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Neptunium concentration profiles in the Purex process

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Abstract

Numerical simulations of neptunium concentration profiles in the co-decontamination step of the Purex process is carried out in order to understand neptunium extraction behavior and to propose a flow sheet for neptunium recovery from the reprocessing process. A simulation result for a flow sheet containing Pu(VI) in the feed solution shows that Pu(VI) plays a role of scavenger of nitrous acid. The rate constant of neptunium reduction with *n*-butyraldehyde is evaluated by using the process data. The determined rate constant is available for the numerical simulation of neptunium concentration profiles in the reprocessing process. © 1998 Elsevier Science S.A.

Keywords: Co-decontamination step; Neptunium recovery; Pu(VI); Nitrous acid; Neptunium reduction; *n*-butyraldehyde

1. Introduction

Neptunium (^{237}Np) is one of most important nuclides in the radioactive waste management from nuclear fuel reprocessing because of its long half life. Great concern has been paid to the pathway of neptunium in the Purex process in order to consider the TRU waste management including actinide recycling. It is very important to understand the extraction behavior of neptunium in the Purex process for determining the pathway of neptunium in the process.

The pathway of neptunium in the process varies with each plant [1–8]. In a previous report [9], we showed that the nitrous acid plays an important role on the neptunium extraction behavior in the co-decontamination step on the Purex process. Some process studies of neptunium extraction behavior by nitrous acid concentration control have been carried out [1,10–18]. One of these studies is to use Pu(VI) [10]. The experimental result shows that most of neptunium supplied to the extraction section is coextracted with uranium and plutonium to organic solvent. Other process studies of neptunium reduction by using butyraldehyde as a reducing agent have also been carried out in order to consider recovery of neptunium from the scrub section [19,20]. These results also show that butyraldehyde works effectively for neptunium reduction from Np(VI) to Np(V) in the scrub section.

In this study, the neptunium extraction behavior under nitrous acid concentration control in the extraction section is made clear with comparison to the simulation result. It is shown that control of nitrous acid in the feed solution is very important for preventing the leak of neptunium to the raffinate. The kinetics of neptunium reduction with butyraldehyde are also analyzed by using the process data.

2. Numerical simulation

2.1. Numerical simulation of neptunium concentration profile in co-decontamination step containing Pu(VI)

It is convenient to coextract neptunium with uranium and plutonium in a co-decontamination step for its recovery. Neptunium is generally reduced from Np(VI) to Np(V) in the presence of high concentrations of nitrous acid. A part of neptunium can be transported to the raffinate stream in the co-decontamination step because Np(V) is not extracted by TBP. Control of nitrous acid concentration in a feed solution is important for preventing neptunium leaking to the raffinate stream. It was recently reported that the concentration of nitrous acid could be reduced when Pu(VI) existed in the solution as follows [10]:

$$PuO_2^{2+} + NO_2^- + 2H^+ \rightleftarrows Pu^{4+} + NO_3^- + H_2O. \qquad (1)$$

This may be effective for preventing Np(VI) being reduced to Np(V) because nitrous acid concentration can be controlled by this reaction. In this report [10], an experiment of neptunium extraction in the co-decontamina-

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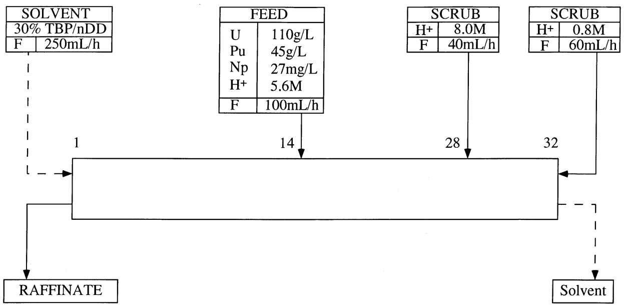

Fig. 1. Flow sheet A.

tion step under the condition containing Pu(VI) in the feed solution was carried out. About 20% of plutonium in the feed solution was hexavalent and the rest was tetravalent. A flow sheet of the experiment is schematically shown in Fig. 1. About 100% of neptunium was coextracted with uranium and plutonium to organic solvent in this experiment [10]. Numerical simulation of neptunium concentration profile is carried out in order to evaluate this result. The numerical simulation code for the mixer-settler which was developed in a previous paper [9] is used for the numerical simulation. In the numerical simulation, it is assumed that nitrous acid does not exist by reaction (1) when Pu(VI) exists in the feed solution and that all of the neptunium in the feed solution exists in the hexavalent state.

Fig. 2 shows the comparison between experimental and calculated concentration profile of total neptunium {[Np(V)] + [Np(VI)]}. This result also indicates that about 100% of neptunium supplied to the process is extracted to organic solvent. This can be explained by the following reason. The reduction reaction from Np(VI) to Np(V) does not occur because nitrous acid does not exist in the feed solution. There is the difference between experimental and calculated values at stages 22 and 28. It is considered that the difference is caused by the following reason. Although the concentration of plutonium in this process is high because of reprocessing for FBR spent fuel, the distribution coefficient of neptunium including our simulation code is obtained for reprocessing of typical LWR spent fuel containing a low plutonium concentration. From the simulation result, it is considered that Pu(VI) plays a role of scavenger of nitrous acid such as hydrazine.

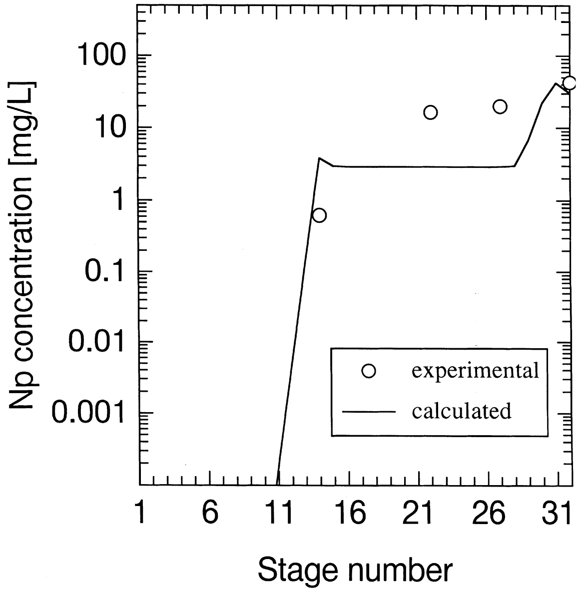

Fig. 2. Concentration profile of Np in flow sheet A.

2.2. Kinetics of neptunium reduction with *n*-butyraldehyde

A method of separating neptunium from coextracted uranium and plutonium by neptunium reduction with *n*-butyraldehyde was proposed [19,20]. A rate equation of neptunium reduction with *n*-butyraldehyde is proposed as follows [21]:

$$-r_{\mathrm{Np(VI)}} = k[\mathrm{Np(VI)}][n-\mathrm{C_3H_7CHO}][\mathrm{H^+}] \qquad (2)$$

where k is the rate constant of the reduction.

In the previous report [9], we proposed an approach for evaluating the rate constant for the reaction of Np(V) with nitric acid using process data. This approach is also used in order to determine the rate constant of Eq. (2). Some experimental concentration profiles in the mixer-settler bank are required for the approach. Uchiyama et al. [20] carried out several experiments of neptunium separation in the mixer-settler bank by using *n*-butyraldehyde as a reductant. A flow sheet of their experiments is schematically shown in Fig. 3. A miniature mixer-settler was also used in this experiment. The volumes of mixer and settler are 6 ml and 17 ml for each stage, respectively. About 70% of neptunium in the feed solution supplied to the 8th stage was pentavalent and the rest was hexavalent. Ammonium vanadium was used as an oxidant of Np(V) in order to extract neptunium fed in the process. The rate equation of neptunium oxidation with vanadium is used [22].

As mentioned above, our numerical simulation code for the mixer-settler is used for the numerical simulation of

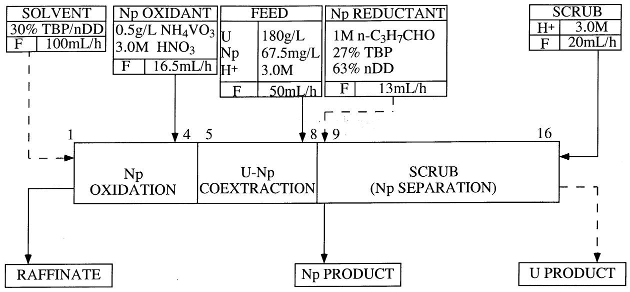

Fig. 3. Flow sheet B.

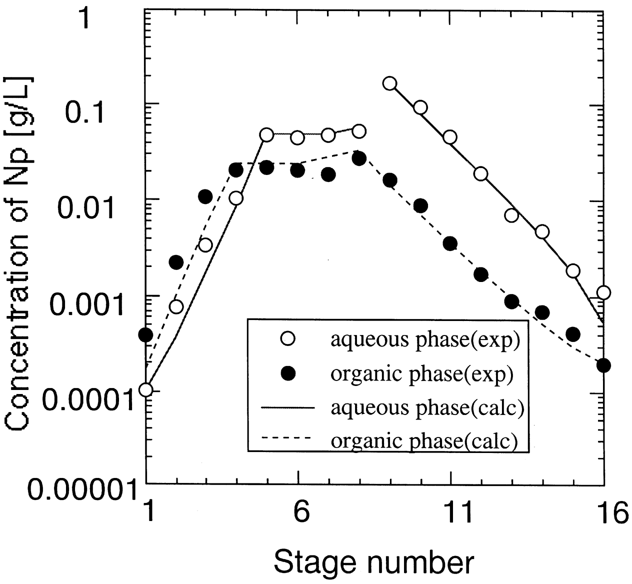

Fig. 4. Concentration profiles of Np in flow sheet B.

neptunium concentration profiles. Eq. (2) is adopted as the rate equation of neptunium reduction with *n*-butyraldehyde. The rate constant of *k* was determined with the non-linear least-squares method and its value is 9.71×10^{-1} [$l^2/(mol^2$ min)]. Fig. 4 shows the comparison between experimental and calculated concentration profiles of total neptunium {[Np(V)]+[Np(VI)]} when the determined rate constant is used. The calculated concentration profiles of neptunium in both the aqueous and organic phase are in good agreement with the experimental ones.

Numerical simulation for another flow sheet [20] shown in Fig. 5 was also carried out in order to evaluate the determined rate constant. The flow rate of the scrub solution in this flow sheet is larger than that in the previous flow sheet. This flow sheet has three outlet flows named RAFFINATE, Np PRODUCT, and U PRODUCT, respectively. The comparison between experimental and calculated ratio of neptunium in the feed solution to that in each outlet flow is listed in Table 1. The calculated values of each outlet flow are in good agreement with the experimental ones. It is, therefore, concluded that the determined rate constant is available for the numerical simulation of neptunium concentration profiles in reprocessing process by using *n*-butyraldehyde as a reductant.

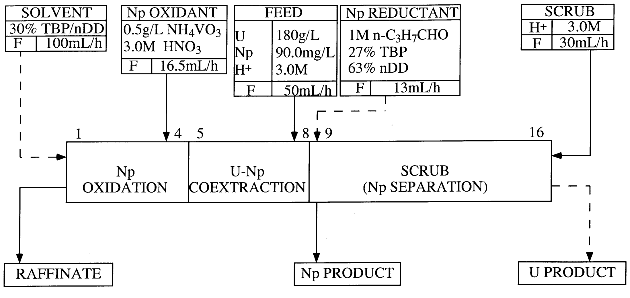

Fig. 5. Flow sheet C.

Table 1
Comparison between experimental and calculated ratio of neptunium in the feed solution to that in each outlet flow

	Experimental (%)	Calculated (%)
Raffinate	0.76	0.23
Np product	99.23	98.97
U product	0.01	0.80

As mentioned above, for neptunium coextraction with uranium and plutonium and selective separation from them, it is effective to use Pu(VI) and *n*-butyraldehyde, respectively.

3. Conclusion

Numerical simulation of neptunium extraction behavior was carried out under nitrous acid concentration control in the co-decontamination step. It was found that from numerical simulation for the flow sheet containing Pu(VI) in the feed solution Pu(VI) plays a role of scavenger of nitrous acid. The kinetics of neptunium reduction with *n*-butyraldehyde was also analyzed by using the process data. The determined rate constant of this reduction reaction was 9.71×10^{-1} [$l^2/(mol^2$ min)]. The determined value was available for the numerical simulation of neptunium behavior in the reprocessing process by using *n*-butyraldehyde as a reductant.

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