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# APPLICATION OF EXTRACTION CHROMATOGRAPHY TO NUCLEAR FUEL REPROCESSING

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## ABSTRACT

The potentialities of applying extraction chromatography to the reprocessing of reactor fuels on an industrial scale have been investigated. The stationary phase was undiluted (100%) tri-n-butyl phosphate (TBP) and the mobile phases were nitric acid or nitrate salt solutions with or without reducing agents for plutonium.

Several extraction chromatographic processes for the recovery of nuclear grade uranium and plutonium are described. The flowsheets are based on a systematic determination of the distribution coefficients of relevant metal species (particularly those of uranium, neptunium, plutonium, americium, ruthenium, zirconium and niobium) in the chromatographic systems employed.

The Purochromex process developed for the recovery of uranium and plutonium from light-water reactor fuels and the Eurochromex process developed for the separation of highly enriched uranium from irradiated U/Al alloy, U/Zr alloy and uranyl sulfate fuels have successfully been hot-tested on a laboratory scale and cold-tested on an "industrial scale."

Some complementary studies related to the separation processes, such as radiation degradation of the stationary phase and the removal of tributyl phosphate from product and waste streams, are also described.

## INTRODUCTION

The discovery of nuclear fission by the chemists Otto Hahn and Fritz Strassmann on the 18th of December 1938 initiated an enormous development of the science and technology of separation with the primary aim to explore nuclear fission phenomena and to apply this new source of energy. Since then until today there is hardly a separation technique known which has not been applied in the nuclear energy industry. Undoubtedly, solvent extraction and chromatography are the most extensively used techniques for analytical and preparative separations in the nuclear fuel cycle, especially in the processing of thorium and uranium and the reprocessing of all kinds of nuclear reactor fuels.

In combining solvent extraction systems with chromatographic techniques one obtains an extremely versatile and effective separation tool, now termed "extraction chromatography," which is a synonym for liquid-liquid partition chromatography and reversed phase partition chromatography. The chromatographers working in the nuclear field have now generally agreed to use the term "extraction chromatography" for that liquid-liquid partition chromatographic technique in which an organic extractant (the less polar substance) sorbed by an organophilic "inert" support forms the stationary phase, an aqueous solution (the more polar substance) acts as the mobile phase, and the substances to be separated are (primarily) inorganic in nature.

The principles governing extraction phenomena and all liquid-liquid chromatographic techniques (elution, frontal analysis and displacement development) are applicable to extraction chromatographic separations. The theoretical aspects and the techniques involved, as well as most of the achievements made in the field of extraction chromatography until the beginning of 1973, have been described in a monograph (1). The present paper summarizes some of the main extraction chromatographic investigations performed by the authors and their collaborators in the field of nuclear fuel reprocessing, and describes specific applications to the recovery of nuclear grade uranium and plutonium needed for the generation of nuclear fission energy.

## BACKGROUND AND SCOPE

In the early years of nuclear fuel reprocessing, attempts were made to use ion exchange chromatography for the separation and purification of uranium and plutonium from the fission products and other impurities. Though the solvent extraction processes — mainly Redox and Purex — were shown to be obviously superior to all other processes under development, at least as a primary means of separating the valuable material from the highly radioactive impurities, ion exchange continued to play an important role in the concentration of intermediate or final product streams and particularly in the final purification of uranium and plutonium.

For about twenty years Eschrich and collaborators have been investigating the potential of chromatographic methods and techniques for the analysis and reprocessing of nuclear fuels and the treatment of radioactive waste solutions (2-5). One of the main aims of these investigations was the development of effective one-cycle chromatographic extraction processes for nuclear fuel reprocessing. Other objectives were to investigate the applicability of chromatographic methods to: (1) the final purification of uranium, neptunium, and plutonium product solutions to fulfill nuclear grade specifications; (2) the recovery of actinides and fission products from waste solutions; (3) the identification and determination of the chemical state of uranium, neptunium, plutonium, and ruthenium in reprocessing solutions (4-7); (4) the separation (enrichment) of uranium isotopes; and (5) the analysis of reprocessing solutions and final products (8-10).

For about 20 years Ochsenfeld and collaborators have also carried out extraction studies which included extraction chromatography in the framework of R&D programs for the realization of a nuclear fuel cycle center in the Federal Republic of Germany.

## CHROMEX PROCESSES

### General

Extraction chromatographic separation processes intended for "industrial scale" application have been termed by us "Chromex Processes." The processes developed up to now aim at the isolation of actinides in the required purity from solutions containing a wide variety of radioactive and inactive impurities. In the processes described below, undiluted 100% TBP is used as the stationary liquid phase, and aqueous nitric acid or nitrate salt solutions are the mobile phase.

Since all chromatographic separations are based on the different distribution of the components to be separated between the stationary and the mobile phase, the distribution coefficients of tracer amounts of all relevant elements between highly pure 100% TBP and nitric acid at 22°C (for U, Np, Pu, and Am at 4, 22, 50, and 75°C) have been determined or redetermined. Table 1 summarizes the results obtained at room temperature in a form sufficiently accurate to predict the chromatographic behavior of the various species under ideal conditions (i.e., not taking account of disturbing influences, such as the degradation of the extractant phase, association of species, and kinetic effects). Figure 1 shows the distribution coefficients of actinides and fission products of greatest significance in fuel reprocessing (17).

For the macro-components uranium and plutonium, which are of prime practical importance, the effect of concentration on their distribution between the aqueous and the organic phase (TBP or TBP-loaded resins) has been determined. Figures 2 and 3 show the equilibrium curves of U(VI) and Pu(IV), respectively, between nitric acid solutions and Levextrel-TBP (see Table 2). The loading concentrations on the organic phase (100% TBP sorbed on Levextrel) for Pu are about five times as high as those achievable with liquid 30% TBP/dodecane (17) without causing difficulties by formation of a third phase because no diluent is present. For ease of comparison with liquid-liquid extraction data, the results obtained were

TABLE 1

Distribution coefficients of various metal species in the system undiluted TBP-$H_2O$-$HNO_3$ at ∿22°C

(The sequence given indicates the approximate decrease in extractability.)

| $D_{Me}$ range | Aqueous equilibrium $HNO_3$ conc. [M] | | | | |
|---|---|---|---|---|---|
| | 0.5 - 1.0 | 1.0 - 3.0 | 3.0 - 6.0 | 6.0 - 8.0 | 8.0 - 11.0 |
| 100 - 1000 | | | Pu(IV), U(VI) | Pu(IV), U(VI), Th, Np(IV) | Pu(IV), Zr, U(VI), Th, Np(IV), Hf |
| 10 - 100 | Pu(IV), U(VI), Np(VI), U(IV)<br>Pu(VI) | Pu(IV), U(VI), Np(VI), Pu(VI), U(IV), Np(IV), Th, Pa | Pu(VI) Np(VI), U(IV), Np(IV), Th, Pa | Np(VI), Pu(VI), U(IV) Zr, Hf | Np(VI), Pu(VI), U(IV) |
| 1 - 10 | , Np(IV) Hg(II), Th, Pa, Ru, Tl(III) Pd, Bi, Pt | Ru, Te, Tl(III), Hg(II) | Hf, Zr, Tl(III), Sc, Cu, Y | Sc, Lu, Y, heavy R.E., Nb | Ti, Os, Nb, Sc, Y, heavy R.E. |
| 0.1 - 1.0 | Sc, Ti, Y<br>light R.E. | Zr, Ru, Sc, Y, Pu(III), Hf<br>all R.E. | Ru, Nb, Np(V) Hg(II), Bi,<br>Heav.R.E. | light R.E. Tl(III), Hg(II), W, | light R.E. V, In, Hg(II), La, W |
| ⟨ 0.1 | heavy La, R.E., Zr, Nb Hf, Pu(III), Np(V), V, Ag, Pb, As, Mo, Ca, Ti, Fe(III), Cr, Al, Cd, Sr, Cu, Mn, In, Cs, K, Na, Rb, Ba, Mg, Zn, Ni, Sb | Np(V), As, Nb, Mo, V, Ti, Ra, Ag, Ca, Fe, Te, Al, Pb, Sr, Na, Mg, Cd, Mn, Cs, K, Cr, Ba, Cu, Rh, Co, In, Zn, Ni, Sb | La, Tl, Pd, As, Ti, Po, Pt, Fe, V, Mo, Ca, Ra, Mg, Ag, Al, Mn, Ca, Sr, In, Te, Na, Ni, Rb, Cs, K, Pb, Co, Cu, Zn, Cr, Ba, Sb | Ti, Bi, Ru, Fe, Po, Tl, V, Mo, As, Pt, Mg, In, Mn, Ca, Ra, Al, Cd, Ag, Ni, Te, Rb, Sr, K, Cs, Na, Zn, Cr, Pb, Co, Cu, Ba | Ru, Bi, Mn, As, Pd, Tl, Mg, Ca, Cr, Pt, Ag, Cd, Rb, Cs, Ra, K, Ca, Zn, Ni, Na, Te, Pb, Co, Sr, Cu, Ba |

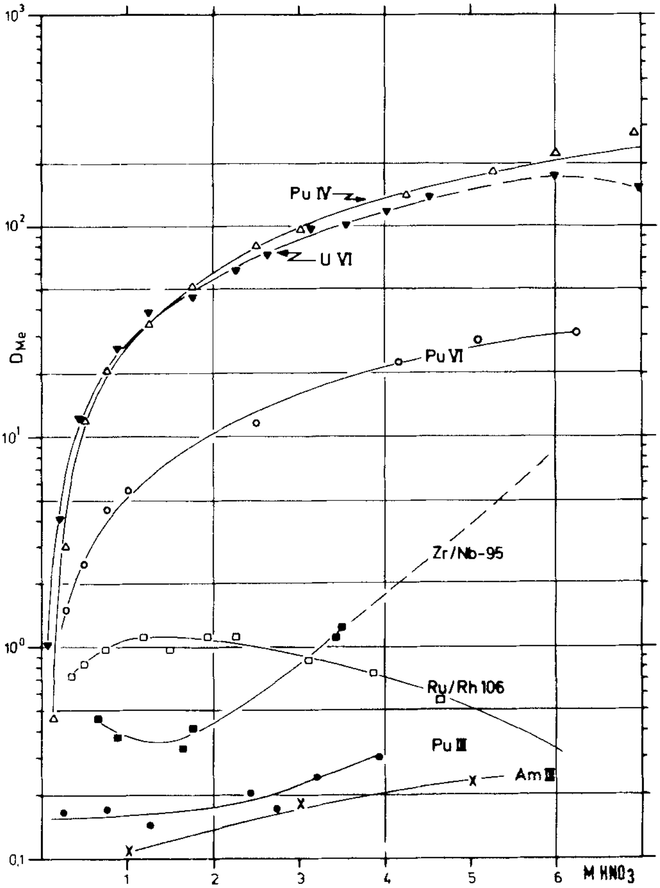

FIGURE 1. Distribution coefficients of actinides and fission products on Levextrel - TBP (containing 60 wt % undiluted TBP) at 22°C.

related to the original volume of the TBP phase sorbed by the Levextrel matrix; the matrix material is considered to function as an inert solid diluent.

Complete sets of data on the simultaneous distribution of nitric acid and uranyl nitrate between aqueous and undiluted TBP phases can be found in Ref. (11). The maximum uranium distribution

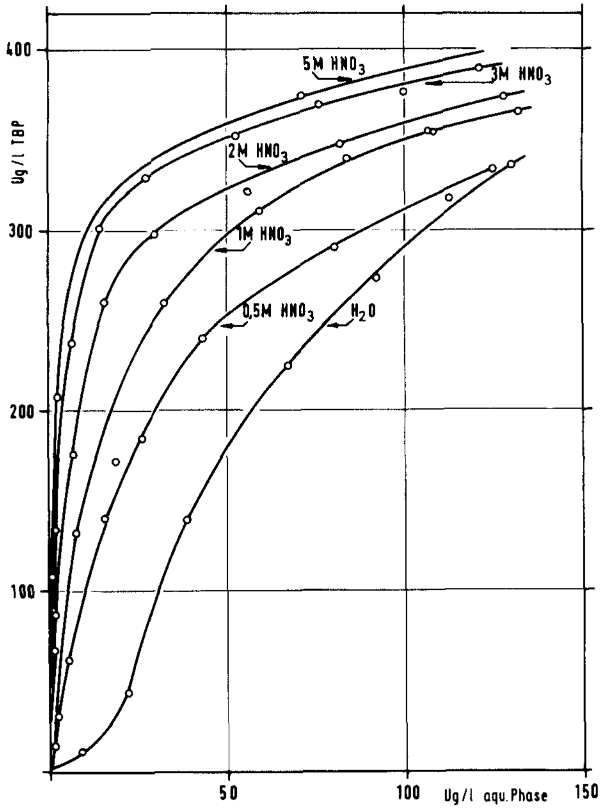

FIGURE 2. Distribution equilibria of uranyl nitrate between Levextrel-TBP and aqueous phases ($HNO_3$) at 22°C.

ratio was always found to occur in the range 5.5 to 6.0 M aqueous equilibrium concentration of nitric acid, independent of the initial uranium concentration. Some equilibrium curves relevant to the Chromex processes described below are presented in Figs. 4 and 5. The indicated concentration of uranium in the TBP-phase represents the maximum possible loadings (capacity) at 100% breakthrough of the corresponding mobile aqueous uranium feed solution (equivalent to the equilibrium aqueous phase in a batch experiment).

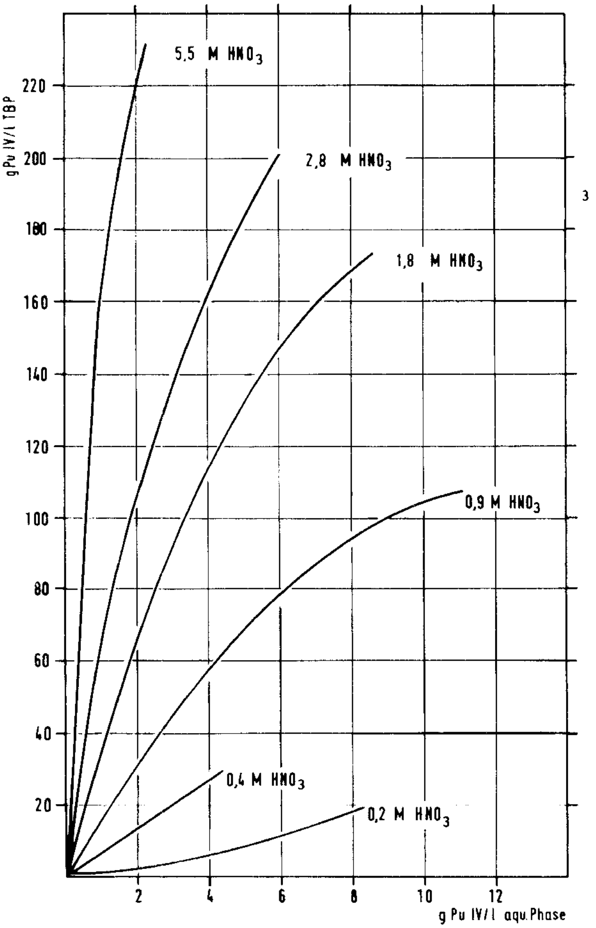

FIGURE 3. Pu(IV) equilibrium distribution between Levextrel-TBP (containing 60 wt % undiluted TBP) and different aqueous $HNO_3$ phases at 22°C.

The Chromex processes described hereafter are based on the high extractability of uranium(VI) and plutonium(IV) by 100% TBP from nitrate media, and the relatively low TBP-extractability of plutonium(III) and the impurities accompanying uranium or plutonium.

TABLE 2

Data on the stationary phases used

| Product | I | II | III |
|---|---|---|---|
| Support material | macroporous polystyrene-divinylbenzene copolymer | polystyrene - (20 %) divinylbenzene containing TBP | polytrifluorochloroethylene |
| Trade name | Lewatit CA 9221 | Levextrel-TBP (Lewatit OC1023) | Voltalef 300 LD |
| Manufacturer | Bayer AG, Leverkusen, FRG | Bayer AG, Leverkusen, FRG | Soc. des Resines Fluorees, France |
| Density matrix material $[g/cm^3]$ | 1.03 | 1.03 | 2.1 |
| Packed density [g/ml] | 0.25 | 0.25<br>0.63 (with TBP) | 0.45 |
| Particle size mm | 0.2 - 0.3 | 0.4 - 0.8 | 0.1 - 0.3 |
| U.S. mesh No. | 70 - 50 | 45 - 25 | 140 - 50 |
| TBP-loading [g/g supp.] | | | |
| maximum | 1.7 | 1.7 | 1.2 |
| stable phase | 1.5 | 1.5 | 1.0 |
| applied (this work) | 1.5<br>(60 wt.-%) | 1.5<br>(60 wt.-%) | 1.0<br>(50 wt.-%) |
| g TBP/l col. bed | 375 | 375 | 450 |
| Max. U(VI) uptake [g/l col. bed] at 5 - 6 M aqu.$HNO_3$ | 150 | 150 | 180 |
| Free col. vol. [%] | 40 | 40 | 40 |

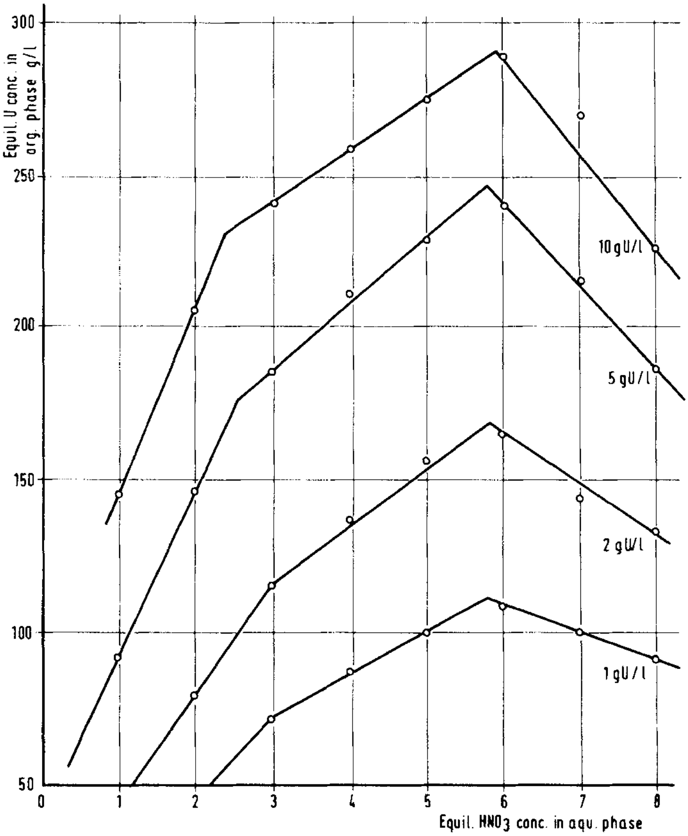

FIGURE 4. Equilibrium distribution of uranium as a function of the equilibrium aqueous uranium and nitric acid concentrations (100% TBP at 22°C).

Support and Stationary TBP Phase

A number of organic granular materials were used as support for the stationary TBP phase in the laboratory scale development studies. For the present work three support-TBP systems were selected in view of their application on an industrial scale. Most of the investigations were carried out using the extraction resin "Levextrel-TBP," developed by the Bayer AG, Leverkusen (FRG) for extraction chromatographic separations (commercially available as Lewatit-resins), and macroporous spheres of a copolymer (also produced by

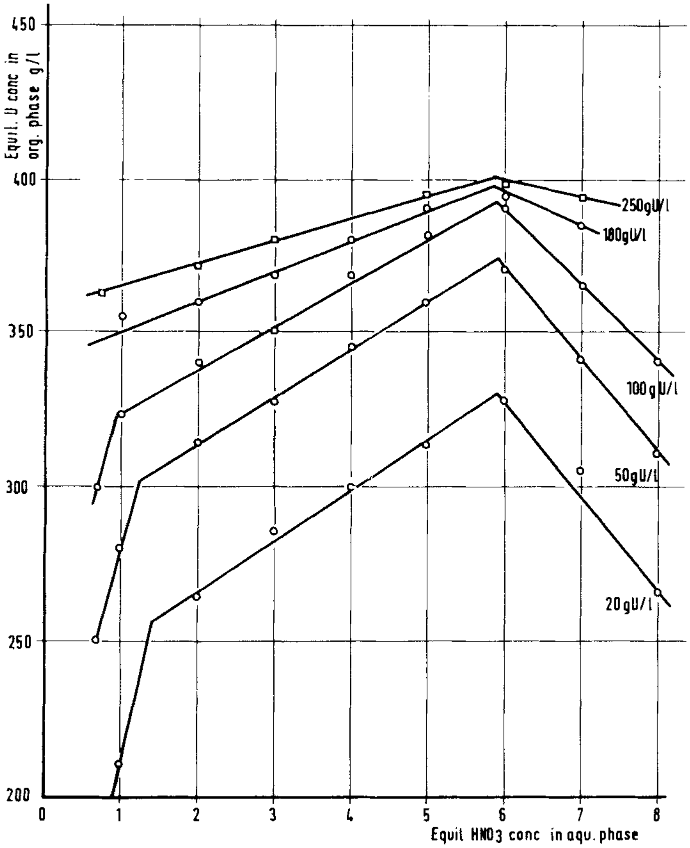

FIGURE 5. Equilibrium distribution of uranium as a function of the equilibrium aqueous uranium and nitric acid concentrations (100% TBP at 22°C).

Bayer AG) coated by us with highly purified TBP. The main characteristics of these support TBP systems are summarized in Table 2.

## The Purochromex Process

Purochromex stands for Plutonium-uranium recovery on chromatographic-extraction columns. The process serves primarily for for the recovery of uranium and plutonium, either individually or as a mixture (e.g., for the fabrication of mixed oxide fuels), from solutions of irradiated reactor fuels or waste materials, and is based on the formerly developed "chromatographic Purex process" (5) and the investigations related thereto (3,6,7-9,11, 16-18).

The recovery of nuclear grade uranium and plutonium from fuel reprocessing feed solutions requires the removal of fission products (in principle the elements with atomic number from 30 to 67), neptunium, americium, curium, activation products, corrosion products, and other impurities such as added chemicals, down to a maximum thermal neutron absorption of the total amount of impurities equivalent to eight parts of natural boron per million parts of uranium or five parts of natural boron per million parts of plutonium; according to U.S. specifications the activity deriving from fission products shall not exceed 8 μCi/g of Pu and the maximum fission product gamma and beta activity of recovered uranium shall be 200% of the corresponding (gamma or beta) activity of aged natural uranium. In a somewhat simplified way one may state that nuclear fuel reprocessing is the art of separating uranium and plutonium from fission product zirconium, niobium and ruthenium, the elements most difficult to separate. Nevertheless, it remains a difficult task to accomplish this separation remotely to the required degree and on an industrial scale.

To reach the specification requirements given above, a three-cycle Purex process is usually necessary. It has been the aim of our studies to explore the possibilities and limitations of the (one-cycle) Purochromex process as a new tool in the back-end of the fuel cycle, in comparison to the processes applied up to now. The process described hereafter for the recovery of uranium and plutonium from light-water reactor (LWR) fuel can obviously be applied to other low-enriched fuels and to a wide variety of waste materials.

## Processing of LWR-fuel (Standard Flowsheet)

Separation unit. Two silica gel columns ($SiO_2$-Col. A and B) provided with a quartz wool or an asbestos filter on top, length/diameter ratio = 5; three identical TBP-columns interconnected in series, with a diameter depending on criticality limitations, flow resistance and desired capacity; length/diameter ratio $\geq 12$.

Dissolution and feed adjustment. The irradiated fuel is dissolved in nitric acid. The dissolver solution is adjusted to a final acidity of 5 to 6 M free nitric acid in such a way that the uranium concentration remains as high as possible, but not higher than 250 g U/l to avoid crystallization. The plutonium is usually almost quantitatively in the tetravalent oxidation state. If analysis shows that this is not the case, the solution is sparged by nitrous gases.

Column operation steps. The adjusted feed solution is fed at a flow rate of less than 3 $ml \cdot cm^{-2} \cdot min^{-1}$ to the chromatographic column system consisting of a silica gel column ($SiO_2$-Col. A) and three TBP-columns (Col. I, II, and III) in series. When the uranium breaks through Col. I, the addition of the feed solution is stopped.

The feed solution present in the interstitial volume of the $SiO_2$-Col. A is displaced to Col. I by washing with 1 bed volume 5 to 6 M $HNO_3$ (preferably 5.7 M) at a rate of less than 1 $ml \cdot cm^{-2} \cdot min^{-1}$.

Col. I is then washed with 2.5 bed volumes 5 to 6 M $HNO_3$ at a flow rate of 2 to 4 $ml \cdot cm^{-2} \cdot min^{-1}$ to displace the residual feed solution and plutonium to the second column, and to remove quantitatively fission products and other impurities from Col. I which, at this stage, is normally loaded with uranium only (sometimes plutonium and zirconium may still be present). The effluent from Col. I flows via Col. II (and at high uranium concentration in the feed, also via Col. III, to avoid losses of plutonium and uranium) to the high-level waste collection tank for subsequent concentration and acid recovery.

The uranium from Col. I is eluted with three bed volumes of distilled water at a flow rate of 1 $ml \cdot cm^{-2} \cdot min^{-1}$ and is collected in the uranium product vessel.

The plutonium present in the tetravalent oxidation state in Col. II is reduced to the TBP-inextractable trivalent state and is eluted, by passing through Col. II, 1.0 to 1.3 bed volumes of one of the following reducing solutions (depending on whether iron and/or sulfate can be tolerated in the subsequent treatment) at a flow of less than 1 $ml \cdot cm^{-2} \cdot min^{-1}$: (a) 0.1 M ferrous sulfamate in 2.5 M nitric acid; (b) 0.1 M ferrous nitrate, 0.1 M hydrazine in 1.8 M nitric acid; (c) 0.1 M sulfurous acid, 0.05 M sulfamic acid in 2 M $HNO_3$.

Subsequently, Col. II is washed with about one bed volume 2.5 M $HNO_3$ at a flow of less than 1 $ml \cdot cm^{-2} \cdot min^{-1}$ to remove quantitatively the reductant; this must be verified by analysis or inline measurements. The effluents of Col. II contain Pu(III), the reducing agents and their oxidation products, possibly uranium, and traces of fission products; they are collected in the Pu-product vessel for further treatment.

The residual uranium is eluted from Col. II by water and collected in a separate vessel; after analysis it is either reworked or added to the uranium final product. After removal of uranium from Col. II (not mandatory for each run) the "forward cycle" is finished and the "backward cycle" can start by forcing the feed solution to pass first downward through the $SiO_2$-Col. B and then directly to Col. III (followed by II and I) until uranium breaks through Col. III.

The feed is then stopped, and the washing and elution flowsheet is followed as described above for the forward cycle. For one complete cycle all solutions should flow at room temperature through the TBP-columns in one direction only, e.g., from the bottom to the top. In one of the subsequent cycles it can be of advantage to reverse the flow direction in order to release gas bubbles, to improve the decontamination, to increase the product concentration, and to reduce a one-sided TBP-depletion.

## Results and Discussion

The Purochromex Process and modifications of it have been tested with real fuel reprocessing feed solutions on a laboratory scale in which columns of 10 to 1000 ml bed volumes were used. Proper design of the column system (low dead corners and volumes) and the application of inline and online instruments for the measurement of the fission product activity (by gamma monitors), plutonium (by alpha and neutron monitors) and uranium (by X-ray fluorescence, gamma-absorption, and spectrophotometry) permitted the attainment in one cycle of gross beta-gamma decontamination factors of the order of $10^7$ for the uranium product (from the "U-displacement columns" number I and III) and $10^4$ to $10^5$ for the plutonium product obtained from the "Pu-elution column" (number II). The uranium product contains practically no plutonium while the plutonium product may contain uranium. A longer Col. II would be advantageous as it prevents to a higher degree the breakthrough of uranium into the plutonium product. The plutonium fraction requires, in most cases, a further purification (see section "Purification of Plutonium") to fulfill present-day nuclear specifications.

The second TBP-column may also be operated in such a way that the uranium to plutonium ratio, as well as the contamination of their mixture by fission products, can be predetermined or adjusted. For a "Civex type" flowsheet or a coprocessing flowsheet the uranium(VI) can be eluted simultaneously with 0.3 $\underline{M}$ nitric acid as they have nearly the same distribution coefficient under the given Purochromex conditions. For the recycling of plutonium in thermal reactors the mass fraction of fissile plutonium should be about 2.8% when natural uranium is used as diluent to achieve an equivalent discharge burnup of fuels with an enrichment of 3.2% uranium-235; a lower mass fraction of plutonium is required if the residual $^{235}U$ enrichment of the processed LWR-fuel is higher than 0.71%.

The high-acid (5 to 6 M $HNO_3$) flowsheet employed assures: (1) the highest possible extractant loading with the macro-component, uranium, causing a considerable decrease of the distribution coefficient of all other elements and, therewith, a higher decontamination; (2) a high decontamination of ruthenium; (3) the minimum gross extractability of zirconium, niobium and ruthenium ($K_d = 0.5$); and (4) a minimum movement of the uranium and plutonium front during the removal of the impurities. Several parameters of the standard flowsheet may be changed with the goal of reducing the volumes of the product and waste and increasing the purity of the plutonium product.

Losses of uranium and TBP-extractable plutonium can be avoided by an appropriate column packing, TBP-loading, column dimensions, flow rate, uranium concentration in the feed and automatic effluent control; thus, uranium and plutonium yields of higher than 99.6% have been achieved. However, the residence time of uranium and plutonium in the TBP-phase has to be kept as short as required. The interstitial space of the columns should be filled with water when not in operation.

The silica gel column retains highly active undissolved fuel particles (on the top), and, in addition, 50 to 90% of the zirconium/niobium (5,12) and more than 60% of the Sb (13). To avoid recontamination of uranium by the ingrowing daughter products, the wash solution for the TBP-columns must bypass the $SiO_2$-Col. The stationary TBP-phase is purified by washing the columns with 0.3 M sodium hydroxide (removal of residual ruthenium and dibutyl phosphate) followed by a water wash. The frequency of the TBP purification depends on the level of the accumulated fission product activity.

At the end of the useful lifetime of the stationary phase (TBP and support) the TBP is removed by elution with kerosene. The resulting solvent waste solution can advantageously be treated by using the Eurowatt process (14), or alternatively, the entire column filling can be incorporated into bitumen or another matrix material, provided that the resulting products meet with established acceptance criteria for their final storage.

Appropriate cutting of the HLW-effluent fraction from the feed loading step permits concentration of the tritium in a small volume. The HLW-solutions can be vitrified by making use of the active silica gel and sodium hydroxide as reagents, or they can be solidified by the Minerva-process (15), in which the active phosphoric acid resulting from the Eurowatt process can also be used as a reagent.

The entire Purochromex process, and particularly the uranium loading and elution steps, have been cold tested extensively on a pilot scale using columns of up to 70 L bed volume, various lots of Levextrel-TBP resins, natural uranium and inactive representative impurities, such as zirconium, cesium, strontium, cerium, nitrosylruthenium nitrato and nitro complexes, and corrosion products (Fe, Cr, Ni). Fully active pilot scale demonstration tests have been planned for years; they will finally be executed in mid-1980 in the framework of an international R&D program.

## The Eurochromex Process

"Eurochromex" is the acronym for enriched uranium reprocessing on chromatographic extraction columns. This process has primarily been designed for the processing of irradiated fuels from research reactors, Materials Testing Reactors (MTR), and ship propulsion reactors to recover the highly enriched uranium in a nuclear grade purity for reuse. Using minor flowsheet changes, the process can also be applied to recover the relatively highly enriched uranium from aqueous sulfate solutions used in homogeneous reactors.

The process principles applied to achieve a high degree of product recovery and decontamination from undesired impurities are the same as in the Purochromex process. An incentive for the present development effort is that plants for the commercial reprocessing of power reactor fuels are usually not suited to process nuclear fuels highly enriched in uranium-235 because of safety, technical, and economic reasons. To avoid significant disturbances of the normal operation, and additional criticality, corrosion and waste problems, it is preferable to process the relatively small, but very valuable, amounts of irradiated highly enriched uranium (HEU) in a tailor-made facility.

In designing the facility and the process the following factors — distinguishing HEU from normal uranium processing — need to be considered: (1) the small amount of plutonium present in the fuel, which is normally not worth recovering (on economical grounds) and is therefore discarded along with the fission products; (2) the large amount of alloying metals which act as salting agents and dictate the solution concentration due to solubility limits; (3) the increased risk of exceeding criticality limitations; (4) the higher decontamination factors required due to the higher burnup (higher fission product to uranium ratio); and (5) the relatively small amounts of uranium involved. Because of these factors, extraction chromatography can offer technical and economical advantages compared to the conventional extraction techniques and equipment.

The Eurochromex process is carried out using basically the same separation principles and equipment as for the Purochromex process; the process chemistry follows in general the solvent extraction processes used or developed at Eurochemic, but adapted to an extraction chromatographic flowsheet. The process steps for the recovery of HEU from three typical reactor fuels by the Eurochromex process will be described hereafter. These steps include dissolution of the fuel (except for homogeneous fuel), adjustment of the aqueous feed solution, feed clarification, extraction of the HEU by the stationary TBP-phase, reductive scrubbing of plutonium and fission products, and elution of uranium (stripping) by an aqueous phase.

### U/Al Alloy Fuel

This process has been designed and tested to recover uranium from aluminum-clad aluminum-uranium alloy (MTR) fuel elements. The initial uranium enrichment prior to irradiation can be as high as 93 wt % $^{235}U$, and the Al/U ratio in an element ranges usually from 15 to 40. Canning and fuel alloy material are dissolved together. The entire process is carried out at room temperature in geometrically safe equipment involving, after feed adjustment and clarification, simple column operation steps which can be controlled completely automatically.

In the following the essential flowsheet data and process steps are given:

Separation unit. Two sintered stainless steel filters (type 304) in parallel (10μ mean pore size), 2 silica gel columns (A and B, ∅ 12 x 60 cm), three TBP columns in series (∅ $\leq$ 12 x 150 to 400 cm, corresponding to a maximum bed volume of 17 to 45 L). For the present flowsheet a height of 250 cm was used (28 L bed volume). Stationary phase: 60 wt % undiluted TBP sorbed on 40 wt % polystyrene-divinylbenzene copolymer (e.g., Lewatit OC 1023).

Dissolution and feed composition. The fuel elements are dissolved in nitric acid (6.2 $\underline{M}$ initially) in the presence of mercury nitrate, acting as catalyst, to obtain a final solution containing less than 7.5 g U/L. As long as the Al/U weight ratio exceeds a value of 6.8, the U concentration in the dissolver product cannot exceed 19 g/L, because of the limited solubility of aluminum nitrate (68 g/L). A typical composition of the feed solution is 1.5 g U/L, 40 g Al/L, 0.5 $\underline{M}$ $HNO_3$, 0.006 $\underline{M}$ Hg, ca. 500 Ci fission products/L, trace concentration of Pu.

Column operation steps. The feed solution is pumped through the stainless steel filter, silica gel column A, and TBP-Col. I, II, and III until breakthrough of uranium occurs through TBP Col. II, at a flowrate of 3 $ml \cdot cm^{-2} \cdot min^{-1}$. [Note: to reduce the radiation dose received by the stationary phase, the uranium-free effluents are sent directly to the waste collection tank, bypassing the next column(s).]

The TBP columns are washed (scrubbed) with 1.5 bed volumes of a 1 $\underline{M}$ aluminum nitrate/0.5 $\underline{M}$ acid deficient solution containing 0.01 $\underline{M}$ ferrous sulfamate and 0.02 $\underline{M}$ hydrazine, at 1 $ml \cdot cm^{-2} \cdot min^{-1}$.

The TBP columns are then washed with 1.5 bed volumes of 4 M $HNO_3$ at 1 $ml \cdot cm^{-2} \cdot min^{-1}$.

The uranium is eluted (stripped) from TBP-Col. I and II with two bed volumes of 0.01 M $HNO_3$ at 0.5 $ml \cdot cm^{-2} \cdot min^{-1}$. A new cycle can now begin by charging first TBP-Col. III and then Col. II until breakthrough of uranium occurs. The operation then continues with the wash (scrub) step, etc.

## U/Zr Alloy Fuel

HEU zirconium alloy fuel can be clad by zirconium or a suitable zirconium alloy (e.g., Zircaloy 2). The present development work was carried out using steam-autoclaved unirradiated fuels containing 98 to 99 wt % Zr and 1 to 2 wt % HEU (225 g HEU/element).

Separation unit. (Same as for U/Al fuel processing, except that the silica gel columns are omitted.)

Dissolution and feed adjustment. The fuel elements are dissolved with a mixture of 5.5 M $NH_4F$/0.5 M $NH_4NO_3$ (Zirflex process); to the hot (80°C) solution an $Al(NO_3)_3$-$HNO_3$ solution is added to stabilize the fuel feed solution and to oxidize uranium quantitatively to the hexavalent state (16). The final feed solutions obtained, which are stable for at least three months, had the following approximate compositions:

Free $HNO_3$: 0.9 to 1.0 M (to avoid hydrolysis $HNO_3$ should be >0.75 M)
U : 0.4 to 0.8 g/L
Al : 0.92 M (as Al-nitrate)
Zr : 0.45 M
F-total : 3.2 M; $NO_3^-$ total: 3.8 M
Spec. density : 1.24 (at 25°C).

Columns operation steps. The feed solution is pumped at a rate of 1.0 to 1.5 $ml \cdot cm^{-2} \cdot min^{-1}$ through stainless steel filter, TBP-Col. I, II, and III until uranium breaks through Col. II.

The TBP-columns are washed by passing two bed volumes of 0.9 M aluminum nitrate/0.01 M ferrous nitrate/0.02 M hydrazine through the column system using a flowrate of 2 $ml \cdot cm^{-2} \cdot min^{-1}$. The aluminum nitrate waste solution containing only small amounts of fluoride is stored separately.

The TBP columns are then washed with two bed volumes of 5 M $HNO_3$ at a rate of 2 $ml \cdot cm^{-2} \cdot min^{-1}$, and the HEU is eluted from Col. I and Col. II with three bed volumes of acidified water at a rate of 1 $ml \cdot cm^{-2} \cdot min^{-1}$.

Uranyl Sulfate Solution (Homogeneous Reactor Fuel)

Following a request to process separately an irradiated uranyl sulfate solution without blending the valuable high-enriched uranium present with a uranium fuel of a much lower enrichment, the applicability of the Eurochromex process to the recovery of the HEU from this type of fuel was tested, with the possibility of operation in a hot cell facility.

The solution to be processed had the following composition:

Total U : 140.4 g/L containing 27.60 g $^{235}U$/L (i.e., 19.66% enrichment)
Free $H_2SO_4$: 0.2 M
Total $SO_4$ : 0.79 M
Pu : 80 mg/L
Activity : 40 Ci/L (mainly due to $^{137}Cs$, $^{90}Sr$, $^{144}Ce$, $^{147}Pm$, and $^{106}Ru$)
$FeSO_4$ : 610 mg/L; $CuSO_4$: 84 mg/L; $Al_2(SO_4)_3$: 32 mg/L.

Several processes were tested using di(2-ethylhexyl) phosphoric acid, trioctylphosphine oxide, a primary amine, and TBP. In order to demonstrate further the versatility of the TBP-Chromex processes in the recovery and purification of actinide elements, we finally selected a Purochromex-type flowsheet. The sulfate content of the fuel solution is sufficiently low to use an aqueous nitrate phase without risking uranium losses to the waste streams. Again, only few chemicals and simple process steps are involved, allowing a fully automated control. The criticality data to be observed were calculated for 20% enrichment to be: concentration =

<45 g U/L; max. diameter of the cylindrical columns = 27 cm; critical mass = 4.0 kg U.

Description of Flowsheet

The process steps given hereafter are valid for the processing of about 3.5 kg U per run. Sub-criticality is maintained by applying geometrically safe equipment and mass limitations.

Separation unit. One silica gel column (Ø 12 x 40 cm) and three columns (Ø 12 x 150 cm) are used in series, each having a bed volume of 17 L. The stationary phase consists of Levextrel-TBP containing 60 wt % TBP (or an equivalent support/TBP system).

Feed adjustment. The uranyl sulfate solution (approximately 25 L) is adjusted by adding a premeasured volume (20 to 23 L) of concentrated $HNO_3$ to obtain a solution which is about 6 M in $HNO_3$. The solution is homogenized by air sparging. About 2 hr is required for this operation.

Column operation steps. The adjusted feed solution is added to the four-column system at a flow of 2 $ml \cdot cm^{-2} \cdot min^{-1}$ (226 ml/min) until uranium starts to break through Col. II. (Time required: 4 hr.)

The columns are washed with 1.5 bed volumes (25 L) or 6 M $HNO_3$/ 0.05 M $Fe(SO_3NH_2)_2$ at 2.0 $ml \cdot cm^{-2} \cdot min^{-1}$, and the effluent of this washing is collected together with the effluent of the feed loading step as "high-level waste." (Time required: 2 hr.)

The TBP columns (not the $SiO_2$ col.) are washed with two to three bed volumes of 6 M $HNO_3$ (breakthrough of U through TBP-Col. III must be avoided) at a rate of 2 $ml \cdot cm^{-2} \cdot min^{-1}$. (Time required: 4 hr.)

The uranium from Col. I and Col. II is eluted by passing three to four bed volumes of distilled water through the columns (preferably at 50 to 60°C) at a rate of 2 $ml \cdot cm^{-2} \cdot min^{-1}$. (Time required: 5 hr.)

The next run is started by feeding the adjusted solution through the $SiO_2$-Col. and then to TBP-Col. III which is already partially loaded with uranium. The following steps are as in the forward cycle. The solution flow through the TBP columns should preferably be from the bottom to the top (upwards).

Depending on the capacity of the TBP columns (proportional to the TBP amount) and the elution volume, the final uranium product concentration is variable but typically in the order of 40 g U/L. For the purification and recovery of about 3 kg HEU, 15 hr are required. The total primary aqueous waste generated amounts to 40 L per kilogram U processed, which can be concentrated to a small volume; the recovered nitric acid can be recycled.

## Results and Discussion

The three Eurochromex process flowsheets have been cold tested on an "industrial scale" (17 to 28 L TBP Col.) and hot tested on a laboratory scale using TBP columns up to 200 ml and synthetic feed solutions spiked with a real MTR-fuel feed solution containing millicurie quantities of fission products. In all uranyl sulfate runs and in some U/Al- and U/Zr-runs, one cycle has been sufficient to obtain a uranium product fulfilling U.S. specifications for uranyl nitrate. However, in several runs intolerably high activities from zirconium, ruthenium, or plutonium and neptunium in the uranium product necessitated a second purification cycle "tailor-made" for a high decontamination from those radionuclides, i.e., purification by silica gel columns of the HEU feed (5 $\underline{M}$ $HNO_3$) and product solution (low acid concentration), high acid wash for ruthenium and a reductive low acid wash for the removal of plutonium, neptunium, and zirconium/niobium prior to the stripping of uranium by 0.01 $\underline{M}$ $HNO_3$.

The loss of uranium to the waste streams was usually less than 0.2%. In principle, any loss of uranium to the acidic waste effluents can be avoided by an appropriate effluent control or the recycling of any uranium-containing waste fractions. The recovery yield thus depends mainly on the quantitative elution of uranium. Application of elevated temperature (60°C) and a low flow rate increases product concentration, but can cause excessive gassing in the column.

It is advisable to wash the TBP column after each cycle with one bed volume of a 0.3 M sodium hydroxide solution to remove residual ruthenium, TBP-degradation products, and possibly non-eluted uranium. Sometimes a small fraction of activity (mainly niobium-95) remained irreversibly sorbed in the columns and could not be eluted by aqueous or alkaline solutions. Monitoring of the gamma activity along the TBP columns, and of the effluent, permits measurement of the decontamination degree and aids in choosing the required mobile phase volumes.

Our investigations have shown that an industrial scale reprocessing of HEU fuels by extraction chromatographic processes is feasible, and that it may offer, due to the separation principle, equipment, and controls involved, economical, safety, and technical advantages over the processes applied up to now.

## PURIFICATION OF PLUTONIUM

With the goal of developing a universally applicable process for the final purification of plutonium solutions originating from fuel reprocessing streams, fuel fabrication scraps, or other waste materials, some fundamental studies were carried out to evaluate optimal process and operating conditions. At first the extraction of pure plutonium nitrate from nitric acid solutions was studied (17). The investigations were then continued using fluoride containing plutonium nitrate solutions, typical products of $PuO_2$ dissolution (18). Subsequently the separation of americium-241, grown in by the radioactive decay of $^{241}Pu$ during storage of plutonium, has been studied.

### Pu Extraction on Levextrel-TBP Columns

The extraction of Pu(IV)-nitrate from nitric acid solutions was investigated using Levextrel-TBP columns (∅ 10 x 110 mm). Some of the experimental data obtained with a resin of 0.16 to 0.3 mm particle size are summarized in Table 3.

Distribution coefficients, calculated by the expression of Martin and Synge (19) from loading experiments of pure plutonium

TABLE 3

Distribution coefficients and HETP at loading of Levextrel-TBP columns

| Exp. No. | Feed composition | | | $D_{Pu(IV)}$ | HETP for Pu(IV) (mm) | Loading of resin for Pu($C=0.5xC_o$) breakthrough | |
|---|---|---|---|---|---|---|---|
| | Pu (g/L) | U (g/L) | $HNO_3$ (M) | | | (g Pu/L) | (g U/L) |
| 1 | 4.29 | - | 4.0 | 42 | 0.8 | 66 | - |
| 2 | 4.6 | 1 | 5.0 | 40 | 0.6 | 67 | 15 |
| 3* | 8.65 | 3 | 6.0 | 27 | 0.6 | 81 | 28 |
| 4 | 3.5 | 3.6 | 3.0 | 35 | 0.4 | 40 | 42 |

5 g Levextrel-TBP (60% TBP), 0.16 to 0.3 mm particle size.

Column: Ø 10 x 110 mm.

Flowrate: 0.83 ml $cm^{-2}\cdot min^{-1}$ (* in exp. No. 3: 1.66 $ml\cdot cm^{-2}\cdot min^{-1}$).

solutions and plutonium solutions containing U(VI) were lower than those obtained from batch equilibrations. The breakthrough capacity (at $C = 0.5 \times C_o$) of a given column for Pu(IV) depends on the concentration of Pu(IV) and nitric acid, on the Pu:U ratio, and on the flowrate of the feed solution. The HETP calculated (height equivalent to a theoretical plate) according to Glueckauf (20) was found to vary between 0.4 and 1.0 mm. Distribution coefficients calculated from column data were found to be 20% lower than those found in batch equilibration experiments. The effects of flowrate on the Pu(IV) loading and on the HETP at breakthrough (at $C = 0.5 \times C_o$) in 10 mm Ø columns have been investigated using 25 g Pu(IV)/L feed solution. The experimental data and results obtained are given in Table 4. The effective linear flowrate, u (cm/min), was calculated from the flowrate, v (ml/min), the cross section of the column, and the average interstitial volume fraction of the resin (0.4). Evaluation of the data by applying

TABLE 4

Effect of flowrate on HETP and loading

| Flowrate |  | HETP (mm) | Pu loading at ($C=0.5\ C_o$) breakthrough (g Pu/L resin) |
|---|---|---|---|
| v (ml/min) | u (cm/min) |  |  |
| 0.7 | 2.2 | 2 | 98 |
| 2.0 | 6.4 | 4 | 96 |
| 3.0 | 9.6 | 6 | 91 |
| 4.0 | 12.8 | 8 | 80 |
| 5.7 | 18.3 | 9 | 74 |
| 8.3 | 26.2 | 16 | 62 |
| 9.2 | 29.5 | 17 | 59 |

Column: Ø 10 mm ($F = 0.78\ cm^2$)

Resin: 10 ml Levextrel-TBP, 0.3 to 0.5 mm

Feed: 24.9 g Pu(IV)/L, 5.1 M $HNO_3$

the van Deemter equation (21) gave the following general expression for the HETP values (in cm) of the column for Pu(IV),

$$HETP = 0.1 + 0.05\ u.$$

Increasing the effective linear flowrate (u) from 2.2 to 29.5 cm/min increased the HETP from 2 to 17 mm and decreased the resin loading at breakthrough from 98 to 59 g Pu(IV) per liter Levextrel-TBP resin.

We tested the validity of the HETP expression for the scaleup of TBP columns. A column with a diameter of 8 cm and a bed volume of 1.2 L, filled with Levextrel-TBP of 0.4 to 0.8 mm particle size, was loaded with 7.5 L of a 5 M $HNO_3$ solution, containing 23.9 g Pu/L, at u = 12.5 cm/min. Experimentally, a HETP of 11 mm was found. The HETP calculated from the van Deemter equation for a small column at a flowrate of u = 12.5 cm/min was 8 mm, which is in quite good agreement with the experimental value.

## Pu-Am Separation

Separation of Am from stored plutonium is often required before using the plutonium for fuel fabrication. Storage of plutonium is preferred in the solid state, usually as the oxide. The oxide, and also scraps from plutonium fuel fabrication, can be dissolved in nitric acid in the presence of fluoride. A process was developed for the extraction of Pu from nitrate solutions containing fluoride, and for the separation of plutonium from americium using Levextrel-TBP resins.

In the presence of fluoride the distribution coefficients of Pu(IV) in TBP are considerably reduced. Complexation of $F^-$ by Al increases the distribution coefficients of Pu(IV). The influence of fluoride and of the Al/F ratio on the distribution of Pu(IV) in the $HNO_3$ Levextrel-TBP system is shown in Fig. 6 (18). Extraction of plutonium by Levextrel-TBP is already satisfactory at an Al/F ratio of 1. Maximum loadings achieved were 140 g Pu/L resin, corresponding to about 370 g Pu/L TBP or almost saturation of the TBP phase.

In column experiments using two columns, each containing 15 ml Levextrel-TBP and connected in series, the loading, washing and elution were studied. Corresponding to the expected composition of solutions from the dissolution of $PuO_2$, the feed solutions contained 25 g Pu/L, 90 mg Am/L, 6 $\underline{M}$ $HNO_3$, 0 to 0.055 $\underline{M}$ F, and 0 to 0.19 $\underline{M}$ $Al(NO_3)_3$. Loadings of 100 to 120 g Pu/L resin were achieved at 5 $ml\cdot cm^{-2}\cdot min^{-1}$ flowrates, with 11 to 22% of the Pu in the effluent of the first and 0.02 to 0.09% of the Pu in the effluent of the second column (Table 5).

Elution of the first column with three bed volumes of 0.3 to 0.5 $\underline{M}$ $HNO_3$ removed 69 to 87% of the Pu from the column (Table 6). The americium content in the plutonium product was in all cases

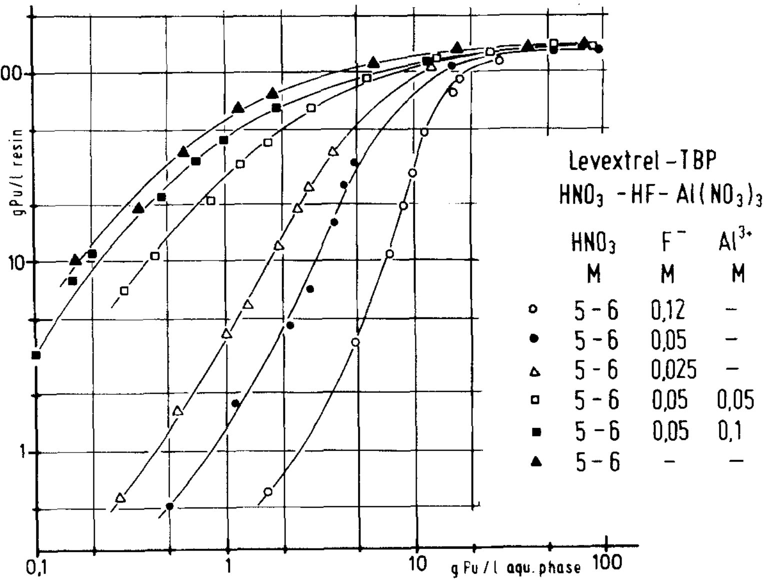

FIGURE 6. Pu distribution in presence of fluoride.

TABLE 5

Loading of Pu(IV) on Levextrel-TBP columns in presence of fluoride

| Exp No | Feed | | Col. I | %- Distribution of Pu | | | |
|---|---|---|---|---|---|---|---|
| | F [M] | Al [M] | Loading after wash [g Pu/l resin] | Col I resin | Col I wash | Col I raffinate | Col II raffinate |
| 1 | 0 | 0 | 74 | 56 | 22 | 22 | 0,08 |
| 2 | 0.055 | 0.05 | 89 | 61 | 21 | 18 | 0,09 |
| 3* | 0.055 | 0.05 | 93 | 65 | 20 | 15 | 0,03 |
| 4* | 0.047 | 0.19 | 95 | 68 | 21 | 11 | 0,02 |

Feed: ~25 gPu/l, ~ 90 mg Am/l, ~ 6 M $HNO_3$, HF, $Al(NO_3)_3$ } Flow 5 ml·$cm^{-2}$ $min^{-1}$
Wash: 5 BV 5 M $HNO_3$ or (•) 5 M $HNO_3$, 0.1 M $Al(NO_3)_3$
Column: Φ 11 × 150 mm

TABLE 6

Pu purification, product quality

| Exp. No. | Feed Al/F | Wash $5M\ HNO_3 + MAl(NO_3)_3$ | Elution $HNO_3$ (M) | Pu-Product (3BV) | | |
|---|---|---|---|---|---|---|
| | | | | Pu g/l | Am ppm | F ppm |
| 1 | no F | 0 | 0,5 | 20.5 | 15 | — |
| 2 | 0.9 | 0 | 0,5 | 20.5 | 45 | 930 |
| 3 | 0.9 | 0.1 | 0,3 | 27.3 | 35 | 50 |
| 4 | 4 | 0.1 | 0,3 | 24,7 | 12 | 45 |

Feed: ~ 25g Pu/l, ~ 90mgAm/l, ~ 6M $HNO_3$, 0-0.055 M HF, 0-0.22 $Al(NO_3)_3$
Elution: 30-55°C
Flow: 5 $ml \cdot cm^{-2} \cdot min^{-1}$

lower than the required 100 ppm. Specifications for fluoride (<100 ppm) were achieved by washing the loaded resin with 5 M $HNO_3$ containing 0.1 M $Al(NO_3)_3$ (experiments 3 and 4). Measured DFs were up to 350 for Am and up to 50 for $F^-$.

Based on our studies the following generalized process for the separation of plutonium from americium has been developed:

Separation unit. Three identical columns 60 wt % TBP, 40 wt % support-(diameter $\leq$ 10 cm) interconnected in series.

Feed adjustment. The acidity is adjusted to 3-6 M $HNO_3$. If not already in the tetravalent oxidation state, plutonium is converted quantitatively to Pu(IV) by sparging the solution with nitrous gases. If $F^-$ is present, its complexation is achieved by addition of $Al(NO_3)_3$ using an Al/F ratio of 3.

Column operation. The adjusted feed solution is fed at room temperature at a flowrate of less than 3 $ml \cdot cm^{-2} \cdot min^{-1}$ to the bottom of Col. I. The feed is stopped when the plutonium breakthrough point of Col. I is reached. Loadings are 120 to 140 g Pu/L resin in Col. I, depending on the feed concentration. The raffinate stream leaving Col. II may contain up to 0.05% of the plutonium after this loading step.

Col. I is washed upwards with 3 to 5 bed volumes of 5 M $HNO_3$ at a flowrate less than 3 $ml \cdot cm^{-2} \cdot min^{-1}$. The effluent flows via Col. II to the waste collection tank. If fluoride has been present in the feed solution, the first 1.5 bed volumes of 5 M $HNO_3$ wash solution should contain 0.1 M $Al(NO_3)_3$.

Plutonium from Col. I is eluted with 2 to 4 bed volumes of 0.3 M $HNO_3$ solution (preferably at 50°C) at $\leq$ 3 $ml \cdot cm^{-2} \cdot min^{-1}$.

## COMPLEMENTARY STUDIES

### Radiation Effects on Stationary Phases

The radiation resistance of the resins is of decisive importance for their use in nuclear technology. First data on gamma irradiation at doses up to 100 Mrad on Levextrel-TBP were reported by Kroebel (22). The effects of gamma radiation on Levextrel-TBP, compared with those on 100% TBP, were extensively studied at the Radiochemical Institute of the University of Munich (23,24) at doses up to 100 Mrad. Formation of dibutyl phosphoric acid (HDBP) and of non-reextractable acidic compounds from TBP was found to be 2 to 5 times lower in TBP resin phases than in liquid 100% TBP. This effect is attributed to aromatic compounds (70% of the C atoms) in the polystyrene matrix. In both cases formation of HDBP and of nonremovable acidic compounds was highest at low nitric acid concentration ($\leq$ 0.5 M) and low organic-to-aqueous ratios during irradiation.

Gamma irradiation of the matrix materials Lewapol (Lewatit CA 9221) and Lewatit OC 1031 up to 130 Mrad showed a decrease of the distribution coefficients for TBP between the matrix and 1 M $HNO_3$ aqueous solutions of about 40%, even at doses of 30 Mrad. Radiolysis of Levextrel-TBP loaded with plutonium and exposed to as much as 100 Mrad of alpha irradiation was studied in Karlsruhe (17). The plutonium retention was 1.5 g Pu/L after an exposure of 38 Mrad and 3.1 g Pu/L after 81 Mrad, with a Pu:HDBP molar ratio of about 1. The measured formation of 37 mg HDBP/Wh is in good agreement with HDBP formation rates in 20% and 30% TBP solutions in dodecane (25, 26).

## Removal of TBP from Aqueous Solutions by Resins

During operation of Levextrel columns,a depletion of TBP takes place,resulting in a reduction of capacity. The TBP loss can be reduced by presaturation of the solutions introduced into the column with TBP, or by topping up the column with TBP after elution.

Product solutions and raffinate streams from the extraction chromatographic processes described above always contain dissolved or entrained TBP. The same is true for aqueous product or raffinate solutions arising in the Purex Process. In both cases removal of organics from the aqueous solutions is highly desirable in order to prevent disturbances in further operations. The methods used so far, steam stripping or scrubbing with kerosene, did not seem to be optimum with regard to purification efficiency and to waste minimization. Therefore we studied the suitability of polystyrene-divinylbenzene resins for removing TBP from aqueous Purex process solutions (27). The experiments were started using Lewatit CA 9221 (Table 2). The most suitable commercial products were found to be Lewatit OC 1031 of the Bayer AG and Amberlite XAD 4 of Roehm and Haas (Table 7). A recently developed Lewatit resin was slightly better than the commercial resins.

The distribution of TBP and HDBP between different resins and aqueous phases is plotted in Fig. 7 as a function of the TBP and HDBP concentration in the aqueous solution. The absorption of HDBP is of the order of 1 to 5% of that of TBP. Amberlite XAD-4 and Lewatit OC 1031 showed nearly identical distribution curves.

The distribution ratios of TBP between the resins and aqueous solutions are equal to or higher than those reported for TBP between dodecane and aqueous solutions. Residual concentrations of TBP in aqueous solutions below 2 mg TBP/L can be obtained in

TABLE 7

Resins for TBP sorption

| Resin | Lewatit OC 1031 | Amberlite XAD-4 |
|---|---|---|
| Surface $m^2/g$ | 400 | 750 |
| Pore size Å | 30-35 | 50 |
| Porosity % | 25 | 51 |
| Density $g/cm^3$ | 1.02 | 1.02 |

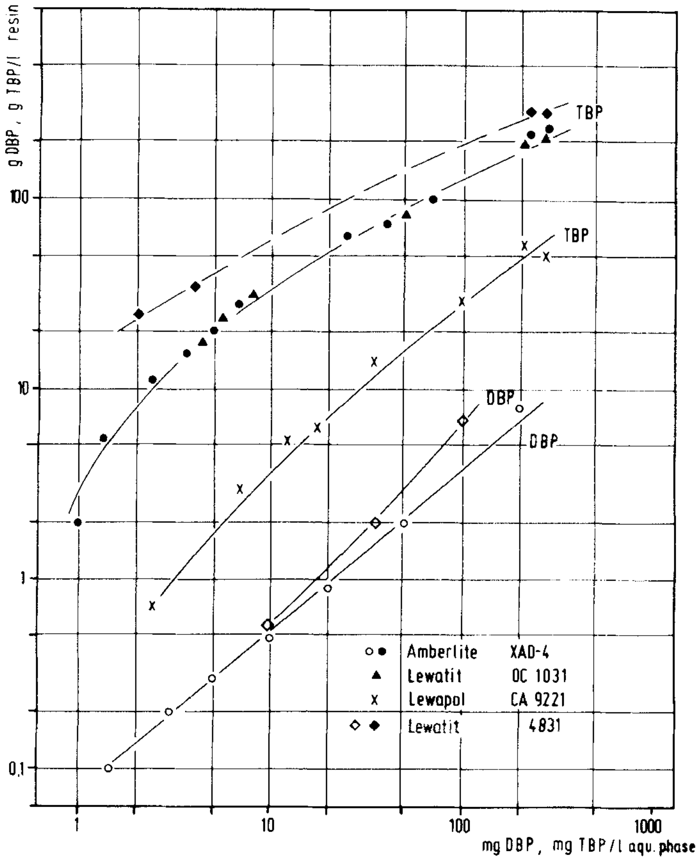

FIGURE 7. DBP and TBP - equilibrium data.

column operation. The resin can be regenerated with an organic solvent without any capacity losses. If solvents with a low boiling point, e.g., methanol, are used, the eluate can be separated by distillation into a TBP fraction and a solvent fraction. The solvent fraction can be reused directly for the regeneration of the resin and the TBP can be recycled after dilution with dodecane and an alkaline washing, or rejected to the waste. Regeneration of the resins requires about 3 to 5 bed volumes of methanol or about twice that volume of dodecane. The quality of resins regenerated by dodecane is inferior, because dodecane is also sorbed by the resin.

TBP and HDBP sorption in columns of ∿5 ml, 1.2 L, 8.8 L, 18 L, and 36 L bed volumes of resin was investigated with feed solutions containing 300 mg TBP/L. At flowrates of 2 $ml \cdot cm^{-2} \cdot min^{-1}$ and at 10 mg TBP/L in the raffinate, loadings were 150 to 160 g TBP/L resin; and at 24 to 27 $ml \cdot cm^{-2} \cdot min^{-1}$, resin loadings of 200 g TBP/L were found at 50% breakthrough. Regeneration of the large columns was coupled with continuous distillation and recycling of the methanol. The effectiveness of TBP-removal remained unchanged after repeated loading and regeneration cycles.

Product solutions of the first and second extraction cycles of highly irradiated fuel were purified from TBP by sorption on resins in the laboratory reprocessing facility MILLI of the Karlsruhe Research Centre (28). The treated uranium and plutonium product solutions came from several reprocessing campaigns with $UO_2$-LWR (∿35,000 MWd/t), LWR-plutonium recycle (<46,000 MWd/t) and fast breeder (<75,000 MWd/t) fuels. In these experiments, Ø 8 x 30 cm and Ø 8 x 40 cm columns, containing 1.3 L or 2 L Lewatit CA 9221 and Amberlite XAD-4 resins, respectively, were used. The purified solutions contained TBP at concentrations below 10 mg/L.

## CONCLUSIONS

The present investigations have shown that extraction chromatography is well-suited to perform difficult radiochemical separations on an industrial scale.

The extremely versatile Purochromex and Eurochromex processes are perhaps the first one-cycle fuel reprocessing processes promising successful application under highly active and remotely controlled operating conditions. Whether they can be applied as primary separation and purification processes, or only for the final purification of the relatively small amounts of plutonium and high enriched uranium, depends on the throughput required, the activity of the feed solutions (burnup and cooling time), and the required purity of the final products.

The availability of a more radiation resistant and chemically stable inert support which has a high extractant take-up and which can repeatedly be reloaded would greatly increase the attractiveness of extraction chromatography for preparative separations of highly active substances.

We hope that our work may contribute to the development of nuclear fission as a low-priced energy source, and that it is used in the sense of its discoverers: for the peaceful application.

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