Minerals Engineering 123 (2018) 8–15

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

The effectiveness of ion exchange resins in separating uranium and thorium from rare earth elements in acidic aqueous sulfate media. Part 2. Chelating resins

Kwang Loon Ang, Dan Li, Aleksandar N. Nikoloski*

Chemical and Metallurgical Engineering and Chemistry, School of Engineering and Information Technology, Murdoch University, Australia

ARTICLE INFO

Keywords:
Thorium
Uranium
Rare earth
Chelating
Ion exchange
Separation
Sulfuric acid

ABSTRACT

Chelating 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 candidate resins included a bis-picolylamine resin, aminophosphonic resins, iminodiacetic resins, and solvent-impregnated resins. The adsorption selectivity of these resins towards 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_2SO_4 (or pH ≥ 1). Depending on their functional groups, the chelating resins displayed varying selectivity towards U(VI), Th(IV) and RE(III). It was found that the iminodiacetic resins exhibited the highest affinity for U(VI) and Th(IV) over RE(III). At 0.005 mol/L H_2SO_4 (or pH 2), the adsorptions of U(VI) and Th(IV) were approximately 90% while adsorption of RE(III) was less than 20%. This can be explained by considering the coordination chemistry of the resins whereby molecular ligands with N- and O-donor atoms were demonstrated to adsorb both U(VI) and Th(IV) strongly. Comparing the different O-donor groups (*i.e.*, sulfonyl, phosphoryl and carboxyl), the carboxyl group from the iminodiacetic resin gave the best separation of U(VI) and Th(IV) from RE (III). The performance of the solvent-impregnated resins has indicated the possibility of exploiting steric effects to obtain a highly selective chelating resin for U(VI) and Th(IV) over RE(III). In addition, the potential application of these resins in an integrated process for sequential 2-stage separation of U(VI) and Th(IV) from RE(III) in sulfuric acid media is also presented.

1. Introduction

It is significant to note that about 95% of the global rare earth metals market is presently supplied by China (Gosen et al., 2014). Although its rare earth deposits are reported to contain very low levels of uranium, they still contain substantial amount of thorium (Zhu et al., 2015). Uranium (VI) and thorium (IV) are invariably associated with the rare earth elements, RE(III), in many ores, particularly of the two most abundant rare earth minerals, *i.e.* monazite and bastnaesite. The effective separation of U(VI) and Th(IV) from RE(III) is thus an important step change in the commercial production of these elements.

Among the different separation techniques, ion exchange (IX) has benefits which warrant further development of its application in removing trace U(VI) and Th(IV) impurities from liquors in the hydrometallurgical processing of rare earths. For instance, IX has advantages over the traditional precipitation method in issues of low recovery of rare earths, disposal of the precipitate, and pollution arising from the storage of radioactive precipitate (Wang et al., 2013). IX also does not have the complications commonly encountered with solvent extraction technique such as issues with liquid waste disposal, phase separation, third phase formation, and solvent loss. Therefore, the effectiveness of various IX resins for the separation of U(VI) and Th(IV) from RE(III) was investigated with the aim not only to identify potential resins, but also to understand their adsorption mechanisms to enable one to deduce with confidence whether a certain resin is feasible for the said application.

The first part of this study reported on the application of conventional anion and cation exchange resins (Ang et al., 2017). In the second part of this study, the use of chelating resins was considered. Chelating resins were developed to overcome the limited selectivity found with conventional anion and cation exchange resins. They exhibit the ability to selectively separate particular elements of interest from others. This is mainly attributed to their surface chemistry which allows modification to contain certain functional groups that are selective for particular

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* Corresponding author at: School of Engineering and Information Technology, Murdoch University, 6150 Western Australia, Australia.
E-mail address: A.Nikoloski@murdoch.edu.au (A.N. Nikoloski).

https://doi.org/10.1016/j.mineng.2018.04.017
Received 12 December 2017; Received in revised form 13 March 2018; Accepted 16 April 2018

elements. The application of chelating resins is common in the separation and purification of individual rare earth elements (Kołodyńska and Hubicki, 2012). However, a thorough search of the literature yielded considerably fewer comprehensive studies of their application in the separation of U(VI) and Th(IV) from rare earths. Moreover, most of the chelating resins studied were either synthesized in-house or specially modified which may not be readily available in the market.

Recently, several chelating resins with mixed sulfonic/phosphonic, aminophosphonic, and iminodiacetic acid functional groups were investigated for the recovery of rare earth elements, RE(III) (Page et al., 2017). It was found that these chelating resins have no selectivity for RE(III) over the impurity metals present in the tested liquor. The study instead indicated potential application of the resins to remove trace Th (IV) from hydrometallurgical processing liquors containing RE(III). For that reason, the second part of this study explored the selective adsorption of U(VI) and Th(IV) from acidic sulfate media in the presence of selected light, medium, and heavy RE(III), specifically, lanthanum (III), cerium (III), gadolinium (III) and ytterbium (III) using various chelating resins with different physicochemical properties. The candidate resins included two solvent-impregnated resins containing extractants commonly used in solvent extraction (SX) processes for rare earths, namely, di-(2-ethylhexyl) phosphoric acid (D2EHPA) and organophosphinic acid. The study also attempted to understand the sorption chemism of these commonly available chelating resins from the perspective of their coordination chemistry.

2. Experimental materials and methods

2.1. Candidate resins

The chelating resins used in this study were selected from commercially-available resins supplied by resin manufacturing companies. Their physicochemical properties and functional groups, as reported in their product data sheets, are tabulated in Table 1. All of the tested resins were macroporous.

Before testing, pre-treatment was applied to ensure that all resins were converted to either sodium form or sulfate form. Solvent-impregnated resins, *i.e.* ChelR 6 and ChelR 7 required no activation before use and hence did not require pre-treatment. The resins were pretreated according to the method described in a previous work (Ang et al., 2017).

2.2. Synthetic solutions

Concentrated stock solution was prepared by dissolving appropriate amounts of $Th(SO_4)_2{\cdot}8H_2O$, $UO_2SO_4{\cdot}3H_2O$, $La_2(SO_4)_3$, $Ce_2(SO_4)_3$, $Gd_2(SO_4)_3$ and $Yb_2(SO_4)_3{\cdot}8H_2O$ in distilled water. The synthetic solution was prepared fresh from the stock solution before each test with a concentration of 2 mmol/L for each metal ion. $Th(SO_4)_2{\cdot}8H_2O$ (99.9%) and $UO_2SO_4{\cdot}3H_2O$ (99.9%) were procured from International Bio-Analytical Industries, Inc. (Florida, USA). $La_2(SO_4)_3$ (99.99%), $Ce_2(SO_4)_3$ (99.99%), $Gd_2(SO_4)_3$ (99.99%) and $Yb_2(SO_4)_3{\cdot}8H_2O$ (99.9%) were obtained locally from Sigma-Aldrich. All other chemicals used were of analytical grade.

Table 1
Physicochemical properties of candidate resins.

Resin ID	Functional group	Total capacity min. eq/L
ChelR 1	Bis-picolylamine	1.10
ChelR 2	Aminophosphonic	1.20
ChelR 3	Aminophosphonic	2.4
ChelR 4	Iminodiacetic	2.2
ChelR 5	Iminodiacetic	2.9
ChelR 6	Di-(2-ethylhexyl) phosphoric acid (D2EHPA)	0.40
ChelR 7	Bis-(2,4,4-trimethylpentyl) phosphinic acid	0.38

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 H_2SO_4 media by different chelating resins. To investigate the effect of acidity for each candidate resin, 100 mL of synthetic solution with varying concentrations of H_2SO_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 taken at the end of the 24-h test. The concentrations of metal ions in each sample were determined by inductively coupled plasma mass spectrometry (ICP-MS iCAP Qc, Thermo Fisher Scientific, Germany).

The adsorption percentage of each metal ion was calculated according to Eq. (1):

$$\%\text{Adsorption} = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where C_0 and C are the initial and equilibrium concentrations, respectively, of metal ion in aqueous solution (mg/L).

The distribution coefficient K_d for each metal ion was calculated according to Eq. (2):

$$K_d = \frac{C_0 - C}{C} \cdot \frac{V}{m} \tag{2}$$

where V is the volume of the synthetic solution (L), and m is the weight of the resin (g).

3. Results and discussion

Seven chelating resins were tested for their adsorption affinity for U (VI) and Th(IV) in acidic sulfate solution containing RE(III). ChelR 1 is a bis-picolylamine functionalised resin. ChelR 2 and ChelR 3 are resins with aminophosphonic acid functionality. ChelR 4 and ChelR 5 are resins with iminodiacetic acid functionality. ChelR 6 and ChelR 7, despite having different functional groups, *i.e.*, D2EHPA and organophosphinic acid, respectively, are categorized as solvent-impregnated resins. The adsorption of U(VI), Th(IV) and RE(III) by these resins at contact times of 2 h and 24 h are tabulated in Table 2 and Table 3 respectively. The distribution coefficient K_d values of each resin for U(VI), Th(IV) and RE(III) are tabulated in Table 4.

3.1. Chelating resins with bis-picolylamine functionality

The bis-picolylamine resin ChelR 1 in Table 2 shows appreciable adsorption of U(VI) and Th(IV) after 2 h of contact in the acidic sulfate solution. It was observed that U(VI) was adsorbed to a greater extent than Th(IV). The adsorption of RE(III) was no more than 10%. After a contact time of 24 h, the adsorption percentage of U(VI) was more than

Table 2
2-h IX adsorption of U(VI), Th(IV) and RE(III) in 0.05 mol/L H_2SO_4.

Resin ID	Adsorption (%)					
	U	Th	La	Ce	Gd	Yb
ChelR 1	44	16	10	10	10	8
ChelR 2	30	27	26	27	27	26
ChelR 3	29	27	24	25	25	24
ChelR 4	29	25	4	5	5	5
ChelR 5	33	30	8	8	8	9
ChelR 6	50	30	2	3	8	24
ChelR 7	93	28	0	1	3	17