

Separation of Uranium Using Microcapsule of Tri-N-Octylphosphine Oxide

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ABSTRACT

A tri-n-octylphosphine oxide (TOPO) microcapsule has been developed for separating uranium from sulfuric acid solutions that have been used to decontaminate uranium waste. The distribution coefficient of the uranium was about 100 ml/g for a sulfuric acid concentration of 0.1–1.0 mol/L. The separation factor for uranium from iron, a representative metal dissolved in waste solution, was about 1000. A 1 g of TOPO microcapsule can remove uranium from about 50 mL of waste solution. The spent microcapsule easily decomposed when heated to about 300–500°C completely decomposed when heated to 300°C. This TOPO microcapsule is thus well suited for volume reduction of uranium-bearing waste.

INTRODUCTION

Several decontamination methods have been developed for lowering the levels of uranium in waste produced by facilities that handle nuclear materials, such as enrichment and fuel-fabrication facilities [1]. Decontaminated waste with a uranium concentration lower than the clearance level can be treated as non-radioactive waste and thus does not need to be disposed of underground.

Using sulfuric acid is a particularly effective method for decontaminating metallic waste [2]. Uranium and a part of the metal, such as iron, dissolve into the solution. Neutralizing the waste sulfuric acid solution causes dissolved ions to precipitate as a sludge, which is then treated as radioactive waste and disposed of underground.

To reduce the amount of radioactive waste, the uranium should be separated from the waste solution. Selective separation removes the uranium from the sludge, so the sludge is no longer radioactive. We investigated selective and quantitative separation of uranium from sulfuric acid solutions.

Solvent extraction, adsorption, and precipitation are the main processes conventionally used to separate uranium. The simplest separation method is to use an adsorption process. However, the most commonly used adsorption process, adsorption by ion exchange resins, has some disadvantages. Cation exchange resin absorbs not only uranium but also many metallic ions,

such as iron. Anion exchange resin absorbs the uranium from a diluted acid solution, but an increase in the acid concentration reduces the degree of absorbability. The distribution coefficient of the uranium between anion exchange resin and a 1 mol/L of sulfuric acid solution is about 1 mL/g, which is relatively small.

Tri-n-octylphosphine oxide (TOPO) is generally used in solvent extraction processes because of its high affinity with uranium over a wide range of sulfuric acid concentrations, up to 1 mol/L. It is one of the most effective reagents for this process. We prepared a TOPO microcapsule and investigated its effectiveness when used for uranium separation using an adsorption process.

EXPERIMENTAL

We investigated the basic adsorption characteristics using batch experiments and the breakthrough characteristics using column experiments. Table I summarizes the conditions for the two types of experiments.

Because TOPO has high affinity with uranium, the elution of absorbed uranium is problematic. If the spent microcapsule decomposes directly instead of passing through the conventional reuse process using ion exchange resins (including the elution of the uranium), the separation process is simpler. We carried out thermal decomposition experiments (500°C, 30 min.) and a thermogravimetric/differential thermal analysis (TG-DTA) to investigate the capsule's basic thermal decomposition characteristics.

Preparation of TOPO microcapsules

Finely smashed TOPO powder was measured and dispersed into a 50-mL sodium alginate solution (1.5 w.%). The kneaded sol was then dropped into a 500-mL calcium chloride solution (about 1 mol/L). This promptly produced small particles of alginate gel [3], which contained fine TOPO powder. These particles were recovered from the calcium chloride solution and transferred to a sulfuric acid solution and equilibrated with it prior to the adsorption experiments.

Batch adsorption

Batch adsorption experiments were carried out to investigate the basic characteristics of the TOPO microcapsule. A 1-g microcapsule was added to 100 mL of simulated waste solution, which contained 0.1–1 mol/L of sulfuric acid, 100 ppm of uranium, and 100 ppm of iron. The solution was agitated vigorously with a magnetic stirrer and, at regular intervals, a small sample was taken, and the concentrations of uranium and iron were measured by ICP-AES. The distribution coefficient was calculated using the following equation. The metal concentration in the TOPO microcapsule was deduced from the difference in the concentration of metal ions in the solution before and after adsorption.

$$\text{Distribution coefficient (mL/g)} = \frac{\text{Metal concentration in the TOPO microcapsule (mg/g)}}{\text{Metal concentration in the simulated waste solution (mg/mL)}}$$

Column adsorption

Small-column adsorption experiments were carried out to investigate the breakthrough characteristics of the TOPO microcapsule. A 4-g microcapsule was placed in a column with an i.d. of 10 mm and a height of 130 mm. The solution (more than 250 mL) simulating a typical decontaminated waste solution was passed through the column at various rates. The solution was analyzed by ICP-AES, and the concentration of uranium was determined.

Table I. Adsorption experiment conditions

Condition		Batch adsorption	Column adsorption
Simulated solution	Sulfuric acid concentration	0.1–1.0 mol/L	0.5 mol/L
	Metal ion concentrations	U(VI): 100 ppm Fe(II): 100 ppm	U(VI): 100 ppm Fe(II): 1500 ppm
	Quantity used	100 mL	> 250 mL
Microcapsule	TOPO content	2–10 w.%	6 w.%
	Average diameter	0.38, 0.86, 2.3 mm	0.86 mm
	Quantity used	1 g	4 g
Adsorption time, Retention time		1–24 hr.	0.6–20 min.
Analysis technique		ICP-AES	ICP-AES

RESULTS AND DISCUSSION

Basic adsorption characteristics (batch experiments)

Figure 1 shows the dependence of the distribution coefficient of uranium on the adsorption time and average microcapsule diameter. The adsorption reaction reached equilibrium in about 3 hours for the microcapsules with an average diameter of 0.38 and 0.86 mm. This indicates the rate-determining step of adsorption is the complex formation reaction of the uranium and TOPO. Thus, the time needed to reach equilibrium is independent of the capsule diameter.

Figure 2 shows the dependence of the distribution coefficient of uranium on the TOPO content in the microcapsule. The coefficient was expected to increase with the content, but the coefficient for 10 w.% was of the same order as that for 6 w.%. This indicates that only a part of the TOPO might form a complex with uranium in case of the microcapsule with TOPO content of 10 w.%.

Given these results, the optimum specifications for the TOPO microcapsule were determined: average diameter of 0.86 mm and TOPO content of 6 w.%.

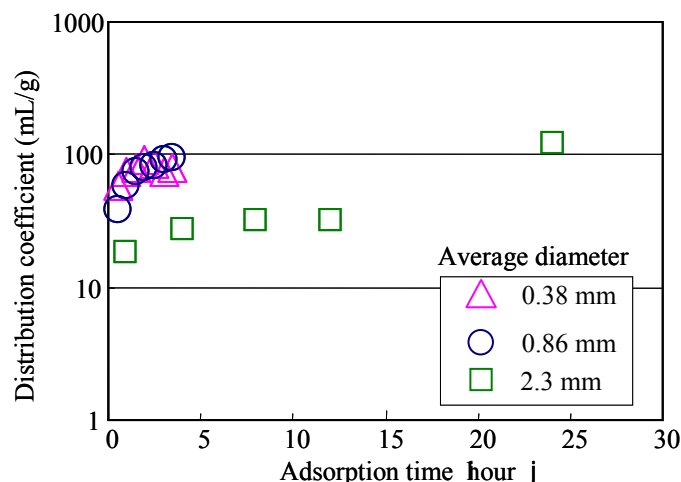


Fig. 1 Dependence of distribution coefficient of uranium on adsorption time and capsule diameter (TOPO content: 6w.%, H₂SO₄: 0.5 mol/L).

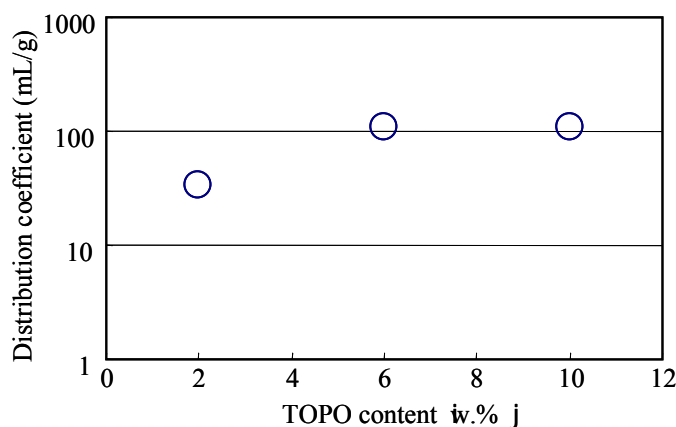


Fig. 2 Dependence of distribution coefficient of uranium on TOPO content (average capsule diameter: 0.86 mm, H₂SO₄: 0.5 mol/L).

Figure 3 shows the dependence of the distribution coefficients of uranium and iron on the sulfuric acid concentration. The coefficients of uranium were about 100 mL/g for the 0.1–1.0 mol/L sulfuric acid concentration, while those of iron were very small (< 0.1 mL/g). The separation factor for uranium from iron exceeded 1000. The TOPO microcapsule thus has high separation performance over a wide range of sulfuric acid concentrations.

The adsorption capacity was determined using iterative batch adsorption experiments using the optimized TOPO microcapsule. The microcapsule was mixed into a solution containing 100 ppm of uranium. After equilibration, all the microcapsule was transferred into a new uranium solution (100 ppm) and equilibration was repeated. This transfer operation was carried out three times. From the total quantity of uranium in the microcapsule and the weight of the microcapsule, the capacity to absorb uranium was determined to be about 6 mg-U/g-capsule, which is comparable to that of conventional ion exchange resins.

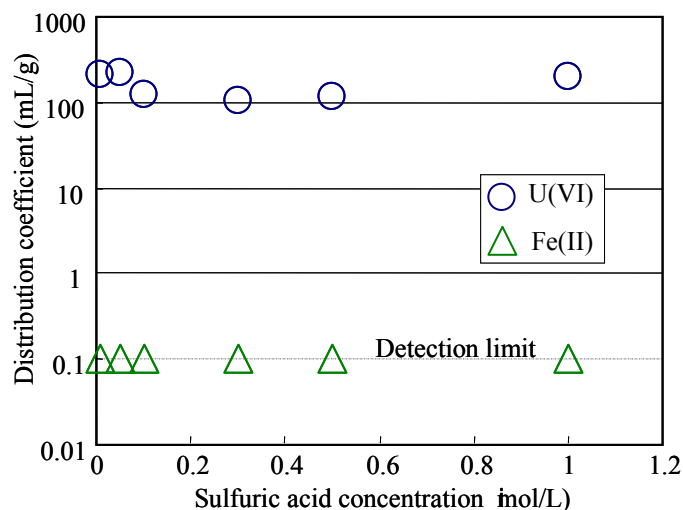


Fig. 3 Dependence of distribution coefficient of uranium on sulfuric acid concentration (TOPO content: 6w.%, average diameter: 0.86 mm).

Breakthrough characteristics (column experiments)

Figure 4 shows the breakthrough curve obtained for various supply rates of simulated waste solution. For effective removal of uranium from the solution, a space velocity (SV) below 3 was needed. Under this condition, the breakthrough of uranium occurred when about 180 mL of waste solution had passed through the column. The average uranium load per microcapsule was about 4.5 mg-U/g-capsule.

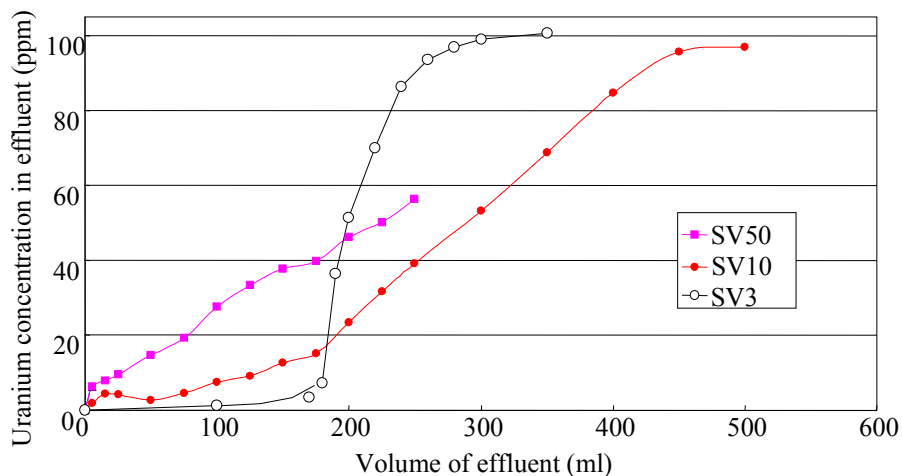


Fig. 4 Breakthrough curve for TOPO microcapsule column (10 mm i.d. × 130 mm H)

Thermal decomposition

As shown in Table II, a TOPO microcapsule decomposed completely at 500°C. The calcium and sodium ions contained in the alginate gel were replaced by protons when the microcapsule was equilibrated using sulfuric acid; therefore, no residue was observed in the thermal decomposition of the TOPO microcapsule. This means that thermal decomposition of a TOPO microcapsule used for uranium separation will yield only uranium, effectively reducing the volume of uranium waste.

Table II. Thermal decomposition of TOPO microcapsule

Microcapsule condition	Weight change after thermal treatment (500°C × 30 min)	Note
As prepared	1 g → 3.5 mg	—
Equilibrated using sulfuric acid	1 g → 0.3 mg	Complete decomposition point: 300°C (TG-DTA) Ca ²⁺ replaced by H ⁺

CONCLUSION

A tri-n-octylphosphine oxide (TOPO) microcapsule was developed for separating uranium from sulfuric acid solutions that have been used to decontaminate uranium waste. The distribution coefficient of the uranium was about 100 ml/g for a sulfuric acid concentration of 0.1–1.0 mol/L. The separation factor for uranium from iron was about 1000. The adsorption capacity was about 6 mg-U/g-capsule. The spent microcapsule was completely decomposed by thermal treatment at 500°C. The use of TOPO microcapsules will thus reduce the volume of uranium-bearing waste.

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