



Comparative study of the application of chelating resins for rare earth recovery



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ABSTRACT

The adsorption properties of chelating ion exchange resins containing mixed sulfonic/phosphonic (SP), aminophosphonic (AP) or iminodiacetic (IDA) acid functional groups were investigated towards the rare earth elements (REE). The aim of this work was to determine the potential for such resins to assist in the isolation of a mixed rare earth product under conditions relevant to the hydrometallurgical processing of rare earth containing minerals. The selectivity of the resins towards La, Sm and Ho, versus the common impurity metals; Al, Fe and Th, was determined in sulfuric acid media. The chelating resins all displayed a similar selectivity with Fe and Th adsorbed in preference to the REE and Al (i.e. $\text{Th} \approx \text{Fe} \gg \text{REE} \approx \text{Al}$). The IDA resin displayed a far superior performance compared to both phosphonic resins (SP and AP) as well as a strong acid cation exchange resin for the adsorption of REE in the presence of very high Na or Ca concentrations. Equilibrium and kinetic adsorption isotherms for La were measured and successfully modelled with all resins, and the elution characteristics of selected resins investigated in both batch and column operation. A number of areas were identified where these resins could be exploited to provide an advantage in the hydrometallurgical processing of REE.

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1. Introduction

The rare earth elements (REE) find application in many fields associated with modernity such as green energy, high performance magnets, lighting and consumer electronics, medical equipment as well as in more traditional industries including glass, ceramics and catalysis (Massari and Ruberti, 2013; Binnemans et al., 2013). The supply of REE to the world market is predominantly from China, resulting from the processing of ionic clays and high grade mineral concentrates such as bastnasite, monazite and xenotime (Chen, 2011). In recent years, a relatively high supply risk index has been assigned to the REE by a number of countries (Massari and Ruberti, 2013). This has spurred interest in the production of REE from mineral concentrates of lower grade and varying sources. To satisfy the demands of these alternative resources the application of new separation methodologies is of interest.

Solid phase extraction with ion exchange resins is a particularly versatile separation technology that can be efficiently applied for the processing of low concentration feed solutions (Kentish and Stevens, 2001). The use of ion exchange resins for the bulk adsorption and concentration of REE has been previously investigated (Stevenson and Nervik, 1961; Strelow, 1966; Strelow and Baxter, 1969; Fritz and Garralda, 1963). This has traditionally involved the use of strong acid (SA) cation exchange resins due to their large adsorption capacity and high selectivity for the trivalent REE over base metal impurities (Strelow, 1960; Strelow et al., 1965). The potential for SA resins to improve the recovery of REE has been highlighted in recent reports, including studies on the recovery of REE values from mining wastewaters (Zhong and Xu, 2010; Chi et al., 2014; Shokobayev et al., 2015); the capture of a REE by-product from the production of phosphoric acid from phosphate rock (Padayachee et al., 1996; Koopman and Witkamp, 2000; Al-Thyabat and Zhang, 2015); and the recycling of rare earth oxide phosphors from technological waste stream (Heytmeijer, 1984; Cardarelli, 2014).

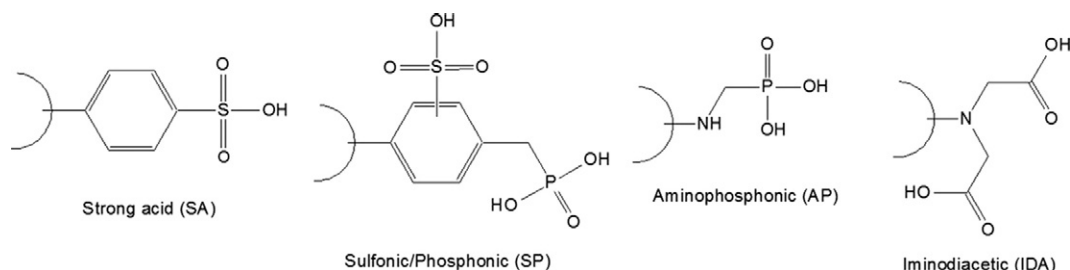
A number of alternative resin types have been developed that offer diverse adsorption properties compared to conventional SA resins. Of particular interest are the “chelating resins” that contain phosphonic acid or iminodiacetic acid functional groups, as opposed to the sulfonic acid groups. Such resins exhibit a high affinity for the adsorption of heavy metal ions and proven performance in established hydrometallurgical applications

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(Hubicki and Kolodynska, 2012). However, the potential use of these resins in REE processing operations has not been widely explored. Early work on resins containing phosphonic acid functional groups revealed a high affinity for the adsorption of REE from acidic liquors (Yamabe et al., 2001; Jyo et al., 1997; Egawa et al., 1994). The selectivity for the REE was found to be superior to bivalent base metal ions although similar to other trivalent metals such as Bi(III), Al(III) and Cr(III), while Fe(III) was adsorbed in preference to the REE. For resins containing iminodiacetic acid functional groups, the pH dependence and kinetic rate of Yb adsorption has been studied by (Xiong et al., 2006). Several reports on the separation of individual REE using phosphonic and iminodiacetic resins are also available (Winget, 1964; Moore, 2000; Kronholm and Anderson, 2015).

This work investigates a range of resins to determine the potential for application in the context of rare earth hydrometallurgical processing. We present comparative sorption and elution data for ion exchange and chelating resins containing the functional groups: sulfonic (SA); mixed sulfonic/phosphonic (SP); aminophosphonic (AP) and iminodiacetic (IDA) acid.



2. Material and methods

The resins used for this study were supplied by Purolite and are commercial products. The exception was the strong acid resin which was a developmental product also supplied by Purolite. The resin properties are summarised in Table 1. All resins were washed with deionised water and then conditioned in an acid solution of composition and pH matching the experimental conditions. Metal ion solutions were prepared by dissolution of the metal oxide (La, Sm and Ho) or sulfate salts (Al, Fe and Th) in HCl or H_2SO_4 .

The pH screening studies were performed by batch contact of the resin with a solution containing a mixture of all metal ions (ca. 50 mg L^{-1} ea.) in H_2SO_4 . The resin to aqueous ratio by volume was 1:10, and contact time was 20 h under continuous agitation on an orbital shaker at room temperature (21°C).

The adsorption isotherms were determined by batch contact of known resin volumes with $LaCl_3$ solution at various conc. ($0.5\text{--}5 \text{ g L}^{-1}$) in HCl media. Kinetic studies were performed by contacting a 100 mL solution of $LaCl_3$ (approx. 2 g L^{-1}) in HCl with 2–3 mL of wet settled resin in a water jacketed beaker at 300 K. The solution was agitated by mechanical stirrer and 1 mL aliquots removed at regular interval for analysis. For both isotherm and kinetic studies an initial solution pH of 1.5 was used for the SA, SP and AP resins and the solution pH remained above 1.0 after equilibration with the resin. For the IDA resin buffering of the solution at pH 4.0 using 0.5 M acetate buffer was used.

Batch elution studies were performed on 2 mL wet settled resin that had been pre-saturated with La, rinsed with water ($3 \times 10 \text{ mL}$), then suspended in the eluent (50 mL) and agitated for 20 h at room temperature (21°C) on an orbital shaker. The column elution of the resins was performed on 9.8 mL wet settled resin, pre-saturated with La, in glass columns of 10 mm internal diameter. The resin was rinsed with 20 bed volumes of water before

introducing the eluent at a flow rate of 0.38 bed volumes per hour (3.70 mL h^{-1}). The eluted solution was collected on an automatic carousel at regular time intervals.

For the acid dependent sorption, sorption rate studies and column elution curves the elemental concentrations were determined by ICP-MS (Perkin-Elmer Elan 9000) or by ICP-OES (Perkin-Elmer Optima 5300DV). For the sorption isotherms and batch elution studies neutron activation analysis (NAA) of the isolated resins was used to determine element concentrations. The resins were dried at 50°C for 20 h then irradiated in the OPAL reactor (neutron flux approx. $5 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$) along with gold wire standards. Gamma spectra were taken 3–6 days after irradiation using Ortec P-type germanium detectors of 25% relative efficiency, connected to Ortec DSPEC Pro or DSPEC-50 digital spectrometers. Concentrations were calculated using the k_0 method of standardisation (van Sluijs et al., 2015).

3. Results

3.1. The impact of acidity on the sorption of La, Sm, Ho, Al, Fe and Th from sulfate media

The sorption of the REE; La, Sm and Ho, as well as metal ions; Al, Fe(III) and Th, routinely found in process liquors, was investigated over a range of sulfuric acid concentrations using the SA, SP, AP and IDA ion exchange resins. The percent sorption versus acid concentration for the various resins is shown in Fig. 1. These results highlight a key difference in the selectivity of the SA resin compared to the three chelating resins. Firstly, the SA resin has a higher affinity for the REE over the Al and ferric impurity ions while Th displays similar adsorption strength to the REE. In comparison the chelating SP, AP and IDA resins all show a similar affinity series with Fe(III) and Th adsorbed in preference to the REE, and Al closely tracking the REE.

Table 1
General resin properties.

Resin ID	Functional group	Resin name	Matrix	Size (mm)	Water retention	Capacity ($\text{g} \cdot \text{L}^{-1}$)
SA	Sulfonic acid	—	Macroporous PS-DVB	425–1200	54–59% (H^+ form)	—
SP	Sulfonic and phosphonic acid	Purolite S957	Macroporous PS-DVB	425–1000	55–70% (H^+ form)	18 (Fe)
AP	Aminophosphonic acid	Purolite S950	Macroporous PS-DVB	300–1000	60–68% (Na^+ form)	26 (Ca)
IDA	iminodiacetic acid	Purolite S930Plus	Macroporous PS-DVB	425–1000	52–60% (Na^+ form)	50 (Cu)

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