Journal of Nuclear and Radiochemical Sciences, Vol. 9, No. 2, pp. 37-39, 2008

Influence of Boric Acid in the Extraction of Uranium (VI), Plutonium (IV) and Europium (III) from Fast Reactor Fuel Dissolver Solution

K.A. Venkatesan, V. Sukumaran, M.P. Antony, and T.G. Srinivasan*

Fuel Chemistry Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 602 102, India.

Received: May 17, 2008; In Final Form: August 16, 2008

Addition of boric acid to dissolver solution has been proposed for minimizing the criticality concern associated with reprocessing of fast reactor fuel. Extraction of uranium (VI) and plutonium (IV) from the resultant nitric acid – boric acid medium by a solution of tri-*n*-butyl phosphate (TBP) in *n*-dodecane (*n*-DD) has been studied at 298 K. The distribution ratios of uranium (VI) and plutonium (IV) were found to be comparable with those obtained in the absence of boric acid. Extraction of europium (III) from nitric acid – boric acid by a solution of 1.2 M TBP–0.2 M *n*-octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) in *n*-DD was also studied. The solubility limit of boric acid as a function of nitric acid concentration was determined and it was found to decrease from 61.5 g/L in 0.1 M HNO_3 to 32.4 g/L in 4 M HNO_3 at 303 K. Extraction of boric acid in 1.1 M TBP/*n*-DD and in a solution of 1.2 M TBP–0.2 M CMPO in *n*-DD was studied and it was found to increase with increase in the concentration of boric acid above ~0.2 M. The study indicated that the interference of boric acid during the extraction of uranium (VI) plutonium (IV) by PUREX solvent and Eu(III) by TRUEX solvent was negligible and the added boric acid could be quantitatively retained in aqueous phase provided the boric acid concentration was fixed below 6 g/L (~0.1 M) in the feed solution.

1. Introduction

PUREX process is being adopted for closing the nuclear fuel cycle and it basically consists of solvent extraction of uranium and plutonium by 1.1 M solution of tri-*n*-butyl phosphate (TBP) in *n*-dodecane (*n*-DD) from 3 – 4 M HNO_3 medium, which is obtained after the dissolution of spent nuclear fuel in nitric acid.[1] The spent nuclear fuel from fast reactor differs remarkably from that of thermal reactors in the composition of fissile elements, yield and amount of fission products. These factors tend to pose several complications such as criticality, third-phase formation, chemical and radiolytic degradation[2-5] etc. during solvent extraction and subsequent re-conversion processes.

The concern over critically arises due to handling of significantly large amounts of fissile element, ^{239}Pu, in addition to other transplutonium elements, in aqueous feed solution during solvent extraction stage. This concern can be minimized by adding strong neutron absorbers such as rare-earth metal ions (e.g. gadolinium), boric acid etc, to aqueous feed. Addition of these external reagents may, however, pose problems during the management of the raffinate, namely high-level liquid waste (HLLW) obtained after extraction. For example addition of trivalent rare-earth metal ion eventually increases the concentration of lanthanide ions in HLLW, which is likely to facilitate third phase formation during minor actinide partitioning by TRUEX process[3-6] and also complicate lanthanide-actinide group separation.[7] Nevertheless, the advantage of adding rare-earth element, from the extraction point of view, is its well-known chemistry and route of trivalent lanthanides in PUREX process flow sheet. In contrary, boron is not formed as a fission product. Therefore, the extraction chemistry of boron, routing of boric acid in PUREX process and influence of boric acid on the extraction of target metals etc. are unknown. However, the merit of using boric acid is that the added boron forms a compatible glass matrix with high-level liquid waste along with other glass formers during immobilization of HLLW, provided it is pushed quantitatively in to HLLW stream. In view of these, the primary aim of the present investigation is to address these unknown issues of using boric acid during reprocessing. In this context, the extraction of behavior of uranium (VI) and plutonium (IV) from nitric acid – boric acid medium by a PUREX solvent (1.1 M TBP/*n*-DD) and Eu(III) by TRUEX solvent (1.2 M TBP–0.2 M CMPO/*n*-DD) was studied and the distribution ratios are compared with those obtained in the absence of boric acid. Solubility of boric acid in nitric acid medium was determined and the quantity of boric acid that can be added to the dissolver solution during reprocessing was recommended.

2. Experimental

Materials. All the chemicals and solvents used in the present study were of analytical grade. Tri-*n*-butylphosphate and uranyl nitrate were obtained from E.Merck, Mumbai. CMPO was synthesized at National Chemical Laboratories, Pune, India and used after purification.

Solubility of boric acid in nitric acid medium. The solubility of boric acid in nitric acid medium was determined by adding a known quantity of boric acid (5–10 mg) to a solution of nitric acid (25 mL) of desired concentration taken in an equilibration tube. This tube was immersed in a constant temperature water bath and the mixture was stirred at a desired temperature. Addition of boric acid (5–10 mg) was continued until the solution under stirring leaves a permanent insoluble residue in solution. The cumulative weight of boric acid obtained after the observation of first insoluble residue was taken as the solubility limit of boric acid in nitric acid medium and it was represented in the units of g/L. The solubility limit thus obtained was plotted against temperature. Solubility of boric acid was also determined in a solution containing uranium (50 g/L) in 4.0 M HNO_3 medium.

Extraction of uranium (VI) by TBP/n-DD. All the extraction studies were carried out at 298 K by mixing equal volume of organic and aqueous phases (3 mL each), unless otherwise

---

*Corresponding author. E-mail: tgs@igcar.gov.in, Fax: +91-44-27480065

TABLE 1: Distribution ratios of uranium (VI) in TBP/*n*-DD at various nitric acid concentrations in the presence and absence of 0.1 M H_3BO_3 at 298 K

$[HNO_3]$/M	TBP concentration in *n*-DD					
	0.2 M		0.5 M		1.1 M	
	Absence of H_3BO_3	Presence of H_3BO_3	Absence of H_3BO_3	Presence of H_3BO_3	Absence of H_3BO_3	Presence of H_3BO_3
0.1	0.08	0.04	0.19	0.11	0.46	0.30
1	0.79	0.99	2.67	2.88	7.28	6.60
2	2.04	1.95	6.49	6.21	14.55	14.05
3	3.62	3.98	11.30	12.76	21.80	21.30
4	4.75	4.69	13.47	13.76	29.20	29.07
5	4.81	5.00	15.56	16.30	30.91	33.20

TABLE 2: Comparison of distribution ratios of uranium (VI) at various nitric acid and boric acid concentrations at 298 K

$[HNO_3]$/M	0.2 M TBP/*n*-DD		0.5 M TBP/*n*-DD	
	0.1 M H_3BO_3	0.5 M H_3BO_3	0.1 M H_3BO_3	0.5 M H_3BO_3
0.1	0.04	0.01	0.11	0.11
1	0.99	0.91	2.88	2.94
2	1.95	2.2	6.21	6.43
3	3.98	4.15	12.76	11.23

TABLE 3: Distribution ratios of plutonium (IV) in 1.1 M TBP/*n*-DD and Eu(III) in 1.2 M TBP-0.2 M CMPO/*n*-DD at various nitric acid concentrations in the presence and absence of 0.1 M H_3BO_3 at 298 K

$[HNO_3]$/M	^{239}Pu(IV) in 1.1 M TBP/*n*-DD		$^{(152+154)}$Eu(III) 1.2 M TBP-0.2 M CMPO/*n*-DD	
	Absence of H_3BO_3	Presence of H_3BO_3	Absence of H_3BO_3	Presence of H_3BO_3
0.1	--	--	0.51	0.11
0.5	0.96	0.91	---	---
1	2.23	2.21	9.58	8.95
2	5.55	5.67	14.0	12.6
3	9.25	9.91	14.6	13.2
4	11.4	12.0	15.2	13.2
5	15.9	15.1	14.8	14.5

mentioned, in a 20 mL capacity test tube. These tubes were clamped in test tube rotator that provides an upside down rotation of tubes at a speed of 50 rpm. Pre-equilibration of organic phase was carried out with desired concentration of nitric acid as well as with boric acid – nitric acid solution. Extraction of uranium (VI) at various nitric acid concentrations (0.1 M to 5.0 M) was studied by mixing organic phase containing TBP solution in *n*-DD (varied, 0.2 M to 1.1 M) with aqueous phase containing desired concentration of nitric acid, boric acid (varied, 0.1 M to 0.5 M), and uranyl nitrate (4.2×10^{-4} M) spiked with ^{233}U tracer in a glass tube. After two hours of equilibration, the distribution ratio (D) of uranium was determined from the radioactivity measurement of ^{233}U present in organic and aqueous phase and by using eq 1.

$$D = \frac{[^{233}\mathrm{U}]_{\mathrm{org}}}{[^{233}\mathrm{U}]_{\mathrm{aq}}} \qquad (1)$$

A similar experiment was carried out for the extraction of ^{239}Pu(IV) and $^{(152+154)}$Eu(III) by using PUREX and TRUEX solvent respectively and the distribution ratios were determined.

Extraction isotherm of boric acid. The extraction of boric acid by 1.1 M TBP/*n*-DD was studied by equilibrating 3 mL of organic phase with 3 mL of aqueous phase containing various concentrations of boric acid. The amount of boric acid remaining in aqueous and organic phases was determined by alkalimetric titration of boric acid in the presence of mannitol. A similar experiment was carried out using TRUEX solvent.

3. Results and Discussion

Extraction studies. The distribution ratios for the extraction of uranium (VI) from nitric acid medium by a solution of TBP in *n*-DD are tabulated in Table 1, and the values are compared with those obtained in the presence of 0.1 M H_3BO_3 in the feed solution. It is observed that the distribution ratios of uranium in the presence and absence of boric acid are similar and they are within the limits of acceptable variations/trend. Increasing the concentration of boric acid to 0.5 M in the feed also does not alter the distribution ratios to any significant extent as shown in Table 2. The boric acid of concentration 0.5 M (~31 g/L) was not completely soluble in 4 M HNO_3 at 298 K. Therefore the distribution ratio of uranium from 4 M HNO_3 medium containing 0.5 M H_3BO_3 could not be generated. The study indicates that the influence of boric acid in the extraction of uranium (VI) by TBP/*n*-DD is negligible.

The distribution ratios for the extraction of ^{239}Pu(IV) in 1.1 M TBP/*n*-DD and $^{(152+154)}$Eu(III) in 1.2 M TBP–0.2 M CMPO/*n*-DD from HNO_3–0.1 M H_3BO_3 medium are shown in Table 3. It is observed that the distribution ratios of plutonium in the presence and absence of boric acid are similar. However, a marginal decrease in the distribution ratio is observed for the extraction of europium (III) by TRUEX solvent.

Solubility of boric acid in nitric acid medium. Solubility of boric acid in nitric acid medium is required for assessing the quantity of boric acid that can be added to the dissolver solution for minimizing the criticality concern. The solubility limit profiles of boric acid in various concentrations of nitric acid at different temperatures are shown in Figure 1. It is seen that the solubility limit of boric acid decreases with increase in the concentration of nitric acid due to common ion effect (eq 2), and the solubility increases linearly with increase of temperature.

$$\mathrm{B(OH)_3 + H_2O \rightleftarrows B(OH)_4^- + H^+}, \quad (\mathrm{p}K_\mathrm{a} = 9.05 \text{ at } 298 \text{ K}, I = 0.1 \text{ M with NaCl}) \qquad (2)$$

The solubility limit of boric acid in 3 M HNO_3 at 303 K is 34.8 g/L and it increases to 58.2 g/L at 318 K. At a constant temperature of 303 K, the solubility limit of 61.5 g/L in 0.1 M HNO_3 decreases to 32.4 g/L at 4 M HNO_3. The solubility of boric acid in a solution of 50 g/L uranium in 4.0 M HNO_3 at 303 K is in different from the value of ~32 g/L observed in the absence of uranyl nitrate.

Extraction of boric acid. The extraction isotherm of boric acid by PUREX and TRUEX solvent is shown in Figure 2. It is observed that extraction of boric acid by 1.1 M TBP/*n*-DD is

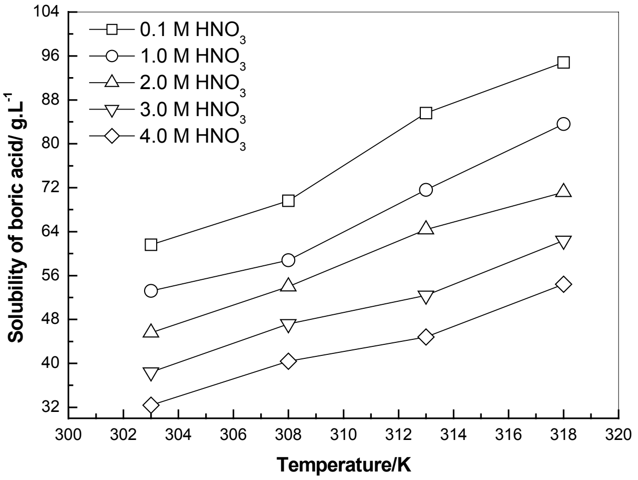


Figure 1. Solubility limit of boric acid in nitric acid medium at various temperatures.

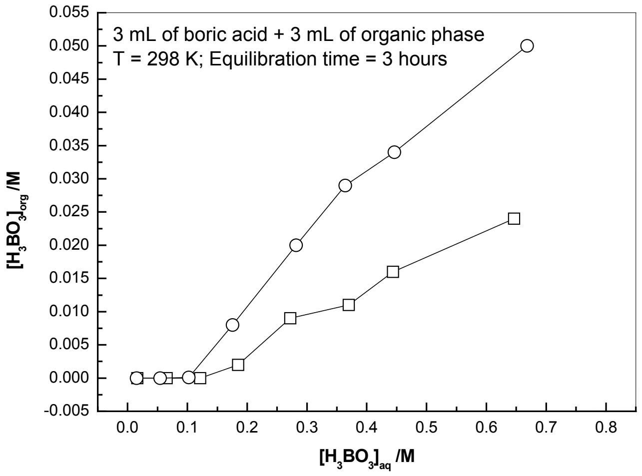
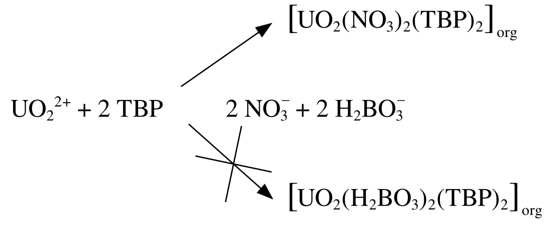


Figure 2. Boric acid extraction isotherm by PUREX and TRUEX solvent at 298 K.

negligible when the aqueous phase concentration of boric acid is below 0.2 M and significant extraction is observed when boric acid concentration in aqueous phase exceeds 0.3 M. It is also observed from Figure 2 that the extraction of boric acid by TRUEX solvent is insignificant when the concentration of boric acid is 0.1 M and thereafter the extraction increases with increase in the concentration of boric acid in aqueous phase. Since boric acid is a weak acid, the extraction could be attributed to the formation of TBP–H_3BO_3 complex in organic phase similar to nitric acid extraction[8] by TBP. In PUREX process, the feed concentration of nitric acid is fixed between 3 and 4 M. In such medium, the solubility limit of boric acid is ~0.4 M (=25 g/L) at 298 K (from Figure 1) and the extraction of boric acid by 1.1 M TBP/*n*-DD from 0.4 M H_3BO_3 medium is ~0.01 M as indicated in Figure 2. However, in the presence of 3 – 4 M HNO_3, the dissociation of boric acid (eq 2) is suppressed significantly. Therefore, it is unlikely that proton from boric acid gets associated with TBP and forms a complex, TBP–H_3BO_3, in preference to strong acid–TBP complex, namely TBP–HNO_3, in organic phase in PUREX process. Nevertheless, it is desirable to fix the boric acid concentration at 0.1 M in aqueous phase to ensure no extraction of boric acid in organic phase and to minimize further the dissociation of boric acid. Under such conditions, the mechanism of uranium (VI) extraction by 1.1 M TBP/*n*-DD could be forced in to a well-established mechanism of extraction, shown in eq 3 involving two molecules of TBP and nitrate ion in the formation of neutral uranyl nitrate–TBP complex, $[UO_2(NO_3)_2(TBP)_2]$, in organic phase. The likely participation of borate ion in the extraction step, shown in eq 4, could thus be excluded by the employment of low concentration of boric acid (0.1 M), where the suppression of dissociation of boric acid is prevailing in 3 – 4 M HNO_3 medium. The similarity in the distribution ratios of uranium (VI) and plutonium (IV) in the presence and absence of boric acid also supports that these metals are not extracted as uranium (VI)–borate or plutonium (IV)–borate complexes. Analysis of boron in the aqueous phase by ICP-AES after stripping of uranium from organic phase also showed that the concentration of boron in it was negligible. In view of this, it is desirable to fix the boric acid concentration at 0.1 M in aqueous phase to ensure no extraction of boric acid in organic phase, to eliminate the contamination of boron in U/Pu/Ln product stream and to retain the added boric acid in aqueous phase after extraction.



$$UO_2^{2+} + 2\,TBP \xrightarrow{2\,NO_3^- + 2\,H_2BO_3^-} [UO_2(NO_3)_2(TBP)_2]_{org} \quad (3)$$

$$UO_2^{2+} + 2\,TBP \xrightarrow{2\,NO_3^- + 2\,H_2BO_3^-} [UO_2(H_2BO_3)_2(TBP)_2]_{org} \quad (4)$$

4. Conclusion

The solubility of boric acid, at 303 K, in 4 M HNO_3 was 31 g/L (~0.5 M) and therefore the maximum concentration of boric acid that can be maintained in PUREX process feed was 0.5 M at 303 K. The extraction behavior of uranium (VI) and plutonium (IV) from the resultant nitric acid – boric acid medium in 1.1 M TBP/*n*-DD was comparable with the behavior observed in the absence of boric acid. Extraction of boric acid by 1.1 M TBP/*n*-DD was negligible when the aqueous phase concentration of boric acid was lower than 0.2 M and significant extraction was observed above 0.3 M. However, extraction of boric acid by TRUEX solvent was significant above 0.1 M in boric acid. Therefore, it is desirable to fix the concentration of boric acid in PUREX feed to 0.1 M (= 6 g/L) to take the advantage of eliminating borate contamination in U/Pu/Ln product stream and route all the added boric acid to HLLW.

References

(1) J. l. Swanson, *PUREX Process Flowsheets*, in *Science and Technology of Tributyl phosphate*, *Vol III*, Eds. W. W. Schulz, L. L. Burger, J. D. Navratil, and K. P. Bender, CRC Press Inc. Boca Raton, (1984), p 55.

(2) K. A. Venkatesan, B. Robertselvan, M. P. Antony, T. G. Srinivasan, and P. R. Vasudeva Rao, Solvent Extr. Ion Exch. **24** 747 (2006).

(3) P. R. Vasudeva Rao and Z. Kolarik, Solvent Extr. Ion Exch. **14,** 955 (1996).

(4) T. G. Srinivasan, R. Dhamodaran, P. R. Vasudeva Rao, and C. K. Mathews, Separation Sci. Technol. **23,** 1401 (1988).

(5) S. Kumar and S.B. Koganthi, Solvent Extr. Ion Exch. **21,** 547 (2003).

(6) E. P. Horwitz, D. G. Kalina, H. Diamond, G. F. Vandegrif, and W. W. Schulz, Solvent Extr. Ion Exch. **3**, 75 (1985).

(7) P. Y. Cordier, C. Hill, P. Baron, C. Madic, M. J. Hudson, and J.O. Liljenzin, J. Alloys Compd. **271–273,** 738 (1998).

(8) D. J. Chaiko and G. E. Vandegrift, Nucl. Technol. **82**, 52 (1988).