The Comparison of Selective Zirconium Removal Between TBP Extraction and POM Complexation

Kyungwon Suh*, Jaeseok Lee, and Jong-Yun Kim
Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon, Republic of Korea
*kyungwon0707@kaeri.re.kr

1. Introduction

Zirconium is one of the significant elements in nuclear materials because of its excellent corrosion resistance, sufficient mechanical properties and low neutron absorption coefficient. For a nuclear application, boron and cadmium in zirconium and its alloy should be present less than 0.5 ppm [1] because of their high neutron absorption cross-section. So it is important to quantify the amount of boron and cadmium in zirconium and its alloys.

ICP-OES (Induced Couple Plasma-Optical Emission Spectroscopy) is routinely used to quantify the amount of metal. However, zirconium is a line rich element, which makes difficult to determine trace elements like boron and cadmium in zirconium and its alloys due to the interference between trace element and zirconium in solution. [2] Therefore, boron and cadmium should be selectively separated from zirconium containing sample solution.

Among several conventional methods for removal of Zr, TBP extraction is a well-established method for zirconium extraction because zirconium has a higher distribution coefficient in nitric acid medium than that of boron and cadmium.

POM (polyoxometalate) is pure inorganic compound which is composed of transition metal like W, Mo, Nb, and Ta and heteroatom such as B, P, and Se. There are two categories of POM: plenary POM and lacunary POM. A plenary POM has no defective sites, while a lacunary POM has defective sites by losing metal-oxide from a plenary POM through the modification of synthetic condition. These lacunary POMs could be used as inorganic ligands, so zirconium could be selective removed from the sample solution containing boron and cadmium.

Herein, we present that the complexation with POM shows a better method for zirconium separation by comparison between TBP extraction and POM complexation.

2. Experimental Section

2.1 General Information

All reagents were used without further purification and purchased from commercial source as follows: TBP (Sigma-Aldrich), boron and cadmium (AccuStandards), $ZrOCl_2 \cdot 8H_2O$ (SHOWA Chemical Co.), $H_3PW_{12}O_{40}$ (Kanto chemical Co.). The amount of each metal was determined using Thermo iCAP 7400 coupled with Teledyne Cetac ASX-560.

2.2 TBP extraction

For TBP extraction in 1:1 (V/V) HNO_3, two kinds of sample solutions were prepared: one contained zirconium only, the other included zirconium, boron, and cadmium. The next experiment procedure was as follows: Dry the sample solution by evaporation. Dissolve the dried sample using 1:1 HNO_3. Mix TBP and HNO_3 by 1:1 volumetric ratio. Separate the HNO_3 from the mixture using a separation funnel.

2.3 POM complexation

As mentioned earlier, a lacunary POM could be ligands for zirconium complexation. So, a lacunary POM was prepared by adding sodium carbonate to dissolved $H_3PW_{12}O_{40}$ in deionized water. As with TBP extraction, two kinds of sample solutions were prepared. And then, zirconium solution made from $ZrOCl_2 \cdot 8H_2O$ was added to each sample solution. To determine the amount of each metal in solution, the suspensions were centrifuged.

3. Results

3.1 Single component case

In TBP extraction, the recovery of Zr in nitric acid was about 7%, meaning most Zr was transferred to TBP. Although the recovery of Zr in POM complexation was dependent on the amount of $H_3PW_{12}O_{40}$, 400 mg $H_3PW_{12}O_{40}$ gave the lowest recovery of Zr in POM complexation, which value(~9%) was similar to that of TBP extraction.

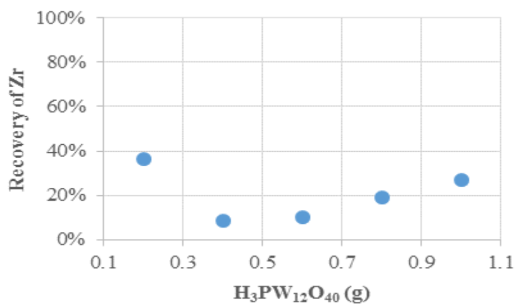

Fig. 1. Recovery of Zr vs the amount of $H_3PW_{12}O_{40}$.

3.2 Ternary component case

In the case of ternary component Zr-B-Cd, the recovery of each metal was summarized in Table 1. POM complexation gave better selective separation of Zr than TBP extraction, although the recovery of each metal was dependent on the volume of sodium carbonate in POM complexation.

Table 1. The recovery of each metal in Zr-B-Cd

Na_2CO_3 (1 M, mL)	Recovery		
	Zr	B	Cd
0.0	0.08	0.96 ± 0.02	1.04 ± 0.01
0.5	0.02	0.97 ± 0.01	1.00 ± 0.01
1.0	0.18 ± 0.01	0.88 ± 0.01	0.46 ± 0.05
2.0	0.84 ± 0.07	0.73 ± 0.04	0.35 ± 0.09
TBP	0.13 ± 0.01	0.83 ± 0.05	0.81 ± 0.04

4. Conclusions

We present that the complexation between POM and oxophilic Zr(IV) provides the better removal than conventional method through the comparison of Zr removal between TBP extraction and Zr-POM complexes.

REFERENCES

[1] ASTM B349, “Standard specification for zirconium sponge and other forms of virgin metal for nuclear application”; ASTM B350, “Standard specification for zirconium and zirconium alloy ingots for nuclear application”; ASTM B352, “Standard specification for zirconium and zirconium alloy sheet, strip, and plate for nuclear application”; ASTM B353, “Standard specification for wroght zirconium and zirconium alloy seamless and welded tubes for nuclear service”.

[2] R. M. Li, Z. S. Li, Y. F. Xin, Appl. Sci. Technol. 2001, 9, 52; Michiko Banno, Eiichi Tamiya, Yuzuru Takamura, Anal. Chim. Acta. 2009 634 153.