NEPTUNIUM DISTRIBUTION IN A HIGH ACID FIRST CYCLE PUREX PROCESS

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This work deals with the extraction behavior
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 d
cooling time was considered. Two consecutive
cold runs were performed in a mock-up facil-
ity at IPEN-CNEN/SP with simulated feed so-
lutions containing: 3M HNO_3; 1M U; 455 ug
^{237}Np labeled with ^{239}Np; 15 mg Zr l^{-1},
12 mg Ce l^{-1}, 7 mg Ru l^{-1} and 13 mg Mo l^{-1}
traced with active isotopes ^{95}Zr, ^{141}Ce,
^{103}Ru and ^{99}Mo 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
25 °C, during 21 h continuous operation,
with O/A ratio of 2 in the extraction sec-
tion and 9 and 13 in the 1st and 2nd scrub-
bing 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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INTRODUCTION

Neptunium-237 is formed by fast neutron irradiation of uranium and as daughter product, by α-decay of americium-241.

A hightly burned-up PWR nuclear fuels contain up to 0.05 wt% neptunium, i.e. 0.5 mg Np g^{-1} U and 50 mg Np g^{-1} Pu. To obtain U and Pu products with a sufficiently low neptunium contamination, separation factors of ca. 100 must be reached during the whole separation process[1,2].

In the Purex Process, neptunium will be distributed through the three different streams: direct discharge with fission products, divided in uranium or plutonium streams or dispersed throughout the process. This chemical behavior of neptunium depends on the complex redox reactions and precise conditions of the process.

After nitric acid dissolution of uranium fuels, neptunium should be mostly as NpO_2^+, which is very slightly extracted in TBP. However, in the reprocessing solutions, neptunium can occur simultaneously in three major valence states, responsible for different extraction behavior. The different neptunium species show different affinities for TBP[3]. Fuel dissolution under oxidizing conditions would favor the higher oxidation states, Np(V) and Np(VI), while the reductant added to convert all the plutonium to Pu(IV) will provide the reduction of Np(VI) to Np(V). Neptunium would be extracted as Np(VI) as well as Np(IV), depending of the redox medium.

The oxidizing system NO_3^-/HNO_2 depends on the acidity on one hand and on the concentration of nitrous acid on the other. It is clear that this system is more oxidizing if the acidity is high and the nitrous acid concentration low, favoring NpO_2^+ oxidation. This reaction

proceeds at a reasonable rate when the HNO_2 concentration is in the range of 10^{-5} to 10^{-3}M, where nitrous acid acts as a catalyst for the oxidation reaction[4]. When the concentration of HNO_2 increases to $>10^{-2}$M, the oxidizing power of nitrate decreases, so that the oxidation of NpO_2^+ to NpO_2^{2+} does not take place even in the presence of a complexing agent such as TBP. At higher concentrations, HNO_2 reduces Np(VI) to Np(V) even in oxidizing media.

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 to the desired product.

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

EXPERIMENTAL

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

The fission products were added as stable isotopes and traced with γ-active isotopes: ^{95}Zr, ^{103}Ru, ^{141}Ce and ^{99}Mo. Neptunium-237 was labeled with ^{239}Np and the intensity of its 0.277 MeV peak was measured for determining the relative neptunium radioactive concentration.

To supply these tracer isotopes, UO_2 was irradiated at 10^{12} n.cm^{-2}.s^{-1} neutron flux for 8 h in an IEA-R1 research reactor and processed after 65 h of 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 h dissolution time with gradual heating (2 h at 60 $^{\circ}C$, 2 h at 80 $^{\circ}C$ and final 2 h at 100 $^{\circ}C$) were the dissolution conditions in both cases.

The resulting solution was adjusted to have 4.2 l final volume feed solution (for each experiment) containing 1M uranium, 3M HNO_3, 455 µg ^{237}Np l^{-1}, 15.25 mg Zr l^{-1}, 6.8 mg Ru l^{-1}, 13.2 mg Mo l^{-1}. The amount of ^{237}Np and these fission products was supplied by ORIGEN program[5], taking into account a PWR fuel type with 3.2% enrichment, 500 MWd/t of burn-up and 100 d cooling time. The tracer isotope γ-activities are given in Table 1. No neptunium valence adjustment was done and the HNO_2 concentration in the feed solution was $<2\times10^{-6}M$.

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 24 V motor. The scheme of the extractor is shown in Fig. 1.

Prior to the planned experiments, the hydrodynamic equilibrium and operational tests were performed. After 4 h operation, two consecutive experiments were carried
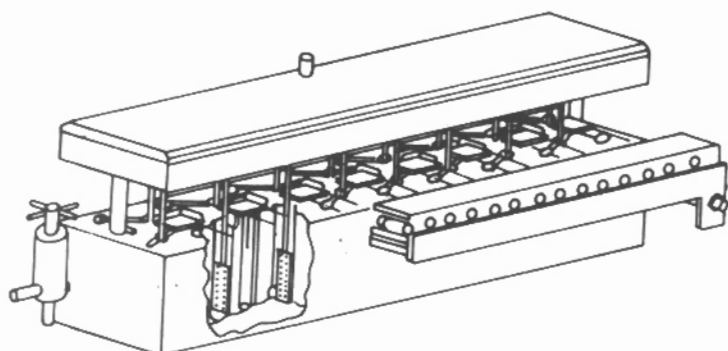
Fig. 1. Schematic view of the mixer-settler sampling
station

TABLE 1

Tracer isotope gamma activities of the feed
solutions

Nuclides	γ-activity, Bq ml^{-1}	
	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

out during 21 h continuous operation for each run. The
process flow-sheet is shown in Fig. 2.

Parameters such as streams flow-rate, mixing speed
(1440 rpm in HA extractor and 1190 rpm in HS extractor)
and room temperature of 21 $^{\circ}$C were rigorously controlled.
In addition, samples for analytical control were taken
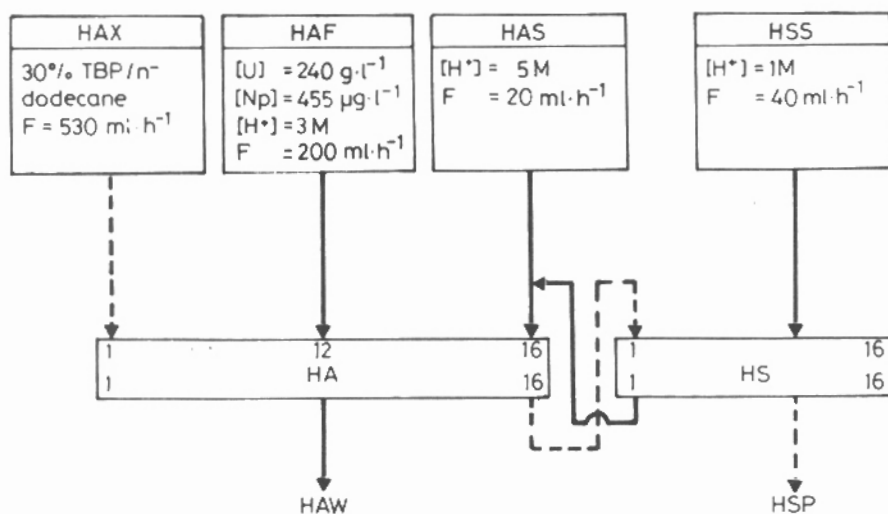at 2 h intervals from aqueous and organic streams.

Fig. 2. Process plowsheet

Methods as X-ray fluorescence[6], γ-spectrometry[7], potentiometry[8], spectrophotometry[9,10] were used for process control purposes.

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

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

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 the organic phase in the first experiment and about 67% in the second one. Under these conditions, 79% of neptu-

TABLE 2

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	-----	----

nium (1st run) and 76% (2nd run) remained in the aqueous phase together with fission products (HAW stream). Neptunium control data taken during 21 h continuous operation at two-hour intervals are given in Table 2.

Concerning nitrous acid concentration, $<10^{-2}$M (detection limit of the method) was maintained in both experiments. The influence of nitrite at 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. This 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
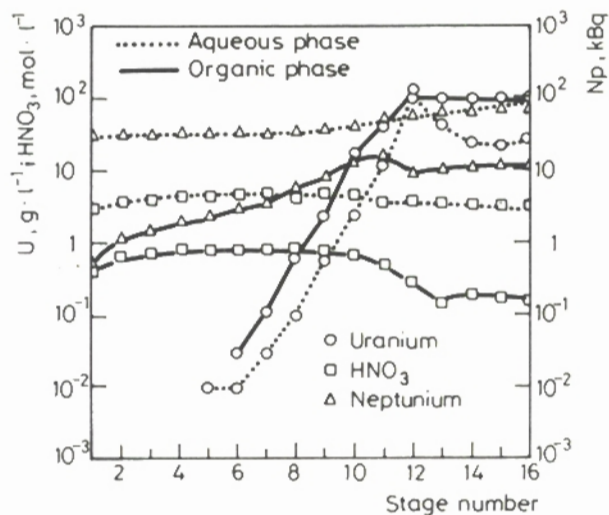
Fig. 3. HNO₃, U and Np distribution profiles in steady state of the HA extractor (aqueous and organic phases, experiment number 1)
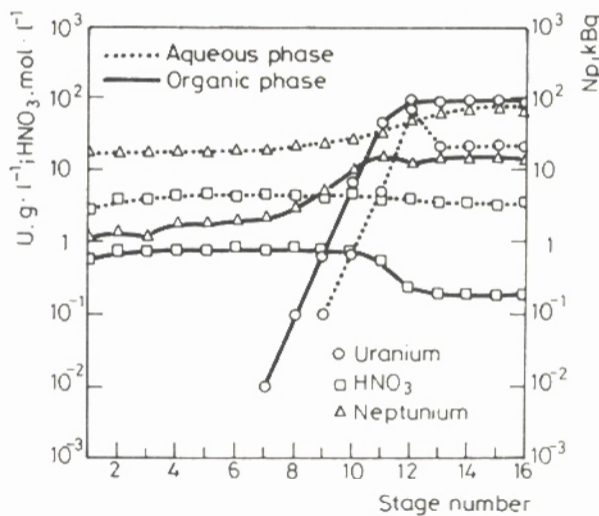

Fig. 4. HNO₃, U and Np distribution profiles in steady state of the HA extractor (aqueous and organic phases, experiment number 2)

phases of the HA mixer-settler. Uranium extraction efficiencies of 80 and 85% were obtained for these two experiments.

These are the partial results for neptunium behavior at trace concentration level concerning to the extraction step of the Purex Process. In these studies no neptunium valence state adjustment in the feed solution was considered.

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

REFERENCES

1. Z. Kolarik, R. Schuler, Separation of neptunium from uranium and plutonium in the Purex Process. Symposium on Liquid-Liquid Extraction Science. I. Chem. E. Symposium Series nº 88, 83-90. Dounreay, Scotland, 1984.

2. W. Ochsenfeld, F. Baumgartner, U. Baunder, H.J. Bleyl, D. Ertel, G. Koch, Experience with reprocessing of LWR, Pu recycle and FBR fuel in the MILLI facility, KFK-2558, 1977.

3. B. Guillaune, J.P. Moulin, Ch. Maurice, Chemical properties of neptunium applied to neptunium management in extraction cycles of Purex Process. Symposium on Liquid-Liquid Extraction Science. I. Chem. E. Symposium Series Nº 88, 31-45, Dounreay, Scotland, 1984.

4. O.L. Keller Jr., Radiochim. Acta, 25 (1978) 211.

5. ORIGEN 2, Oak Ridge National Lab., ORNL-TN- 7175.

6. V.H. Cohen, H.T. Matsuda, B.F. Araujo, X-ray fluorescence spectrometry applied to uranium determination. Proc. of X. Symposium on Actinides and Lanthanides, São Paulo, 1983.

7. M.A. Gonçalves, H.T. Matsuda, Fission products con-
   trol by gamma spectrometry in simulated Purex pro-
   cess solutions. Proc. of XXIII Brazilian Meeting on
   Chemistry, Blumenau, 1982.

8. V.H. Cohen, H.T. Matsuda, B.F. Araujo, J.A. Araujo,
   Potentiometric determination of uranium in simulated
   Purex process solutions by acidimetry. Proc. of
   XXIV Brazilian Meeting on Chemistry, São Paulo, 1983.

9. I.C. Araujo, H.T. Matsuda, B.F. Araujo, J.A. Araujo,
   Spectrophotometric determination of nitrite in
   simulated Purex process solutions. Proc. of XXIV
   Brazilian Meeting on Chemistry, São Paulo, 1983.

10. I.C. Araujo, H.T. Matsuda, B.F. Araujo, J.A. Araujo,
    Separation of microamounts of uranium from radio-
    active waste and its photometric determination with
    DBM. Proc. of XXV Brazilian Meeting on Chemistry,
    Fortaleza, 1985.