Papers

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Separation of Fission Products, Nitric Acid, Plutonium and Uranium by Extraction Chromatography with TBP-Polystyrene

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Extraction chromatography with tributylphosphate (TBP) impregnated on a polystyrene support (Lewatit OC 1023) has been investigated with a view to its application in the first part of a general actinide separation scheme. In a first step uranium and plutonium is to be recovered from solutions of irradiated fuels or from waste solutions. In a following stage nitric acid is to be partially removed from the non-extractable fission products and transplutonium elements, yielding the low acidity solutions required for most partition processes with these elements [1].

Two types of simulated fuel solutions have been tested. The first contained uranium and simulated fission products corresponding to a burn-up of 3.3%. The transplutonium elements Am and Cm were simulated by the homologous lanthanides Eu and Gd. In the other solution 18% of the uranium was replaced by plutonium. The operation sequence of a system with two columns, each of a volume of 2 l, was as follows: 200 ml of the solution (50 g U or U + Pu, 4 *M* HNO_3) were fed onto a first column to extract uranium and plutonium. The bulk of the fission products and the higher simulated actinides were washed with 6 *M* HNO_3 onto a second column. Both columns were then eluted with distilled water. Uranium and the fission product fractions were detected by photometry. Additionally, for the fission products Gd, Eu, Ru, Sr, Cs, Zr and Nb, tracers were added for their determination by γ-spectroscopy. The plutonium was measured by α-spectroscopy and nitric acid by titration.

Plutonium can be separated from uranium by eluting the first column with an Fe(II) solution to reduce Pu(IV) to the non-extractable Pu(III) and then eluting the U(VI) with water.

By eluting the second column, fission products and higher actinides are obtained as a fraction well separated from nitric acid (Fig. 1).

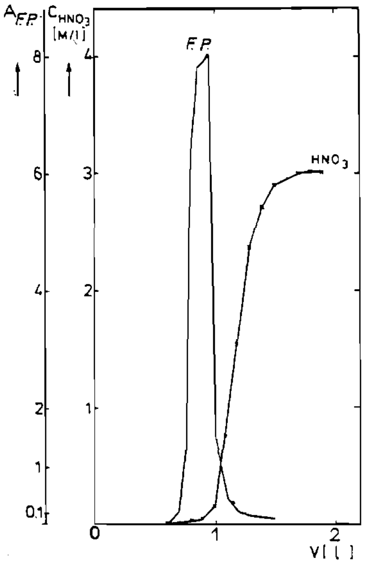

Fig. 1. Separation of fission products (F.P.) from HNO_3. $A_{F.P.}$: absorbance of fission products.

More than 99% of these elements can be recovered in a solution with an acidity of less than 0.5 *M* HNO_3. This acididity is sufficiently low for the later recovery of the actinides. An additional denitration step can thus be avoided.

The troublesome elements Ru and Zr distribute with their main part in the fission-product fraction and a smaller part in the U/Pu fraction [2, 3]. Whereas the non-extracted Zr part is eluted with all the other fission products and is clearly separated from HNO_3, the Ru peak is slightly retarded and shows a stronger tailing. The extracted part of the Ru can be eluted from the first column, separated from uranium, if the column has been previously washed with 6 *M* HNO_3. Ru has a low extraction coefficient with TBP at high acidities in contrast to Zr. For this reason Zr is eluted with uranium when the first column is washed with water (Figs. 2, 3).

It is thus possible to separate on TBP-impregnated polystyrene columns fission products and transplutonium elements from uranium, plutonium and from HNO_3.

1 J. O. Liljenzin, J. Rydberg and G. Skarnemark, *Symp. Sep. Sci. Tech.*, Gatlinburg, 1979.
2 J. V. Holder, *Radiochim. Acta, 25*, 171 (1978).

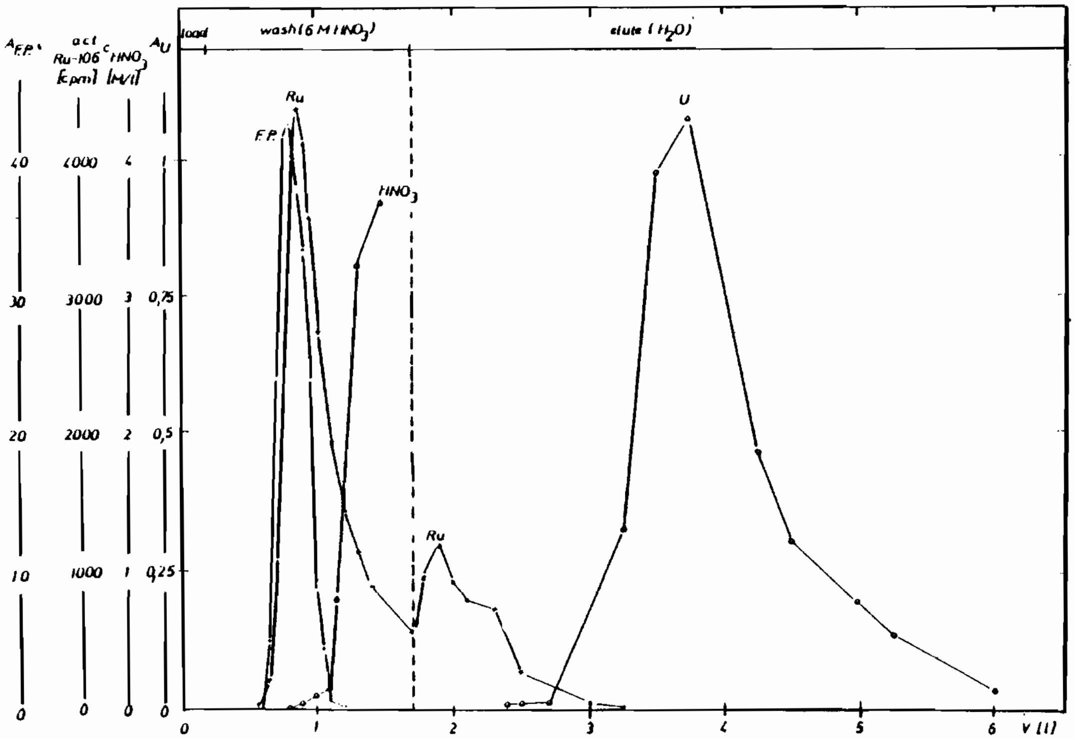

Fig. 2. Separation of Ru and other fission products (F.P.) from HNO3 and U. $A_{F.P.}$: absorbance of fission products, act.: activity, A_U: absorbance of uranium.

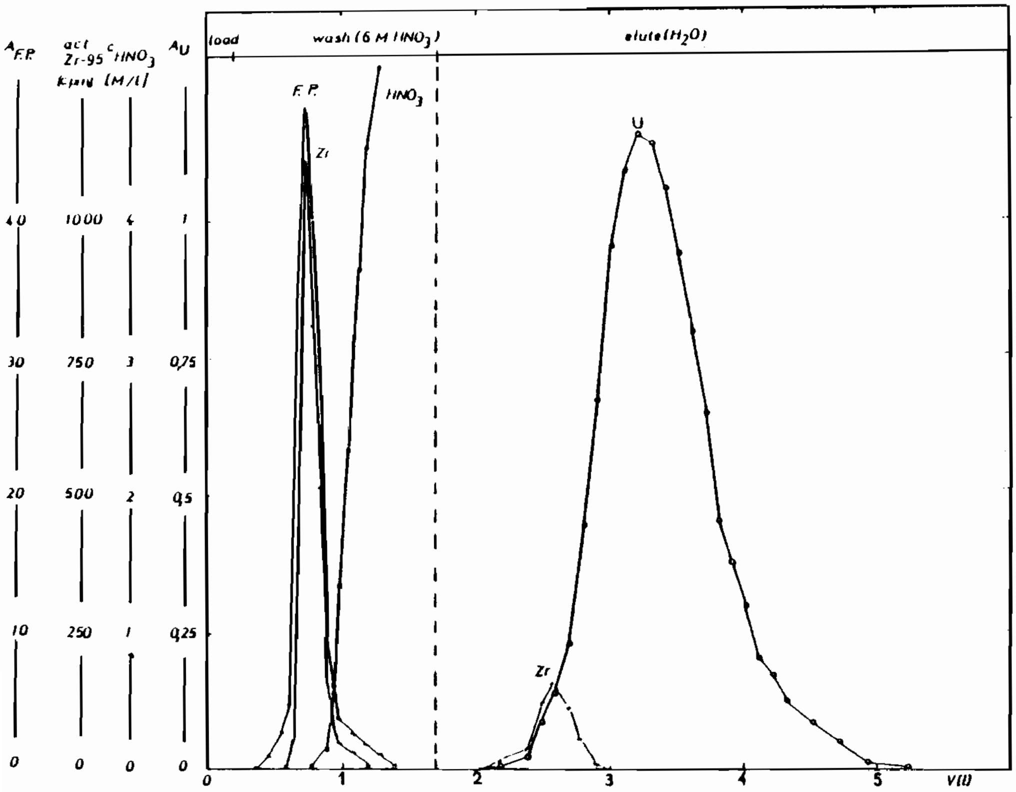

Fig. 3. Separation of Zr and other fission products (F.P.) from HNO3 and U. $A_{F.P.}$: absorbance of fission products, A_U: absorbance of uranium, act.: activity.

3 D. Scargill, C. E. Lyon, N. R. Large and J. M. Fletcher, *J. Inorg. Nucl. Chem.*, *27*, 161 (1965).

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Head-End Scheme for Reprocessing of Advanced Nuclear Fuels by Direct Dissolution in Nitric Acid

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Advanced nuclear fuels—mixed carbides MC, mixed carbonitrides M(C, N), mixed nitrides MN ($M = U_{0.8}Pu_{0.2}$)—show promise for use in future fast breeder reactors (FBR). One precondition for their acceptability as fuels is the mastering of the complete fuel cycle, especially the reprocessing step. In principle, the Purex solvent extraction process, developed for LWR fuel, is also applicable to the recovery of uranium and plutonium from mixed oxide FBR fuel. Additional preparative steps in the head-end of the process are needed for advanced fuels, if the reprocessing is based on the controlled oxidation of the fuel to MO_2 with O_2 or CO_2. Another way of preparing the feed to meet the requirements of the Purex process is the direct dissolution of the carbides or nitrides in nitric acid, as described in this paper.

Specimens of 5–10 g of MC, M(C, N) or MN with burn-ups between 0 and 6.7 at % were dissolved under reflux in 2–12 *M* HNO_3 kept at constant temperatures between 30 and 85 °C for up to 24 hours. The evolved gases were continuously measured by infrared absorption (Miran-80) or samples were taken during and after the dissolution and analysed by mass spectrometry. In the case of MC- and M(C, N)-dissolutions, the CO_2 formed was trapped in NaOH and the carbonate/bicarbonate titrated with HCl under computer control [1].

The resulting solutions were analysed for uranium and plutonium by titration (unirradiated MC), according to the methods of Eberle *et al.* [2] and Davies and Townsend [3], respectively. Additionally, spectrophotometric measurements in the range 400–850 nm were made.

The remotely controlled spectrometer (Cary 17D and HP 9835A) was used to determine the oxidation states of U and Pu along with the total concentrations of these elements by multicomponent analysis, taking the carbon containing compounds in the solution into account [1]. The organic species, mainly mellitic acid and oxalic acid [4], were also identified by ion chromatography (Dionex D 10) [5].

The solutions were filtered through 1.6 μm fritted glass filters, the residues determined by weighing and characterized by x-ray diffraction analyses. After dissolution of the residue in H_2SO_4 and $(NH_4)_2SO_4$ the radioactive fission products were determined by γ-spectrometry, the uranium concentration was measured by isotope dilution mass spectrometry and the plutonium concentration by α-spectrometry.

Gaseous Phase

The off-gas from MC dissolution contains the gases N_2O, NO, NO_2 and CO_2; no hydrocarbons are formed when the nitric acid molarity is above 2 *M*. About 50% of the carbide carbon is released as CO_2, the remainder forms soluble organic compounds. The evolution of the predominant gas, NO, ceases at the end of the carbide dissolution, whereas the formation of NO_2 and CO_2 continues for many hours, indicating an oxidation of the carbonaceous by-products in the solution. Only small amounts of N_2O are found in the off-gas.

Liquid Phase

The MC-fuel dissolves in nitric acid producing a solution containing U(VI), Pu(IV) and carbon containing species [1]. Unirradiated or low burn-up fuels dissolve completely (>99.9%), whereas high burn-up fuels (>4 at%) give rise to minor amounts of residues, which can be removed by filtration. The oxalic acid complexes the plutonium and decreases its extractability with tributylphosphate (TBP) [6]. The carbon containing species can, however, be destroyed by oxidizing chemicals, such as MnO_2 or BiO_3^- [7], or by photochemical treatment [8]. The nuclear radiation absorbed by the sample solution also affects the organic compounds, so that their deleterious influence on the Pu-extraction disappears after storage. MN-fuels dissolve faster than MC under violent NO_x evolution. The solution obtained contains U(VI) and Pu(IV). During M(C, N)-dissolution large amounts (20%) of Pu(VI) were occasionally observed; however Pu(VI) is unstable and transforms to Pu(IV) upon standing.

Solid Phase

The amounts of residues found by dissolution of high burn-up MC and MN are minimized in 8 *M* HNO_3 at 80 °C (*e.g.* 0.5% and 0.3%, respectively). The MC residues contain only very small amounts of uranium and plutonium (*e.g.* 0.04% and 0.3% of the initial fuel amounts, respectively), with a U/Pu ratio in the residue of 0.6, strongly deviating from the U/Pu ratio in the solution (about 3.9). Small amounts of PuO_2 were also found in the residue.

1 H. Bokelund, M. Caceci and M. Ougier, *Radiochim. Acta*, *39*, 49 (1982).