Chemical Separation of Fission Products in Uranium Metal Ingots

from Electrolytic Reduction Process

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1. Introduction

Chemical characterization of various process materials is required for the optimization of the electrolytic reduction process in which uranium dioxide, a matrix of spent PWR fuels, is electrolytically reduced to uranium metal in a medium of $LiCl-Li_2O$ molten at 650 °C [1]. In the uranium metal ingots of interest in this study, residual process materials and corrosion products as well as fission products are involved to some extent, which further adds difficulties to the determination of trace fission products. Besides it, direct inductively coupled plasma atomic emission spectrometric (ICP-AES) analysis of uranium bearing materials such as the uranium metal ingots is not possible because a severe spectral interference is found in the intensely complex atomic emission spectra of uranium. Thus an adequate separation procedure for the fission products should be employed prior to their determinations. In present study ion exchange and extraction chromatographic methods were adopted for selective separation of the fission products from residual process materials, corrosion products and uranium matrix. The sorption behaviour of anion and tri-n-butylphosphate (TBP) extraction chromatographic resins for the metals in acidic solutions simulated for the uranium metal ingot solutions was investigated. Then the validity of the separation procedure for its reliability and applicability was evaluated by measuring recoveries of the metals added .

2. Experimental and Results

2.1 Reagent and Instrumentation

All chemicals were of analytical reagent grade. The mixed metal solutions, which were simulated for the uranium metal ingot solutions, were prepared by combining and diluting the calibration standard solutions for ICP-AES analysis (1,000 µg/mL, Spex) to the appropriate concentrations. Chemical components of a synthetic uranium metal ingot sample are as follows; U: 922.2 mg/g, Fe: 871.0, Cr: 335.2, Ni: 120.8, Mg: 81.6, Li: 88.6 µg/g and Ba, Sr, La, Ce, Nd, Pr, Y, Zr, Mo and Cs: 1~5 µg/g, respectively. Measurements were made in triplicate with ICP-AES (Jobin Yvon, Ultima 2, Franc) and the selected wavelengths of the metals with the precision data are listed in Table 1. Cs was analyzed with flame atomic absorption spectrometer of Perkin Elmer (AA-400).

Table 1. Wavelength and determination reliability at analytical concentration

Element	Wavelength nm	Analytical concentration, mg l^{-1}	RSD %
La	379.478	0.01	3.1
Ce	418.660	0.05	2.0
Nd	430.357	0.02	4.9
Y	371.029	0.01	1.2
Ba	455.403	0.01	1.1
Sr	407.771	0.01	3.3
Zr	343.823	0.05	1.2
Mo	202.030	0.1	1.9
Li	670.784	0.01	2.1
Cr	267.716	0.01	2.0
Ni	221.647	0.05	2.4
Fe	259.940	0.02	2.6

2.2. Dissolution of uranium metal ingot samples

Five grams of a uranium metal ingot sample was refluxed for more than 10 h in 40~50 mL of 8 M HNO_3. The dissolved solution was transferred into a weighed 100 mL volumetric flask and the reflux flask was rinsed with an aliquot of 8 M HNO_3. The washings were transferred to the flak and the combined solution was accurately weighed.

2.3 Separation of minor amounts of Mo, Zr and lanthanides by TBP extraction chromatography

To investigate the separation behaviour of the metals from the mixed metal solution containing 60 mg of uranium in 1 mL of 4 M HNO_3 was passed through TBP/XAD-16 resin column (TBP resin ; 1.5 g) at a flow rate of 0.17 mLmin^{-1}. The effluents were collected fractionally in a 2 mL and the amount of the metals in each fraction was determined by ICP-AES. As shown in Fig. 1, the elution curves showed that Mo, Zr, Fe, Cr and Ni were completely eluted by 30 mL of 4 M HNO_3, while no remarkable leakage of U(VI) was found after elution with 40 mL of 4 M HNO_3. From this result and the previous study on the separation of Sr, Ba, Rh, Eu, Gd, Sm, Y, Nd, Cd and Te from 10 mg of U in the system of 4 M HNO_3 and TBP/XAD-16 resin column (TBP resin ; 300 mg) [2], the fission products, residual

process materials and corrosion products from uranium matrix can be quantitatively recovered in a group.
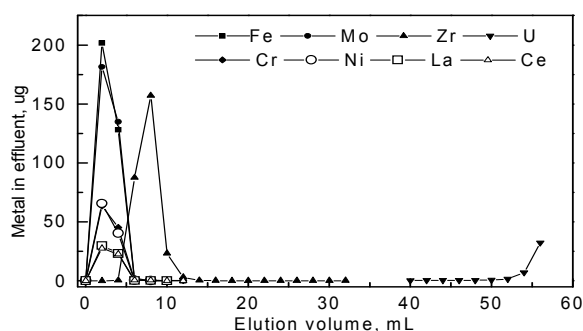

Fig. 1. Separation behaviour of Mo, Zr, La, Ce and U on the TBP/XAD-16 extraction resin column. Column; TBP/XAD-16: 1.5 g, bed volume: 2.6 mL, ID: 9 mm.

2.4 Separation of trace amounts of Cs, Sr, Ba and lanthanides by anion exchange chromatography

Through this metallization process, some fission products such as alkali metals, alkaline earths and several lanthanides, which are fission products with high gamma, high heat decay or high neutron cross section, are transferred from the spent fuel matrix into the LiCl-Li_2O molten salt [3,4]. Therefore, it is thought that Cs, Sr and Ba in the uranium metal ingots are markedly reduced in quantity when contrasted with the spent PWR fuels. An anion exchange chromatography in hydrochloric acid medium was selected as a possible technique for the separation of trace Cs, Sr, Ba and some lanthanides from about 1 g of uranium because of its selectivity for uranium [5] in 10 M HCl medium.

To investigate the separation behaviour of the metals from a uranium metal ingot, a mixed metal solution containing about 1 g of uranium and trace metals in 4 mL of 10 M HCl was passed through an anion exchange resin column at a flow rate of 0.15 mLmin^{-1}. The effluents were collected fractionally and the amount of the metals in each fraction was determined by ICP-AES. As shown in Fig. 2, Sr, Ba, La, Ce, Y, Ni and Cr were completely eluted by 45 mL of 10 M HCl while U, Fe, Mo and Zr was retained on the resins during elution of more than 55 mL.
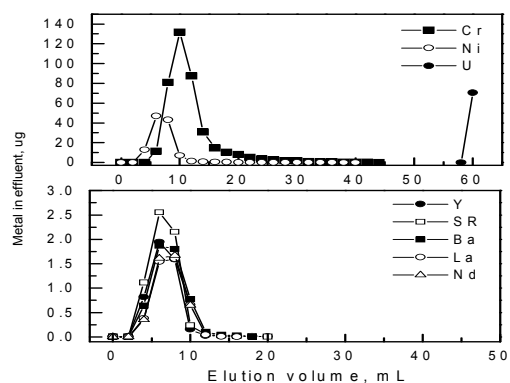

Fig. 2. Separation behaviour of metal ions on the anion exchange resins of 10 M HCl. Column; Bio Rad 1X8, 200-400 mesh, bed volume: 12 mL, ID., 15 mm. Sample (4 mL/10 M HCl); Y, Sr, Ba, La, Nd : 5 ug/each, Cr: 350 ug, Li and Mg: 90 ug/each, U: 1 g.

The recoveries of the metals were also measured and the result listed in Table 2 shows that the trace fission products can be quantitatively separated from corrosion products, residual process materials and uranium matrix by anion exchange chromatography.

Table 2. Recovery of metals from U, Mo, Zr and Fe by anion exchange chromatography

Metal	Recovery, %				RSD, %
	T-1	T-2	T-3	Mean	
Cs	98.1	97.4	96.5	97.3	0.82
Sr	99.8	99.4	98.8	99.3	0.5
Ba	111.5	115.0	115.8	114.1	2.0
La	96.1	100.0	98.8	98.3	2.0
Ce	98.7	99.2	100.4	99.4	0.9
Nd	98.4	98.2	99.6	99.1	0.6
Y	99.6	100.8	100.4	100.3	0.6
Pr	97.9	99.6	99.6	99.0	1.0
Sm	100.4	101.6	100.8	100.9	0.6
Eu	97.4	98.0	97.2	97.5	0.4
Gd	98.4	99.2	100.0	99.2	0.8

3. Conclusion

A chromatographic separation procedure has been developed for the determination of fission products in uranium metal ingot samples produced from electrolytic reduction process of the spent PWR Fuels. Trace Cs, Sr and Ba as well as minor Mo, Zr and lanthanides could be quantitatively recovered with relative standard deviation of less than 2.0% from corrosion products, residual process materials and uranium matrix. It indicates that the separation procedure can be applied to the chemical characterization of the uranium metal ingots with a high reliability.

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