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Redox Behaviour of Neptunium in the Presence of U, Pu, and Am Applied in their Separation by TBP and Ion Exchange (HPLC)*

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In the reprocessing of nuclear fuels by the conventional Purex process, about equal parts of the neptunium follow the uranium and the plutonium product streams [1]. Many chemical flowsheets for neptunium reflect the efforts to lead this element into the highly active waste stream and dispose of it with the fission products, e.g. ref. 2.

In this paper a flowsheet is presented for the recovery of neptunium and other actinides such as uranium, plutonium, americium and curium from solutions of dissolved fuels. Essentially, the neptunium is adjusted to the pentavalent oxidation state by Fe(II) under spectrophotometric control in such a way that plutonium remains tetravalent.

The uranium and the plutonium are sorbed on a chromatographic column containing polystyrene beads impregnated with TBP [3], whereas the neptunium and the higher actinides leave the column with the fission products. In a second column the neptunium and the higher actinides are then recovered individually from the fission product solution by high pressure liquid chromatography, HPLC (cation exchange), in a pH gradient with α-hydroxyisobutyric acid as eluant.

The reduction reactions for neptunium are acid- and time-dependent. In weak HNO_3 (1.2 M) the following reactions take place sequentially, according to the corresponding redox potentials:

$$\mathrm{Np(VI)} \longrightarrow \mathrm{Np(V)} \quad E^\circ \text{ in } 1\ \mathrm{M}\ \mathrm{HNO_3} = 1.14\ \mathrm{V}\ [4,5] \tag{1}$$

$$\mathrm{Pu(IV)} \longrightarrow \mathrm{Pu(III)} \quad E^\circ \text{ in } 1\ \mathrm{M}\ \mathrm{HNO_3} = 0.91\ \mathrm{V} \tag{2}$$

$$\mathrm{Np(V)} \longrightarrow \mathrm{Np(IV)} \quad E^\circ \text{ in } 1\ \mathrm{M}\ \mathrm{HNO_3} = 0.74\ \mathrm{V} \tag{3}$$

The species U(VI) and Am(III) are not influenced by the Fe(II) reduction.

Figure 1 shows absorption spectra for different added amounts of Fe(II) (0.1 M in 2 M HNO_3). The peaks of interest in the reactions (1), (2) and (3) have been marked on the curves with arrows, indicating an increase or decrease upon Fe(II) addition. The reduction can be carried out in such a way that Np(V) is selectively obtained, without reducing the Pu(IV).

In 8 M HNO_3, the sequence of the steps (2) and (3) is interchanged (see Fig. 2) and in 4 M HNO_3 the two reactions run concurrently, as shown in Fig. 3. The Pu(IV) species are stabilized in strong

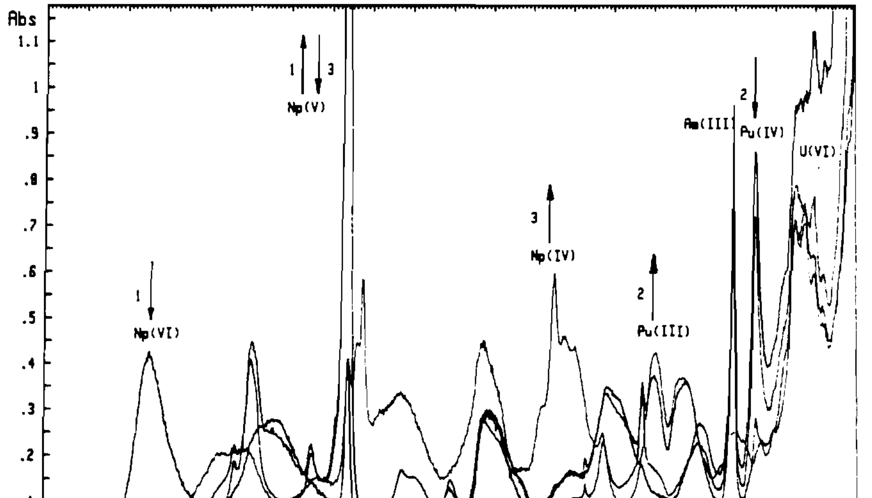

Fig. 1. Absorption spectra of Np-, Pu-, U- and Am-ions in nitric acid solution (1.2 M) + Fe(II).

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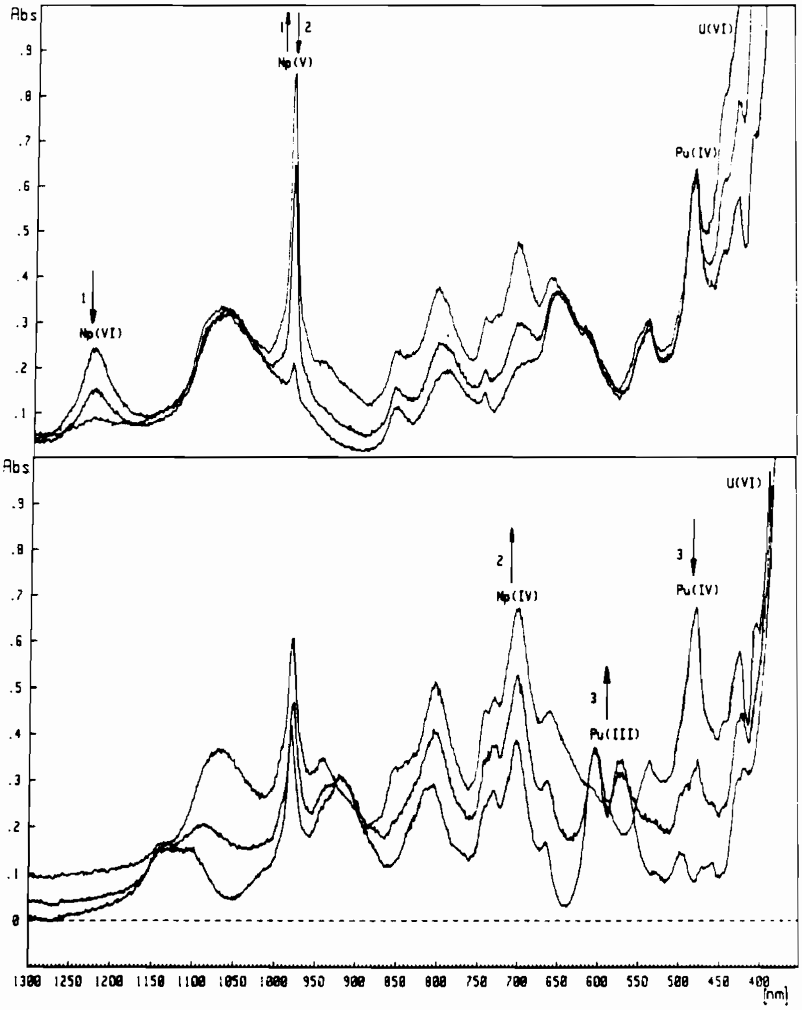

Fig. 2. Absorption spectra of Np-, Pu- and U-ions in nitric acid solutions (8 M) + Fe(II).

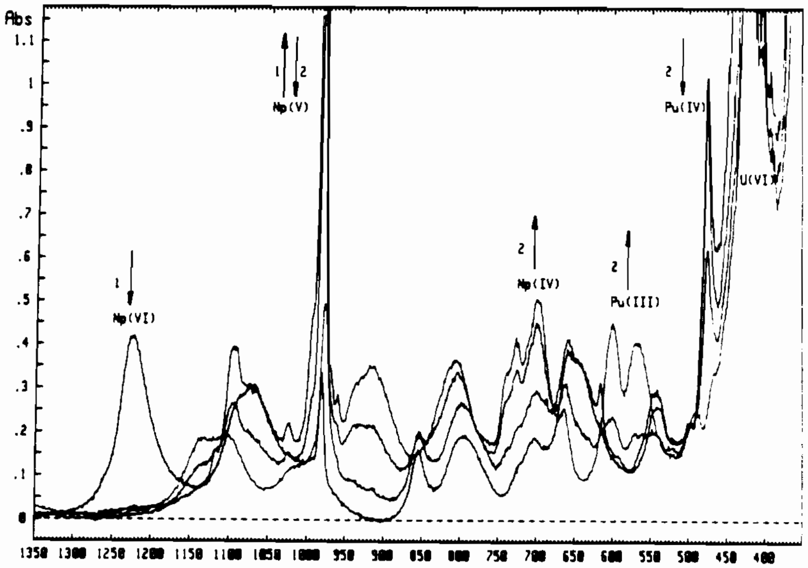

Fig. 3. Absorption spectra of Np-, Pu- and U-ions in nitric acid solution (4 M) + Fe(II).

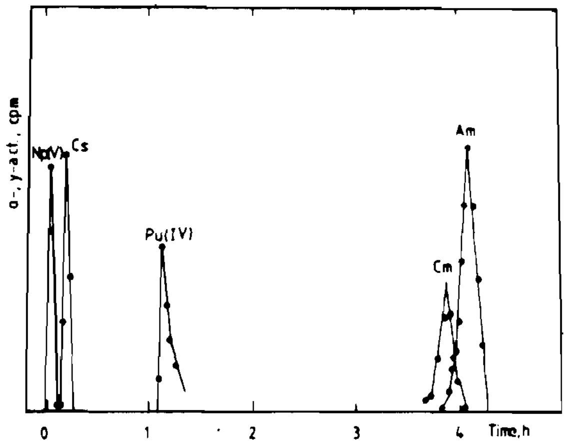

Fig. 4. Chromatogram showing separation of Np(V) from actinides and fission product Cs (HPLC in a pH gradient).

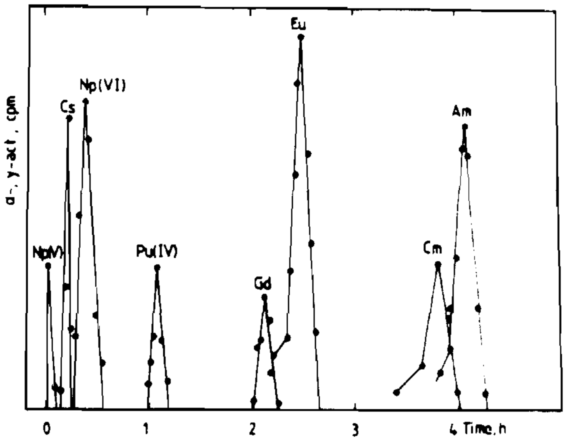

Fig. 5. Chromatogram showing separation of Np(V) and Np(VI) from actinides and fission products (HPLC in a pH gradient).

nitric acid as $Pu(NO_3)_6^{2-}$ ions, thus hampering the reaction path (2); similarly, the formation of a $Np(NO_3)_6^{2-}$ complex facilitates step (3) [6, 7].

In the medium strength acid prevailing in the Purex feed solution, a selective reduction of Np to the non-extractable Np(V) state is possible with Fe(II). The Np will thus pass with the fission products into the HAW solution. The raffinate from the U/Pu separation is fed onto the HPLC column. Here the monovalent Np(V) ion appears ahead of fission product Cs (see Fig. 4); on the other hand, Np(VI) would be positioned just after the Cs peak, as indicated in Fig. 5.

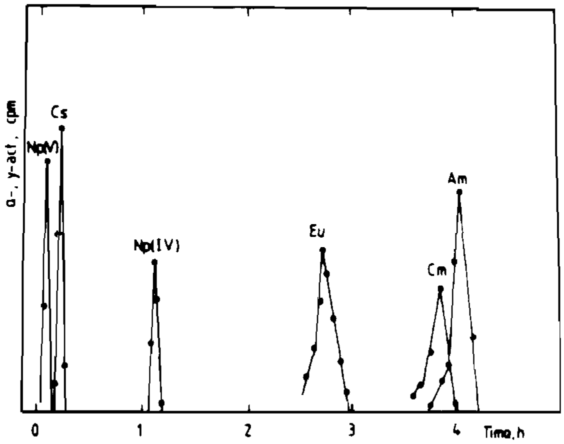

Fig. 6. Chromatogram showing separation of Np(V) and Np(IV) from actinides and fission products (HPLC in a pH gradient).

Figures 5 and 6 show further separations of actinide elements (Np, Pu, Cm and Am) from lanthanides (Gd and Eu) and fission product Cs.

The two tetravalent ions Np(IV) and Pu(IV) elute nearly at the same position, as is seen from the Figs. 5 and 6; however, under the experimental conditions used for the separation, these ions hardly co-exist.

References

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