

TECHNOLOGY FOR RECOVERY OF BYPRODUCTS

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ABSTRACT

Products of conventional nuclear fuel processing plants are uranium and plutonium, and any other recovered material is considered to be a byproduct. Some byproducts have been recovered from past nuclear fuel processing operations, either as a normal mode of operation or by special campaigns. Routine recovery over an extended period has been limited to neptunium, but extended campaigns were used at Hanford to recover strontium for radioisotope thermoelectric generators. Krypton is recovered at Idaho Chemical Processing Plant on a campaign basis, and isotope separation of krypton is done at Oak Ridge National Laboratory. Past campaigns at Hanford PUREX have recovered cesium, promethium, americium, cerium, and technetium. Past byproduct recovery efforts were usually severely constrained by the status of flowsheet development and availability of existing facilities at the time decisions were made to recover the byproducts. Additional processes were developed to accommodate other unit operations and in response to changes in waste management objectives or user requirements. Now an impressive variety of recovery technology is available for most potential byproducts, with varying degrees of demonstration under conditions which satisfy today's environmental protection and waste management constraints.

For purposes of this paper, a byproduct is considered to be any product from a nuclear fuel reprocessing plant other than the principal products of uranium and plutonium. We will review the byproducts of interest, compare and contrast byproduct recovery with waste management, describe current and past byproduct recovery operations, development status of alternative processes, and bases for selection among alternative processes in developing an integrated byproduct recovery plant.

Technology for the recovery of byproducts from nuclear fuel reprocessing has developed over the years to the current status which allows efficient recovery of many byproducts on a large scale using well-demonstrated technology, or even a choice among well developed technologies. Other byproducts have less well developed recovery technology. A study of byproduct recovery completed in 1978 by Exxon Nuclear Company¹ reviewed the status of process technology and selected preferred flowsheets for recovery of either individual byproducts or groups of byproducts. The present paper describes the demonstrated technology for recovery of byproducts and alternative technology which could be easily adapted to large scale production.

BYPRODUCTS OF INTEREST

Byproducts have been recovered for many purposes: heat sources, gamma radiation sources, light sources, beta energy sources, alpha radiation sources, raw materials for production of other useful radioisotopes, and for their value as chemical elements. Those which have been recovered on a large scale include: ^{237}Np , ^{90}Sr , ^{137}Cs , ^{85}Kr , ^{147}Pm , ^{241}Am , ^{244}Cm , and ^{144}Ce . The first three of these have been recovered over extended periods in more than one facility, while the others were recovered on a large scale either in a single facility or by periodic campaigns rather than on a regular basis. Other potential byproducts have been recovered in small amounts during development efforts, but have not been

recovered on a large scale. This latter group includes the elements Tc, Ru, Rh, Pd, and Xe.

RELATIONSHIP OF BYPRODUCT RECOVERY TO WASTE MANAGEMENT

Byproduct recovery is often closely related to waste management, but the fundamental objectives are somewhat different. The goal of byproduct recovery is an adequate yield of a separated byproduct with adequate chemical and radiochemical purity, in an acceptable chemical form, and packaged to satisfy a user's need. Waste management is directed toward satisfying current criteria for both storage and disposal of all plant effluents. Both byproduct recovery and waste management are oriented to satisfy fully all safety and environmental protection requirements, and to accomplish objectives in a cost effective manner. The principal differences are that byproduct recovery is not necessarily concerned about the quantity of the byproduct that remains in the waste but is concerned about the purity of the recovered byproduct, while waste management is concerned about the quantity of the material that remains in the waste but is not necessarily concerned about the purity of the separated material.

A synergistic effect can often be achieved between waste management and byproduct recovery. One clear illustration is the Hanford waste management program in which a large amount of both strontium and cesium are removed from high level wastes so that waste tanks will not continue to boil for very long periods. The materials are recovered in a single facility but by separate processes, and are converted to stable solids for separate encapsulation and storage. The products are potentially useful as if they were recovered for byproduct purposes, but there are still appreciable differences. Product purity is maintained to optimize the number of containers and the costs of preparing and storing each container. This purity is rather high, but is less than would be desired for use as byproducts. Also, container size and amount of product per container is optimized for

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storage rather than for use. Thus, although there are many similarities between this particular waste management operation and a potential byproduct recovery operation, it is clear that the Hanford program is oriented toward waste management rather than toward byproduct recovery.

NEPTUNIUM

The Savannah River Plant processes spent nuclear fuel by solvent extraction and recovers not only plutonium and uranium, but also recovers neptunium.² While processing normal fuel at the Savannah River Plant neptunium is routed to the high-level waste (HLW) as Np(V), and after reduction to Np(IV), is recovered with agitated anion exchange beds. Neptunium (IV) is selectively removed from solutions with high nitrate ion concentration along with any Pu(IV) which is present. The neptunium is subsequently purified by additional anion exchange processes and a cation exchange process. While processing highly enriched uranium fuels, Savannah River uses a solvent extraction process to recover neptunium.

Neptunium was also recovered at the Hanford PUREX and Redox Plants by co-extraction as Np(VI) with plutonium and uranium. The neptunium was refluxed in the plant until a sufficiently high concentration was achieved, and was subsequently partitioned by solvent extraction and purified by anion exchange. The Hanford PUREX Plant used a 30 percent tributyl phosphate (TBP) solvent extraction flowsheet and the Hanford Redox Plant used a hexone solvent extraction flowsheet.

STRONTIUM

Strontium¹ is currently recovered at Hanford using a solvent extraction process, and was previously recovered at Hanford using a carrier precipitation process to obtain a crude which was then purified using an organic cation exchange process.

Hanford currently uses a di-(2-ethyl hexyl) phosphoric acid (D2EHPA) solvent extraction process to recover strontium from acidic wastes. The process is based on a procedure developed at ORNL and modified at Hanford.

A carrier precipitation process was developed and used at Hanford to recover megacurie quantities of strontium from HLW. HLW was adjusted to pH 1, lead nitrate and sodium sulfate were added, and strontium and the rare earths were carried into the resulting lead sulfate precipitate. The precipitate was metathesized with sodium hydroxide and sodium carbonate to dissolve the lead and convert the residual precipitate to carbonates. After dissolution of the precipitate in nitric acid, the recovered byproducts were purified by cation exchange.

Multikilocurie quantities of crude strontium from the carrier precipitation process were purified at Hanford using an organic cation exchange process. The feed was loaded onto hydrogen form Dowex 50W resin, and eluted through successively smaller columns containing resin loaded with a metal ion such as nickel or zinc. The eluting solution used a complexing agent such as ethylenediamine tetraacetic acid or nitrilotriacetic acid in ammonium hydroxide to cause the metal ions to separate into compact bands as the elution progressed. High strontium purity was achieved.

CESIUM

Cesium¹ has been recovered on a plant scale by ion exchange on several media including an aluminosilicate gel and synthetic zeolites, by phosphotungstic acid precipitation, and by ferro- or ferricyanide precipitation. It has been purified on a large scale by alum co-crystallization.

Large scale recovery of cesium from alkaline supernatant liquid has been accomplished at Hanford by cation exchange. Several different exchangers have been used: an aluminosilicate gel exchanger (DECALSO), synthetic zeolites (Linde AW-500 or Zeolon), and an organic exchanger (Duolite ARC-359). In the current Hanford cesium recovery process, cesium is eluted from the exchanger with ammonium carbonate solution. The product is separated from the eluant by evaporation and the eluant is recovered for recycle. The product from the initial recovery process usually requires further purification by cation exchange due to high levels of sodium and potassium.

Cesium can be recovered from highly acidic wastes using heteropoly acids such as phosphotungstic or phosphomolybdic acid. The former has been used at Hanford to recover cesium from clarified HLW as part of their waste management activities. The precipitate is washed and then dissolved in sodium hydroxide. Purification of the product is required using another type of process.

A process for recovery of cesium from a slightly alkaline solution by precipitation of cesium nickel ferrocyanide followed by metathesis with silver nitrate and cation exchange was developed and used at Hanford on a plant-scale. Subsequently, a similar process using cesium zinc ferrocyanide was developed on a laboratory scale but not used on a plant scale.

Alum co-crystallization is applicable to purification of cesium, but is not practical for initial recovery from HLW. The process uses ammonium alum to saturate a crude cesium fraction at elevated temperature. A precipitate of cesium alum $[\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$ forms when the solution cools. Several successive crystallizations are required to achieve high purity.

KRYPTON AND XENON

The separations processes¹ potentially applicable to noble gas recovery include adsorption, diffusion, cryogenic distillation, and preferential absorption. The chemical processing plant at Idaho Falls recovers ^{86}Kr by low-temperature adsorption on a campaign basis depending on need for the material, the type of fuel being processed, and other production commitments. Occasional operation of the facility permits development of much useful data applicable to a plant designed for regular use, but significant process improvements would be required for upgrading the plant to routine recovery operations.

Adsorption processes use packed columns of charcoal or molecular sieves, operated at either ambient or reduced temperature, to remove krypton and xenon from offgas streams. Reduced temperature operation, usually at liquid nitrogen temperature, results in increased capacity and permits a slightly more concentrated product. A reduced temperature process has been operated on a plant scale at the Idaho Chemical Processing Plant, and the product has been further refined at ORNL. The reduced temperature process requires alternate heating and cooling of the adsorbent, which requires appreciable energy. Preliminary gas cleaning must be done to avoid possible plugging

of equipment by condensed phases as the gas is cooled. Ozone may be a particular problem because of its reactivity. Ambient temperature operation does not require the energy-consuming refrigeration step or as extensive preliminary gas cleaning. However, the equipment must be much larger and the process has not been demonstrated on a large scale.

TRIVALENT LANTHANIDES AND ACTINIDES

Because of the strong chemical similarity among the lanthanides and actinides, there are usually two separate steps in recovery of elements of this group. First a crude separation is made to recover the group without appreciable separation into individual elements, followed by a second process to separate the elements from each other. The crude separation may be made by solvent extraction, ion exchange, or precipitation. The final purification requires many stages of separation, and is usually done by ion exchange or solvent extraction in continuous operations so that the required number of stages can be supplied easily.

Crude separations have been performed on a plant scale at Hanford using the same processes that were mentioned earlier for strontium (solvent extraction using D2EHPA and precipitation using lead sulfate carrier). Separation by individual elements has been demonstrated on an engineering scale at Hanford using compact-band ion exchange chromatography to purify promethium, americium and curium.

CERIUM

Cerium has been recovered at Hanford along with the trivalent rare earths, and separated from the trivalent rare earths by oxidation and solvent extraction of Ce(IV). Oxidation and separation were accomplished using silver persulfate and nitric acid to oxidize Ce(IV) in the aqueous phase and it was extracted into an organic solution containing both D2EHPA and TBP in an inert hydrocarbon diluent. Oxidation, which required several minutes of contact at 35°C, proceeded more rapidly at elevated temperature, at the expense of reduced life of persulfate. Lifetime of the persulfate was also reduced by silver concentrations above 0.02M and HNO₃ concentrations above 2M. Prolonged radiation of the solvent adversely affected the Ce(IV) distribution ratio.

ALTERNATIVE PROCESSES

A solvent extraction flowsheet for the recovery of neptunium from fluorination plant residues with triethylamine has been developed. Two solvent extraction flowsheets using either a di-(2-ethylhexyl)phosphoric acid or a dibutyl butyl phosphonate solvent have been studied. In addition, there are many other solvents that could be used for the recovery and purification of neptunium.

For strontium recovery, an inorganic cation exchange process was developed by the French and Belgians using polyantimonic acid. HLW is denitrated to 2 M HNO₃, centrifuged to remove precipitated impurities, and then treated by cation exchange. Flow rates are on the order of 0.1 to 0.5 ml min⁻¹ cm⁻² because of slow loading kinetics. After loading the exchanger is washed with nitric acid, eluted at elevated temperature with silver nitrate in nitric acid, and regenerated with 6 M nitric acid. The eluate is treated with sodium chloride to precipitate silver chloride, concentrated, and then purified by solvent extraction.

High molecular weight substituted phenols such as 4-sec-butyl-2-(α -methylbenzyl) phenol (BAMBP) will extract cesium from alkaline solutions. This forms the basis of the PHENEX process developed at ORNL and tested on a pilot scale at Hanford. The process gives good separation of cesium from sodium. A similar process (CSREX) was developed at Hanford, using both BAMBP and D2EHPA for simultaneous recovery of cesium, strontium, and rare earths. However, BAMBP does not appear to be practical for large scale operations since it is rapidly degraded at the required pH of the process.

Cesium can also be extracted from neutral or alkaline solutions using dipicryl amine dissolved in nitrobenzene. The process is highly selective for cesium and has been demonstrated at Hanford on a laboratory and engineering scale. However, the reagents required have undesirable properties for use on a large scale.

Cesium can be extracted over a wide pH range using tetraphenylboron solutions. However, a process for solvent recycle has not yet been developed.

A process for cesium extraction by polyhalides was developed at Brookhaven and used on an engineering scale by the British. Although the process was successful, it has the disadvantage of problems associated with halide corrosion of equipment.

Other inorganic exchangers, developed principally in France and Belgium, are capable of removing cesium selectively from highly acidic solutions. They include ferrocyanide molybdate, titanium phosphate, and zirconium phosphate. Of these, titanium phosphate appears to be best because of a combination of high selectivity for cesium and high chemical stability.

For recovery of krypton and xenon, diffusion processes have been proposed based on thermal diffusion, diffusion through selective membranes, and electrostatic diffusion. None of these processes has been developed very extensively, and may not be satisfactory for large-scale operations.

Cryogenic distillation has been used for decades in liquid air plants. Thus the technology is well defined for all of the operations, materials of construction, and items of equipment. After preliminary gas cleaning to remove oxygen, water, oxides of nitrogen and other easily condensable gases, the residual gas is compressed, cooled and introduced to a column countercurrent with liquid nitrogen. The liquified product gases accumulate in the bottom of the column, from which they may be periodically removed and purified by fractional distillation.

In the fluorocarbon process for noble gas recovery, certain liquids are used to dissolve appreciable quantities of noble gases at low temperatures. Carbon tetrachloride, Freon-11, Freon-12 and other organic solvents have been studied for this process. Freon-12 (dichlorodifluoromethane) is frequently considered since it has good radiation stability and good selectivity. The gas stream is pretreated to remove oxides of nitrogen and then passed through the fluorocarbon at low temperature. Krypton and xenon are recovered together by distillation to desorb the dissolved gases.

Technetium, palladium and rhodium were recovered from neutralized HLW at Hanford both by using a strong base anion exchange resin and by using tricapryl ammonium chloride on an inert support. However, this process requires neutralization of the HLW and is not

considered to be viable unless the HLW is to be neutralized for other purposes.

Palladium and rhodium have been recovered on a laboratory scale by contacting glass made from HLW with lead and a reducing agent. Ruthenium may also be recovered by this process. Although this process could be used, it is not applicable unless the HLW is to be vitrified.

Japanese data show that palladium is removed from a nitric acid solution by a strong base anion exchange resin, or by extraction with tri-isooctyl amine. Palladium may be precipitated with dimethylglyoxime.

Rhodium recovery has not been demonstrated by solvent extraction or ion exchange from nitric acid solutions. Precipitation processes have been investigated on a laboratory scale, but no fully satisfactory process has been developed.

Technetium may be recovered from fluorination plant residues by solvent extraction using tri-laurylamine, and it is removed from nitric acid solution by strong base anion exchanger resins. Other solvents have also been used to recover and purify technetium.

PROCESS SELECTION

Many factors affect the selection of a process for recovery of byproducts, including the following: feed material, required product yield and purity, state of development of available processes, other byproducts to be recovered, safety, cost, impact on waste management, similarity to other plant operations, available facilities and the need for compatibility with existing materials of construction. Byproduct recovery operations have usually been added to existing plants or established in existing facilities, rather than being included in the initial design of a facility. Thus, selection of unit operations was limited by the available space, materials of construction, processing rates and services. A plant for recovering multiple byproducts would ideally use the same unit operations and chemicals for recovering many of the byproducts, be based on well developed technology, use no corrosive or unstable chemicals and require only small amounts of chemicals.

Solvent extraction using about 30% TBP is the usual process for recovery of uranium and plutonium and can also be used for recovery of neptunium. A similar process would be desirable for byproduct recovery. Other byproducts cannot be recovered using this concentration of TBP, but higher concentrations could be used for recovery of lanthanides and actinides. Use of two different concentrations of TBP would require separate solvent systems. A greater benefit could be obtained by using a different solvent in the second system so that a greater variety of byproducts could be recovered. The solvent with the most advanced state of development work is D2EHPA, which has been used for recovery of strontium, trivalent lanthanides and actinides, and cerium. Thus many byproducts can be recovered using solvent extraction technology and two solvent systems, one for uranium, plutonium and neptunium, and the other for a variety of byproducts.

Cesium has been recovered using ion exchange or precipitation technology, but no suitable solvent extraction process has been demonstrated. Ion exchange is usually the method of choice since it is more easily used as a continuous process and has been applied on a large scale to radioactive materials.

The noble gases are recovered from a gas stream rather than from solution, so the selection of a recovery process is independent of the process selected for recovery of materials from solution.

Other potential byproducts are technetium and noble metals. None of these have been recovered on a large scale, and even the pathway through the normal separations process is not well established. Separations processes could probably be developed using strong base anion exchange resins, or the solvent extraction equivalent which is long chain tertiary amines such as tri-laurylamine.

The Exxon Nuclear study¹ selected preferred processes for an integrated byproduct recovery plant. Krypton and xenon would be recovered by cryogenic distillation. Neptunium, strontium and rare earths would be recovered by a solvent extraction process using D2EHPA. Neptunium would extract at 1M HNO₃, rare earths at a pH of about 2.5, and strontium at a pH of about 4.5. Cesium would be recovered from 1M HNO₃ by ion exchange using titanium phosphate. Palladium and technetium would be recovered by solvent extraction using tri-laurylamine, but the acidity for this extraction was not established. Rhodium would be recovered from the combined dissolver solids and solids formed when the HLW is adjusted to pH 2.5. Recovery of krypton, xenon, neptunium, strontium and rare earths is based on well established technology, but no established technology is available for recovery of technetium and the noble metals.

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