

Effective extraction performance of a fluorous phosphate for Zr(IV) from HNO₃ solution: comparison with a tri-*n*-butyl phosphate

Y. Ueda^{1,3}, K. Kikuchi^{1,2}, T. Sugita¹, R. Motokawa^{1,3}
1): R. G. for Interfacial Reaction-Field Chemistry, JAEA
2): Ibaraki Univ. 3): R. G. for Hierarchical Structure, JAEA

An efficient separation technology for various radionuclides is important to reduce the amount and toxicity of radioactive waste and to concentrate high radioactivity in small waste volumes. The separation of metal ions such as radionuclides is carried out by a hydrometallurgical process mainly based on a solvent extraction method. Solvent extraction is a separation technique for concentrating and separating a certain target component by using distribution of a solute between two immiscible solutions. The solvent extraction method has been widely adopted to practical process for reprocessing spent nuclear fuel and refining valuable metals. The extraction and separation of Zr(IV) as a fission product from aqueous HNO₃ solutions has been investigated extensively because the presence of Zr species in the tri-*n*-butyl phosphate (TBP)-based reprocessing of spent nuclear fuel is problematic [1]. Zr species are likely to form a liquid–liquid (water, oil) interfacial crud or third phase during Zr extraction procedure by TBP from HNO₃ aqueous solution (Figure 1). Formation of third phase is an undesirable process in the reprocessing of spent fuel, as it could potentially cause safety and criticality concerns due to the high metal concentrations. We have recently reported that a Zr-loaded organic phase from liquid–liquid extraction with TBP shows hierarchical aggregation behaviors of Zr(NO₃)₄(TBP)₂ coordination complexes, which self-assemble into primary clusters that coalesce further to form superclusters [2]. This supercluster formation portends the formation of third phase and interfacial crud. However, there are still few proposals for development of the extraction system with a new extractant that does not suffer from these problems.

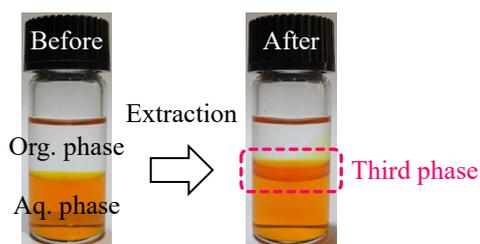


Fig. 1 Snapshot of the third phase formation.

In this contribution, we developed a fluoroalkylated phosphate (TFP) for Zr(IV) extraction to increase the extraction performance and prevent third-phase formation (Figure 2) [3]. Fluorous solvents such as perfluorinated alkanes have unique chemical properties, including low toxicity, non-flammability, and immiscibility with both water and organic solutions. The high hydrophobicity of a fluorous solvent reduces the formation of a third phase and interfacial crud.

The dependences of the Zr(IV) extraction from HNO₃ solution by 0.05 M TFP and 0.5 M TBP on HNO₃ concentration were determined to compare the fluorous and conventional organic extraction systems. Figure 3 shows the effect of the initial HNO₃ concentration in the aqueous phase on the distribution ratio of Zr(IV) ($= [\text{Zr(IV)}]_{\text{ext,eq}} / [\text{Zr(IV)}]_{\text{aq,eq}}$). From

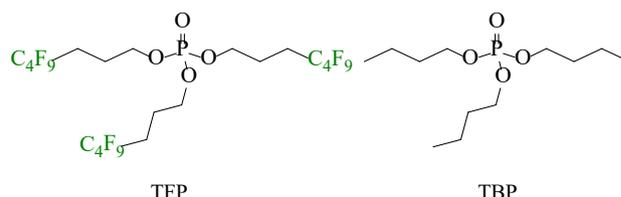


Fig. 2 Chemical structures of the fluorous phosphate (left) and the conventional organic phosphate (right).

this result, 0.05 M TFP had a much higher Zr(IV) extraction performance than 0.5 M TBP despite the TFP concentration in the fluorous phase being one-tenth of that of TBP. Moreover, no third phase formed even in the high concentration-TFP system. To verify the reason for the superior Zr(IV) extraction performance of TFP compared with TBP, the compositions of each phase before and after water, HNO₃, and Zr(IV) extraction were determined. The concentrations of water and HNO₃ molecules in the fluorous phase become low during the Zr(IV) extraction, indicating that water and HNO₃ molecules do not preferentially interact with TFP in contrast to TBP. We believe that the superior performance of TFP makes it suitable as an alternative extractant to TBP in the Zr(IV) extraction system and to other conventional organic extraction systems.

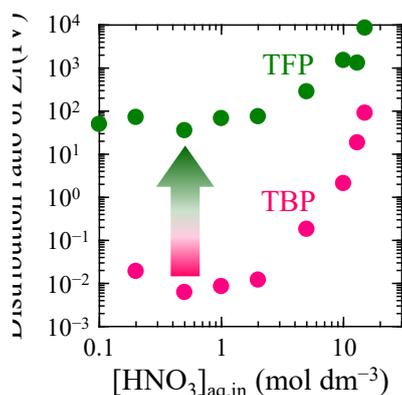


Fig. 3 Effect of HNO₃ concentration on the distribution ratio of Zr(IV) by TFP and TBP. [TFP] = 0.05 M in perfluorohexane, [TBP] = 0.5 M in *n*-octane, [Zr(IV)] = 0.01 M, [HNO₃] = 0.1–15.6 M.

References

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- [3] Y. Ueda *et al.*, *Solvent Extr. Ion Exch.* **37**, 347 (2019).