

ABSTRACT

Author: Choi, Hoon, PhD

Institution: Purdue University

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Title: Development of separation and purification methods for producing rare earth elements from coal fly ash

Major Professor: Nien-Hwa Linda Wang

Rare earth elements (REEs) are critical materials in many electronics and green technology products. Though the demand for REEs is growing rapidly, China controls over 90% of the REEs supply and the US currently is not producing any REEs. As most of the REEs occurred together in the mineral ores with low concentrations and they have similar chemical and physical properties, the extraction and purification processes are challenging. Conventional methods for producing REEs require large amounts of toxic chemicals and generate large amounts of hazardous wastes. Therefore, it is important to develop alternative REE sources as well as efficient and environmentally friendly processes to produce REEs domestically. In this dissertation, coal fly ash, a major coal combustion product, was explored as a potential source for REEs. Novel separation and purification methods were developed for producing high purity REEs from coal fly ash.

First, a sequential separation process was developed to recover and concentrate REEs from coal fly ash. The ash was first digested using a NaOH solution and subsequently dissolved in an acid to extract REEs as well as other chemicals. About 74% of REEs, 92 % of SiO₂, 74% of Al₂O₃, 24% of Fe₂O₃, and 65% of CaO were extracted. Most (>99%) of the extracted REEs and cations (Al⁺³, Fe⁺³, Ca⁺²) were captured in a cation exchange column. Negatively charged Si species were eluted by water. The captured REEs were separated from the other cations in the column. A solution of NaCl was used to elute the cations and most of the REEs, which were strongly adsorbed

in the column, were eluted using a solution of diethylenetriaminepentaacetic acid (DTPA). In this separation process, high purity SiO_2 (>99%), $\text{Al}(\text{OH})_3$ (>99%), and $\text{Fe}(\text{OH})_3$ (>95%) were produced. The eluted DTPA-REEs solution was then loaded in a cation exchange column. The REEs accumulated in the column could be further separated into pure REE fractions using a ligand-assisted displacement chromatography method (LAD), instead of the the conventional liquid-liquid extraction method.

Detailed rate model simulations were developed for LAD and verified with experimental and literature data. The dynamic column profiles in simulations showed that a prestant which has a higher ligand affinity and a lower sorbent affinity than REEs is required to develop an isotachic train in LAD. When a constant-pattern isotachic train is developed, high concentration bands with high purity and high yield can be achieved. Further increase in column length is not needed. Thus, if purity, yield, sorbent, and ligand are fixed, the constant-pattern state gives the highest sorbent productivity and the highest ligand efficiency. It is critical to develop a method to find the general conditions required for developing constant-pattern states. Key dimensionless parameters affecting the constant-pattern states were formulated first based on the h-transformation theory for an ideal system and the shock layer theory for a nonideal system. Strategic combinations of the key dimensionless groups were developed to express a dimensionless minimum column length as a function of the combined dimensionless groups. Rate model simulations were used to find various minimum column lengths for developing constant-pattern states from transient states. The simulation results were used to generate a correlation curve in a two-dimensional plot or map where the curve divided the map into two regions, the transient region, and the constant-pattern region. The map can be used to find the minimum required conditions for developing a constant-pattern state for a general LAD system at any scale.

A constant-pattern design method for both ideal and non-ideal (with significant mass transfer effects) LAD systems was developed based on the general correlation equation for the map. In addition, an equation for the yield of a target component as a function of the key dimensionless groups was derived based on the constant-pattern mass transfer zone lengths. The column length and operating velocity solved from the two equations ensured the yields and the constant-pattern state for the target components. A selectivity weighted composition factor was developed to allow the design method to specify a minimum target yield for one or multiple components. The design method is robust and scalable because it provides the optimal operating conditions to meet the minimum target yield and purity of one or multiple components for LAD systems at any scale. The design method was verified using simulations and experiments for different target yields, ligand concentrations, and feed compositions for ternary mixtures. The minimum target yields were achieved or exceeded in all cases tested. The results showed that high ligand concentration, long column length, and high effective sorbent selectivity can increase sorbent productivity. The minimum column length required to achieve a constant-pattern state and the productivity of LAD are limited by the lowest selectivity or by a minority component with a low concentration in the feed, even when it does not have the lowest selectivity. If both minor and major REE components in a mixture need to be recovered in the same LAD process, the overall productivity could be significantly limited. Thus, separating major components first and recycling/separating the minor components in a separate LAD process could increase the total productivity significantly. The productivities achieved using this design method are two orders of magnitude higher than the literature results with similar REE yields and purities.