Continuous Extraction and Stripping of Neptunium By Fresh and Degradated Tributyle Phosphate Using Co-60 Cell

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Abstract

The behaviour of Np-239 during the Continuous extraction and stripping was followed . Three Continuous extraction experiments were carried out . In the first experiment the extraction and stripping were carried out by using Tributyl Phosphate / treated odorless kerosene as the organic phase , while the aqueous phase was uranium and neptunium-239 dissolved in 3M HNO_3 . In the second experiment irradiation of organic phase up to 30 M rad were carried out , while keeping the aqueous phase as it is in the first experiment. In the third experiment , the acidity of the aqueous phase was 1.5M instead of 3M and keeping the organic phase as it is in experiment 1. The results obtained in tables 1-3 show the possibility of rejection Np-239 according to the conditions of run 1. The degradation product of the tributyl phosphate namely di and monobutyl phosphate plays an important role in the difficulty of Np stripping. The third experiment conditions were the best.

Introduction

In hot nitric acid solution neptunium can be existed in three valence states (IV, V, VI) depending on the acidity, oxidation potential of the solution , nitrous acid concentration and nitrate ion concentration. So the neptunium behaviour appears very complicated while the trivalent state can not be observed in nitric medium except as transient species . the hexavalent state is the stable form in high concentrations of nitric acid (> 5M) while the pentavalent state is the most stable form in lower nitric acid solution < 2M [1-4] . The pentavalent state exists as NpO_2^+ ion which disproportionates at higher acid concentration to Np IV and Np VI. This disproportionation reaction can be represented by the following equation which is strongly dependent on acidity .

$$2NpO_2^+ + 4H^+ \longrightarrow Np^{4+} + NpO_2^{2+} + 2H_2O$$

Since the reduction to Np^{4+} involves the breaking of the strong Np-O bond of the NpO_2^+ , the oxidation to NpO_2^{2+} is favored in this reaction because it takes place with a simple electron transfer [4-7]

It is desirable that neptunium would be rejected to the high activity waste , preferably in the first extraction cycle , but it is not clear that the necessary extent of rejection could be accomplished in one cycle . The following reaction might occur and it is not possible to control precisely the position of equilibrium

$$NpO_2^{2+} + 1/2\ HNO_2 + 1/2\ H_2O \rightleftharpoons NpO_2^{+} + 2/3\ H^{+} + 1/2\ NO_3^{-}$$

The oxidation of NpO_2^+ by NO_3^- is favored by high acidity and low nitrous acid concentration in the 10^{-3} M range [4] , while even at high acidities , nitrous acid (10^{-2}M) reduces NpO_2^{2+} to NpO_2^+.

Thus maintenance of the desired inextractable pentavalent state , depends on maintaining the nitrous acid concentration in the proper range.

Published work on Neptunium distribution ratios of tetra and hexavalent by TBP in xylene from 3M HNO_3 shows that the distribution ratio of the hexavalent is much higher than tetravalent state [3].

It is well known that radiolysis is by far the greatest contributor to solvent degradation and that the main products from radiolysis of TBP are H_2MBP and HDBP , and it is reported that HDBP is produced in a greater yield than H_2MBP [2,4].

The presence of nitric acid increases the yield of HDBP and H_2MBP.

The aim of the present work is to investigate the continuous extraction and stripping behaviour of neptunium by carrying out 3 continuous extraction runs to follow the Neptunium behaviour:

1- In the first run , fresh 20% TBP/kerosene/3M HNO_3 system was used.
2- In the second run , irradiated 20% TBP/kerosene/3M HNO_3 system was used.
3- In the third run , fresh 20% TBP/kerosene/1.5M HNO_3 system was used.

Experimental

Three samples of U_3O_8 of about 20,15 and 10 mgs were irradiated separately for 72 hours in the research reactor. The neutron flux was 0.5×10^{13} n/cm^2 .Sec. and the reactor power was (5MW). The Np-239 resulting from the uranium irradiation was used after a short cooling time of about two days.

Each sample was dissolved in 6M nitric acid and diluted with more than 20 mls of 6M Nitric acid , the first two samples were refluxed for about 30 minutes , then added to the feed solution .The third sample was heated until the brown fumes of nitric acid covered the whole container.

Irradiation of the extractant

Five liters of the extractant (20%TBP/Kerosene/HNO_3) were exposed to a γ -ray source of Co-60 for 105 hours up to 30 Mrad to study the effect of organic degradation products namely monobutyl phosphate and dibutyl phosphate that could be formed due to γ – rays emitters that are actually present in such a process. i.e a simulation of real conditions . This irradiated extractant was by used in the second run.

The estimation of the degradation product , resulting from the above irradiation of the TBP , was analysed using HPLC and found to be 0.56%.

Continuous extraction experiments

The feed solution for the continuous extraction and then stripping run was prepared from the following constituents:

- A portion of the dissolved irradiated uranium sample containing Np-239.
- 35g/l uranium as UO_2.
- 7g/l aluminium as $Al(NO_3)_3.9H_2O$.
- 7g/l magnesium as $Mg(NO_3)_2.6H_2O$.
- 0.02M sodium nitrite.
- 3M nitric acid.

Hydraulic equilibrium was carried out for both extraction and stripping batteries (fig-1) according to the following parameters:

Aqueous phase:

- Strip solution , 0.1M HNO_3 , 0.6 l/hr.
- Scrub solution , 3M HNO_3 , 0.12l/hr.
- Feed solution , 35g/l uranium in 3M HNO_3 , 0.36 l/hr , 7g/l aluminum and 7g/l Mg As nitrate , and 0.02M $NaNO_2$.

Organic phase.

- 20% TBP – Kerosene - 0.6 l/hr.

The above parameters were set for the first continuous extraction run.

For the second run the organic phase was irradiated by using Co-60- source up to 30M Rad . In the third run , the same conditions and parameters as in the first continuous extraction run except the acidity of the scrub and feed solutions were made 1.5M HNO_3 instead of 3M.

Measurements

Np-239 activity were measured by using 277 keV γ energy with the aid of Ge detector of (97) cm^3 active volume and 4096 – multichannel analyser, camac ADC type 9060 linked with HP-computer (Princeton-Gamma Tech, W. Germany).

Result and Discusion

Continuous extraction- stripping run no.1

The result of the first Continuou extraction run table 1 shows (at the steady state i.e. after 3 hours of operation) that neptunium is almost completely extracted by TBP.

Only 3- 3.9% of Neptunium follows the aqueous waste stream (A.W) . This behaviour could be explained that the nitric acid morality of the extraction battery (3M HNO_3) is quite suitable to make Np in the extractable VI and IV valence state.

Stripping with 0.1 HNO_3 is very efficient with 100% of Np being stripped (A.P in table.1) and 0.2 - 0.7% of Np in organic waste , for a couple of samples only , the remaining , samples gave undetectable activity , thus complete stripping was accomplished.

Continuous extraction- stripping run no.2

The effect of the degradation products of the organic solution (formation of HDBP and H_2MBP) was followed in this run ,the results were tabulated in table 2 , it can also be concluded that all Neptunium is extracted to the organic phase , even more than the case of the non-irradiated solvent. This is also evident from the very low percentages of Neptunium in aqueous waste streams between 0.9-2.0% at the steady state (i.e. after 3hr s of operation).

A major difference in results of the first continuous extraction run and the second is observed in the stripping stages , were a poor stripping was clearly noticed , ranging between 61-75%.The remaining Neptunium not stripped ranging between 25-38% is left in the organic waste stream (O.W). This poor stripping may be explained on the basis that certain degradation products are forming with Neptunium , difficulty stripped complexes.

Continuous extraction- stripping run no.3

In table 3 were neptunium in the extraction stages is being separated among the aqueous waste stream (58-60% after 4 hours of operation) and the organic product (40-44% after 4 hours of operation). This indicates that both extractable Np IV,VI valence state and non extractable V valence state were formed in solution at such low acidity (1.5M HNO_3) . A complete stripping of Np is observed in the stripping stages.

Conclusion

1- Almost complete extraction of neptunium in the first run made us to conclude that little amounts of the neptunium is in a pentavalent state.

2- Neptunium stripping is difficult when irradiated solvent is being used .

3- Lowering the acidity of nitric acid from 3M to 1.5M reduced greatly the percentage of Neptunium coextracted with uranium.

Therefore to have better results in rejection of neptunium to the high activity waste , a lower nitric acid conc.(1.5M) of the feed is recommended rather than 3M .Also, more than one extraction cycle is required.

References

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Table (1): Continuous extraction and stripping run using fresh 20% TBP-kerosene as extractant , and feed solution 35 gU/l , 7 gAl/l ,7 gMg/l in 3M HNO_3 and 0.02M $NaNO_2$, scrubbing with 3M HMO_3 and stripping with 0.1 HNO_3.

Times in hours	Extraction		Stripping	
	%Np in A.W.	%Np in O.P.	%Np in A.P.	%Np in O.W.
1	2.0	50		
2	3.4	81.1	100	Nil
3	3.9	100.0	100	0.7
4	3.0	95.9	100	0.2
5	3.6	95.4	100	Nil
5.5	3.8	96.1	100	Nil

Table (2):Continuous extraction and stripping run using irradiated 20% TBP-kerosene as extractant , and the feed , scrub and strip is the same as in table (1).

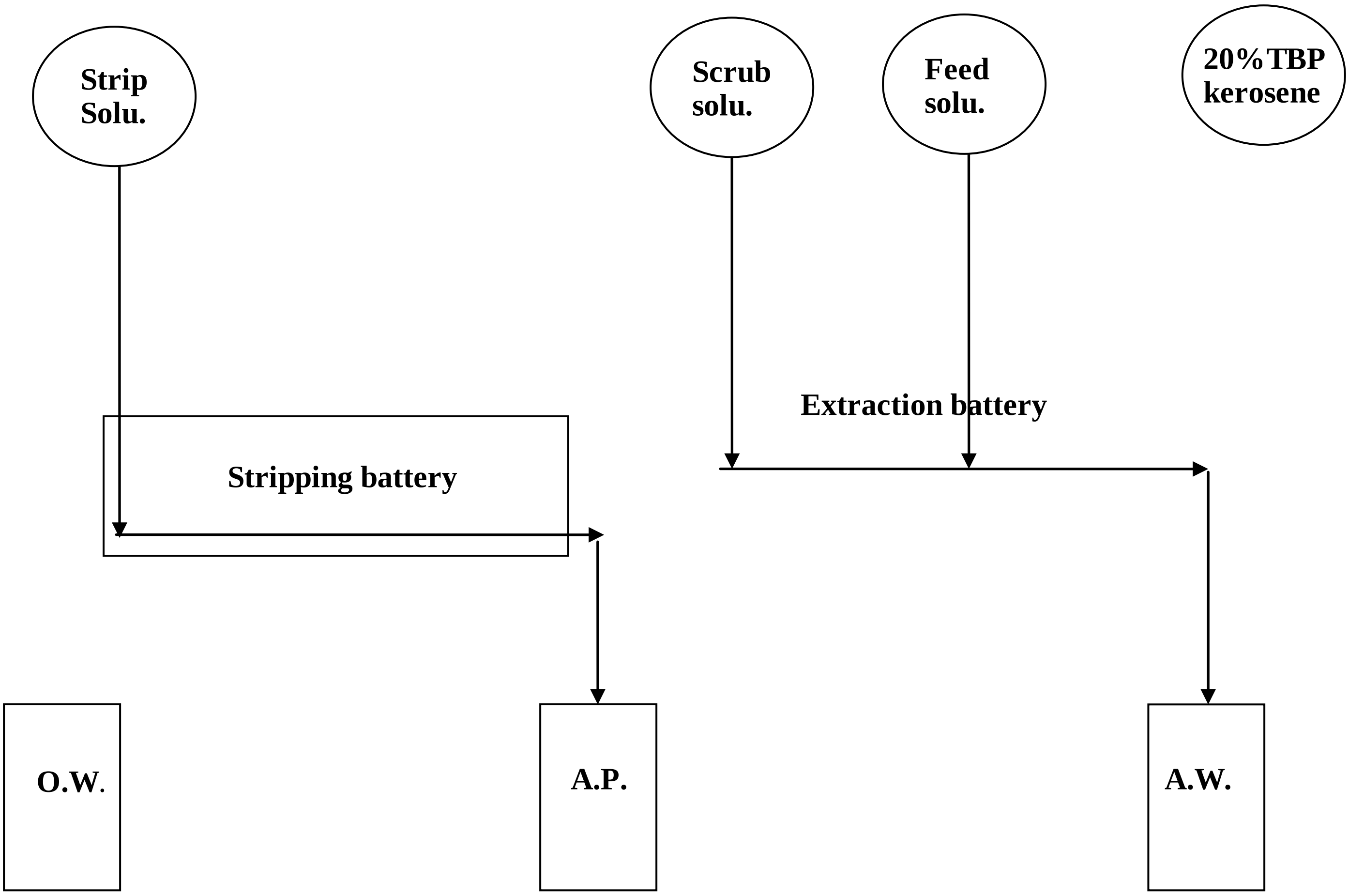
Times in hours	Extraction		Stripping	
	%Np in A.W.	%Np in O.P.	%Np in A.P.	%Np in O.W.
1				
2				
3	2.0	100	75	25
4	1.5	93	62	38
5	0.9	100	73	31
5.5	0.9	100	61	36

Table(3): Continuous extraction and stripping run using fresh 20% TBP-kerosene as extractant , and feed solution 35 gU/l , 7 gAl/l ,7 gMg/l in 1.5M HNO_3 and 0.02M $NaNO_2$, scrubbing with 1.5M HMO_3 and stripping with 0.1 HNO_3.

Times in hours	Extraction		Stripping	
	%Np in A.W.	%Np in O.P.	%Np in A.P.	%Np in O.W.
2.5	43	57	100	Nil
3.0	48	52	100	Nil
4.0	58	42	100	Nil
5.0	60	40	100	Nil
5.5	56	44	100	Nil

Where

A.W. is aqueous waste stream
O.P. is organic product stream
A.P. is aqueous product stream
O.W. is organic waste stream


Strip Solu.
Scrub solu.
Feed solu.
20%TBP kerosene
Extraction battery
Stripping battery
O.W.
A.P.
A.W.

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1	2.0	50		
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4	3.0	95.9	100	0.2
5	3.6	95.4	100	Nil
5.5	3.8	96.1	100	Nil

Table 2:Continuous extraction and stripping run using irradiated 20% TBP-kerosene as extractant , and the feed , scrub and strip is the same as in table 1.

Times in hours	Extraction		Stripping	
	%Np in A.W.	%Np in O.P.	%Np in A.P.	%Np in O.W.
1				
2				
3	2.0	100	75	25
4	1.5	93	62	38
5	0.9	100	73	31
5.5	0.9	100	61	36

Table 3. Continuous extraction and stripping run using fresh 20% TBP-kerosene as extractant , and feed solution 35 gU/l , 7 gAl/l ,7 gMg/l in 1.5M HNO_3 and 0.02M $NaNO_2$, scrubbing with 1.5M HMO_3 and stripping with 0.1 HNO_3.

Times in hours	Extraction		Stripping	
	%Np in A.W.	%Np in O.P.	%Np in A.P.	%Np in O.W.
2.5	43	57	100	Nil
3.0	48	52	100	Nil
4.0	58	42	100	Nil
5.0	60	40	100	Nil
5.5	56	44	100	Nil

Where

A.W. is aqueous waste stream
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