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OBSERVATIONS ON THE PROCESS CHEMISTRY OF NEPTUNIUM

by

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I. INTRODUCTION

The purex process is used for the reprocessing of irradiated uranium fuel at the Trombay Plutonium Plant. Analysis of the process solutions at various stages for neptunium has revealed that in the codecontamination cycle neptunium is extracted, along with uranium and plutonium, into TBP almost quantitatively while in the partitioning cycle the extraction is reduced to about half, though the conditions of extraction are almost alike in both cycles⁽¹⁾. To understand this behaviour of neptunium, it was found necessary to analyse the first cycle feed solution for different oxidation states of neptunium.

The effect of nitric acid concentration and TBP saturation with uranium on the extraction of Np(IV) and Np(VI) into 30% TBP-Shell-sol T has been studied at 45°C and 60°C. These data are relevant from the point of view of neptunium recovery in the purex process.

II. EXPERIMENTAL

Oxidation state analysis

The neptunium present in the sample as Np(IV) was estimated by adjusting a known aliquot of the sample to 1M in HNO₃ and then extracting into 0.5M TTA in xylene. The extracted neptunium was purified from plutonium and estimated by TTA extraction method⁽²⁾.

LaF₃ precipitation was used to separate Np(IV) and Np(V) together from Np(VI) and

neptunium carried with LaF_3 was purified and estimated by TTA extraction. The difference in the values of neptunium content obtained with direct TTA extraction and that carried by LaF_3 was taken as the amount of Np(V) present in the sample. The difference between the total neptunium content and that carried by LaF_3 was taken as the amount of Np(VI) .

Alternatively Np(V) was estimated by the TTA extraction method starting with a sample from which Np(IV) and Np(VI) together were quantitatively removed by extraction with hexone from the sample which was adjusted to 1M HNO_3 and nearly saturated with NH_4NO_3 . The results of the oxidation state analysis are given in table I.

Extraction of Neptunium into TBP

The experimental procedure for the extraction of Np(IV) and Np(VI) with varying nitric acid and uranium concentration into 30% TBP is the same as described in an earlier paper⁽³⁾. 30% TBP-Shell sol-T was pre-equilibrated with nitric acid of corresponding concentration and the equilibrations were carried out at 45°C and 60°C in a thermostated water bath. The results are shown in table II.

III. RESULTS AND OBSERVATIONS

The Behaviour of Neptunium in the purex process

It is clear from the data presented in table I that neptunium is present mainly as Np(V) in the feed solution. The presence of about 35% Np(IV) in the samples 1, 2 and 3 may be due to the high acidity, in those samples, which is known to favour disproportionation of Np(V) .

Assuming that neptunium was present as Np(V) in the second cycle feed also, the higher extraction of neptunium in the first cycle may be due to the presence of rate accelerating materials which enhance the rate of oxidation of Np(V) to Np(VI) .

by nitrous acid⁽⁴⁾. It was recently reported⁽⁵⁾ that a rate accelerating material is produced in the first cycle of the purex process during the reprocessing of metallic uranium fuels.

Effect of temperature on neptunium extraction

From the data presented in table II it is seen that the distribution coefficient of Np(VI) decreases with increase in the temperature to 60°C in the nitric acid concentrations of 1-4M as also reported by Bahr⁽⁶⁾. It has been observed that the decrease becomes smaller with increasing concentration of uranium in the organic phase. This is similar to the effect observed in the extraction of Pu(VI)⁽⁷⁾ and U(VI)⁽⁸⁾.

The distribution coefficient of Np(IV) increases with increase in the temperature to 60°C. The relative increase in the distribution coefficients is enhanced by the presence of uranium. This effect is similar to that observed in the case of Pu(IV)⁽⁷⁾.

REFERENCES

1. N. Srinivasan et al, BARC-428 (1969).
2. F.L. Moore; Anal. Chem. 29, 941 (1957).
3. "Investigations on the process chemistry of neptunium, Part I", N. Srinivasan et al, DAE Chemistry Symposium, 23-26, September 1969 at Chandigarh (1969).
4. T.H. Siddall (III) and E.K. Dukes; J.Am.Chem. Soc., 81, 790 (1959).
5. J.L. Swanson; BNWL-1017 (1969).
6. W. Bahr, KFK-797 (1968).
7. S.M. Stoller and R.B. Richards (Editors); Reactor Handbook, Vol.II, 2nd Ed. p.156 (1961), Interscience Publishers Inc.
8. S.M. Stoller and R.B. Richards (Editors); Reactor Handbook, Vol.II, 2nd Ed.p.155 (1961), Interscience Publishers Inc.

TABLE I

Oxidation state analysis of neptunium in the first cycle feed

S.No.	[HNO ₃]M	Total Np µg/ml	Np(IV) µg/ml	Np(V) µg/ml	Np(VI) µg/ml
1	5.3	1.09	0.35	0.69	0.05
2	4.8	0.98	0.35	0.66	nil
3	4.8	0.98	0.35	0.65	"
4	2.2	1.83	0.07	1.75	"
5	1.9	1.48	0.01	1.49	"
6	3.5	0.96	0.07	0.94	"
7	3.5	0.96	0.07	0.92	"
8	1.9	1.74	0.02	1.66	0.06
9	3.6	1.00	0.09	0.89	nil
10	3.6	1.00	0.09	0.91	"

TABLE II

Variation of distribution coefficient of Np(IV) and Np(VI) with uranium saturation of 30% TBP-SST

Temp.	Organic phase uranium concn mg/ml	Distribution coefficient							
		Np(IV)				Np(VI)			
		1M HNO ₃	2M HNO ₃	3M HNO ₃	4M HNO ₃	1M HNO ₃	2M HNO ₃	3M HNO ₃	4M HNO ₃
45°C	0	0.8	2.3	4.1	6.2	3.6	7.9	10.8	12.5
	20	0.6	1.7	2.9	4.6	2.8	6.2	8.3	9.5
	40	0.4	1.2	2.1	3.2	2.1	4.5	5.9	6.6
	60	0.2	0.8	1.3	1.9	1.4	2.9	3.8	4.0
	80	0.15	0.45	0.7	0.95	0.9	1.5	2.0	1.8
60°C	0	0.8	2.8	4.8	7.0	2.7	6.0	8.1	8.7
	20	0.5	2.0	3.7	5.2	2.2	4.7	6.3	6.7
	40	0.35	1.4	2.6	3.7	1.6	3.6	4.4	4.45
	60	0.3	0.95	1.5	2.35	1.1	2.4	2.6	2.55
	80	0.15	0.6	0.7	1.1	0.7	1.3	1.1	1.2

N.B : Data taken from the graphs of distribution co-efficient vs organic phase uranium concentration.