

CHROMATOGRAPHIC SEPARATION OF RARE EARTH ELEMENTS AS ANIONIC COMPLEXES BY ION EXCHANGE

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ABSTRACT

Separation and purification of rare earth elements (REE) is known to be a troublesome issue. Reaching significant (> 99%) purities requires multiple steps. Mass production of purified REEs is often done by solvent extraction (SX) methods. Large number of consecutive steps in solvent extraction mean large quantities of SX chemicals and it also requires large number of mixer-settler units. Ion exchange (IX) methods are alternative option for REE production. Most research on IX methods in REE separation relies on HPLC technology. High pressure makes the scalability of the production expensive. REE separation by IX could be profitable if the separation could be done in a low-pressure system and with simple chemistry. IX as separation method allows collection of multiple different product fractions after the separation process by combining individual fractions after single step. With SX the collection of multiple (> 2) different products from single unit operation is not possible.

Phosphogypsum, waste material of phosphoric acid production, is known to contain trace amount of REEs. These precious metals can be extracted from this high calcium containing matrix by IX. Recovery of REE from the loaded resin can be done by alkaline complexing agents. Rare earth mixture ($c(\text{REE}) \approx 3 \text{ g/L}$) with high purity (98%) can be obtained as product. REEs are in form of metal-chelate complex in this alkaline mixture. Major REEs present in the mixture are La (15.2%), Ce (45.0%), Pr (5.9%) and Nd (23.5%). Ce can be removed from the solution by oxidating Ce(III) to Ce(IV) and adjusting pH to the suitable level. All the other REEs are present but in low concentrations compared to the others.

In this study, chromatographic REE separation is done by utilizing net negative charge of these REE-ligand complexes. Stationary phase in the separation process is a strong base anion (SBA) resin. REE-ligand complexation is known to enhance the affinity differences of individual elements in the REE series. Typically, with SBA resin in REE separation the mobile phase contains excess amount of free complexing agent or ligand. In these processes the elution order of REEs is often shown to be from Lu to La. This kind of approach requires usually large amounts of mobile phase since the REE-ligand complex affinities to stationary phase are strong. Strongest complex is first to exit the column carried by mobile phase. REE-ligand complexes remain negative throughout the whole process. In our research, the REE-ligand complex is fed to the column system as complexes and dilute HCl is used as mobile phase. Separation is still based on the differences on the complex strength but HCl as the mobile phase protonates weakest complexes first and thus elution order is reversed from La to Lu. This approach decreases the amount of eluent spent in the separation process.

Optimal conditions for REE separation were studied by using a synthetic REE mixture as the feed solution because the composition and properties could be varied systematically. The feed volume, flow rate, temperature, feed pH, mobile phase concentration (pH), and the selection of the acid and the resin were investigated to find most suitable conditions for the separation. With suitable feed composition and pH control the interactions of REE-ligand with SBA resin can be adjusted.

It was shown with an authentic feed mixture (from leaching of phosphogypsum) that the purity of individual REEs can be enhanced by means of IX process with dilute HCl as eluent. Product fractions of desired metal(s) ((Pr+)Nd) can be collected with enhanced purity and reprocessed to create new feed. In sequential separation cycles the purities can be furthermore enhanced. First cycle improved Nd purity from 46.5% to 75.5% (Yield 52.3%) and second cycle furthermore improved purity from 75.5% to 81.2% (Yield 86.9%). For Pr+Nd product fraction the purity is 95.5% after second cycle.

Keywords: rare earth element, ion exchange, MGDA, complex, separation