

Entrou como resumo, porque está faltando a pg. da Introdução. foi solicitado 2 vezes, mas a Harco não mandou

NEPTUNIUM DISTRIBUTION IN A HIGH ACID FIRST CYCLE PUREX PROCESS

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COLEÇÃO PTC

DEVOLVER AO BALÇÃO DE EMPRÉSTIMO

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Abstract

This work deals with the extraction behaviour of neptunium in a high acid Purex Process. The composition of PWR fuel type with 3.2% enrichment, 500 Mwd/t burn-up and 100 days coolig time was considered. Two consecutive cold runs were performed in a mock-up facility at IPEN-CNEN/SP with simulated feed solutions containing: 3M HNO₃; 1M U; 455ug ²³⁷Np labelled with ²³⁹Np; 15mgZr/L, 12mgCe/L, 7mgRu/L and 13mgMo/L traced with active isotopes ⁹⁵Zr, ¹⁴¹Ce, ¹⁰³Ru and ⁹⁹Mo as FP. A 30 vol.% TBP/n-dodecane was used as solvent. Counter-current experiments were carried out using two 16 stages plexiglass mixer-settlers, at 25⁰C, during 21h continuous operation, with O/A ratio of 2 in the extraction section and 9 and 13 in the 1st and 2nd scrubbing sections, respectively. For a 65% organic loading, ca 77% of neptunium remains in the waste stream, without any Np valence adjustment.

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so that the oxidation of NpO_2^+ to NpO_2^{++} does not take place even in the presence of complexing agent as TBP. In higher concentrations, HNO_2 reduces Np(VI) to Np(V) even in oxidant medium.

Maintenance of the desired valence state depends on the rigorous control of nitrous acid concentration in the proper range. This control is difficult due to the HNO_2 production from fuel dissolution, radiolysis of HNO_3 and also by the high distribution into TBP. These conditions must be balanced in the first uranium and plutonium extraction cycle, according of desired product.

The present work deals with the extraction behaviour of neptunium in the presence of uranium and fission products in the first cycle of Purex Process.

II- Experimental

Two consecutive experiments were performed in laboratory with simulated solutions containing uranium, neptunium, fission products and nitric acid. A 30 vol.% tributylphosphate in a mixture with n-dodecane was used as solvent.

The fission products were added as stable isotopes and traced with gamma active isotopes: ^{95}Zr , ^{103}Ru , ^{141}Ce and ^{99}Mo . Neptunium-237 was labelled with ^{239}Np and the intensity of its 0.277MeV peak was measured for determining the relative neptunium radioactive concentration. To supply these tracer isotopes, UO_2 was irradiated at $10^{12}\text{n.cm}^{-2}.\text{s}^{-1}$ neutron flux during eight hours in IEA-R1 research reactor and processed after 65 hours cooling time.

- Feed solution

The simulated feed solution was prepared by dissolving UO_2 pellets, stable fission product isotopes and ^{237}Np (first solution). The dissolution of irradiated UO_2 was performed separately under the safety conditions and then added to the first solution. 8M HNO_3 and 6 hours dissolution

time with gradual heating (2h at 60⁰C, 2h at 80⁰C and final 2h at 100⁰C) were the dissolution conditions in the both cases.

The resulting solution was adjusted to have final 4.2L volume feed solution (for each experiment) containing 1M uranium, 3M HNO₃, 455ug ²³⁷Np/L, 15.25mg Zr/L, 6.8mg Ru/L, 13.2mg Mo/L. The amount of ²³⁷Np and these fission products was supplied by ORIGEN program⁽⁵⁾, taking in account a PWR fuel type with 3.2% enrichment, 500MWd/t of burn-up and 100 days cooling time. The tracer isotope gamma activities are given in Table I. Any neptunium valence adjustment was not done and HNO₂ concentration in the feed solution was <2x10⁻⁶M.

- Process and equipment description

Counter-current experiments were carried-out with two 16 stages plexiglass mixer-settlers with 430 mL total capacity, provided with 16 stainless-steel mixer paddles system driven by a 24V motor. The scheme of the extractor is shown in Figure 1.

Prior to the planned experiments, the hydrodynamic equilibrium and operational tests were performed. After four hours operation, two consecutive experiments were carried-out during 21 hours continuous operation for each run. The process flow-sheet is shown in Figure 2.

Parameters as streams' flow-rate, mixing speed (1440rpm in HA extractor and 1190rpm in HS extractor) and room temperature of 21⁰C were rigorously controlled. Add to that, samples to analytical control were taken at two hours intervals from aqueous and organic streams.

Methods as X-ray fluorescence⁽⁶⁾, gamma spectrometry⁽⁷⁾, potentiometry⁽⁸⁾, spectrophotometry^(9,10) were used for process control purposes.

Uranium, neptunium, nitric acid and fission products distribution profiles were obtained by chemical analysis at the steady state in the final of the process.

Effectiveness was determined by comparative study between theoretical profiles supplied by URAPEX program and experimental profiles.

III- Results and Discussion

Two runs were carried-out under the same experimental conditions. The thermodynamic equilibrium was reached after 6 hours operation with 65% uranium saturation in organic phase in the first experiment and about 67% in the second one. Under these conditions, 79% of neptunium (1st run) and 76% (2nd run) was remained in the aqueous phase together with fission products (HAW stream). Neptunium control data taken during 21 hours continuous operation in two hours intervals is given in Table II.

Concerning to nitrous acid concentration, $< 10^{-2}M$ (detection limit of the method) was maintained in both experiments. The influence of nitrite in this concentration level on the valence state of neptunium is not expected.

The increase of neptunium concentration either in the aqueous or organic phase in the scrubbing section of the HA mixer-settler had been observed. It is probably due to the reextraction of neptunium in the HS contactor, resulting in a recycle to HA extractor.

Figures 3 and 4 show the distribution profiles of uranium, neptunium and nitric acid in aqueous and organic phases of the HA mixer-settler. The extraction effectiveness of uranium of 80 and 85% was obtained for two experiments, respectively.

These are the partial results for neptunium behaviour in trace level concentration concerning to the extraction step of the Purex Process. In these studies any neptunium valence state adjustment in the feed solution was not considered.

The works will be continued with neptunium behaviour studies in the scrubbing and partition steps, as well as in the final product decontamination and neptunium partitioning from HAW stream.

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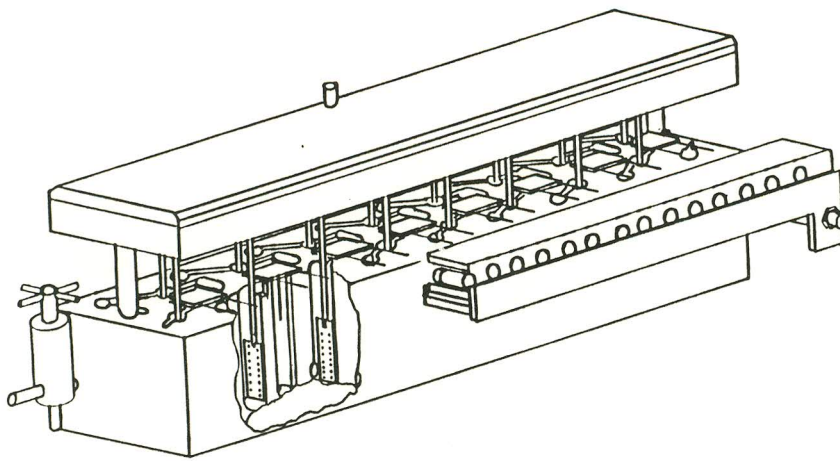
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TABLE I: Tracer isotope gamma activities of the feed solutions

Nuclides	gamma activity (Bq/mL)	
	Experiment 1	Experiment 2
^{239}Np	4.669×10^4	3.640×10^4
^{95}Zr	7.481×10^2	4.588×10^2
^{103}Ru	2.463×10^2	1.931×10^2
^{141}Ce	3.675×10^2	3.559×10^2
^{99}Mo	1.938×10^3	1.991×10^3

TABLE II: Neptunium control data in the aqueous and organic streams

Δt (h)	Experiment 1		Experiment 2	
	HAW (%)	HSP (%)	HAW (%)	HSP (%)
02	80.3	1.7	77.7	1.0
04	74.2	2.0	76.0	2.5
06	68.8	4.8	75.6	3.0
08	80.0	6.5	75.8	8.5
10	74.7	6.5	69.1	7.1
12	85.0	5.0	78.5	7.9
14	78.0	7.0	74.5	19.8
16	83.1	8.1	80.2	20.1
18	82.0	6.3	81.3	22.0
20	83.2	5.1	—	—



**FIGURE 1 - SCHEMATIC VIEW OF THE MIXER-SETTLER
SAMPLING STATION**

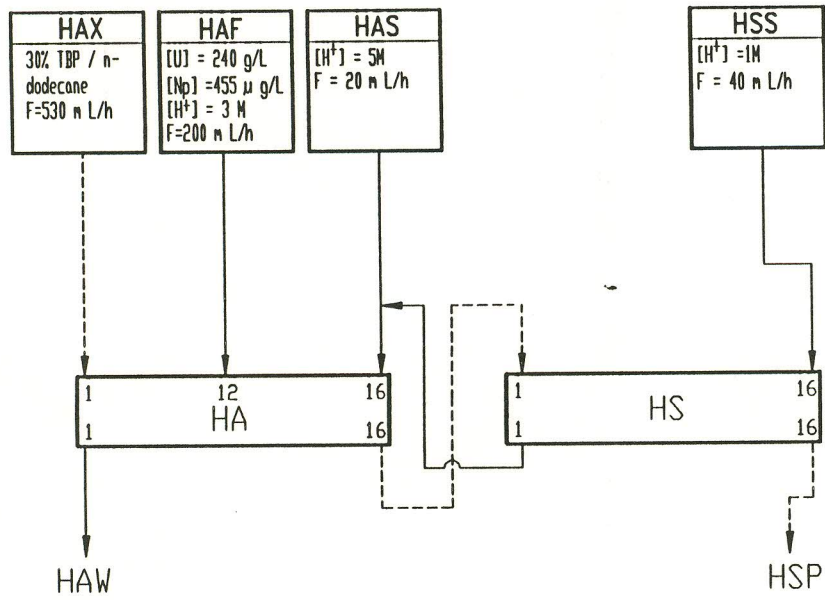


Figure 2 - Process Flowsheet

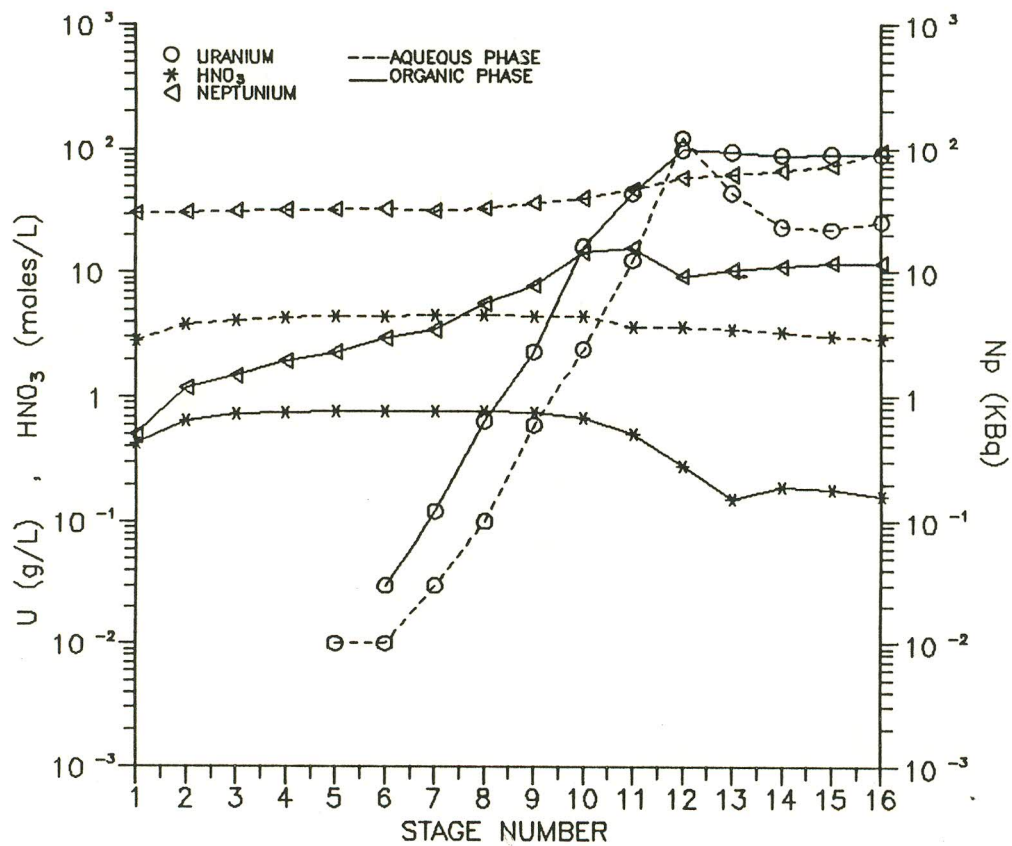


FIGURE 3 - HNO₃, U AND Np DISTRIBUTION PROFILES AT STEAD STATE OF THE HA EXTRACTOR (AQUEOUS AND ORGANIC PHASES, EXPERIMENT NUMBER 1).

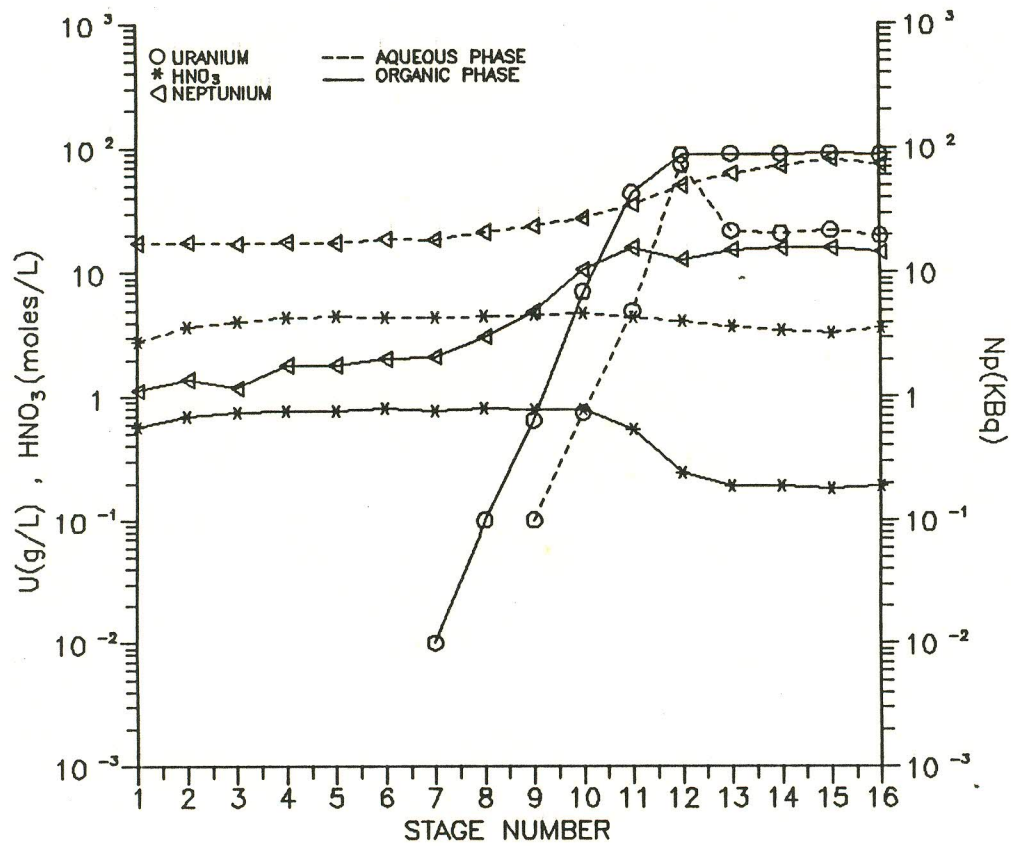


FIGURE 4 - HNO₃, U AND Np DISTRIBUTION PROFILES AT STEAD STATE OF THE HA EXTRACTOR (AQUEOUS AND ORGANIC PHASES, EXPERIMENT NUMBER 2).