



Separation of thorium and uranium in nitric acid solution using silica based anion exchange resin



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ABSTRACT

To separate thorium and uranium in nitric acid solution using anion exchange process, a strong base silica-based anion exchange resin (SiPyR-N4) was synthesized. Batch experiments were conducted and the separation factor of thorium and uranium in 9 M nitric acid was about 10. Ion exchange chromatography was applied to separate thorium and uranium in different ratios. Uranium could be eluted by 9 M nitric acid and thorium was eluted by 0.1 M nitric acid. It was proved that thorium and uranium can be separated and recovered successfully by this method.

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1. Introduction

As known, thorium is 3–4 times more abundant than uranium on earth and ^{232}Th can be transferred to ^{233}U by neutron capture and decay [1]. ^{233}U can be used as nuclear fuel in reactors meaning thorium is a potential nuclear fuel. Furthermore, a new reprocessing process for thorium fuel is required and the separation of thorium and uranium is the key point [2]. However, until recently, the radioactivity of the spent fuel of thorium fuel cycles has been considered an intrinsically proliferation-resistant feature due to the formation of the ^{232}U isotope [3,4]. While ^{232}Th is transferred to ^{233}U , a (n, 2n) reaction on ^{233}Pa or ^{233}U will produce ^{232}U , the decay chain of which contains hard gamma emitters [4,5]. In addition, ^{232}U is also formed in UO_2 and MOX fuels in significant quantities and will go along with the depleted uranium during reprocessing [6,7]. The daughter nuclides of ^{232}U , in particular ^{212}Bi and ^{208}Tl , emit strong γ radiation and cause occupational radiological hazard in the working environment [6]. As a result, the concentration of ^{232}U is limited and the time between production of reprocessed uranium fuels and receipt of the fuel at the reactor should not exceed 1.5 years to limit accumulation of ^{232}U [8].

It is reported that the daughter products of ^{228}Th will reach equilibrium within a month and ^{232}U is an alpha emitter with a 72-year half-life [5,7]. Hence the dose rate due to high energy gamma radiations of thorium daughters will depend only on the buildup of ^{228}Th

from ^{232}U [7]. So, if it is possible to separate the few ^{228}Th from large amount of uranium, the radiological hazard of the reprocessed fuels could be reduced effectively in a relatively long period of time for the manufacturing of fresh fuel assemblies and the subsequent handling of these assemblies at nuclear power plants.

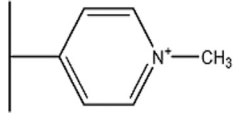
Traditional spent fuel reprocessing process use organic solvent extraction to separate and recover thorium and uranium [9]. For example, THOREX process uses TBP as extractant [10]. Whereas, the liquid–liquid extraction process generates a large amount of the secondary waste and a large scale of extraction equipment is required [11]. Ion exchange technology has been applied to reprocess spent fuel for over 70 years for its simple operation, organic solvent free feature and compacted equipment [12]. For conventional gel-type ion exchangers are of slow adsorption-elution rate, unsatisfactory decontamination factor and poor radiation resistance [12,13]. In recent years, silica-based anion exchange resins have been developed, with fast retention kinetics, good radiation resistance and low pressure loss in a packed column [14,15]. These materials perform well in the recovery of uranium, plutonium and neptunium from spent nuclear fuels [13,16,17]. They also reveal great affinity to some specific fission products such as Pd, Ru and Tc [12,13,18].

Previously, we have studied the adsorption behavior of thorium from nitric acid solutions by the use of silica-based anion exchange resins [19]. In this paper, we report our investigation on separation of thorium and uranium in nitric acid solutions using silica-based anion exchange resin and chromatographic method. We also discuss the potential applications in removing little amount of thorium from uranium.

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Table 1
Characterization of the SiPyR-N4 anion exchange resin.

Functional group	
Carrier bead	Porous SiO ₂
Bead diameter (μm)	37 ~ 74
Mean pore size of beads (nm)	600
Pore fraction in beads	0.69
Resin content (wt%)	24.6%
Total capacity (meq/g-resin)	4.2
Quaternary capacity (meq/g-resin)	4.2

2. Experimental

2.1. Reagents and materials

The strong base silica-based anion exchange resin, called SiPyR-N4, with macro-reticular resin embedded in porous silica beads was used in this study. Its structure and properties are listed in Table 1. The resin was synthesized according to the methods reported earlier [19]. The diameter of the silica particles is 37–74 μm and the mean pore size of the beads is 600 nm, which provide a rapid ion-exchange rate compared to conventional resins. Fig. 1 shows the surface structure of the resin under Scanning Electron Microscope (SEM). Commercial anion exchange resin (IR-900) was purchased from Sinopharm Chemical Reagent Co. Ltd.

In the experiments, the solutions containing thorium and uranium were prepared by dissolving their nitrates in nitric acid. The nitrates, such as Th(NO₃)₄ and UO₂(NO₃)₂ were purchased from Aladdin Chemistry Co. Ltd and the nitric acid was provided by Sinopharm Chemical Reagent Co. Ltd. All these materials were analytical grade reagents.

Deionized water was produced by a laboratory water purification system (DW-200) with a resistance of 18 MΩ.

2.2. Batch experiments

In order to investigate the adsorption behavior of thorium and uranium, batch experiments were conducted in a thermostatic air shaker. The batch experiments studied the influence of a wide range of acidity. The nitric acid ranged in concentration from 0.1 M to 9 M. The initial concentration of thorium and uranium was 10 mM.

Throughout all the batch experiments, the temperature of the air shaker was set at 298 K and the phase ratio was 0.1 g of resin to 5 ml of solution. The mixture of the resin and solution was shaken for a given time at a frequency of 120 r/min. After a phase separation using membrane filters with mean pore size of 0.45 μm, the concentration of metal ions before and after the adsorption in aqueous phase were determined with ICP-AES instrument (Shimadzu ICP-7510).

The distribution coefficient (K_d , cm³/g) and separation factor (SF) were calculated as follows:

$$K_d = (C_o - C_e) \cdot V / C_e \cdot m \quad (1)$$

$$SF = K_{d,Th} / K_{d,U} \quad (2)$$

where C_o and C_e denote the initial and equilibrium concentration of metal ions in aqueous phase (mg/L); m represents the mass of the resin (g); V is the volume of the aqueous phase (ml).

Prior to contact with aqueous phase, the resin was conditioned with HNO₃ solution in concentrations ranging from 0.1 to 9 M according to the respective acidity of batch experiments.

2.3. Column experiments

Column experiments were carried out using Pyrex-glass columns. Fig. 2 shows the schematic diagram of the column apparatus. The temperature of the column and the solution were kept at 298 K using a low temperature circulator and cold trap instrument. SiPyR-N4 anion exchange resin was charged into the column in slurry state. Prior to the column experiments, the resin was conditioned by passing 9 M HNO₃ solution through the column. Feed solutions were pumped to the column at a constant flow rate. Then the eluent solutions containing 9 M HNO₃, 0.1 M HNO₃ and distilled water were supplied to the column successively. The effluents from the column were recovered by auto-fractional collector with the volume of 2.5 ml or 5 ml and the metal concentrations in each fraction were determined by ICP-AES spectroscopy.

2.3.1. Breakthrough and elution curves

To study the dynamic adsorption behavior of thorium and uranium, the adsorption and elution of thorium and uranium from monometallic solution were performed by SiPyR-N4 packed column. The adsorption of thorium using IRA-900 packed column was also carried out to compare uptake kinetics plot of the present commercial resins and the silica based anion exchange resin. The experiment aimed at studying the dynamic adsorption and elution behavior and obtaining the breakthrough and elution curves. Too large a size of the column would result in unnecessary cost of the resin, material and time. So, a small column with an inner diameter of 8 mm and a length of 50 mm was used. The concentration of HNO₃ in the feed solution was 9 M and the initial concentration of metal ions was 10 mM. The flow rate was controlled to 0.5 ml/min and the space velocity (SV) was 12.

2.3.2. Separation of thorium and uranium

To examine the separation behavior of thorium from uranium, a column experiment was carried out for 9 M HNO₃ solution containing 10 mM Th(IV) and 10 mM U(VI).

Longer column would be favorable to separation of thorium and uranium. However, longer column and faster flow rate would cause higher column pressure which was negative. Overall consideration, the column with an inner diameter of 10 mm and a length of 500 mm was used. The flow rate was set as 0.7 ml/min.

2.3.3. Separation of little amount of thorium from uranium

As mentioned above, if it is possible to separate the few ²²⁸Th from large amount of uranium, the radiological hazard of the reprocessed fuels could be reduced effectively in a relatively long period of time. However the amount of ²²⁸Th is quite small compared to uranium. So, another column separation experiment was conducted for 9 M HNO₃ solution containing 0.1 mM Th(IV) and 10 mM U(VI).

Considering the fine separation result, a column with a length of 100 mm could have already met the requirement. The column with an inner diameter of 10 mm and a length of 100 mm was used. Since shorter column had been used, while assuring a safe column pressure, the flow rate could be faster to improve the efficiency and it was set as 2 ml/min.

3. Results and discussion

3.1. Batch experiments

As shown in Fig. 3, with the increase of the acidity, the distinction of distribution coefficient between thorium and uranium becomes more and more significant. The same as results obtained from earlier investigation, the resin reaches the best adsorption of thorium in 9 M HNO₃ solution [19]. However, the adsorption

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