DEGRADED TBP SOLVENT REGENERATION TECHNOLOGY USING BUTYLAMINE AS A SOLVENT WASHING TO REDUCE SOLID SALT WASTE

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ABSTRACT

Normal butylamine compounds are studied as salt-free wash reagents for degraded solvent used in PUREX process in spent fuel reprocessing. The solvent wash tests were carried out with two types of butylamine compounds, n-butylamine oxalate and n-butylamine bicarbonate, by counter-current mode using a small size mixer-settler composed of two 4-stage wash steps. Di-n-butyl phosphoric acid (HDBP), the main degradation product from TBP, was removed from real degraded solvent with decontamination factor of 2.5~7.9.

The study on electrolytic decomposition of butylamine compounds was also conducted for waste treatment.

INTRODUCTION

The mixed organic solvent of tri-n-butyl phosphate (TBP) and hydrocarbon diluent is utilized in a PUREX process in spent fuel reprocessing. The solvent is radiolitically and chemically degraded. Decomposed organic compounds, di-n-butyl phosphoric acid (HDBP) as the most typical product, are formed during plant operation. The products reduce solvent extraction efficiency of uranium and plutonium (1). Therefore, the degraded solvent is washed before being recycled. In conventional plants, sodium carbonate and sodium hydroxide have been used as solvent wash reagents. A drawback of the reagents is the production of large amount of solid sodium salt waste. Hydrazine oxalate and hydrazine carbonate was proposed to substitute for the sodium compounds from the viewpoint of reducing radioactive waste volumes (2,3), because hydrazine compounds can be decomposed to water and gases. Hydrazine compounds, however, are unstable and difficult to prepare and store because hydrazine produces the volatile and explosive hydrazoic acid (4).

The authors have already proposed a new solvent wash process using normal butylamine compounds instead of hydrazine compounds as salt-free solvent wash reagents by experiments with simulated degraded solvent (5,6,7). The present paper describes results of solvent washing tests with real degraded solvents that have been produced in actual PUREX reprocessing tests with spent fuel (8,9,10).

Basic study on the electrolytic decomposition of n-butylamine using silver ion as a mediator oxidant was performed for waste treatment (11). The optimum condition for decomposition of butylamine was investigated by changing the concentration of nitric acid, the concentration of silver ion, temperature and applied electric potential, and the decomposition rate was obtained.

EXPERIMENTAL

Solvent Wash Tests

In the present study, two types of butylamine compounds, n-butylamine oxalate and n-butylamine bicarbonate, were used as solvent wash reagents at the concentration of 0.25M. A solution of n-butylamine oxalate was prepared by adding the equivalent amount of oxalic acid to n-butylamine aqueous solution. The pH of the solution was 8. The n-butylamine oxalate solution of pH 2 was prepared by adding nitric acid to the above solution. A solution of n-butylamine bicarbonate was obtained by bubbling carbon dioxide through n-butylamine aqueous solution until the pH of the solution became constant (pH7).

Three kind of degraded solvent from 30% TBP - n-dodecane used in the present study, named Solvent 1, 2 and 3, were obtained by three different reprocessing tests, as listed in Table I. The reprocessing tests that produced Solvent 2 and 3 were carried out using the same dissolved solution of the spent fuel burned up to 44GWd/t in the different extraction condition (7,8). Concentrations of HDBP and radionuclides in the degraded solvent are shown also in Table I.

Table I Degraded Solvent Used in the Present Study

Name of degraded solvent used	Burn-up of spent fuel used	Concentration of HDBP (g/L)	Concentration of radionuclide (Bq/ml)				
			α-emitters	β-emitters	Cs-137	Ru-106	Zr-95*
Solvent 1	29 GWd/t	0.192	8.0×10^{2}	6.0×10^{2}	8.7×10^{2}	6.4×10^{0}	0.57
Solvent 2	44 GWd/t	1.26	3.2×10^{3}	NA**	4.5×10^{2}	1.5×10^{2}	-
Solvent 3	44 GWd/t	0.397	5.8×10^{3}	5.1×10^{2}	3.4×10^{2}	2.9×10^{2}	-

* Added to the dissolved solution of the spent fuel of 29 GWd/t before extraction test

** Not analyzed

Experimental condition of counter-current solvent wash test is shown in Fig.1. A small size mixer-settler of 8 stages installed in a glove box was used in the tests. The process consists of two 4-stage wash steps with different wash reagent. The solvent wash behaviors were studied under various conditions varying the kind of butylamine compounds and pH in aqueous phase.

The concentration of HDBP was analyzed by ion chromatography. The concentration of α- and β-emitters were measured by 2π gas flow counter and that of γ-emitters was analyzed by γ spectrometry.

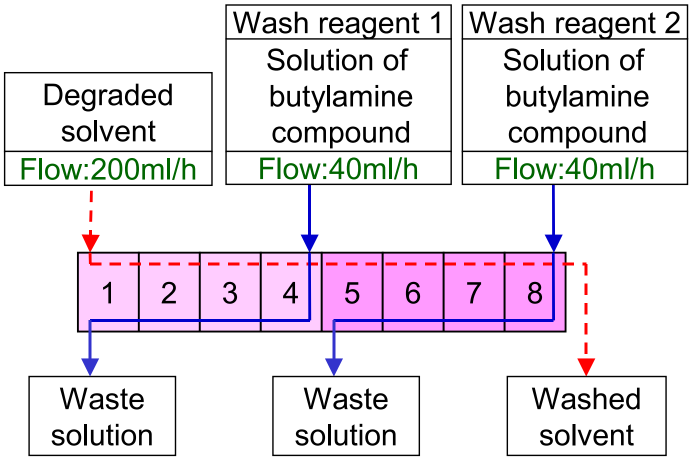

Fig.1 Experimental condition of counter-current solvent wash test

Electrolytic Decomposition of Butylamine Compounds

Decomposition of the butylamine compounds was examined by electrochemical oxidation process using silver ion as a mediator oxidant. The electrolytic decomposition cell used in the present study has the capacity of 100 ml and one pair of platinum-coated titanium electrodes (anode : 10×5 mm, cathode : 20×5 mm). The cathode was covered with a small tube where porous glass flit was attached as isolation wall. Decomposition tests were carried out by constant potential electrolysis using saturated calomel electrode (SCE) as the reference. Parameters examined were nitric acid concentration (0.01, 1.0, 2.0, <u>3.0</u> M), silver concentration (0, 2, 4, 6, <u>8</u>, 16 g/L), butylamine concentration (<u>0.18</u>, 0.36, 0.72 g/L), electrolytic potential (1.5, <u>1.6</u>, <u>1.7</u>, 1.8, 1.9, 2.0 V vs. SCE) and temperature (40, 50, <u>60</u> °C). The underlined values are the value taken in the experiments to examine the influence of other parameters.

RESULTS AND DISCUSSION

Solvent Wash Tests

The counter-current solvent wash tests were conducted six-times varying the degraded solvent and wash reagent. Table II shows the experimental conditions and the results on the decontamination factor (DF) for HDBP. For the Solvent 1, four kinds of experiments were carried out, but they did not give much difference in the DF for HDBP. In the Test No. 1 and 3, where the butylamine bicarbonate was used as wash reagent 2, bubbles of carbon dioxide appeared in the mixer-settler. Since this phenomenon would make some troubles in plant operation, only butylamine oxalate was used as a wash reagent for Solvent 2 and 3.

Table II Experimental conditions and the results on the decontamination factor (DF) for HDBP

Test No.	Degraded solvent	Wash reagent 1	Wash reagent 2	DF for HDBP
1	Solvent 1	Butylamine oxalate, pH2	Butylamine bicarbonate, pH 7	7.5
2		Butylamine oxalate, pH2	Butylamine oxalate, pH8	6.1
3		Butylamine oxalate, pH8	Butylamine bicarbonate, pH 7	5.1
4		Butylamine oxalate, pH8	Butylamine oxalate, pH8	7.9
5	Solvent 2	Butylamine oxalate, pH2	Butylamine oxalate, pH8	2.5
6	Solvent 3	Butylamine oxalate, pH2	Butylamine oxalate, pH8	5.1

Profiles of HDBP concentration in the organic phase and pH in the aqueous phase in the Test No. 2, 4, 5 and 6 are shown in Figure 2. In the Test No. 4, where the butylamine oxalate at pH 8 was used as wash reagent 1, accumulation of HDBP in the first wash step was observed, as shown in Figure 2, which is due to the decrease of pH caused by nitric acid contained in the degraded solvent. In the first wash step, nitric acid and metal ion such as Zr, U and Pu, rather than HDBP, should be removed by butylamine oxalate at low pH (5). The removal of HDBP from the organic phase in the second wash step is less effective in the Test No. 5 and 6 than in the Test No. 2 in spite of the higher pH. Normally, distribution ratio of HDBP decreases with the increase of pH in the wash solution.

Figure 3 shows distribution ratio of HDBP obtained in the counter-current wash tests plotted by the pH measured. Results of batch experiments using simulated degraded solvent that contains TBP and HDBP

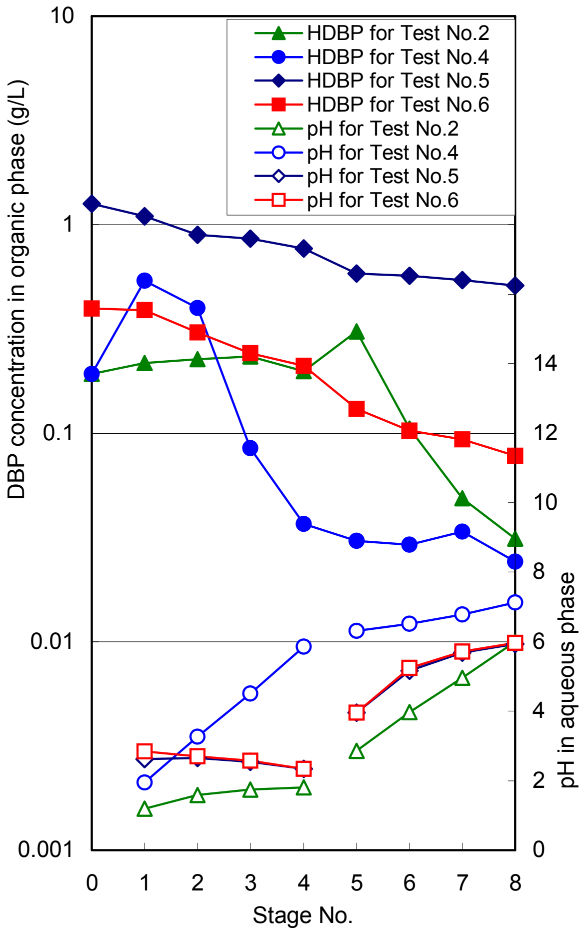

Fig. 2 Profiles of HDBP concentration and pH obtained in counter-current solvent wash tests

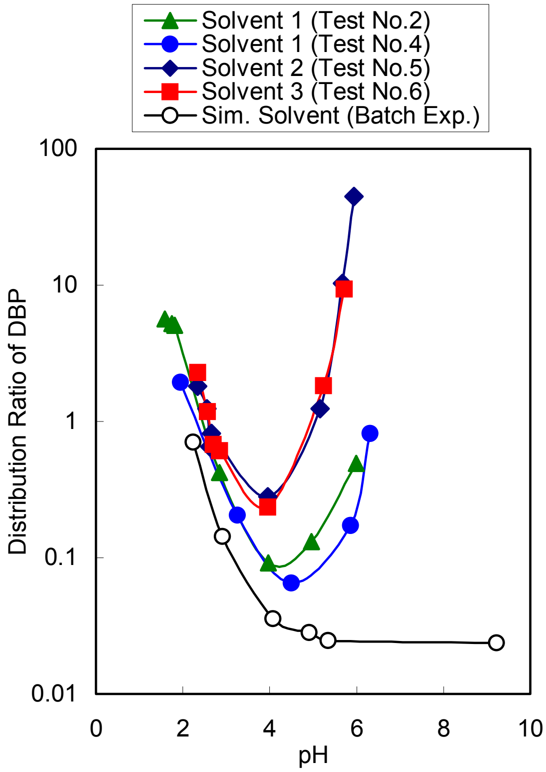

Fig. 3 Distribution ratio of HDBP

in n-dodecane were shown also in Figure 3 for comparison. At higher pH, distribution ratios of HDBP obtained by the tests with real degraded solvent were unexpectedly high compared with the results of the batch experiment. The chemical state of HDBP in the real degraded solvent would be different from that in the simulated one. The higher absorbed dose (in the Test No. 5 and 6) makes the distribution ratio of HDBP higher. Investigation on this difference between real and simulated degraded solvent should be undertaken, examining the wash behavior of not only HDBP but also metal ions, particularly Zr.

Decontamination factors for α- and β-emitters obtained the counter-current solvent wash tests are shown in Table III. The decontamination factors for α- emitters in Test No. 5 and 6 were high as in Test No.2 and 4, but that is not the case for β-emitters. This would be a key point to be examined in order to improve the decontamination factor for HDBP.

Table III Decontamination factor for radionuclide

Test No.	α- emitters	β- emitters	Cs-137	Ru-106	Zr-95
2	2.9×10^{2}	56	8.8×10^{2}	2.3	3.2
4	1.6×10^{2}	54	1.6×10^{2}	2.7	3.8
5	8.7×10^{2}	-	1.8×10^{1}	1.9	-
6	7.0×10^{3}	4.9	5.3×10^{1}	1.4	-

Electrolytic Decomposition of Butylamine Compounds

The optimum condition for electrolytic decomposition of butylamine was the nitric acid concentration of 3M, the silver concentration of 8 g/L, the solution temperature of 60 °C and the decomposition electric potential of 1.7 V vs. SCE. Observed decomposition curves for butylamine (0.18 g/L) and butylamine oxalate (0.18g/L as butylamine) at the optimum condition are shown in Figure 4. The two curves were almost the same. An experiment for oxalic acid solution showed that oxalic acid was decomposed very rapidly. Decomposition rate was fast in the initial period and 90 % of butylamine decomposed within 120 minutes. The decomposition rate constant (decomposition to 70 %) was 3.09×10^{-1} mg/min when the decomposition reaction was considered as 0th- order. On the other hand, decomposition to 95 % takes 270 minutes. The slow rate of the decomposition in the proceeded period should be improved from the engineering point of view.

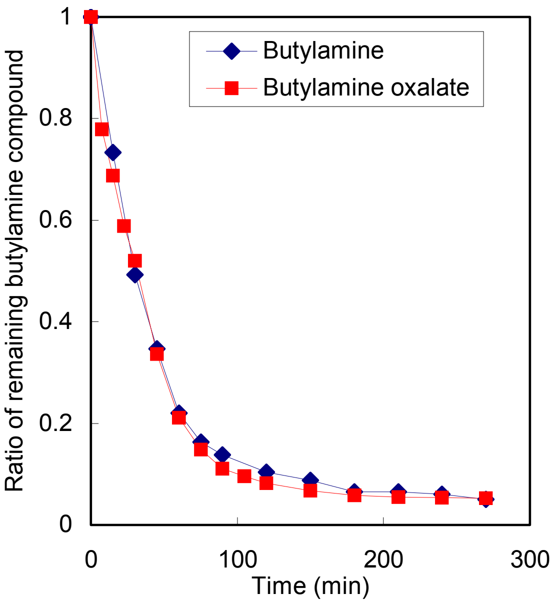

Fig. 4 Decomposition of butylamine and butylamine oxalate at the optimum condition (3M HNO_3, 8 g/L Ag, 60 °C, 1.7 V vs. SCE)

CONCLUSION

The results of the present study showed the possibility to use of n-butylamine compounds as a salt-free solvent washing reagent for spent fuel reprocessing. The difference in distribution ratio of HDBP was, however, observed between the real and simulated degraded solvent. Investigation on this difference should be undertaken, examining the wash behavior of not only HDBP but also metal ions, particularly Zr. The further subjects to be examined are to improve the wash efficiency of n-butylamine compounds by a process optimization and to improve n-butylamine decomposition by electrolysis from the engineering point of view.

Acknowledgement

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