oxidation states of Am. The approach is to use a strong oxidant (standard potential of 1.7 V for the Am(III)/Am(VI) redox couple) to oxidize Am(III) to Am(VI), leaving the lanthanides as Ln(III) (with the exception of Ce) and extracting the Am(VI). The most mature process being developed in the US uses sodium bismuthate.³² The solid sodium bismuthate oxidizes Am(III) to Am(VI) and 1M diamylamylphosphonate (DAAP) in n-dodecane extracts the Am(VI). The sodium bismuthate also oxidizes Ce(III) to Ce(IV) and the DAAP co-extracts the Ce(IV). A selective strip using dilute HNO₃ or H₂O₂ is accomplished based on the large difference in stability between Am(VI), which is unstable, and Ce(VI) which is stable. This process has been tested using a radiotraced simulant in 5-cm centrifugal contactors with a resulting removal efficiency of 62% as compared to a batch contact removal efficiency of 65% obtained immediately prior to the radiotracer test. These results demonstrated that Am(VI) can remain oxidized long enough to accomplish a separation using solvent extraction in engineering-scale equipment. Current work is focused on developing the selective stripping and testing of alternative extractants such as butyramides.³³

7.5. *Group Hexavalent Actinide Precipitation*

Another promising approach being developed by the US DOE-NE STAAR program focuses on a group separation of all actinides from U to

Am in the hexavalent form.³⁴ This process would forgo a required upfront PUREX type process to separate and Pu prior to the minor actinide separation process, thus further simplifying the overall reprocessing flowsheet. The main challenge to such a process is the oxidation and stability of Am(VI). Sodium bismuthate has been shown to be an effective oxidant for Am.³² As such, the concept behind this group hexavalent actinide separation process is to oxidize U, Pu, Np and Am to the hexavalent state using sodium bismuthate. The solution is then cooled to 2C, resulting in co-crystallization of the hexavalent actinides. Results to date indicate near proportional removal in the range of 61% to 71% with a single crystallization.³⁴ Multiple recrystallizations have the potential to significantly increase the recovery of the hexavalent actinides. Study of the fission products Zr, Cs, Ce and Nb indicate on Nb is separated significantly (12%). The fission products Nb, and to a lesser extent Zr, Cs and Ce showed some separation under the highly oxidizing conditions created with the sodium bismuthate.³⁴

7.6. DIAMEX/SANEX Process

The Diamide Extraction (DIAMEX)/Selective Actinide (SANEX) process, developed in France in collaboration with European researchers, is a two-step process which would follow a PUREX type U/Pu separation process. First, the lanthanides and trivalent actinides are separated from the remaining fission products (DIAMEX) and then the trivalent actinides are separated from the lanthanides in the SANEX process.³⁵

The DIAMEX process uses a malonamide, such as 1M N,N'-dimethyl-N,N'-dioctyl-hexylethoxy-malonamide (DMDOHEMA) in a hydrogenated tetrapropylene, to co-extract the lanthanides and trivalent actinides.³⁶ After scrubbing with a HNO₃/oxalic acid/HEDTA scrub and a second 1M HNO₃ scrub, the actinides and lanthanides are back-extracted into a 0.3M HNO₃ stream. This strip product is feed for the SANEX process.

The SANEX process uses an extractant consisting of 15mM 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[2,2']bipyridine (CyMe4-BTBP) and 0.25M DMDOHEMA in an octanol

diluent.³⁵ The acidity of the aqueous feed from the DIAMEX process is increased to 2M HNO₃. A dilute HNO₃ scrub is used to back-extract the lanthanides and 0.5 M glycolic acid at pH 4 is used to strip the actinides from the solvent.

The DIAMEX and SANEX processes are relatively well developed. The DIAMEX process has been tested with simulated and actual used nuclear fuel solutions in a variety of equipment – mixer settlers, pulse columns and centrifugal contactors.^{36,17} The SANEX process has been demonstrated in laboratory-scale centrifugal contactors with actual used fuel solutions.³⁵

7.7. DIAMEX-SANEX/HDEHP Process

A single-step process has been developed by the French CEA by combining di-(2-ethyl-hexyl)-phosphoric acid (HDEHP) with the DMDOHEMA from the DIAMEX/SANEX process to co-extract the lanthanides and trivalent actinides and selectively strip first the actinides and then the lanthanides.^{37,17} The HEDTA holds the lanthanides in the organic phase during the actinide strip. The actinide strip solution uses HEDTA and citric acid to back-extract the actinides followed by dilute nitric acid to back-extract the lanthanides. Zr, Mo, and Fe co-extract with this process, requiring a citric acid strip prior to the actinide strip, to remove the Mo, and an oxalic acid/nitric acid strip to remove the Zr and Fe.¹⁷ Simulant testing and hot testing with actual used fuel solution (ATALANTE facility) have been successfully performed using laboratory-scale equipment.¹⁷

7.8. I-SANEX

The Innovative Selective Actinide Separation (I-SANEX) process uses TODGA and octanol in a TPH diluent to extract the minor actinides and lanthanides from a PUREX raffinate.³⁸ A series of two scrub solutions back-extract Mo, Zr, Sr, and HNO₃ from the solvent. Trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (CDTA) is added to the feed and scrub as a complexing agent for Zr and Pd. Selective stripping of the actinides from the lanthanides is accomplished using SO₃-Ph-BTP

in HNO_3 to back-extract the actinides and citric acid solution buffered to pH3 to back-extract the lanthanides. This process has been demonstrated at the laboratory scale using centrifugal contactors and radio-traced PUREX raffinate simulant.³⁸ Results of the testing indicate >99.9% recovery of the Am(III), Cm(III), and Ln(III) with <0.1% contamination of the actinide product with lanthanides. The scrub section was effective in back-extraction of Mo, Zr, and Sr. Ruthenium was found to extract (16%) and mostly remained in the solvent, requiring further research.

7.9. 1-Cycle SANEX

The one-cycle Selective Actinide Separation (1-Cycle SANEX) process uses CyMe₄BTBP and TODGA in a TPH/1-octanol diluent to extract the minor actinides from a PUREX raffinate.³⁸ Scrub solutions, consisting of oxalic acid and HNO_3 is used to back-extract Zr and residual lanthanides and L-cysteine in HNO_3 is used to back-extract Pd(II). The minor actinides are then stripped using a solution of glycolate at pH4. This process has been demonstrated at the laboratory scale using centrifugal contactors and radio-traced PUREX raffinate simulant.³⁸ Results of the testing indicate >99.8% recovery of Am(III), >99.4% recovery for Cm(III), and satisfactory decontamination of the actinide product from fission products and lanthanides. Slow extraction kinetics and limited loading capacity of the organic phase are issues requiring further research.³⁸

7.10. CEA-GANEX and Euro-GANEX Processes

The Group Actinide Extraction (GANEX) process was developed by the French CEA. This process supports homogenous recycle of actinides by first separating a pure uranium product in a first cycle solvent extraction process that uses DEHiBA (N,N-di-(ethyl-2-hexyl)isobutyramide) as a U(VI) extractant, followed by a second cycle in which the TRU is separated together for recycle. DEHiBA is used instead of TBP due to increased selectivity for U(VI) over Pu(IV) and its high loading capacity for U. This portion of the CEA-GANEX process has been demonstrated

at the Atalante facility, using actual used nuclear fuel dissolved in nitric acid, with good results.³⁹

The second cycle of the CEA-GANEX process uses *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxymalonamide (DMDOHEMA) and bis(2-ethylhexyl)phosphoric acid (HDEHP) extractants to co-extract the actinides and lanthanides, and a few other extractable fission products (Mo, Ru, Tc).⁴⁰ The Mo, Ru and Tc are stripped from the solvent prior in a series of two strip sections. The actinides and lanthanide are then selectively stripped using a mixture of HEDTA and citric acid at pH 3 for the actinides and a TEDGA/oxalic acid/nitric acid solution to strip the lanthanides. This second cycle of the CEA-GANEX process was demonstrated at the Atalante facility, using actual used nuclear fuel dissolved in nitric acid, with good actinide recovery but higher than expected contamination of the actinide product with lanthanides.^{40,17}

As part of the European Union Actinide Recycling by Separation and Transmutation (ACSEPT) and Safety of Actinide Separation processes (SACSESS) programs, the EURO-GANEX process was developed.⁴¹ This process consists of a first cycle as described above, followed by a second cycle that utilizes TODGA and *N,N'*-dimethyl-*N,N'*-dioctyl-2-(2-hexyloxyethyl) malonomide (DMDOHEMA) extractants. (CDTA) is used in the extraction/scrub aqueous phase to suppress Zr and Pd extraction. The TRU and lanthanides are selectively stripped using SO₃-Ph-BTP, AHA, and HNO₃ to back-extract the actinides and dilute nitric acid to back-extract the lanthanides.^{17,41} Testing of the process with fast reactor carbide fuel that was oxidized and dissolved in nitric acid, and processed in a U-extraction cycle, was performed at the European Joint Research Centre Institute of TransUranium elements (ITU). Results were positive – good recovery of Am, Np and Pu (>99%) with very little lanthanide contamination (<0.1%).⁴¹

7.11. Japan – DGA extraction Process

Diglycolamide (DGA) extractants are being developed in Japan for the separation of minor actinides from used nuclear fuel.⁴² One of the more promising DGA's is *N,N,N',N'*-tetraoctyldiglycolamide (TODGA). TODGA effectively extracts Am, Cm and rare earth elements at acidities

greater than 1M HNO_3 . Back-extraction can be accomplished at low acidity. Third phase formation was noted with the extraction of Nd. To alleviate this issue, N,N,N',N'-tetradodecyldiglycolamide (TDdDGA) was developed.⁴² Alternative methods to address third phase formation include the addition of N,N-dihexyloctanamide (DHOA) to the TODGA/dodecane solvent, or through the use of TBP or octanol as a phase modifier.^{43,44} Also, Russian researchers at the Khlopin Radium Institute have developed several alternative polar-fluorinated diluents for DGA extractants that increase the extraction capability of TODGA for Am and Eu.¹⁷

Counter-current flowsheet testing with HLW simulant in mixer-settler equipment has been performed in Japan using TDdDGA in n-dodecane.⁴⁵ With the flowsheet tested, minor actinides and lanthanides are extracted by the TDdDGA and back-extracted, together, using dilute HNO_3 . Zirconium and Pd extraction is suppressed through the use of HEDTA and H_2O_2 in the feed and scrub. Separation of the minor actinides from the lanthanides is then accomplished using extraction chromatography. The countercurrent flowsheet test of the TRU recovery step achieved >99.99% recovery of Am and 62% recovery of Np.⁴⁵

7.12. Diamides of Dipicolinic Acid

Diamides of dipicolinic acid (DPA) are being investigated in Russia and other countries for the separation of actinides and lanthanides from used fuel.^{46,47} Mixtures of cobalt dicarbollide and DPA in an FS-13 diluent have been investigated in Russia. The study included N,N,N',N'-tetrabutyl- dipicolinic acid (TBDPA) and the ortho, meta, and para isomers of N,N-diethyl-N',N'-ditolyl diamides. Results indicate that the ortho-position is the most favorable and the ethyl-tolyl isomer Et(o)TDPA has good selectivity between the heavy and light lanthanides.⁴⁶ In the Czech Republic, N,N'-diethyl-N,N'-di-meta-tolyldipicolinamide (Et(m)TDPA) was found to have the high Am extractability while maintaining good Am(III)/Eu(III) selectivity.⁴⁷

Alternatively, at the Khlopin Radium Institute, dipyriddyldicarboxylic acid in polar fluorinated diluents has been studied.⁴⁸ Diamides of 2,2-dipyriddyldi-6,6-dicarboxylic acid can be used for the separation of minor

trivalent actinides from lanthanides with good separation factors (>10) obtained.

7.13. EXAm

The Extraction of Americium (EXAm) process is being developed in France by the CEA for the recovery of only Am, as the main contributor to long-term heat generation and radiotoxicity, from PUREX raffinate.^{49,50} The solvent consists of DMDOHEMA and HDEHP in TPH. TEDGA is used as a complexing agent to maintain Cm and heavy lanthanides in the aqueous phase, thus improving the Am/Cm selectivity. Molybdenum, Pd and Ru are stripped from the solvent using citric acid and NaOH prior to stripping of the Am. A selective strip is then employed which first back-extracts Am using DTPA at a low acidity and then back-extracts the lighter lanthanides using oxalic acid and TEDGA.

Hot testing of the EXAm process has been performed using actual PUREX raffinate.⁴⁹ Greater than 99% of the Am was extracted with a decontamination factor of >500 relative to Cm. Approximately 0.7% of the extracted Am was lost to the Mo strip effluent. Good decontamination from the light lanthanides was obtained for the Am product.

Recent efforts have focused on operation of the EXAm process using a concentrated PUREX raffinate.⁵⁰ These efforts have included countercurrent flowsheet testing with simulants and actual PUREX raffinate to produce AmO₂ pellets for irradiation testing. These tests resulted in an acceptable Am product; however, there was a 10% loss of Am to the raffinate.

8. Summary

Historically, there is a great deal of experience with aqueous separation technologies for the separation of U and Pu from used nuclear fuel. Much of this experience is based on the use of the PUREX process on an industrial-scale for decades. As countries move forward with development of advanced separation processes, considerable effort has

focused on modified PUREX processes in which there is not a pure Pu product. Additionally, a great deal of progress has been made in development of aqueous separation processes for the separation and recycle of minor actinides from used nuclear fuel. This is the primary area of ongoing research and development in the nuclear separations community with several processes having been demonstrated with actual used nuclear fuel in laboratory-scale equipment.

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