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Applicability of insoluble tannin to treatment of waste containing americium

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Abstract

The applicability of insoluble tannin adsorbent to the treatment of aqueous waste contaminated with americium has been investigated. Insoluble tannin is considered highly applicable because it consists of only carbon, hydrogen and oxygen and so its volume can be easily reduced by incineration. This report describes measurements of the americium distribution coefficient in low concentration nitric acid. The americium distribution coefficients were found to decrease with increasing concentration of nitric acid and sodium nitrate, and with increasing temperature. At 25°C in 2.0×10^{-3} M HNO_3, the distribution coefficient was found to be 2000 ml g^{-1}. The adsorption capacity was determined by column experiments using europium as a simulant of americium, and found to be 7×10^{-3} mmol g^{-1}-dried tannin in 0.01 M HNO_3 at 25°C, which corresponds to approximately 1.7 mg-^{241}Am/g-adsorbent(dried). The prospect of applying the adsorbent to the treatment of aqueous waste contaminated with americium appears promising.

Keywords: Insoluble tannin; Americium adsorption; TRU waste treatment; TRU recovery

1. Introduction

Treatment of wastes containing transuranic (TRU) elements in terms of safety and waste management is an important issue for fuel cycle backend facilities, and americium is one of the major TRU elements in wastes.

Recently, insoluble tannin adsorbent, TANNIX^R, has been developed as a practical adsorbent for the treatment of aqueous waste containing uranium from fuel fabrication plants [1]. The adsorbent is a gelled material containing only carbon, hydrogen and oxygen, and so its volume is easy to reduce by drying and incinerating. In general the residue after incineration will be the oxide of the adsorbed metal.

For uranium, adsorption in the insoluble tannin adsorbent occurs under the conditions of pH 4 to 8 and the residue after the incineration is uranium oxide. Numata et al. [2] have reported adsorption data for plutonium which is also adsorbed under the conditions from pH 4 to 8.

Kamei et al. [3] presented an abstract on adsorption ratios of neptunium, americium and curium from pH 4 to 10; they found high adsorption ratios for neptunium between pH 6 to 8 and low adsorption ratios for americium over pH 5. Marsh et al. [4] described adsorption data for americium in simulated high level liquid waste (pH 0.58, 3.5 and 13.85) in the Hanford tanks. There is, however, few published data on the adsorption of TRU in acidic solution.

In this paper, we determine the suitability of insoluble tannin for americium adsorption by measuring the distribution coefficient and the adsorption capacity. In the case of the adsorption capacity experiments, europium tracer was used instead of americium. The viability of using europium simulant is detailed in Section 3.2.

2. Experimental

2.1. Materials and measurements

The insoluble tannin adsorbent used was TANNIX^R [1] which is a product of Mitsubishi Nuclear Fuel Co. Ltd. It is wattle tannin gelated in aqueous ammonia by mixing aldehyde and has a particle size of 500–1180 μm. Prior to the adsorption experiments, the insoluble tannin adsorbent was washed with 0.1 M (mol/l) HNO_3 solution. The dried weight of the adsorbent was measured at 110°C.

Radioisotopes, ^{241}Am and ^{152}Eu, were used as tracers with their concentrations determined by using a well-type

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high purity germanium detector. The concentration of nitric acid was measured using a conductivity meter.

In order to determine the distribution coefficient and adsorption capacity, it is necessary to measure the density, the water content and packing rate. The water content is measured by comparing the weight of the tannin gel when immersed in water to the dry weight of the gel. Solubility of the gel in nitric acid was examined to know usable concentration of nitric acid as a practical adsorbent.

2.2. Determination of distribution coefficient

The distribution coefficients, K_d, is defined as follows:

$$K_d = [(C_0 - C)/C](V/M)\ (\text{ml g}^{-1}) \tag{1}$$

where C_0 and C are the ^{241}Am concentrations in initial and final solutions, and V and M the solution volume (ml) and dried weight of the adsorbent (g), respectively.

In order to determine the distribution coefficient, equilibration time of americium adsorption on insoluble tannin was determined by batch experiments.

2.3. Determination of adsorption capacity

The americium adsorption capacity of insoluble tannin was determined by column experiments by using europium solution as simulant of americium solution. Prior to the experiments, adsorption behavior of europium was compared with that of americium by batch experiments to validate the use europium as a simulant for americium.

For the column experiment, the insoluble tannin adsorbent was packed with 0.1 M HNO_3 in a glass column. Adsorption capacity was calculated from the following equation:

$$A_c = \frac{[\sum(C_0 - C_i)V_i] - C_0V_c}{M} \tag{2}$$

where A_c is adsorption capacity of the adsorbent, C_0 and C_i the europium concentrations in the initial feed solution and each fraction, V_i the volume of each fraction, V_c the volume of water in the column, and M the dried weight of the adsorbent in the column. 6.0×10^{-4} M of europium solution containing ^{152}Eu tracer in 0.01 M HNO_3 was used as the feed solution. The concentration of nitric acid was the same as that in the concentration in the waste from fuel cycle facilities to obtain a realistic adsorption capacity. The solution was supplied to the column by means of a piston pump and the flow rate was held constant. Fractions of 2.4 ml volume were collected by an automatic fraction collector.

3. Results and discussion

Table 1
Specifications of the insoluble tannin adsorbent (TANNIN®)

Particle size (μm)	500–1180
Content of H_2O (%) (dried in 110°C)	76±1
Density in swelling (g cm^{-3})	1.14±0.03
Packing rate in column (%)	60±5
Limit of applicable nitric acid concentration (M)	<2.0

The water content, density, packing rate and solubility in nitric acid are summarized in Table 1. Since it is dissolved in more than 2 M HNO_3, data on distribution coefficient were obtained for less than 0.5 M HNO_3.

3.1. Distribution coefficient

Fig. 1 shows the distribution ratios (concentration in HNO_3/concentration in adsorbent) of Am(III) in 0.02 M HNO_3 at 25°C as a function of contact time. To obtain the distribution coefficients, the adsorbent was contacted with nitric acid containing americium for three hours which was the time required for equilibration.

Fig. 2 shows a logarithmic plot of Am(III) distribution coefficients at 25°C as a function of nitric acid concentration. It is clear that the distribution coefficients decreased rapidly with increased nitric acid concentration. Americium(III) was strongly adsorbed in low acid concentration, and the distribution coefficient was approximately 2000 ml g^{-1} at 2×10^{-3} M HNO_3. In more than 0.1 M HNO_3, Am(III) was weakly adsorbed on the adsorbent. The reason for this adsorption behavior is currently under investigation. While uranium, neptunium and plutonium are not adsorbed in the low concentration nitric acid, they are adsorbed in pH 6 to 10 [1–3], which is not the case for americium [3]. The difference between the adsorption behavior of americium and that of plutonium, neptunium and uranium may be due to the difference in oxidation state in solution, although further experiments are required in order to determine the adsorption mechanism. From the viewpoint of practical waste treatment, there is a possibility of mutual separation between

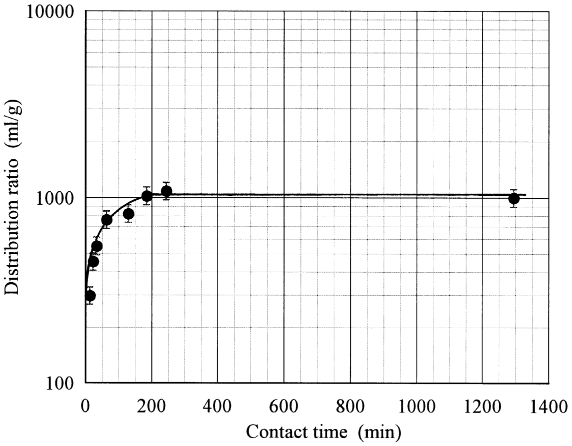

Fig. 1. Contact time dependency of distribution ratio of Am(III) in 0.02 M HNO_3 at 25°C.

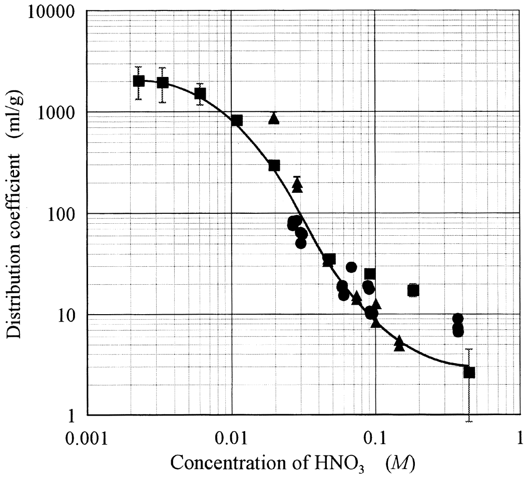

Fig. 2. Acid dependency of distribution coefficient of Am(III) on the insoluble tannin adsorbent at 25°C. ■: 2.0 ml of the adsorbent contacted with 40.0 ml of HNO_3, ●: 2.0 ml of the adsorbent contacted with 8.0 ml of HNO_3, △: 1.0 ml of the adsorbent contacted with 4.0 ml of HNO_3.

americium and other TRU elements including uranium by applying insoluble tannin. Note that curium which has oxidation state 3 is anticipated to behave similarly to americium during practical waste treatment. However, further experiments are clearly necessary to demonstrate the feasibility of waste treatment by insoluble tannin.

Fig. 3 shows a logarithmic plot of Am(III) distribution coefficients in 0.02 M HNO_3 as a function of temperature. The distribution coefficients were found to decrease with increasing temperature. If wastes containing americium have a high temperature due to decay heat, the temperature should be lowered in order to apply the treatment process.

Fig. 4 is a plot of distribution coefficients at 25°C as a function of sodium nitrate concentration in 0.01 and 0.02 M HNO_3. The distribution coefficients also decreased with increasing concentration of sodium nitrate. Liquid wastes from fuel cycle backend facilities often have high nitric acid concentration. To treat the wastes by the adsorbent, neutralization or denitration are required to lower the acid concentration because Am(III) was strongly adsorbed only in low acid concentration as shown in Fig. 2. In this case, it is necessary to lower the acid concentration without increasing concentrations of salts.

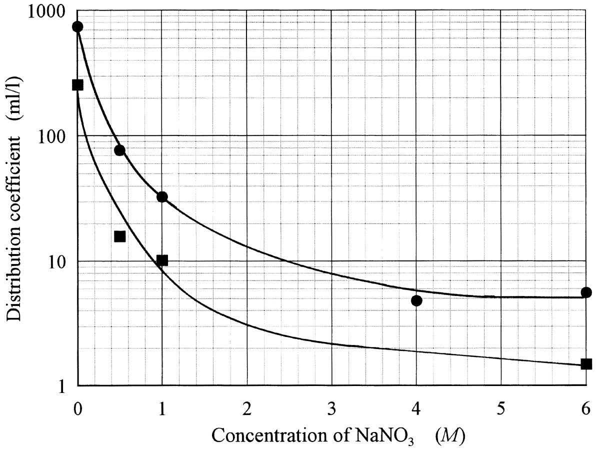

Fig. 4. Concentration of $NaNO_3$ dependency of distribution coefficient of Am(III) at 25°C. ■: 0.02 M HNO_3, ●: 0.01 M HNO_3.

Although it is clear from these results that the distribution coefficients of americium on the insoluble tannin in low concentration nitric acid at room temperature are effective for waste treatment, it is difficult to discuss in detail the adsorption mechanism of americium. In order to explain the adsorption behavior of americium, further experiments to determine the adsorption mechanism are required.

3.2. Adsorption capacity

Fig. 5 shows the result of the batch experiment using nitric acid containing ^{241}Am and ^{152}Eu tracers. Distribu-

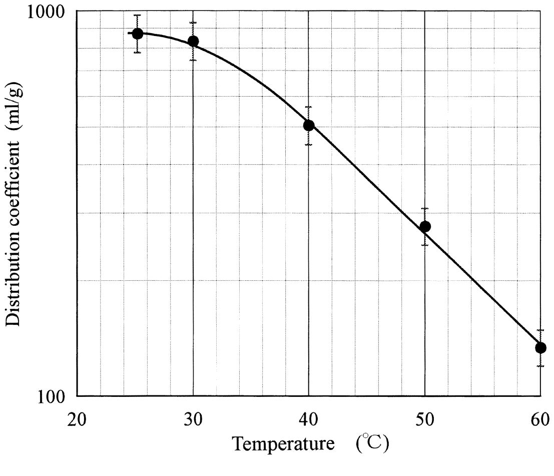

Fig. 3. Temperature dependency of distribution coefficient of Am(III) in 0.02 M HNO_3.

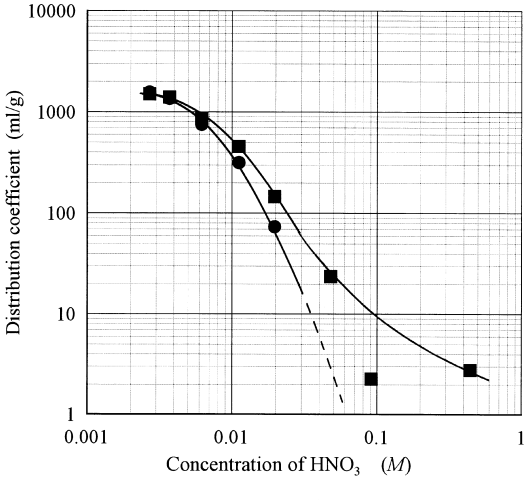

Fig. 5. Comparison of distribution coefficients between Am(III) and Eu(III) at 25°C. ■: Am(III), ●: Eu(III).

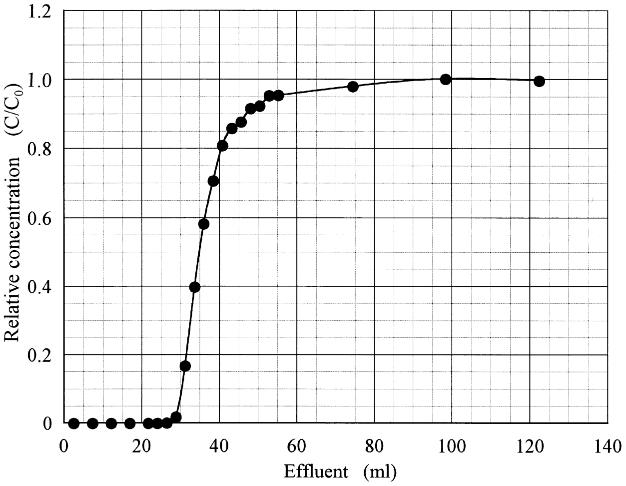

Fig. 6. Breakthrough curve; 6.0×10^{-4} M Eu; 0.01 M HNO_3; 0.076 $ml\cdot cm^{-2}\cdot min^{-1}$.

tion coefficients of europium and americium appear to be very similar at low nitric acid concentration, but significantly different at higher acid concentration (0.01–0.50 M). Given that the column experiment was conducted using europium in 0.01 M HNO_3, the measured adsorption capacity will be a slight underestimate of the value for americium. This is due to the difference in the europium and americium distribution coefficients at 0.01 M HNO_3.

The breakthrough curves for europium column experiments are shown in Fig. 6. The column used was 10 mmϕ by 200 mm long and the feed solution was supplied to the column at 0.06 ml min^{-1} (0.076 $ml\cdot cm^{-2}\cdot min^{-1}$). Before the breakthrough point, europium was not detected and was adsorbed effectively. The adsorption capacity, as given in Eq. (2), was found to be 7×10^{-3}mmol-Eu/g-adsorbent(dried) which corresponds to approximately 1.7 mg-^{241}Am/g-adsorbent (dried).

4. Conclusions and future perspective

The main conclusions that can be drawn from the experimental work described here and future perspective are as follows:

1. Insoluble tannin adsorbent is applicable to waste treatment because of a high distribution coefficient and the adequate adsorption capacity of Am(III) in low nitric acid concentration.
2. Adsorption kinetics of the insoluble tannin adsorbent were found to be slow.
3. Distribution coefficients of Am(III) were found to decrease with increasing temperature and increasing concentration of nitric acid and sodium nitrate. Therefore, the insoluble tannin adsorbent is applicable to treatment of wastes containing americium only in low nitric acid and salt concentrations.
4. In order to explain the adsorption behavior of americium, further experiments to determine the adsorption mechanism are required.
5. To demonstrate the feasibility of mutual separation between americium (III) and other elements (uranium, neptunium and plutonium) by applying insoluble tannin, further experiments are clearly necessary.

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