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EXTRACTION CHROMATOGRAPHIC REMOVAL OF Np AND Pu DURING THE REPROCESSING OF SPENT Th-U FUEL

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ABSTRACT

Spent high enriched U-Th mixed oxide fuels contain small amounts of the actinides Np and Pu. Although these elements cannot be economically recovered for fuel value, current fuel cycle and waste treatment concepts tend to require that processes be developed to include both elements in one of the Thorex reprocessing effluent streams. Chromatographic separation is described as a method to isolate Pu and Np for subsequent disposal.

INTRODUCTION

Spent Th-containing fuel of the HEU-type (Highly Enriched Uranium) contains small amounts of Np and Pu. Both these actinides are valueless components due to their quantity and isotopic composition. However, they are rather hazardous radiotoxic materials, and therefore the recycling of Np and Pu through a reactor is discussed as an alternative to the direct disposal in a final waste repository.

The disposal of Np and Pu is facilitated if these elements can be combined into a single process end stream, either in the waste for final storage after waste treatment, or in the uranium product for recycling through the reactor, or in the thorium stream, for the isolation of Np and Pu and subsequent recycling through the reactor.

Under these premises, the reprocessing of spent Th-U fuel was investigated with regard to the chemical behavior of Np and Pu. In addition, a separation method was developed which can be used without significant modification to purify each of the reprocessing end streams from Np and Pu.

SIMULTANEOUS REMOVAL OF Np AND Pu IN THE COURSE OF REPROCESSING

The two-cycle Thorex-process was used as the reference scheme for the reprocessing of Th-containing fuel. This process consists of two stages: (1) decontamination with a simultaneous extraction and backextraction of Th and U, and separation from the bulk of the fission products, and (2) an extraction-partition stage with a simultaneous extraction of the heavy metals followed by selective backextractions of Th and U. The process is discontinuous between the two stages.

The Np and Pu are distributed throughout the reprocessing end streams since they are present in the feed solution as non-extractable Np(V) and as extractable Pu(VI) species. While Np ends up quantitatively in the waste, Pu appears in the product streams (90% in the thorium product and 10% in the uranium product). This unfavorable behavior can be simply altered by stabilizing those oxidation states of Pu and Np which exhibit suitable extractabilities, or by preparing non-extractable actinide complexes (1). With these modifications, both actinides can be combined in either one of the reprocessing end streams except the uranium product stream. Further treatment then depends on the concept selected for their final disposal. Alternative schemes for the removal and subsequent disposal of these actinides are presented in Fig. 1.

Removal of Np and Pu for Direct Final Storage

Neptunium and plutonium will have no influence on already-tested waste management procedures (denitration, calcination,

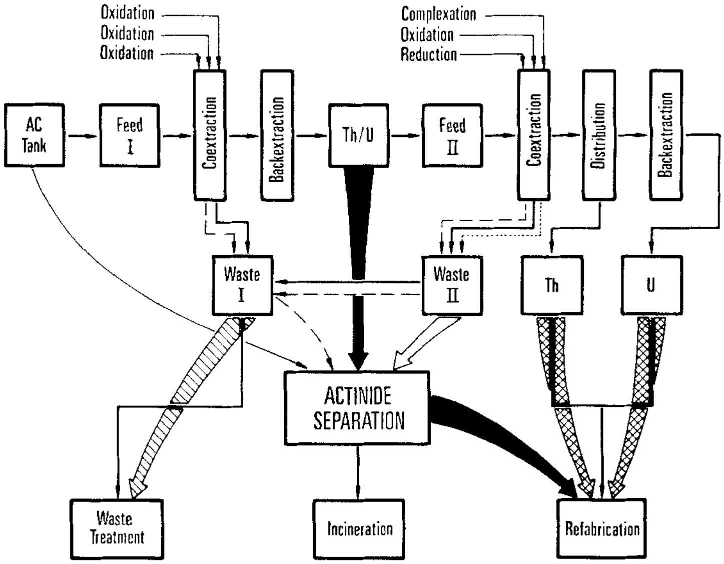

FIGURE 1. Alternative schemes for actinide removal and disposal.

vitrification), since their concentrations are comparatively small. Without changes in the Thorex flowsheet, the first feed solution contains Np(V) and Pu(IV). Consequently, Np ends up in the waste stream of the first extraction cycle, while Pu accompanies the heavy metals and can be withdrawn in the aqueous waste of the second extraction cycle by applying reducing agents. Thus, it may be combined with Np (hatched arrow in Fig. 1).

Coextraction of Np and Pu for the Direct Recycling Through a High Temperature, Gas-Cooled Nuclear Reactor (HTR)

Actinide separation is not necessary if hot refabrication of the total heavy metal (Th + U) is assumed. Np and Pu can be oxidized with VO_4^{3-} to an extractable species during both coextraction steps (crosshatched arrow in Fig. 1) and distributed between the Th- and U-product streams.

Isolation of Np and Pu for Recycling

In case a partial hot refabrication of the recovered heavy metals is desired, Np and Pu must be isolated and hence combined quantitatively in a single process stream. Presumably, isolation of the Pu from the thorium product would be necessary if the recovered thorium is to be refabricated in an unshielded facility after an intermediate storage time. The same is true if the immediate disposal of the thorium is sought, without applying extra stringent measures for thorium storage. As a consequence, the starting solutions for an actinide separation are restricted to the following process streams:

<u>Fuel solution</u> (thin full arrow in Fig. 1). The separation of the actinides takes place before the actual partitioning of the fuel constituents, i.e., before entering the extraction flowsheet. The high fission product dose rate, however, is a great disadvantage.

<u>Waste I</u> (thin broken arrow). The combination of the actinides in the waste stream has already been discussed. The high dose rate complicates the separation in this case also.

<u>Th-U stream</u> (solid arrow). Stabilized as extractable compounds (VO_4^{3-}-oxidation during the first cycle coextraction), the actinides accompany the heavy metals and can be separated from the intermediate product stream of the first cycle. The advantages are that this stream has a low fission product concentration, and that the Thorex-process is discontinuous here. However, the insertion of a new component into an established process flow sheet poses complications.

<u>Waste II</u> (open arrow). After co- and backextraction of the actinides in the first cycle, Np is reduced to non-extractable Np(V) by NO_x formed during the process. Pu can be retained in the aqueous phase with a complexing agent, such as citric acid, which must not interfere with the Th/U-coextraction. This stream has a low fission product content and its use as a starting solution for the actinide separation will not significantly affect the Thorex flowsheet. It should be noted, however, that the feasibility of this process variant must still be proven by mixer-settler experiments.

Provided Np and Pu can be combined in waste II, this stream is the most suitable starting solution for the separation; otherwise, the Th-U stream may be chosen.

After separation, the Np and Pu can be recombined with any fissile material for the refabrication process; this addition should not have any deleterious effects on the refabrication. The isolated transuranium elements may also be used as starting material for incineration in a fast breeder reactor, or in recently developed high flux irradiation facilities.

SEPARATION OF Np AND Pu FROM THE REPROCESSING END STREAMS

Np and Pu isotopes exert a significant influence on the performance of the Th-U fuel cycle, although they are only present in trace quantities. They are separated from the spent fuel solutions mainly to purify the reprocessing end streams, and not for their recovery as species of value. For this purpose, methods with a high separation power are preferred over those with a high separation capacity. Therefore, an extraction chromatographic procedure was chosen to isolate these two actinides.

Separation System

Tetravalent actinides can be easily extracted from HNO_3-solutions by tertiary amines. The sovlent (Alamine 336^R, ∿95% trioctyl amine) is polymerized into polystyrene (2) and combined with the matrix to form the separation compound (Lewextrel type). The distribution coefficients (K_D) of the actinides are nearly independent of acid concentration in the range from 2 M HNO_3 to 6 M HNO_3; these coefficients are compiled in Table 1, whereas the characteristics of the Lewextrel resin is presented in Table 2. The chromatographic support does not show any synergistic effect on the separation.

TABLE 1

Actinide Distribution Coefficients in the System TOA/2 M HNO_3

Aqueous phase	K_D Th(IV)	U(VI)	Np(IV)	Pu(IV)
Infinite dilution	200	<0.01	4600	19,000
30 g Th/L 3 g U/L	1.3	<0.01	110	520

TABLE 2

Characteristics of the Lewextrel-TOA Resin

Composition (weight %)	37.5% trioctyl amine; 23.4% divinyl benzene; 39.1% styrene
Density	0.96 g/cm^3
Grain size	<0.1 mm
Average porosity	47%
Capacity	0.15 mmol/ml resin

This separation system enables the purification of all Thorex-reprocessing end streams from Np and Pu and requires only small variations of the feed adjustment procedure.

Separation Unit

Column operation depends on the capacity of the resin bed, the desired decontamination factors (DK) of the purified solution, and the loading time. As a first approximation, the decontamination factors and the total effluent volume are a function only of the concentration c_u of the separated component in the column effluent at a given column volume (Fig. 2).

The overall column capacity cannot be exploited entirely to obtain a particular DK value since the separation has to be

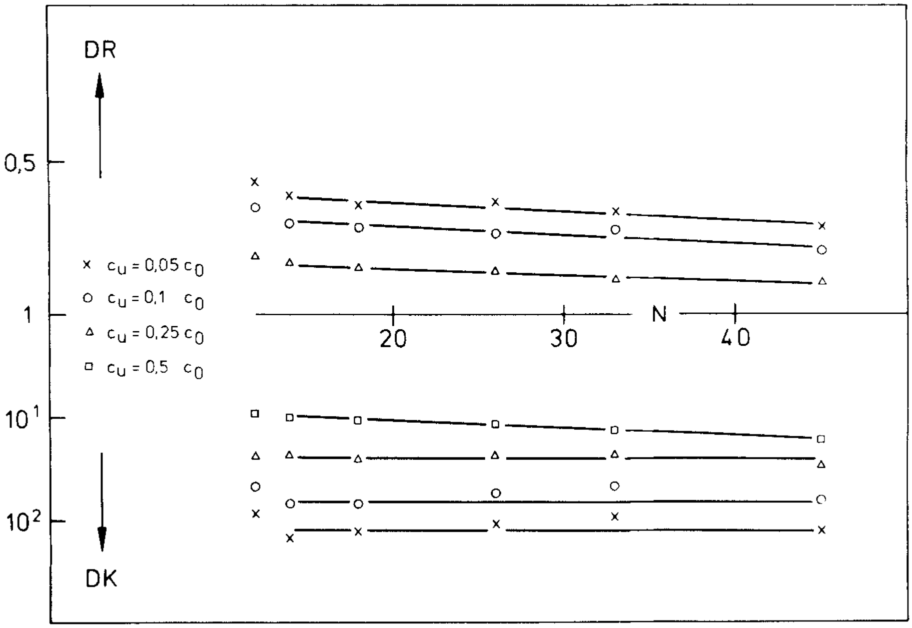

FIGURE 2. Discontinuance ratio DR(=V_u/V_D) and decontamination factors (DK) of a chromatographic separation column as a function of effluent concentration c_u and number of theoretical plates, N. The concentration of feed is designated c_o; V_u is the total effluent volume at initial breakthrough and V_D that for which $c_u = 0.5\ c_o$.

discontinued at that concentration which corresponds to the particular DK value. The highest DK value obtained by one-stage column separation is determined by the detection limit of the analytical method used. The decontamination factors can only be improved by using a two-stage separation unit, with the detector between both stages.

The quantity of the resin is determined by the feed solution volume which must be treated in a single operation. The column dimensions can be calculated with the aid of the equations of van Deemter (3) and Poiseulle (4) (Fig. 3). Thus the column length _l_, the linear velocity _u_, and the residence time _t_ can be

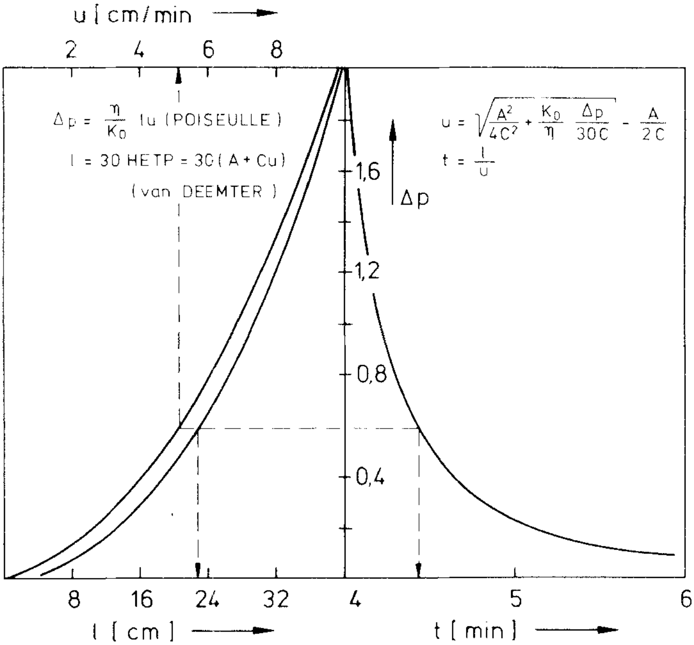

FIGURE 3. Operational criteria of a chromatographic column. η = viscosity; K_0 = permeability; A, C = van Deemter terms; Δp = pressure difference between head and end.

optimized. The degradation of the resin by radiolysis and mechanical strain is taken into consideration when the column is packed.

Separation Process

Extraction chromatography is a discontinuous process and consists of the following steps: (1) preparation of the column to obtain suitable separation conditions; (2) feed adjustment of the starting solution; (3) sorption of Np and Pu on the chromatographic column; (4) desorption of Np and Pu from the chromatographic column; and (5) regeneration of the column. The chromatographic removal of Np and Pu was tested in glove boxes and will be employed in a small semitechnical hot cell facility which is presently under construction (Fig. 4). The starting solution (Th-U

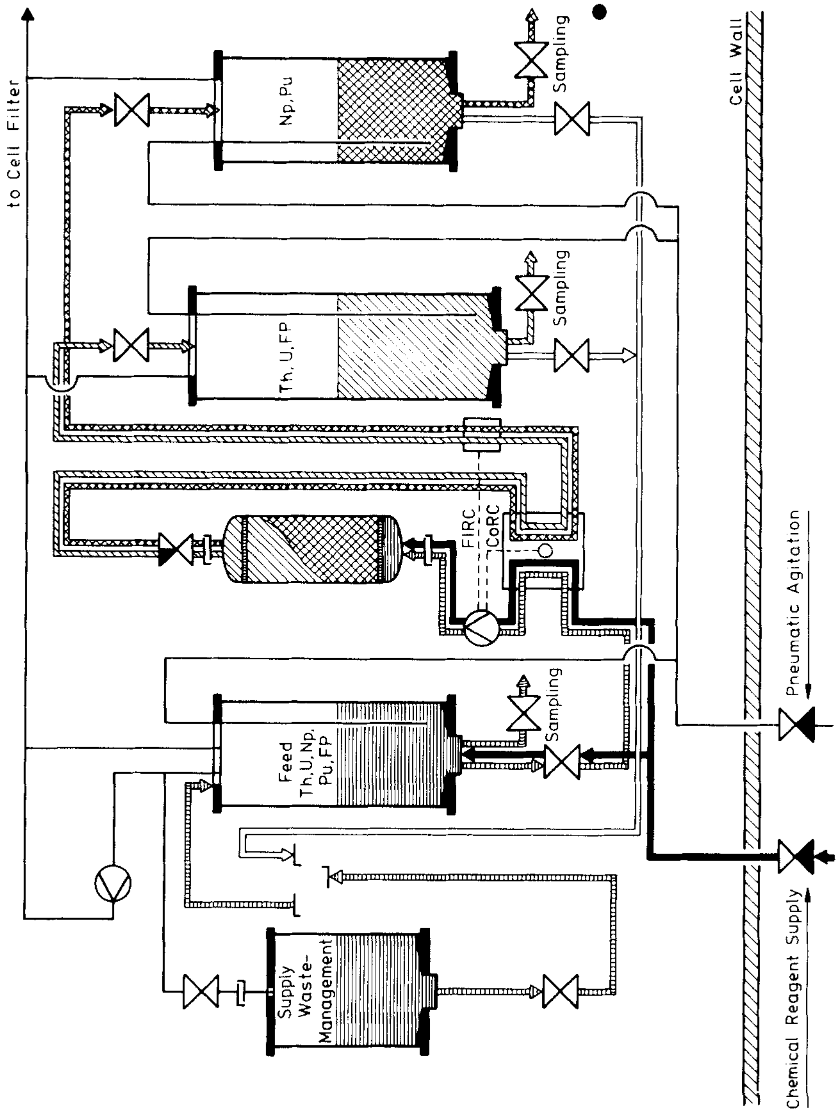

FIGURE 4. Hot cell facility for actinide removal.

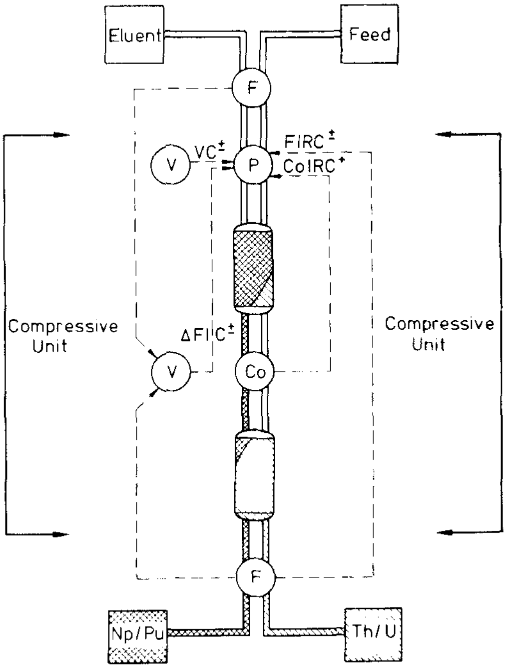

FIGURE 5. Process monitoring of a chromatographic separation column.

intermediate product stream from nuclear fuel reprocessing) is brought inside the hot cell in a transport container and pumped into the feed tank. Feed adjustment is performed by adding concentrated nitric acid through the chemical reagent supply tube from a container located outside the cell. Np is stabilized with $Fe(NH_2SO_3)_2$, and Pu with NO_x; both actinides can be stabilized simultaneously in the tetravalent state by a Fe^{2+}/Fe^{3+} mixture of a definite composition (5,6). Subsequently, the feed solution passes through the column where Np and Pu are absorbed on the resin and the purified Th-U stream is collected in the product tank. Np and Pu are eluted from the column with 0.1 $\underline{M}$ HNO_3/0.1 $\underline{M}$ citric acid, which is added through the chemical reagent supply tube, and collected in the Np-Pu tank. The waste solutions are removed from the hot cell in the transport container.

Monitoring of the Process

Since it is discontinuous, the chromatographic process can only be monitored by determining the concentration of the separated component in the column effluent. For this purpose alpha counters with semiconductor detectors or solid scintillators are used, although a polarographic method is now under development. The chemical analysis is combined with flow rate measurements to monitor the total separation process (Fig. 5). The process is interrupted by the control circuit CoIRC^{+} (Concentration Indicator Recorder Controller) which switches off the pump when the concentration limit has been reached. The flow is regulated by the control circuit FIRC$^{\pm}$ (Flow Indicator Recorder Controller). Leakages and the resulting liquid losses are detected by the control circuit ΔFIC$^{\pm}$ (Differential Flow Indicator Controller) which switches off the pump at an upper and lower limit of the flow rate difference. Lastly, dislocations and obstructions in the resin bed are detected by the circuit VC^{+} (Voltage Controller) which turns the pump off if the voltage of the pump is increased or decreased.

REFERENCES

1. U. Wenzel, C. L. Branquinho, D. Herz, and G. Ritter, American Chemical Society Symposium Series (1979) in press.

2. R. Kröbel and A. Mayer, DBP-2244306 (1974).

3. J. J. van Deemter, F. J. Zuiderweg, and A. Klingenberg, Chem. Eng. Sci. 5, 271 (1956).

4. P. C. Carman, *Flow of Gases Through Porous Media*, Butterworths, London, 1956.

5. D. Gourisse and A. Chesné, Anal. Chim. Acta 45, 321 (1969).

6. H. H. Remagen, JÜL-1505 (1978).