Kirk-Othmer Encyclopedia of Chemical Technology.

NUCLEAR REACTORS, CHEMICAL REPROCESSING

The process of separating the components of irradiated nuclear reactor fuel into several streams, usually uranium, plutonium, and wastes, is called chemical reprocessing. Within the context of the nuclear fuel cycle, synonyms for chemical reprocessing include reprocessing, fuel reprocessing, separations, and chemical separations. The term separations is also used to describe isotopic separation techniques, which fall outside the scope of this article. At times additional products have been recovered from the waste stream. Both flow sheet selection and the resulting economics depend on the context in which the reprocessing is performed. This context is commonly referred to as the fuel cycle. The fuel cycles of interest as of this writing (ca 1995) are illustrated in Figure 1. Even before the end of the Cold War, essentially all nations possessing nuclear weapons had stopped or drastically curtailed production of nuclear weapons materials. Thus weapons-related fuel cycles are not of interest herein, except for historical background and in the case where weapons materials may be recycled as a source of energy.

The raw material for nuclear reactor fuel, uranium, exits the mining–milling sequence as uranium oxide. Because of its color, it is called yellow cake. The yellow cake is converted to uranium hexafluoride and enriched in ^{235}U (see Diffusion separation methods; Nuclear reactors, isotope separation). The energy required by the enrichment process is measured in terms of separative work units (SWU). The enriched uranium hexafluoride is then reduced to the oxide and formed into pellets, which are fabricated into reactor-fuel elements (see Nuclear reactors, nuclear fuel reserves). The cost of reactor fuel is thus the sum of the costs for yellow cake, the conversion, enrichment, and fabrication. Other fuel-cycle costs are associated with the waste streams originating at each of the fuel-cycle facilities (see Nuclear reactors, waste management).

The classical fuel cycle is based on the recovery and recycle of energy values contained in spent fuel, where energy values are defined in terms of the four components of reactor fuel cost. The classical fuel cycle begins with an initial reactor charge of low enriched uranium (approximately 2.5–3.5% ^{235}U). During reactor operation, the amount of ^{235}U is reduced by the fission reactions which occur, a phenomenon referred to as burn-up, but at the same time ^{238}U is absorbing neutrons to create plutonium. As a result, at the time of discharge the irradiated fuel rods contain recoverable energy in the form of both residual fissile uranium and plutonium. The uranium and plutonium are chemically separated from the fission products for recycle in the form of mixed uranium and plutonium oxide (MO_x) fuel. During each recycle, the energy level of the recycled uranium is maintained either by blending with more highly enriched uranium ($>3.5\%$ ^{235}U), or by routing the recovered uranium through a conversion and enrichment step and adding virgin low enriched uranium ($\sim 3.5\%$ ^{235}U) to make up for the depleted ($\sim 0.2\%$ ^{235}U) uranium tails stream.

As the recycled fuel composition approaches steady state after approximately four cycles (1), the heat and radiation associated with ^{236}U and ^{238}Pu require more elaborate conversion and fuel fabrication facilities than are needed for virgin fuel. The storage, solidification, packaging, shipping, and disposal considerations associated with wastes that result from this approach are primarily concerned with the relatively short-lived fission products. The transuranic isotopes are recycled to and burned in the reactors. Commercial reactor fuel is being reprocessed and recycled in the U.K., France, Japan, India, and the former Soviet Union. Essentially all other nuclear nations, except the United States, have contracted to have these services performed.

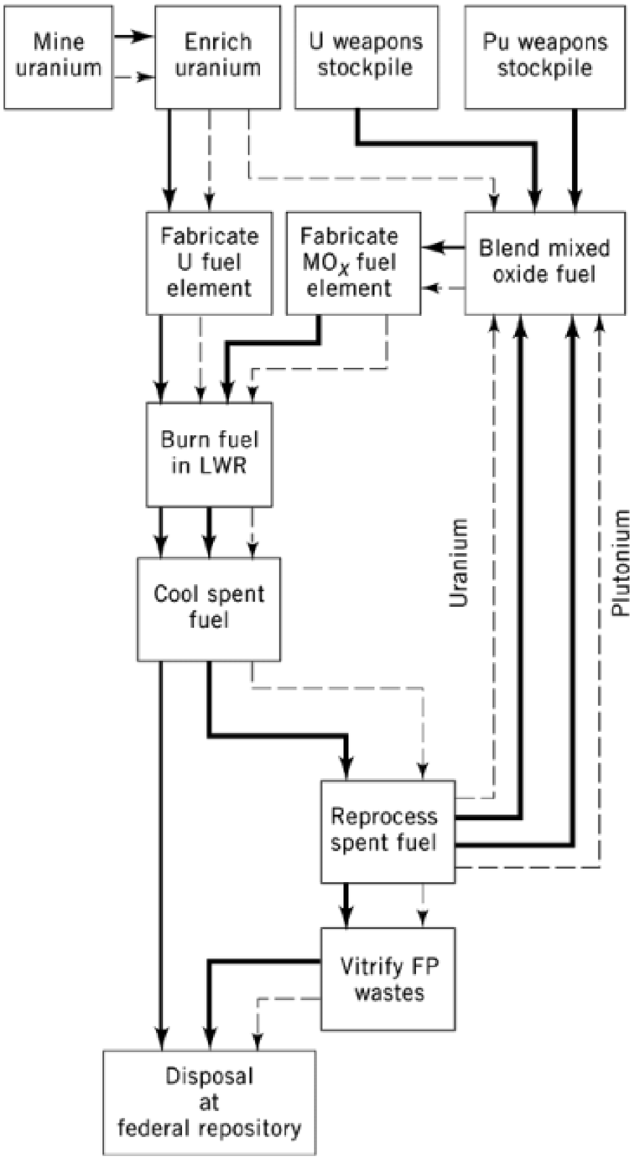

Fig. 1. Alternative fuel cycles for nuclear fuel, where (_) corresponds to the classical fuel cycle, (_) the throwaway fuel cycle, and (▬▬) the recycle weapons fuel cycle. FP = fuel processing; LWR = lightwater reactor.

A variation of the classical fuel cycle is the breeder cycle. Special breeder reactors are used to convert fertile isotopes into fissile isotopes, which creates more fuel than is burned (see Nuclear reactors, reactor types). There are two viable breeder cycles: ^{238}U/^{239}Pu, and ^{232}Th/^{233}U. The thorium fuels were, however, not in use as of 1995. A breeder economy implies the existence of both breeder reactors that generate and nonbreeder reactors that consume the fissile material. The breeder reactor fuel cycle has been partially implemented in France and the U.K.

The throwaway fuel cycle does not recover the energy values present in the irradiated fuel. Instead, all of the long-lived actinides are routed to the final waste repository along with the fission products. Whether or not this is a desirable alternative is determined largely by the scope of the evaluation study. For instance, when only the value of the recovered yellow cake and SWU equivalents are considered, the world market values for these commodities do not fully cover the cost of reprocessing (2). However, when costs attributable to the disposal of large quantities of actinides are considered, the classical fuel cycle has been the choice of virtually all countries except the United States.

The recycle weapons fuel cycle relies on the reservoir of SWUs and yellow cake equivalents represented by the fissile materials in decommissioned nuclear weapons. This variation impacts the prereactor portion of the fuel cycle. The post-reactor portion can be either classical or throwaway. Because the availability of weapons-grade fissile material for use as an energy source is a relatively recent phenomenon, it has not been fully implemented. As of early 1995 the United States had purchased highly enriched uranium from Russia, and France had initiated a modification and expansion of the breeder program to use plutonium as the primary fuel (3). All U.S. reactor manufacturers were working on designs to use weapons-grade plutonium as fuel.

1. History

The nuclear fuel cycle was developed in the United States during World War II. Two paths were pursued: a uranium weapon, which required the development of a means of separating the fissionable and fertile isotopes of uranium (enrichment); and a plutonium weapon, which required the manufacture and recovery of plutonium (reactors and chemical reprocessing). Since that time, many techniques have been developed for recovering uranium and plutonium from spent fuel. The first large-scale process for recovering plutonium from irradiated nuclear fuel was based on a bismuth phosphate precipitation reaction in Hanford, Washington, ca 1944. This was essentially a throwaway fuel cycle, because everything except the plutonium was routed to the waste stream. In an effort to reduce both the demand for uranium and the problems associated with the large waste stream, liquid–liquid solvent extraction processes were developed that recovered both the plutonium and uranium. A portion of the uranium was recycled for enrichment (see also Extraction, liquid–liquid).

The first solvent extraction plant, REDOX, utilized methyl isobutyl ketone [108-10-1] (hexone) as the solvent (4). Aluminum nitrate nonahydrate [7784-27-2] (ANN) was used as the salting agent to enhance uranium and plutonium extraction. An advantage of the process was that a simple distillation (qv) step removed radiation degradation products from the solvent. Disadvantages of this process include the large quantities of unrecoverable aluminum nitrate in the wastes, the potential fire hazard from the hexone, and poor ruthenium decontamination (5). During this same period, the British developed the BUTEX process, which used dibutoxy diethyl ether as the extractant at Windscale in 1952. No salting agent was required, resulting in a much smaller waste stream. The Windscale facility was also the first to use mechanical decladding. In the American plants fuel cladding was chemically removed from the fuel.

The American facilities also differed fundamentally from the British facilities in regard to maintenance philosophy. The American plants were designed to employ remote maintenance, ie, to remove and replace equipment using shielded cranes operating inside the shielded structure. The British developed a contact approach based on simplified designs for equipment downstream of the fission product removal step. The British approach has been used at all commercial facilities.

An improved solvent extraction process, PUREX, utilizes an organic mixture of tributyl phosphate solvent dissolved in a hydrocarbon diluent, typically dodecane. This was used at Savannah River, Georgia, ca 1955 and Hanford, Washington, ca 1956. Waste volumes were reduced by using recoverable nitric acid as the salting agent. A hybrid REDOX/PUREX process was developed in Idaho Falls, Idaho, ca 1956 to reprocess high burn-up, fully enriched (97% ^{235}U) uranium fuel from naval reactors. Other separations processes have been developed. The desirable features are compared in Table 1.

Table 1. Separations Processes for Chemical Reprocessing[a,b]

	Feature					Equipment		
Process	Flexi-bility	Contin-uous operation	Fission-product separation	U/Pu separation	Ease of waste handling	Size	Remote handling	Corrosion resistance
precipi-tation								X
solvent extraction	X	X	X	X	X	X	X	X
ion exchange	X		X	X	X			X
zone melting/slagging			X		X	X		
molten salt/pyrometal-lurgical			X			X		
fluoride volatility			X	X		X		

[a] Ref. 6.
[b] X represents desirable process characteristic.

1.1. Commercial Experience

The Nuclear Fuel Services (NFS) plant in West Valley, New York, is the only separations facility in the United States to have reprocessed commercial power reactor fuel (7). This facility was a significant improvement over the government-owned PUREX process, in that a mechanical head-end eliminated the chemical decladding step and the resulting liquid waste stream. After successfully processing the entire available backlog of U.S. commercial power reactor fuel (ca 250 t) as well as a small amount of government-owned fuel from the Hanford reactor, the facility was shut down for modification to increase its capacity. Changing licensing requirements prevented the plant from restarting. As of this writing, it is being decontaminated and decommissioned.

A facility designed to process one metric ton per day of discharged or spent fuel was built by General Electric in Morris, Illinois, to demonstrate their proprietary Aquafluor process (8). This process had the potential for significant cost savings over the classic PUREX process in that the solvent extraction cycles for uranium purification were eliminated. Final uranium purification was to be accomplished during conversion to the uranium hexafluoride product. Technical problems encountered during facility cold checkout, coupled with changing market conditions and an unstable licensing environment, all contributed to cancellation of the project. As of 1995 the plant's fuel storage basin is being used to store lightwater reactor (LWR) fuel.

Plans to construct reprocessing facilities were also pursued by Exxon, Atlantic Richfield, and Allied-General Nuclear Services (AGNS) using variations of the PUREX process. Only the AGNS project proceeded through construction and checkout. The AGNS flow sheet was unique in that it used an electrolytic reduction technology and a nitric oxide oxidation step for plutonium valance adjustments (9). As a result, the high level liquid waste contained only fission-product salts. This reduced the volume of high level waste and simplified its vitrification, packaging, and transportation. Cold check-out runs in the 1500-t/yr AGNS facility were completed in 1981, but the plant never entered hot operation, owing to an unstable licensing environment combined with changing market conditions.

As of 1995, there were no nuclear fuel reprocessing plants operating in the United States. Other nuclear nations have constructed second- or third-generation reprocessing facilities. These nations have signed the nuclear nonproliferation treaty, and the facilities are under the purview of the International Atomic Energy Agency (IAEA).

The UP2 plant located at La Hague, France, began processing gas-cooled reactor and fast breeder reactor fuels in 1965, and in 1987 began reprocessing LWR fuel for utilities located throughout Europe and Japan. A newer, 800-t/yr plant, UP3, was constructed at the same site and was commissioned in 1990. The UP2 plant was subsequently refurbished and upgraded to the same capacity, with the added ability to handle MO_x and high burn-up fuels. The facility was renamed UP2-800 and was brought on line in 1994. The site capacity should gradually increase to 1600 t/yr of LWR fuel. Between 1950 and 1991, 80% of the power reactor fuel reprocessed worldwide was reprocessed in France (10).

Site preparation for the British thermal oxide reprocessing plant (THORP) at Sellafield, Seascale Cumbria, began in 1983, and the plant began hot operation in 1994. British Nuclear Fuels Limited (BNFL), the owners of the 1200-t/yr plant, have contracted to process spent fuel from utilities throughout Europe and Japan. The THORP facility, the third reprocessing plant to be built at the Sellafield site, was conceived in the mid-1970s when it became apparent that a new facility would be required to process LWR fuel from U.K. power reactors. The design and construction time scale of the reprocessing plant is typical of nuclear projects in the regulatory environment of the latter twentieth century. The features incorporated were thus developed and tested more than a decade before the plant began hot operation (11).

During the early 1970s, the French assisted a Japanese company, PNC, in the design of a small, 150-t/yr reprocessing facility which was built at Tokai-mura primarily to gain experience in the back-end of the fuel cycle. The plant was commissioned in 1977 and continues to operate. Based on this experience, the Japanese have built an 800-t/yr reprocessing plant at Rokashamura that is very similar to the French UP3 facility. As of 1994 it was undergoing testing and start-up (11). Smaller, 100-t/yr plants are also in operation in India, at Prefre and Kalpakkam (12).

2. Reprocessing Strategy

The radioactive isotopes associated with spent fuel emit substantial amounts of α-, β-, and γ-radiation as a result of radioactive decay. These radioisotopes (qv) have half-lives, $t_{1/2}$, of up to thousands of years. The storage of spent fuel prior to reprocessing allows the shorter lived isotopes to decay, thus reducing the costs associated with shielding and heat removal. These savings are balanced by the higher costs associated with maintaining a large spent fuel inventory. Under the economic conditions that existed during design of the AGNS facility, the optimum cooling time was 180 d for fuel having a burn-up of 33×10^3 MW·d/t. The average fuel processed thus far, however, has a substantially lower burn-up and has been cooled for a number of years.

A second consideration affecting reprocessing strategy is the preservation of separative work units (SWU), a measure of the relative value of enriched uranium. Fuel is campaigned through a reprocessing facility in batches having similar discharge enrichments. However, a single utility rarely has enough fuel of the same enrichment and burn-up to avoid SWU degradation. Batches are therefore a mix of similar discharge enrichments from a number of utilities, and the utility/reprocessor differences in fissile measurements become important. The amount of fissile material in spent fuel is calculated by the utility based on reactor physics models. The reprocessor determines fissile content based on analysis of the dissolver solutions and the dissolver solids. Reconciliation is an ongoing effort. The process steps involved in reprocessing irradiated fuel are illustrated in Figure 2.

2.1. Fuel Characteristics

Historically, chemical reprocessing of irradiated fuel was developed specifically to handle the U.S. government's defense-related fuels. These were of two types. There were the very low enrichments and burn-ups, eg, 0.9% ^{235}U and 2000 MW·d/t, as was used for plutonium production, and very high enrichments and burn-ups, eg, 97% ^{235}U and 10^5 MW·d/t, as is used in naval reactors. In both cases, metallic uranium is used. The low burn-up fuels are clad in aluminum; the higher burn-up fuels are clad in zirconium.

By contrast, uranium fuels for lightwater reactors fall between these extremes. A typical pressurized water reactor (PWR) fuel element begins life at an enrichment of about 3.2% ^{235}U and is discharged at a

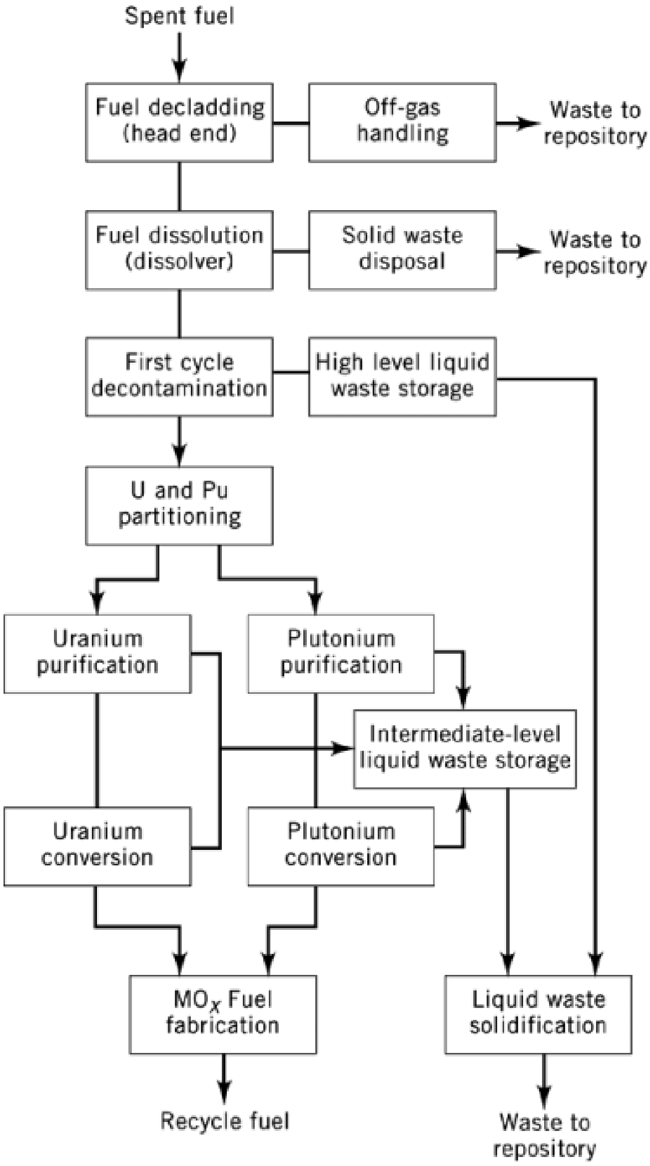

Fig. 2. Processing steps for irradiated fuel.

burn-up of about 30×10^3 MW·d/t, at which time it contains about 0.8 wt % ^{235}U and about 1.0 wt % total plutonium. Boiling water reactor (BWR) fuel is lower in both initial enrichment and burn-up. The uranium in LWR fuel is present as oxide pellets, clad in zirconium alloy tubes about 4.6 m long. The tubes are assembled in arrays that are held in place by spacers and end-fittings.

MO$_x$ fuel designed for use in existing LWRs is typically exposed to burn-ups greater than 40×10^3 MW·d/t. The discharged MO$_x$ fuel has essentially the same uranium enrichment as uranium oxide fuel, but has a greater total amount of plutonium.

Canadian reactors (CANDU) are fueled using natural uranium. The discharged fuel contains small amounts of plutonium, but the fissile uranium content is below that of natural uranium. Therefore, the irradiated fuel is not normally considered a candidate for economic reprocessing.

2.2. Head-End

2.2.1. Fuel Decladding

A power reactor fuel assembly consists of uranium or mixed uranium/plutonium oxide pellets enclosed in a zirconium metal tube which is nominally 1.27 cm in diameter by about 4.6 m long, referred to as a fuel pin. The fuel pins are then arranged in an array nominally 17×17 for a PWR fuel assembly, or 6×6 for a BWR fuel assembly. The pins are held in place by massive metal end fittings and the configuration is stabilized by stamped sheet-metal spacer grids located at intervals along the length of the pins. Depending on the fuel design, some of the LWR pin locations are occupied by instrument tubes or burnable poisons. The British Advanced Gas Reactor (AGR) fuel assemblies contain graphite moderators.

All operating facilities shear the spent fuel elements into segments several centimeters long to expose the oxide pellets to nitric acid for dissolution. This operation is often referred to as chop-leach. The design and operation of the shear is of primary importance because (*1*) the shear can be the production bottleneck, and (*2*) the shear is the point at which tritium and fission gases are released.

2.2.2. Fuel Dissolution

In the American and British plants, LWR fuel pieces typically fall directly from the shear into a dissolver basket, which fits inside the dissolver vessel. A soluble poison such as gadolinium is added to the nitric acid to prevent criticality. The massive end fittings are sometimes separated from the fuel pieces before the latter enter the dissolver. The French have installed continuous rotary dissolvers in the UP3 and UP2-800 plants at La Hague. The units each consist of a drum rotating within a geometrically favorable slab tank (13).

Fast reactor fuel assemblies are shrouded with a relatively heavy metal envelope. This envelope is removed before shearing by either laser cutting (14) or stress cracking (15).

The rate (kinetics) and the completeness (fraction dissolved) of oxide fuel dissolution is an inverse function of fuel burn-up (16–18). This phenomenon becomes a significant concern in the dissolution of high burn-up MO_x fuels (19). The insoluble solids are removed from the dissolver solution by either filtration or centrifugation prior to solvent extraction. Both financial considerations and the need for safeguards make accounting for the fissile content of the insoluble solids an important challenge for the commercial reprocessor. If hydrofluoric acid is required to assist in the dissolution, the excess fluoride ion must be complexed with aluminum nitrate to minimize corrosion to the stainless steel used throughout the facility. Also, uranium fluoride complexes are inextractable and formation of them needs to be prevented.

2.3. Chemical Separation

A reprocessing facility typically utilizes multiple extraction/reextraction (stripping) cycles for the recovery and purification of uranium and plutonium. For example, a co-decontamination and partitioning cycle is followed by one or more cycles of uranium and plutonium purification. The basic process is illustrated in Figure 3.

2.3.1. Chemistry

Chemical separation is achieved by countercurrent liquid– liquid extraction and involves the mass transfer of solutes between an aqueous phase and an immiscible organic phase. In the PUREX process, the organic phase is typically a mixture of 30% by volume tri-*n*-butyl phosphate (solvent) and a normal paraffin hydrocarbon (diluent). The latter is typically dodecane or a high grade kerosene (20). A number of other solvent or diluent systems have been investigated, but none has proved to be a substantial improvement (21).

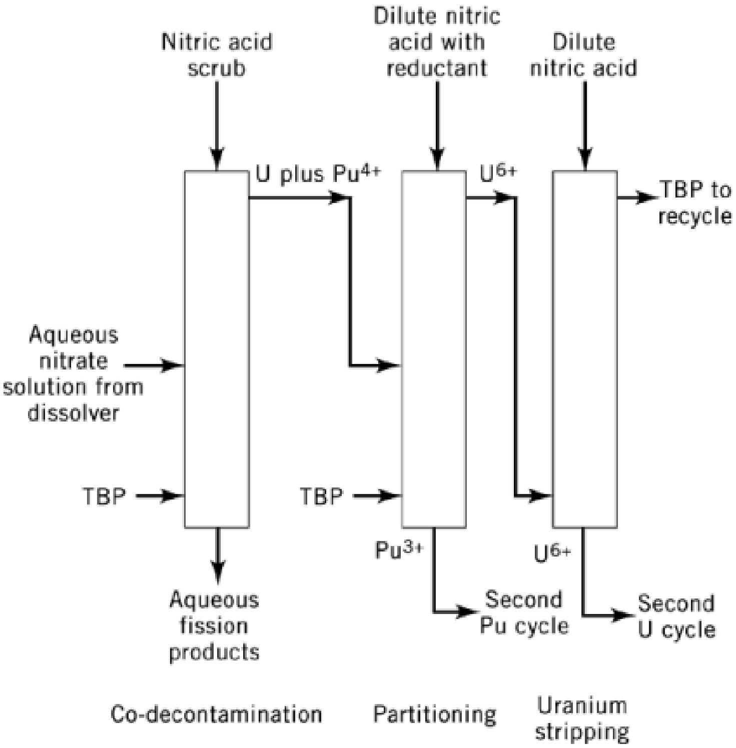

Fig. 3. Basic PUREX process where TBP=tri−*n*−butyl phosphate.

The distribution of highly extractable solutes such as U^{6+} and Pu^{4+} between the aqueous and organic phases is strongly dependent upon the nitrate anion concentration in the aqueous phase. This salting effect permits extraction or reextraction (stripping) of the solute by controlling the nitric acid concentration in the aqueous phase. The distribution coefficient, *D,* of the solute is expressed as

$$D = \frac{\text{concentration in organic solution}}{\text{concentration in aqueous solution}} \qquad (1)$$

which is influenced by many factors. For instance, the salting effect of the anion (nitrate) plays a role as does the approach to the saturation of the solvent (loading), competition of the solutes for free solvent, and temperature.

Two ions *a* and *b* can be separated by countercurrent extraction as long as the ratio of the distribution coefficients, that is, the separation factor Ω, is not unity:

$$\Omega_{a-b} = \frac{D_a}{D_b} \neq 1 \qquad (2)$$

The solubility of the actinides in the organic phase, the right-hand side of equation 3, is achieved by the weak complexes that tri-*n*-butyl phosphate [126-73-8] (TBP), $(n\text{-}C_4H_9O)_3PO$, forms with the neutral metal nitrates:

$$UO_2^{2+} + 2NO_3^- + 2\,TBP \rightleftharpoons UO_2\,(NO_3)_2 \cdot 2TBP \qquad (3)$$

The equilibrium constant for uranium, K_U, is

$$K_U = \frac{[UO_2(NO_3)_2 \cdot 2TBP]_o}{[UO_2^{2+}]_a [NO_3^-]_a^2 [TBP]_o^2} \qquad (4)$$

where the subscripts *a* and *o* correspond to organic and aqueous, respectively. The distribution coefficient, therefore, is

$$D_U = K_U[NO_3^-]_a^2 [TBP]_o^2 \qquad (5)$$

where the brackets indicate activities. A similar expression can be written for NO_3^- and plutonium:

$$H^+ + NO_3^- + TBP \rightleftharpoons HNO_3 \cdot TBP \qquad (6)$$

$$Pu^{4+} + 4\,NO_3^- + 2\,TBP \rightleftharpoons Pu(NO_3)_4 \cdot 2TBP \qquad (7)$$

Each of the actinides has more than one valence state and most tend to hydrolyze. Uranium in nitric acid is usually hexavalent and stable as uranyl ion, UO_2^{2+}, although U^{4+} can be prepared under strong reducing conditions. Plutonium in nitric acid can exist in the +3, +4, and +6 valence states. It can be oxidized readily to the extractable +4 valence using NO_2^- prior to extraction; it can also be reduced using Fe^{2+} or hydroxylamine, or electrolytically to the less extractable +3 valence. This characteristic is exploited to transfer Pu^{4+} and U^{6+} from the aqueous phase to the organic phase, or to selectively strip the plutonium back into the aqueous phase, leaving the uranium in the organic. The selective stripping of plutonium from the organic phase back into the aqueous phase is called partitioning (Fig. 3).

Computer simulation programs for process design optimization have been developed for the PUREX process utilizing these relationships (22). A subroutine has also been developed which describes the behavior of fission products (23).

2.3.2. First-Cycle Decontamination

In the first cycle, clarified dissolver solution containing the uranium, plutonium, other transuranics, fission products, and excess nitric acid are contacted with the organic phase in the extraction column. A strong nitric acid stream is introduced at the top of the column to remove (scrub) residual impurities that extract or are entrained in the organic phase. Approximately 99.9% of the uranium and plutonium nitrates transfer to the organic phase, and conversely, 99.9% of the fission products and nitric acid remain in the aqueous phase. This acidic aqueous solution from the first cycle of the separations process is the high level liquid waste stream. It is collected in underground storage tanks pending solidification (see Nuclear reactors, waste management).

Relative values for the various TBP distribution coefficients of the feed constituents are as follows:

Species	D
U^{6+}	8.1
Pu^{4+}	1.55
Pu^{6+}	0.62
HNO_3	0.07
Zr	0.02
Ce^{3+}	0.01
Ru	0.01
Pu^{3+}	0.008
Nb	0.005
rare earths	0.002
combined β-emitters	0.001
Cs	>0.0001

These variations permit the separation of other components, if desired. Additional data on uranium, plutonium, and nitric acid distribution coefficients as a function of TBP concentration, solvent saturation, and salting strength are available (24, 25). Algorithms have also been developed for the prediction of fission product distributions in the PUREX process (23).

2.3.3. Uranium–Plutonium Partitioning

The uranium and plutonium are separated in the partitioning column by reducing the plutonium to a less extractable valence state. The plutonium nitrate transfers back to the aqueous phase and the uranium remains with the organic.

Historically, ferrous sulfamate, $Fe(NH_2SO_3)_2$, was added to the HNO_3 scrubbing solution in sufficient excess to ensure the destruction of nitrite ions and the resulting reduction of the Pu^{4+} to the less extractable Pu^{3+}. However, the sulfate ion is undesirable because sulfate complexes with the plutonium to complicate the subsequent plutonium purification step, adds to corrosion problems, and as SO_2 is an off-gas pollutant during any subsequent high temperature waste solidification operations. The associated ferric ion contributes significantly to the solidified waste volume.

Hydroxylamine is used as a substitute for the ferrous sulfamate (26). These systems are called salt-free flow sheets. The main purpose is to ease the problems associated with the processing and storage of the liquid waste streams (27). Another approach is to use an electropulse column to electrolytically produce U^{4+} to reduce Pu^{4+} to Pu^{3+} on a continuous basis (28, 29). The half reactions for the flow sheets are

$$U^{6+} + 2\,e^- \xrightarrow{}_{N_2H_4} U^{4+} \qquad (8)$$

$$2\,Pu^{4+} + U^{4+} \xrightarrow{}_{N_2H_4} 2\,Pu^{3+} + U^{6+} \qquad (9)$$

During electrolytic reduction of U^{6+} to U^{4+} and the subsequent reduction of Pu^{4+} to inextractable Pu^{3+} hydrazine is added as a holding agent to destroy excess nitrite ions and prevent reoxidation of U^{4+} and Pu^{3+} to their higher valence states.

In the uranium-stripping step, a dilute HNO_3 solution is used to remove uranium from the organic phase. The aqueous effluent containing the uranium product is evaporated to a concentrated uranyl nitrate $UO_2(NO_3)_2$ solution that is adjusted to about 1.8 M uranium and 1.0 M HNO_3 and fed to the second uranium purification cycle.

2.3.4. Uranium Purification

Subsequent uranium cycles provide additional separation from residual plutonium and fission products, particularly zirconium– niobium and ruthenium (30). This is accomplished by repeating the extraction/stripping cycle. Decontamination factors greater than 10^6 at losses of less than 0.1 wt % are routinely attainable. However, ruthenium can exist in several valence states simultaneously and can form several nitrosyl–nitrate complexes, some for which are extracted readily by TBP. Under certain conditions, the nitrates of zirconium and niobium form soluble compounds or hydrous colloids that complicate the liquid–liquid extraction. Silica-gel adsorption or one of the similar liquid–solid techniques may also be used to further purify the product streams.

Improvements in the ability to control operating conditions and in contractor designs have allowed a steady reduction in the number of purification steps required. The THORP facility, commissioned as of 1994 in the U.K., uses only a single purification step.

2.3.5. Plutonium Purification

The aqueous feed for the second plutonium cycle is typically prepared by adding HNO_3 and an excess of sodium nitrite, $NaNO_2$, to destroy the excess reductant and oxidize the Pu^{+3} to the more extractable Pu^{4+}. An alternative approach which reduces the amount of salt in the liquid waste involves absorbing nitrogen tetroxide, N_2O_4, as a substitute for the $NaNO_2$:

$$N_2O_4 + H_2O \longrightarrow 2\ H^+ + NO_3^- + NO_2^- \qquad (10)$$

The excess nitric acid is recovered during waste concentration and is recycled for fuel dissolution (12).

After the second extraction/stripping cycle, the plutonium is concentrated by evaporation or by preferential adsorption (qv) on ion-exchange resins. As in the case for uranium, the newer facilities, such as THORP, use only a single purification step.

2.4. Product Conversion

2.4.1. Uranium

The uranium product from the PUREX process is in the form of uranyl nitrate which must be converted to some other chemical depending on anticipated use. One route to MO_x fuel is to mix uranium and plutonium nitrates and perform a coprecipitation step. The precipitate is heated to form a mixed U–Pu oxide. Another approach is to convert the uranium to an oxide, either directly (31) or via an ammonium diuranate intermediate precipitation step (32), followed by a U–Pu oxide powder blending step. The resulting mixed oxide can then be reenriched by blending with more highly enriched uranium. The option of fluorinating recycle uranium to UF_6 for recycle to a cascade-type enrichment process (that is, diffusion or centrifuge) is not usually attractive because of the presence of ^{236}U. As of this writing, the ^{236}U problem had been addressed for laser enrichment. The value of the uranium product at this point is a function of the residual separative work (SWU) it contains and the cost of disposal. If the uranium has ^{235}U concentrations in excess of natural uranium, it can be recycled in lieu of virgin feedstock. This approach has both economic and has environmental benefits in that less uranium mining is required.

2.4.2. Plutonium

The plutonium nitrate product must be converted to MO_x fuel if it is to be recycled to lightwater reactors. Whether from a plutonium nitrate solution or a mixed U/Pu nitrate solution, the plutonium is typically precipitated as the oxalate and subsequently calcined to the oxide for return to the fuel cycle (33).

2.4.3. By-Products

The PUREX process is efficient at separating uranium and plutonium from everything else in the spent fuel. Within the high level waste stream are a number of components which have, from time to time, been sufficiently interesting to warrant their recovery. The decision to recover a particular isotope is usually based on a combination of market incentives and desired waste reduction.

Neptunium has been recovered during the reprocessing of defense-related fuels. The ^{237}Np is recycled back to a reactor where it is transmuted to ^{238}Pu. The ^{238}Pu has seen application as a long-lived isotopic heat source. Plutonium-238 is most useful in space programs, but is also of interest as part of a proliferation-resistant fuel cycle (2).

The 30-yr half-lives of ^{137}Cs and ^{90}Sr make these attractive isotopic heat or radiation sources. However, $_{144}$Ce and ^{134}Cs are shorter lived alternatives. Each has been recovered and used in various quantities. Rhodium, palladium, and technetium have also been recovered for potential catalytic or precious metal applications (34, 35).

2.5. Waste Handling

2.5.1. Off-Gas Treatment

Before the advent of the shear, the gases released from the spent fuel were mixed with the entire dissolver off-gas flow. Newer shear designs contain the fission gases and provide the opportunity for more efficient treatment. The gaseous fission products krypton and xenon are chemically inert and are released into the off-gas system as soon as the fuel cladding is breached. Efficient recovery of these isotopes requires capture at the point of release, before dilution with large quantities of air. Two processes have been developed, a cryogenic distillation and a Freon absorption. Neither method has seen widespread use (36).

Tritium differs from the noble gases. Tritium is very reactive and readily combines to form water. The voloxidation process, which controls the point at which the oxidation occurs and recovers the resulting tritiated water, has been developed. As of this writing it has not yet been used.

A large portion of the ^{14}C can be released from the reprocessing facility as CO_2. Thus a recovery process has been developed using an alkaline absorbent column (37).

In the reprocessing environment there are many ruthenium compounds, some of which are gaseous. Some reprocessing approaches, notably the REDOX process, require a ruthenium removal step in the off-gas system. The PUREX process maintains ruthenium in one of its nonvolatile states.

In contrast, iodine recovery is both highly developed and universally used throughout the industry. Iodine can be absorbed on solid sorbents or in an off-gas scrub of caustic, mercuric nitrate solution, or hyperazeotropic nitric acid (qv) (38). The last process, called Iodox, is effective, particularly for trace amounts of organic iodides. Stable periodic acid forms as a precipitate in concentrated nitric acid, and can be stored as a slurry, pending decay of ^{131}I. The periodic acid is converted into a stable compound, for instance barium iodate, and packaged for terminal disposal. Solid absorbers, eg, silver nitrate deposited on Berl saddles or silver zeolite granules, are reliable and effective (39). The disposal of silver reactors has a negligible environmental impact. These are, however, costly and have the potential for forming highly reactive compounds if operated at excessively high temperatures.

2.5.2. Hulls Handling

After the fuel has been dissolved, the residual pieces of zirconium cladding, referred to as hulls, are rinsed and removed from the dissolver vessel. The decay of activation products provides sufficient heat to ensure drying of the hulls and preclude hydrogen formation caused by the radiolysis of water.

The hulls are the first material removed from the process to merit concern in respect to safeguards. These represent a possible route for special nuclear material (SNM) to be clandestinely removed from the system.

Special instrumentation is used to assay the hulls containers for residual SNM. This step not only monitors the dissolver for proper functioning, but also serves an accountancy function as a material access area portal and enables the satisfaction of contractual requirements regarding process losses (40).

The volume of hulls generated is nominally 62 m^3/t of fuel, which is about 10 times the actual volume of metal. Whereas they are not yet in commercial use, both compaction and melting processes are being developed to improve waste handling economics (41).

2.5.3. High Level Waste Management

The technical challenges related to the interim storage, solidification, and disposal of irradiated fuel using the throwaway fuel cycle (see Fig. 1) are driven by the nuclear properties of the actinides and the configuration of the irradiated fuel. The technical challenges of the high level waste from the recycle option are driven by the nuclear properties of the fission products, and the solidification of a liquid. The United States is wrestling with the daunting environmental challenges associated with disposing of large quantities of actinides. Most other nations have elected to address the more tractable problems associated with fission-product disposal. The U.S. experience with high level wastes (HLW) is thus limited to the interim storage of spent LWR fuel and liquid wastes from the weapons program (see Nuclear reactors, waste management).

In the United States, liquid HLW from the reprocessing of defense program fuels was concentrated, neutralized with NaOH, and stored in underground, mild steel tanks pending solidification and geologic disposal (see Tanks and pressure vessels). These wastes are a complex and chemically active slurry. Suspended in the supernatant liquid are dissolver solids which never went into solution, insoluble reaction products which formed in the tank, and salts which have exceeded their solubility limit. The kinetics of many of the reactions taking place are slow (years) so that the results of characterization attempts are sometimes transient. This is a problem made more difficult by the lack of homogeneity, which frustrates representative sampling (42). After the first few months, the decay heat in the HLW is dominated by ^{137}Cs and ^{90}Sr, which are found in the supernatant liquid and sludge, respectively. To ease the problems of heat removal and mitigate the consequences of spills, these isotopes can be removed and stored separately (43). The cesium capsules have been used as radiation sources for food preservation, and the strontium capsules are available for heat sources. Removal of these radioisotopes has simplified waste management and may position some of the waste for a less costly management option than geologic disposal.

By contrast, HLW from LWR fuel reprocessing is stored in cooled, well-agitated, stainless steel tanks as an acidic nitrate solution having relatively few solids. Modern PUREX flow sheets minimize the addition of extraneous salts, and as a result the HLW is essentially a fission-product nitrate solution. Dissolver solids are centrifuged from the feed stream and are stored separately. Thus the HLW has a low risk of compromising tank integrity and has a favorable composition for solidification and disposal (11).

3. Reprocessing Equipment

3.1. Fuel Shear

At the NFS plant in West Valley, New York, fuel assemblies were transferred from the fuel storage pool via an underwater conveyor and fed horizontally into the head-end cell, where the end fittings were removed by an abrasive disk saw and placed in a scrap drum (9). A hydraulic pneumatic feed pusher advanced the fuel into the shear. The shear chopped the fuel into preselected lengths ranging from 1.25–5 cm. The blade was driven by a hydraulic ram which developed a force adjustable between 250 and 320 t. The hydraulic power unit for the shear-blade drive and gag actuators was located outside the process cell. The shear blade was arranged to cut diagonally across the fuel bundle. The throat of the shear housing had a 23-cm opening and could accommodate bundles up to 232 cm^2 and up to 4.9 m long. Gamma detectors automatically stopped the shear when either the basket was full or the chute became plugged. An inert gas sweep and a fire-retardant injection system were also part of the design. The capability to cool the fuel bundle in the shear magazine was provided but never needed.

The NFS shear successfully processed irradiated LWR fuel between 1966 and 1972. Among the lessons learned were that the chute that channeled sheared fuel pieces to the dissolver basket was susceptible to bridging, the gag drives required a disproportionate amount of maintenance, and insufficient throat clearance led to jamming of chopped fuel.

The French chop-leach efforts began at La Hague in 1970. The first implementation was a vertically fed shear installed at the UP2 facility. The design has proven robust and the unit continues to operate as of this writing (1995). A horizontally fed unit of French design which extended this technology to include BWR fuel and the diversion of end fittings was installed in the PNC facility at Tokai-mura, Japan. It went into hot operation in 1977, and is operative as of 1995. The same technology was used in the AGNS shear which was also manufactured by the French (44). The UP3 plant at La Hague and the more recently upgraded UP2 facility continue to use this technology.

The AGNS shear was designed to cut the entire fuel assembly, thus eliminating the need for prior removal of end fittings. The necessity of physically moving sheared fuel to different processing locations was eliminated by installing multiple multicycle dissolvers (45). Specialized equipment facilitated hulls removal. Fission gases, released during the shearing operation, were routed into the vessel vent system by an inert gas sweep at the cutting blade, and at this point, provisions were made to install noble gas recovery equipment when a suitable technology was demonstrated (12).

The General Electric shear was a small unit. The fuel assembly end fittings were mechanically removed in a separate operation prior to shearing. The fuel rods were pulled from the fuel assembly frame and were inserted into the shear feed chamber as a single layer of rods. The shear feed chamber was then sealed to the shear, and the rods were cut into 7.6-cm lengths. The shear and feed chamber were vented to the dissolver, trapping the fission gases without having to handle the extra gas volumes associated with a sweep (10).

The thermal oxide reprocessing plant (THORP) at Sellafield, U.K., uses a hydraulically operated shear to cut fuel rods into pieces between 2.5 and about 10 cm in length. Because of wear on the shear blade, the moving blade and gag are remotely replaceable as a module. The hydraulic equipment for this, the feed envelope charge ram, and the shear incremental feed ram, are mounted outside the biological shielding. Modular redundancy allows off-line maintenance and high equipment availability (46).

The Japan Nuclear Fuel Service Company reprocesses LWR fuel in facilities which take advantage of French shear and dissolver designs, German iodine removal technology, and British reduced-pressure evaporation.

Reprocessing facilities use equipment capable of shearing entire fuel assemblies. This accounts for a significant portion of the reprocessing cost in terms of size of the equipment needed and the consequent size of the cell required to house it. Shear blade maintenance requirements are also important. There are active programs aimed at reducing these costs. For instance, an operation involving only a single fuel pin would require a significantly smaller shear and cell to house it. Less oxide dust and cladding fines might also be anticipated. However, a fuel disassembly step with its attendant equipment and the space to house it must be added (7).

A number of alternatives to shearing have been investigated wherein the cladding is breached by lasers (qv), plasma torches (see Plasma technology), or inductive heating (47). In one proposal the oxide pellets are crushed while still inside the cladding and the fuel is tipped or vibrated out into a dissolver (48). Another approach is to chemically embrittle the cladding, which can then be crushed along with the oxide pellets before being fed to the dissolver (49). The crushing step would substitute for both the shear and the subsequent hulls volume reduction step.

3.2. Liquid–Liquid Contactors

A variety of contactors have been developed for liquid–liquid extraction processes. These designs include equilibrium-stage contactors such as mixer–settlers and centrifugal contactors, and differential contactors, such as packed and sieve-tray pulse columns. Each design has advantages and disadvantages; for example, mixer–settlers and centrifugal contactors are compact and require substantially less cell space than do columns. Centrifugal contactors have the additional advantage of high throughput capacities with minimal liquid holdup, ie, short residence times, and can perform over a wide range of organic-to-aqueous flow ratios. They are, however, subject to pluggage by entrained solids, and the high mixing energies can create stable emulsions in the presence of contaminates such as silicates. Other disadvantages include the difficulties of remotely maintaining rotating equipment. Compact annular centrifugal contactors are under development for application in the next generation of reprocessing plants (50).

Pulse columns have proven to be reliable, but have long residence times, ie, high volumetric holdup, which result in radiation damage to the solvent when reprocessing high burn-up fuels. They also must be housed in large shielded cells, are subject to flooding, and have only limited capacity if a geometrically safe configuration is required (51). The THORP facility in the U.K. uses conventional nozzle plate pulse columns having hafnium components which act as neutron absorbers to ensure nuclear safety (52). The French plants at La Hague use annular, baffel plate columns to maintain criticality safety (53).

The overall decontamination factor of fission products and other impurities in the process is often limited, not by mass-transfer relationships, but by hydrodynamic characteristics, such as the entrainment of one liquid phase in the other or poor solvent quality. Mono- and dibutyl phosphate degradation products, which are caused by radiation and chemical damage to TBP, form complexes with plutonium and with some of the fission products (54–57). Good extraction equipment designs provide efficient separation of the phases between contactors. Sequential washing of the organic phase using Na_2CO_3 and HNO_3, or alternatively treatment with a macroreticular resin, enhances the solvent quality (58).

3.3. Liquid Waste Storage Tanks

Reprocessing of high burn-up, short-cooled LWR fuel required improvements in the design of the liquid waste storage tanks. Modern tanks are fabricated from stainless steel, and are placed in underground, stainless steel-lined concrete vaults. Advancements in the reprocessing flow sheet minimize salt concentrations and preclude discharge of dissolver solid to the storage tanks. The tanks are equipped with pneumatically activated, liquid-discharge pulsers to prevent the settling of heat-emitting solids on the bottom of the tank. The tanks are also equipped with air-lift circulators which maintain the solids in suspension and enhance heat transfer to the cooling coils. The coils are suspended from the tank ceiling to minimize interference with performance of the pulsers (11, 59).

A mathematical model of the operating characteristics of a modern HLW storage tank has been developed (60). This model correlates experimental data for the rate of radiolytic destruction of nitric acid, the rate of hydrogen generation owing to radiolysis of water, and cooling coil heat transfer. These are all functions of nitric acid concentration and air-lift circulator operation.

The capacity of any specific tank configuration, in terms of metric ton equivalents, is determined by one of three parameters. (*1*) The solubility of waste salts. Precipitates can settle and cause thermal hot spots, which in turn can result in accelerated corrosion rates. Thus it is important to maintain the tank contents below the solubility limits. (*2*) The density of the waste solution. The tank footings are designed for a specific loading which translates to a waste solution density. As fuel burn-ups change or as process improvements are made, it is possible for the waste concentration to exceed the allowable density before the solubility limits are reached. (*3*) The decay heat-removal capacity. The heat-removal capacity of the tank is a function of the cooling-coil area and the overall heat-transfer coefficient. As the fuel burn-up or age changes, the specific heat generation rate of the waste changes. This, coupled with potential fouling of the cooling coils, could result in a heat-removal limitation, even when concentration and density are well below their limits. Waste tank operations consists in managing each of the above parameters so as to maximize the capacity of the available waste storage facilities.

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