SECTION 1 : PROCESS CHEMISTRY

1.1   Process Chemistry of Neptunium

N. Srinivasan*, M.V. Ramaniah, M.N. Nadkarni*, S. V. Kumar*,

S. K. Patil, V. V. Ramakrishna, R. Swarup, G.V.N. Avadhany,

R. R. Sonawane* and P. K. S. Kartha*

Neptunium-237 is formed in significant amounts in uranium-fuelled power reactors. This is an important isotope as it is used as the starting material for the production of ^{238}Pu which is one of the most suitable heat sources for radioisotopic power sources. Kilogram quantitites of ^{237}Np are produced in power reactors making its recovery a matter of considerable importance.

The work on the process chemistry of neptunium was continued with a view to establishing the flowsheet conditions for its recovery during the Purex Process of reprocessing of irradiated uranium. It is known that in the Purex Process, ^{237}Np can be forced to follow the desired process stream by a careful choice of the acidity, uranium concentration in the organic phase and the oxidation state of neptunium. As it is proposed to recover ^{237}Np from the final cycle of uranium purification it was necessary to establish conditions so that ^{237}Np can be coextracted into TBP in the first and second cycles along with uranium and plutonium. It was reported[1,2] that in the feed solution of the first cycle of the Purex Process neptunium exists mainly as Np(V) which is not extractable by TBP. Of the several methods suggested to oxidize Np(V) to TBP-extractable Np(VI) the use of nitrous acid[3] and vanadium(V)[4,5] were considered to be most suitable. The results of investigations on the following aspects of neptunium chemistry are described here.

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* Fuel Reprocessing Division.

a) The use of vanadium(V) for the oxidation of Np(V) to
   Np(VI) in the counter-current extraction of neptunium
   under the Purex Process conditions.

b) Path of neptunium under partitioning column conditions with
   (i) ferrous sulphamate and (ii) uranium(IV) as the reducing
   agents.

c) Extraction of Np(IV) by long-chain alkyl amines.

1.1.1   Use of Vanadium(V) for oxidisation of Np(V) to Np(VI)

The mixer-settler unit used in the present studies was described earlier[6]. All the inactive solutions were fed to the unit using micro-flow metering pumps whereas the active feed solution was fed by using a capillary attached to a constant overflow system. ^{238}Np was added to ^{237}Np to enable the estimation of neptunium by gamma counting. The oxidation state of neptunium was adjusted to Np(V) which was subsequently added to a uranium solution of known uranium and nitric acid concentrations.

The results of a counter current experiment carried out by adding V(V) to the aqueous feed containing Np(V) are given in Table 1. The results of the experiment carried out in which V(V) was introduced in the second stage (from the feed stage) mixer in the extraction section are given in Table 2.

The results of these experiments show that by using V(V), added either in the feed or preferably in the extraction section, neptunium can be coextracted to the extent of about 90%. Although the conditions used by Bahr and Koch[5] for similar studies are not known, the present results are in good agreement with their results.

TABLE 1

Use of V(V) for the oxidation of Np(V) to Np(VI).

Feed: $[HNO_3]$ = 3 M; $[U]$ =328 mg/ml; $[V(V)]$ = 9.4 x 10^{-4}M; $[^{238}Np]$ = 8.5 x 10^4 c/50 sec/ml

Scrub: $[HNO_3]$ = 3 M

Flow rates (ml/min): Feed = 1.25, scrub = 0.6; solvent = 5.4

Time (hrs.)	^{238}Np activity in the outgoing streams: c/50 sec/ml x 10^{-4}		Concentration of U in the outgoing organic stream mg/ml
	Aq.	Org.	
14	0.25	1.23	-
15	0.17	1.60	-
16	0.17	1.63	-
17	0.21	1.50	72
18	0.28	1.60	75
19	0.43	1.53	73

Note: % of neptunium extracted into TBP (calculated from the average ^{238}Np activity in the organic stream)= 80%.

TABLE 2

Use of V(V) for the oxidation of Np(V)

Feed: $[HNO_3]$ = 2M; $[U]$ = 344 mg/ml; $[^{238}Np]$ = 2.08 x 10^5 c/50 sec/ml

Scrub: 3 M HNO_3. Vanadium(V): = 1.08 x 10^{-2}M; $[HNO_3]$ = 3 M

Flow rates (ml/min): Feed = 1.2; scrub = 1.1; solvent = 6.2; V(V) = 0.5

Time (hrs.)	^{238}Np activity in the outgoing streams:c/50 sec/ml x 10^{-4}		Concentration of U in the outgoing organic stream mg/ml
	Aq.	Org.	
14	0.19	4.11	-
15	0.19	3.73	-
16	0.11	3.80	-
17	0.12	3.92	71
18	0.15	4.07	71
19	0.13	4.01	71

Note: % of Np extracted into TBP = 95%.

Path of neptunium under partitioning column conditions

Counter-current data on the behaviour of neptunium present as
n the uranium-loaded organic phase, under partitioning column
ns with $U(IV)$ as the reducing agent are given in Table 3.

TABLE 3

Path of neptunium during partitioning

-loaded
solvent) $\angle HNO_3 \underline{7} = 0.3M; \angle \overline{U} \underline{7} = 65$ mg/ml ; $\angle^- {}^{238}Np \underline{7} = 3.6 \times 10^4$ c/50 sec/ml

scrub $\angle U(IV) \underline{7} = 7$ mg/ml; $\angle N_2H_4 \underline{7} = 0.06M; \angle HNO_3 \underline{7} = 2$ M

es Feed (org) = 6.7; Reducing scrub = 0.9

tages = 5

HNO_3 conc. in outgoing Aq. stream	${}^{238}Np$ activity in the outgoing streams c/50 sec/ml x 10^{-5}		Conc. of U in the outgoing stream mg / ml	
	Aq.	Org.	Aq.	Org.
2.6	1.20	0.15	6.9	62
-	1.04	0.16	7.8	62
2.5	1.12	0.20	7.7	63
-	1.07	0.19	8.4	63
2.4	1.14	0.19	7.9	62
-	1.21	0.19	8.1	63
2.4	1.24	0.19	9.1	63

of neptunium following the organic stream = 48 - 53%.

entration of $U(IV)$ and the flow rates used in the present experiment
arable to those proposed to be used in the Tarapur Plant. It is seen
se data that about 50% of neptunium follows the aqueous stream as is
since the reduction of Np(V) to Np(IV) by $U(IV)$ is slow.

Two counter-current runs were carried out using ferrous sulphamate as reducing agent in a similar way. The results of one of these runs are given in Table 4.

TABLE 4
Path of neptunium during partitioning

Feed (org) $[HNO_3]$ = 0.3M; $[U]$ = 64 mg/ml; $[^{238}Np]$ = 2.08 x 10^4 c/50 sec/ml

Reducing scrub $[Fe^{++}]$ = 0.12M; $[HNO_3]$ = 1M

Flow rates (ml/min) Feed (org) = 6.7; Reducing scrub = 0.8

No. of stages = 5

Time (Hrs.)	HNO$_3$ conc. in the outgoing Aq. stream	^{238}Np activity in the outgoing streams c/50 sec/ml x 10^{-4}		Conc. of U in the outgoing streams mg/ml	
		Aq.	Org.	Aq.	Org.
15	-	2.28	0.9	10.6	62
16	2.2	1.90	1.63	6.4	61
17	-	1.86	1.78	6.0	61
18	2.0	1.85	1.78	6.8	62
19	-	1.85	1.84	7.5	61
20	2.4	1.83	1.83	7.4	60

% of neptunium following the organic stream = 87%.

The reduction of Np(VI) to Np(IV) by Fe(II) is quite rapid and most of the Np(IV) thus formed continues to follow uranium in the organic stream. These results are in good agreement with those reported by Lewis[7]

1.1.3 Co-stability of Np(IV) and Pu(IV)

In the Purex Process if Np is present as Np(IV) it can be coextracted with U(VI) and Pu(IV) and the extracted Np(IV) could be made to follow

uranium in the organic stream in the partitioning step irrespective of the reducing agent used. The co-stability of Np(IV) and Pu(IV) in a synthetic solution was studied and the results are given in Table 5.

TABLE 5
Co-stability of Np(IV) and Pu(IV)

Initial composition	Mixing time (hrs.)	% Np(IV) remained
$/^-$ U(VI) $_7$ = 33 mg/ml	2	99.0
$/^-$ Pu(IV) $_7$ = 80 μg/ml	5	98.6
$/^-$Np(IV) $_7$ = 2-3 μg/ml	6	98.5
$/^-$HNO$_3$ $_7$ = 2 M	48	93.3
$/^-$U(VI) $_7$ = 50 mg/ml	2	96.9
$/^-$Pu(IV) $_7$ = 116 μg/ml	4	96.9
$/^-$Np(IV) $_7$ = 5 μg/ml	24	96.8
$/^-$HNO$_3$ $_7$ = 3 M	54	96.6
$/^-$U(VI) $_7$ = 352 mg/ml	2	96.4
$/^-$Pu(IV) $_7$ = 2 mg/ml	4	92.6
$/^-$Np(IV) $_7$ = 135 μg/ml	8	85.9
$/^-$HNO$_3$ $_7$ = 2.4 M	24	57.7
$/^-$ U(VI) $_7$ = 294 mg/ml	0	99.4
$/^-$ Pu(IV) $_7$ = 1 mg/ml	2	95.3
$/^-$Np(IV) $_7$ = 67 μg/ml	4	90.4
$/^-$HNO$_3$ $_7$ = 2.1 M	6	85.8
	20	54.8

Note: All the above experiments were done in the absence of light.

From these data it is seen that more than 80% Np(IV) remains unoxidized
in the presence of Pu(IV) upto 8 hrs.

To recover any neptunium which follows plutonium in the partitioning
step it is necessary to adjust it to Np(V) which follows the raffinate in
the plutonium purification cycle. From the oxidation potential data it
appears that the oxidation of Np(IV) to Np(V) by Pu(IV) is thermodynamically
possible. At room temperature, however, this oxidation was found to be too
slow. The same was, therefore, attempted at higher temperatures (at 50°C
and 60°C), and it was found that Np(IV) can be oxidized almost quantitatively
in 2M nitric acid by Pu(IV) at these temperatures in about 30 minute.

These data would be useful in selecting the proper conditions to
optimize the recovery of neptunium without affecting the recovery of plutonium.

1.1.4   Extraction of Np(IV) by tricaprylmethyl ammonium nitrate

Long-chain amines are known to be good extractants for actinides
and are particularly useful in the reprocessing of high burn-up fuels.
While tertiary amines permit the extraction of Pu(IV) only since the
extraction of U(VI) from aqueous nitric acid is poor, quaternary amines
extract both Pu(IV) and U(VI)[8]. In continuation of our earlier studies on
the extraction of Np(IV) by TLA, the work was extended to the extraction of
Np(IV) using tricaprylmethyl ammonium nitrate.

Experiments were carried out on the extraction of Np(IV) into
% tricaprylmethyl ammonium nitrate (Aliquat-336, nitrate form) in
Solvesso-100. The extraction on Np(IV) from 2M nitric acid was studied
at different concentrations of Aliquat-336 ranging from 1 - 30%. The log-log
plot of Kd of Np(IV) vs Aliquat-336 concentration was found to be linear
with a slope of about 1.3. The value of the slope less than 2 may be the
result of aggregation of the extractant[9]. The dependence of the extraction
of Np(IV) into 10% Aliquat-336 nitrate on aqueous nitric acid and uranium

concentrations was studied and the data are presented in Table 6 and 7, respectively.

TABLE 6

Variation of K_d of Np(IV) with nitric acid concentration

Conc. of HNO_3, M	1	2	3	4	5	6	7	8
K_d	964	1780	1990	1920	1760	1450	1100	685

TABLE 7

Effect of U(VI) conc. on the distribution coefficient of Np(IV) in 2 M HNO_3

Initial Aq. conc. of U(VI) g/ml	4	10	20	40	60	80
K_d	2030	1710	1500	1180	623	435

A maximum around 3-4M nitric acid was observed which is usually common for all alkyl amine extractions. From the data in table 7 it can be seen that the K_d of Np(IV) decreases with increasing uranium concentration.

The stripping of Np(IV) from 10% Aliquot-336 nitrate was studied using acetic, formic, perchloric, sulphuric and hydrochloric acids. It was found that all these reagents strip Np(IV) quantitatively. However, from the process point of view, acetic or formic acid is preferred as these could be removed easily, if desired, in the process.

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✓ 1.2   Transplutonium elements

C. K. Sivaramakrishnan, A. V. Jadhav, K. Reghuraman,

K. A. Mathew, P. S. Nair and M. V. Ramaniah

1.2.1   Recovery and purification of americium

Development work on the separation and purification of trans-plutonium elements was continued. Recovery of 55 mg of ^{241}Am from solutions containing large amounts of rare earths was reported in the last annual report[1]. Americium was separated from rare earths using Dowex-1 (x 4, 50 -100 mesh) and using 8 M ammonium thiocyanate as the eluant. The americium so separated contained small amounts of rare earth impurities. The following procedure was adopted successfully for removal of these impurities. Americium was precipitated as hydroxide and the hydroxide was dissolved in 0.5M HNO_3 + 0.1M $(NH_4)_2S_2O_8$ containing trace amounts of silver ions. On heating the solution to 90°C for one hour all americum was oxidised to Am(VI). By adding conc. HF to the solution all the rare earth impurities were precipitated as