

## REPROCESSING: A NOVEL APPROACH TO WASTE MANAGEMENT

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### ABSTRACT

The current waste management scenario for civilian reactor fuel is direct disposal. With renewed interest in nuclear power due to the environmental issues of global warming and acid rain, reprocessing to recover fuel values from reactor fuel may become a viable option. The Purex process developed for recovery of plutonium from military fuel is readily adaptable to civilian power fuel. The Purex process is based on solvent extraction of uranium and plutonium from nitric acid solution using tributyl phosphate in a hydrocarbon diluent as the solvent. Several waste streams result from reprocessing of reactor fuel. Disposal of these wastes will require some additional development effort.

### A NOVEL APPROACH

With the advent of civilian nuclear power, it was accepted that reprocessing and waste management would be an integral part of the fuel cycle. The Nuclear Fuel Services plant in New York was constructed with the full support of the federal government; in fact, the government guaranteed a base load of "N" reactor fuel as an added inducement to the owners. Early licensing activities for the proposed Barnwell Nuclear Fuel Plant proceeded with no opposition from the government; and in the mid 1970s, Exxon plans for a 2000 ton per year reprocessing plant had progressed as far as the submission of a Preliminary Safety Analysis Report.

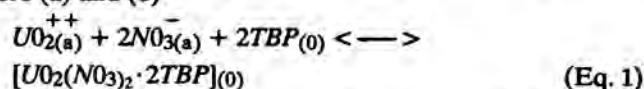
These activities came to an abrupt halt in 1977 when President Carter announced there would be a ban on commercial fuel reprocessing in the United States. This edict was based on the faulty assumption that other countries would follow suit, thereby reducing the threat of proliferation of nuclear weapons. The ban on reprocessing was lifted in 1981, but the political climate had become so anti-nuclear that no prudent business man would invest corporate funds in a reprocessing/waste management venture.

Fifteen years have passed since the initial ban on commercial reprocessing and a new generation of nuclear engineering students has graduated essentially unaware of the subject. In that period of time, the waste management scenario for civil reactor fuel has become direct interment without recovering the fuel values. However, with increasing concerns about global warming and acid rain from fossil fuel electricity generation, there may be a resurgence in nuclear power. If such a resurgence does take place, there may be renewed interest in reprocessing and recycle of the recovered products. In this case, waste management emphasis would shift back to the disposal of wastes from reprocessing--in particular, the high level wastes, i.e., the fission products and the transuranics.

Reprocessing was initially developed to recover plutonium from irradiated uranium for military purposes. The first production scale recovery of plutonium from irradiated uranium was by the bismuth phosphate process, a batch precipitation method somewhat reminiscent of radium recovery as practiced by the Curies. Following the conclusion of World War II a continuous solvent extraction process (Redox) using methyl isobutyl ketone as the solvent was developed and installed at Hanford. In the early 1950s an improved solvent extraction process (Purex) was developed using tributyl phosphate (TBP) in a hydrocarbon diluent as the solvent. In early work with TBP refined kerosenes were used as the diluent,

but now the preferred diluent is a mixture of straight chain hydrocarbons, C<sub>10</sub> to C<sub>14</sub>. Small amounts of aromatic hydrocarbons in the kerosenes proved to be deleterious to the process.

The Purex process is based on the equilibrium reaction where (a) and (o)



denote the aqueous and organic phases respectively. At 2M nitric acid the reaction proceeds to the right wherein uranium as a complex compound with TBP is extracted; and at very low acid concentrations, the reaction proceeds to the left wherein uranium is stripped from the solvent phase. Plutonium in the plus four and six valence states follows the uranium while plutonium in the plus three valence state is not extracted by TBP. Most of the fission products and the transuranics--neptunium, americium and curium do not form extractable complexes with TBP under Purex conditions, so remain in the aqueous phase when uranium is extracted.

In practice, the uranium and plutonium are extracted from the fission products and then separated by reducing the plutonium to the plus three valence state. The uranium is then stripped from the solvent by dilute acid. The three main components of the irradiated fuel are thus separated for further treatment.

The long-cooled civil power reactor fuel currently in storage was originally enriched to about 3.5 percent U-235. After a burn up of 33,000 MWD/T the U-235 content has been reduced to about 0.8 percent, the plutonium content is about one percent, and the fission product concentration is about three percent. In recent years some of the utilities have shifted to higher initial enrichments and correspondingly higher burnups so the fission product content will be higher.

Civilian reactor fuel is clad in a zirconium alloy that is inert to nitric acid. In order to prepare the fuel for reprocessing, it is necessary to chop the fuel into small segments to expose the fuel to the nitric acid dissolver solution. Massive shears have been developed to chop fuel bundles. A few hours exposure to hot nitric acid dissolves the fuel leaving the leached cladding pieces as the first waste component. The off gas from the dissolver is treated for recovery of nitrogen oxides and iodine and then filtered through high efficiency filters before discharge through a tall stack to the atmosphere. The iodine absorber and the filters are solid waste forms to be

packaged for disposal. This head-end process is illustrated in Fig. 1.

The dissolver solution is analyzed for uranium and plutonium for accountability purposes and nitric acid for process control. The dissolver solution is then adjusted to the proper acid concentration to prepare feed for solvent extraction. The first solvent extraction cycle is shown in Fig. 2. The prepared feed is introduced near the center of the first extraction unit (1A).

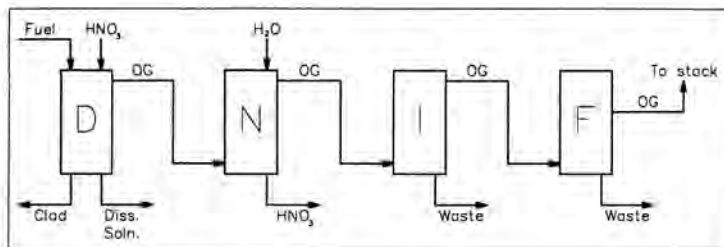


Fig. 1. Typical head end process.

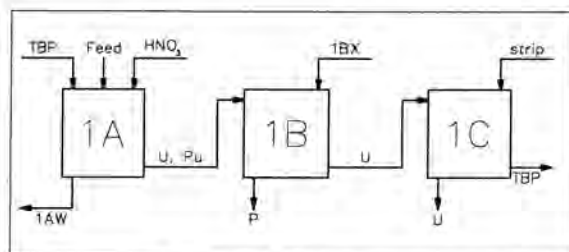


Fig. 2. Schematic of first extraction cycle.

A counter current flow of TBP (usually 30 percent in the hydrocarbon diluent) extracts the uranium and plutonium. Near the organic discharge a counter current flow of 2M nitric acid is introduced to scrub fission products from the TBP solution. The separation factor for uranium and fission products is about  $10^4$ , i.e., 99.99 percent of the fission products remain in the aqueous phase as the high level waste. The transuranics plus a small amount of unextracted uranium and plutonium are also included in the waste stream.

The TBP product stream is contacted with a plutonium reductant (1BX) in the second extraction unit (1B). Ferrous sulfamate was the commonly used reductant in early Purex work, but reduced uranium,  $U^{+4}$ , has been developed, particularly in France, as it avoids the addition of extraneous materials. An in situ process that reduces the plutonium directly has been developed in the United States and Germany. The reduced plutonium transfers to the aqueous phase affecting the separation from uranium. The uranium is stripped from the TBP in the third contactor (1C) by a very dilute nitric acid stream. The TBP is routed to solvent cleanup and is then recycled.

Although there is a high level of decontamination in the first extraction cycle, both the uranium and plutonium products require further decontamination from fission products. Both the uranium and plutonium streams are subjected to at least one additional solvent extraction cycle. A typical second (or third) cycle is shown in Fig. 3. The solution from the first cycle is concentrated and acid added to prepare a new feed solution. The aqueous feed is contacted with TBP solution in

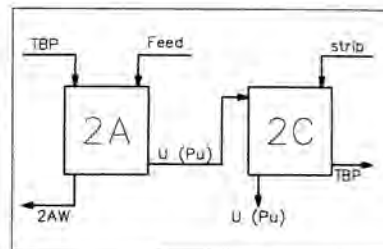


Fig. 3. Schematic of second (or third) extraction cycle.

the 2A contactor extracting the uranium (or plutonium), resulting in further separation from fission products. The aqueous stream from the 2A contactor is low activity waste. The product is stripped from the TBP in a second contactor (2C), the TBP being routed to another solvent treatment system. The solvent systems from the first and second cycle are usually kept separate as the first cycle solvent is more heavily exposed to radiation.

Depending on the flowsheet preferred by the plant operations staff, there may be a third plutonium cycle in which the concentration of plutonium in the product stream may be raised by use of a reducing strip similar to the 1B. Plutonium can also be further decontaminated from traces of fission products and uranium by ion exchange. There are other flowsheet adaptations in which uranium and plutonium are costripped in the first cycle and then separated in the second cycle. There are a variety of options discussed in the reprocessing literature.

Three types of contactor have found use in reprocessing plants--pulse columns, centrifugal contactors, and mixer-settlers. In the pulse column, the aqueous and organic phases are dispersed through perforated plates by a pulsing action on one of the liquid streams. This thoroughly mixes the phases, resulting in a high extraction efficiency. In the mixer-settler, the two phases are mixed by pumping or stirring and then drained into the settling section where the phases separate. Usually 12 to 16 stages comprise an extraction battery. The two phases move counter current through the battery. In the centrifugal contactor, the two phases are mixed rapidly in the inlet section and then separated by centrifugal action. Again several of these units will be combined in an extraction battery.

One of the problems in solvent extraction of irradiated fuels is radiation damage to the organic materials producing compounds that interfere with the process. One of the advantages of the centrifugal contactor is short contact time between phases minimizing solvent damage. The centrifugal contactor has high extraction efficiency; however, it is a complex piece of machinery requiring maintenance.

Contact time between phases is longer with the pulse column than the centrifugal contactor. In order to attain the required separation factors, a pulse column must be about ten meters in height requiring large volume hot cells. On the other hand, the pulse column is essentially a no-maintenance device.

The mixer-settler has the longest contact time between phases of the three devices. With long-cooled fuels, the radiation dose per unit time is lower so a longer contact time is not a serious problem. Little headroom is required in the hot cells, the motors that drive the mixing stages can be located externally.

Besides radiation damage to the solvent, TBP is also subject to hydrolysis from contact with nitric acid. The

hydrolysis products--mono and dibutyl phosphate--form complexes with uranium and plutonium that strongly favor the organic phase, hence are more difficult to strip. If these compounds were allowed to accumulate in the solvent, losses of uranium and plutonium would be unacceptable. Contact with a basic scrub such as sodium carbonate followed by a nitric acid wash effectively removes both the radiation damage products and mono and dibutyl phosphates from the solvent. A solvent treatment flowsheet is shown in Fig. 4. Both pulse columns and mixer-settlers have been used as contactors for solvent treatment.

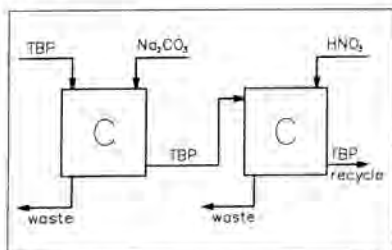


Fig. 4. Solvent treatment.

Reprocessing results in several waste streams to be processed. The first is the leached cladding from the head end. Early plans were to discharge the cladding into concrete containers for eventual burial. Some consideration has been given to melting this scrap for volume reduction. This waste material is intermediate in activity; there is induced activity from neutron exposure and trace contamination from fission products.

The major waste stream is the aqueous from the first extraction cycle containing most of the fission products and the transuranics. Originally it was planned to concentrate this stream and then store the concentrate in cooled tanks awaiting some yet-to-be-developed disposal scheme. Subsequently the government decreed that this waste could be stored in tanks for five years only--a moot point at the moment. In the United States there is a backlog of over 25,000 tons of discharged fuel, some with a cooling time of over 20 years. The high level waste from reprocessing this long-cooled fuel would not require additional tank cooling, it could be solidified directly.

Since the government decree on storage of high-level waste, processes have been developed for solidification of high-level waste particularly for the so-called defense waste. There had also been a demonstration project with waste from civilian reactor fuel. The preferred process and one variation are shown in Fig. 5. The high-level waste is sent to an evaporator where about 90 percent of the water and nitric acid are removed. With short-cooled fuel, the concentrate would be

stored in tanks; but with long-cooled fuel, the concentrate would be routed directly to the calciner where the fission products and transuranics are converted to metal oxides. The calcine is then mixed with glass frit in a glassmaking furnace, the mixture melted and then cast into the final storage canister. The canister is cooled, capped, decontaminated, and transferred to interim storage awaiting transfer to the federal repository (wherever that may be). An alternate to the calciner/glass furnace is the liquid fed ceramic melter. Here the concentrate from the evaporator is fed directly to the melter where calcining and glass making take place simultaneously. The overheads from the concentrator and calciner, or the ceramic melter, are routed to the low activity waste concentrator. The glass product from five tons of fuel could be encapsulated in a canister two feet in diameter by ten feet long.

Besides the overheads from high-level waste treatment, there are other streams that qualify as low activity waste. The aqueous streams from the additional uranium and plutonium decontamination cycles are low activity waste as are solutions used in solvent cleanup. There are miscellaneous wastes such as decontamination solutions and analytical residues that are low activity. All these low activity liquid wastes can be concentrated by evaporation. The overheads from low activity waste concentration and the  $\text{NO}_x$  scrubber solution would be sent to the nitric acid fractionator. The bottoms from the evaporator containing residual fission products and some dissolved salts could be returned to the high-level waste concentrator so that all the radioactive species would be combined in one package for disposal.

The overheads from the acid fractionator can be recycled to the process as weak nitric acid strip solution. The recovered acid can be used for dissolution of the fuel.

The iodine absorber material is another low activity waste form. One possible disposal scheme is to include it in the cemented cladding from the head end. If the volume of the cladding waste is reduced by melting, inclusion of the iodine waste would not be practical, so the iodine waste could be included in some other solid waste package.

If reprocessing is resumed in the United States, some additional research and development on waste processing and disposal will be needed. In particular development of procedures for volume reduction has an incentive in cost reduction. As mentioned, melting of cladding scrap is one such procedure. There has also been research on alternate solvent treatment methods that eliminate sodium salts. As examples, hydrazine and oxalic acid are possible solvent treatment materials that would be destroyed in the calciner leaving no solid residues. Some research on a phosphate glass has shown promise for the inclusion of highlevel waste. The higher the loading of waste in the glass, the lower the interment costs.

Finally one might ask, when will reprocessing be accomplished and by whom? From an evaluation of the political climate, it appears that some type of partnership between the federal government and industry is about the only viable option. If the government is directly involved, some opposition to reprocessing might be lessened. As to reprocessing plants, the Hanford Purex plant has processed "N" reactor fuel that had some similarity to civilian fuel. With the addition of a chop-leach headend to Hanford Purex, ten tons per day of LWR fuel (3000 tons per year) could be reprocessed. The completed Barnwell separations facility was designed for five tons per day. Both plants would require the addition of waste

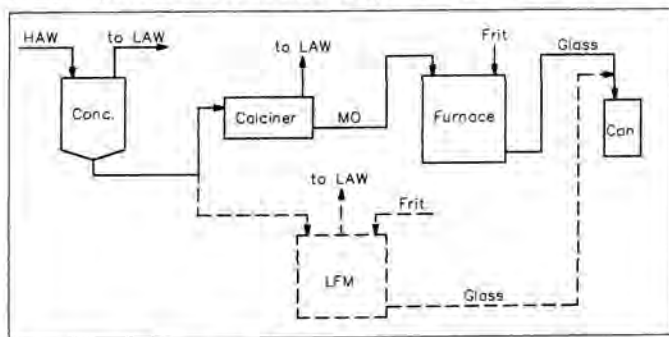


Fig. 5. High activity waste treatment.

facilities and licensing could be completed, the backlog of irradiated fuel would have grown to over 30,000 tons. Under this scenario, long-cooled fuel could be reprocessed for many years.

At the present time there is no economic incentive to reprocess in the United States. Uranium is cheap, enrichment is cheap and there are no new reactor projects underway. Both the plutonium and uranium have fuel values and several coun-

tries have plans to reprocess and recycle plutonium in LWRs. In the long term, reprocessing and recycle are in the best interests of this country. To reach this happy (?) state of affairs will require a concerted effort on the part of the nuclear community. Those involved in waste management must convince the relevant authorities that nuclear waste from reprocessing can be sequestered without harm to the general public or the environment.