

Neptunium control in co-decontamination step of purex process

Zhang Zefu*, He Jianyu*, Zhu Zhaowu*, Ye Guoan*, Zhao Zhiqiang*

A new alternative method for separation of Np in the first co-decontamination step is proposed. It comprises two steps, namely, preconditioning of Np valence state in the dissolved solution of spent fuel by NO gas bubbling in HNO₃ medium to produce HNO₂, which is considered as salt-free process to convert Np(VI) to Np(V) and stabilization of Np(V) with urea, finally, the demonstrative counter current cascade extraction of Np(IV) and Np(V) in a miniature mixer-settler was carried out. The batch experiments show that Np(V) produced after conditioning may be slowly oxidized again to Np(VI) during standing time. Addition of urea in the HNO₃ solution might enhance the stability of Np(V). On the other hand, the solvent extraction by 30% TBP/kerosene could greatly accelerate the oxidation rate of Np(V). The chemical flow sheet study at 25°C shows that, more than 98% of Np could be routed into HLLW if urea is added in the HNO₃ solution. The operating temperature has great influence on the kinetics of Np(V) oxidation. If operation temperature rises to 36°C and urea is not added, about 38% of Np will go along with U and Pu into organic phase. The behavior of Np(IV) during extraction shows great accumulation in the middle stages of battery.

Keywords: reprocessing, neptunium, valence state

1 Introduction

Since 1980, the potential radiotoxicity of Np-237 has been considered as one of the most dangerous nuclide. The amount of Np in the world increases years by years due to development of nuclear power station. The production of Np-237 rises also with burnup of spent fuel and Pu content in nuclear fuel. The control of Np routing in reprocessing plant is one of key task, especially in the co-decontamination step in order to avoid Np splitting over the whole flowsheet. Some efforts have been made to route Np into HLLW which was considered as a first option [1,2], unfortunately, it is unsuccessful up-to now due to chemical complication of Np in the HNO₃ solution. On the other hand, the electro-reduction method with potential control was suggested in the co-decontamination step to drive Np into HLLW[3], but, construction of such facility in the high radioactive zone is not a reliable choice. The above situation leads to look for more effective way to separate Np from U after co-decontamination step and some successes have been achieved in recent years[4-6]. The Np remained in Pu fraction could be burned in the reactor. But first of all, the Np in the co-decontamination step must be quantitatively oxidized to Np(VI) with salt free reagent in order to extract Np into 30% TBP/kerosene along with U and Pu, this is not a easy work, although the high concentration of HNO₃ favours Np(VI) formation. The present proposal of routing Np(V) into HLLW is based on the new idea, that is the preconditioning of Np to Np(V) and stabilization of Np(V) with urea in the feed solution. It is hopeful to depress reoxidation of Np(V) to minimum during extraction process and force Np into HLLW.

2 Oxidation and disproportionation of Np(V) in HNO₃ solution

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2.1 Chemicals

All chemicals were of reagent or analytical pure grade, additional purification was not done before use. The solution of 0.5M thenoyltrifluoacetone(TTA) in xylene was kept in the refrigerator after its preparation ($M=\text{mol}\cdot\text{dm}^{-3}$).

2.2 Purification of neptunium-237 and preparation of Np(IV), Np(V) and Np(VI)

The NpO₂ powder was dissolved in the concentrated HNO₃ by heating, then evaporated to dryness and dissolved in 5~6 M HNO₃, and then the hydrazine nitrate was added to make solution to 0.2M in N₂H₄HNO₃, the above solution was heated at 80°C for 40~60 minutes to reduce Np to Np(IV). After cooling, the solution was passed through an anion exchange column to remove impurity. A portion of Np(IV) was taken and acidified to 7M in HNO₃, evaporated until the residue became black in color, and then dissolved in the 2M HNO₃ containing 0.05M urea, the obtained Np(VI) was kept in the dark vessel. A portion of above Np(VI) solution was taken and diluted to make solution to 0.2M in HNO₃ with distilled water, finally, NH₄NO₂ was added to make solution to 0.1M in HNO₂, and the Np(V) was ready obtained.

2.3 Analysis

The mixture of Np valence state was analyzed first by extraction of Np(IV) with 0.5M TTA in xylene, and then another probe was taken to determine Np(VI) by extraction with 0.1M TOPO(trioctylphosphine) in xylene. In this way, Np(VI) and Np(IV) were extracted together. The remaining of Np in aqueous phase is referred to Np(V). The fraction of Np(VI) could be calculated by the difference in activity between TTA and TOPO extractions. In all probes for Np valence states determination, the urea was added to avoid valence change during extraction. The activity of each probe was measured by α -counting. The nitrite was analyzed by colorimetric method[7].

Tables 1,2 and 3 show the tendency of oxidation and disproportionation of Np(V) in HNO₃ solution. It shows that both oxidation and disproportionation depend strongly on the concentration of HNO₃ and standing duration. The results

obviously demonstrate that the longer standing time and higher HNO_3 concentration are in favor of both oxidation and disproportionation. Siddle[8] has studied the kinetics of Np(V) oxidation in HNO_3 solution and pointed out that the oxidation rate of Np(V) in HNO_3 solution increase with HNO_2 concentration up to $5 \times 10^{-5} \text{M}$. The present work shows that Np(V) oxidation increase with HNO_2 up to concentration $5 \times 10^{-3} \text{M}$, but when concentration of HNO_2 rises up to $5 \times 10^{-2} \text{M}$, the portion of Np(VI) lowers. The similar phenomena was observed by Flanary[9]. In case of latter, the excess of HNO_2 plays a role as reductant towards the Np(VI) produced

previously. Such behavior of HNO_2 in HNO_3 solution can explain the routing of Np in the co-decontamination step of Purex process. When HNO_3 concentration is low and HNO_2 is high in the extraction zone of battery, the reduction of Np(VI) will be in advance, and Np will go into HLLW. In the opposite, if concentration of HNO_3 is high and HNO_2 is relatively low, the oxidation of Np(V) to Np(VI) will occur, and Np will go along with U and Pu into organic phase. The experiment also indicates that, a small portion of Np(IV) always appears, which increases with standing time elapsing even at low concentration of HNO_3 . If comparison of data in presence of urea with that

Table 1. Oxidation and disproportionation of Np(V)
1M HNO_3 , 0.04g/L Np Np(V)>99% 25°C

Standing Time(day)	Np(VI)%					Np(IV)% in average
	$1 \times 10^{-2} \text{M CO(NH}_2)_2$	$\text{HNO}_2 \text{ M}$				
		5×10^{-2}	5×10^{-3}	5×10^{-4}	5×10^{-5}	
1	0.32		0.72	0.55	0.51	0.21
2	0.36	1.35	2.08	1.81		0.33
4		1.56	2.30	2.12	0.55	0.50
5	0.56		2.41	2.24	0.62	0.53
8	0.71		2.73		0.73	0.67
12	0.83	1.71	3.14	2.32	0.85	0.82
17	0.92		3.20	2.22	0.92	0.88

Table 2. Oxidation and disproportionation of Np(V)
2M HNO_3 , 0.04g/L Np Np(V)>99% 25°C

Standing Time(day)	Np(VI)%					Np(IV)% in average
	$1 \times 10^{-2} \text{M CO(NH}_2)_2$	$\text{HNO}_2 \text{ M}$				
		5×10^{-2}	5×10^{-3}	5×10^{-4}	5×10^{-5}	
1	0.38	1.45	1.62	0.43		0.35
2	0.50	1.47	1.82	1.43	0.51	0.46
4		2.01	2.24	1.50	0.62	0.68
5	0.72	2.38		2.49	1.13	0.95
8	0.86	2.51	2.74	2.64	1.83	1.20
12	1.14	2.70	3.52	3.38	2.02	1.39
17	1.42	2.73	3.67	3.41	2.28	1.55

Table 3. Oxidation and disproportionation of Np(V)
3M HNO_3 , 0.04g/L Np Np(V)>99% 25°C

Standing Time(day)	Np(VI)%					Np(IV)% in average
	$1 \times 10^{-2} \text{M CO(NH}_2)_2$	$\text{HNO}_2 \text{ M}$				
		5×10^{-2}	5×10^{-3}	5×10^{-4}	5×10^{-5}	
1	0.34		0.42	0.37		0.29
2	0.62	2.91	3.01	1.21	0.72	0.73
4	1.37	3.81	4.00	2.24	1.76	1.30
5	1.20		4.59	4.41	2.28	1.36
8	1.55		5.84	6.89	2.55	1.80
12	2.12	6.51	7.44	8.48	2.70	1.39
17	2.41	7.05	8.02		3.09	2.63

Table 4. Oxidation of Np(V) in the extraction process with 30% TBP-kerosene, 2M HNO₃, 0.04g/L Np, Np(V)>99%, 25°C

Standing Time(day)	Np(VI)%				
	1 × 10 ⁻² M CO(NH ₂) ₂	HNO ₂ M			
		5 × 10 ⁻²	5 × 10 ⁻³	5 × 10 ⁻⁴	5 × 10 ⁻⁵
10	0.4		3	1	
15	0.8	11	13	4	1
20	0.8	17		17	
30	1.7	25	43	25	18
40	2.0	25	43	25	20

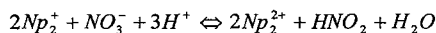
Table 5. Oxidation of Np(V) in the extraction process with 30% TBP-kerosene, 3M HNO₃, 0.04g/L Np, Np(V)>99%, 25°C

Standing Time(day)	Np(VI)%				
	1 × 10 ⁻² M CO(NH ₂) ₂	HNO ₂ M			
		5 × 10 ⁻²	5 × 10 ⁻³	5 × 10 ⁻⁴	5 × 10 ⁻⁵
5	2			4	2
10	2	21	30	34	10
20	3	39	46	42	17
25	4	43	61	43	35
30	4.3	47	66	68	46

data without urea is carried out, it seems that part of Np(VI) in presence of urea comes not from direct oxidation of Np(V), but from disproportionation of Np(V). It means that, Np(V) could be stabilized by urea.

Tables 4 and 5 demonstrate the results of Np(V) oxidation during extraction with 30%TBP/kerosene. The general tendency of Np(V) oxidation during extraction is similar to those results obtained in the static standing experiment.

The results convince that the extraction process greatly accelerates the rate of the Np(V) oxidation. The reason for rate increase in case of extraction is as follows:



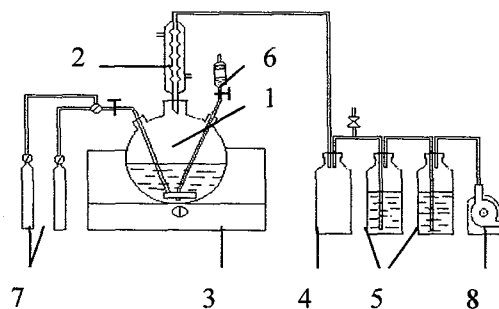
The apparent equilibrium constant of equation in 3M HNO₃ solution K' is 4.5 × 10⁻⁷ at 25°C[10], the above reaction is a convertible one. When Np(VI) is extracted from aqueous phase into organic phase, the equation will shift from left to right in order to establish a new equilibrium. It means that extraction process always creates a favorable condition for continuous oxidation of Np(V).

3 Conditioning of valence state and stabilization of Np(V) in Purex process

Usually, there is a co-existence of Np(IV,V,VI) in the dissolved solution of spent fuel in HNO₃ medium[11]. Neptunium in the oxidizing atmosphere of dissolution step with high concentration of HNO₃ should be oxidized to high valence state, namely Np(V) and Np(VI). But in the dissolution step, the formed Np(V) would concurrently disproportionate to

Np(IV) and Np(VI). From the thermodynamic point of view, the Np(IV) in HNO₃ solution must be oxidized to high valence state. Unfortunately, kinetics shows that Np(IV) in HNO₃ is quite stable at ambient temperature, therefore, a small amount of Np(IV) always exist together with Np(V) and Np(VI). The ratio of Np(V) to Np(VI) mainly depends on the ratio of HNO₂ to HNO₃ concentration. The higher HNO₂ is, the more Np(V) will be formed.

Figure 1 shows the apparatus for Np valence conditioning. The nitrogen monoxide(NO) was introduced into vessel to bubble 3M HNO₃ solution containing a mixtures of Np(IV,V,VI) at (20~80)°C. When HNO₂ reached maximum concentration, the bubbling of NO stopped. The experiment shows that maximum concentration of HNO₂ occurred at ~50°C, the

**Fig.1. Schematic diagram of apparatus. for generation of HNO₂ by NO bubbling in HNO₃ solution.**

1. reaction vessel, 2. condenser, 3. controlling heater, 4. bottle for safety, 5. absorption bottle, 6. bypass, 7. high pressured container of NO and N₂ respectively, 8. vacuum pump.

concentration of HNO_2 produced can reach 0.15M. After stopping bubbling, let the solution cool down to about 25°C. The analysis shows that about 96%Np was converted to Np(V), and then stabilization of Np(V) was done by adding urea alone or the mixture of urea and hydrazine, the latter has higher reduction rate than urea for HNO_2 sweeping.

4 Chemical flow sheet study on Np control

Based on the above data, a new alternative method for Np separation in co-decontamination step is proposed to demonstrate its feasibility for practical application. Four runs were conducted to check the chemical flowsheet in a miniature mixer-settle.

4.1 Experimental

4.1.1 Analysis

Macro amount of U(VI) and HNO_3 mixture were determined by combining titration in the saturated K_2SO_4 solution adjusted previously to pH4, and then a probe containing U and HNO_3 was added. The concentration of HNO_3 was determined with NaOH titration till pH4, and then portion of 30% H_2O_2 was added to determine U(VI) concentration by titration again. The low concentration of U(VI) was determined by colorimetric method with Arsenaz(III). In the chemical flowsheet study, Np concentration was determined by γ -ray spectrometry with high resolution HPGe detector. In practice, the γ -ray with 86.5keV from Np was measured. The contribution of 86.59keV from protactinium and absorption of γ -ray by U was corrected.

4.1.2 The parameter of facility and flowsheet

The construction of miniature mixer-settler is as follows: there are 16 stages in total, of which 8 stages are serves as extraction section, rest for washing. Each mixer volume is 3ml, and 8ml for each settler. The whole volume of the battery is about 176ml. The flow ratio: F: X: S=1: 2.4: 0.57; the flow rate:0.75ml/min(F), 1.8ml/min(X), 0.43ml/min(S). Usually, the feed solution containing 225g/l U, 0.1g/l Np, and 3mol/l HNO_3 was fed at stage 8, washing solution of 3M HNO_3 was fed at stage 16, and 30% TBP/kerosene at stage 1. The pure Np(IV) and Np(V) were used in the experiment, the operation temperature was kept at 25°C unless otherwise specified.

4.2 Results and Discussion

Run A: As it claimed above, the presence of certain amount of Np(IV) in feed solution is an inevitable fact. It is interest to demonstrate the behavior of Np(IV) in the co-decontamination step. The feed solution contains 0.14g/l Np(IV), U and HNO_3 . Figures 2, 3 and 4 show the concentration profile of U, HNO_3 and Np(IV) respectively. Table 6 shows Np distribution ratio in each stage. Both of Fig.4 and Table 6 for run A indicate the heavy accumulation of Np(IV) occurred in the middle of battery, especially at stage 9 of aqueous phase and stage 7 of organic

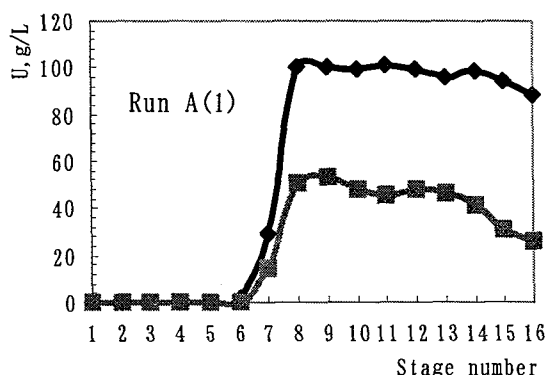


Fig 2. Concentration profile of U

—●— Organic phase —■— Aqueous phase

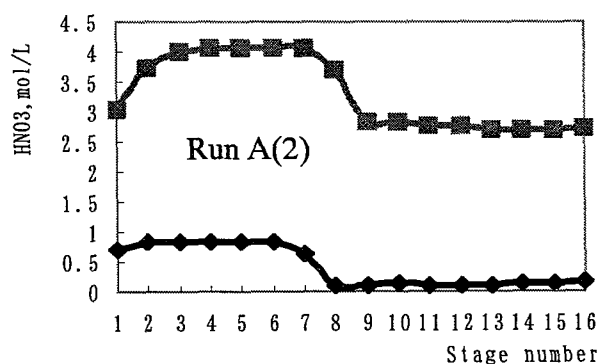


Fig 3. Concentration profile of HNO_3

—●— Organic phase —■— Aqueous phase

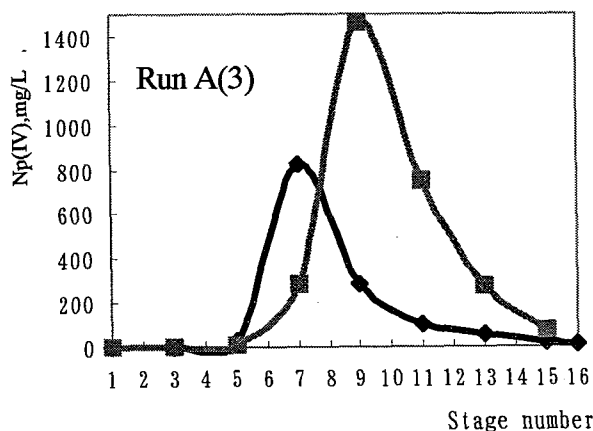


Fig 4. Concentration profile of Np(IV),mg/L

—●— Organic phase —■— Aqueous phase

phase. The material balance is poor(-21%). It is obvious that the Np(IV) is easy to be extracted in the extraction zone where the U concentration is low, regardless of low distribution ration of Np(IV)(~3). But the extracted Np(IV) will be washed out in the washing zone where the U concentration is high. It should notify that the extraction process has not yet reached the stationary state in present experiment.

Table 6. Distribution ratio of Np in each stage 25°C

NO.	Stage Number							
	1	3	5	7	9	11	13	15
RUN A	0.01	0.14	3.06	0.27	0.19	0.14	0.19	0.23
RUN B	0.003	0.009	0.022	0.24	0.13	0.17	0.16	0.16
RUN C	0.004	0.008	0.048	0.16	0.082	0.12	0.1	0.1

Run B: The feed solution contains 0.1g/L Np(V), 5×10^{-3} M NaNO₂, U and HNO₃. The concentration profile of Np is shown in Fig.5, it is a quite typical figure for normal operation and the distribution ratio of each stage is shown in Table 6 for Run B.

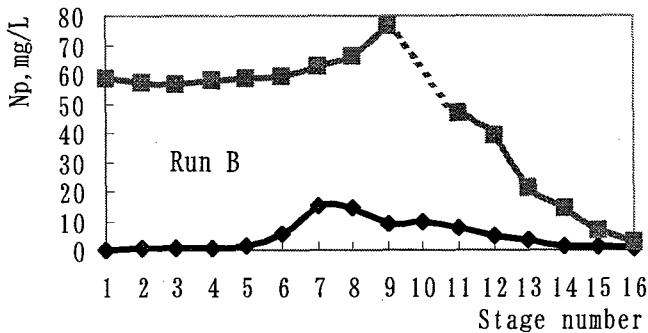


Fig 5. Concentration profile of Np in presence of HNO₂ at 25°C

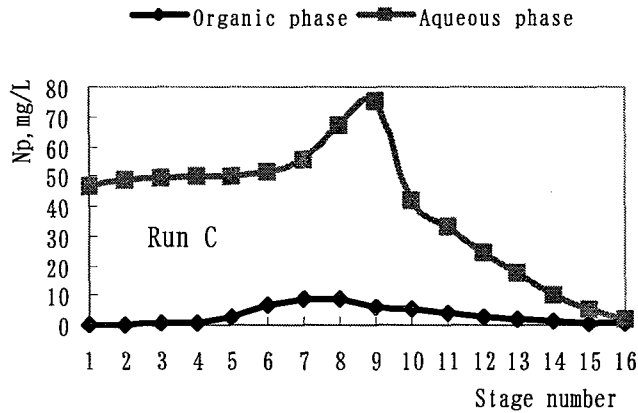


Fig 6. Concentration profile of Np in presence of urea at 25°C

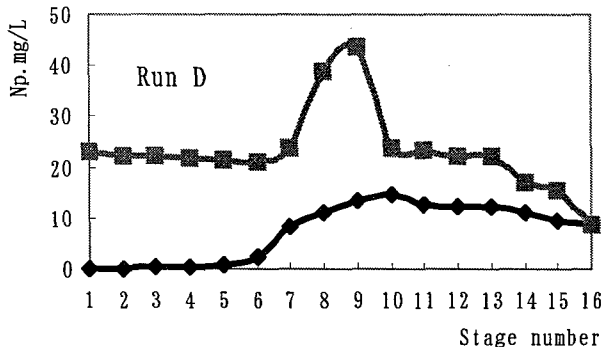


Fig 7. Concentration profile of Np in presence of HNO₂ at 36°C

The Np in HLLW is about 98%. The material balance is satisfied.

Run C: The feed solution contains 0.05M urea, 0.1g/L Np(V), U and HNO₃. The result is showed in Fig.6 and Table 6. The Np in HLLW is more than 98%.

Run D: The feed solution contains 0.1g/L Np(V), 5×10^{-3} M HNO₂, U and HNO₃. The experiment was carried out at 36°C. The result is shown in Fig. 7. It shows that rising temperature can accelerate oxidation rate of Np(V) to a great deal and drive Np to go along with U and Pu. There are about 38% Np is kept in the organic phase. In case of 0.05M urea added in feed solution at 36°C, about 98% Np will be in HLLW. It shows clearly that urea could lower oxidation of Np(V). In all case, the recovery of U and Pu is more than 99.9%

5 Conclusion

The oxidation of Np(V) in HNO₃ solution during standing and solvent extraction by 30% TBP/kerosene was studied. The results show that oxidation increases with standing time elapsed, but, such oxidation can be depressed by adding of urea. The small amount of Np(IV) is always appeared due to disproportionation of Np(V) which increases in proportion to the standing time and HNO₃ concentration. The solvent extraction process will greatly accelerate the Np(V) oxidation rate in favor of Np(VI) formation.

The chemical flowsheet study in a miniature mixer-settle shows that Np(IV) is accumulated in middle section of battery during the extraction process. The oxidation of Np(V) to Np(VI) in the battery is dependent on the acidity, contact time and temperature. Under present experiment condition, about 98% of Np was found in HLLW at 25°C when urea is not added. If temperature rises to 36°C, more than 38% of Np will go along with U and Pu. If urea is present in feed solution at 36°C, more than 98% Np will go to HLLW. The urea was selected for HNO₂ scavenger. The products of the reaction with HNO₂ mainly are the N₂ and CO₂. In addition, the urea may possess a weak complexing ability towards the Pu(IV). It requires more detail investigation for practical application and the hot experiment campaign with genuine feed solution is needed to demonstrate its reality and feasibility.

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