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AQUEOUS PROCESSES FOR SEPARATION AND
DECONTAMINATION OF IRRADIATED FUELS

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INTRODUCTION

Much of the basic technology developed in the United States for processing irradiated fuels has been reviewed in the published proceedings of earlier conferences. (1,2) It is the purpose of this paper to review recent developments and improvements in aqueous processes for accomplishing separation and decontamination of irradiated fuels from power reactors.

It is well known that production of nuclear power in the United States at the present time at a cost below that of power produced from fossil fuels represents a formidable problem. The problem is being attacked by a diversified research and development program in which a number of different types of power reactors will be tested and different approaches for the reprocessing of fuel elements from these reactors will be simultaneously tested. It is expected that this test program will permit selection of optimum combinations of reactor types and reprocessing methods which may prove capable of producing nuclear power at costs competitive with power produced from fossil fuels.

Accordingly, research and development is currently being pursued in the United States on three distinct types of fuel processing methods; pyrometallurgical processes, which are reviewed in Reference 3, fluoride volatility processes, which are discussed in Reference 4, and aqueous processes, which are the subject of the present paper. Although the ultimate role of these processing methods in a nuclear power economy cannot be accurately assessed at the present time, it is felt that the proven reliability and versatility of aqueous processes guarantees them a prominent role in power reactor fuel reprocessing. Aqueous solvent extraction processes, for example, are ideally suited for installation in central processing plants which are designed to handle fuels from a number of power reactors generating a total of several thousand megawatts or more of power. Under these circumstances, nuclear fuels can be processed by continuous processes at high throughputs and at high on-stream efficiency and therefore at low unit cost.

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DESIGN AND OPERATING PHILOSOPHIES FOR AQUEOUS PROCESSING PLANTS

Philosophies of design, construction, and operation of aqueous processing plants are under continual review with respect to the special problems posed by power reactor fuel processing. Present philosophies and probable future trends are reviewed in paper 18.⁽⁵⁾ Operational practices for plants employing both remote maintenance and direct maintenance are being continually refined and unit operating costs are being continually reduced as additional experience is gained in operating both types of plant. It is felt that the concept of remote maintenance is most appropriate to a central processing plant designed to handle fuels and blankets of low enrichment from a number of power reactors. Such plants will necessarily employ large-scale equipment and the added capital investment in the equipment necessary to apply remote maintenance techniques will represent a smaller fraction of the total capital cost of the plant than would be the case for a smaller plant processing fuels of high enrichment.

Contact maintenance is also less practical for large-scale plants because of the inherently greater difficulty of decontaminating large equipment pieces and because the economic incentives are greater for operating such a plant at high on-stream efficiency and at rates approaching peak capacity. In plants designed to process fuels of high enrichment, small-scale equipment can be used, volume processing requirements are low, and the plant can be designed to operate at lower on-stream efficiency without adding exorbitantly to the capital cost. Periodic shutdowns of several weeks' duration to decontaminate equipment and perform maintenance by contact methods can therefore be tolerated. In such small-scale plants the frequency of maintenance can be reduced by installing multiple parallel assemblies of such critical units as pumps, jets, and valves so that consecutive failures of two or more units may be tolerated before production need be interrupted, and the investment in multiple units does not add greatly to the capital cost of the plant.

IMPROVED SOLVENT EXTRACTION PROCESSES

Continued development effort at several laboratories in the United States has disclosed refinements and improvements which can be made in the basic solvent extraction processes discussed in the proceedings of earlier conferences. These refinements make it possible to reduce operating costs in existing plants employing these processes and suggest ways in which the capital costs of new plants could be reduced.

PROCESSES FOR NATURAL OR SLIGHTLY ENRICHED URANIUM FUELS

Flowsheets Employing Backcycle of Aqueous Wastes

A simple concept which is capable of reducing significantly the consumption of chemicals and the investment in waste storage facilities is the concept of recycling aqueous wastes in solvent extraction plants. This concept is illustrated by the schematic flowsheet of Figure 1. This flowsheet shows one way in which aqueous wastes can be recycled in a three-cycle solvent extraction plant. Fresh salting agent is fed only to the final uranium and plutonium cycles. The aqueous wastes from the final uranium and plutonium cycles are combined, evaporated to the desired volume and employed as the scrub stream in

the second solvent extraction cycle. The aqueous waste from the second cycle is similarly evaporated and employed as the scrub stream for the first extraction cycle. The net result is that three complete solvent extraction cycles are operated but the quantities of salting agent required, the waste storage capacity required, and the quantities of plutonium and uranium lost to the aqueous waste are no greater than if only a single cycle of solvent extraction were operated. Such flowsheets have the additional important advantage that operating conditions which result in incomplete extraction of uranium or plutonium and which would therefore not be tolerable in a conventional plant can be considered for the second or final cycles in plants employing backcycle of aqueous wastes. Any plutonium or uranium which is lost to the aqueous wastes in the second or final cycles is simply recycled to the first cycle where conditions are adjusted to yield high recovery of both uranium and plutonium.

Considerable experimental evidence has been obtained with a wide range of equipment types and scales which indicates that fission product decontamination is not significantly altered by recycling aqueous wastes in this fashion.

Waste backcycle flowsheets are particularly appropriate for solvent extraction processes which employ non-volatile salting agents. For example, the Redox process⁽⁶⁾ employs methyl isobutyl ketone ("hexone") as the solvent and aluminum nitrate as the salting agent. Operation of a three cycle Redox process without backcycle of aqueous wastes would require waste storage capacity of almost 3000 gallons per ton of uranium processed. By employing waste recycle as shown in Figure 1, it is possible to reduce the waste storage requirement to less than 1000 gallons per ton of uranium and to reduce uranium and plutonium losses by a factor of about three.

However, it should be noted that the flowsheet of Figure 1 obtains these savings at the expense of installing two additional evaporators. With flowsheets in which the major portion of the salting agent can be satisfactorily added to the feed it is possible to reduce the number of evaporators required by employing a single evaporator to concentrate both the product from an earlier cycle and waste recycled from a later cycle.

The concept of waste recycle can be profitably applied in Purex-type processes also.^(7,8) Figure 2 shows a Purex flowsheet employing backcycle of second cycle aqueous wastes. Although this flowsheet has to date been tested only in bench-scale equipment, it is considered to be workable in plant applications. In this flowsheet uranium and plutonium are processed through a typical extraction-scrub column, the HA column. Additional decontamination is obtained in the HS column in which the organic extract from the HA column is subjected to exhaustive scrubbing. (The additional scrubbing could be obtained by simply increasing the length of the scrub section in the HA column. A separate column is employed in the flowsheet of Figure 2 because of the additional flexibility which it provides.) Separation of uranium and plutonium is accomplished in the LBX column which is of sufficient size to handle the desired uranium processing rate and in the smaller LBS column which has a diameter small enough to avoid criticality problems. The separated plutonium(III) fraction is oxidized to plutonium(IV) and processed through a conventional final plutonium solvent extraction cycle. The uranium is retained in the organic stream emerging from the LBX column. Re-extraction of uranium into an aqueous phase is accomplished in the LC column. The aqueous uranium-bearing

LCU stream is reduced in volume in a continuous evaporator and made into feed for a conventional final uranium solvent extraction cycle in the 2D and 2E columns. The decontaminated uranium product from the 2E column is processed through a second continuous evaporation step and is transferred to further processing steps as a concentrated uranyl nitrate solution (ca. 2 M $\text{UO}_2(\text{NO}_3)_2$).

The aqueous wastes from the final uranium and plutonium cycles are combined, reduced to an appropriate volume in a continuous evaporation step and recycled to a point just below the feed entry point in the HA column. Considerable flexibility is made possible in the final uranium and plutonium cycles by this provision for recycling aqueous wastes from the final cycles to the first cycle. In particular, the following advantages may be noted for this flowsheet in comparison with flowsheets not employing recycle of wastes.

- (1) Lower concentrations of salting agent (nitric acid) can be employed in the final uranium and plutonium cycles. This yields improved decontamination from the fission products zirconium and niobium but would not be permissible in flowsheets not employing waste recycle because of the higher losses of uranium and plutonium which would result.
- (2) A higher concentration of plutonium is permissible in the uranium feed to the final uranium cycles than would be the case with flowsheets not employing waste recycle. A reducing agent is routinely added to the aqueous phase in the 2D column to reduce any plutonium in the feed to this column to plutonium(III) and thereby prevent its extraction with uranium. In the absence of waste recycle, temporary failures of the LEX column to reduce the plutonium content of the final uranium cycle feed to amounts which can be economically discarded to waste would require a non-routine rework operation to recover this plutonium. With the waste recycle flowsheet shown in Figure 2, such momentary failures in the LEX column can be tolerated since the aqueous waste from the 2D column is routinely recycled.
- (3) With the provision for recycle of the aqueous waste from the 2A column shown in the flowsheet of Figure 2, it is unnecessary to add additional nitric acid salting agent to the plutonium stream after the final separation from uranium in the LBS column. The aqueous phase in the 2A column is maintained at only about 2.5 M HNO_3 . This results in less efficient extraction of plutonium (but more efficient fission product separation) in the 2A column. Operation at this low feed acidity would not be permissible in the absence of waste recycle. Further, since the nitric acid in the feed to the 2A column is added prior to the LBS column where final separation of plutonium from uranium is accomplished, it is possible to use nitric acid contaminated with uranium for this purpose. Thus, it is possible at this point to use nitric acid which has been recovered as a by-product in the final processing of uranium in which uranyl nitrate is converted by thermal decomposition to uranium trioxide.(9)

- (4) By comparison with more conventional Purex processes such as have been reviewed in earlier publications^(7,8), the flowsheet of Figure 2 accomplishes significant reductions in operating costs. Principally through decrease in the amounts of nitric acid required, essential materials costs are reduced by about 30%. The necessary capital investment in waste storage facilities is reduced by a factor of 3. Uranium and plutonium losses are reduced by factors of 2 and 3, respectively. In comparison with three-cycle Purex processes⁽⁸⁾, equipment requirements are reduced through elimination of two extraction columns, the HC column and the 1A column, and through elimination of one intercycle concentrator.

Quite apparently the two-cycle flowsheet of Figure 2 demands more efficient decontamination in each cycle than is necessary in more conventional three-cycle flowsheets. Experimental evidence has been obtained which indicates that the improved decontamination performance required for the flowsheet of Figure 2 is possible in plant-scale equipment through recently developed improvements both in solvent extraction equipment and in chemical flowsheets.

Effect of Temperature on Fission Product Decontamination in Purex Processes

Operation of Purex-type processes at elevated temperature was shown by Alter and associates at the Knolls Atomic Power Laboratory to yield improved fission product decontamination in bench-scale mixer-settler units. Recently, Karraker and associates at the Savannah River Laboratory have conducted a more exhaustive study of the effect of temperature on fission product decontamination in tributyl phosphate solvent extraction processes, again in bench-scale mixer-settlers. Studies at Hanford have also shown beneficial effects of operation at elevated temperature on fission product decontamination in both bench-scale mixer-settlers and in pulse columns.

Results of the Savannah River study are summarized in paper 224.⁽¹⁰⁾ Conditions which were found to be most effective for obtaining improved fission product decontamination are shown in the schematic flowsheet of Figure 3. Gross gamma decontamination factors as high as 2.4×10^6 for uranium and 4.6×10^5 for plutonium have been demonstrated in bench-scale mixer-settlers with this flowsheet. Excellent recovery of both uranium and plutonium was obtained, plutonium losses to the aqueous waste being normally about 0.01% and uranium losses ranging from 0.0001% to 0.01%. Separation of plutonium from uranium in the 1B unit was good, the uranium product ranging from 14 to 30 parts plutonium per 10^9 parts uranium. Plutonium contamination in uranium processed through additional solvent extraction cycles is normally only a factor of 2 or 3 less than these values.

The principal departures from a conventional Purex flowsheet are the additional scrubbing of the organic extract of uranium and plutonium at 70°C in the 1A' unit and the operation of the 1B unit at 70°C. Insertion of the 1A' unit operated at 70°C increased the decontamination from gamma-emitting fission products by a factor of 370 over that obtained with the 30°C 1A unit alone.

The gross gamma decontamination was increased by a factor of 7 as the temperature of the 1A' unit was increased from 30°C to 70°C. Operation of the 1B unit at 70°C increased the decontamination of uranium by causing more than 90% of the fission products in the entering organic extract to be extracted into the aqueous plutonium-bearing phase. Improved separation of uranium from fission products was therefore obtained in the 70°C 1B unit at the expense of increasing the concentration of fission products in the plutonium product obtained from this unit. This is preferred since anion exchange methods of proven efficiency exist for accomplishing the final decontamination of plutonium.

Operation of the 1A unit also at elevated temperature yields poorer fission product decontamination than the conditions shown in Figure 3. Operation of the 1A unit at 70°C decreases decontamination from zirconium and niobium in this unit by a factor of about 8. Although decontamination from ruthenium in the 1A unit is increased by a factor in excess of 14 by operating this unit at 70°C the decreased zirconium-niobium decontamination offsets this and results in a net decrease in overall gamma decontamination by a factor of about 3.5.

Additional decontamination of the uranium product from such a flowsheet can be obtained by percolating the concentrated aqueous uranium solution over an adsorbent bed such as silica gel. Fairly efficient decontamination from zirconium and niobium is possible in such an adsorption step; overall gamma decontamination factors in excess of 20 have been obtained in such operations. Additional decontamination of uranium from ruthenium can be obtained by volatilization of ruthenium species during the thermal decomposition step in which uranyl nitrate is converted to uranium trioxide powder. Decontamination factors for ruthenium of the order of 10 have been obtained in this operation.

The operating conditions shown in Figure 3 are considerably more stringent than those customarily employed in Purex-type flowsheets. Careful consideration must be given to selection of a solvent system for operation at 70°C. In addition to the obvious requirement that the diluent for TBP have a boiling point and flash point high enough to permit it to be safely used at 70°C, it must be more inert to attack by nitric acid solutions than are most commercial kerosene blends. Most commercial kerosenes on exposure to nitric acid at elevated temperature undergo reactions yielding products which promote extraction of fission products and thereby hinder separation of plutonium and uranium from fission products. Highly purified paraffin diluents such as n-dodecane are sufficiently stable that they can be successfully used at 70°C.

Similarly, care must be used in selection of a reducing agent to be employed in a partition solvent extraction unit at 70°C. The work presented in paper 224 indicates that ferrous sulfamate may be satisfactorily used under the conditions of that work. However, the rate of hydrolysis of sulfamic acid in nitric acid solution at 70°C is appreciable and consideration should be given to the residence time of the aqueous phase at 70°C in the 1B contactor to be used in attempting to employ the flowsheet of Figure 3.

ALTERNATE PROCESSES FOR FINAL DECONTAMINATION AND CONCENTRATION OF PLUTONIUM AND URANIUM

Concentration Processes for Plutonium

The plutonium product which results in most solvent extraction plants is a dilute solution of plutonium in dilute nitric acid. For convenience in transferring and in subsequent processing steps the volume of this solution is generally reduced by simple evaporation and the plutonium product transferred as a solution approximately one molar in plutonium. Although simple and direct, evaporation obviously accomplishes no further purification of plutonium and indeed may introduce impurities into the plutonium through corrosion of the evaporator.

Accordingly, attention has been given to alternate methods for concentrating plutonium, in particular to methods which are capable of accomplishing simultaneous concentration and purification of plutonium feeds which have been only partially decontaminated.

Reflux Solvent Extraction Cycles

Use of so-called "reflux flowsheets" to accomplish purification of plutonium from non-radioactive impurities was discussed in an earlier symposium.⁽¹¹⁾ Such flowsheets are capable of efficient fission product decontamination also and are applicable in principle to any solvent extraction system in which the extracted salt is present in the feed at concentrations well below its solubility limit. Under such circumstances substantial purification and concentration can be accomplished simultaneously in a two-column solvent extraction cycle such as is illustrated by the schematic flowsheet of Figure 4.

An aqueous feed containing plutonium at low concentration is fed to an intermediate point in a dual-purpose extraction-scrub column (column "A"). The plutonium in the organic extract from the "A" column is stripped into an aqueous phase in column "B". Only a small portion of the aqueous effluent from column "B" is withdrawn as product, however. The remainder (>99% in the case illustrated in Figure 4) is recycled and blended with the aqueous scrub solution which enters at the top of column "A". It is apparent that in the case illustrated in Figure 4, steady state operation requires that the concentration of plutonium in the aqueous solution emerging from column "B" be 22-fold greater than it would be in a conventional final plutonium solvent extraction cycle in which the entire aqueous flow in column "B" is withdrawn as product.

Experimental data obtained in bench-scale and pilot-scale equipment indicate that decontamination is significantly improved by such flowsheets employing either TBP solvent systems and nitric acid as the salting agent (Purex processes) or employing methyl isobutyl ketone as the solvent and aluminum nitrate as the salting agent (Redox processes). It is apparent that those fission products which are extracted with plutonium in the "A" column and which strip with plutonium in the "B" column are recycled to the "A" column in the same ratio as is plutonium. Thus, provided the reflux operation does not produce increased extraction of fission products introduced in the dilute

feed to the center of the "A" column, overall fission product decontamination will be improved by a factor which has as a maximum value the factor by which plutonium is concentrated in the reflux operation. An additional gamma decontamination factor in excess of 10^4 was obtained in laboratory studies on processing the plutonium product from a Redox first cycle through a reflux cycle similar to that of Figure 4.

With equipment of appropriate design this reflux operation does not increase waste losses. Losses to the aqueous waste in the "A" column are not substantially increased since the entire length of the "A" column is available for extracting plutonium out of the concentrated reflux stream. Increased losses in the "B" column can be avoided by addition of reducing agents to effect reduction to plutonium(III) or by employing complexing agents in the aqueous stripping solution if the "B" column is of insufficient length.

Reflux flowsheets thus offer a workable means of accomplishing simultaneous decontamination and concentration of plutonium. However, it should be noted that they pose severe control problems. Large inventories of fissionable material are accumulated in such reflux operations and extreme care should be used in design of both the extraction equipment and the receivers and handling equipment for both aqueous and organic wastes to assure that supercritical quantities of fissionable material cannot be accumulated in unsafe geometries.

Ion Exchange Processes for Plutonium

Both cation and anion exchange processes have been developed for concentrating plutonium which has been previously purified from fission products and uranium by solvent extraction methods. Cation exchange processes for isolation of both plutonium and uranium-233 were reviewed in some detail in an earlier publication.⁽¹²⁾ Results of recent work on cation exchange methods for plutonium and uranium and methods of operating ion exchange equipment are reviewed by Tober in paper 225.⁽¹³⁾ Anion exchange methods for the concentration and purification of plutonium are discussed by Ryan and Wheelwright in paper 814.⁽¹⁴⁾

Both cation and anion exchange processes are capable of yielding product solutions containing as high as 50 to 60 g Pu/l. Both types of process are also capable of yielding some purification from fission products and other impurities. However, anion exchange processes appear inherently capable of more efficient separation of plutonium from uranium, fission products and other impurities and employ simpler flowsheets and nitric acid as the only process chemical. Anion exchange process have the further advantage that the final product is a dilute nitric acid solution (0.35 M to 0.75 M HNO_3) which is more conveniently handled in subsequent processing operations than is the product from cation exchange processes which is generally in the range 5 to 6 M HNO_3 .

Since anion exchange processes for plutonium are discussed in some detail in other papers in this symposium it will suffice here merely to point out that experimental data indicate that a completely decontaminated plutonium product of 50 g Pu/l can be readily obtained by coupling a single cycle of anion exchange to an improved Purex solvent extraction partition cycle. A flow-sheet illustrating such a process is presented in a later section.

Concentration Processes for Uranium

In the United States, natural uranium which has been only partially depleted in the uranium-235 isotope is customarily recycled to isotope separations processes where a usable uranium-235 content is restored by a diffusional process employing uranium hexafluoride. Conversion of the aqueous solvent extraction product to uranium hexafluoride is ordinarily accomplished in several steps in which aqueous uranyl nitrate is converted by thermal decomposition into uranium trioxide which in turn is reduced to uranium dioxide with cracked ammonia. Uranium dioxide is converted to anhydrous uranium tetrafluoride by reaction with hydrogen fluoride. The uranium tetrafluoride is finally converted to uranium hexafluoride by reaction with fluorine.

Although economic methods have been developed for these several operations, decontamination from fission products cannot be conveniently obtained in the existing processes. There is, therefore, an incentive for development of an aqueous process which can employ as feed partially decontaminated aqueous uranyl nitrate solutions and produce fully decontaminated anhydrous uranium tetrafluoride as the product.

Since anhydrous uranium tetrafluoride is an appropriate intermediate for production of either uranium hexafluoride or uranium metal or alloys, such processes may find application also to power reactor fuels which do not require isotopic enrichment for further use.

Two processes are under investigation for conversion of aqueous uranyl nitrate solutions to anhydrous uranium tetrafluoride (or to anhydrous double salts of uranium tetrafluoride with alkali fluorides or ammonium fluoride). These are the Excer process⁽¹⁵⁾, which is under development at the Oak Ridge National Laboratory and the Flurex process, which is under development in the Hanford Laboratories. These processes are discussed in detail in papers 660⁽¹⁶⁾ and 618.⁽¹⁷⁾

Excer Process

One application of the Excer process is illustrated in the schematic flowsheet of Figure 5. Uranyl ion is separated from nitrate ion by absorbing the uranium on a cation exchange resin. A continuous ion-exchange contactor is indicated in Figure 5, but fixed bed equipment has also been satisfactorily employed. The uranium is eluted from the cation exchange resin with hydrochloric acid. Reduction of uranyl ion to uranium(IV) is effected in a compartmented electrolysis cell in which the anode is shielded from the chloride solution by a cation exchange resin in membrane form. Sulfuric acid can be used as the electrolyte in the anode compartment. Typical reduction rates are 1.5 lbs/hr, ft². In the flowsheet of Figure 5, uranium(IV) is precipitated as the salt $UF_4 \cdot 0.75 H_2O$ by addition of a stoichiometric amount of hydrofluoric acid to the uranium(IV) chloride solution. The precipitated hydrated salt is removed by filtration and converted to anhydrous uranium(IV) fluoride by heating at 400°C in nitrogen. Products containing about 0.1% H₂O, less than 1% UO₂, less than 1% uranium(VI), and of tap densities averaging about 2.7 g/cc (but on occasion as high as 3.5 g/cc) were obtained in this operation. The supernatant from the precipitation step is evaporated and the hydrochloric acid

distillate recycled and re-used as the elutriant in the cation exchange step. The bottoms from the evaporation step are recycled to the cation exchange step to recover the uranium which is normally present at 1 to 5 g/l U in the supernatant from the $\text{UF}_4 \cdot 0.75 \text{ H}_2\text{O}$ precipitation step. Contaminants in the uranium feed are therefore recycled and are lost from the system only in the waste from the cation exchange step or in the product. Decontamination factors of 10^3 to 10^4 were obtained for Fe, Cr, Ni, Mn, V, and Mo in the precipitation of $\text{UF}_4 \cdot 0.75 \text{ H}_2\text{O}$. Fission product decontamination factors of 10 to 100 for zirconium, niobium, and ruthenium but only 1 to 5 for cesium, strontium, and rare earths were obtained in the precipitation step. Fortunately, cesium, strontium, and the rare earths are ordinarily effectively separated in solvent extraction processes and, therefore, should not constitute a major problem in applying this process to uranium partially decontaminated by solvent extraction.

Many types of electrolysis cells were examined. Solid cathode cells are acceptable for the two-step reduction and precipitation shown in Figure 5 and are preferred by the Oak Ridge investigators because of their simplicity of construction and operation. Of many electrode materials tested, Hastalloy C or graphite is preferred for the cathode and platinized tantalum for the anode. Current efficiencies ranged from 80 to 90% with single-stage uranium reduction efficiencies of 90 to 95%.

With cells employing an agitated mercury cathode, uranium may be eluted from the cation resin in hydrofluoric acid, this solution fed directly to the electrolysis cell and uranium simultaneously reduced and precipitated. Elution of uranium from the cation resin in hydrofluoric acid gives more efficient separation of uranium from contaminants. Typically, uranium is recovered at a concentration of 125 g U/l by elution in hydrofluoric acid. The eluted product contains only about 50 ppm nitrate and the 0.4 M HNO_3 waste only about 4 ppm fluoride. The fission products zirconium, niobium, and ruthenium are not strongly absorbed in the resin loading step and, therefore, appear in the dilute nitric acid waste. Decontamination factors of about 50 for zirconium-niobium and about 20 for ruthenium were observed. Cesium, strontium, and the rare earths are not eluted in hydrofluoric acid and overall decontamination factors of about 10^3 were obtained for these fission products. These fission products may be eluted from the resin in a separate step employing hydrochloric, nitric, or sulfuric acid.

Use of a hydrofluoric acid feed in conjunction with solid cathode electrolysis cells was not successful because of reduced efficiency arising from precipitation of the solid fluoride on the cathode. Flowsheets employing hydrofluoric acid feeds and cells with agitated mercury cathodes are discussed in paper 660.

Flurex Process

In the Flurex process separation of uranyl ion from nitrate ion and reduction and precipitation of uranium as a double salt of uranium tetrafluoride with ammonium fluoride or an alkali metal fluoride is accomplished simultaneously in a continuous three-compartment electrolysis cell containing both cation and anion exchange resins in membrane form. A simplified schematic flowsheet for this operation is shown in Figure 6. Aqueous uranyl nitrate solution is introduced continuously into the center compartment of the cell, which is

bounded on one side by a cation-permeable membrane and on the other side by an anion-permeable membrane. Under the applied electrical potential uranyl ions diffuse through the cation exchange membrane into the catholyte compartment. Nitrate ions diffuse in the other direction, through the anion exchange membrane and into the anolyte compartment. Hydrofluoric acid and ammonium fluoride are continuously introduced into the catholyte compartment and as uranyl ion is reduced at a stirred or flowing mercury cathode it is precipitated as the salt $\text{UF}_4 \cdot \text{NH}_4\text{F}$. As indicated in Figure 6 the precipitated salt would be continuously removed by filtration or centrifugation, dried and converted to anhydrous uranium tetrafluoride by heating at 400° to 500°C . A small portion of the supernatant, which would include washes of the precipitated uranium product, would be discarded to waste. The remainder would be evaporated to the desired volume and recycled to the catholyte compartment. Operating at 60°C and maintaining the anolyte at a pH of 8 to 9, current efficiencies of 85 to 90% have been demonstrated, with current densities of 2 amps/in² at the cathode and 1 amp/in² at the ion exchange membranes. Platinum has proven the most satisfactory anode material tested to date although recent results indicate type 304L and 347 stainless steels may be satisfactory anode materials in alkaline media.

The extent of recovery of uranium in a single-stage operation has not been thoroughly evaluated yet, nor has multistage operation been studied. Fission product decontamination has not yet been studied in detail but early experiments indicated substantial fission product decontamination may be possible in this process.

Simplified Flowsheet for Irradiated Uranium

From the foregoing discussion it is apparent that further simplification in processes for irradiated uranium will probably be possible with continued technological development. In particular, the schematic flowsheet of Figure 7 in which a single Purex solvent extraction cycle (employing operation at elevated temperature for improved fission product decontamination) is combined with an anion exchange step for plutonium and a final uranium purification and concentration step such as the Excer process or the Flurex process, may be within range of attainment in the near future.

Processing of Power Reactor Fuels of Low Enrichment

It is expected that power reactor fuels of low enrichment can be processed by slightly modified Purex processes. Flanary and co-workers at the Oak Ridge National Laboratory have demonstrated that feeds containing up to 215 g/l uranium and up to 50 g/l of stainless steel components can be processed by TBP extraction. With the flowsheet shown in Figure 8, two theoretical extraction stages were required to reduce the plutonium loss to 0.01%.

Most low-enrichment fuels which contain zirconium contain the fissionable material in a form (uranium or uranium dioxide) which is readily soluble in nitric acid but clad in zirconium or zirconium alloys. Decladding operations such as the Zirflex process⁽¹⁸⁾ developed at the Hanford Laboratories will permit the cladding to be preferentially dissolved and the fissionable material to be then dissolved in nitric acid and processed by conventional Redox or Purex processes.

Low-enrichment fuels which are alloyed with zirconium will probably contain 10 weight % or less zirconium. It is expected that such fuels can be processed in Purex processes by dissolving in mixtures of nitric and hydrofluoric acid and adding aluminum nitrate to complex excess fluoride. The work of Maness at the Hanford Laboratories indicates that Hastelloy F is an acceptable material of construction for dissolvers to employ mixtures of nitric and hydrofluoric acids. For example, the corrosion rate of low carbon Hastelloy F in boiling 1 M HNO_3 , 2 M HF was only 2 mils/month.

Processing of uranium-zirconium alloys at the lower feed acidities appropriate for Redox processes may be possible at somewhat reduced processing rates. Work at Hanford indicates that feed solutions containing 1.2 moles zirconium per mole uranium, 4 moles fluoride per mole zirconium, and 0.2 M to 1 M aluminum nitrate are not stable at zirconium concentrations higher than 0.2 M if the acidity is limited to 0.25 M HNO_3 . Increasing the nitric acid concentration increases the composition range of stable solutions. A feed containing 0.53 M zirconium, 0.42 M uranyl nitrate, 0.9 M aluminum nitrate, and 0.85 M nitric acid is sufficiently stable for processing.

SOLVENT EXTRACTION PROCESSES FOR THORIUM FUELS AND BLANKETS - THOREX PROCESS

The basic Thorex process, in which TBP extraction is applied to the recovery and purification of uranium-233 and thorium from irradiated thorium, has been described by Gresky.⁽¹⁹⁾ Results obtained in the testing of this flowsheet in the Thorex Pilot Plant at the Oak Ridge National Laboratory have been reviewed by Bruce.⁽²⁰⁾ This flowsheet, which comprises one solvent extraction cycle for thorium and one solvent extraction cycle plus an ion exchange isolation step for uranium-233, is considered adequate for feeds irradiated to not more than 1500 grams uranium-233 per ton and allowed to decay at least 180 days before processing.

Continued pilot-scale testing of the Thorex process at the Oak Ridge National Laboratory has employed flowsheets such as that shown in Figure 9, consisting of two solvent extraction cycles for thorium and three solvent extraction cycles plus an ion exchange isolation step for uranium. This flowsheet has yielded consistently satisfactory decontamination performance with fuels irradiated to 3500 grams uranium-233 per ton and allowed to decay for at least 400 days before processing. The tentative specifications for both fission product activity and chemical purity for both the uranium and thorium products were met with this flowsheet. The pilot plant experience indicates that modification of this flowsheet will be required to assure consistently low losses of thorium and uranium, however.

In the most recent phase of the pilot plant test program the flowsheet of Figure 9 was tested for the processing of fuels irradiated to 3500 grams of mass 233 per ton and aged only 30 days. With these very radioactive feeds the flowsheet of Figure 9 yielded a uranium product which met the tentative specification for both fission product activity and chemical purity. Fission product activity in the thorium product exceeded the specification by a factor of about 200, however. Overall gamma decontamination factors averaged 4×10^4 for thorium and 5×10^7 for uranium-233. Ruthenium limited decontamination in both the uranium and the thorium stream.

Supporting laboratory studies indicated that formation of nitrite by radiation effects in these highly radioactive feeds caused the ruthenium to become more extractable by tributyl phosphate. These studies also indicated that digesting acid-deficient Thorex feeds with 0.04 M NaHSO_3 for one hour sufficed to convert the bulk of the ruthenium to inextractable species. With the sulfite treatment single stage decontamination factors for ruthenium as high as 200 were obtained as compared with factors of only 2 for feeds which were not subjected to the sulfite treatment. This treatment was not effective with feeds of higher acidity.

Application of the sulfite treatment to both the first and second cycle feeds in the pilot plant resulted in an improvement in ruthenium decontamination by a factor of about 10 in each cycle. The fact that lesser improvement factors were observed with this treatment in the pilot plant is attributed to partial destruction of the added sulfite in the pilot plant feeds, through radiation and/or oxidation. A minimum of about 0.06 M NaHSO_3 appeared necessary to improve ruthenium decontamination in the pilot plant.

PROCESSES FOR HIGHLY ENRICHED URANIUM FUELS

Solvent extraction processes for highly-enriched uranium fuels ($\geq 90\%$ U-235) have been reviewed by Stevenson.⁽²¹⁾ These differ from processes for natural or slightly-enriched uranium primarily in that the residual uranium-235 is the only fissionable material to be recovered, the process must handle feeds containing such diluents or alloying agents as aluminum, zirconium, or stainless steel at molar concentrations much greater than the uranium concentration*, and the process is normally conducted in much smaller equipment.

Processes developed for application at the Idaho Chemical Processing Plant and reviewed by Stevenson include several processes for dilute alloys of uranium with aluminum. In these the fuel and the aluminum cladding are dissolved in nitric acid and the enriched uranium recovered by:

- (1) Three consecutive hexone solvent extraction cycles employing aluminum nitrate as the salting agent, or
- (2) A cycle of tributyl phosphate extraction, employing 4.5 volume % TBP in kerosene and aluminum nitrate salting followed by two cycles of hexone extraction, or
- (3) A cycle of TBP extraction employing 6 volume % TBP and aluminum nitrate salting followed by a cycle employing 18 volume % TBP and nitric acid salting followed in turn by a silica gel adsorption step.

* The cores from the Experimental Breeder Reactor (EBR) are exceptions. These are essentially pure uranium of high enrichment.

A process has been developed for the same plant in which uranium-zirconium alloys containing up to about 2 weight % zirconium are dissolved in aqueous hydrofluoric acid and aluminum nitrate is added to complex excess fluoride ion and to oxidize uranium to uranium(VI) and render it extractable by TBP. Separation of the uranium from zirconium and the bulk of the fission products is accomplished in a TBP extraction cycle employing 10 volume % TBP. The necessary additional (and essentially complete) fission product decontamination is obtained in two additional cycles of hexone extraction. The experience at the Idaho Chemical Processing Plant with this flowsheet is reviewed by Reid, Stevenson, and Lemon in paper 259.⁽²²⁾ Greater than 99.5% recovery of uranium and decontamination factors in excess of 10^6 are routinely realized. The uranium product solution may be safely handled without shielding.

A similar process has been developed for enriched fuels which employ stainless steel as a cladding or alloying agent. The stainless steel is dissolved in dilute (4 - 6 M) sulfuric acid after which nitric acid is added to dissolve the uranium. The uranium is separated from the stainless steel in a TBP solvent extraction cycle similar to that discussed in the preceding paragraph, and essentially complete fission product decontamination is obtained by two additional cycles of hexone extraction.

Processes have also been developed for recovery and purification of enriched uranium from unalloyed cores by either hexone or TBP extraction.

Recent work in solvent extraction processes for enriched fuels has been directed at improving fission product decontamination and adapting existing processes to handle fuels of different composition.

Karraker and associates have studied the effect of temperature on fission product decontamination in TBP extraction processes for uranium-aluminum alloys. Their work is reported in paper 224⁽¹⁰⁾ of this symposium. The flowsheet of Figure 10 illustrates conditions which yielded satisfactory performance in bench-scale mixer-settlers with enriched uranium fuels irradiated to from 7 to 30% burnup. The first cycle employs 6 volume % TBP in n-dodecane and aluminum nitrate salting. The second cycle employs 18 volume % TBP and nitric acid salting. Both cycles are operated at 70°C. As in the case of Purex processes, operation at this temperature resulted in significant improvement in fission product decontamination, by a factor of 50 in the first cycle and 2 to 4 in the second cycle. Ruthenium decontamination in particular was improved by operation at elevated temperature. The decontamination factor for ruthenium in the first cycle was greater by a factor of 100 at 70°C than at 30°C. Zirconium-niobium decontamination in the first cycle was increased by a factor of 10 on increasing the temperature from 30°C to 70°C. Overall gamma decontamination factors for the indicated flowsheet averaged about 4×10^8 , with overall uranium losses of the order of 0.02%. Essentially identical decontamination performance was obtained over a fairly wide range of stream compositions and flow ratios.

Flanary and Goode at the Oak Ridge National Laboratory have developed the flowsheet shown in Figure 11 for recovery and purification of enriched uranium from Army Package Power Reactor fuel. This fuel consists of 10 weight % uranium dioxide dispersed in and clad in stainless steel. The indicated first cycle flowsheet is designed to employ feeds prepared by the Darex process⁽²³⁾ in which the fuel is dissolved in a mixture of nitric and hydrochloric acids and the chloride then removed by oxidative distillation.

Separation of the uranium from the stainless steel components and from the bulk of the fission products is effected by extraction of a dilute feed (5 g U/l) with 5 volume % tributyl phosphate in a hydrocarbon diluent. The organic phase is scrubbed with a $\text{HNO}_3\text{-Al}(\text{NO}_3)_3$ solution to improve fission product separation. Ferrous sulfamate is added in the scrub stream to reduce the traces of plutonium in the feed and prevent the extraction of plutonium with uranium. Uranium is recovered in an aqueous solution by a conventional stripping operation in the second column.

The uranium having been separated from the stainless steel components in the first cycle, subsequent processing can be performed by conventional, proven processes.

Laboratory data indicate that with the flowsheet of Figure 11, 4 theoretical stages in the extraction section of the first column and 4.5 theoretical stages in the stripping column will suffice to reduce uranium losses in each column to 0.01%. Tests of this flowsheet in bench-scale mixer-settler units with feeds prepared from highly irradiated APPR fuel specimens yielded decontamination factors of 4.8×10^5 for beta and 6.0×10^4 for gamma activity. Decontamination factors of 3.3×10^2 for beta and 2.5×10^3 for gamma activity are anticipated for a second cycle, or overall decontamination factors slightly greater than 10^8 through two cycles. Since decontamination by a factor in excess of 2×10^8 will probably be desired, a third solvent extraction cycle or other final purification step may have to be applied to the two-cycle product.

The reactor proposed by the Power Reactor Development Company for construction near Detroit, Michigan, will employ a fuel which is rather unique in the power reactor field, consisting of 27% enriched uranium alloyed with 10% molybdenum and clad in zirconium. Pierce and associates at the Brookhaven National Laboratory are studying the processing of this fuel by TBP solvent extraction methods. A complication is the limited solubility of molybdenum in acid feeds. Employing a mixture of nitric and hydrofluoric acids in the dissolving step this fuel may be dissolved to yield a feed containing 2.5 M HNO_3 , 0.06 M F^- , 23 g U/l, 0.028 M Mo(VI), 0.012 M Zr(IV) which can be satisfactorily processed by a TBP extraction process. Tests in bench-scale mixer-settlers indicate that molybdenum is not extracted by the TBP solvent. It has also been observed that addition of ethylene diamine tetraacetic acid in a molar concentration equal to that of the molybdenum permits the molybdenum to be stabilized in solution at uranium concentrations as high as 130 g U/l and at acidities appropriate for nitric acid salted TBP extraction processes.

Workers at the Oak Ridge National Laboratory have demonstrated that satisfactory separation of uranium from precipitated molybdic acid can be accomplished by washing the precipitate with nitric acid or by selectively dissolving the molybdic acid in an alkaline solution, leaving the uranium as a hydrous oxide which can then be dissolved in nitric acid and blended with the feed.

RECOVERY OF MINOR COMPONENTS OF IRRADIATED FUELS

An expanding interest in research employing neptunium-237 and americium-241 has prompted studies at several United States laboratories of means of recovering these products.

Recovery of Neptunium-237

Neptunium-237 arises in neutron-irradiated uranium by two routes, as follows.

With uranium fuels of low enrichment the first process is predominant at relatively low exposures but the second process becomes important at high exposures, accounting for about half the neptunium-237 formed at 1400 MWD/t. With highly enriched uranium fuels the second process is of course the only one of importance.

Since significant quantities of neptunium are present in irradiated natural uranium, considerable attention has been given to the recovery of neptunium-237 as a third product in the Purex processes presently employed to recover uranium and plutonium from these fuels. The extraction behavior of neptunium-237 in TBP extraction processes has been studied by Siddall and associates at the Savannah River Laboratory, by Sheppard and Keder at the Hanford Laboratories, and by Lewis, Flanary, and Goode at the Oak Ridge National Laboratory. Simultaneous recovery of neptunium with uranium and plutonium is complicated by the existence of three oxidation states of neptunium of relative extractability neptunium(VI) > neptunium(IV) >> neptunium(V). In nitrate systems, neptunium(V) is virtually inextractable by TBP solvent systems. The equilibrium distribution coefficients* for both neptunium(IV) and neptunium(VI) increase with increasing aqueous nitrate and decrease with increasing uranium concentration in the organic phase (i.e., with increased solvent saturation). With 30 volume % TBP in a hydrocarbon diluent, distribution coefficients at constant 70% solvent saturation are in the range 0.1 to 0.2 for neptunium(IV) and 1 to 2 for neptunium(VI) at aqueous phase acidities of 1.5 to 2.0 M HNO_3 . Extraction as neptunium(VI) obviously represents the best chance of co-extracting neptunium with plutonium and uranium. It has been demonstrated that co-extraction of neptunium with uranium and plutonium can be effected by adding oxidants such as bromate or nitrite to the scrub stream in a typical Purex dual-purpose extraction-scrub column.

* Distribution Coefficient = Distribution Ratio = $\frac{\text{Concentration in organic}}{\text{Concentration in aqueous}}$

Reductants such as iron(II) which are customarily used to reduce plutonium to plutonium(III) to accomplish separation from uranium reduce neptunium to neptunium(IV), which is moderately extractable in the TBP solvent system. A combination of high aqueous phase nitrate concentration and a low ratio of aqueous to organic flow rate in a Purex uranium-plutonium partition column will therefore result in recovery of neptunium(IV) in the organic uranium-bearing stream. A low aqueous phase nitrate concentration and larger ratio of aqueous to organic flow rates will yield recovery of neptunium(IV) in the aqueous, plutonium(III) bearing stream. Within the range of conditions which yield acceptable separation of uranium and plutonium, neptunium can therefore be forced into either the uranium stream or the plutonium stream, or split between the two streams. The choice is dictated by the rangeability of the partition cycle contactors and the relative ease with which neptunium may be recovered from the uranium or plutonium streams in a given plant.

Tober and associates at the Savannah River Laboratories and Sheppard at the Hanford Laboratories have demonstrated that neptunium(IV) is efficiently absorbed by strong-base anion exchange resins out of nitrate solutions. A complication is the necessity of using a reductant to maintain neptunium in the tetra-valent state in the anion exchange step and the fact that most of the reducing agents which can be used result in gas formation in the resin bed. However, the Savannah River workers have found that digestion of the reduced feed at elevated temperature prior to the anion exchange loading step minimizes the gassing problem and still permits excellent recovery of neptunium. The work at Savannah River on the processing of neptunium by anion exchange is discussed by Tober in paper 225.(13)

If neptunium(IV) is recovered in the plutonium(III) product from a partition cycle and if an additional solvent extraction cycle is to be used for final purification of plutonium, a convenient means of separating neptunium and plutonium is to oxidize to plutonium(IV) and neptunium(V), e.g., with nitrite, whereupon the neptunium is diverted into the aqueous waste in the plutonium extraction column. The neptunium in this waste can then be reduced to neptunium(IV) and recovered by anion exchange methods such as are discussed by Tober or by cation exchange methods such as are discussed by Lewis, et.al., in paper 704.(24)

If neptunium is diverted into the uranium stream in the partition cycle it can be delivered to the aqueous waste in a subsequent uranium extraction cycle by reducing to neptunium(IV) and employing relatively low concentrations of salting agent in the aqueous phase and relatively high solvent saturation. Recovery from such wastes can be effected by ion exchange methods as indicated previously. It is usually necessary to add a reducing agent in the final uranium cycle to avoid contamination of the uranium product with plutonium. This necessity precludes forcing neptunium into the aqueous waste as neptunium(V) or recovering it by extraction with uranium as neptunium(VI). Recovery of neptunium with the uranium product can be accomplished without contaminating the uranium with plutonium by adding a reducing agent in the final cycle to convert plutonium and neptunium to plutonium(III) and neptunium(IV) and employing conditions (somewhat higher concentrations of salting agent and lower solvent saturation) which enable extraction of neptunium(IV). If neptunium is forced into the uranium product it can be conveniently recovered from the solid residue ("ash")

which remains after conversion of the uranium product to UF_6 . Lewis and associates at the Oak Ridge National Laboratory have demonstrated a solvent extraction flowsheet for recovery of neptunium from this "ash". The fluoride salts are dissolved in aluminum nitrate-nitric acid solution. Extraction of residual uranium and the neptunium are accomplished by extraction into 15 volume % TBP in the first of a series of three contactors. Removal of impurities is effected using an aluminum nitrate-nitric acid scrub in the scrub section of this contactor. The scrubbed organic extract cascades to a second contactor where neptunium is preferentially stripped from the uranium by 0.5 M HNO_3 . In the third contactor, uranium is stripped into 0.01 M HNO_3 . This flowsheet yielded recovery of 99% of the neptunium and separation from uranium by a factor of 10^5 in the Metal Recovery Pilot Plant at the Oak Ridge National Laboratory.

The Oak Ridge workers, on the basis of their experience in recovery of neptunium from depleted uranium obtained from the Canadian Chalk River plant, have advanced the modified Purex flowsheet of Figure 12 for recovery of uranium, plutonium, and neptunium. The development studies on which this flowsheet is based are discussed by Lewis, et.al., in paper 704. The principal departure from a conventional Purex flowsheet is the insertion of a neptunium-uranium partition column in the second uranium cycle.

This flowsheet has not been tested in its entirety. However, the conditions stipulated for the neptunium-uranium partition column are essentially those which resulted in retention of only 1% of the neptunium with the uranium and less than 0.001% of the uranium with the neptunium in the pilot plant processing of the Chalk River uranium. The specification of 1.5 M HNO_3 in the plutonium product (1BP) from the uranium-plutonium partition column reflects experience gained in the pilot plant processing of the Chalk River feed in which it was found that an acidity of 1.4 M HNO_3 in the aqueous effluent from the uranium-neptunium partition column forced more than 95% of the neptunium into the uranium stream. A supplemental 67 hour run confirmed the feasibility of recovering neptunium in the 1A column by adding 0.05 M nitrite in the 1AS. The loss of neptunium was less than 1% when nitrite was added to the scrub but increased to 100% when the nitrite was omitted. It is noteworthy that addition of 0.04 M $FeSO_4(NH_4)_2SO_4$, 0.08 M NH_2SO_3H to the 1AS permitted efficient recovery of neptunium from the Chalk River feeds under conditions identical in other respects to the 1A flowsheet of Figure 12. Omission of the reductant resulted in an 80% loss of neptunium. Thus neptunium recovery can be effected in this column with either an added oxidant or reductant, but not otherwise.

A process for recovering neptunium from irradiated highly enriched fuels was also tested in the Oak Ridge National Laboratory Metal Recovery Pilot Plant. The uranium-aluminum alloy fuel was dissolved in HNO_3 and processed through two cycles of solvent extraction using TBP solvent systems and aluminum nitrate salting. In the first cycle uranium and neptunium were recovered and decontaminated from fission products and other impurities by extraction into 2 volume % TBP. Separation and further decontamination of uranium and neptunium was accomplished in a second cycle using 15 volume % TBP. Recovery exceeded 99% for both uranium and neptunium.

Exploratory studies by Sheppard and Wilson at the Hanford Laboratories indicates that extraction with diluted solutions of trialkyl amines holds promise as a means of recovering and purifying neptunium.

Neptunium(IV) can be efficiently extracted out of nitric acid solutions into diluted solutions of tri-n-octyl amine or tri-laurylamine. Efficient separation from uranium and fission products appears possible. Stripping can be effected by oxidizing to neptunium(V) with nitrite. This work has been discussed by Sheppard.(25)

Recovery of Americium

Solvent extraction with TBP was successfully applied by Lewis and associates to recover americium from aged plutonium metallurgical wastes in the Metal Recovery Pilot Plant at the Oak Ridge National Laboratory. The plutonium was extracted in a conventional solvent extraction cycle employing 30 volume % TBP in Amsco. The aqueous waste from this cycle contained the americium. This waste was neutralized with ammonia and processed according to the flowsheet shown in Figure 13. Separation of americium from the bulk of the residual plutonium was accomplished in a dual-purpose stripping column in which americium was preferentially stripped into 0.05 M HNO_3 . The americium was isolated by a cation exchange cycle employing Dowex-50. Principal cationic impurities which accompanied the americium were rare earths (primarily lanthanum) and stainless steel corrosion products, and some plutonium. Final purification of the americium was accomplished in further cation exchange steps in which Dowex-50 columns were loaded to $\leq 30\%$ of their length out of a feed in which the concentrations of hydrogen ion and ammonium ion were adjusted to 0.1 - 0.2 M, and 0.5 M, respectively. Elution with either concentrated HCl or with 0.15 M citric acid - 0.10 M diammonium citrate (pH 3.2) resulted in removal of americium ahead of the lanthanum and produced an americium product of acceptable purity.

CHEMICAL AND RADIATION DAMAGE EFFECTS IN SOLVENT SYSTEMS

The widespread use of TBP solvent systems in the processing of irradiated fuels in nitrate solutions has prompted studies in several United States laboratories of the chemical reactions which these solvents undergo with aqueous nitrate systems and of the effects of ionizing radiations on these solvent systems. A detailed discussion of this work is beyond the scope of this paper and since excellent reviews have already been published in this field, attention is herein confined to recent and hitherto unpublished work.

Chemical reactions of TBP which are pertinent to fuel processing applications have been reviewed by Burger.(26) Previously-unpublished information which supplements this review is discussed in the sections following.

Oxidation Reactions

Tributyl phosphate is quite stable toward both thermal decomposition and chemical oxidation. The reactions of TBP with acid dichromate or with acid or alkaline permanganate are quite slow at room temperature and these reagents may be used to remove easily oxidized impurities from TBP. Indeed, treatment with

alkaline permanganate is shown in a later section to be an effective method for purifying process solvents for re-use. The stability of TBP toward reactions with nitric acid is, of course, one of its main virtues in nuclear fuel processing. However, it should be recognized that TBP can undergo violent reaction with nitrates or nitric acid under extreme conditions. In particular, the work of Wagner at Hanford and of Colven, Nichols, and Siddall at Savannah River discloses that:

- (1) TBP-uranyl nitrate-nitric acid - water systems will undergo highly exothermal reactions at temperatures above 135°C, the normal boiling point of uranyl nitrate hexahydrate. Reactions of explosive violence can result with rapid external heating to above 135°C.
- (2) Violent reactions can be initiated in TBP-nitric acid - water systems by rapid heating to above 130°C in the case of 15 M HNO_3 and to above 160°C in the case of 4 M HNO_3 . The threshold temperatures for violent reactions can be reduced by from 300 to 400°C by introducing glass wool into the system.
- (3) Nitric acid promotes the reaction between TBP and uranyl nitrate.
- (4) The vigor of the reaction increases as the ratio of TBP to uranyl nitrate is increased.
- (5) At high pressures, sustained reactions are possible at lower concentrations.

The implications of these reactions in the design of evaporators for nitric acid or uranyl nitrate solutions in fuel processing plants employing TBP are readily apparent.

Hydrolysis

The hydrolysis of TBP has been studied by a number of investigators. Rate constants for the process in both acid and alkaline media have been compiled by Burger. The acid-catalyzed hydrolysis is probably the most important reaction of TBP from the standpoint of nuclear fuel processing. It occurs in both the organic and aqueous phases and proceeds in stepwise fashion, yielding in turn dibutyl phosphate ("DBP"), monobutyl phosphate ("MBP"), and finally H_3PO_4 . The complicating effects of these on product recovery and fission product decontamination in TBP extraction processes are well known. In most processing applications the first hydrolysis reaction (yielding DBP) is the only one of importance. The TBP solvent is ordinarily subjected to an alkaline wash after each use. This suffices to remove the acidic DBP and the second and third hydrolysis reactions are therefore given little opportunity to occur.

It should be noted that in typical fuel processing applications the "hydrolysis" reaction (according to the work of Blumenthal and Herbert⁽²⁷⁾ perhaps more properly termed dealkylation) which occurs in the organic phase is by far the more important source of DBP. Although the rate constants are higher by a factor of 10 to 100 in the aqueous phase than in the organic phase, the solubility of TBP in the aqueous phase is so low that with typical organic/aqueous flow ratios the organic phase reaction contributes more than 90% of the DBP formed.

Burger has studied the partition of DBP between 20 volume % TBP in a kerosene diluent (Shell Spraybase) and aqueous nitrate solutions.⁽²⁸⁾ These (hitherto unpublished) data are presented in Figure 14.

From these data Burger has estimated the distribution coefficient of undissociated DBP to be 7.2 and the association constant for the dimerization reaction to be 4. Thus at an organic phase concentration of 100 ppm DBP more than 99% of the DBP is monomolecular.

Applying the data of Figure 14 to typical continuous countercurrent uranium stripping contactors it is seen that reflux of DBP can occur in such contactors. However, calculations for a stripping contactor comprising 2 or 3 theoretical stages indicates that although DBP reflux by a factor of 10 may occur, by far the major portion of the DBP will leave the contactor in the organic stream. The aqueous product from such a contactor should contain no more than 1 to 2 ppm DBP with as much as 500 ppm DBP in the entering organic feed.

Chemical Reactions of Hydrocarbon Diluents

Studies of the chemical degradation suffered by TBP-hydrocarbon mixtures on prolonged exposure to nitric acid solutions at elevated temperature lead to a conclusion that the hydrocarbon diluents are the primary source of the offending substances which have a long-term effect on process performance. The products of TBP hydrolysis are easily removed in the solvent treatment steps which normally employ alkaline washes. Offending substances formed by reaction with the diluent resist removal in this operation, however, and therefore accumulate as the solvent is continually recycled.

R. H. Moore has identified several of the classes of compounds which are formed in prolonged recycle of a TBP-Shell Spraybase solvent.⁽²⁹⁾ The major fractions identified were compounds containing carbonyl or carboxyl groups, compounds containing nitro groups, and compounds containing nitroso groups. Compounds containing carbonyl and carboxyl groups presumably result from oxidative attack on the hydrocarbon diluent. Nitro compounds presumably arise through direct nitration reactions. Nitroso compounds may arise through secondary reactions between nitrous acid and nitro compounds (or other active intermediates). The further observation that the fraction containing the nitroso derivatives was capable of drastically reducing the efficiency of fission product separation prompted further study of the role of nitrous acid in the chemical degradation of TBP-hydrocarbon compounds.

Moore has therefore conducted experimental studies in which TBP-hydrocarbon solvents were agitated with solutions of nitric and nitrous acid at temperatures ranging from 25°C to the reflux temperature for prolonged periods of time. Concentrations of nitric and nitrous acid in both phases were determined as a function of time and the process utility or "quality" of the solvent was evaluated by measuring its optical density at 330 m μ and by measuring the distribution coefficient for uranium when the degraded solvent was contacted with an equal volume of an aqueous uranyl nitrate solution containing 1 g/l U. The degraded solvent was washed with sodium carbonate solution to remove DBP and other highly acidic impurities prior to contact with the uranium solution. Previous work had shown that this simple index yields results paralleling those obtained by evaluating the ability of degraded solvents to irreversibly extract radiozirconium tracer or gross fission product activity.

Perhaps the most significant conclusion to be drawn from this work is the fact that nitrous acid must be present in order to generate products capable of altering the extraction of uranium. For example, exposure of 30 volume % TBP - 70 volume % Shell E-2342* for 48 hours at 70°C to a solution which initially contained 6 M HNO_3 , 0.05 M NaNO_2 resulted in an increase in the uranium distribution coefficient ($E_Q(\text{U})$) from 0.014 to 2.70. By contrast, exposure of the same solvent for 72 hours at 70°C to a solution which contained initially 6 M HNO_3 , 0.1 M $\text{NH}_2\text{SO}_3\text{H}$ resulted in no change in the value of $E_Q(\text{U})$ which remained at 0.005 to 0.006 throughout the entire exposure. It may be noted that experience indicates that fission product decontamination suffers when the value of $E_Q(\text{U})$ increases above about 0.02. Addition of urea gave results comparable to those obtained in the above-described experiment with sulfamic acid.

Examination of the variation of $E_Q(\text{U})$ with time, nitric acid concentration, and nitrous acid concentration shows the data to be consistent with a mechanism such as the following.

- (1) Nitric acid reacts with the solvent in reactions which are catalyzed by nitrous acid and which produce both oxidation products and nitro compounds. Since nitrous acid is one of the products, certain of these reactions at least are autocatalytic. Further, an indeterminate fraction of the products are innocuous in the sense that they do not alter the value of $E_Q(\text{U})$.
- (2) Certain of the products formed in (1) react with nitrous acid to yield products (e.g., nitroso compounds or nitrolic acids), which strongly and adversely affect the process utility of the solvent, as measured by the change in $E_Q(\text{U})$ value.

Although most of Moore's work employed Shell-E-2342, the generally similar behavior of a number of other hydrocarbon diluents in earlier studies suggests that nitrous acid plays an important role in the degradation of these as well. The work of Karraker, Siddall, and others at the Savannah River Laboratory indicates that highly purified paraffinic hydrocarbons such as n-dodecane are sufficiently resistant to attack by nitric-nitrous acid systems to be used in Purex systems at 70°C. Moore's work indicates that less expensive diluents may be acceptable for use at elevated temperatures provided agents such as sulfamic acid are added to destroy nitrous acid.

Effects of Ionizing Radiation on Solvent Systems

The effects of ionizing radiation on TBP-diluent systems are receiving increased attention in connection with the processing of reactor fuels in which solvent systems may be exposed to aqueous feeds containing several hundred curies per liter of beta-gamma radiation. Contributions by United States investigators in this field include the work of S. S. Jones at the Knolls Atomic Power Laboratory, Baldwin, Cathers, Goode, and Burr at the Oak Ridge National Laboratory, Nichols at the Savannah River Laboratories, and Burger and McClanahan at the Hanford Laboratories. Recent (and hitherto unpublished)

* A naphthenic base kerosene fraction.

work by Blanco and Goode at the Oak Ridge National Laboratory, Wagner and Kinderman at the Stanford Research Institute, and Wymer at the Georgia Institute of Technology is summarized in the sections following.

Radiation Effects in Amsco 125-82

The effects of ionizing radiation upon a typical hydrocarbon diluent, Amsco 125-82, have been studied by Wymer and by Wagner and Kinderman. This kerosene fraction is composed of about 17 highly branched saturated hydrocarbons ranging from $C_{16}H_{26}$ to $C_{14}H_{30}$, with five present in greater than 9 mole %. Major components are 2,2,4,6,6 pentamethyl heptane and 2,2,3,4,5,5 hexamethyl hexane. Principal degradation products resulting from radiations of the 2,2,4,6,6 pentamethyl heptane fraction with a 50 kvp X-ray source were hydrogen and methane, with G values* of 1.15 and 0.78, respectively. Gas chromatography showed 20 degradation products in the range C_1 to C_8 with 7 major peaks of C_4 hydrocarbons, principally butanes and butenes.

Irradiation of Amsco 125-82 with 1 Mev electrons, cobalt-60 gamma radiation, and gamma radiation from mixed fission products resulted in formation of unsaturated hydrocarbons as one of the major chemical effects in both wet and dry systems. The iodine number for the irradiated product increased with radiation up to a dose of 1000 watt-hrs/liter, but remained constant at higher doses. The absence of further increase in the iodine number at higher doses is attributed to polymerization of the unsaturated products. Approximately 16 weight % polymer was formed when Amsco was irradiated to 1900 watt-hrs/liter. Irradiation of dry Amsco 125-82 to 780 watt-hrs/liter produced gaseous products with G values as follows: total gas, 4.62; C_1 - C_4 hydrocarbons, 1.95; hydrogen, 2.10. Nitration, in amounts proportional to the radiation dose, occurred in samples irradiated in the presence of aqueous nitrates.

Radiation Effects in TBP and TBP-Diluent Systems

Gaseous products formed on irradiation of pure, dry TBP include hydrogen and hydrocarbon gases ranging from C_1 to C_4 . Comparing the data of Burr with more recent results reported by Wagner and Kinderman, little change in G values for gaseous products is noted on increasing the dose from 123 watt-hrs/liter to 1420 watt-hrs/liter. Burr found G values of 1.73 for hydrogen, 0.072, 0.177, 0.129, and 0.525 for C_1 , C_2 , C_3 , and C_4 hydrocarbons, respectively, or a G value of 3.10 for all gases, on irradiating TBP to a dose of 123 watt-hrs/liter with 1.56 Mev electrons. Wagner and Kinderman found slightly lower G values of 1.59 and 0.95 for hydrogen and C_1 - C_4 hydrocarbons, respectively, or a total gas G value of 2.54 on irradiating TBP to 1420 watt-hrs/liter with 1 Mev electrons.

* G value - number of molecules of indicated product formed per 100 ev absorbed.

Liquid products formed on irradiation of pure, dry TBP include the products of dealkylation reactions DBP, MBP, and H_3PO_4 , and polymeric species of incompletely defined composition. Burger and McClanahan(30) also identified butyl alcohol among the liquid products formed on irradiating TBP with cobalt-60 gamma radiation. Increase in the radiation dose results in increase in the G values of MBP, H_3PO_4 , and polymer, and decrease in the G value of DBP. Burr found G values of 2.44 and 0.14 for DBP and MBP, respectively, with a dose of 123 watt-hrs/liter (1.56 Mev electrons). At a dose of 250 watt-hrs/liter (cobalt-60 gamma radiation), Burger and McClanahan found DBP and MBP formed with G values of 1.8 and 0.3, respectively, but found no H_3PO_4 or polymer. At a dose of 1420 watt-hrs/liter, Wagner and Kinderman found G values of 0.39 for DBP, 2.25 for MBP + H_3PO_4 , and 0.91 for polymer, the latter value computed on the basis of the average molecular weight of 840 to 850 determined for the polymer by cryoscopic measurements.

Studies of the effect of additives on the radiolysis of TBP afford particularly interesting comparisons. Rather surprisingly, Burger and McClanahan found that the G value for DBP formation (when computed on the basis of the energy absorbed by TBP) was reduced from 1.8 to 1.2 (at 250 watt-hrs/liter) when an equimolar amount of water was added to TBP or when TBP was diluted with an equal volume of n-butyl alcohol. These investigators also found that addition of benzene decreased the yield of DBP in direct proportion to the mole fraction of benzene in the mixture. Addition of carbon tetrachloride produced the expected large increase in DBP yield, the DBP yield increasing by a factor of 9 as the concentration of CCl_4 in the mixture was increased to 90 volume %.

Wagner and Kinderman found that irradiation of TBP containing dissolved nitric acid resulted in a substantial increase in gaseous products, which included nitrogen oxides formed by degradation of HNO_3 and CO and CO_2 formed by radiation-induced oxidation of the organic material. Irradiation of TBP containing 2 M HNO_3 to 80 watt-hrs/liter yielded G values of 2.17 for hydrogen, 0.81 for CO_2 , 0.41 for N_2O , 1.62 for NO, 1.08 for $\text{N}_2 + \text{CO}$, and 0.41 for $\text{C}_1\text{-C}_4$ hydrocarbons, or 6.49 for total gas. Similar increases in gaseous products were noted on irradiating 5 volume % TBP - 95 volume % Amsco 125-82 in contact with an aqueous 2 M HNO_3 solution.

Burger and McClanahan found that G values for DBP and MBP (computed on the basis of energy absorbed by TBP on irradiation to 250 watt-hrs/liter) were not significantly altered when TBP was diluted with iso-octane or a typical kerosene diluent, Soltrol-170. Wagner and Kinderman found the G values for DBP and MBP + H_3PO_4 (computed on the basis of energy absorbed by TBP) were, respectively, greater by a factor of 2.4 and lower by a factor of 5 for 50 volume % TBP - 50 volume % Amsco 125-82 irradiated to 1455 watt-hrs/liter than for pure, dry TBP irradiated to 1420 watt-hrs/liter.

Effects of Ionizing Radiations on Other Organophosphorus Compounds

Wagner and Kinderman have also studied the radiolysis of other organophosphorus compounds of potential interest as solvents. G values for total gas and total acid for these compounds are compared with those for TBP in Table I.

The stabilizing effect of an aromatic structure is seen in the considerably enhanced stability of dibutyl phenylphosphonate as compared with the other compounds. The phosphonate structure must in itself account for some of the enhanced stability, however, as indicated by the fact that the alkyl phosphonates are also somewhat more stable than TBP.

Process Implications of Solvent Radiolysis

The degradation products resulting from solvent radiolysis (which it may be noted are identical to those resulting from chemical degradation) may complicate fuel processing through the formation of emulsions and the formation of organic-soluble complexes with uranium, plutonium, thorium, and fission products. Blanco and Goode at the Oak Ridge National Laboratory have evaluated the effects of the products of solvent radiolysis on the Thorex and other processes. Emulsion formation promoted by formation of thorium dibutyl phosphate may require that the radiation dose per cycle in the Thorex process be limited to less than 10 watt-hrs/liter. Emulsion formation in the Purex system or in the TBP process for enriched uranium-235 fuels did not appear to be significant below doses of about 400 watt-hrs/liter. In these latter systems, therefore, the working limit will be determined by the effects of the radiolysis products on decontamination and product losses and appears to be in the range 15 to 30 watt-hrs/liter.

Laboratory studies at the Oak Ridge National Laboratory have shown that TBP-Amsco solvent contacted with Thorex dissolver solution to 300 watt-hrs/liter was successfully purified by successive washing with sodium carbonate and nitric acid and was indistinguishable from fresh solvent in subsequent extraction and stripping tests.

Addition of DBP, phosphate "polymer", or irradiated TBP to Purex systems in amounts corresponding to radiation doses of 1000 watt-hrs/liter did not cause significant emulsification. Retention of uranium in the solvent phase did occur; DBP accounted for about 65% of the uranium retention, the polymer accounted for about 20% of the effect.

A summary of predicted and measured effects of radiolysis on process performance is shown in Figures 16 and 17.

In connection with problems of emulsion formation in TBP processes, it should be noted that processes handling significant amounts of zirconium may be expected to be sensitive to emulsion formation, in similar fashion as found for Thorex feeds. Brite⁽³¹⁾ has shown that the DBP content of a TBP-hydrocarbon solvent is directly related to the increased time required for the phases to disengage when the solvent is contacted with a colloidal zirconium aqueous phase. Indeed, this phenomenon has been made the basis of a highly sensitive and useful, albeit empirical, analytical method for DBP.

Solvent Recovery Methods

A number of techniques have been studied for accomplishing removal of fission product activity and offending organic degradation products from TBP-diluent solvents. Vacuum distillation apparently represents a method for complete solvent purification. Steam distillation is also capable of removing both fission product activity and the solvent degradation products.

Aqueous washing operations which yield efficient purification of solvents from both fission products and degradation products include washes with 1.0 M NaOH - 1.0 M NH_4OH , or washes with alkaline permanganate solutions.

POTENTIAL NEW SOLVENTS

The work of a number of investigators has contributed much useful information on other organic compounds which may find advantageous use in the future as solvents for the processing of nuclear fuels. A comprehensive review of this work is beyond the scope of this paper. However, two classes of compounds, organophosphorus compounds and alkyl amines, which show particular promise for the processing of nuclear fuels are briefly discussed in the sections following.

Organophosphorus Compounds

The desirable properties of chemical stability and high extraction capability and selectivity for actinide elements which have led to widespread use of TBP in the processing of nuclear fuels have prompted a rather intensive study of the solvent properties of other organophosphorus compounds. United States investigators who have made notable contributions to this study include Katzin and co-workers at the Argonne National Laboratory, C. E. Higgins, Baldwin, and Ruth, and K. D. Brown and associates at the Oak Ridge National Laboratory, Burger at the Hanford Laboratories, and Siddall at the Savannah River Laboratories. For purposes of discussion, distinction is made between two classes of organophosphorus solvents, i.e., neutral compounds and acidic compounds.

Neutral Organophosphorus Solvents

The solvent properties of four classes of compounds containing the phosphoryl ($\text{P}=\text{O}$) group have been studied;

Burger⁽³²⁾ has shown that the extraction ability of diluted solutions (0.5 M solvent in carbon tetrachloride) of these compounds for uranium(VI) and plutonium(IV) and plutonium(VI) out of nitrate solutions can be correlated in terms of the basicity of the phosphoryl oxygen, as measured by the infrared stretching frequency of the phosphoryl group. His data are shown in Figure 17. The curve for uranium(VI) extraction represents data obtained with 14 phosphates, 18 phosphonates, 3 phosphinates, and 3 phosphine oxides. The curves for plutonium(IV) and plutonium(VI) extraction comprise data for 3 phosphates, 3 phosphonates, and 2 phosphinates. Infrared absorption maxima attributed to the P - O stretching vibration occurred at frequencies of about 1270 cm^{-1} for alkyl phosphates, 1242 cm^{-1} for alkyl phosphonates, 1192 cm^{-1} for alkyl phosphinates, and 1157 cm^{-1} for alkyl phosphine oxides. The extraction efficiency for uranyl nitrate, as measured by the distribution ratio for extraction out of a solution initially 0.2 M in uranyl nitrate and into a 0.5 M solution of the organic compound in carbon tetrachloride, was greater by a factor of over 100 for alkyl phosphine oxides than for alkyl phosphates. It might be noted that a wider variation in distribution coefficients would be expected under conditions of constant ionic strength in the aqueous phase. In the measurements of Figure 16, the ionic strength of the equilibrium aqueous phase decreased as the extraction of uranyl nitrate increased.

Burger found also that introduction of electronegative substituents such as chlorine in the alkyl groups virtually destroyed the solvent power of phosphates. Uranium distribution coefficients were less than 0.01 for tri (*B*-chloroethyl) phosphate as compared with a value of 0.19 for tributyl phosphate. The inductive effect in phenyl groups linked to the phosphorus by a C - O - P bond also virtually destroyed the solvent power; the uranium distribution coefficient with triphenyl phosphate was less than 0.01. The presence of an ether oxygen in the substituents had only a slight effect on uranium extraction; uranium distribution coefficients of 0.14 were obtained with both dibutyl ethoxyethyl phosphate and tributoxyethyl phosphate as compared with a value of 0.19 for tributyl phosphate.

Linkage of phenyl groups through a direct C - P bond does not reduce the solvent power to as great an extent as phenyl groups linked through a C - O - P bond. For example, uranium extraction distribution coefficients for extractions of uranium by dioctyl phenyl phosphonate and diethyl phenyl phosphonate were 0.31 and 0.30, respectively, as compared with values of 0.9 to 1.1 under the same conditions with alkyl phosphonates.

Burger also prepared crystalline compounds of the structure $\text{UO}_2(\text{NO}_3)_2(\text{Ester})_2$ with butyl dibutyl phosphinate, with dibutyl phenyl phosphonate, with tributyl phosphine oxide, and with triphenyl phosphine oxide. In all cases, water was not present in the solid salt. The triphenylphosphine oxide complex proved highly stable, no evolution of oxides of nitrogen being observed below about 290 to 310°C.

The selectivity of these classes of compounds for the actinide elements has not been thoroughly studied. Siddall presents a comparison in paper 226⁽³³⁾ of the extraction of uranium, thorium, and zirconium by tri-n-butyl phosphate, and by several alkyl phosphonates. The greater extraction capability exhibited by the phosphonates permits a lower concentration of nitric acid salting agent to be used to obtain extraction of uranium or thorium. This in itself permits

improved separation from zirconium. Also, even at these lower aqueous phase acidities a higher mole ratio of uranium or thorium to extractant can be established than is possible even at the higher acidities required for extraction with TBP. Thus the concentration of uncomplexed extractant available for extraction of fission products is reduced.

An additional advantage of di n-amyl n-amyl phosphonate (DAAP) in the processing of thorium is pointed out by Siddall. No third phase is formed on extraction of thorium nitrate into a solution of DAAP in a paraffinic hydrocarbon diluent until organic phase concentrations of thorium so high as to be of little practical interest in thorium processing are reached. This is in sharp contrast to the behavior with TBP, in which case organic phase thorium concentrations must be limited to rather low values to avoid formation of a third phase with typical kerosene diluents.

It should be noted that the greater solvent strength of the more polar organophosphorus compounds has certain disadvantages in that it complicates the re-extraction of the products into an aqueous phase. In extraction of uranium by a phosphonate, for example, the product must be stripped as a rather dilute aqueous solution. Increasing the temperature or introduction of complexing agents can be used to improve equilibria in the stripping operation, however.

K. D. Brown and associates at the Oak Ridge National Laboratory have shown that efficient extraction of uranium(VI) or plutonium(IV) can be effected by trialkyl phosphine oxides out of sulfuric acid. For example, uranium(VI) exhibited a distribution coefficient of 20 between 3, 4, or 5 M H_2SO_4 and a 0.3 M solution of tri-n-decyl-phosphine oxide in kerosene. Plutonium(IV) was extracted out of 3 M H_2SO_4 into a 0.3 M solution of tri-n-octylphosphine oxide in Amsco 125-82 with a distribution coefficient of 17. Distribution coefficients were much lower (about 0.1) out of 3 M SO_4^{2-} solutions adjusted to a pH of 1 but addition of a relatively small amount of nitrate sufficed to establish usable distribution ratios.

Acidic Organophosphorus Solvents

K. D. Brown and co-workers⁽³⁴⁾ at the Oak Ridge National Laboratory have conducted an extensive study of solvent extraction methods for recovering and purifying uranium from ore leach liquors. Since the uranium values in uranium ores are generally obtained as a dilute solution in sulfuric acid or sodium carbonate, more powerful uranium extractants are required for this application than are customarily used for processing irradiated uranium fuels in nitrate solutions. One class of compounds which has proved particularly useful in the recovery of uranium from sulfuric acid leach liquors are the dialkyl phosphates. These extract uranium out of acidic chloride, sulfate, or nitrate solutions by a cation exchange mechanism, which may be represented by the equation.

Stripping of the uranium can be effected with concentrated acids which reverse the above equilibrium or, preferably, with aqueous solutions of ammonium or sodium carbonate which accomplish uranium stripping according to the equations.

Uranium is recovered in the aqueous phase as the soluble tricarbonat complex and the dialkyl phosphate is converted into the sodium or ammonium salt. The sodium salts (but not the ammonium salts) tend to precipitate from the organic phase either as solids or as a third liquid phase. However, it is possible to avoid this by adding a long chain, aqueous-insoluble alcohol.

The Dapex process⁽³⁴⁾, which recovers uranium by extraction into a solution of di 2-ethylhexyl phosphate in kerosene, has been applied on a commercial scale to the processing of sulfate leach liquors.

A particularly interesting outgrowth of the search for reagents to prevent the aforementioned third phase formation when stripping with sodium carbonate was the discovery that certain organic phosphorus compounds, in addition to preventing third-phase formation, gave in combination with di 2-ethylhexyl phosphate uranium extraction coefficients greater than could be accounted for by simply summing the extraction coefficients for either reagent alone. This synergistic enhancement of uranium extraction is most pronounced for phosphine oxides and decreases from phosphine oxides to phosphinates to phosphonates to phosphates. For example, the uranium extraction coefficient from 0.5 M sulfate solution at a pH of 1 into 0.1 M di 2-ethylhexyl phosphate is 135. Addition of 2% 2-ethylhexanol reduces the coefficient to 40. Addition of 0.08 M TBP increases the coefficient to 800 while addition of 0.05 M tributyl phosphine oxide increases the coefficient to 7000. Since none of the neutral compounds alone will extract uranium from sulfate solutions at these concentrations the increased extraction must be attributed entirely to synergistic effects.

Recently, Brown and associates have considered application of solvent extraction with dialkyl phosphates to certain radiochemical separations, notably the recovery of such potentially useful fission products as strontium-90 and cesium-137. Strontium in dilute sodium nitrate solutions displaces sodium from sodium dialkyl phosphate salts with high efficiency over a wide range in pH. The separation factor for strontium and sodium (i.e., $E_a^{\text{O}}(\text{Sr})/E_a^{\text{O}}(\text{Na})$) was nearly constant at about 50 (corresponding to $E_a^{\text{O}}(\text{Sr}) = 10$ and $E_a^{\text{O}}(\text{Na}) = 0.2$) for extraction into 0.1 M di 2-ethylhexyl phosphate out of 0.5 M NaNO_3 solution containing 10 ppm Sr and varying in pH from 7 to 13. At a pH of about 5 the extraction coefficient for strontium increased to about 200 and since about half of the extractant was in the acid form the separation factor increased to about 2000.

Distribution coefficients for cesium into di 2-ethylhexyl phosphate from 0.5 M nitrate solutions are slightly lower than those for sodium and no pH region of enhanced extraction has been found. Cesium was extracted preferentially (separation factors for Cs/Na of 30 maximum) by 0.1 M solutions of such mono alkyl phosphates as mono-1-(3-ethylpentyl)4-ethyloctyl phosphate but the extraction coefficients were low, only 0.2 to 0.7.

Alkyl Amine Solvents

Long chain alkyl amines have also been studied in some detail by Brown⁽³⁵⁾ and associates for application to recovery of uranium from ore leach liquors. When alkyl amines in appropriate organic diluents are contacted with aqueous mineral acid solutions they form the organic-soluble salts as exemplified by the equations.

In the salt form the amines are therefore functionally similar to weak base anion exchange resins and extract uranium out of aqueous mineral acid solutions by an anion exchange mechanism which, in oversimplified form, can be represented by the equations.

Actually the experimental evidence indicates that combining ratios are of the order of 6 amines per uranium in some cases, 4 in others.

Stripping can be accomplished by displacement by other anions such as chloride or nitrate, by complexing the uranium into aqueous solution as the tricarbonat complex or by precipitating the uranium directly from the organic phase as a granular polyuranate by contacting the amine extract with a slurry of magnesium oxide.

Certain amines show very high extraction power for uranium from acidic sulfate solutions, e.g., the uranium extraction coefficient is greater than 1000 for extraction out 1.0 M SO_4^{--} , pH = 1 into a 0.1 M solution of N-benzl-heptadecyl amine in kerosene.

The Amex process⁽³⁵⁾ for recovering uranium from leach liquors by amine extraction is presently under test on a pilot plant scale.

Although amines have as yet found no large-scale application in the processing of irradiated fuels, experimental studies by Brown and associates at the Oak Ridge National Laboratory, by Sheppard and Wilson at the Hanford Laboratories, and by Maraman and co-workers at the Los Alamos Laboratories, indicate considerable potential for these compounds in this field, particularly for plutonium processing. Sheppard and Wilson have demonstrated excellent plutonium extraction and separation from uranium and fission products by extraction out of

nitric acid solutions into diluted solutions of such tertiary amines as tri-n-octyl-amine or tri-lauryl-amine. The Los Alamos workers have preferred extraction with secondary amines for plutonium purification in applications not requiring separation from uranium. This work is discussed in detail in papers 578⁽³⁶⁾ and 819.⁽³⁷⁾

It may be noted that amines may very possibly have one very significant advantage over organophosphorus compounds for processing irradiated fuels, i.e., their degradation products are likely to be relatively innocuous, in sharp contrast to organophosphorus compounds. For example, Sheppard found that irradiation of tri-n-octyl-amine to 80 watt-hrs/liter did not significantly alter plutonium extraction behavior.

Alkyl amines and the more polar phosphorus compounds have in common another substantial advantage over solvents presently in use for irradiated fuels, viz, they are efficient extractants for uranium out of solutions containing such complexing anions as sulfate or phosphate. Thus they may well find application in the processing of power reactor fuels not conveniently dissolved in nitric acid. For example, such solvents could possibly be applied to the recovery of uranium from feed solutions prepared by dissolving stainless steel bearing fuels in sulfuric acid.

IMPROVED SOLVENT EXTRACTION CONTACTORS

The processing of irradiated fuels demands a higher order of separation efficiency than is required in any other current application of liquid-liquid solvent extraction. Further, experience gained in many years of continuous operation of solvent extraction plants indicates that the limit on performance is generally established by the contactors rather than by the chemical flowsheet.

Accordingly, studies have been pursued at several United States laboratories in recent years with the aim of developing solvent extraction contactors of increased capacity and improved separation efficiency.

The advent of the TBP solvent system, which performs poorly in packed towers, has caused experimental effort to be focused on contactors in which the solvent and aqueous phases are mixed by mechanical agitation. Contactors of this type in use in the United States for processes employing TBP solvents include pulsed columns (employing sieve plates or packing)⁽³⁸⁾ and pump-mix mixer-settlers.⁽³⁹⁾ The improved performance possible with pulse column cartridges of new design is discussed by Geier in paper 94.⁽⁴⁰⁾ The performance of a mixer-settler of nuclearly safe geometry is described by Colven in paper 222.⁽⁴¹⁾

Improved Pulse Column Internals

Pilot plant studies by Geier and associates at Hanford indicate that significant improvements can be made in both the capacity and separation efficiency of pulse columns by tailoring the cartridge specifically to the function to be performed. Pulse column cartridges which proved superior to previously described designs⁽³⁸⁾ are discussed in the paragraphs following. It should be noted that this work was done in behalf of developing improved pulse column cartridges for processing irradiated uranium by a Purex process employing 30 volume % TBP in a kerosene diluent. Caution should be used in applying these findings to other systems.

Uranium Extraction

Two cartridges which proved superior to conventional stainless steel sieve plate cartridges for effecting extraction of uranium from an aqueous phase into an organic phase are the graded cartridge and the nozzle plate cartridge. The graded cartridge is a stainless steel sieve plate cartridge tailored to yield essentially uniform dispersion throughout the length of the uranium extraction section. In a typical uranium extraction column in the Purex system the bulk of the uranium is extracted rapidly in a fairly short section just below the entry point of the aqueous uranium feed. Similarly, in a fairly short region in the bottom of the column just above the entry joint of the organic phase, rapid extraction of nitric acid occurs. These two regions are separated by a region in which the solvent is essentially in equilibrium with the only bulk extractable component, nitric acid, present in the aqueous phase. Thus, two regions of substantial net mass transfer (from aqueous to organic) are separated by an intermediate region of little net mass transfer. The systems in the regions of high net mass transfer show little tendency to disperse while the two-phase systems in the intermediate region of low net mass transfer show a significantly greater tendency to disperse. These effects are consistent with the known surface properties of TBP-hydrocarbon diluent systems. In these systems TBP acts as a surfactant, addition of TBP tending to lower the interfacial tension between aqueous and hydrocarbon phases. The complexes formed between TBP and uranyl nitrate or nitric acid have the opposite effect, however, tending to increase the interfacial tension between aqueous and organic phases. Thus, it may be surmised that in the column regions where rapid net transfer of uranium or nitric acid is occurring the predominant species at the aqueous-organic interfaces are the complexes formed between TBP and uranyl nitrate or nitric acid, the "free" TBP concentrations at the interface are low, interfacial tensions are high, and the energy required to effect extension of the interfacial area (i.e., dispersion) is high. In the region of near-equilibrium where little net mass transfer occurs the concentration of "free" TBP at the interface is greater, the interfacial tension is lower, and energy requirements for dispersion correspondingly lower.

In the graded cartridge closely-spaced plates having small holes were employed to increase the relative energy input in the two regions of difficult dispersion while wider plate spacings and/or larger hole diameters were employed to reduce the relative energy input in the intermediate region where dispersion is readily obtained.

Nozzle plates are stainless steel sieve plates in which each hole is slightly indented so that each hole serves as a tiny jetting nozzle. Nozzles extending at least 0.04 inch past the surface of the plate were required to obtain performance substantially different from that obtained with conventional planar sieve plates. In sharp contrast to conventional stainless steel sieve plates, nozzle plates are usable with either the aqueous phase or the organic phase as the continuous phase. When organic continuous operation is attempted with conventional stainless steel sieve plates, the dispersed aqueous phase has a tendency to wet the plates and coalesce into large globules and poor transfer efficiency results. However, when stainless steel nozzle plates are employed in columns operated with the organic phase continuous (and the nozzles oriented downward, opposite to the direction of flow of the organic) the coalescence of the aqueous phase does not occur and the aqueous phase remains dispersed.

Performance data for these two cartridges and for the conventional sieve plate cartridge are compared in Table II. A substantial increase in flooding frequency and correspondingly improved extraction efficiency is noted for the graded cartridge as compared with the conventional cartridge. Some increase in flooding frequency is noted also for the nozzle plate cartridge and this cartridge has the additional advantage that it may be operated satisfactorily with either the aqueous phase or the organic phase as the continuous phase.

With respect to the graded cartridge it should be noted that increased capacity and efficiency are obtained but flexibility is reduced. For example, changes in chemical flowsheet or changes in feed entry points which might be possible with the other cartridges would probably not be possible with this cartridge.

Uranium Stripping

Two cartridges which proved superior to conventional stainless steel sieve plate cartridges for uranium stripping are the nozzle plate cartridge and a sieve plate cartridge using plastic plates. The plastic plates are preferentially wetted by the organic phase and therefore this cartridge is usable only with the organic phase as the continuous phase. The nozzle plate cartridge is again usable with either phase as the continuous phase while the conventional cartridge is usable only with the aqueous phase as the continuous phase.

On the basis of the comparison of performance data in Table III the nozzle plate cartridge is an obvious choice for uranium stripping columns.

Scrub Sections

Operation with the organic phase as the continuous phase was adopted as a primary criterion in the design of cartridges for scrub sections. This desire stems from experience which indicates that accumulation of finely divided solids which adsorb fission products strongly and which tend to concentrate at static organic-aqueous interfaces is virtually inevitable in long-term operation of solvent extraction plants processing irradiated fuels. If the interface in a dual-purpose uranium extraction-scrub column is located at the top of the column (as in aqueous-continuous operation) a high concentration of these interfacial "cruds" will be established at a point (the interface) not far removed from the point of removal of the product organic stream and occasional inadvertent withdrawal of these solids with the product can mask entirely satisfactory decontamination performance for those fission products which are in solution.

Thus, operation of a dual-purpose uranium extraction-scrub column with the organic phase as the continuous phase is preferred since the interface is then positioned at the bottom of the column (near the point of discharge of the aqueous waste) and radioactive solids which tend to accumulate at the interface are removed in the aqueous waste stream rather than with the product stream.

The best of the cartridges which have been tested to date for organic-continuous scrub sections consists of alternate pairs of stainless steel sieve plates (0.08 inch hole diameter, 21% free area) and plastic sieve plates (0.188 inch hole diameter, 23% free area) with a one inch spacing between adjacent plates.

The conventional stainless steel sieve plate cartridge was of course inoperable with the organic phase as the continuous phase. Even under conditions of aqueous-continuous operation its capacity was lower than that of the mixed plate cartridge operated with the organic phase continuous. Under scrub section conditions the nozzle plate cartridge exhibited satisfactory capacity but transfer efficiency was low and sensitive to pulse frequency.

The relative scrubbing efficiency of these cartridges was evaluated for the transfer of chloride from organic uranium-bearing phases to an aqueous scrub solution. In these systems chloride exhibited an equilibrium distribution ratio of 0.12 to 0.13, comparable to certain of the fission products. Later studies with fission products indicate the relative efficiencies based on chloride transfer to be appropriate.

With the conventional stainless steel sieve plate cartridge and the aqueous phase as the continuous phase, HTU values for chloride transfer ranged from 3.2 feet at a pulse frequency of 60 cycles/minute to 1.8 feet at 180 cycles/minute at flows of 250 to 500 gallons/hr, ft². HTU values with the mixed-plate cartridge in organic-continuous operation were significantly better, ranging from 2.9 feet at a pulse frequency of 50 cycles/minute to 1.2 feet at 100 cycles/minute at flows of 250 to 500 gallons/hr, ft².

The increased efficiency of the mixed-plate cartridge arises from the fact that the aqueous phase coalesces on the stainless steel plates and then is again dispersed into the continuous organic phase in the region of the plastic plates. The column in operation thus comprises alternating aqueous-continuous and organic-continuous bands. The organic phase from which contaminants are being scrubbed is therefore frequently coalesced and re-dispersed in its passage through the column and improved transfer efficiency results, in keeping with laboratory studies which indicate that transfer is most rapid from freshly formed interfaces and decreases as the interface ages. The "banding" phenomenon that occurs in such cartridges has caused them to be dubbed "zebra" cartridges. This type of operation is stable and persists as long as the stainless steel plates are preferentially wet by the aqueous phase.

Although fluorothene can be used for the plastic plates in such a mixed plate cartridge, polyethylene manufactured by the Ziegler process is preferred because of improved radiation stability and more efficient wetting by the organic phase.

Uranium-Plutonium Separation

Some concentration of plutonium is desirable in the step in which plutonium is reduced and scrubbed from a uranium-bearing organic phase as plutonium(III). Accordingly, pulse column cartridges were tested for this application at flow ratios of aqueous to organic of about 0.06 with the aqueous phase as the continuous phase. A cartridge which proved superior to conventional stainless steel sieve plate cartridges for this application is a mixed plate cartridge in which sections of four stainless steel sieve plates (0.188 inch hole diameter, 33% free area) are separated by a single plastic sieve plate (0.188 inch diameter holes, 23% free area). The spacing between adjacent plates was 2 inches throughout. This cartridge proved to have a capacity about 1.5 times that of the conventional stainless steel cartridge when both were operated aqueous continuous.

The principal limitation in the capacity of the conventional stainless steel cartridge arises from the fact that the dispersion becomes increasingly finer from the bottom to the top of the column, approaching a stable emulsion at the top which limits the capacity. Substituting a plastic (organic-wet) plate for every fifth stainless steel plate forces the organic phase to coalesce at every fifth plate with the result that the very fine, capacity-limiting dispersion does not form. Again either fluorothene or polyethylene made by the Ziegler process could be used as the plastic plates in such a cartridge, with the latter being preferred.

Plutonium Extraction

Pulsed packed towers employing Raschig ring packing have been successfully employed for plutonium extraction. The performance of aqueous-wet (stainless steel) and organic-wet (fluorothene) one inch by one inch Raschig rings were compared with a conventional stainless steel sieve plate cartridge for extracting uranium out of a dilute solution of uranium in nitric acid.

The stainless steel packing showed essentially identical performance with either the aqueous phase or the organic phase as the continuous phase, and exhibited higher capacity than the other cartridges but its transfer efficiency was good only at high pulse frequency (1.2 feet HTU at 100 cycles/minute) and decreased rapidly as the pulse frequency was reduced.

The fluorothene packing exhibited a capacity intermediate between that of the other two cartridges but was highly efficient over a wide range of pulse frequencies, the HTU for uranium transfer varying only from 1.1 feet at 80 cycles/minute to 1.3 feet at 40 cycles/minute.

The stainless steel sieve plate cartridge had lower capacity than either of the other two cartridges and efficiency intermediate between the other two cartridges. With this cartridge also the efficiency decreased greatly as the pulse frequency was reduced below 80 cycles/minute.

Preferred Cartridges for Processing of Irradiated Uranium

In summary, pulse column cartridges which exhibited significantly improved performance over conventional stainless steel sieve-plate cartridges and are considered workable in Purex processes for irradiated uranium are the following.

(1) Dual-Purpose Extraction-Scrub Columns (e.g., HA or 1A)

Organic-continuous operation with nozzle plates in extraction section, mixed-plate cartridge (2 s/s, 2 plastic) in scrub section.

(2) Uranium-Plutonium Partition (e.g., 1B)

Aqueous-continuous operation with mixed-plate cartridge (4 s/s, 1 plastic).

(3) Uranium Stripping (e.g., HC or 1C)

Organic-continuous operation with nozzle plates.

(4) Plutonium Extraction (e.g., 2A)

Fluorothene Raschig rings (1" x 1").

If aqueous-continuous operation were desired in the extraction sections of "A" columns the graded cartridge could be used and if increased capacity were desired in the plutonium extraction columns the stainless steel rings could be employed (with high pulse frequencies).

Nuclear Safety in Equipment Design

Nuclear safety is a paramount consideration in the design of processing equipment for fissionable materials. Considerable background information relative to the design of nuclearly safe equipment and adoption of nuclearly safe operating techniques has been developed through both experimental and theoretical studies. A detailed discussion of this work is beyond the scope of this paper. However, references to much of this work are included in references 42 through 47 in the bibliography.

Design of mixer-settler solvent extraction contactors of adequate capacity in nuclearly-safe geometry represents a recent engineering endeavor in this field. This work is discussed in the section following.

Mixer-Settlers of Critically Safe Geometry

The applicability of "pump-mix" mixer-settlers to solvent extraction processes for nuclear fuels has been pointed out in earlier publications.⁽³⁹⁾ The possibility of constructing such units in a geometry such that fissionable materials could be safely processed at high concentrations has been explored in recent work at the Savannah River Laboratory, with results as reported in paper 222.

Units which have been studied are in the shape of horizontal slabs 3 inches high. If these units are positioned such that the large faces of the slabs are no closer than 6 feet to neutron reflectors they can be safely employed for processing fissionable materials at concentrations up to 400 grams/liter.

A test unit which had a liquid holdup of 1.8 gallons per stage had a maximum capacity of about 2 gallons/minute (sum of total flow of both phases). A similar unit which had a liquid holdup of 5.4 gallons per stage had a maximum capacity of about 6 gallons/minute. The principal factor limiting the capacity is the necessity for allowing a liquid holdup of about one minute in each settling chamber in order to obtain satisfactory phase separation.

A six-stage test unit was operated for over 1000 hours without mechanical breakdown. Conditions were established for obtaining stage efficiencies for uranium transfer greater than 85% for extraction of uranium out of aluminum nitrate salted or nitric acid salted aqueous solutions into 1.5, 6, and 30 volume % solutions of TBP in kerosene. Flow ratios of aqueous:organic of 6:1, 3:1, 1:1, 1:7, and 1:10 were tested. Colven presents an equation correlating performance with the pertinent variables in paper 222.

Continuous Solvent Washer of Critically-Safe Geometry

A continuous solvent washer of a shape designed to preclude a nuclear reaction in the event of accumulation of fissionable material in the unit is described by Colven in paper 222. The entire unit is housed in a cylinder of sufficiently small diameter to avoid accumulation of fissionable material in an unsafe geometry even in the event of build-up and precipitation of fissionable material in the unit. A mixing impeller is housed in a cylindrical insert in this unit so that it discharges through a shrouded housing. The solvent wash solution (typically 4% Na_2CO_3 solution) fills the outer chamber to above the level of the mixer. Solvent is introduced at the bottom of the cylindrical insert and the mixed solvent-aqueous wash dispersion is discharged through the shroud housing into the outer chamber, which serves as a settling section. The washed solvent is withdrawn at the top of the unit.

Performance data for such a unit are presented by Colven, for 6 and 30 volume % TBP in kerosene solvents. Typically, entrainment of wash solution in the washed solvent was less than 0.05%. Processing capacities up to 0.5 gallons/minute were demonstrated.

Such continuous solvent washers could be coupled to two mixer-settler banks in such a way as to provide a closed solvent circuit and permit a solvent extraction cycle to be conducted in rather compact equipment with a minimum inventory of solvent. Such a flowsheet is illustrated by Colven in paper 222.

"IN-LINE" ANALYSIS OF PROCESS STREAMS

As a result of the special problems associated with the operation of remote-operated processing plants for irradiated fuels, the field of instrument development for such plants has evolved into a major area of nuclear fuel processing technology. In addition to a continuing experimental program aimed at the development of improved control instrumentation (for temperature, flow rate, pressure, tank liquid level, etc.), vigorous research programs are in progress at several United States laboratories with the aim of developing methods for "in-line" analysis of process streams. The purpose of such instrumentation is to obtain quantitative analytical data directly and virtually instantaneously from process streams. Conventional sampling followed by laboratory analyses has an inherent time lag of several hours which constitutes a severe limitation in the operation of continuous plants. In particular, if dependence must be placed on delayed analyses, plant operating variables must be conservatively chosen and the plant cannot be operated at its maximum capability. In addition to reducing the time lag in obtaining analytical data, in-line analytical instruments represent a first step toward completely automatic control of nuclear fuel processing plants and the continuous data derived from them is extremely useful in elucidating process dynamics.

However, it should be recognized that the original cost of such instruments is generally high and frequently cannot be justified solely on the basis of savings in analytical costs. Such instruments can, however, be justified for many applications on the basis of improved safety, improved process control and the aforementioned increased rangeability in plant operating variables.

In most applications of "in-line" instruments to date it has not been feasible to install the sensing component directly in the process stream, as would normally be most desirable. Rather, it has been necessary to devise automatic sampling techniques which deliver a continuous or intermittent sample to an instrument located in a "sample gallery". This necessity has limited the utility of some in-line instruments and considerable effort is currently being directed toward developing sensing components which can be placed directly in the process line or vessel.

Analytical methods under study for possible in-line application embrace virtually all instrumental analytical methods. No attempt will be made to discuss all the exploratory work which is in progress in this field. Rather, attention will be confined to those methods and instruments which have attained a firm state of development and are considered workable in plant applications. These are briefly described in Table IV. The performance of a number of these instruments in a pilot plant application has been discussed by Pleasance.⁽⁴⁸⁾

It will be noted that the degree of precision stipulated for these instruments in Table IV is considerably lower than could normally be obtained with these techniques in typical laboratory applications. In many instances this is deliberate and stems from a philosophy which has evolved from operating experience. It has been found expedient in many instances to sacrifice high precision in favor of increased reliability and dependability. Experience indicates that such in-line analytical instruments must be reliable, mechanically strong and stable, and simplified to whatever extent is feasible, in order to be of real value in nuclear fuel processing plants.

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FIGURE 1

THREE-CYCLE SOLVENT EXTRACTION PROCESS EMPLOYING BACKCYCLE OF AQUEOUS WASTES

<u>Stream</u>	<u>Relative Flow</u>	<u>Composition</u>	<u>Temperature, °C</u>
HAF	75	1.8 M U, 1.0 M HNO ₃ , Pu (IV)	50
HAX	333	30 vol. % TBP	35
HSR	57	0.066 M U, 2.42 M HNO ₃	60
1BSU	32	0.065 M U, 0.75 M HNO ₃ , 30 vol. % TBP	Ambient
HAO	33	30 vol. % TBP	35
HSS	56	2.0 M HNO ₃	30
1BX	25	0.5 M HNO ₃ , 0.03 M Fe(NH ₂ SO ₃) ₂	Ambient
1BS	31	30 vol. % TBP	35
1BXP	26	0.08 M U, 1.9 M HNO ₃ , Pu(III), Fe(NH ₂ SO ₃) ₂	Ambient
1BU	407	0.33 M U, 0.063 M HNO ₃ , 30 vol. % TBP	Ambient
1BP	30	2.75 M HNO ₃ , Pu(III), Fe(NH ₂ SO ₃) ₂ , γ DF $\sim 10^4$	Ambient
1CX	407	0.01 M HNO ₃	50
1CU	418	0.32 M U, 0.07 M HNO ₃ , γ DF $\sim 10^4$	50
2DF	89.4	1.5 M U, 0.29 M HNO ₃ , 0.013 M Fe(NH ₂ SO ₃) ₂	40
2DS	33	H ₂ O	30
2DIS	36	2.5 M HNO ₃	30
2DX	345	30 vol. % TBP	35
2EX	357	0.01 M HNO ₃	50
2EU	368	0.367 M U, 0.035 M HNO ₃ , γ DF $\sim 10^7$	50
2AF	31.3	2.70 M HNO ₃ , Pu(IV), 0.06 M Na, 0.029 M Fe(III)	45
2AS	3.75	0.6 M HNO ₃	Ambient
2AX	7.5	30 vol. % TBP	35
2BX	3	0.01 M HNO ₃	Ambient
2BP	3	0.28 M HNO ₃ , Pu(IV), γ DF $\sim 10^8$	Ambient

FIGURE 2

TWO-CYCLE PUREX FLOWSHEET EMPLOYING BACKCYCLE OF AQUEOUS WASTES

(Part 2)

<u>Stream</u>	<u>Relative Flow</u>	<u>Composition</u>
1AF	100	1.5 M U, 0.7 M HNO ₃ , Pu(IV), 1.2×10^9 g c/m, ml
1AS	67	3.0 M HNO ₃
1AX	420	30 vol. % TBP, 70 vol. % n-dodecane
1BX	75	0.04 M Fe(NH ₂ SO ₃) ₂ , 0.1 M HNO ₃
1BS	123	30 vol. % TBP, 70 vol. % n-dodecane
1CX	700	0.03 M HNO ₃
1BP	75	Pu(III), 1.4 M HNO ₃ , 6.7×10^3 g c/m, ml, $\gamma_{DF} = 2.4 \times 10^5$
1CU	700	0.21 M U, 260 g c/m, ml, $\gamma_{DF} = 6.6 \times 10^5$

FIGURE 3

HIGH TEMPERATURE PUREX PROCESS

FIGURE 4

REFLUX PLUTONIUM CYCLE

FIGURE 5

EXCER PROCESS

FIGURE 6

FLUREX PROCESS

FIGURE 7

ONE-CYCLE PUREX PROCESS

<u>Stream</u>	<u>Relative Flow</u>	<u>Composition</u>
HAF	100	215 g/l U, 50 g/l SS, 1 M HNO ₃ , 0.01 M NaNO ₂ , Pu(IV)
HAS	50	3 M HNO ₃
HAX	250	30 vol. % TBP, 70 vol. % Amsco 125-82
HCX	500	0.01 M HNO ₃
1AF	66	324 g/l U, 2 M HNO ₃ , 0.01 M NaNO ₂ , Pu(IV)
1AS	45	3 M HNO ₃
1AX	220	30 vol. % TBP, 70 vol. % Amsco 125-82
1BX	30	0.5 M HNO ₃ , 0.03 M Fe(NH ₂ SO ₃) ₂
1BS	59	30 vol. % TBP, 70 vol. % Amsco 125-82
1CX	440	0.01 M HNO ₃

FIGURE 8

MODIFIED PUREX FLOWSHEET FOR FUELS CONTAINING STAINLESS STEEL

FIGURE 9

THOREX CO-DECONTAMINATION FLOWSHEET

(Part 1)

<u>Stream</u>	<u>Relative Flow</u>	<u>Composition</u>
1AF	100	350 g/l Th, 1.40 g/l U, 0.6 M $\text{Al}(\text{NO}_3)_3$, 0.3 N Acid Deficient, 0.06 M F^- , 0.004 M Hg, 0.002 M PO_4^{3-}
1AS	100	0.5 M $\text{Al}(\text{NO}_3)_3$, 0.2 N Acid Deficient, 0.003 M PO_4^{3-} , 0.005 M Fe^{++}
1AX	500	42.5 vol. % TBP
1AW	180	0.2 g/l Th, < 0.0005 g/l U, 0.56 M $\text{Al}(\text{NO}_3)_3$, 0.28 N Acid Deficient
1CX	910	0.008 M HNO_3
1CP	930	37.4 g/l Th, 0.15 g/l U, 0.008 M HNO_3
2AF	100	350 g/l Th, 1.40 g/l U, 0.6 M $\text{Al}(\text{NO}_3)_3$, 0.3 N Acid Deficient
2AS	100	0.5 M $\text{Al}(\text{NO}_3)_3$, 0.2 N Acid Deficient, 0.003 M PO_4^{3-} , 0.005 M Fe^{++}
2AX	500	42.5 vol. % TBP
2AW	180	0.2 g/l Th, < 0.0005 g/l U, 0.56 M $\text{Al}(\text{NO}_3)_3$, 0.28 N Acid Deficient
2BX	100	Demineralized H_2O
2B'X	480	0.24 M HNO_3
2BS	160	42.5 vol. % TBP
2BT	600	58 g/l Th, 0.2 M HNO_3
2BTC	70	466 g/l Th, 1.6 M HNO_3
2BU	660	0.01 g/l Th, 0.27 g/l U in TBP-Diluent
2CX	330	0.008 M HNO_3
2CU	330	0.42 g/l U, 0.02 M HNO_3
IF	330	0.42 g/l U, 0.02 M HNO_3
IW	330	0.05 M HNO_3
Elutriant	0.93	3 M Ammonium Acetate, 1.5 M Acetic Acid, 0.75 M Ammonium Citrate
IP	0.93	150 g/l U as Acetate-Citrate Complex

FIGURE 9

THOREX CO-DECONTAMINATION FLOWSHEET

(Part 2)

<u>Stream</u>	<u>Relative Flow</u>	<u>Composition</u>
(First Cycle)		
Feed	100	3 g/l U, 1.2 M $\text{Al}(\text{NO}_3)_3$, 0.5 M HNO_3
Scrub	15	1.2 M $\text{Al}(\text{NO}_3)_3$, pH 1.3
Extractant	35	6 vol. % TBP, 94 vol. % n-dodecane
Strip	5	0.01 M HNO_3
Product	5	60 g/l U, $\beta_{\text{DF}} = 2.6 \times 10^6$, $\gamma_{\text{DF}} = 4.3 \times 10^5$
(Second Cycle)		
Feed	7.1	42.3 g/l U, 3.0 M HNO_3
10 M HNO_3	2.1	
Scrub, Stage 4	3	3.0 M HNO_3
Scrub, Stage 1	3	0.01 M HNO_3
Extractant	21	18 vol. % TBP, 82 vol. % n-dodecane
Strip	14	0.01 M HNO_3
Product	14	21.4 g/l U, $\beta_{\text{DF}} = 2.6 \times 10^8$, $\gamma_{\text{DF}} = 4.3 \times 10^8$

FIGURE 10

HIGH TEMPERATURE FLOWSHEET FOR HIGHLY-ENRICHED URANIUM FUELS ALLOYED WITH ALUMINUM

FLWSHEET FOR HIGHLY-ENRICHED URANIUM FUELS CONTAINING STAINLESS STEEL

Stream	Relative Flow	Composition
1AF	100	324 g/l U, 2.0 M HNO_3 , Pu, Np
1AS	67	3.0 M HNO_3 , 0.05 M NaNO_2
1AX	333	30 vol. % TBP
1EX	45	0.30 M HNO_3 , 0.03 M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$
1BS	89	30 vol. % TBP
1CX	666	H_2O
1DF	97	334 g/l U, 2.0 M HNO_3 , 0.05 M NO_2^- , Np
1DS	67	3.0 M HNO_3 , 0.05 M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$
1DX	333	30 vol. % TBP
1D'X	90	0.01 M HNO_3
1D'S	110	30 vol. % TBP
1D'P	90	0.001 g/l U, 0.75 M HNO_3 , Np
1EX	516	H_2O
1EU	538	60.2 g/l U, 0.125 M HNO_3

FIGURE 12

MODIFIED PUREX FLOWSHEET FOR RECOVERY OF URANIUM, PLUTONIUM, AND NEPTUNIUM
(Part 1)

<u>Stream</u>	<u>Relative Flow</u>	<u>Composition</u>
2AF	67	6.0 M HNO ₃ , 0.1 M NO ₂ ⁻ , Pu(IV)
2AS	8.2	0.5 M HNO ₃
2AX	16.4	30 vol. % TBP
2BX	4.1	0.05 M HNO ₃ , 0.05 M (NH ₂ OH) ₂ ·H ₂ SO ₄
2BP	4.1	0.52 M HNO ₃ , 0.05 M (NH ₂ OH) ₂ ·H ₂ SO ₄ , Pu

FIGURE 12

MODIFIED PUREX FLOWSHEET FOR RECOVERY OF URANIUM, PLUTONIUM, AND NEPTUNIUM

(Part 2)

Stream	Relative Flow	Composition
1AF	100	6.0 M HNO ₃ , 1.22 M Mg, 0.28 M Al, 0.11 M Ca, 0.14 M F, Pu, Am
1AS	17	0.5 M HNO ₃
1AX	45	30 vol. % TBP
1BX	25	0.05 M NH ₂ OH·0.5 H ₂ SO ₄
Elutriant	4	5.7 M HNO ₃ , 0.3 M NH ₂ SO ₃ H
Waste	20	0.3 M HNO ₃ , ~0.4 g/l Pu
Pu Product	4	~4.8 M HNO ₃ , 500 g Pu/Column
1AW	117	5.2 M HNO ₃ , 1.03 M Mg, 0.24 M Al, 0.09 M Ca, 0.12 M F, Am
2AF	150	5.0 M NH ₄ NO ₃ , 0.2 M Al, 1.0 M Mg, 0.08 M Ca, 0.10 M F, Am
2AS	25	4 M NH ₄ NO ₃
2AX	75	30 vol. % TBP
2BX	15	0.05 M HNO ₃
2BS	25	30 vol. % TBP

FIGURE 13

RECOVERY OF PLUTONIUM AND AMERICIUM FROM METALLURGICAL WASTES

FIGURE 14

DISTRIBUTION OF DBP BETWEEN AQUEOUS SOLUTIONS
 AND 20% TBP - SHELL SPRAY BASE AT 25 AND 50°C

	BURNUP	COOLING TIME (days)	SOLVENT EXPOSURE (μ watt-hr/l)
GRAPHITE (BROOKHAVEN) (FEED: 320 g/l U)	588 MWD/T	90	0.01
THERMAL POWER FUEL (FEED: 320 g/l U)	10,000 MWD/T 10,000 MWD/T	10 100	0.48 0.27
FAST POWER FUEL (APDA) (FEED: 237 g/l U)	5% U-235 5% U-235	10 50	1.9 0.57
THOREX (FEED: 1 M Th)	4,000 g/T U-233	30	1.3

FIGURE 15
CALCULATED SOLVENT IRRADIATION LEVELS PER CYCLE
(assuming 5 minute solvent residence time)

SOLVENT EXPOSURE (S watt-hr/l)	OBSERVED EFFECT
0.01	NONE
0.5	2-FOLD DECREASE IN R_u DF (THOREX)
4.3	2-FOLD DECREASE IN 25 PROCESS DF SIGNIFICANT P_u LOSS
5 - 10	SEVERE EMULSIONS IN THOREX
18	SIGNIFICANT U LOSS
24	25-FOLD DECREASE IN 25 PROCESS DF

FIGURE 16

EFFECT OF RADIATION ON TBP EXTRACTION PROCESSES

FIGURE 17

VARIATION OF DISTRIBUTION COEFFICIENT
WITH PHOSPHORYL STRETCHING FREQUENCY

TABLE I

Yields of Gaseous and Acidic Products
on Irradiation of Organophosphorus
Compounds with 1 Mev Electrons

(Data of Wagner and Kinderman)

<u>Compound</u>	<u>G (Total Gas)</u>	<u>G (Total Acid)</u>
<u>Pure Compounds</u>		
Tributyl Phosphate	2.54	2.64
Dibutyl Phosphate	3.40	----
Dibutyl Butylphosphonate	1.79	1.40
Diamyl Amylphosphonate	1.30	1.90
Dibutyl Phenylphosphonate	0.45	0.36
<u>50 Volume % Solution in Amsco 125-82</u>		
Tributyl Phosphate	2.78(a)	0.60(a)
Dibutyl Butylphosphonate	2.05(a)	0.80(a)
Diamyl Amylphosphonate	1.79(a)	1.50(a)
Dibutyl Phenylphosphonate	1.04(a)	0.24(a)

(a) Computed on basis of total energy absorbed by mixture.

TABLE II

Comparison of Performance of Uranium Extraction Column
Cartridges

<u>Cartridge</u>	<u>Continuous Phase</u>	<u>Flooding Frequency</u> (cycles/min. at 1000 gal/hr, ft ²)	<u>HTU for U</u> (feet)	
			<u>HTU</u>	<u>f-cyc/min.</u>
Conventional SS Sieve Plate	Aqueous	~ 75	0.8	70
			1.0	40
Graded	Aqueous	~ 105	0.6	90
			0.7	70
Nozzle Plate	Organic	~ 95	0.9	100
			1.0	80

TABLE III

Comparison of Performance of Uranium Stripping Column
Cartridges

<u>Cartridge</u>	<u>Continuous Phase</u>	<u>Maximum Capacity</u> (gal/hr, ft ² at 80 cyc/min)	<u>HTU for U</u> (feet at 500-600 gal/hr, ft ²)	
			<u>HTU</u>	<u>f-cyc/min</u>
Conventional SS Sieve Plate	Aqueous	~ 800	~ 1.9	80
Fluorothene Sieve Plate	Organic	~ 900	1.1	80
Nozzle Plate	Aqueous	~ 1200	0.9	100
			1.0	80
Nozzle Plate	Organic	~ 1800	0.9	90
			4.1	60

TABLE IV

In-Line Analysis of Process Streams

<u>Method - Instrument</u>	<u>Process Application</u>	<u>Accuracy</u>	<u>Range</u>	<u>Comments</u>
pH - By measurement of EMF with glass-calomel electrode cell. Includes provision for intermittent calibration against standard solutions.	Determination of concentration of acid or base in aqueous streams.	± 0.1 pH unit	pH of 0 to 14	(References 49, 50, 51)
Polarography - Current resulting from reduction of ions in solution is measured. Measured current is proportional to concentrations of reducible ions.	Concentrations of reducible ions in aqueous solutions. Particularly useful for determining U(VI) at low concentrations.	± 20%	0.05 to 10 g/l U	Requires compensation for interfering substances, e.g., dissolved organic, Fe(III), etc. Performance proven in test applications. Operation cyclic but automatic. (References 52, 53)
Alpha Printer - Measures, washes, dries sample in cyclic, automatic operation. Counts electrical pulses from phototube activated by visible light arising from interaction of alpha radiation from dried sample with ZnS phosphor.	Total alpha activity of streams suitable for evaporation to dryness. To date applied principally for plutonium in aqueous solution.	± 15%	10 ⁻⁶ to 0.1 g/l Pu	Although complex electrical, mechanical device, performance has proved satisfactory. (Reference 54)

<u>Method - Instrument</u>	<u>Process Application</u>	<u>Accuracy</u>	<u>Range</u>	<u>Comments</u>
<u>Colorimeter</u> - Measures specific wave length visible light absorption by process solutions, using phototube as detector.	Materials absorbing in visible region. Particularly useful for U(VI), $\text{Cr}_2\text{O}_7^{=}$.	$\pm 5\%$ (UO_2^{++}) $\pm 20\%$ ($\text{Cr}_2\text{O}_7^{=}$)	30 to 500 g/l U(VI) 2 to 32 g/l $\text{Cr}_2\text{O}_7^{=}$	Subject to interference by other colored materials, e.g., solvent decomposition products require compensation for determining U(VI) in organics. (References 55, 56)
<u>Gamma Absorptiometer</u> - Measures attenuation by process solution of gamma radiation from external gamma source, using ion chamber or scintillation crystal as detector. Absorption proportional to concentration, mass absorption coefficient of solution species.	Determination of total concentration of heavy elements in aqueous or organic solution. Absorption practically unaffected by light elements.	$\pm 7\%$	5 to 300 g/l U, Pu, Th	Requires little maintenance. Can be installed in remote area. (References 57, 58, 59)
<u>Contact Alpha</u> - Alpha radiation detected directly by phosphor in contact with process solution.	Total alpha activity. To date used primarily for moderate concentrations of Pu in aqueous solution.	$\pm 20\%$	0.1 to 10 g/l Pu	Requires little maintenance. Can be installed in remote area. (Reference 60)

<u>Method - Instrument</u>	<u>Process Application</u>	<u>Accuracy</u>	<u>Range</u>	<u>Comments</u>
<u>Gamma Activity Monitor</u> - Measures gamma radiation from process stream using NaI or TlI scintillation crystal and phototube as detector. Can be employed to monitor wide spectrum of gamma energies or radiation in selected energy ranges.	Gamma radiation, total or in selected energy ranges, in solids, liquids, or gases.	$\pm 15\%$	10 μc to $3 \times 10^4 \mu\text{c}$	Versatile and reliable. Careful design required to avoid deposition of activity in sample cell. (References 61, 62)
<u>Conductivity</u> - Resistance of process stream measured with A.C. bridge. Conductivity measured is function of total concentration of electrolytes.	Determination of concentrations of electrolytes in aqueous solutions. Must be used in conjunction with other methods to differentiate individual electrolytes. Can be used to determine level of conducting solutions in vessels.	$\pm 7\%$	0.01 to 10^6 ohms	Can be used directly in stream or vessel. No sampling required. (References 63, 64)
<u>Oxidation Potential</u> - Measures EMF between appropriate measuring and reference electrodes.	Valence state, e.g., for Pu. Concentrations of certain ionic constituents, e.g., Cl^- .	----	----	Suitable instrumentation available. Additional work required on application and on interpretation of data.

<u>Method - Instrument</u>	<u>Process Application</u>	<u>Accuracy</u>	<u>Range</u>	<u>Comments</u>
<u>Neutron Monitor</u> - Employs BF ₃ counter or other neutron detector to measure neutron flux resulting from (, n) reactions in process streams.	Determination of concentrations of alpha emitting elements, e.g., U, Pu, Am, Cm.	± 5%	ca. 1 to 60 g/l Pu	Requires little maintenance. Can be installed in remote area. No sampling required.
<u>Dielectric Constant</u> - Measures capacitance in condenser in which process stream forms part of the dielectric.	Concentration of TBP in diluent solution. Concentrations of electrolytes in organic solutions. Very useful for monitoring location of aqueous-organic column interfaces.	TBP to ± 0.5 Volume % Interface Location to ± 1/8 in.	20 to 30 Volume % TBP 0 to 48 in.	Used routinely for column interface control. (Reference 65)
<u>Turbidimeter</u> - Measures attenuation of light by absorption or scattering, using photocell as detector.	Detection of turbidity in process streams. Detection of emulsions in liquid-liquid extraction systems.	----	----	(Reference 66)