

BEHAVIOR AND STRUCTURES OF ^{99}Tc -SPECIES IN SOLVENT

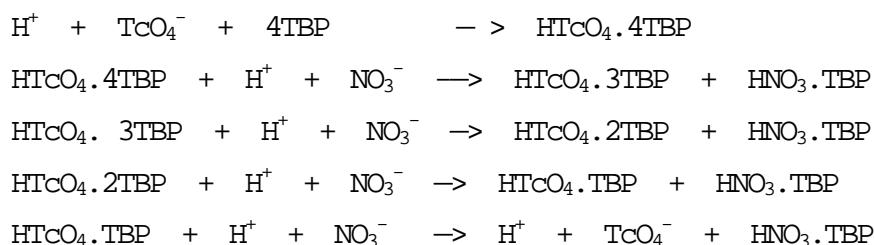
EXTRACTION SYSTEMS OF THE NUCLEAR FUEL CYCLE

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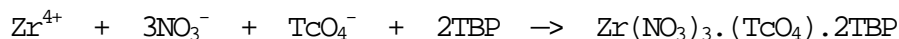
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The objectives of the present study are to analyze the distribution behavior of technetium (Tc) in the tri-n-butylphosphate (TBP) extraction system and to clarify the chemical forms of Tc(VII)-extractant complexes in various extraction systems by means of EXAFS method.

The extraction of Tc(VII) with TBP from nitric acid solution proceed through the following stepwise equilibrium reactions with increasing HNO_3 concentration.



In the presence of metallic ions, i.e., U(VI), Pu(IV) and Zr(IV), the extraction of Tc(VII) is enhanced by the coextraction mechanism as,



Firstly the distribution ratio of Tc(VII), D_{Tc7} , was measured in 30vol% TBP-n-dodecane- HNO_3 extraction system at 25 °C as functions of the aqueous concentrations of HNO_3 , U(VI) and Zr(IV), and the data obtained were added to the Purex distribution database: DISTEXFP and the numerical equations to calculate D_{Tc7} were established by using DISTEXFP, which contains about 500 points of D_{Tc7} values including our own data. Due to the fact that Tc(VII) is extracted as HTcO_4 and coextracted as TcO_4^- with other metals by replacing NO_3^- of the TBP-metal complexes, D_{Tc7} is expressed as the sum of extraction of Tc(VII) by all mechanisms like Kolarik's model[1]. In the present study, it was modified and the following equation was adopted,

$$D_{\text{Tc7}} = D_{\text{Tc7}}^{\circ} + D_{\text{Tc7}}^{\text{U}} + D_{\text{Tc7}}^{\text{Pu}} + D_{\text{Tc7}}^{\text{Zr}},$$

where

$$D_{\text{Tc7}}^{\circ} = P_1 C_{\text{N}}^{\text{P2}} / (1 + C_{\text{N}}^{\text{P3}} + P_4 C_{\text{Zr4}})$$

$$D_{\text{Tc7}}^{\text{U}} = P_5 C'_{\text{U6}} (1 + P_6 C_{\text{N}}^{\text{P7}})$$

$$D_{\text{Tc7}}^{\text{Pu}} = P_8 C'_{\text{Pu4}} (1 + P_9 C_{\text{N}}^{\text{P10}})$$

$$D_{Tc7}^{Zr} = P_{11} C'_{Zr4} C_N^{P12}$$

where P_1, P_2, \dots, P_{12} are parameters of which value were to be determined by a best fit method, and

$$C_N = C_H + 4(C_{U6} + C_{Pu4} + C_{Zr4} + C_{Tc7}).$$

C_i and C'_i are respectively the aqueous and the organic concentrations of species i .

After having been determined the parameter values, dependencies of D_{Tc7} on C_H for several solute systems were obtained by using the model. D_{Tc7} has a maximum at C_H of 0.6 M, where D_{Tc7} value is less than unity at 25 °C.. The enhancing effect of U(VI) is significant only in the region of low C_H , whereas that of Zr(IV) is appreciable only in a high acidic region where Zr(IV) is extractable. The positive influence of Pu(IV) is prominent not only in low C_H but also in high C_H region.

By comparing D_{Tc7} values between calculated by the model and experimental, it became clear that D_{Tc7} data are still lacking in Tc(VII)-Pu(IV)-HNO₃ system in which a limited reliability was shown by scatter of the data points.

The distribution model developed above was put into a Purex process simulation code; EXTRA-M [2], and the effects of some flow sheet conditions, e.g., flow rate, concentrations of HNO₃ and Zr(IV), on the concentration profile of Tc(VII) were analyzed by setting a reference flowsheet. The undesired catalytic effect of Tc on the redox reactions of Pu and hydrazine at the partitioning cycle[3] suggests that it should be rejected to an aqueous waste stream or recovered prior to the partitioning cycle.

A sufficient flow rate of a high-acid strip, such as 5 M HNO₃, is necessary depending on the Zr(IV) concentration to achieve a complete stripping of Tc into the aqueous waste stream. Under a relatively high concentration of Zr(IV) and the high-acid strip, the concentration profile of Tc(VII) showed an accumulation of Tc(VII) in the process. Then the complete rejection of Tc into the waste stream is to be accomplished by a large flow rate of the aqueous/strip solution or by employing a bypass flow sheet in which the aqueous strip solution containing Tc in high concentration passes by most of the extraction stages and enter the stage near the aqueous outlet.

From a view point of Tc recovery, the accumulation phenomenon should be

taken into account, the maximum concentration of Tc is observed in the aqueous phase of 7th stage. Change of the aqueous concentration of Tc in the 7th stage as a function of operation time was calculated by EXTRA-M. The increase of Tc-concentration is drastic, e.g., more than 100 times of the feed concentration and higher than 100g dm^{-3} after the operation of one day and 4 days, respectively. Consequently, it would be considered to recover Tc effectively from the aqueous phase of 7th~8th stage, where radioactivity of the fission products is very low compared with that in the aqueous waste stream coming out from 1st stage. One proposed method is to set up a loop at the specific stage to recycle the aqueous stream going through a Tc-recovery station (Tc-RS). The extent of Tc-recovery can be flexibly controlled because it depends on the timing; concentration of Tc increasing in the loop, and recycling ratio of the flow introduced by the loop, and of course on separation yield at the Tc-RS. The place to set up the Tc-RS should be apart from the 1st cycle extractor to avoid strong radiation field. The method of Tc recovery is not mentioned in the presentation.

As is well known, Tc(VII) takes the form of TcO_4^- which is very stable anion in acidic solutions. Thereby the chemical form of extracted Tc(VII)-complex is very interesting. We have measured EXAFS of some organic samples of Tc(VII) extracted by TBP, amides etc. The analyzed chemical form of Tc(VII) will be presented.

REFERENCES

1. Z. Kolarik, P. Dressler : Solv. Ext. Ion Exch., 7(4), 625 (1989).
2. S.Tachimori : EXTRA-M ; A Computing Code System for Analysis of the Purex Process with Mixer Settlers for Reprocessing (in Japanese), (1994).
3. J. Garraway : Extraction'84, I. Chem. E. Symp. Ser. No.88, (1984).

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