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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.

Keywords: ion exchange, rare earth, thorium, chelating resin, adsorption, elution, kinetics

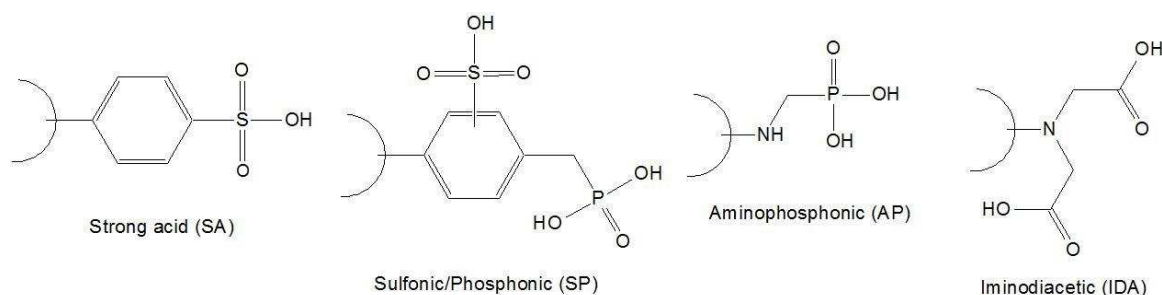
1. INTRODUCTION

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.¹ 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.² In recent years, a relatively high supply risk index has been assigned to the REE by a number of countries.^{1a} 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.³ The use of ion exchange resins for the bulk adsorption and concentration of REE has been previously investigated.⁴ 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.⁵ 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;⁶ the capture of a REE by-product from the production of phosphoric acid from phosphate rock;⁷ and the recycling of rare earth oxide phosphors from technological waste stream.⁸

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 hydrometallurgy applications.⁹ 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.¹⁰ 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.¹¹ Several reports on the separation of individual REE using phosphonic and iminodiacetic resins are also available.¹²

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 H₂SO₄.

Table 1: General resin properties.

Resin ID	Functional group	Resin name	Matrix	Size (mm)	Water retention	Capacity (g.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)

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 H₂SO₄. 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 LaCl₃ solution at various conc. (0.5-5 g L⁻¹) in HCl media. Kinetic studies were performed by contacting a 100 mL solution of LaCl₃ (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 (3×10 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. 5×10¹² cm⁻²s⁻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 k₀ method of standardisation.¹³

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 Figure 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.

For the SA resin it is possible to extract the separation factors from the data displayed in Figure 1a. The separation factor (β_y^x) is defined as the difference in the distribution ratios (D) for any two adsorbing species (x and y) according to equation 1:

$$\beta_y^x = \frac{D_x}{D_y} = \frac{Q_x}{C_x} \times \frac{C_y}{Q_y} \quad (1)$$

Where Q is the resin capacity and C the solution concentration of the adsorbing species x or y. The separation factors measured at 0.83 M H⁺ for La, Sm and Ho versus Al and Fe(III) are

summarised in Table 2. For the IDA resin, the separation factors for Fe(III) and Th cannot be measured as the distribution ratios for the REE and Fe(III) or Th are either very high or very low. It is therefore more useful to estimate the ion selectivity by comparing the acid concentration at which 50 % adsorption is obtained, i.e. the $\Delta[\text{H}^+]_{50}$ value. The $\Delta[\text{H}^+]_{50}$ values for La, Sm and Ho versus Th and Fe(III) are also summarised in Table 2. To illustrate the difference between separation factors (β) and $\Delta[\text{H}^+]_{50}$ values by example; a $\Delta[\text{H}^+]_{50}$ value of 0.2 (as determined for the REE:Fe pairs) corresponds to a separation factor in the order of $\sim 10^4$.¹⁴ The significance of these results is discussed in more detail in Section 4 below. Unfortunately for the SP and AP resins the selectivity for Fe(III) and Th over the REE cannot be quantified from this data as the adsorption of Fe(III) and Th is very high even at the highest acid concentrations investigated.

Another key difference to note between the performance of the SA and chelating resins is the influence of acid concentration on the adsorption of REE. Both SA and SP resins have a similar affinity for the REE and are able to efficiently extract these metals from acid solutions up to approx. 0.5 M H^+ . The adsorption of the REE was found to be slightly stronger for the AP resin, which could tolerate acid concentrations up to approx. 1.0 M H^+ . However, for the IDA resin the weakly acidic nature of the acetate functional groups results in the effective adsorption of REE only at acid concentrations less than 0.001 M (or $\text{pH} > 3$).

Table 2: Separation factors (β) and $\Delta[\text{H}^+]_{50}$ values for SA and IDA resins, respectively.

ion pair	SA resin	IDA resin
	β^a	$\Delta[\text{H}^+]_{50}$ (β est.) ^b
La:Fe	37	0.2 ($\sim 10^4$)
Sm:Fe	18	0.2 ($\sim 10^4$)
Ho:Fe	10	0.2 ($\sim 10^4$)
La:Al	18	-
Sm:Al	9	-
Ho:Al	5	-
La:Th	-	0.3
Sm:Th	-	0.3
Ho:Th	-	0.3

^a The separation factors for the SA resin were calculated at 0.83 M H^+ using the data presented in Figure 1a.

^b The separation factors for the IDA resin were estimated from the $\Delta[\text{H}^+]_{50}$ values determined from Figure 1d.¹⁴

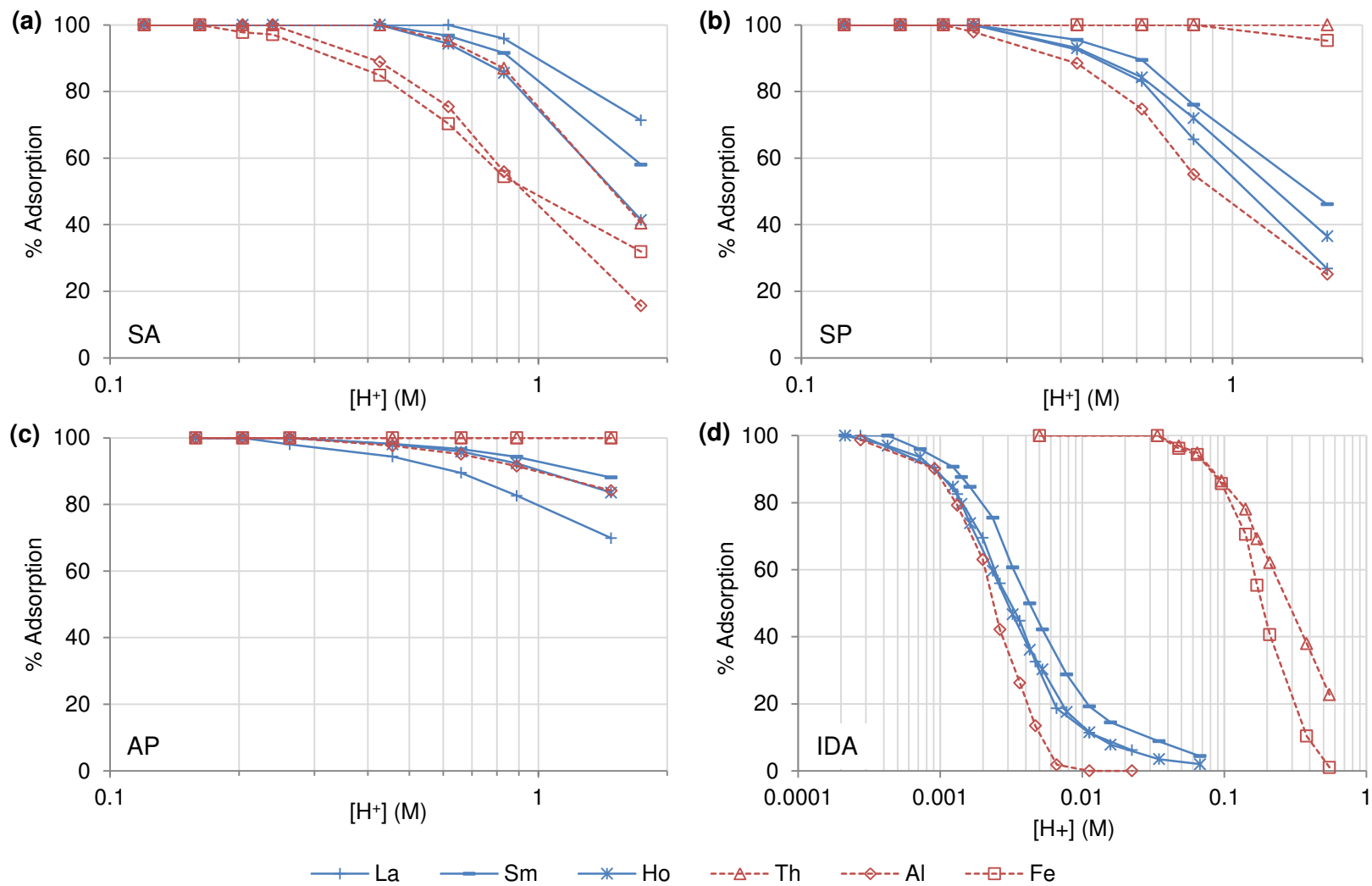


Figure 1: Metal ion sorption as a function of H^+ concentration for the: (a) strong acid (SA), (b) mixed sulfonic/phosphonic (SP), (c) aminophosphonic (AP) and (d) iminodiacetic resins (IDA).

3.2 Equilibrium isotherm and rate determination for La adsorption

The equilibrium adsorption isotherms for La were determined as a model for REE behaviour. The adsorption experiments were performed in HCl to minimise coordination effects of the anion (c.f. SO_4^{2-}) between solutions of different ionic strength. Measurements were made at pH 1.5 for SA, SP and AP resins and pH 4.0 (buffered with 0.5 M acetate) for the IDA resin (Figure 2). The isotherms were modelled using a least squares regression on the linear form of the Langmuir adsorption equation:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{bQ_{\max}} \quad (2)$$

Where C_e is the solution concentration at equilibrium, Q_e is the resin capacity at equilibrium, Q_{\max} is the maximum possible resin capacity and b is the Langmuir constant which defines the strength of the adsorption interaction. A close fit between the model and the experimental data was observed and the Langmuir constant (b) and maximum adsorption capacity (Q_{\max}) of the resins were determined (Table 3). The Langmuir constant was found to be highest for the SA resin indicating it has the greatest affinity for rare earth adsorption for all resins investigated, however very strong adsorption was observed for all resins as indicated by the sharp right-angle profile of the isotherms, and little practical difference in their adsorption strength can be seen from this data. The most notable difference in the isotherm behaviour is the much lower maximum adsorption capacities observed for the chelating resins; SP (52 g.L^{-1}), AP (39 g.L^{-1}) and IDA (49 g.L^{-1}), compared to the SA resin (64 g.L^{-1}).

The adsorption kinetics for La were also measured in HCl media, at pH 1.5 for SA, SP and AP resins, and pH 4.0 (buffered with 0.5 M acetate) for the IDA resin. Due to the different adsorption mechanism between SA and chelating resins (as discussed later in Section 4), the adsorption kinetics are controlled by different rate controlling steps. For SA ion exchange resins the adsorption kinetics are controlled by diffusion of the metal ions through the polymer bead.¹⁵ However, for chelating resins the adsorption kinetics are controlled by formation of the coordination bond at the functional group of the resin.¹⁶ To effectively compare the reaction kinetics between SA and chelating resins here, an empirical model was chosen that does not consider the mechanism of adsorption. For this purpose the pseudo second-order rate equation developed by Ho and McKay was applied due to its proven efficacy in modelling the adsorption of heavy metal ions from solution.¹⁷ The kinetic data was modelled using a least squares regression on the linear form of the equation:

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{t}{Q_e} \quad (3)$$

Where Q_e is the equilibrium adsorption capacity, Q_t is the adsorption capacity at time t , and k is the kinetic rate constant. The rate of La adsorption is shown in Figure 3, for ease of comparison the adsorption capacity of the resins have been normalised to their equilibrium concentration. The kinetic rate constants (k) are summarised in Table 3. The largest rate constant was obtained with the SA resin ($0.102 \text{ L.g}^{-1}.\text{h}^{-1}$), followed in order by the chelating resins; AP ($0.092 \text{ L.g}^{-1}.\text{h}^{-1}$), IDA ($0.042 \text{ L.g}^{-1}.\text{h}^{-1}$) and SP ($0.035 \text{ L.g}^{-1}.\text{h}^{-1}$).

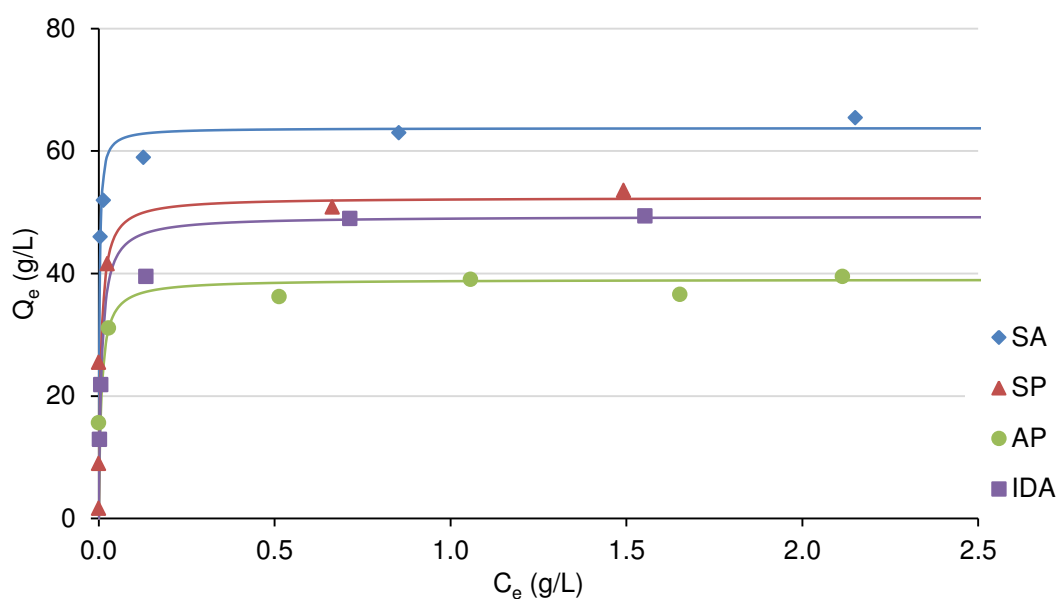


Figure 2: Equilibrium adsorption isotherms for La in HCl at pH 1.5 (SA, SP and AP resins) and 4.0 (IDA resin; buffered with 0.5 M acetate).

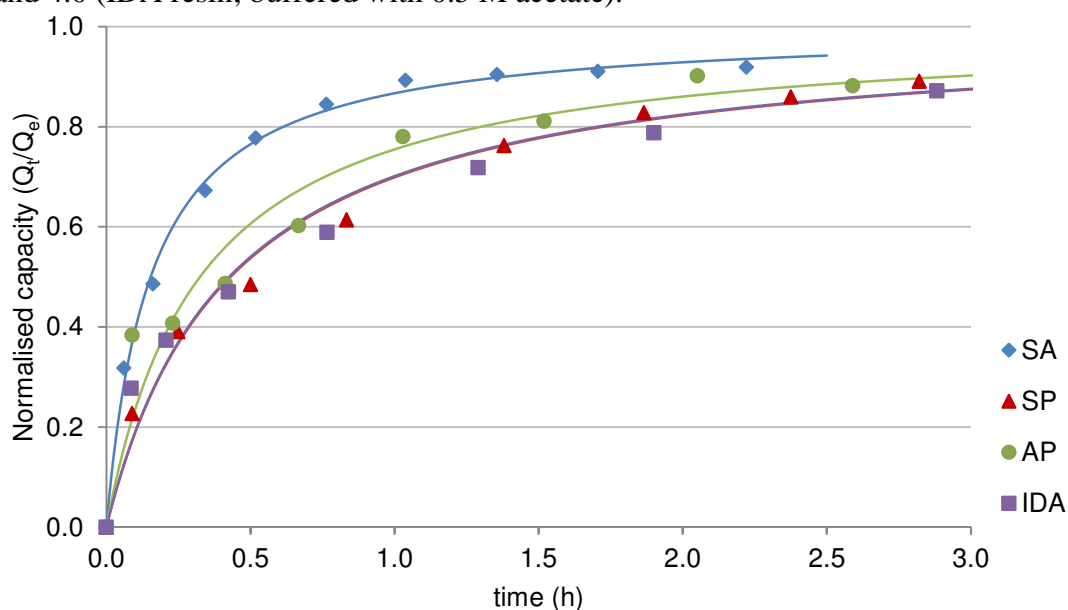


Figure 3: La adsorption rate from HCl at pH 1.5 (SA, SP and AP resins) and 4.0 (IDA resin; buffered with 0.5 M acetate).

Table 3: Adsorption isotherm and kinetic parameters for La adsorption.

Resin (pH)	SA (1.5)	SP (1.5)	AP (1.5)	IDA (4.0)
Q_{\max} (g.L ⁻¹)	64	52	39	49
b (L.g ⁻¹)	541	161	137	128
k (L.g ⁻¹ .h ⁻¹)	0.102	0.035	0.092	0.042

3.3 Elution of La from SA, SP and IDA resins using HCl, NaCl and CaCl₂ eluents

Elution of La from the SA, SP and IDA resins was investigated with HCl solutions of various concentrations (0.1–4 M). Concentrated NaCl (4 M) and CaCl₂ (2 M) solutions were also investigated as qualitative indicators of how effective the resins would perform in the presence of high concentrations of alkali and alkaline earth metal cations. The results are summarised in Table 4.

The 4 M HCl solution achieved similar elution values for both the SA (80 %) and SP (79 %) resins, however at lower acid concentration a stronger affinity between La and the SA resin was discernible. For example, the 1 M HCl solution eluted 54 % of the La from the SP resin and only 38 % of the La from the SA resin. This is consistent with the observed pH dependence of La adsorption described above in Figures 1(a) and 1(b). In contrast, the IDA resin was almost entirely stripped of La in quite dilute acid solutions, with elution values of 99.8 % and 97 % in 0.5 and 0.1 M HCl, respectively. This is consistent with the weakly acidic nature of the acetate functional groups on the resin and the observed pH dependence of La adsorption shown in in Figure 1(d).

A large difference between the resins was observed when elution of La was attempted using 4 M NaCl and 2 M CaCl₂ solutions. For the SA resin these solutions achieved a high recovery of La with 87 % (4 M NaCl) and 96 % (2 M CaCl₂) elution. In comparison, elution of La from the SP resin was less effective with 4 M NaCl (52 %) and 2 M CaCl₂ (76 %), and almost no La was eluted from the IDA resin (<1 %) with either eluent. These results highlight a key advantage of the chelating resins over conventional SA resin types, and that is a high selectivity for metals that form strong coordination bonds to the functional groups of the resin, over weakly-coordinating alkali and alkaline earth metals. The results in Table 4 show that this selectivity is exceptionally high for the IDA resin, but is much less pronounced for the SP resin.

Table 4: Elution of La by batch contact of 2 mL wet settled resin with 50 mL of solution.

solution	% Elution		
	SA	SP	IDA
0.1 M HCl	3	11	97
0.5 M HCl	21	34	99.8
1 M HCl	38	54	99.9
2 M HCl	58	69	-
4 M HCl	80	79	-
4 M NaCl ^a	87	52	<1
2 M CaCl ₂ ^a	96	76	<1

^a The pH of the NaCl and CaCl₂ solutions was adjusted with HCl for consistency with adsorption studies; equilibrium pH= 1.1 (SA, SP) and 3.5 (IDA).

3.4 Column elution of La from SA and IDA resins with HCl

The batch desorption studies described above highlight the relative ease of recovering adsorbed REE values from an IDA resin using dilute HCl solutions. To investigate this in more detail the elution of La from the IDA resin using HCl was performed in a column operation, and the results compared to the elution of La from a column of SA resin. Figure 4 shows the elution profile for the following resin:eluent combinations; SA:4 M HCl, IDA:3 M

HCl and IDA:0.5 M HCl. The same resin bed volume (BV= 9.8 mL) and flow rate (0.38 BV h^{-1}) was used throughout.

An important difference between the SA and IDA resin is the elution peak shape. The SA resin shows a sharp elution front and a long trailing tail, whereas the IDA resin shows a broad elution front and a very sharp tail (for both eluent solutions). For the SA resin this tailing effect greatly reduces the efficiency of the column. This is illustrated by the % elution curves in Figure 4, which describes how the return on recovered La per volume of eluent increasingly diminishes as the SA resin is stripped. In comparison, a linear relationship between La recovery and eluent volume is observed for the IDA resin with both eluent solutions.

Some key metrics have been summarised in Table 5 which highlight the difference in elution efficiency between the two resins. For example, 80 % of the La may be eluted from the SA resin within the first 3.2 BV of eluent, yet an additional 6.2 BV is required to elute 98 % of the La. For the IDA resin, >99 % of La is eluted with either 1.5 BV (3 M HCl) or 3.8 BV (0.5 M HCl) of eluent. Elution of the IDA resin with 3 M HCl also yields a higher La tenor in the eluate (30.4 g.L^{-1} and >99 % recovery) compared to elution of the SA resin with 4 M HCl (17.5 g.L^{-1} La and only 80 % recovery). Another measure of column efficiency is captured in the reagent cost of the elution process, quantified here as the acid efficiency, and defined by the equivalents of La eluted per equivalents of acid added to the column (Table 5). The acid efficiency for elution of the IDA resin with 0.5 M HCl is 50 % (i.e. for every equivalent of H^+ added to the column half an equivalent of La is eluted). This drops to an acid efficiency of 22 % for elution with 3 M HCl, and is less than 4 % for complete elution of the SA resin. The difference in acid efficiency for the two IDA eluents is likely a consequence of the slow desorption kinetics, and a higher equilibrium La concentration in 3 M HCl. Therefore a higher proportion of the acid passes to the eluate before exchange with the resin can occur. Of course in practice all of these elution metrics are dependent on the mode of column operation (flow rate, temperature, moving bed, continuous counter-current, etc.) and by no means represent an absolute difference between the resins. However, the general trends between resins, in terms of acid consumption and eluate concentration, are expected to hold for a given set of operating conditions.

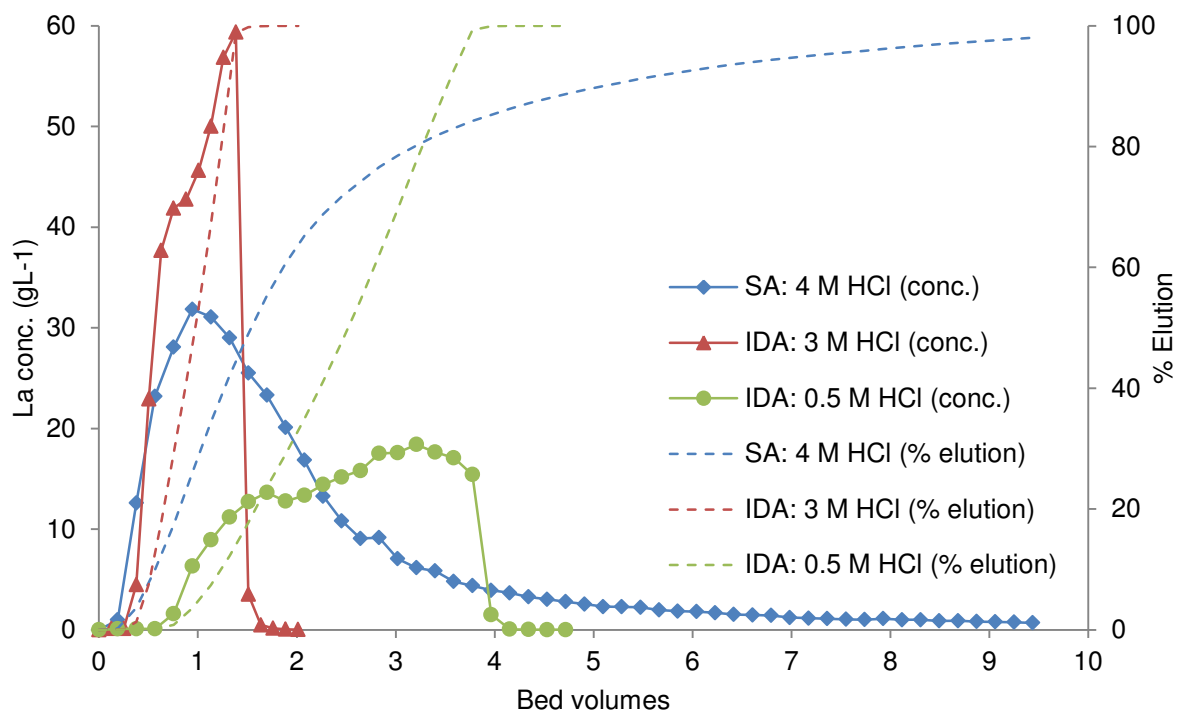


Figure 4: The elution of La from SA and IDA resins with HCl (flow rate= 0.38 BV.h⁻¹).

Table 5: Elution metrics for the recovery of La from SA and IDA resins.

Resin: Eluent	Bed volumes collected	La eluted (meq.)	La recovered (%)	av. La conc. (g.L ⁻¹)	Acid added (meq.)	Acid efficiency ^a (%)
SA: 4 M HCl	3.2	11.9	80	17.5	126	10
SA: 4 M HCl	9.4	14.6	98	7.3	370	4
IDA: 3 M HCl	1.5	9.7	>99	30.4	44.4	22
IDA: 0.5 M HCl	3.8	9.2	>99	11.5	18.5	50

^a Acid efficiency is defined as the equivalents of La eluted per equivalents of acid added, expressed as a percent.

4. DISCUSSION

To investigate the use of ion exchange in the production of REE from low grade mineral concentrates, we considered a sulfuric acid bake/water leach route as the simplest first step to producing suitable feed liquor. For this reason the impact of acidity on the adsorption of rare earth and impurity ions was conducted in sulfate media (Section 3.1). These adsorption studies highlighted a key difference in metal ion selectivity between the SA resin and the three chelating resins. The selectivity trends observed in Figure 1 can be understood by considering the different adsorption mechanisms operating within the different resin types. For the SA resin (Figure 1a), adsorbed metal ions retain their hydration shell and no direct bonding between the sulfonate functional groups on the resin and the metal cation occurs.¹⁸ In this case the strength of the adsorption is determined primarily by the valence of the metal ion, whereby metal ions of higher charge are adsorbed in preference to metal ions of lower charge. In the case of tetravalent Th(IV) its position amongst the trivalent REE appears anomalous, however, unlike the REE, the Th(IV) ions are strongly associated with the sulfate

ions in solution which moderates their affinity for the resin. This is reflected in the previously reported distribution coefficients (D) for Th(IV) adsorption onto a SA resin from 1 N HCl (2049), HNO₃ (1180) and H₂SO₄ (52)⁵. For cations that have the same valence the strength of adsorption onto a SA resin is determined by the hydration energy of the cation, so that small cations with a high charge density and hence high hydration energy are displaced by larger cations with a lower hydration energy.¹⁹ This accounts for the selectivity of the REE over Al and Fe(III) (and also for the selectivity between the REE; La > Sm > Ho).

For the chelating resins (Figure 1b-d), a coordination bond between the metal ion and the functional group of the resin (i.e. phosphonate or carboxylate) is possible, and the strength of adsorption is determined by the strength of this metal-ligand bond.¹⁸ As the strength of a metal-ligand bond is determined by numerous factors, including the geometry and energy of the bonding orbitals, it is difficult to predict general trends in adsorption strength across the periodic table. However the exceptional adsorption strength of Fe(III) and Th(IV) ions onto both phosphonate and carboxylate resin types has been described previously.²⁰

The results shown in Figure 1a highlight the current limitation of SA resins to separate REE from the impurity ions Al, Fe(III) and Th. Considering the relatively high concentration of Al and/or Fe(III) typically encountered in low grade leach liquors, the separation factors determined here ($\beta_{Al}^{Ho} = 5$ and $\beta_{Fe}^{Ho} = 10$) are not sufficiently large to practically separate the REE from these metals. For example if the Fe(III) concentration in solution was only 10 times the concentration of Ho then both metals would adsorb to the same capacity on the resin. In such circumstance the cost of adsorbing and eluting unwanted ferric impurity over the desired REE ions would be a costly burden on operating a SA resin for rare earth recovery. As for Th, due to its attenuated adsorption in sulfate media no selectivity between it and the REE is provided by the SA resin.

The results described in Figures 1b-d indicate that the chelating resins have no selectivity for the REE over Al, Fe(III) or Th. Therefore, such ion exchange systems can only be applied to feed liquors that contain low concentrations of these impurity metals. However, they do display a high selectivity for Fe(III) and Th over the REE; for example the IDA resin displayed very large $\Delta[H^+]_{50}$ values for the REE:Fe (0.2 M) and REE:Th (0.3 M) pairs. As noted above, a $\Delta[H^+]_{50}$ of 0.2 for the REE:Fe pair corresponds to a separation factor in the order of $\sim 10^4$. Therefore the chelating resins may be useful in controlling trace impurity by selectively removing low concentrations of Fe(III) or Th from a mixed rare earth product without significant loss of REE. This is particularly relevant for Th removal from sulfate media as the conventional SA resin displayed no selectivity between Th and REE in sulfate media. Th is often associated with rare earth feedstocks like monazite, and its removal requires special consideration due to its radioactivity.²¹

The chelating resins display a significant difference in the adsorption of REE versus acid concentration. Both phosphonic chelating resins will adsorb REE from strongly acidic solutions ($[H^+] = 0.5-1.0$ M), however the higher acid tolerance of the AP resin could make regeneration of the resin more difficult. Conversely, The IDA resin only effectively adsorbs the REE at relatively high pH (> pH 3). This may at first seem a severely restrictive requirement for application of the IDA resin, however process liquors of pH 3 or above are routinely produced where some form of impurity control process has been applied to the original leach liquor. For example, the common practice to remove impurity ions such as Al, Fe(III) and Th is to precipitate their hydroxides from solution by partial neutralisation of an acidic leach liquor to pH 3-4, alternatively a rare earth concentrate that has undergone a

caustic conversion process may be selectively leached at $\text{pH} > 4$ to remove the rare earths and leave the impurity ions in the leach residue. In the weakly acidic liquors produced the IDA resin is an effective adsorbent for REE.

The IDA resin offers two key advantages over conventional SA resins and the phosphonic chelating resins. Firstly, adsorbed REE are easily eluted from the IDA resin using acid, resulting in lower acid consumption and a higher REE tenor in the eluate (Section 3.4). Secondly, the IDA resin displays a very high selectivity for adsorption of REE over alkali and alkaline earth cations such as Na and Ca (Section 3.3). These impurity ions are often present in high concentrations in liquors that have been partially neutralised by the addition of caustic salts. With these considerations it is anticipated that the IDA resin would be particularly advantageous in the recovery of dilute REE values from waste process streams.

Another important consideration when choosing an ion exchange resin is to determine the impact of the resin capacity and adsorption kinetics on a process. The chelating resins display lower capacity and slower adsorption kinetics for La compared to the SA resin (Section 3.2). This can increase the amount of resin and reagent required for a given separation process and add to the expense of an ion exchange operation. However, the small difference in capacity and adsorption rate between the resins studied here is not expected to pose a significant barrier to their application.

5. CONCLUSIONS

The fundamental adsorption properties of SP, AP and IDA chelating resins were characterised and compared to a conventional SA resin. The following key observations were recorded:

- All chelating resins displayed a similar selectivity series with Fe and Th adsorbed in preference to the REE and Al (i.e. $\text{Th} \approx \text{Fe} \gg \text{REE} \approx \text{Al}$). This was strikingly different to the SA resin which displayed the following selectivity series in sulfuric acid media; $\text{REE} \approx \text{Th} > \text{Fe} \approx \text{Al}$;
- A varied response to REE adsorption towards acid concentration was observed, with the SA, SP and AP resins displaying a tolerance for REE adsorption from high acid concentrations ($< 0.5 \text{ M H}^+$), whereas the IDA resin effectively adsorbed REE only at low acid concentrations ($< 0.001 \text{ M H}^+$);
- The sensitivity of the IDA resin to acid concentration resulted in superior elution performance with HCl eluent compared to both phosphonic and SA resins;
- The IDA resin also displayed superior selectivity for the adsorption of REE in the presence of high Na and Ca concentrations;
- Equilibrium and kinetic adsorption isotherms were measured and successfully modelled for all resins. The chelating resins displaying lower capacity and slower kinetics for La adsorption compared to the SA resin.

These results have highlighted opportunities for the application of chelating resins in the hydrometallurgical processing of REE, namely:

- The application of chelating resins for removing trace Th impurity from REE liquors, especially with regard to sulfate solutions where no separation of Th and the REE is possible using conventional SA resins;
- The application of IDA resins in the recovery of dilute REE values from waste process streams, where cost advantages may be obtained in the facile regeneration of the resin with acid and its high selectivity for REE adsorption over alkaline metal impurities such as Na and Ca.

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