



# The effectiveness of ion exchange resins in separating uranium and thorium from rare earth elements in acidic aqueous sulfate media. Part 1. Anionic and cationic resins



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## ABSTRACT

Conventional ion exchange resins with different functional groups were evaluated for their potential application in separating uranium U(VI) and thorium Th(IV) from rare earth elements RE(III). The resins studied comprised strong- and weak-base anion exchange resins, and strong- and weak-acid cation exchange resins. The selectivity of these resins to adsorb U(VI) and Th(IV) in the presence of selected RE(III) was examined in sulfuric acid media of varying concentrations. It was evident that the adsorption performance of the resins was acid concentration-dependent. Most candidate resins had potentially feasible selective adsorption at or below 0.1 mol/L H<sub>2</sub>SO<sub>4</sub> (pH ≥ 0.7). Within the group of anion exchange resins, both the strong- and weak-base resins exhibited a similar selectivity with U(VI) adsorbed in preference to RE(III). The difference between them was their adsorption of Th(IV). The weak-base resin with primary amine functional group demonstrated superior separation of Th(IV) from RE(III). For this resin, 78% of U(VI) and 68% of Th(IV) were adsorbed while RE(III) co-adsorption was < 5% at 0.0005 mol/L H<sub>2</sub>SO<sub>4</sub> (pH 3). In the case of the strong-acid cation exchange resins, Th(IV) and RE(III) were adsorbed in preference to U(VI), *i.e.*, RE(III) > Th(IV) > U(VI). The weak-acid cation exchange resins, on the other hand, displayed limited adsorption of all elements.

## 1. Introduction

The separation of uranium and thorium from rare earths is one of the most important tasks in the hydrometallurgical production of these elements. This is because U(VI) and Th(IV) invariably coexist with the two most abundant rare earth minerals, *i.e.* monazite and bastnaesite. The method of removing U(VI) and Th(IV) in conventional hydrometallurgical processing of rare earths has problems pertaining to the disposal of solid and/or liquid waste, in addition to substantial loss of rare earths to waste (Gui et al., 2014; Zhu et al., 2015). For that reason, in the past decade there has been a resurgence of investigations into U(VI) and Th(IV) separation involving the use of different methods (Cheng et al., 2011; Deng et al., 2013; Fan et al., 2011; Gao et al., 2012; Nasab et al., 2011; Song et al., 2009; Zhang et al., 2012; Zhong and Wu, 2012; Zuo et al., 2008).

A literature review into the separation of U(VI) and Th(IV) from rare earths shows that extensive work has been conducted to separate U(VI) and Th(IV) using liquid or solvent extractants. This is considered a convenient and efficient method to purify the rare earths because of its simplicity and ease of operation (He et al., 2013). However, one of its

drawbacks is the need to dispose of organic waste generated in the recovery process (Gui et al., 2014). In contrast, ion exchange (IX) is known to produce less liquid waste, whether aqueous or organic in nature, and hence there are fewer waste disposal issues. IX also does not have issues of phase separation, third phase formation, or solvent loss, and is particularly advantageous for adsorption of metals present in low concentrations, *e.g.*, from bastnaesite ores with a low content of U(VI) and Th(IV). These merits of IX therefore justify research into the technology to further develop its potential for separation of U(VI) and Th(IV) from rare earths.

The objective of this study was to evaluate the adsorption affinity of various IX resins with different physicochemical properties for U(VI) and Th(IV) in sulfuric acid media containing selected light, medium, and heavy RE(III), *i.e.*, lanthanum (III), cerium (III), gadolinium (III) and ytterbium (III). Comparative adsorption data for the resins were presented to demonstrate the ones that are most selective towards U(VI) and Th(IV) over RE(III). Rather than focusing on a single element system, the impact that the presence of RE(III) have on the adsorption ability of the resins to selectively adsorb U(VI) and Th(IV) was investigated. The scope of this investigation was limited to readily

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available commercial IX resins rather than chemically modified IX resins that might not be economically viable. The candidate resins comprised anion and cation exchange resins, and chelating resins including two solvent-impregnated resins containing extractants commonly used in SX processes for rare earths separation, namely, di-(2-ethylhexyl) phosphoric acid (D2EHPA) and organophosphinic acid.

The first part of this study is reported in this present paper, and focuses on conventional anion and cation exchange resins. It is interesting that the majority of IX studies on the extraction of U(VI), Th(IV) and RE(III) only involve strong-acid cation and strong-base anion exchange resins, with few studies on weak-acid cation exchange resins (Korkisch, 1989a,b). A thorough search of the literature yielded only one study involving weak-base anion exchange resin, namely Amberlite CG-4B which is no longer manufactured (Kuroda et al., 1972). Arguably, Amberlite CG-4B is better classified as a polyamine chelating resin (Hubicki and Wójcik, 2006). This paper presents, for the first time, the application of a weak-base anion exchange resin with primary amine functional group to the separation of U(VI) and Th(IV) from RE(III). The results from this paper will also be compared with the IX performance of chelating resins reported elsewhere (Ang et al., 2017).

## 2. Experimental materials and methods

### 2.1. Candidate resins

The ion exchange resins used in this study were selected from commercially-available resins supplied by resin manufacturing companies. Their physicochemical properties, as reported in their product data sheets, are tabulated in Table 1.

Schematics of the functional groups belonging to the various ion exchange resins used in this study are shown in Table 2.

Before testing, pre-treatment was applied to ensure that all resins were converted to sodium form for cation exchange resins and sulfate form for anion exchange resins. The pre-treatment method was adapted from the work reported by Zagorodni (2007). Resins with a wide bead size distribution were manually dry-sieved to the size range of 0.50–0.71 mm. Monodispersed resins within the size range of 0.50–0.71 mm and resins with bead size > 0.71 mm (i.e., AnIXR 6 and AnIXR 7) were not dry-sieved. All conditioned resins were stored in sealed glass bottles.

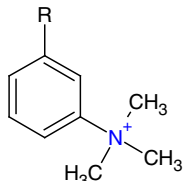
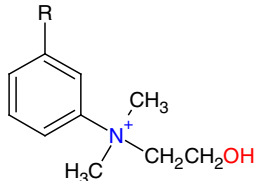
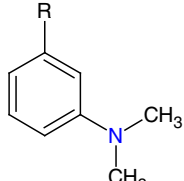
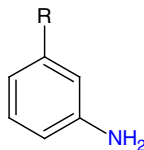
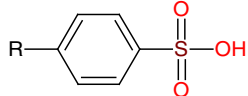
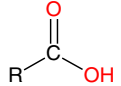
### 2.2. Synthetic solutions

Concentrated stock solution was prepared by dissolving appropriate amounts of  $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{La}_2(\text{SO}_4)_3$ ,  $\text{Ce}_2(\text{SO}_4)_3$ ,  $\text{Gd}_2(\text{SO}_4)_3$  and  $\text{Yb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  in distilled water. The synthetic

**Table 1**  
Physicochemical properties of candidate resins.

Resin ID	Functional group	Structure	Total capacity min. eq/L
AnIXR 1	Primary amine	Macroporous	2.2
AnIXR 2	92%-tertiary, 8%-quaternary amine	Macroporous	1.6
AnIXR 3	80%-tertiary, 20%-quaternary amine	Macroporous	1.6
AnIXR 4	Quaternary amine, type I	Gel	1.4
AnIXR 5	Quaternary amine, type I	Gel	1.6
AnIXR 6	Quaternary amine, type I	Macroporous	1.15
AnIXR 7	Quaternary amine, type II	Gel	1.2
AnIXR 8	Quaternary amine, type II	Macroporous	1.1
AnIXR 9	Quaternary amine, type II	Macroporous	1.0
CatIXR 1	Sulfonic	Gel	2.0
CatIXR 2	Sulfonic	Macroporous	1.8
CatIXR 3	Carboxylic	Porous	4.5
CatIXR 4	Carboxylic	Macroporous	4.3

**Table 2**  
Schematics of functional groups of various ion exchange resins.

Types of resin	Functional groups	Chemical structures
Strong-base anion exchange resin	Quaternary amine, type I	
	Quaternary amine, type II	
Weak-base anion exchange resin	Tertiary amine	
	Primary amine	
Strong-acid cation exchange resin	Sulfonic acid	
Weak-acid cation exchange resin	Carboxylic acid	

solution was prepared fresh from the stock solution before each test with a concentration of 2 mmol/L for each metal ion.  $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$  (99.9%) and  $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  (99.9%) were procured from International Bio-Analytical Industries, Inc. (Florida, USA).  $\text{La}_2(\text{SO}_4)_3$  (99.99%),  $\text{Ce}_2(\text{SO}_4)_3$  (99.99%),  $\text{Gd}_2(\text{SO}_4)_3$  (99.99%) and  $\text{Yb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  (99.9%) were obtained locally from Sigma-Aldrich. All other chemicals used were of analytical grade.

### 2.3. Adsorption procedure

The adsorption experiments were carried out in a batch setup to examine the adsorption of U(VI), Th(IV) and RE(III) in  $\text{H}_2\text{SO}_4$  media by different ion exchange resins. The following steps were repeated for each candidate resin.

To investigate the effect of acidity, 100 mL of synthetic solution with varying concentrations of  $\text{H}_2\text{SO}_4$  (0.0005–2.0 mol/L) was added to a conical flask containing 1 g resin (dry, free-rolling). The mixture was equilibrated in a Thermoline Scientific BT-350R refrigerated shaking water bath machine at constant temperature of 20 °C for 24 h. The solution was sampled 2 h after the start of equilibration, and a second sample was extracted at the end of the 24-h test. The concentrations of metal ions in the sample were determined by inductively coupled plasma mass spectrometry (ICP-MS iCAP Qc, Thermo Fisher Scientific, Germany).

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