DEVELOPMENT OF SEPARATION AND PURIFICATION METHODS FOR PRODUCING RARE EARTH ELEMENTS FROM COAL FLY ASH

by

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To my family who devotedly supported me

and

to my love Ellie and Elli

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TABLE OF CONTENTS

TABLE OF CONTENTS
LIST OF TABLES
LIST OF FIGURES
NOMENCLATURE
ABSTRACT
CHAPTER 1. INTRODUCTION
1.1 Background
1.1.1 Rare earth elements
1.1.2 Coal fly ash as a potential source of REEs
1.2 Motivations and Objectives
1.3 Dissertation Outline
CHAPTER 2. SEPARATION METHODS TO RECOVER RARE EARTH ELEMENTS,
SILICA, ALUMINUM HYDROXIDE, AND IRON HYDROXIDE FROM COAL FLY ASH 34
2.1 Introduction
2.1.1 Literature review of REEs extraction methods from coal fly ash
2.1.2 Overview of the sequential separation process
2.1.3 Highlights
2.2 Experimental
2.2.1 Materials and characterization
2.2.2 NaOH digestion of coal fly ash
2.2.3 Acid dissolution to extract REEs
2.2.4 Magnetic separation of residual solids 40

2.2.5	Cation exchange steps to capture REEs
2.2.6	REEs concentration in a REEs concentration column
2.2.7	Precipitation of iron hydroxide, and aluminum hydroxide from NaCl effluents 41
2.2.8	Silica gel precipitation and NaOH recovery from sodium silicate solution
2.3 Re	sults and discussion
2.3.1	Characterization of coal fly ash
2.3.2	Overview of the process to recover Si, Al, Fe, and REEs 45
2.3.3	Step 1 - NaOH digestion
2.3.4	Step 2 - Acid dissolution
2.3.5	Step 3 – Cation exchange steps to capture REEs
2.3.6	Step 4 – REEs concentration in a REEs concentration column
2.3.7	Step 5 - Magnetic separation of residual solids
2.3.8	Precipitation of iron hydroxide, and aluminum hydroxide from NaCl effluents (Step
3-3B)	
2.3.9	Silica gel precipitation and NaOH recovery from sodium silicate solution
2.3.10	Scale up of the overall process
2.4 Co	nclusions
CHAPTE	R 3. STUDY ON KEY PARAMETERS CONTROLLING A CONSTANT-
PATTERN	N STATE OF LIGAND-ASSISTED DISPLACEMENT CHROMATOGRAPHY FOR
SEPARAT	TING RARE EARTH ELEMENTS
3.1 Int	roduction
3.2 The	eory
3.2.1	Effective sorbent selectivity and separation mechanism for LAD

3.2.2 The minimum column length to develop an isotachic train of a binary mixture in an
ideal system (Liso-id)
3.2.3 Constant-pattern mass transfer zone length ($L_{MTZ,CP}$) for binary mixture in a nonideal
system
3.2.4 Rate model simulations and simulation parameters to find the transient-pattern mass
transfer zone lengths and the minimum dimensionless column length to reach the constant-
pattern state
3.2.5 Key dimensionless parameters or groups controlling the development of constant-
pattern isotachic train for a nonideal system90
3.3 Material and Methods
3.3.1 Materials
3.3.2 Separation of REEs using ligand-assisted displacement chromatography
3.4 Results and Discussion
3.4.1 Determination of model parameters
3.4.2 Verification of the Rate Model
3.4.3 Dynamic mechanism of LAD compared with conventional displacement and LAE
104
3.4.4 Effects of key dimensionless parameters on the development of a CPIT 108
3.4.4.1 Effects of the feed composition and feed volume on the minimum column length
for a nonideal system, L _{iso-nid} 108
3.4.4.2 Effects of nonlinear distribution coefficient and breakthrough cut on the minimum
column length for a nonideal system, L _{iso-nid}

3.4.4.3 Effects of the effective sorbent selectivity on the minimum column length for a
nonideal system, Liso-nid
3.4.5 Development of a general map to identify constant-pattern and transient-pattern
regions using dimensionless group analysis and rate model simulations
3.4.6 Verification of the minimum dimensionless column length curve and the general map
3.5 Conclusions
CHAPTER 4. CONSTANT-PATTERN DESIGN METHOD FOR THE SEPARATION OF
TERNARY MIXTURES OF RARE EARTH ELEMENTS USING LIGAND-ASSISTED
DISPLACEMENT CHROMATOGRAPHY
4.1 Introduction
4.2 Theory
4.2.1 Maximum loading fraction to develop an isotachic train for a ternary mixture in ideal
systems
4.2.2 Constant-pattern mass transfer zone length for ternary nonideal systems
4.2.3 Derivation of the yield equation for a given component in a ternary nonideal system.
4.2.4 Constant-Pattern Design Method
4.2.4.1 Productivity in LAD
4.2.4.2 Assumptions and limits for the Design Method
4.2.4.3 Breakthrough cut and yield on the minimum column length ϕmin and
productivity
4.3 Material and Methods 145

4.3.1 Separation of REEs using ligand-assisted displacement chromatography 145
4.4 Results and Discussion
4.4.1 Experimental verification of the design method for the separation of equimolar
mixtures with target yields for all three components
4.4.2 Effects of effective ligand concentration on the yield and productivity 152
4.4.3 Constant-pattern design to recover for a single component 155
4.4.4 Effects of pressure drop limit and band concentration limit on the productivity for the
target yield 157
4.4.5 Effects of the lowest effective sorbent selectivity on the productivity for the target
yield
4.4.6 Effects of feed composition on the yield and productivity
4.5 Conclusions
CHAPTER 5. CONCLUSION AND RECOMMENDATION 167
5.1 Conclusions
5.2 Recommendations
REFERENCES 171
APPENDIX A. SCALE UP AND ECONOMIC FEASIBILITY OF THE OVERALL PROCESS
APPENDIX B. MINIMUM COLUMN LENGTH TO FORM AN ISOTACHIC TRAIN FOR
BINARY SEPARATION IN DISPLACEMENT CHROMATOGRAPHY FOR AN IDEAL
SYSTEM
APPENDIX C. CONSTANT-PATTERN MASS TRANSFER ZONE LENGTH (L _{MTZ,CP}) FOR A
NONIDEAL SYSTEM

APPENDIX D. ESTIMATION OF MODEL PARAMETERS	192
APPENDIX E. PROCEDURE TO CALCULATE THE MINIMUM COLUMN LI	ENGTH FOR A
NONIDEAL SYSTEM	193
VITA	195

LIST OF TABLES

Table 1.1 Occurrence of rare earth elements in mineral sources and class F coal fly ash, normalized
weight percentage with respect to rare earth oxides [19,20]
Table 2.1 Chemical compositions of coal fly ash 43
Table 2.2 ICP-MS analysis of REE contents (ppm) of the coal fly ash
Table 3.1 Key dimensionless parameters controlling the development of a constant-pattern state
Table 3.2 Simulation parameters used for experimental data in Figures. 3.5 and 3.6
Table 3.3 Simulation parameters used for experimental data in Figure 3.6 100
Table 3.4 Simulation parameters used for Figure 3.7a. 102
Table 3.5 Simulation parameters used for Figures 3.7b and 3.7c. 103
Table 3.6 Comparison of displacement, LAD and LAE
Table 3.7 Simulation parameters used for experimental data in Figure 3.9. 109
Table 4.1 Parameters for design and rate model simulations 149
Table 4.2 Yield, purity, and productivity obtained from experimental results. Designs 1-3 are based
on the minimum target yields for recovering all components, while Design 4 is for the recovery of
only the major component, Nd, with a minimum target yield. The designs did not consider film
resistance and were based on 0.8 minimum target yield. The unit of productivity (P _R) is kilogram
per bed volume (m ³) per day151
Table 4.3 Parameters for design and rate model simulations 162
Table 4.4 Yield, purity, and productivity of each component obtained from rate model simulations
for different feed composition cases. The parameters used for the design and simulations were

listed in Table 2. Total feed concentration in all cases was 0.5 N. Dead volume in all cases was 2% of column volume. The unit of productivity (P_R) is kilogram per bed volume (m^3) per day. 164

Table A. 1 Estimated equipment list, size, and cost for 1 ton ash/day capacity (The estimated c	ost
was referred from vendors in Alibaba (https://www.alibaba.com/)1	83
Table A. 2 Economic analysis based on the chemical cost and processing cost (2,000 ton ash/d	ay)
	84
Table A. 3 Business case for large scale production 1	85

LIST OF FIGURES

Figure 1.1 Global production of rare earth elements (raw data obtained from USGS mineral
information [7])
Figure 2.1 Overview of the sequential separation process to recover REEs and other components
from coal fly ash
Figure 2.2 High purity products produced from coal fly ash via sequential separation process 37
Figure 2.3 XRD pattern of ash samples: (a) original ash, (b) ash after NaOH digestion, (c) residual
solids after acid dissolution. (Q: quarts, M: mullite, G: magnetite, S: hydroxyl-sodalite)
Figure 2.4 SEM images of (a) original ash, (b) enlarged part of ash, (c) ash after NaOH digestion,
(d) residual solids after acid dissolution, (e) Fe-enriched residual solids, and (f) EDS image of (e).
Figure 2.5 Schematic flowchart of the sequential separation process
Figure 2.6 Dissolution of Si (circle) and Al (triangle) in base during NaOH digestion - S/L mass
ratio was 1 to 2.5
Figure 2.7 Extraction efficiency of SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , CaO, and REEs in NaOH digestion and
acid dissolution steps
Figure 2.8 REEs Extraction efficiency and their concentrations in acid solution in the acid
dissolution step
Figure 2.9 Overview of cation exchange step (Step 3) and REEs concentration step (Step 4) to
recover REEs and other components from an acid solution containing Fe, Si, Al, Ca, and REEs
Figure 2.10 Effluent histories during acid loading and water washing steps (Step 3-1 and 3-2A)

Figure 2.11 (a) Scheme of Step 3-2B, (b) SEM-EDS images and (c) XRD data of the silica gel
produced from an acid effluent in Step 3-2B
Figure 2.12 Effluent histories during 2 M NaCl elution (Step 3-3A)
Figure 2.13 Effluent histories during DTPA elution (Step 3-4)
Figure 2.14 (a) Recovery of REEs in DTPA-REEs fraction and DTPA-Ca fraction collected in
Step 3-4; (b) Concentrations of Fe, Al, Ca, and total REEs in DTPA-REEs fractions; (c)
Enrichment factor of Fe, Al, Ca, and total REEs. The enrichment factors were calculated based on
the ratio of the normalized total REEs concentration in the DTPA-REEs fractions to that in original
ash 58
Figure 2.15 Effluent histories during 0.015 M EDTA elution of captured REEs in Step 4. A
synthetic feed solution containing 18 mN DTPA-Fe and 1 mN DPTA-Nd was loaded onto a Cu-
saturated bed (455 column volumes) and the captured Nd were eluted by loading 0.015M EDTA-
Na (pH 8.4)
Figure 2.16 Overall mass balance of major components and REEs after NaOH digestion, acid
dissolution, and magnetic separation steps
Figure 2.17 (a) Scheme of the sequential precipitation process (Step 3-3B) and SEM-EDS images
of obtained products, (b) Fe(OH) ₃ and (c) Al(OH) ₃
Figure 2.18 Schematic flow chart of silica gelation processes to produce silica gel and NaOH from
a sodium silicate solution
Figure 2.19 (a) SEM-EDS image, (b) XRD data, and (c) BED data of the silica gel produced from
sodium silicate solution in the gelation process
Figure 2.20 Flowchart of the large scale separation processes with the material mass balance of
major components

Figure 3.1 (a) Development of an isotachic train in an ideal system and (b) development of a
constant pattern isotachic train in a nonideal system in conventional displacement chromatography.
The sorbent affinity order from low to high: $C1 < C2 < Displacer$
Figure 3.2 Overview of research strategy to develop a map for constant-pattern and transient
pattern regions in nonideal LAD systems
Figure 3.3 (a) LAD operation; adsorption; reaction; and separation of REE1 and REE2; (b) Column
profiles showing the development of a constant-pattern isotachic train (CPIT) in LAD at t ₈ 80
Figure 3.4 Definition of mass transfer zone length L_{MTZ} and θ : (a) L_{MTZ} in column profiles and (b)
t _{MTZ} in effluent histories
Figure 3.5 Comparison of rate model simulations (dashed lines) with experimental data (solid
lines). (a) Separation of equimolar Sm and Nd (0.18 N each, 94 mL), (b) Separation of equimolar
Nd and Pr (0.18 N each, 94 mL) using 0.03 M EDTA-Na (pH 8.4) in a column (1.16 cm id. x 39.5
Nd and Pr (0.18 N each, 94 mL) using 0.03 M EDTA-Na (pH 8.4) in a column (1.16 cm id. x 39.5 cm L_c) packed with AG MP50
Nd and Pr (0.18 N each, 94 mL) using 0.03 M EDTA-Na (pH 8.4) in a column (1.16 cm id. x 39.5 cm L _c) packed with AG MP50
Nd and Pr (0.18 N each, 94 mL) using 0.03 M EDTA-Na (pH 8.4) in a column (1.16 cm id. x 39.5 cm L _c) packed with AG MP50
Nd and Pr (0.18 N each, 94 mL) using 0.03 M EDTA-Na (pH 8.4) in a column (1.16 cm id. x 39.5 cm L _c) packed with AG MP50
Nd and Pr (0.18 N each, 94 mL) using 0.03 M EDTA-Na (pH 8.4) in a column (1.16 cm id. x 39.5 cm L_c) packed with AG MP50
Nd and Pr (0.18 N each, 94 mL) using 0.03 M EDTA-Na (pH 8.4) in a column (1.16 cm id. x 39.5 cm L_c) packed with AG MP50
Nd and Pr (0.18 N each, 94 mL) using 0.03 M EDTA-Na (pH 8.4) in a column (1.16 cm id. x 39.5 cm L _c) packed with AG MP50
Nd and Pr (0.18 N each, 94 mL) using 0.03 M EDTA-Na (pH 8.4) in a column (1.16 cm id. x 39.5 cm L_c) packed with AG MP50
Nd and Pr (0.18 N each, 94 mL) using 0.03 M EDTA-Na (pH 8.4) in a column (1.16 cm id. x 39.5 cm L _c) packed with AG MP50
Nd and Pr (0.18 N each, 94 mL) using 0.03 M EDTA-Na (pH 8.4) in a column (1.16 cm id. x 39.5 cm L _c) packed with AG MP50

Figure 3.8 The dynamic column profiles of (a) Sm and Nd, and (b) Nd and Pr separations shown in Figure 3.5. A constant-pattern isotachic train (CPIT) of Sm and Nd is formed at 150 minutes. Figure 3.9 (a) Effects of feed compositions on the development of a CPIT in binary separations; (b) Distance-time diagram of case that has molar feed composition as 1 to 3; (c) Distance-time diagram of case that has molar feed composition as 3 to 1. Notice that LMTZ, 1 * and LMTZ, 2 * in (a) are represented in (b) and (c), respectively. For simulations, particle radius was doubled and flowrate was ten times reduced from Figure 3.5b in order to see the change of L_{MTZ} clearly.... 111 Figure 3.10 Effects of K_d on the minimum column length to develop a CPIT (Liso-nid) with respect to (a) t_{MTZ} and (b) L_{MTZ}. In simulations, L_c and the effective ligand concentration were changed but L_{feed} and other parameters were the same as those used in Table 3.7. Dashed vertical lines Figure 3.11 Effects of breakthrough cut (θ) on the dimensionless mass transfer zone length. Red dashed line indicates the same ϕmin for all cases. One of L_{MTZ}/L_c curves obtained from Fig. 3.10b Figure 3.12 Comparison of $L_{MTZ,CP}/L_{feed}$ at different αe values obtained from simulations (squares) with analytical solutions calculated using Eq. (3.18) (circles). In simulations, L_c was changed until $L_{MTZ,CP}$ was reached for each αe case. Other parameters were the same as those listed in Table 3.7. Figure 3.13 Effects of the effective sorbent selectivity on the dimensionless mass transfer zone length to develop a CPIT ($L_{iso-nid}$) with respect to (a) 1/kf * and (b) right hand side of Eq. (3.17a). Each curve corresponds to different αe when feed length L_{feed} is kept constant while the column length is varied. Other simulation parameters were the same as those in Table 3.7. Dashed vertical Figure 3.14 (a) General relationship among mass transfer coefficients, feed loading, effective sorbent selectivity, and L_{MTZ}/L_{feed} based on Eq. (3.18) and (b) General relationship between the dimensionless column length (ϕ) and the combined dimensionless groups of Lf, kf *, and αe , showing the minimum dimensionless column length (ϕmin) as the boundary between the Figure 3.15 Map identifying the general conditions to develop a constant-pattern state. The region above the ϕ min curve shows the conditions to develop a constant-pattern state while the region below the ϕmin curve indicates transient-pattern state. Points for each data in Figure. 3.5, 3.6, and 3.7 are expressed on the map to identify L_{MTZ} status. The correlation of ϕmin curve was Figure 4.1 Simulated dynamic column profiles for the separation of a ternary mixture of Sm, Nd, Figure 4.2 Research approach to develop constant-pattern design method for ternary separation. 132 Figure 4.3 (a) Separation of three components by loading a displacer and (b) corresponding band Figure 4.4 Definition of mass transfer zone length: (a) L_{MTZ} in column length and (b) t_{MTZ} in effluent histories. The shaded regions are the lengths of the mass transfer zones for a specific cut θ......135

Figure 4.5 General map identifying constant-pattern and transient pattern regions and (b) Effects of Yi and θ on Lfkf * values and corresponding ϕ values. The designed experiments (Design 1~4) Figure 4.6 Yield of a middle component from an isotachic band in (a) an ideal system and (b) a Figure 4.7 Yield correlation with combined dimensionless groups Lfkf * and selectivity weighted Figure 4.9 LAD separation experiments designed for the minimum target yield (a) 95%, (b) 80%, and (c) 70%, respectively, for (>99%) purity (θ : 0.05); and (d) comparison of the yield and productivity of the middle component (Nd) (dashed line) estimated from the design method with experimental results and literature data; Sm (round), Nd (triangle), Pr (square); Solid lines are effluent histories and dashed lines are simulation results. Literature data obtained from [30] is Figure 4.10 (a) LAD chromatograms using doubled ligand concentration for the same target yield as Design 2A (Fig. 9b) and (b) Comparison of the yield and productivity for different ligand concentrations; Sm (round), Nd (triangle), Pr (square); Solid lines are effluent histories and dashed Figure 4.11 (a) LAD chromatograms using different feed composition (Sm:Nd:Pr = 1:2.7:1.3) when designed a process for target yield of 80% for Nd with >99% purity (Design 4), (b) Yieldproductivity plot comparing different feed composition with equimolar composition feed mixture

Figure 4.12 Productivity plot versus column length and effective ligand concentration for the target
yield (80%) of the middle component (a) in Design 2A and (b) in Design 4, the different feed
composition case (1:2.7:1.3)
Figure 4.13 (a) Effects of the lowest sorbent selectivity on the loading fraction (Lf) and
dimensionless overall mass transfer coefficient ($kf *$) for the target yield of 80% for Nd with >99%
purity (Design 2A case) and (b) Effects of the lowest sorbent selectivity on the on the productivity
for target yield (80%)

Figure A. 1 SEM-EDS image of cenosphere collected in CaO removal process	181
Figure A. 2 Flowchart of the large scale separation processes with water balance	181
Figure A. 3 Detailed flowchart of the large scale processes	182

NOMENCLATURE

A_c	Cross sectional area of a column				
C _d	Effective ligand (displacer) concentration				
$c_{f,i}$	Feed concentration of component <i>i</i>				
c _p	Particle phase concentration in equilibrium				
D_b	Brownian diffusivity				
D_p	Intra-particle diffusivity				
E _b	Axial dispersion coefficient				
h _i	Nontrivial roots of the H-function of component <i>i</i>				
ID	Inner diameter of a column				
K _d	Nonlinear distribution coefficient				
K_f	Lumped mass transfer coefficient				
K _{se}	Size exclusion factor				
k_f	Film mass transfer coefficient				
k _{f,overall}	Overall mass transfer coefficient				
k_f^*	Dimensionless overall mass transfer coefficient				
L _c	Column length				

L_f	Loading fraction				
$L_{f,max,id}$	Maximum loading fraction for an ideal system				
L _{feed}	Column length occupied with feed in ideal system				
L _{iso-id}	Minimum column length to develop an isotachic train in an ideal system				
L _{iso-nid}	Minimum column length to develop a constant-pattern isotachic train in a nonideal system				
$L_{MTZ,CP}$	Constant-pattern mass transfer zone length				
L _{MTZ,T}	Transient pattern mass transfer zone length				
N_D	Ratio of intraparticle diffusion rate to convection rate				
N_{f}	Ratio of film mass transfer rate to convection rate				
Р	Phase ratio				
Peb	Peclet number in axial direction				
$P_{R,i}$	Productivity of component <i>i</i>				
ΔP_{max}	Pressure limit				
Q_f	Flow rate				
q_{max}	Column capacity				
q_p	Particle phase concentration in equilibrium				
R_p	Particle radius				
t _{MTZ,CP}	Constant-pattern mass transfer zone length with respect to elution time				
u_0	Interstitial velocity				

u _d	Displacer's shock wave velocity				
V _c	Column volume				
V_f	Feed loading volume				
x _i	Mole fraction of component <i>i</i> in the feed				
Y _i	Yield of component <i>i</i>				
$lpha^e_{i,j}$	Effective sorbent selectivity				
$lpha_{i,j}^{ligand}$	Ligand selectivity				
$\alpha_{i,j}^{sorbent}$	Sorbent selectivity				
β	Natural log of the ratio of maximum band concentration to minimum band concentration				
Υi	Selectivity weighted composition of component <i>i</i>				
ε_b	Bed void fraction				
$arepsilon_p$	Particle porosity				
ε_t	Total void fraction				
θ	Breakthrough curve cut used for mass transfer zone definition				
μ	Viscosity				
ϕ	Dimensionless column length; a column length relative to the minimum column length required to form an isotachic train in an ideal system				
ϕ_{min}	Minimum dimensionless column length to form a constant-pattern isotachic train in a non-ideal system				

ABSTRACT

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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 byproduct, was explored as a potential source for REEs. Novel separation and purification methods were developed for producing high purity REEs from class F coal fly ash.

First, a sequential separation process was developed to recover and concentrate REEs from class F 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 SiO₂ (>99%), Al(OH)₃ (>99%), and Fe(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 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 prestaurant 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 htransformation theory for an ideal system and the shock layer theory for a nonideal system. Strategetic combinations of the key dimensionless groups were developed to express a dimensionless mininum column length as a function of the combined dimensionless groups. Rate model simulations were used to find various minimum column lengths for developing constantpattern 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.

CHAPTER 1. INTRODUCTION

1.1 Background

1.1.1 Rare earth elements

Rare earth elements (REEs) include scandium, yttrium, and 15 elements in the lanthanide series. Because of their unique physicochemical properties, REEs have been widely used in high technology products such as catalysts, magnets, phosphors, high-performance motors, and turbines [1–3]. Although the total quantity of REEs that are in need is minute, they are decisive materials for high-tech industries [4–6]. Despite their significance, more than 85 % of the global REEs supply has been controlled by China as shown in Figure 1.1[7,8]. At present, the US has not produced any REEs and 78% of REEs consumption in the US was imported from China as of 2018 [7,8]. China has not only produced REEs raw materials but also manufactured REEs products, leading to control a whole REEs value chain [4]. Because of the growing demand of REEs and potential supply risk, the US Department of Energy regards REEs as critical materials, especially neodymium (Nd), dysprosium (Dy), terbium (Tb), europium (Eu), and Yttrium (Y) [8].

The supply challenges mainly result from low concentrations of REEs in ores and similar physical and chemical properties of REEs [1,5,9]. The minable REEs sources are limited in few locations in the world. Furthermore, purification of REEs is the most difficult step in the production process because of similar physical and chemical properties [10]. Currently, the solvent extraction method is extensively used in industries [11,12]. However, this method needs hundreds to thousands of mixer-settler units in series and in parallel and requires large amounts of acid and organic extractants [11]. For those reasons, the REEs production processes consume large amounts of chemicals and generate them as toxic wastes resulting in serious environmental issues. According to a report, commercial processes can produce up to 60,000 m³ of acidic waste gas and

200 tons of acidic waste water per ton of REE-oxide produced [13,14]. Furthermore, the current method is inefficient, not easily adaptable to different feed compositions, and not environmentally sustainable. Therefore, it is important to develop efficient, economical, and environmentally sound technologies to produce REEs in the US [4,11].





1.1.2 Coal fly ash as a potential source of REEs

Coal fly ash is a coal combustion byproduct, which consists of silicon dioxide (SiO_2) , aluminum oxide (Al_2O_3) , iron oxide (Fe_2O_3) , calcium oxide (CaO) and other metal oxides [15]. It has been reported that coal ash can contain more than 1,000 ppm of REEs, depending on coal sources and coal combustion types [8,16–18]. Specifically, coal and coal combustion byproducts

from near the Appalachian region were reported to contain 400-1,000 ppm of REEs [19]. The relative REEs concentrations with respect to rare earth oxides (REO) in US domestic fly ash is compared with those in ores in Table 1.1. The REO concentrations in ores often vary from 0.2 to 6 wt.% [20]. Coal fly ash produced in Kentucky regions also contain comparable amounts of REEs. Especially, the distribution of REEs showed that coal fly ash contains relatively more heavy rare earth elements (Eu-Y) compared to other ores.

In the US, more than 100 million tons of coal ash including 44 million tons of coal fly ash is produced annually [8,21]. However, only 54% of it has been recycled while the rest has been stored in ponds or landfills, posing a serious threat to the environment [8,22]. Since the year of 2000, half a billion tons of coal fly ash has been stored or landfilled across the US [23]. Given that the fly ash contains from 300 to 2,000 ppm REEs it is possible to meet the US domestic REEs demand for decades if a fraction of the REE in coal fly ash could be recovered and purified. Also, since the ash is already produced as small particles, a mining step that is difficult to get approved in the US can be avoided. Producing REE from coal fly ash is thus beneficial not only for reducing the potential supply risk but also for solving the waste disposal problems.

Element	Bastnasite,	Bastnasite,	Monazite,	Coal fly ash
	Mountain Pass,	Bayan Obo, Nei	Nangan,	from Kentucky,
	California, U.S.	Monggol,	Guangdong,	U.S.
		China	China	
La	33.2	23	23.35	17.89
Ce	49.1	50	42.70	35.78
Pr	4.34	6.2	4.10	4.14
Nd	12	18.5	17.00	15.86
Sm	0.789	0.8	3.00	3.35
Eu	0.118	0.2	0.10	0.32
Gd	0.166	0.7	2.03	2.58
Tb	0.0159	0.1	0.70	0.44
Dy	0.0312	0.1	0.80	2.91
Но	0.0051	trace	0.12	0.58
Er	0.0035	trace	0.30	1.61
Tm	0.0009	trace	Trace	0.39
Yb	0.0006	trace	2.40	1.47
Lu	0.0001	trace	0.14	0.04
Y	0.0913	0.5	2.40	12.6

Table 1.1 Occurrence of rare earth elements in mineral sources and class F coal fly ash, normalized weight percentage with respect to rare earth oxides [19,20]

1.2 Motivations and Objectives

Extracting REEs from coal fly ash has several advantages with respect to addressing in REEs supply problems as well as ash disposal problems. First, the feed stock cost is low, considering that coal power plants pay \$10 per ton of coal ash for the ash disposal in the US. Second, since ash was already generated as waste, the extraction process does not require mining sites nor mining processes, which would take more than 10 years for permission in the US [24]. Third, the average particle size of fly ash is less than 100 μ m, which is sufficiently small for the extraction processes. Furthermore, potential ash disposal problems can be solved given that ash spill by a dike broke at Tennessee resulted in causing serious environmental problems and took \$1 billion and 5 years to recover the surroundings [22].

Several studies have shown that the potential extraction methods for extracting REEs from coal fly ash [25–27]. However, since the concentration of REEs in fly ash is very low, the methods require the consumption of large amounts of chemicals. Thus, the economic feasibility of the methods in large scale still remains as an open question. Additionally, since the major components were extracted together with REEs, the separation of REEs from the major impurities are critical to recover REEs with high yield and high purity. However, the efficient separation of REEs from major components has not been studied extensively. Therefore, it is important to develop an efficient and economical extraction method to recover REEs. For this reason, the recovery of high-value byproducts from coal fly ash could lead to an advancement making process economically efficient.

Ligand-assisted displacement chromatography (LAD) is an efficient and environmentally benign method for purifying REEs. Ligands used in LAD are generally regarded as nontoxic materials [28]. Since the surface area per reactor volume is huge in the chromatography method, the mass transfer efficiency in LAD is orders of magnitude higher than the solvent extraction methods [12,29]. Furthermore, the column is fully utilized and the ligand-REEs complex ratio is almost close to one to one molar ratio in LAD, the ligand efficiency in LAD are orders of magnitude higher than those in the solvent extraction methods. The feasibility of the LAD process at preparative scale has been shown since the 1950s [30–38]. However, the dynamic mechanisms were not well understood. Since no design method considering mass transfer effects have existed till now, all the experimental works were performed by trial and error [29]. For this reason, the LAD method has not been considered for the use in large scale processes [12,39]. Therefore, it is important to understand the separation mechanisms of LAD and to develop a robust and scalable design to implement LAD into REEs purification processes.

This dissertation has three objectives. The first objective is to develop an efficient sequential separation process to recover crude mixtures of REEs from class F coal fly ash and to produce byproducts with high purity. The second objective is to develop a rate model to study the dynamic mechanisms of LAD and to find the general conditions to achieve binary LAD separations under constant-pattern states. The third objective is to develop a robust and scalable design for ternary REEs separations using the LAD and to understand the effects of key parameters on the yield and productivity.

1.3 Dissertation Outline

This dissertation is divided into two parts of studies: (1) the development of methods to extract REEs from class F coal fly ash and (2) the development of a design method of ligandassisted displacement chromatography for an efficient and environmentally benign REEs purification process. The first part is discussed in Chapter 2 and the second part is discussed in Chapter 3 and 4, respectively. In Chapter 2, sequential separation methods were developed to recover REEs from class F coal fly ash. Technical feasibility of the developed sequential separation process to extract REEs with other byproducts was discussed in a step by step manner. Major components of coal fly ash were also recovered as valuable byproducts to reduce the processing cost. REEs were extracted and recovered from coal fly ash, which can be a crude mixture of REEs in the purification process.

In Chapter 3, a detailed rate model is developed for LAD and is verified experimentally in order to study the dynamic mechanisms of LAD and to find key parameters and dimensionless groups controlling a constant-pattern state. The dynamic mechanism of LAD was compared with ligand-assisted elution chromatography and conventional displacement chromatography. The effects of the material properties, intrinsic parameters, operating parameters on the development of a constant-pattern state were discussed using a dimensionless group analysis. The key dimensionless groups on developing a constant-pattern were found and their general correlation was developed as a map.

In Chapter 4, a constant-pattern design method was developed based on the general map. To validate the design method, ternary REEs separations using LAD systems were conducted. This chapter also studies the effects of design parameters on the product yield, purity, and productivity. Different scenarios of targeting a single component or multicomponent were discussed using rate model simulations.

CHAPTER 2. SEPARATION METHODS TO RECOVER RARE EARTH ELEMENTS, SILICA, ALUMINUM HYDROXIDE, AND IRON HYDROXIDE FROM COAL FLY ASH

2.1 Introduction

In this chapter, a sequential separation process was developed to recover REEs, silica, aluminum hydroxide, and iron hydroxide from class F coal fly ash. To develop efficient REEs extraction processes, the REEs extraction mechanisms were studied from the literature review in Section 2.1.1. A brief overview of the developed processes was explained in Section 2.1.2. Some highlights were shown in section 2.1.3. The experimental methods and results of each step in the processes were shown in a step by step manner in Section 2.2 and 2.3, respectively.

2.1.1 Literature review of REEs extraction methods from coal fly ash

Several studies have been reported for extracting REEs from class F coal fly ash [1,8,27]. Direct acid leaching or ammonium sulfate leaching methods were found to be relatively simple and less inexpensive than ionic liquid or eutectic solvent leaching methods to extract ion-exchangable REEs on the surface of ash particles [1,27]. However, those methods showed high REEs extraction yields only when a feed has ion-exchangable REEs, such as fire clay. Because most REEs were in the glassy matrix of class F coal fly ash, those methods were not effective for coal fly ash [17,18,27].

Lin et. al. conducted physical separations and NaOH hydrothermal treatment for class F coal fly ash [40,41]. The physical separation steps including sieving and magnetic separations helped to enrich REEs by removing iron-rich fractions in ash. The following NaOH hydrothermal treatment removed the glassy matrix so that the concentrations of REEs were enriched in the

leftover solids by 3 times. However, 12 to 18% of REEs were lost in the physical separation step and methods to recover REEs from the leftover solids were not discussed.

Taggart et al. found that the REEs extraction efficiency of direct acid leaching (<40%) was lower than that of the two-step leaching process which includes a NaOH digestion step and followed by a nitric acid leaching step (50~85%) [8]. NaOH digestion helps to extract REEs by removing the glassy matrix but the REEs extraction yields can be varied from feed composition, coal sources, and acid leaching conditions.

Recently, King et al. reported that NaOH digestion and a subsequent acid leaching process using HCl can extract up to 85% of the REEs [24]. However, the required acid and base amounts were large since the solid to liquid volume ratio was 1 to 50 with 1 to 12 M HCl and 6.25 M NaOH, resulting in a high chemical cost. Also, the leached acid solution contains high concentrations of Al, Si, Fe, and Ca, which are orders of magnitudes higher than those of REEs. Furthermore, the hydrochloric acid leaching solution turned into a gel due to a high concentration of Si [42]. However, all those problems were not further discussed.

Since the concentrations of REEs are very low in fly ash and they are co-extracted with major components, a subsequent separation process after the leaching step is needed to recover REEs. However, the method for separating REEs from the other major components of coal ash (Si, Al, Fe, Ca) have not been reported in the literature. Therefore, it is a major goal of this study to develop an efficient separation process to recover REEs with high purity and high yield from class F coal fly ash.

Additionally, it should be mentioned that a process using NaOH digestion and acid dissolution is effective to dissolve REEs from class F fly ash. However, this process may not work

for class C fly ash because class C fly ash has high contents of CaO, which accelerates the formation of acid-insoluble calcium aluminosilicates, instead of sodium aluminosilicates [24,43].

2.1.2 Overview of the sequential separation process

A brief flow chart of the sequential separation process to recover REEs and major products. is shown in Figure 2.1. For effective extraction of REEs, coal fly ash first went through NaOH digestion step to dissolve silica and to form aluminosilicate zeolite structures. In next step, the separated solids were mixed with acid to dissolve REEs with the aluminosilicates, iron oxide, and calcium oxides. The extracted REEs were captured in the cation exchange column and separated from most of the major component. The captured REEs were sent to a REEs concentration column using a diethylenetriaminepentaacetic acid (DTPA) ligand elution. REEs were accumulated until the column is saturated so that they are concentrated in the following elution step. The residual solids were magnetically separated to collect Fe-riched solids. The high purity products produced by the developed processes are shown in Figure 2.2.



Figure 2.1 Overview of the sequential separation process to recover REEs and other components from coal fly ash


Figure 2.2 High purity products produced from coal fly ash via sequential separation process

2.1.3 Highlights

The highlights of this study are as follows. About 74% of REEs were extracted from class F coal fly ash by NaOH digestion and acid dissolution processes. Most (>99.9%) of the REEs extracted in the acid solution were captured in a cation exchange column. The captured REEs were efficiently separated from the major components (Si, Al, and Fe) using sequential NaCl and DTPA ligand elution. Most (>99%) of REEs were recovered as DTPA-REEs and the normalized average REEs concentration was enriched 284 times. The recovered REEs was redeposited and accumulated in another REEs concentration column. High purity silica gel (98-99.9%), Al(OH)₃ (>99%) Fe(OH)₃ (>95%) and Fe-enriched solids were produced during separation processes.

2.2 Experimental

2.2.1 Materials and characterization

The coal fly ash used in this study was generated at Miami Fort Generating Station (North Bend, Ohio). Sodium hydroxide (NaOH) and sodium chloride (NaCl) were purchased from Mallinckrodt Baker. Hydrochloric acid (HCl), nitric acid (HNO₃), copper sulfate (CuSO₄), erbium nitrate pentahydrate (Er(NO₃)₃·5H₂O), diethylenetriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA), and calcium hydroxide (Ca(OH)₂) were purchased from Sigma-Aldrich. Distilled deionized water (DDW) was obtained from a Millipore four stage cartridge system. The strong cation exchange resin, AG-MP50 resin (100-200 mesh), was purchased from Bio-rad. Millipore glass column (1.16 cm *ID* and 100 cm L_c) and Omnifit column (1 cm *ID* and 10 cm L_c) used for sorbent packing were purchased from VWR International.

Elemental analysis of major components was conducted using an Atomic Absorption Spectroscopy (AAS) (AAnalyst 300, Perkin Elmer) and Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy (SEM-EDS) (JCM-6000PLUS, JEOL). The REEs concentration was analyzed using an Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) (Element 2, Thermo Finnigan) with the standard addition method. For REEs elemental analysis, the ash samples (0.5 g) were dissolved in 30% hydrofluoric acid (10 g) to dissolve all components except the hydrocarbons. The solution is followed by a heat-up process to vaporize all the liquid so that white precipitates could be collected. The white precipitates were dissolved in a mixture of 33 % HCl (30 g) solution and 30 % hydrogen peroxide (5 g). The acid solution dissolving the white precipitates was diluted with 2% nitric acid and then analyzed to measure the concentrations of REEs using ICP-MS.

X-ray diffraction (XRD) patterns were obtained using Rigagku SmartLab X-Ray with CuKα radiation (40 kV, 40 mA). Chromatography experiments were performed using a ÄKTA explorer 100 (GE Healthcare). Effluent fractions were collected and analyzed by AAS. The average pore size and surface area of silica gel products was measured using BET analysis (NOVA 2200e, Quantachrome).

2.2.2 NaOH digestion of coal fly ash

The class F coal fly ash (20 g) was mixed with 10 M sodium hydroxide solution with a solid to liquid (S/L) mass ratio of 1 to 2.5 in a round-bottom flask. The flask was boiled in an oil bath at 120 °C with stirring and refluxing. After 4 hours of reaction, the flask was removed from the oil bath and cooled down to room temperature. The leachate, called sodium silicate solution, was collected via filtration and the solids were washed with DDW (200 g) to remove the NaOH solution remaining in the pore phase. Separated solids were collected and dried in an oven at 80 °C. The crystalline structure and elemental analysis of the solids after NaOH were conducted using XRD and SEM-EDS. The concentration of major components in the sodium silicate solution was measured using AAS. For a kinetic test, during the base digestion reaction, aliquots (0.5 mL) of the mixtures were taken periodically. The aliquots were filtered using syringe filters and then diluted to measure Si and Al concentration in the aliquots using AAS.

2.2.3 Acid dissolution to extract REEs

The filtered solids (19.6g) from the NaOH digestion step was mixed with 2 M HCl solution (196 g) with a solid to liquid (S/L) mass ratio of 1 to 10. The mixtures were sonicated for 30 minutes and then separated by centrifugation (6000 rpm, 10 min). The separated solution was collected, and the concentration of Fe, Si, Ca, and Al concentration was analyzed using AAS.

2.2.4 Magnetic separation of residual solids

The separated solids were washed with DDW (1 to 15 volume ratio). The washing steps were repeated until the solution became clear after the particle settled down. The washed solids were separated by putting a strong magnet on the beaker wall. The solids attracted by the magnet were separated from nonmagnetic particles. The separated magnetic fractions and nonmagnetic fractions were dried in an oven. The elemental analysis was conducted for the dried samples using SEM-EDS.

2.2.5 Cation exchange steps to capture REEs

A column was packed with AG-MP50 resins using a slurry packing method [ref]. The packed column volume was 93 mL (i.d.1.16 cm by L_c 88 cm). Before loading the acid solution, the column was saturated with Na⁺ ions by eluting with 1 M NaCl and washing with DDW for 2 column volume (CV).

To capture cations in the leaching solution, the acid leaching solution was loaded on the column. Erbium ions (Er^{3+}) were spiked (600 mg/kg) in the solution in order to track the REEs. A 50 mL of the leaching solution was loaded onto the column with superficial velocity 2 cm/min and then the column was washed with 1 column volume of DDW at the same velocity. The eluate was collected every 3 minutes to measure the concentration of major components (Si, Al, Ca, Er, and Fe) using AAS. The eluted solution was kept at 80°C overnight to form a silica gel.

The captured cations in the column were first eluted with 1 CV of 2 M NaCl solution at 5 cm/min of superficial velocity. Then, the column was further washed using 0.03 M DTPA-Na (pH 8.2) solution at 2 cm/min of superficial velocity. The eluate fractions were collected periodically to analyze the concentration of the Si, Al, Ca, Fe, and Er using AAS. The concentrations of REEs in the first four fractions and other fractions were measured using ICP-MS.

2.2.6 REEs concentration in a REEs concentration column

A cation exchange column was packed (1 cm i.d. and 8.5 cm L_c) with AG-MP 50 and prepared as a Cu-saturated column by loading copper sulfate (0.5 M). A synthetic mixture of DTPA-Fe (0.018 N) and DTPA-Nd (1 mN or 50 ppm) were loaded on the column at 12 cm/min until the column is saturated. After the column was washed with 1 column volume of DDW, Nd was eluted by loading 0.015 M EDTA-Na (pH 8.4) at 2.5 cm/min. The effluent histories were observed using the AKTA system with DAD detector (Agilent, G1315D).

2.2.7 Precipitation of iron hydroxide, and aluminum hydroxide from NaCl effluents

To precipitate Fe and Al, a sequential titration method was used. 10 mL of each eluate fraction collected from the 2 M NaCl elution step were combined. The sodium hydroxide solution (1 M) was added into the obtained eluate (60 mL) until the pH reached 12.5. The mixture was continuously stirred for 1 hour and then was separate from iron hydroxide (Fe(OH)₃) precipitates via filtration. Next, 1 M NaOH solution was slowly added into the filtered solution to precipitate Al at pH 8. After mixing for 1 hour, the white aluminum hydroxide (Al(OH)₃) precipitates were separated from the solution via filtration. The iron precipitates and aluminum precipitates were washed three times with excessive amounts of DDW and then were dried for characterization.

2.2.8 Silica gel precipitation and NaOH recovery from sodium silicate solution

The filtered sodium silicate solution (50 g) from the NaOH digestion step was diluted by half by adding DDW (50 g). CO_2 gas was bubbled into the sodium silicate solution at a flow rate of 26 mL/min for 1 hour. The precipitated silica gel was separated using centrifugation. The separated silica gel was re-suspended in DDW 100 g and the supernatant was decanted using centrifugation. This washing step was repeated two times to remove the excess Na⁺ ions left in the silica gel solid phase. The separated NaOH solution and the washed solution containing sodium carbonate (Na_2CO_3) was mixed with 10 grams of $Ca(OH)_2$ to precipitate $CaCO_3$ for 30 min. Then the solution was separated via centrifugation. The Ca concentration in the separated solution was measured using AAS and then the collected solution was titrated with 1 N HCl to measure the concentration of NaOH.

2.3 Results and discussion

2.3.1 Characterization of coal fly ash

The chemical composition of the fly ash used in this study was shown in Table 2.1. According to the XRF analysis, the major components were SiO₂, Al₂O₃, Fe₂O₃, and CaO. The ash composition represents a class F fly ash, where the sum of concentrations of silica, alumina, and iron oxide is greater than 85% [21,44,45]. As shown in Figure 2.3a, the X-ray diffraction pattern of the original ash indicated that the major minerals are mullite, magnetite, and quarts [46–48]. The SEM images in Figure 2.4a showed that ash consists of spherical particles which have a wide range of size distribution. The concentrations of typical rare earth elements (REEs) in the original ash are listed in Table 2.2. The total concentration of REEs is greater than 700 ppm, which could be a promising REEs source.



Figure 2.3 XRD pattern of ash samples: (a) original ash, (b) ash after NaOH digestion, (c) residual solids after acid dissolution. (Q: quarts, M: mullite, G: magnetite, S: hydroxyl-sodalite)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	Loss
									on
									ignition
wt.%	43.97	20.54	21.35	5.33	0.99	1.27	0.75	1.98	1.73

Table 2.1 Chemical compositions of coal fly ash

Table 2.2 ICP-MS analysis of REE contents (ppm) of the coal fly ash

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Yb	Sc	Y	Total
ppm	93	180	44	114	43	5	17	5	16	10	98	72	709



Figure 2.4 SEM images of (a) original ash, (b) enlarged part of ash, (c) ash after NaOH digestion, (d) residual solids after acid dissolution, (e) Fe-enriched residual solids, and (f) EDS image of (e).

2.3.2 Overview of the process to recover Si, Al, Fe, and REEs

An overview of the process flowchart is shown in Figure 2.5. First, coal fly ash is digested with 10 M NaOH solution (Step 1). The solids were separated from the NaOH solution, washed with DDW, and sent to the acid dissolution step. The NaOH and DDW solutions contained sodium silicates. Both solutions were mixed and sent to the gelation step to produce a silica gel and to recover NaOH (See section 2.3.9). In the acid dissolution step, major components of ash and REEs were dissolved using 2 M HCl in Step 2.

The acid solution containing Si, Al, Fe, Ca, and REEs was sent to a capture process, where the acid solution was loaded on a Na-saturated ion exchange bed (Step 3). Since the Si species were negatively charged, they do not adsorb on the cation exchanger bed and eluted as a high purity fraction. Then, the captured Al and Fe cations were eluted using a 2 M NaCl solution. Most (88%) of Fe and almost all Al in the acid solution were eluted in the same effluent fraction, which was sent to a sequential precipitation step to produce high purity Fe(OH)₃ and Al(OH)₃ (See Section 2.3.8).

The REEs captured in the cation exchanger bed and the rest of the Fe and some Ca were then eluted using a ligand solution 0.03 M DTPA. In the ligand elution step, Fe, REEs, Ca were eluted as DTPA-cation complex species. DTPA-Fe and DTPA-REEs fractions were sent to another REE concentration column to redeposit and accumulate REEs and Fe in the column (Step 4). The accumulated REEs were eluted as EDTA-REEs, which was the feedstock for the LAD purification step (Chapter 3 and 4). The residual solids were washed with water and magnetic separation was used to collect a Fe-enriched solid (Step 5).



Figure 2.5 Schematic flowchart of the sequential separation process

2.3.3 Step 1 - NaOH digestion

Since REEs are mostly in the aluminosilicate glassy phase, the REEs dissolution rate is limited by acid diffusion in the glassy phase [8,24]. Therefore, it is more efficient to eliminate the glassy matrix prior to the acid dissolution process.

In the NaOH digestion, amorphous silica and aluminosilicates dissolve into base solution and then quickly forms zeolite structures on the surface of ash particles [46–48]. The dissolved aluminum was converted to zeolite structures. Excessive silica species dissolves as sodium silicate in NaOH solution. The mechanisms of aluminosilicate dissolution and zeolite formation are shown below [47].

$$\begin{split} SiO_2 + 2 \, NaOH &\to Na_2 SiO_3 + H_2O \\ Al_2O_3 + 2 \, NaOH &\to 2Na_2 AlO_2 + H_2O \\ &3Al_2O_3 * 2SiO_2 + 10NaOH &\to 6NaAlO_2 + 2Na_2SiO_3 + 5H_2O \\ &6NaAlO_2 + 6Na_2SiO_3 + 8H_2O &\to Na_8Al_6Si_6O_{24}(OH)_2(H_2O)_2 \ (s) + 10 \, NaOH \end{split}$$

The AAS results indicate that 48% of SiO₂ was dissolved in the NaOH solution within 5 hours (Figure 2.6). The XRD pattern in Figure 2.3c of the particles showed that the newly formed sodium aluminosilicates have sodalite structures [47,49]. When compared with the surface of ash particles (Figure 2.4b), in the ash after NaOH digestion (Figure 2.4c), the particle surface showed a more irregular shape indicating the formation of small crystals, hydroxyl-sodalite structure, on the surface.

In the NaOH digestion step, REEs and iron oxides were left in the solid phase due to low solubility. Therefore, the solids separated from the NaOH solution were washed with DDW to remove excessive NaOH left in the pore phase and then sent to the acid dissolution step (Step 2) to extract the REEs. The separated NaOH solution containing sodium silicates was sent to the gelation step to produce silica gel and regenerate the NaOH solution (See Section 2.3.9).



Figure 2.6 Dissolution of Si (circle) and Al (triangle) in base during NaOH digestion - S/L mass ratio was 1 to 2.5.

2.3.4 Step 2 - Acid dissolution

The ash particles were mixed with 2 M HCl solution to dissolve REEs, aluminosilicates, and Fe₂O₃. Since the sodium aluminum silicates formed in the previous step easily reacted with the acid, the REEs could also easily diffuse into acid solution [24,27]. We chose HCl because it is less expensive than nitric acid, and it has been reported that HCl has a relatively higher REEs extraction yield [24].

The overall dissolution processes are explained below. Iron oxide, calcium oxide, and sodium aluminosilicates react with the hydrochloric acid. When the aluminosilicates are removed, the glassy matrix of ash particles is significantly reduced so that REEs can be easily extracted from the acid solution.

$$\begin{split} Na_8Al_6Si_6O_{24}(OH)_2(H_2O)_2(s) + 32HCl \\ \rightarrow 8NaCl + 6AlCl_3 + 6Si(OH)_3(OH)_2Cl + 4H_2O \\ Fe_2O_3(s) + 6HCl \rightarrow FeCl_3 + 3H_2O \\ CaO(s) + 2HCl \rightarrow CaCl_2 + H_2O \\ REE_2O_3(s) + 6HCl \rightarrow 2REE(Cl)_3 + 6H_2O \\ 2REE(OH)_3(s) + 6HCl \rightarrow 2REE(Cl)_3 + 6H_2O \end{split}$$

The S/L mass ratio was fixed at 1 to 10. The acid concentration was determined as the equivalent amount of acid to dissolve all aluminum silicates and iron oxides. Because the dissolution of aluminosilicates accelerates the extraction of major components, the concentration of the extracted components in acid solutions reached a plateau within 30 minutes at room temperature.

The extraction yields of major components (SiO₂, Fe₂O₃, Al₂O₃, and CaO) and REEs in acid solution were shown in Figure 2.7. The extraction yield for individual REE was shown in Figure 2.8. In acid dissolution step, 44% of SiO₂, 74% of Al₂O₃, and 24% of Fe₂O₃, and on average 74% of REEs were extracted in the HCl solution. The extraction efficiencies of REEs were close to that of Al, indicating that most of REEs were in aluminum phase. The results were consistent with the data from previous literature [24,41].

At this step, although the REEs extraction efficiency showed high yields, the solution also contains significant amounts of Si, Al, and Fe species. The concentration of REEs were orders of magnitudes lower than that of major components. Therefore, it is important to collect REEs without loss and to reduce the concentration of other components in further purification processes.



Figure 2.7 Extraction efficiency of SiO₂, Al₂O₃, Fe₂O₃, CaO, and REEs in NaOH digestion and acid dissolution steps



Figure 2.8 REEs Extraction efficiency and their concentrations in acid solution in the acid dissolution step

2.3.5 Step 3 – Cation exchange steps to capture REEs

To recover the extracted REEs with high yields and to separate from major components, the cation exchange processes were conducted as shown in Figure 2.9. There were several steps in the capture processes: loading, washing, and elution steps. In Step 3-1, the acid solutions were directly loaded on the column packed with a strong cation exchange column. In Step 3-2A, the column was washed with water to elute the nonadsorbing silica species. The collected effluent solution was heated up to form silica gel in Step 3-2B. In Step 3-3, the captured cations were eluted by 2 M NaCl and followed by 0.03 M DTPA solutions in Step 4. The eluted NaCl solution containing Al and Fe was sent to the sequential precipitation processes to produce Al(OH)₃ and Fe(OH)₃ at different pH (Step 3-3B). The eluted DTPA-REEs fractions were sent to another REEs capture column, which is saturated with Cu^{2+} , to accumulate REEs in Step 4. The accumulated REEs were eluted by forming EDTA-REEs complex species so that the concentrated REEs can be further purified into individual REEs using ligand-assisted displacement chromatography (LAD) process.

To scale up the processes, the operating conditions can be designed based on the dimensionless groups [50]. For instance, loading volume is calculated based on the loading fraction (L_f) , which is the ratio of the equivalent of total components to the total column capacity. The flowrate is calculated based on the dimensionless group N_D, which is the ratio of intraparticle diffusion rate to the convection rate. The definition of L_f and N_D can be found in Table 3.1.



Figure 2.9 Overview of cation exchange step (Step 3) and REEs concentration step (Step 4) to recover REEs and other components from an acid solution containing Fe, Si, Al, Ca, and REEs

To ensure REEs capture and to leave a sufficient column length for the elution steps, the loading volume was determined to have the total loaded cations take less than 60% of total capacity in the column. The concentrations of H^+ , Al^{3+} , Fe^{3+} , Ca^{2+} , and Si in the acid solution were 1 M, 0.28 M, 0.05 M, 0.06 M, and 0.31 M, respectively. Additionally, Er^{3+} (3.6 mM) was spiked in the acid solution to trace REEs using AAS. Based on the column capacity of REEs and Fe^{3+} (2 equivalent/liter), about half of the column volume of the acid solution was loaded and thus, the total cation concentrations took up 57% of the total column capacity.

The effluent histories of acid loading and water washing steps, Step 3-1 and 3-2A, were shown in Figure 2.10. Since the column was preloaded with Na⁺ ions, the trivalent cations, REEs³⁺, Fe³⁺, and Al³⁺, were easily captured in the column. Since the silica species is in the form of silicic

acid (Si(OH)₄) which is non-adsorbing, the Si species can be eluted by flushing with water [51]. According to the AAS results, the concentrations of Al^{3+} and Fe^{3+} were less than 1.5 ppm and neither Ca^{2+} nor Er^{3+} were detected. The ICP-MS results further confirmed that no REEs³⁺ were in the effluents. These results demonstrated that the silica species were effectively separated from other cations.



Figure 2.10 Effluent histories during acid loading and water washing steps (Step 3-1 and 3-2A)

Since the Si concentration was orders of magnitudes higher than other elements, it can form a high purity silica gel. In Step 3-2B, by increasing the temperature, the silica species spontaneously formed gel structures as shown in Figure 2.11a. The purity was higher than 99.9% based on the total cation concentrations. The SEM-EDS scan also showed only Si and O components, demonstrating the high purity (>99%) silica gel (Figure 2.11b). The XRD data (Figure 2.11c) of the silica gel showed a smooth peak between 20 and 30 degree, which is the distinctive peak of the amorphous silica gel [52,53].



Figure 2.11 (a) Scheme of Step 3-2B, (b) SEM-EDS images and (c) XRD data of the silica gel produced from an acid effluent in Step 3-2B

In Step 3-3A, the captured H⁺, Al³⁺, and Fe³⁺ ions were eluted by loading 2 M NaCl. Because of high concentrations of NaCl, the isotherms can be favorable to Na+ ions to displace divalent or trivalent cations according to the mass action law [54]. As a result, cations, which have lower sorbent affinity, elutes faster than other cations. In Figure 2.12, the pH curve shows that H+ ions elute first and then Al³⁺ and Fe³⁺ were eluted out. It was noted that the sorbent affinity of Ca²⁺ was higher than that of Al³⁺ or Fe³⁺ when the total cation concentrations were higher than 1 N [55,56]. As a result, Ca^{2+} ions were less readily displaced by Na ions compared to Fe^{3+} and Al^{3+} ions. According to the AAS, >99% of the captured Al^{3+} and 88% of the captured Fe^{3+} were eluted by loading 3 column volumes of NaCl solution. Only 2% of the captured Ca^{2+} were detected at the end of the fractions. Since REEs³⁺ have much higher sorbent affinity than that of Ca^{2+} , it was expected that the REEs³⁺ remained in the column [56]. As expected, AAS data showed that there was no Er^{3+} detection in all fractions. The ICP-MS data showed blank intensity for REEs, meaning that REEs were still captured in the column. The collected effluents containing Fe and Al were titrated with NaOH to precipitate Fe and Al in Step 3-3B, which will be further discussed in Section 2.3.8.



Figure 2.12 Effluent histories during 2 M NaCl elution (Step 3-3A)

In Step 3-4, the REEs³⁺, Ca²⁺, and the Fe³⁺ leftover in the column were effectively eluted using 0.03 M DTPA-Na solution via the ligand-assisted chromatography method. One can use either EDTA or DTPA for ligand elution but DTPA was chosen in this step because of its high solubility at low pH conditions. Since DTPA and cations can form complex species, they can migrate the column without adsorption when the solid phase is saturated with Na⁺ ions. The dynamic mechanisms of ligand-assisted chromatography are explained in detail in Section 3.4.3.

Since DTPA prefers Fe³⁺ to REEs to Ca²⁺, the elution order follows the ligand affinity from Fe to Ca, as shown in Figure 2.13. According to the AAS data, the spiked Er³⁺ peak indicated that DTPA-REEs were eluted together with DTPA-Fe and thus it was separated from most of DTPA-Ca. Based on the AAS data, the first four fractions, which have a high concentration of Fe and Er, were combined as DTPA-REEs fraction (48 mL) and the rest of the fractions were combined as a DTPA-Ca fraction. In order to confirm the recovery of REEs, DTPA-Fe and DPTA-Ca fraction were analyzed using ICP-MS. The results are shown in Figure 2.14a. Most of the REEs were coeluted with Fe so 92~99% of REEs were collected in the DTPA-REEs fractions. The overall mass balances between feed and the effluents were close to 100 % for most REEs. However, Nd and Pr had relatively large errors. This was probably caused by the inhomogeneity of samples that may have affected experimental errors during the dilution of the samples.

It should be noted that the concentrations of major components were significantly reduced (Figure 2.14b). When the total REEs concentration (41 ppm) was compared with the concentrations of Fe, Al, and Ca, the normalized total REEs concentration was increased by 226 times in the DTPA-REEs fractions as represented in Figure 2.14c. Since Al and Si were separated from previous steps, Fe and Ca were the main contributions of the total concentrations. The extracted REEs were 7% of the total cation concentrations in DTPA-REEs fractions because the extracted REEs in acid solution were successfully recovered without any significant losses.



Figure 2.13 Effluent histories during DTPA elution (Step 3-4)



Figure 2.14 (a) Recovery of REEs in DTPA-REEs fraction and DTPA-Ca fraction collected in Step 3-4; (b) Concentrations of Fe, Al, Ca, and total REEs in DTPA-REEs fractions; (c)
Enrichment factor of Fe, Al, Ca, and total REEs. The enrichment factors were calculated based on the ratio of the normalized total REEs concentration in the DTPA-REEs fractions to that in original ash.

2.3.6 Step 4 – REEs concentration in a REEs concentration column

The collected DTPA-REEs fraction can be transferred to another capture column, which is saturated with Cu^{2+} ions. According to the separation mechanism of ligand-assisted displacement chromatography (LAD), Cu^{2+} has higher ligand affinity and lower sorbent selectivity than that of REEs. As a result, the DTPA-Cu complex forms and REEs can be deposited in the column. Since H^+ or Fe³⁺ have higher ligand affinity and lower sorbent affinity than REEs, one can use those ions, alternatively.

Ideally, the continuous loading of DTPA-REEs can accumulate REEs in the capture columns until the column is saturated. However, the average concentration of REEs in DTPA fractions were 3.7 ppm, which is a very small amount to demonstrate the capture process at the laboratory scale. Therefore, a synthetic solution of DTPA-REEs fractions (DTPA-Fe/Nd) was used to show the feasibility of the capture process. The feed solution containing 50 ppm of Nd was loaded with 3 liters or 455 CV, which was presumably the volume resulted from processing 4 kg of ash. Due to a low concentration, the Nd was not detected during the feed loading so the loading was continued until the pre-loaded Cu was completely eluted out.

The effluent profiles in Figure 2.15 show the elution curve of EDTA-Nd. The EDTA-Nd band concentration was increased almost 15 times from the feed concentration. This suggests that the low concentration of REEs can be accumulated in the column and can be concentrated using EDTA elution, which is favorable for further LAD purification processes. Even if Ca²⁺ or Fe³⁺ can be captured together, REEs are separated in the LAD processes because EDTA-Fe elutes ahead of EDTA-REEs and EDTA-Ca elutes behind of EDTA-REEs in LAD, similar to the elution order in Figure 2.14.



Figure 2.15 Effluent histories during 0.015 M EDTA elution of captured REEs in Step 4. A synthetic feed solution containing 18 mN DTPA-Fe and 1 mN DPTA-Nd was loaded onto a Cu-saturated bed (455 column volumes) and the captured Nd were eluted by loading 0.015M EDTA-Na (pH 8.4).

2.3.7 Step 5 - Magnetic separation of residual solids

The residual solids after acid dissolution showed about 70% mass reduction from original ash, which is close to the expected results based on the extraction yields of major components within experimental errors. Magnetic separations were conducted to separate Fe-riched solids from others. Because the aluminum silicates glass matrix was removed, solids separated by a magnet had approximately 15 times higher concentration of Fe compared to that of Al or Si. The Fe content in the magnetically separated fraction was about 45% and this can meet the Fe ore commodity requirements so that the Fe-riched solids can be a promising source for Fe ores [57]. After magnetic separations, the mass of the residual solids was reduced to 16% of the original ash. The overall mass balance of major components and REEs were summarized in Figure 2.16.



Figure 2.16 Overall mass balance of major components and REEs after NaOH digestion, acid dissolution, and magnetic separation steps.

2.3.8 Precipitation of iron hydroxide, and aluminum hydroxide from NaCl effluents (Step 3-3B)

In Step 3-3B, Fe and Al can be precipitated as hydroxide salts at different pH by adding NaOH into the collected NaCl effluent solutions containing both Fe and Al as shown in Figure 2.17. Because of the different solubility at high pH, Fe(OH)₃ were first precipitated and separated from the solution at pH 12.5. The pH of the recovered solution was adjusted by adding 1 M HCl to precipitate Al(OH)₃ at pH 8. Both products have relatively high purity according to SEM-EDS as shown in Figure 2.17b and c. The purity of Fe(OH)₃ and Al(OH)₃ showed >95% and >99%, respectively. After precipitation, the leftover solution contains NaCl, which can be recycled for the separation processes.



Figure 2.17 (a) Scheme of the sequential precipitation process (Step 3-3B) and SEM-EDS images of obtained products, (b) Fe(OH)₃ and (c) Al(OH)₃

2.3.9 Silica gel precipitation and NaOH recovery from sodium silicate solution

The separated NaOH solution from the NaOH digestion step dissolved 48% of SiO_2 as sodium silicates. Since the NaOH digestion step requires large amounts of NaOH, efficient

separation processes need to be developed for the NaOH solution to recycle NaOH and to produce SiO₂ gel. Thus, a process to produce high purity silica gel and NaOH were developed as shown in Fig. 2.18. The separated sodium silicate solution and the solid washed solution from the washing step were combined and mixed with CO₂. The reaction between NaOH and CO₂ generated sodium carbonate and silica gel. The overall chemical reactions are shown below.

$$2NaOH(aq) + CO_2(g) \rightarrow Na_2CO_3(aq) + H_2O$$

 $Na_2SiO_3(aq) + CO_2(g) \rightarrow SiO_2(s) + 2Na^+ + CO_3^{2-}(aq)$



Figure 2.18 Schematic flow chart of silica gelation processes to produce silica gel and NaOH from a sodium silicate solution

By bubbling CO₂ gas in the sodium silicate solution, NaOH reacted with CO₂ to generate sodium bicarbonates. Since the pH of the solution decreased to 9 so that the silica gel was produced via the sol-gel process [58,59]. As shown in Figure 2.19a, the silica gel products had high purity (>98%). The XRD data in Figure 2.19b represents the amorphous structures of silica gel [58].

Furthermore, the surface area measured from BED analysis was 459 cm³/ml, showing a large surface area of common silica gel [58]. The results in Figure 2.19 demonstrate that high purity silica gel can be produced in the gelation process.

After separating the silica gel, the separated solution and the gel-washed solution contained sodium carbonates. By mixing with calcium hydroxide, sodium hydroxide was regenerated and calcium carbonate was precipitated.

$$Na_2CO_3 + Ca(OH)_2(s) \rightarrow NaOH(aq) + CaCO_3(s)$$

The separated NaOH solution was analyzed using AAS, confirming that there was no Ca left in the solution. Titrating the NaOH solution with 1 N HCl showed that 46% of the total NaOH used in the NaOH digestion step was recovered. According to the chemical reactions forming the sodium aluminosilicates, 47% of NaOH can be left in the solid phase while 53% of NaOH remained in the sodium silicate solution. Therefore, up to 88% of recovery efficiency of NaOH was achieved experimentally from the recoverable amount of NaOH remaining in the solution. The precipitated CaCO₃ can be a potential product or reused after calcination.



Figure 2.19 (a) SEM-EDS image, (b) XRD data, and (c) BED data of the silica gel produced from sodium silicate solution in the gelation process

2.3.10 Scale up of the overall process

As shown in previous sections, each unit operation from Step 1 to 5 and product producing steps can be combined as an overall process. For large scale processes, however, Ca extraction in acid dissolution is inefficient because it increases the required volume of a capture column and also requires a large elution volume of DTPA. Therefore, it is reasonable to remove Ca in CaO removal process before performing the NaOH digestion process so that the required volume of the capture column and DTPA solution. For CaO removal, ash is washed with HCl, where the amount of acid is equivalent to Ca equivalent. The washed ash is sent to the rest of the separation processes. By removing CaO before NaOH digestion, the capture column volume is reduced by 20% and the DTPA elution volume is reduced by 80% because the DTPA solution is mainly used for REEs elution. Additionally, it is assumed that all the extracted Fe and Al are separately eluted out using NaCl elution. The flowchart of an overall process in large scales is shown in Figure 2.20 with

material mass balance. The detailed process flowchart and the economic analysis of the overall process are shown in Appendix A.



Figure 2.20 Flowchart of the large scale separation processes with the material mass balance of major components

2.4 Conclusions

Sequential separation methods were developed to recover REEs from coal fly ash. Since most REEs were trapped in the aluminosilicates glassy matrix of ash particles the NaOH digestion step was first performed to assist efficient extraction of REEs in subsequent acid leaching. In the NaOH digestion step, 48% of silica was dissolved in 10M NaOH solution (1 to 2.5 S/L ratio) by removing the glassy matrix and also the aluminosilicates glassy matrix was converted into sodalite structures. In the subsequent acid dissolution step, REEs, Si, Al, Ca, and Fe were easily dissolved in 2 M HCl. The extraction yields of Si, Al, Fe, Ca, and REEs were 44%, 74%, 24%, 65%, and 74%, respectively. The similar yields of REEs and Al indicated that most of REEs were trapped in the aluminosilicates matrix.

The acid solution containing REEs and other major components were sent to a cation exchange step in order to recover REEs. By loading the acid solution into a capture column, >99.9% of Al, Ca, and REEs, were captured while Si species were selectively eluted out during feed loading and water washing steps. The captured Al and Fe ions were eluted by loading 2 M NaCl solutions. More than 99% of Al and 88% of Fe were eluted and produced as Al(OH)₃ and Fe(OH)₃ with the purity of >99% and >95%, respectively.

In the ligand elution step, the captured REEs, 22% of Fe, and 98% of Ca were eluted by loading 0.03 M DTPA-Na (pH 8.2). The elution results showed that most of DTPA-Fe and (>99%) DTPA-REEs were eluted together at the front of the DTPA breakthrough curve. The average concentration of the recovered REEs was 3.7 ppm, where the concentration ratio of REEs to total concentrations was increased 284 times compared to that ratio in original ash. The recovered DTPA-REEs was transferred to a REEs concentration column, which is saturated with Cu ions. Loading a large volume (455 CV) of a synthetic mixture of DTPA-Fe and DPTA-Nd and a

subsequent EDTA-Na elution showed the concentrated EDTA-Nd band, demonstrating the feasibility of the concentration step at large scale. The scale up of this process can be easily conducted by using dimensionless groups such as loading fraction and N_D , which is the intraparticle diffusion rate relative to convection rate.

For efficient and economical processes, major components of coal fly ash, SiO₂, Fe₂O₃, and Al₂O₃ were also extracted and produced as valuable byproducts with high purity and high yield. The sodium silicate solution was reacted with carbon dioxide gas to produce high purity (>98%) silica gel by adjusting the pH to 9. The leftover solution was mixed with calcium hydroxide to precipitate calcium carbonate and to recover NaOH, which was about 46% of the total NaOH used in the process. The NaCl effluents containing Fe and Al were sent to sequential precipitation process to produce Fe(OH)₃ and Al(OH)₃. By adding NaOH and HCl sequentially, Fe(OH)₃ and Al(OH)₃ were produced with the purity of >95% and >99%, respectively.

After acid dissolution, the residual solids were further treated with magnetic separations. A fraction collected from magnetic separations had high contents of Fe, which can meet the Fe ore grade. The mass of final residual solids, which were nonmagnetic fractions, were 16 % of the original ash. Overall, 84% of the ash contents were extracted and generated as high purity products, which contribute to reducing chemical costs in the processes.

CHAPTER 3. STUDY ON KEY PARAMETERS CONTROLLING A CONSTANT-PATTERN STATE OF LIGAND-ASSISTED DISPLACEMENT CHROMATOGRAPHY FOR SEPARATING RARE EARTH ELEMENTS

3.1 Introduction

The purification of REEs is the most challenging step in the production of REEs because most REE have similar physical and chemical properties [9,60]. Thousands of mixer-settler units are used in the purification of REE using two-phase liquid-liquid extraction [37]. The extraction method requires large amounts of acids, bases, extractants, and organic solvents, and it generates a large amount of wastes [12,14,60]. To produce 1 ton of REE oxide, 10 tons of concentrated acid, (31 wt.% HCl), 2-3 tons of sodium hydroxide, 100 tons of extractants, and 120 tons of organic solvent (kerosene) are required. Furthermore, 120 tons of waste water are discharged into the environment [11,14].

An alternative approach is to utilize chromatography for the purification of REEs, which does not require organic solvents or the separation of two immiscible liquid phases. It has orders of magnitude higher surface area per unit volume, resulting in a smaller processing volume and a smaller footprint than the extraction method. However, no chromatography sorbents with significant selectivity for REEs are available for production scale purification. Stationary phases with chelating functional groups have been developed for analytical applications [61–64]. However, the sorbents have limited stability and they are not economical for large scale purification of REEs [10].

Recently, ligand-assisted elution chromatography (LAE) based on titania and ethylenediaminetetraacetic acid (EDTA) was developed for the separation of REEs [10]. While titania does not have selectivity for REEs, many chelating agents (ligands) have significant selectivity for REEs. Prior to feed loading, the column was presaturated with EDTA. REEs adsorbed strongly on the EDTA-coated stationary phase due to the chelating reactions between REEs and EDTA. The EDTA solution was also used for REE elution. The reversible complexation of REEs with the EDTA in the mobile phase resulted in the desorption of REEs. The REEs with higher ligand affinity eluted earlier. Mixtures of Sm, Nd, and Pr were separated with high purity (>95%) and high yield (>95%) using either stepwise elution or linear-gradient elution [10]. Most of the EDTA used in the purification process can be recycled [37]. LAE is expected to have a much smaller footprint than the liquid-liquid extraction processes [10].

Ligand-assisted displacement chromatography (LAD) is the focus of this study, because it has higher ligand efficiency and sorbent capacity utilization. Spedding and Powell were the first to show the feasibility of LAD for producing three pure REE fractions. Citric acid or EDTA was used as the ligand and the columns were packed with a strong cation exchange resin with sulfonic acid functional groups [30,31,65]. Lindstrom et al. demonstrated that LAD could be used to separate mixtures of six REEs from rare earth ores [35]. Moore et al. found that a combination of EDTA and a resin with iminodiacetic acid functional groups can have a higher selectivity for heavy REEs (e.g. Er, Ho, Tb, and Gd) than the EDTA-cation exchange systems [37]. It was observed in the previous studies that the REE chromatograms in LAD were similar to conventional displacement chromatograms [37,66,67].

Formation of an isotachic train is a distinct feature of conventional displacement chromatography [68–71]. A column is presaturated with a weak presaturant. A feed mixture is loaded into the column. A displacer which has the highest sorbent affinity is used to displace the most strongly adsorbed component in the feed, which in turn displaces the component with a lower affinity. Such "chain" displacement results in separation of the solute bands with sharp boundaries

(or concentration waves). In an ideal system, an isotachic train is developed when all the solute bands are fully separated, and all the shock waves move at the same velocity (Figure 1a). In a nonideal system, an isotachic train is developed when all parts of the concentration waves are moving at the same velocity, showing "constant-pattern" (Figure 1b). In this study, we call an isotachic train for a nonideal system as a "constant-pattern isotachic train (CPIT)" to avoid any confusion with an isotachic train in an ideal system.



Figure 3.1 (a) Development of an isotachic train in an ideal system and (b) development of a constant pattern isotachic train in a nonideal system in conventional displacement chromatography. The sorbent affinity order from low to high: C1 < C2 < Displacer.
Figure 3.1 compares the development of an istotachic train in an ideal system with that in a nonideal system. Figure 3.1a shows an example of the formation of an isotachic train of two components (C1 and C2) in an ideal system. The column is pre-equilibrated with a presaturant (not shown in Figure 3.1), which has the lowest sorbent affinity. The displacer has the highest affinity for the sorbent. The affinity sequence is the following: displacer > C2 > C1 > presaturant. When the feed mixture is loaded onto the column, the solutes C1 and C2 in the feed adsorb at the top of the column, displacing the presaturant. The band of the weaker component (C1) is "rolled-up" because C1 is displaced by the stronger component (C2) during loading (t_1) . When the displacer is fed into the column, adsorbed C1 and C2 are both displaced by the displacer. The displaced solutes re-adsorbed in front of the displacer band and C1 are subsequently displaced by C2 (t_2 - t_5). Since the migration of all the band boundaries (or concentration waves) are caused by displacement of a lower affinity solute by a higher affinity solute, all the boundaries are sharp, as a result of "thermodynamic sharpening". Eventually, the solutes separate into successive pure bands with sharp boundaries, which migrate at the same velocity as the displacer front to form an isotachic train (t_6) .

In displacement chromatography for a nonideal system, the bands are separated as a result of displacement of a low-affinity solute by a high-affinity solute as in an ideal system. In addition, all the concentration waves are spread because of axial dispersion, film mass transfer, and intraparticle diffusion. Because of wave spreading, the bands partially overlap as shown in Figure 3.1b. The overlapping regions in the column are called the mass transfer zones (MTZ). Eventually, at t_7 , the thermodynamic sharpening effects counterbalance the wave spreading effects; all parts of the waves migrate at the same velocity. At this time, the length of MTZ becomes constant, called the "constant-pattern mass transfer zone length" or L_{MTZ, CP}. If all the concentration waves migrate

at the same velocity, the band shape remains constant as the bands migrate down the column. Thus, a "constant-pattern isotachic train" (CPIT) is observed at t_7 and t_8 in Figure 3.1b. Before the formation of the constant pattern waves at t_7 , the MTZ length continues to change during migration and it is called the "transient-pattern mass transfer zone length" or $L_{MTZ,T.}$ The analytical solution of the $L_{MTZ,CP}$ was derived for conventional displacement chromatography, and is discussed in section 3.2.3 [72,73].

After a CPIT forms, the shapes of the bands remain fixed as the concentration waves propagate further down the column. This means that any additional column length does not affect the purity or the yield of the products. Figure 3.1 shows that it takes a longer time and a longer column to develop a CPIT in a nonideal system than it takes to form an isotachic train in an ideal system.

Helfferich developed the "h-transformation" theory for LAD to calculate the minimum column length ($L_{c,iso}$) required to develop an isotachic train in an ideal system [74]. The minimum column length was calculated based on selectivity, feed composition, and feed length, which is the column length occupied by feed components at the end of loading. For a nonideal system, however, there is no general theory for predicting the minimum column length required for developing a CPIT. The parameters which control the formation of a CPIT are also unknown.

Knowing the minimum column length to develop a constant-pattern state is important for achieving high yields of high purity products, high sorbent productivity, and high ligand efficiency. If the column length is insufficiently long, the components do not fully separate, resulting in low yields of high purity products. If the column length is too long, a CPIT forms in the middle of the column. As a result, the remaining column is wasted, reducing the average sorbent productivity and ligand efficiency without increasing the yield. Since the conditions for developing the constant-pattern state were unknown, previous studies used a trial and error method to design LAD processes. Design and optimization of the numerous parameters by trial and error can be timeconsuming and costly. Each experiment can take a few days or a few weeks. Furthermore, the designs based on trial and error cannot be easily adapted to different feed compositions, column sizes, ligand concentrations, or flowrates.

In this study, we first develop a reliable rate model and simulations for nonideal systems to reduce the number of experiments in LAD design. Simulations can be used to predict effluent histories and column profiles when multiple variables are changed. They can also be used to gain fundamental understanding of displacement mechanisms. Furthermore, the model and simulations are useful for developing a method for finding the minimum column length and the general conditions required to achieve the constant-pattern state for a nonideal system. The general method is important because it is applicable to different feed conditions, adsorbents, ligands, solute properties, material properties, or system parameters. Only a few small-scale experiments are required for measuring the key parameters controlling a CPIT (see theory section). The minimum column lengths for the formation of a CPIT at different scales can be predicted from the general method without process simulations or experiments.

The specific objectives of this study are (1) to develop an efficient rate model and simulations for LAD in nonideal systems and to validate the model using experimental data, (2) to use the simulations to understand the separation mechanism of LAD and to elucidate the differences between LAD, LAE, and conventional displacement, (3) to develop key dimensionless groups controlling the mass transfer zone lengths in nonideal systems and to use the simulation to find the transition points from a transient state to a constant-pattern state, and (4) to develop a general theory for the conditions required to form a constant-pattern state in LAD.

An overview of the strategy to develop a general theory for finding the minimum column length to reach a constant-pattern state is summarized in Figure 3.2. The parameters in Figure 3.2 are defined in Table 3.1 and explained in detail in Theory. The goal is to develop a map which separates the constant-pattern region from the transient-pattern region. First, the conditions required to develop an isotachic train for binary mixture in an ideal system are found using local equilibrium analysis. Second, the key dimensionless parameters controlling the constant-pattern mass transfer zone length in a nonideal system are derived from the shock layer theory. Third, to bridge the gap between the two theories, transient-pattern mass transfer zone lengths are obtained from rate model simulations. Finally, the effects of the parameters for a nonideal system (listed in the top of Figure 3.2) on the transient-pattern and constant-pattern mass transfer zone lengths are analyzed using dimensionless groups to reduce the number of variables. Strategic combination of the dimensionless groups is developed to reduce the multi-dimensional solutions into a twodimensional solution, or a user-friendly map. This map can be used to find, without trial and error, the minimum column length and the general conditions required to achieve the constant-pattern state.



Figure 3.2 Overview of research strategy to develop a map for constant-pattern and transient pattern regions in nonideal LAD systems

Dimensionless			Tested
naramatars	Physical description	Definition	range of
parameters			parameters
x _i	Relative fraction of a component i among feed	$\frac{C_{f,i}}{\sum_{i=1}^{N} C_{f,i}}$	0.25 ~ 0.75
	components		
K _d	Weighted retention factor	$\frac{(1-\varepsilon_b)q_d}{\varepsilon_b c_d}$	64~460
$\alpha^{e}_{i,j}$	Sorbent selectivity	$\alpha_{i,j}^{sorbent}$	1.3 ~ 10
	Ligand selectivity	$\alpha_{i,j}^{iigana}$	
φ	Column length relative to the minimum column length to develop an isotachic train in an ideal system	$\frac{L_c}{L_{iso-id}}$	0.56~2.1
ϕ_{min}	The minimum column length	$\frac{L_{iso-nid}}{L}$	
	nonideal system relative to that for an ideal system	L _{iso} –id	
k_f^*	Overall mass transfer rate	$\left(\frac{1}{1}+\frac{1}{1}+\right)$	
	Convection rate	$\frac{\left(N_{f} Pe_{b}\right)^{-1}}{\frac{1}{15N_{D}}}$	
ND	Intraparticle diffusion rate	$\frac{K_{se}(1-\varepsilon_b)\varepsilon_p D_p L_c}{\varepsilon_1 u_s P^2}$	7.5 ~ 158
	Convection rate	e _b u ₀ n _p	
Peb	Axial dispersion rate	$\frac{u_0L_c}{\Gamma}$	616 ~ 9,052
	Convection rate	E _b	
θ	Fraction of breakthrough	C _{i,bot} C _{i,band}	0.01 ~ 0.15
		N	
L_{f}	Dynamic loading amount	$\frac{\sum_{i=1}^{N} C_{f,i} V_f}{q_{max} V_c}$	0.04 ~ 1
	Equilibrium capacity	inux · t	

Table 3.1 Key dimensionless parameters controlling the development of a constant-pattern state

3.2 Theory

3.2.1 Effective sorbent selectivity and separation mechanism for LAD

In conventional displacement chromatography, the feed component which has the lowest sorbent affinity elutes first, whereas in ligand-assisted displacement (LAD) the component which has the highest ligand affinity elutes first. The elution order of the feed components in LAD is determined by the sorbent selectivity relative to the ligand selectivity, which is defined as the effective sorbent selectivity (α^e) (Eq. (3.1)) [10]. If there is no sorbent selectivity, the effective selectivity is the inverse of the ligand selectivity.

$$\alpha_{i,j}^{e} = \frac{\alpha_{i,j}^{sorbent}}{\alpha_{i,j}^{ligand}} \approx \frac{1}{\alpha_{i,j}^{ligand}}$$
(3.1)

An example of the development of a CPIT in LAD for the separation of two REEs (REE₁ and REE₂) is shown in Figure 3.3. In this example, a cation exchange column is pre-equilibrated with a presaturant (P) and the counter ion of the ligand (L) is sodium (Na⁺). The presaturant should have a higher ligand affinity and a lower sorbent affinity than the REEs. Next a mixture of REE₁ and REE₂ is fed onto the column. Because the presaturant (P) has a lower sorbent selectivity than the REEs, it is displaced by REEs and a sharp boundary is formed between the presaturant zone and a mixed band of REEs near the column inlet. When a ligand (L-Na⁺) is fed into the column, it competes with the sorbent to form a ligand-REE complex (L-REE). The REE desorbed from the sorbent is then replaced by Na⁺, resulting in an apparent displacement of REE by Na⁺. Because the L-REE complex does not adsorb, the complex migrates downstream.





Figure 3.3 (a) LAD operation; adsorption; reaction; and separation of REE1 and REE2; (b) Column profiles showing the development of a constant-pattern isotachic train (CPIT) in LAD at

If the ligand has selectivity of REE₁ over REE₂, then the REE₁ band will migrate ahead of REE₂ band causing a separation between the two REE bands. When the L-REE₁ complex reaches the part of the column loaded with the presaturant (P), the ligand prefers to form a complex with the presaturant P. As a result, REE₁ is released from the ligand and readsorbs on the sorbent (Figure 3.3a). Similarly, as more ligand is fed into the column, the L-REE₂ complex will reach the boundary between the two REE bands and will release REE₂ to form a complex with REE₁. A similar mechanism takes place at the boundary between the REE₂ band and the displacer front. As this process continues, if the column length is sufficiently long, the two REEs are separated into two successive bands that move at the same velocity as two box cars of a train (Figure 3.3b). In nonideal systems, when all parts of waves move at the same velocity, a CPIT is developed in LAD (t₈ in Figure 3.3b) as that in conventional displacement chromatography (Figure 3.1b).

3.2.2 The minimum column length to develop an isotachic train of a binary mixture in an ideal system (L_{iso-id})

The minimum column length required to develop an isotachic train for an ideal system (L_{iso-id}) can be calculated from the wave velocities using local equilibrium analysis (Appendix B). The analysis is based on the following assumptions: first, the complexation reaction stoichiometry between REEs and a ligand is one-to-one. Second, the complexation reactions and the adsorption/desorption rates are much faster than the mass transfer rates such that the reactions are always in equilibrium and the effective selectivities defined in Eq. (3.1) are constant. Third, volume changes in the column are negligible.

For binary separations, L_{iso-id} is only a function of α^e and the feed length (L_{feed}), Eq. (3.2).

$$\frac{L_{iso-id}}{L_{feed}} = \frac{\alpha}{\alpha^e - 1} \tag{3.2}$$

The feed length is defined as the column length occupied by feed components at the end of loading for an ideal system.

$$L_{feed} = \frac{\sum_{i=1}^{N} c_{f,i} V_f}{q_{max} A_c}$$
(3.3)

where $c_{f,i}$ is the concentration of component *i* in the feed, V_f is the feed volume, q_{max} is the column capacity based on the total bed volume, and A_c is the cross-sectional area of a column. A detailed derivation of Eq. (3.2) is shown in Appendix B. Eq. (3.2) indicates that if the effective sorbent selectivity is very large, the minimum column length to form an isotachic train approaches the feed length in an ideal system. In other words, the isotachic train forms immediately upon introduction of the ligand. Eq. (3.2) indicates that for a binary system the minimum column length to form an isotachic train in an ideal system L_{iso-id} is independent of feed composition. In systems with three or more components, L_{iso-id}/L_{feed} is a function of both feed composition (x_i) and α^e [75]. For an equimolar feed mixture, the minimum column length for an ideal multicomponent system is controlled by the lowest selectivity pair. This study focuses on understanding the development of isotachic trains for binary feed mixtures.

Furthermore, the isotachic band concentrations are determined by the effective ligand (displacer) concentration (c_d), not by the feed concentrations. Since the bands are moving at the same velocity as the displacer velocity and if all components have the same q_{max} , the band concentrations are determined by the effective ligand concentration as seen in Eq. (3.4). Therefore, when L_{feed} and the C_d are the same, the effluent histories are identical.

$$u_{i} = \frac{u_{0}}{1 + P_{\Delta c_{i}}^{\Delta q_{i}}} = \frac{u_{0}}{1 + P_{\Delta c_{i}}^{q_{max}}} = u_{d} = \frac{u_{0}}{1 + P_{\Delta c_{d}}^{\Delta q_{d}}} = \frac{u_{0}}{1 + P_{\Delta c_{d}}^{q_{max}}}$$
(3.4)

where u_0 is the linear (interstitial) velocity, P is the phase ratio, ε_b is the bed void fraction, ε_p is the particle porosity, q_d is the column capacity (q_{max}) per bed volume in an ion exchange system, and $\Delta q_d / \Delta c_d$ (= q_d / c_d) is the change in the stationary phase concentration relative to the change in the mobile phase concentration across a shock wave in an ideal system.

3.2.3 Constant-pattern mass transfer zone length (L_{MTZ,CP}) for binary mixture in a nonideal system

For a nonideal system, the length of the mass transfer zone in terms of column length (L_{MTZ}) or elution time (t_{MTZ}) is defined by the cut θ , which is the ratio of a selected breakthrough concentration $C_{i,bot}$ relative to the plateau concentration $C_{i,top}$, Figure 3.4.

$$\frac{c_{i,bot}}{c_{i,band}} = \theta \tag{3.5a}$$

$$\frac{c_{i,top}}{c_{i,band}} = 1 - \theta \tag{3.5b}$$

$$t_{MTZ} = \left| t(C_{i,top}) - t(C_{i,bot}) \right| \tag{3.6a}$$

$$L_{MTZ} = u_d t_{MTZ} \tag{3.6b}$$

The wave center velocity of a CPIT in a non-ideal system is approximately the same as the displacer wave velocity (u_d) in an ideal system.

$$u_d = \frac{u_0}{1+K_d} \tag{3.7}$$

where K_d denotes a nonlinear distribution coefficient, which is defined as,

$$K_d = P\varepsilon_p + \frac{q_d}{\varepsilon_b c_d} \tag{3.8}$$



Figure 3.4 Definition of mass transfer zone length L_{MTZ} and θ : (a) L_{MTZ} in column profiles and (b) t_{MTZ} in effluent histories

When a CPIT is developed, the constant-pattern mass transfer zone length $L_{MTZ,CP}$ in the column can be estimated from the elution time $t_{MTZ,CP}$ in the effluent history. Analytical solutions for $L_{MTZ,CP}$ or $t_{MTZ,CP}$ in conventional displacement chromatography were previously derived in the literature, as shown in Eq. (3.9) [72,73]. These analytical solutions are based on the assumptions that the adsorption and desorption waves in the mass transfer zone are symmetric and the mass transfer coefficients of the two components are the same.

$$L_{MTZ,CP} = \left[\frac{E_b(1+K_d)}{u_0 K_d} + \frac{u_0}{K_f(1+K_d)}\right] \left(\frac{\alpha+1}{\alpha-1}\right) \ln \left|\frac{1-\theta}{\theta}\right|$$
(3.9a)

$$t_{MTZ,CP} = u_d L_{MTZ,CP} = \left[\frac{E_b (1+K_d)^2}{u_0^2 K_d} + \frac{1}{K_f} \right] \left(\frac{\alpha+1}{\alpha-1} \right) ln \left| \frac{1-\theta}{\theta} \right|$$
(3.9b)

where E_b denotes axial dispersion coefficient, α denotes the sorbent selectivity between the adjacent components, the lumped mass transfer coefficient (K_f) is defined in a system that the driving force for mass transfer is based on the difference in the concentrations of the solid phase.

$$\frac{\partial q_p}{\partial t} = K_f \left(q_p^* - q_p \right) \tag{3.10}$$

where q_p is the average particle phase concentration, and q_p^* is the particle phase concentration in equilibrium with the mobile phase concentration.

To relate the mass transfer coefficient (K_f) with the parameters in the rate model simulations, we employ an overall mass transfer coefficient $(k_{f,overall})$ in the linear driving force model based on the concentration difference in the mobile phase (c) [76].

$$\frac{\partial q_p}{\partial t} = k_{f,overall}(c - c^*) \tag{3.11}$$

where $k_{f,overall}$ is the overall mass transfer coefficient, c* is the mobile phase concentration in equilibrium with the average particle phase concentration q_p , and c is the mobile phase concentration. Note that two different mass transfer coefficients, the overall mass transfer coefficient $k_{f,overall}$ and the lumped mass transfer coefficient (K_f), can be related at a constantpattern state as shown below [77].

$$\frac{1}{k_{f,overall}} = \frac{1}{K_f} \frac{c_d}{q_{d,p}}$$
(3.12)

where $q_{d,p}$ is the particle phase concentration in equilibrium with the mobile phase concentration of a displacer. The $k_{f,overall}$ for a linear isotherm system can be expressed in terms of the dimensionless groups related to the rates of film mass transfer, axial dispersion, and intraparticle diffusion (Appendix C) [76].

$$\frac{1}{k_{f,overall}} = \left(\frac{PL_c}{u_0}\right) \left(\frac{1}{N_f} + \frac{1}{Pe_b} + \frac{1}{15N_D}\right)$$
(3.13)

where N_f is a dimensionless group defined as the ratio of the film mass transfer rate to the convection rate, Pe_b is the Peclet number for the axial direction, the ratio of axial convection rate to axial dispersion rate, and N_D is a dimensionless group defined as the ratio of the intraparticle diffusion rate to the convection rate [78]. Notice that for low Reynolds number (<1), Eq. (3.14b) can be further simplified using the Chung and Wen correlation ($E_b = 10\varepsilon_b R_p u_0$) [79].

$$N_f = \frac{3L_c}{R_p} \frac{(1-\varepsilon_b)k_f}{\varepsilon_b u_0}$$
(3.14a)

$$Pe_{b} = \frac{u_{0}L_{c}}{E_{b}} = \frac{u_{0}L_{c}}{10\varepsilon_{b}R_{p}u_{0}} = \frac{L_{c}}{10\varepsilon_{b}R_{p}}$$
(3.14b)

$$N_D = \frac{K_{se}(1-\varepsilon_b)\varepsilon_p D_p L_c}{\varepsilon_b u_0 R_p^2}$$
(3.14c)

where K_{se} is size exclusion factor, ε_b is bed void fraction, ε_p is the particle porosity, D_p is the intraparticle diffusion coefficient, R_p is the particle radius, and k_f is film mass transfer coefficient.

The dimensionless constant-pattern mass transfer zone length is derived as seen in Eq. (3.15). The detailed derivation of Eq. (3.15) is explained in Appendix C.

$$\frac{L_{MTZ,CP}}{L_c} = \left[\frac{1}{Pe_b} + \frac{1}{15N_D} + \frac{1}{N_f}\right] \left(\frac{\alpha^e + 1}{\alpha^e - 1}\right) \ln \left|\frac{1 - \theta}{\theta}\right|$$
(3.15a)

$$\frac{t_{MTZ,CP} u_0}{L_c} = K_d \left[\frac{1}{Pe_b} + \frac{1}{15N_D} + \frac{1}{N_f} \right] \left(\frac{\alpha^e + 1}{\alpha^e - 1} \right) \ln \left| \frac{1 - \theta}{\theta} \right|$$
(3.15b)

Here, we define the dimensionless overall mass transfer coefficient (k_f^*) as expressed in Eq. (3.16). When Eq. (3.16a) is substituted into Eq. (3.13), the relationship between k_f^* and $k_{f,overall}$ can be found.

$$\frac{1}{k_f^*} = \frac{1}{Pe_b} + \frac{1}{15N_D} + \frac{1}{N_f}$$
(3.16a)

$$\frac{1}{k_f^*} \approx \frac{1}{Pe_b} + \frac{1}{15N_D}, \text{ if film resistance is negligible}$$
(3.16b)

Based on the definition of the dimensionless overall mass transfer coefficient (k_f^*) , Eq. (3.15) can be simplified into Eq. (3.17).

$$\frac{L_{MTZ,CP}}{L_c} = \frac{1}{k_f^*} \left(\frac{\alpha^e + 1}{\alpha^e - 1} \right) ln \left| \frac{1 - \theta}{\theta} \right|$$
(3.17a)

$$\frac{t_{MTZ,CP} u_0}{L_c} = \frac{K_d}{k_f^*} \left(\frac{\alpha^e + 1}{\alpha^e - 1} \right) \ln \left| \frac{1 - \theta}{\theta} \right|$$
(3.17b)

For ideal systems, the minimum column length to form an isotachic train L_{iso-id} can be calculated from the feed length L_{feed} and the effective sorbent selectivity, Eq. (3.2). One can choose L_{feed} for an ideal system as the characteristic length to make the $L_{MTZ,CP}$ for a non-ideal system in Eq. (3.17a) into a dimensionless group, yielding Eq. (3.18).

$$\frac{L_{MTZ,CP}}{L_{feed}} = \frac{1}{k_f^* L_f} \left(\frac{\alpha^e + 1}{\alpha^e - 1} \right) \ln \left| \frac{1 - \theta}{\theta} \right|$$
(3.18a)

$$\frac{L_{MTZ,CP}}{L_{feed}} = \frac{1}{k_f^* L_f} \left(\frac{\alpha^e + 1}{\alpha^e - 1}\right) \beta$$
(3.18b)

where β in the natural log of the ratio of upper boundary to lower boundary (=ln $\left|\frac{1-\theta}{\theta}\right|$), the ideal loading fraction (L_f) is defined as the ratio of the feed length for an ideal system to column length.

$$L_f = \frac{L_{feed}}{L_c} \tag{3.19}$$

The dimensionless constant-pattern mass transfer zone length $L_{MTZ,CP}/L_{feed}$ in Eq. (3.18) has an explicit dependence on α^{e} , L_{f} , and k_{f}^{*} .

3.2.4 Rate model simulations and simulation parameters to find the transient-pattern mass transfer zone lengths and the minimum dimensionless column length to reach the constant-pattern state

A detailed rate model was developed to simulate LAD. The following assumptions are made to take into account the complex mechanisms in the rate model. First, the complexation reactions between the ligand and REEs and the adsorption/desorption reactions can be assumed to be in equilibrium, such that the effective sorbent selectivity, Eq. (3.1), is valid and is a constant for each solute pair [10]. For such systems, the constant separation factor isotherm model and the detailed general rate model equations developed previously can be used. The assumptions used to derive the general rate equations, boundary conditions, and numerical solution methods for solving the coupled differential and algebraic equations were reported previously [50,80]. Pore diffusion is assumed to be the major mechanism for intra-particle diffusion in the rate model. The Chung and Wen correlation is used to estimate the axial dispersion coefficient and Wilson and Geankoplis correlation is used to estimate the film mass transfer coefficient [79,81].

The constant separation factor isotherm model is equivalent to the multi-component Langmuir isotherm model if all the components have the same maximum adsorption capacity. It is also equivalent to the multicomponent mass-action isotherm model for monovalent ion exchange. To take into account the stoichiometry of ligand reactions with ions of different valences, all the concentrations in the mobile phase and the stationary phase are expressed in equivalents per liter. The isotherm for component *i* is shown in Eq. (3.20)

$$q_{i} = \frac{q_{max}\alpha_{i,ref}^{e}c_{p,i}}{\sum_{j=1}^{N}\alpha_{j,ref}^{e}c_{p,j}}$$
(3.20)

where q_{max} is the column capacity (mequiv./mL bed volume), $C_{p,i}$ is the concentration of component *i* in the stationary phase, and $\alpha_{i,ref}^{e}$ is the effective separation factor that can be defined according to Eq.(3.1) as follows.

$$\alpha_{i,ref}^{e} = \frac{q_i c_{p,ref}}{c_{p,i} q_{ref}} = \frac{\alpha_{i,ref}^{sobent}}{\alpha_{i,ref}^{ligand}}$$
(3.21)

The presaturant was chosen as the reference component, where $\alpha^{e}_{ref,ref}$ is 1. The solutes with larger effective sorbent selectivity $\alpha^{e}_{i,ref}$ elute later.

The rate model and simulations were first verified with experimental data. Verified simulations were then used to find the transient-pattern mass transfer zone length $L_{MTZ,T}$ and the constant-pattern mass transfer zone length $L_{MTZ,CP}$ in nonideal systems. In a nonideal system, the minimum column length to develop a constant-pattern isotachic train ($L_{iso-nid}$) in the column effluent is longer than that for an ideal system (L_{iso-id}). The value of $L_{iso-nid}$ depends on material properties, intrinsic parameters, feed loading, and flowrate.

A dimensionless column length (ϕ) is defined by using L_{iso-id} as the characteristic length.

$$\phi = \frac{L_c}{L_{iso-id}} \tag{3.22}$$

The ϕ also corresponds to a loading fraction (L_f) for a given column length. For binary separation, the following relation can be derived from Eqs. (3.2) and (3.22).

$$L_f = \frac{L_{feed}}{L_c} = \frac{L_{feed}/L_{iso-id}}{L_c/L_{iso-id}} = \frac{(\alpha^e - 1)/\alpha^e}{\phi}$$
(3.23)

The minimum dimensionless column length to develop a CPIT (ϕ_{min}) is defined below.

$$\phi_{min} = \frac{L_{iso-nid}}{L_{iso-id}} \tag{3.24}$$

If the dimensionless column length ϕ is greater than ϕ_{min} , a CPIT is formed within the column. If the dimensionless column length ϕ is less than ϕ_{min} , the column length is too short to reach the constant-pattern state.

3.2.5 Key dimensionless parameters or groups controlling the development of constantpattern isotachic train for a nonideal system

The development of a CPIT in a non-ideal system is affected by the key parameters that are listed in the first row in Figure 3.2. These parameters were combined to form the dimensionless parameters or dimensionless groups in Table 3.1. The dimensionless parameters which affect the minimum column length to develop a CPIT (L_{iso-id}), Eq. (3.2), and the constant-pattern mass transfer zone length ($L_{MTZ,CP}$), Eqs.(3.17) and (3.18), include the following: feed composition (x_i), effective sorbent selectivity (α^e), dimensionless overall mass transfer coefficient (k_f^*), nonlinear distribution coefficient (K_d), and loading fraction (L_f). The effects of the dimensionless parameters on the development of a CPIT were studied using rate model simulations. The range of the dimensionless parameters studied are also listed in Table 3.1.

3.3 Material and Methods

3.3.1 Materials

Neodymium (III) nitrate hexahydrate (Nd(NO₃)₃·6H₂O), samarium (III) nitrate hexahydrate (Sm(NO₃)₃·6H₂O), praseodymium (III) nitrate hexahydrate (Pr(NO₃)₃·6H₂O), copper sulfate pentahydrate (CuSO₄·5H₂O), and ethylenediaminetetraacetic acid (EDTA) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl), sodium hydroxide (NaOH) were purchased from Mallinckrodt Baker. Distilled Deionized Water (DDW) was obtained from a Millipore filter system. The strong cation exchange resin, AG-MP50 resin (100-200 mesh), was purchased from Bio-rad. Millipore glass columns (1.16 cm *ID* x 50 cm L_C) used for sorbent packing were purchased

from VWR international. Chromatography experiments were performed using a ÄKTA explorer 100 (GE Healthcare). A diode array detector (Agilent 1260 infinity II) was attached to the column outlet to monitor effluent absorbance at multiple wavelengths. The absorbance of each component was monitored at 700 nm, 575 nm, 404 nm, and 444 nm for Cu, Nd, Sm, and Pr, respectively. When Nd is the first REE band in the effluent, the deconvolution of Nd and Cu peaks was done by subtracting the Cu absorbance at 575 nm, which is calculated based on the absorbance at 700 nm, from the total absorbance at 575 nm.

3.3.2 Separation of REEs using ligand-assisted displacement chromatography

Before packing the column, the resins were soaked in DDW and sonicated for an hour to remove air bubbles and impurities in the particle pore phase. After the resins settled down, the solution was dumped out to remove impurities and fines. This washing step was repeated for several times. The washed resin was packed in a column for pretreatment. The column was washed with 5 column volumes of 1 M NaOH, 1M HCl, and DDW, sequentially to remove any impurities. The column was then unpacked, and the pretreated resins were recollected. Two Millipore column was packed again with the pretreated resins using a slurry packing method. The column was pre-equilibrated with Cu^{2+} by loading 0.1 M CuSO₄ solution (5 mL/min) until the Cu breakthrough curve appeared. The column was then flushed with DDW to remove excess ions in the mobile phase until the conductivity dropped below 0.005 mS/cm. The packed column sizes were 1.16 cm (*ID*) x 39.5 cm (*L_c*), and 1.16 cm (*ID*) x 44.0 cm (*L_c*), respectively.

For parameter estimation, the separation of equimolar mixture of Sm and Nd, and Nd and Pr was carried out. The column (39.5 cm L_c) pre-equilibrated with Cu²⁺ was fed with 94 mL of the feed solution containing equimolar mixture of Sm and Nd (0.06 M each) at 2 mL/min. The ligand solution, EDTA-Na, was prepared by dissolving the calculated amount of EDTA and sodium

hydroxide in DDW and then titrating to pH 8.4 after diluting the solution into a certain volume so that the final concentration of the EDTA is 0.03 M. After feed loading, 0.03 M EDTA-Na (pH 8.4) was fed into the column at 2 mL/min. After REEs were fully eluted, the column was saturated with Na⁺ ions. Thus, the column was regenerated by loading 0.1 M CuSO₄ solution. The LAD experiment was repeated with the feed solution containing 0.06 M Nd and Pr at the same condition.

To verify the formation of a constant pattern isotachic train, binary mixture separations were tested using a column (44 cm L_c) pre-equilibrated with Cu²⁺. The binary equimolar mixture containing 0.05 M Nd and Pr was fed into the column and then eluted with 0.03 M EDTA (pH 8.4). The feed loading volume and flowrates were varied for each run: (a) 99.8 mL and 1 mL/min, (b) 91.8 mL and 1.8 mL/min, (c) 84.8 mL and 1.9 mL/min, (d) 82.4 mL and 2.0 mL/min, and (e) 65.8 mL and 2.5 mL/min, respectively. After REEs were fully eluted, the column was regenerated to Cu²⁺ form by flushing with 0.1 M CuSO₄ and followed by DDW.

3.4 Results and Discussion

3.4.1 Determination of model parameters

To simulate LAD experiments using the constant separation factor isotherm, the effective sorbent selectivity, effective ligand concentration, sorbent capacity, Brownian diffusivity, and intraparticle diffusivity must be determined. Column parameters including column length, bed void, particle porosity, and dead volume are also required. In cases where the column capacity (q_{max}) is the same for all components, the constant separation factor isotherm is equivalent to the widely used multi-component Langmuir isotherm [54,82]. The constant separation factor isotherm has the added benefit of requiring fewer adsorption parameters (a single q_{max} and $\alpha_{i,ref}^{e}$ for each component) than the multi-component Langmuir isotherm (a_i and b_i for each component). This allows for accurate estimation of parameters with only a few experiments. Additionally, the

simulation time required for the constant separation factor isotherm is shorter than that required for the multi-component Langmuir isotherm.

Some parameters for the rate model simulations were estimated from the experimental data in Figures 3.5a and 3.5b, which show the separation of an equimolar binary mixture of Sm and Nd, and Nd and Pr, respectively. The column was pre-saturated with Cu^{2+} and EDTA-Na solution was used as a ligand displacer for both experiments. Since EDTA prefers Cu^{2+} to the REEs, Cu^{2+} band (not shown) eluted ahead of the REE bands. The elution order of REEs, from Sm to Nd to Pr, followed the affinity sequence of the REEs with the ligand.

Simulation parameters, listed in Table 3.2., were estimated as follows. The bed void fraction (ε_b) and the particle porosity (ε_p) were measured using pulse test methods [83]. The ligand selectivities for Pr, Nd, and Sm were available from the literature [10]. Since the sorbent does not have selectivity for REEs, the effective sorbent selectivity for REEs were assumed to be the inverse of the ligand selectivities, Eq. (1). The effective sorbent selectivity $\alpha_{Sm,Nd,}^e$ and $\alpha_{Nd,Pr}^e$ were found to be 3.2 and 1.8, respectively.

The values of Brownian diffusivities D_b for all REEs and ligand-REE complexes were assumed to be the same as that of La reported in the literature [10]. Because all the REEs have similar physical properties, the pore diffusivities ($D_{p,i}$) for all REEs or complex species were assumed to be the same, and they were estimated by matching the simulated concentration waves between the two REE bands with the corresponding data in Figure 3.5.



Figure 3.5 Comparison of rate model simulations (dashed lines) with experimental data (solid lines). (a) Separation of equimolar Sm and Nd (0.18 N each, 94 mL), (b) Separation of equimolar Nd and Pr (0.18 N each, 94 mL) using 0.03 M EDTA-Na (pH 8.4) in a column (1.16 cm id. x 39.5 cm L_c) packed with AG MP50.

System param	neters								
L _c (cm)	ID (cm)	$R_p(\mu m)$	Еb	ε _p	q _{max} (meq BV)	./mL	C _{f,i} (N)	Feed volum (mL)	ne Q _f (mL/min)
39.5	1.16	56	0.33	0.34	1.45		0.18 each	94	2
Isotherm para	ameters								
Component	Cu (ref)	Sm	Nd	P	r	EDT	TA-Na		
(a) $\alpha_{i,ref}$	1	5	16			90)		
(b) $\alpha_{i,ref}$	1		5	Ç)	45	i		
Mass transfer	paramete	ers							
Component	B diff (c	Brownian diffusivity, D_b (cm ² /min) Pore diffusivity D_p (cm ² /min)		e ity, in)	Axial dispersion coefficient, E _b (cm ² /min)		ion Fi E _b	n Film mass transfer coefficient, k _f (cm/min)	
All species	4×10-2) ⁻⁴ 9×10 ⁻⁵			Chung and Wen (1968)		W: G (19	Wilson and Geankoplis (1966)	
Numerical pa	rameters								
	Collocation			n points		Tolera	ince		
Axial element	(L/u_0)	L/u ₀) Axial Particl		cle		Absol	ute Re	lative	
100	0.01	4	2			1x10 ⁻⁴	1x	10-3	

Table 3.2 Simulation parameters used for experimental data in Figures. 3.5 and 3.6

The ligand selectivity for Cu^{2+} relative to Sm^{3+} was greater than 100 [84]. The sorbent selectivity of Sm^{3+} to Cu^{2+} was greater than 5. Therefore, according to Eq. (1), the effective sorbent selectivity of Sm^{3+} to Cu^{2+} ($\alpha_{Sm,Cu}^{e}$) was expected to be greater than 200. However, an effective sorbent selectivity $\alpha_{Sm,Cu}^{e}$ of 5 was sufficiently large to match closely the simulated waves of Cu^{2+} and Sm with the data in Figure 3.5a. Any $\alpha_{Sm,Cu}^{e}$ value greater than 5 did not increase the sharpness of the waves. Similarly, a value of 5 for $\alpha_{Pr,Na}^{e}$, the effective sorbent selectivity for Pr^{3+} relative to the displacer, EDTA-Na, gave sufficiently sharp simulated waves to match with the data in Figure 3.5b.

The constant separation factor model requires that all components have the same maximum sorbent capacity. Because the isotachic train is controlled by the elution of the copper band, the maximum sorbent capacity for copper was determined using a frontal test (Appendix D). The measured capacity was 1.68 eq./L. When copper was stripped from the column using 0.03 M EDTA, a band concentration of 0.039 M copper resulted. This result indicates that EDTA binds with copper in a molar ratio of roughtly 1:1.3. When copper binds with EDTA, it exchanges with either sodium or hydrogen and forms hexadentate structure [36] that has a net charge of -2. In the process of forming this complex, all four carboxylic acid groups chelate with the copper ion and the other counterions are only bound electrostatically. Because this complex has a charge of -2 and copper has a charge of +2, it has the capability to bind with another Cu^{2+} electrostatically, raising the EDTA to copper ratio above 1:1. The H⁺ and Na⁺ in solution are also available to bind electrostatically with the EDTA-Cu complex. Additionally, as H⁺ from EDTA is released into the solution as a results of the formation of the EDTA-Cu complex, the pH is lowered, which can also lower the number of available COO⁻ groups, further lowering the ideal molar binding ratio of EDTA to copper from 1:2 down to the observed ratio of 1:1.3.

The REEs have a slightly different binding structure with EDTA because of their large sizes. Some REEs form a hexadentate structure, while others form a pentadentate structure depending on the atomic radius [85]. Although the structures are slightly different, when REEs bind with EDTA, H^+ and Na^+ are released. However, because REEs have a charge of +3, the complex that is formed with EDTA has a net charge of -1 instead of -2 as in the case of copper. This means that the EDTA-REE complex binding with REEs is less likely. While the EDTA solution was loaded at a pH of 8.4, the EDTA-REE bands elute at a pH <3.0. The pH lowering effect is similar to that observed upon the binding of Cu^{2+} with EDTA. The model assumes that the complexation reaction between REEs and EDTA followed the one-to-one stoichiometry, but because the decreased pH hinders the binding availability, the band concentration for REE was lower than expected. The eluted REE band concentration (0.0228 M) was lower than the nominal ligand concentration (0.03 M). The overall result is that the average molar binding ratio between EDTA and REE is 1:0.76.

In the model, the effective ligand concentration for REEs (0.0228 M) was chosen as the displacer concentration because the focus was on the elution behavior of REE bands. Because the copper bands were more concentrated than the REE bands, choosing the effective ligand concentration for REEs lowered the concentration of the copper band in the model, causing a delay in the elution of all of the bands. To match the experimental band position with the simulation, the maximum sorbent capacity was lowered from 1.68 eq./L to 1.45 eq./L. The reduction was applied to reflect the ligand binding efficiency difference between the copper and the REE bands. The concentration of the REE bands were matched by adjusting the displacer concentration and then the positions of the bands were matched by adjusting the simulated maximum sorbent capacity to reflect the difference in ligand binding efficiency.

3.4.2 Verification of the Rate Model

The simulation parameters determined in the previous section were used to simulate various equimolar binary separations of Nd and Pr done using the sulfonic acid resin. The column used in this experiment was longer than that used in the experiments for determining the intrinsic parameters. The simulations and experimental results can be seen in Figure 3.6, and a summary of the experimental and simulations parameters is given in Table 3.3. The simulated chromatograms show good agreement with the experimental chromatograms. The differences between the simulated and the experimental mass transfer zone lengths are within the experimental error.

Additionally, the model was applied to simulate three sets of experimental data reported in the literature. Figure 3.7a. shows the separation of an equimolar mixture of REEs using Er^{3+} as the presaturant [37]. Figures 3.7b and 3.7c show the separation of mixtures of REEs from mineral ores using Cu²⁺ as the presaturant [35]. In all three cases, EDTA was used as a ligand and sulfonic acid resins (AG50X12 for Figure 3.7a, Dowex 50X8 for Figures 3.7b and 3.7c) were used. The effective sorbent selectivity for each REE was assumed to be the inverse of its ligand selectivity. The rest of the parameters were estimated similarly as for Figure 3.6. The simulation parameters for Figures 3.7a and 3.7b-c are listed in Table 3.4 and 3.5, respectively. The model accurately predicted the three chromatograms for LAD systems reported in the literature. The results of Figure 3.7 demonstrate that the developed model can be used to predict the separation of various REE mixtures that have more than two components.



Figure 3.6 The separation of equimolar mixture of Nd and Pr (0.15 N) using 0.03 M EDTA-Na (pH 8.4). The experimental conditions were based on the minimum dimensionless column length ϕ_{min} : (a) 1.0, (b) 1.1, (c) 1.2, (d) 1.3, and (e) 1.5, respectively, and (f) comparison of the dimensionless mass transfer zone length L_{MTZ}/L_c with L_{MTZ,CP}/L_c for different ϕ_{min} cases. Solid lines in (a) to (e) were experimental data and dashed lines were simulation results.

System pa	arameters									
L _c (cm)	ID (cm)	$R_p(\mu m)$	Еb	ε _p	q _{max} (meq. BV)	/mL	C _{f,i} (N)	Fee vol	d ume L)	Q _f (mL/min)
								(a)	99.8	(a) 1
								(b)	91.8	(b) 1.8
44	1.16	56	0.33	0.34	1.45		0.15 each	(c)	84.8	(c) 1.9
								(d)	82.4	(d) 2.0
								(e)	65.8	(e) 2.5
Isotherm	parameters									
Componer	nt Cu (ref)	Nd	Pr	EDTA	A-Na					
α _{i,ref}	1	5	9	45	5					
Mass tran	sfer param	eters								
Componer	nt d	Brownian liffusivity, D _b (cm ² /min)		Pore diffusivi D _p (cm ² /mi	ty, n)	Axi co	al dispersi efficient, E (cm ² /min)	on E _b	Film m coef (cr	ass transfer ficient, k _f m/min)
All species	s 4×1	0 ⁻⁴	9 ×1	10-5		Chur Wen	ng and (1968)	(Wilson Geank (1966)	and oplis
Numerica	l parameter	rs								
Axial	Step size	Collocation	ı point	S		To	lerance			
element	(L/u ₀)	Axial	Parti	cle		Ab	solute Rel	ative	•	
100	0.01	4	2			1x.	10 ⁻⁴ 1x1	0-3		

Table 3.3 Simulation parameters used for experimental data in Figure 3.6



Figure 3.7 Comparison of rate model simulations (solid lines) with literature data (dots): (a) Chromatogram of the separation of heavy REEs using EDTA, Fig 2A of Moore et al. (1995), (b) and (c) Chromatograms of the separation of REE using EDTA with different flowrates, Fig 3A and 3B of Lindstrom (1959) [35,37] Simulation parameters for (a) and (b)-(c) are listed in Table 3.4 and 3.5, respectively.

System parameters									
L _c (cm)	ID (cm)	R _p (µm)	Еb	ε _p	qı (mea B	^{max} q./mL V)	V_f (mL)		Q _f (mL/min)
40	2.2	112.5	0.35	0.45	1.	.82	1]	L	3.8
Isotherm an	nd input p	arameters							
Component	t Er	Но	Dy	Tb		Gd	Eu	Sm	EDTA-NH4
$\alpha_{i,1}$	1	1.95	3.9	10.5	3	6.86	40.54	60.81	182.43
$C_{f,i}(mN)$	-	33	33	33		33	33	33	32.6
Mass transf	er param	eters							
Compone	ent di	Brownian ffusivity, D _b (cm ² /min)	Pore (c	diffusiv D _p em²/min	vity, Axial dispersion Film mas coefficient, E _b coeffic n) (cm ² /min) (cm		n mass transfer Defficient, k _f (cm/min)		
All specie	es	4×10 ⁻⁴		5×10 ⁻⁵		Chun (g and Wen 1968)	Gea	Wilson and nkoplis (1966)
Numerical parameters									
Axial	Step size	p size Collocation points Tolerance			ance				
element	(L/u ₀)	Axial		Partie	cle	Absolute Relative		Relative	
100	0.05	4		2			1x10 ⁻³		1x10 ⁻³

Table 3.4 Simulation parameters used for Figure 3.7a.

ameters							
ID (cm)	$R_p(\mu m)$	ε _b	ε _p	V_f (mL)	(m	q _{max} eq./mL BV)	Q _f (mL/min)
1.7	75	0.32	0.6	635.2		2.25	22.7 (b) 11.3 (c)
nd input p	arameters						
Cu	Eu	Sm	Nd	Pr	Ce	La	EDTA- NH4
1	12.3	18.45	59.04	106.27	210.5	520	1600
-	19.8	40.8	457.8	144.9	12.6	217.	8 39
fer parame	eters						
E ent diff ((Brownian Fusivity, D _b cm ² /min)	Pore d	iffusivity, D _p ²/min)	Axial dispe coefficien (cm ² /mi	ersion t, E _b n) co	Film ma	ass transfer t, k _f (cm/min)
les	4×10 ⁻⁴	5>	×10 ⁻⁵	Chung and (1968)	Wen W	Vilson an (1	d Geankoplis 966)
parameter	S						
Step size	Col	location	points		Т	olerance	
(L/u ₀)	Axia	al	Particle	Absolute Relative		tive	
0.01	4		2	1x10 ⁻³		1x1	0-3
	ID (cm) ID (cm) 1.7 Id input pa Cu 1 - fer parameter fer size (L/u ₀) 0.01	ametersID (cm) R_p (µm)1.775Tot input parametersCuEu112.3-19.8Fer parametersentBrownian diffusivity, Db (cm²/min)es 4×10^{-4} parametersStep sizeCol (L/u_0)Axia0.014	ametersID (cm) R_p (µm) ε_b 1.7750.32nd input parametersCuEuSm112.318.45-19.840.8Fer parameters40.8Fer parameters(cm²/min)entBrownian diffusivity, Db (cm²/min)Pore d (cm²/min)es 4×10^{-4} 5:parametersCollocation(L/u_0)Axial0.014	ametersID (cm) R_p (µm) ε_b ε_p 1.7750.320.6InterpretenderCuEuSmNd112.318.4559.04-19.840.8457.8Fer parametersBrownian diffusivity, Db (cm ² /min)Pore diffusivity, Dp (cm ² /min)es 4×10^{-4} 5×10^{-5} Step size (L/u_0)Collocation points0.0142	ametersID (cm) R_p (µm) ε_b ε_p V_f (mL)1.7750.320.6635.2dinput parametersCuEuSmNdPr112.318.4559.04106.27-19.840.8457.8144.9Fer parametersent diffusivity, Db (cm ² /min)Pore diffusivity, Dp (cm ² /min)Pore diffusivity, Axial dispectorgrametersStep sizeCollocation points(L/u_0)AxialParticleAbsolut0.01421x10 ⁻³	ameters ID (cm) R_p (µm) ϵ_b ϵ_p V_f (mL) (m 1.7 75 0.32 0.6 635.2 nd input parameters Cu Eu Sm Nd Pr Ce 1 12.3 18.45 59.04 106.27 210.5 - 19.8 40.8 457.8 144.9 12.6 Ger parameters ent Brownian diffusivity, Db (cm ² /min) Pore diffusivity, Axial dispersion coefficient, Eb (cm ² /min) c es 4×10^{-4} 5×10^{-5} Chung and Wen V (1968) V parameters Step size Collocation points T (L/u_0) Axial Particle Absolute 0.01 4 2 1x10 ⁻³	ametersID (cm) R_p (µm) ε_b ε_p V_f (mL) $\begin{pmatrix} q_{max} \\ (meq./mL \\ BV) \end{pmatrix}$ 1.7750.320.6635.22.25ad input parametersCuEuSmNdPrCeLa112.318.4559.04106.27210.5520-19.840.8457.8144.912.6217.Cer parametersBrownian diffusivity, D_b Pore diffusivity, $Axial$ dispersion (cm^2/min) Film m. coefficient, E_b coefficient, E_b $coefficient, E_b$ es 4×10^{-4} 5×10^{-5} Chung and Wen Wilson an (1968) Step size(L/u_0)AxialParticleAbsoluteRela0.0142 $1x10^{-3}$ $1x1$

Table 3.5 Simulation parameters used for Figures 3.7b and 3.7c.

The formation of a constant-pattern isotachic train (CPIT) in LAD was investigated using the verified rate model and simulations. Figure 3.8a shows the simulated dynamic concentration profiles for the experiment in Figure 3.5a. The Sm and Nd bands developed a CPIT at 150 minutes, since the mass transfer zone lengths at 150 minutes and 175 minutes are the same. After the formation of a CPIT, further migration through the column does not increase the yield of high purity product (Figure 3.8a). On the other hand, the dynamic profiles in Figure 3.5b shows that the column length for Figure 3.5b was too short for the Nd and Pr bands to fully develop a CPIT, and the profiles show transient-pattern mass transfer zone length $L_{MTZ,T}$.

The simulated dynamic column profiles in Figure 3.8a indicate that the band separation and the development of a constant-pattern isotachic train in LAD is similar to those in conventional displacement chromatography. However, the detailed mechanisms are quite different in the two systems. In conventional displacement chromatography, the component with the lowest sorbent affinity elutes first, while in LAD, if the sorbent has no selectivity, the component with the highest ligand affinity elutes first. In displacement chromatography, an isotachic train develops and migrates through the column because the bands are displaced by a high sorbent affinity displacer. Sharp waves form due to the displacement of low affinity solutes by high affinity solutes. The mass transfer zone length is controlled by sorbent selectivity and mass transfer resistance. However, in LAD, the migration of the isotachic bands is driven by the complexation reaction between the ligand and the presaturant in LAD. Sharp waves are developed by complexation reactions between the ligand and the solutes. The mass transfer zone length primarily depends on the ligand selectivity and intraparticle diffusion.



Figure 3.8 The dynamic column profiles of (a) Sm and Nd, and (b) Nd and Pr separations shown in Figure 3.5. A constant-pattern isotachic train (CPIT) of Sm and Nd is formed at 150 minutes. Nd and Pr bands did not reach a constant-pattern state in the column.

In LAD, the presaturant has the highest affinity for the ligand or the lowest effective sorbent affinity. The example shown in Figure 3.2 is used here to elucidate the dynamics. As the complex of the ligand with REE₂ (fast migrating REE) enters the region occupied by the presaturant (Figure 3.2a), the ligand prefers to form a complex with the presaturant, causing desorption of the presaturant from the sorbent and release of REE₂ into the mobile phase. The released REE₂ then readsorbs onto the sorbent, resulting in apparent displacement of the presaturant by REE₂. Since the ligand-presaturant complex is stable and does not adsorb, the boundary between the REE₂ band and the presaturant band is sharp (Figure 3.2b). This phenomenon is similar to the formation of a self-sharpening wave (or sharp wave in short) as a high sorbent affinity species displaces a low sorbent affinity species in conventional displacement chromatography.

In a CPIT in LAD, the desorption wave of the fast migrating REE₂ band is also sharp. As the ligand-REE₁ complex enters the REE₂ zone, the ligand prefers to form a complex with REE₂. It releases REE₁ to form a complex with REE₂ (Figure 3.2a). The released REE₁ then readsorbs, resulting in a sharp boundary and an apparent displacement of REE₂ by REE₁. Similarly, the desorption wave of REE₁ is also sharp, because the ligand prefers REE₁ to Na⁺. Because the main driving force is the reaction between the ligand and the presaturant, all the boundaries of the separated REE bands migrate at the same velocity as the desorption wave of the presaturant. Furthermore, the ligand concentration controls the migration velocity of the desorption wave of the presaturant, and consequently the isotachic REE band concentrations. The pH of the ligand solution is also important, because it controls the fraction of the active functional groups of the ligand, or the effective ligand concentration.

Although the ligand complexation reactions drive the desorption of REEs in both LAD and LAE, the chromatograms of LAD and LAE are different. The elution order of ligand-assisted

elution chromatography (LAE) is the same as in LAD, but the migration velocities of the solutes are different in LAE and LAD. The migration speed of each solute band is controlled by both the affinity of the solute with the sorbent and the affinity of the solute with the ligand [10]. The main differences between LAE and LAD are the presaturant and the effective sorbent selectivities. In LAE, the column is presaturated and eluted with $EDTA-NH_4^+$ which is a weakly adsorbing species on titania. The REE adsorption waves are sharp because REEs displace ammonium, which has a lower effective sorbent affinity than REEs. The REE desorption waves are diffuse because the desorption is mainly driven by the displacement of REEs by a weakly adsorbing eluent (NH_4^+) [86]. A comparison of conventional displacement, LAD, and LAE is summarized in Table 3.6.

	Displacement	LAD	LAE
Elution order	Component with low	Component with high	Component with high
	sorbent affinity elutes	ligand affinity elutes	ligand affinity elutes
	first	first	first
Driving force	Displacement by a	Complexation reaction	Complexation reaction
for band	higher sorbent affinity	between the ligand and	between the ligand and
migration	displacer	the presaturant	the solutes
Wave sharpness	Sharp waves due to displacement of low affinity solutes by high affinity solutes	Sharp adsorption and desorption waves due to the displacement of a low effective sorbent affinity species by a high effective sorbent affinity species	Sharp adsorption waves due to the displacement of NH4 ⁺ by REE (with a higher effective sorbent selectivity); Diffusive desorption waves due to displacement of REE by NH4 ⁺

Table 3.6 Comparison of displacement, LAD and LAE

3.4.4 Effects of key dimensionless parameters on the development of a CPIT

The key parameters controlling the minimum column length to form a constant-pattern isotachic train (CPIT) and the constant pattern mass transfer zone length $L_{MTZ,CP}$ for nonideal systems are shown in the first row in Figure 3.2. To reduce the number of variables, key dimensionless groups were found from Eq. (2-3), (17), and (18), and summarized in Table 3.1. The effects of the key dimensionless group on the minimum column length and the mass transfer zone length were investigated using the rate model simulations. To clearly see the transition from the transient state to the constant pattern state, a wide range of conditions were simulated and analyzed. Table 3.1 lists the range of the variables and the dimensionless groups studied. The intrinsic parameters used in each simulation were in Table 3.7 and the value of θ was 0.01 for all the cases, unless noted otherwise.

3.4.4.1 Effects of the feed composition and feed volume on the minimum column length for a nonideal system, L_{iso-nid}

For an ideal system, feed composition (x_i) and loading volume (V_f) are related to the feed length L_{feed} . Both concentration overload and volume overload result in the same feed length and the minimum column length as expected from Eqs. (3.2) and (3.3). Simulations were used to test the effects of feed concentration and loading volume on the minimum column length for nonideal systems. The feed composition, column length, and elution velocity in the simulations were kept the same as those for Figure 3.5b, except the feed concentrations and loading volume. In Case 1, the feed concentrations of both Nd and Pr were doubled to 0.36 N, and the loading volume was reduced by one half to 47 mL. In Case 2, the feed concentrations of both Nd and Pr were reduced by 10 fold to 0.018 N each, whereas L_f was kept the same by increasing the loading volume by 10 fold to 940 mL. The resulting effluent histories for both cases were identical to Figure 3.5b (results not shown). The results indicate that concentration overload (Case 1) and volume overload (Case
2) gave essentially the same effluent histories when L_f is held constant and all the other dimensionless groups in Figure 3.2 were kept the same.

System paran	neters									
L _c (cm)	ID (cm)	$R_p(\mu m)$	Еb	Еp	q _{max} (meq BV)	./mL	C _{f,i} (N)	Feed volume (mL)	Q _f (mL/min)	
30 - 60	1.16	112	0.33	0.34	1.45		0.18 each	94	0.2	
Isotherm para	ameters									
Component	Cu (ref)	Sm	Nd	Р	Pr	EDT	ΓA-Na			
α _{i,ref}	1	-	5	ç)	45	5			
Mass transfer	r paramet	ers								
Component	Brownian diffusivity, D _b (cm ² /min))	Pore diffusivity, D _p (cm ² /min)		Axial dispersion coefficient, E _b (cm ² /min)		sion Film E _b cc)	Film mass transfer coefficient, k _f (cm/min)	
All species	4×10 ⁻⁴	9×10 ⁻⁵			Chung and Wen (1968)		Wils Gea (196	Wilson and Geankoplis (1966)		
Numerical pa	rameters									
Axial element	Step size Collocation points					Tolerance				
	(L/u ₀)	Axial	Particle			Absolute Relative				
100	0.01	4	2			1x10 ⁻²	⁴ 1x	10-3		

Table 3.7 Simulation parameters used for experimental data in Figure 3.9.

For an ideal binary system, the minimum column length to form an isotachic train (L_{iso-id}) is only a function of the effective sorbent selectivity, Eq. (3.2), Appendix B. For a nonideal system, the minimum column length to form a constant-pattern isotachic train $(L_{iso-nid})$ is longer than for an ideal system. To study the effects of feed compositions, binary separations for non-ideal systems were simulated based on the parameters given in Tables 3.7. The particle radius was doubled, and flowrate was reduced ten-fold to observe the change of L_{MTZ} clearly. The feed compositions of Nd and Pr were varied from 1:3, 1:1, and 3:1 on a molar basis, respectively.

As shown in Figure 3.9a, as the dimensionless column length increases, the transient dimensionless mass transfer zone length decreases until it eventually reaches a constant length $L_{MTZ,CP}$ after forming a CPIT. For the nonideal systems, the column length required to form CPIT is 22 % longer than the length required to form an isotachic train in an ideal system, or ϕ_{min} (or $L_{iso-nid}/L_{iso-id}$) = 1.22. Figure 3.9a shows that L_{MTZ} reaches constant-pattern in the binary systems at the same column length, $L_{iso-nid}$ (dashed vertical line) regardless of feed compositions. The results of Figure 3.9a show that if a system develops fully separated isotachic bands with plateaus, the feed composition does not affect $L_{iso-nid}$, the minimum column length to form a CPIT.

In contrast, if a column length is too short to form a CPIT, the mass transfer zone lengths in the transient state ($L_{MTZ,T}$) will depend on the feed composition. Figures 3.9b and 3.9c show the migration of the concentration waves obtained from rate model simulations for 1:3 and 3:1 composition, respectively. In both cases, the overlapping region of the Nd desorption wave and the Pr adsorption wave define the mass transfer zone between the two adjacent bands. The transient mass transfer zone lengths in the 1:3 case $L^*_{MTZ,1}$ (Figure 3.9b) are longer and migrate faster than for the 3:1 case $L^*_{MTZ,2}$ (Figure 3.9c) during the transient state. However, the mass transfer zone lengths at the constant-pattern state are the same for both cases.



Figure 3.9 (a) Effects of feed compositions on the development of a CPIT in binary separations; (b) Distance-time diagram of case that has molar feed composition as 1 to 3; (c) Distance-time diagram of case that has molar feed composition as 3 to 1. Notice that $L^*_{MTZ,1}$ and $L^*_{MTZ,2}$ in (a) are represented in (b) and (c), respectively. For simulations, particle radius was doubled and flowrate was ten times reduced from Figure 3.5b in order to see the change of L_{MTZ} clearly.

3.4.4.2 Effects of nonlinear distribution coefficient and breakthrough cut on the minimum column length for a nonideal system, L_{iso-nid}

The value of nonlinear distribution coefficient (K_d) is determined by the ratio of column capacity and the effective ligand concentration, Eq. (3.8). It controls the wave velocity of the displacer and thus the velocity of the constant-pattern isotachic bands in LAD, Eq. (3.4). As a

result, the K_d value affects the constant-pattern shock layer thickness t_{MTZ} observed in the effluent history, Eq. (3.17b). However, it is unknown from the literature whether K_d affects the minimum column length for developing a constant-pattern isotachic train in a non-ideal system (L_{iso-nid}). Rate model simulations were used to answer this question. The material properties, operating parameters, and L_{feed} were kept constant as in Table 3.3, but column length was varied from 40 to 70 cm (40, 45, 50, 60, and 70 cm) and K_d was varied from 64 to 460 by changing the effective ligand concentration.

The dimensionless t_{MTZ} values were found from simulated effluent histories and analyzed according to Eq. (3.17b). As shown in Figure 3.10a, for a fixed K_d value, as the column length increases, the dimensionless t_{MTZ} decreases and eventually follows a straight line, indicating the formation of a constant pattern isotachic train. In the constant pattern region, the dimensionless t_{MTZ} is proportional to K_d as predicted by Eq. (3.17b). The transition from the transient region to the constant–pattern region for all the six K_d curves occurs at the same x-axis value, which is indicated by the vertical dashed line. The transition point corresponds to the minimum column length for the formation of constant pattern. The results indicate that the K_d values do not affect the minimum column length for nonideal systems.

The dimensionless mass transfer zone lengths were also found from simulated column profiles and analyzed according to Eq. (3.17a). The results are shown in Figure 3.10b. As expected from Eq. (3.17a), all the six straight lines for the various K_d values in the constant-pattern region of Figure 3.10a merge into a single straight line. More importantly, all six curves in the transient region in Figure 10a also merge into a single curve in Figure 3.10b. The results indicate that one can use Figure 3.10b to identify the minimum column length without considering the K_d values or the feed composition for binary systems as discussed in the previous section.

Although the effective ligand concentration (c_d) does not affect L_{iso-nid}, it affects the isotachic band concentrations. As the effective ligand concentration increases, the concentrations of the isotachic bands increase and thus the bands are compressed. When the band width of a component is smaller than the sum of the mass transfer zone lengths between the adjacent bands, the band no longer has a flat-top. Therefore, there is a maximum ligand concentration to form isotachic bands with flat tops. If the bands do not have flat tops, the constant-pattern shock layer thickness analysis no longer applies. Additionally, the maximum ligand concentration could be limited by ligand solubility, which may depend on pH.

Breakthrough cut (θ) is a variable used to calculate the mass transfer zone lengths in Eq. (3.17). However, it should be noted that θ does not affect the value of ϕ_{min} because θ is an arbitrary cut chosen for defining the mass transfer zone length. As shown in Figure 3.11, breakthrough cut changed the value of L_{MTZ,CP}. However, a red dashed line pointed out the same ϕ_{min} for all cases, indicating the independence of ϕ_{min} from θ .



Figure 3.10 Effects of K_d on the minimum column length to develop a CPIT ($L_{iso-nid}$) with respect to (a) t_{MTZ} and (b) L_{MTZ} . In simulations, L_c and the effective ligand concentration were changed but L_{feed} and other parameters were the same as those used in Table 3.7. Dashed vertical lines indicated the same ϕ_{min} to develop a CPIT for all cases.



Figure 3.11 Effects of breakthrough cut (θ) on the dimensionless mass transfer zone length. Red dashed line indicates the same ϕ_{min} for all cases. One of L_{MTZ}/L_c curves obtained from Fig. 3.10b was re-analyzed with varied θ values.

3.4.4.3 Effects of the effective sorbent selectivity on the minimum column length for a nonideal system, L_{iso-nid}

Effective sorbent selectivity (α^e) affects not only the constant-pattern mass transfer zone length (L_{MTZ,CP}) but also the minimum column length to reach a constant-pattern state. Rate model simulations were designed to study the effects of the effective sorbent selectivity (α^e) on the mass transfer zone length in the transient and the constant-pattern regions. The simulation parameters were the same as those in Table 3, except the α^e values were varied from 1.3 to 10 and the column lengths were varied from 25 cm to 170 cm to ensure that constant pattern region was observed. The transient and constant-pattern mass transfer zone length was measured from simulated column profiles.

First, we compare the analytical solutions for the constant-pattern mass transfer zone lengths obtained from Eq. (3.18) with those from simulations in Figure 3.12. The simulated values

closely agreed with the analytical solutions at lower α^e (<2). At higher α^e , the analytical solutions were higher than those from simulations. This is because the overall mass transfer coefficient in the analytical solution was estimated based on the Ruthven's correlation, which was derived for linear adsorption isotherms. Wave sharpening effects due to highly nonlinear isotherms for high α^e are not considered in the Ruthven's correlation. Eq. (3.18) can provide conservative estimates of the constant-pattern mass transfer zone lengths for high α^e systems.



Figure 3.12 Comparison of $L_{MTZ,CP}/L_{feed}$ at different α^e values obtained from simulations (squares) with analytical solutions calculated using Eq. (3.18) (circles). In simulations, L_c was changed until $L_{MTZ,CP}$ was reached for each α^e case. Other parameters were the same as those listed in Table 3.7.

According to Eq. (3.17a), dimensionless constant-pattern mass transfer zone length $L_{MTZ,CP}/L_c$ is proportional to $1/k_f^*$, with a slope related to the value of α^e and θ . Rate model simulations were used to test this linear relation in the constant pattern state and study the transition

from the transient state to the constant pattern state. The results for different α^e were compared in Figure 3.13a. Increasing column length in the simulations increases N_D, and Pe_b, resulting in a smaller value of the x-axis $(1/k_f^*)$. It also results in a smaller value of the loading fraction (L_f) . The transition from the transient state to the constant pattern state is indicated by the decreasing of the dimensionless mass transfer zone length as the value of $1/k_f^*$ becomes smaller. The slope of the curve also decreases abruptly and reaches a constant value in the constant pattern state. The transition point for each α^e curve corresponds to the minimum column length or the maximum loading fraction for the system to reach the constant pattern state.

Figure 3.13a also shows that in the constant-pattern region, each L_{MTZ}/L_c curve is linearly proportional to $1/k_f^*$ as predicted from Eq. (3.17a). As $1/k_f^*$ increases, each of the α^e curves eventually enters the transient region with a larger slope and larger transient mass transfer zone lengths $L_{MTZ,T}/L_c$. The systems with larger α^e values have smaller dimensionless mass transfer zone lengths and require a smaller value of k_f^* or a smaller column length to reach the constantpattern state.

After constant-pattern is reached, the curves for different α^e values should merge into a single straight line if the x-axis includes the α^e term in Eq. (3.17a). The curves in Figure 3.13a were plotted with the α^e term in the x-axis in Figure 3.13b. The results show that all the α^e curves in the constant-pattern region merge into a single line as expected. Furthermore, the curves in the transient regions of Figure 3.13a also merge into a single curve with the same transition point. The end point of the constant-pattern region (the linear portion of the merged curve, indicated by the vertical dashed line in Figure 3.13b) corresponds to the minimum column length (or the maximum loading fraction) for the various systems with different α^e values and loading fractions.



Figure 3.13 Effects of the effective sorbent selectivity on the dimensionless mass transfer zone length to develop a CPIT ($L_{iso-nid}$) with respect to (a) $1/k_f^*$ and (b) right hand side of Eq. (3.17a). Each curve corresponds to different α^e when feed length L_{feed} is kept constant while the column length is varied. Other simulation parameters were the same as those in Table 3.7. Dashed vertical lines indicated the same ϕ_{min} for all cases.

3.4.5 Development of a general map to identify constant-pattern and transient-pattern regions using dimensionless group analysis and rate model simulations

To find the effects of loading fraction (L_t) and mass transfer coefficients on the minimum column length to reach constant-pattern for a non-ideal system $L_{iso-nid}$, we first examined their effects on the constant-pattern mass transfer zone length. Instead of using the column length as the characteristic length, the feed length for an ideal system L_{feed} was used as the characteristic length for the dimensionless mass transfer zone length in Eq. (3.18) to incorporate loading fraction in this equation. This equation predicts that at the constant-pattern state, if the values for the left-handside term $L_{MTZ,CP}/L_{feed}$ are plotted versus the right hand-side term of Eq. (3.18), one should obtain a straight diagonal line. The transient mass transfer zone lengths are longer than the constant-pattern mass transfer zone lengths and they should be located above the diagonal line. This plot enables to examine the transition from the transient state to the constant-pattern state for systems with different loading fractions and dimensionless mass transfer coefficients k_f^* . Furthermore, the transition points help identify the minimum column length to reach the constantpattern state.

The first vertical line on the upper right corner in Figure 3.14a corresponds to the single curve shown in Figure 3.13b for $\alpha^e = 1.6$, which was obtained by keeping $L_f k_f^*$ constant. The vertical line shows the transition from transient pattern $L_{MTZ,T}$ to constant-pattern $L_{MTZ,CP}$ as L_c increases. By increasing k_f^* values while keeping all other dimensionless parameters constant, other vertical lines were obtained. Decreasing particle sizes and linear velocities resulted in larger k_f^* values. Connecting the simulated constant-pattern points from the various vertical lines forms a straight line with a slope of 1.04. This simulated constant-pattern (CP) line is close to the diagonal line, which is the theoretical constant-pattern line from Eq. (3.18). This small difference is due to



Figure 3.14 (a) General relationship among mass transfer coefficients, feed loading, effective sorbent selectivity, and L_{MTZ}/L_{feed} based on Eq. (3.18) and (b) General relationship between the dimensionless column length (ϕ) and the combined dimensionless groups of L_f , k_f^* , and α^e , showing the minimum dimensionless column length (ϕ_{min}) as the boundary between the constant-pattern and transient pattern region. The circles in (b) are from Figure 3.13b.

All the transient-pattern points of $L_{MTZ,T}/L_{feed}$ in Figure 3.14a fall on the region above the CP line as expected. Along each vertical line, the feed length is kept constant while column length is increased to reduce the loading fraction until CP is reached and the vertical line meets the simulated CP line. By connecting the transient mass transfer zone length points having the same loading fraction and α^e but different k_f^* on the various vertical lines, one can find a straight line. Because the feed length is kept constant along the constant loading fraction line, the column length or the dimensionless column length ϕ is also constant. Along the constant ϕ line, as the k_f^* value increases, the transient mass transfer zone length decreases until the constant ϕ line meets the simulated CP line. This intersection point corresponds to the transition from the transient-pattern state to the constant-pattern state for the given ϕ . At this point, the ϕ value is the minimum dimensionless column length to reach the constant-pattern state or ϕ_{min} . For each constant ϕ line, the corresponding x-axis value of the intersection point gives the required condition for the ϕ_{min} . By plotting the various ϕ_{min} values versus the inverse of the corresponding x-axis values without θ term, one can obtain a ϕ_{min} curve in Figure 3.14b.

The simulation results for the effective sorbent selectivity series in Figure 3.10 also can be reanalyzed to generate five more points on the ϕ_{min} curve in Figure 3.14b. The y-axis value of the transition point in Figure 3.14b is L_{MTZ,CP}/L_{iso-nid}. One can rewrite Eq. (3.17a) as Eq. (3.25).

$$\frac{L_{MTZ,CP}}{L_{iso-nid}} = \frac{1}{k_f^*} \left(\frac{\alpha^e + 1}{\alpha^e - 1} \right) \ln \left| \frac{1 - \theta}{\theta} \right|$$
(3.25)

The x-axis value at this point of Figure 3.14b is a unique value, which corresponds to the systems with the various α^{e} values and the maximum loading fractions L_{fmax} . The minimum column length for an ideal binary system is related to the effective sorbent selectivity, Eq. (3.2), which can be used to relate L_{fmax} to the minimum dimensionless column length, ϕ_{min} as follows:

$$L_{fmax} = \frac{L_{feed}}{L_{iso-nid}} = \frac{L_{feed}/L_{iso-id}}{L_{iso-nid}/L_{iso-id}} = \frac{(\alpha^e - 1)/\alpha^e}{\phi_{min}}$$
(3.26a)

One can then rearrange Eq. (3.26a) to relate ϕ_{min} to L_{fmax} .

$$\phi_{min} = \frac{(\alpha^e - 1)/\alpha^e}{L_{fmax}} \tag{3.26b}$$

The x-axis value at the transition point of Figure 3.13b (0.044) corresponds to the various L_{fmax} values obtained from the simulations for the systems with the various α^e values. One can use Eq. (3.26b) to calculate the five ϕ_{min} values corresponds to the five α^e (1.3, 1.5, 1.8, 2.0, and 2.2) and the corresponding five L_{fmax} values. The x-axis value (0.044) of Figure 3.13b can be multiplied by $1/L_{fmax}$ and inverted to obtain five x-axis points in Figure 3.14b. One can then plot the corresponding five ϕ_{min} values on the y-axis to obtain five more points on the general ϕ_{min} curve in Figure 14b. Although the physical systems for the selectivity series and the loading fraction series are different, the ϕ_{min} points obtained from Figure 3.13b are consistent with those from Figure 3.14a. The results of Figure 3.14b indicate the ϕ_{min} curve has general significance.

Based on the aforementioned results, a general map was developed in Figure 3.14b. The ϕ_{min} curve can be correlated empirically using an exponential function.

$$\phi_{min} = 1.745e^{-0.04737X} + 0.6503 \quad for (X < 34)$$
where X is $L_f k_f^* \left(\frac{\alpha^e - 1}{\alpha^e + 1}\right)$.
(3.27)



Figure 3.15 Map identifying the general conditions to develop a constant-pattern state. The region above the ϕ_{min} curve shows the conditions to develop a constant-pattern state while the region below the ϕ_{min} curve indicates transient-pattern state. Points for each data in Figure. 3.5, 3.6, and 3.7 are expressed on the map to identify L_{MTZ} status. The correlation of ϕ_{min} curve was empirically found in Eq. (3.27).

The region above the ϕ_{min} curve represents the constant-pattern region, in which a system has sufficient column length and other conditions $(L_f, k_{f,}^* \alpha^e)$ to develop a CPIT. The ϕ_{min} curve represent the minimum required conditions to develop the constant-pattern state. As k_f^* increases to above 34, the minimum dimensionless column length ϕ_{min} approaches one, which means that the minimum column length to reach the constant-pattern state for a nonideal system (L_{iso-nid}) approaches that for an ideal system. The region below the ϕ_{min} curve represents the transientpattern region, in which a system has not reached the constant-pattern state. The general map can be used to determine, without simulations, whether a set of material properties and operating conditions can reach the constant-pattern state. A procedure to calculate the minimum column length to reach the constant-pattern state is described in Appendix E. Because the map is based on dimensionless groups, this method is applicable to LAD systems at any scale.

3.4.6 Verification of the minimum dimensionless column length curve and the general map

The ϕ_{min} curve obtained from simulations and theoretical analysis (Figure 3.14b) was also verified using five sets of LAD experiments. The ϕ_{min} curve was tested experimentally for the separation of equimolar mixture of Nd and Pr. The chromatograms are shown in Figure 3.6. The design of the experiments was based on five different values of ϕ_{min} , ranging from 1 to 1.5. A procedure to calculate the operating conditions is reported in Appendix E.

Figure 3.6 shows the effluent histories for the five cases marked on the ϕ_{min} curve in Figure 3.15. The dimensionless mass transfer zone lengths L_{MTZ}/L_c obtained from the experimental effluent histories agree closely with those obtained from simulations as shown in Figure 3.6f, indicating that a constant-pattern isotachic train was developed in all the experimental systems. The system in Figure 3.6a was designed to have a low dimensionless column length, $\phi = 1$, whereas the system in Figure 3.6e was designed for $\phi = 1.5$. The mass transfer zone length was smaller, the feed loading was larger, and the yields of high purity products were higher for Figure 3.6a than for Figure 3.6e. However, the productivity is smaller for Figure 3.6a because the linear velocity was reduced to achieve the low ϕ .

This general map works not only for binary systems but also for multicomponent systems based on the most difficult separation or the lowest selectivity pair. The experimental data and the literature data discussed in the previous section were analyzed and marked on the general map in Figure 3.15 to compare their operating conditions. The marked point for Figure 3.5a is in the constant-pattern region in Figure 3.15, which shows the column length was longer than needed to reach constant-pattern. The column length can be reduced to improve sorbent productivity without reducing the product purity or yield.

The points for Figure 3.6 are on the ϕ_{min} curve, as expected. Figure 3.5b and all the literature data in Figure 3.7 are in the transient-pattern region below the ϕ_{min} curve. These cases did not develop constant-pattern isotachic trains. Either the column length should be increased, or mass transfer resistances should be reduced by reducing flowrate or particle size. Moreover, the point for Figure 3.7c is close to the ϕ_{min} curve, but this system could not develop a constant-pattern state because the Pr loading was too small to develop a flat-top band. A longer column and a higher loading should be used to move the point on or above the ϕ_{min} curve to develop a CPIT with flat-top bands.

3.5 Conclusions

A detailed rate model and associated simulations were developed for the first time for nonideal LAD systems. The model and associate parameters were verified with experimental data for the separation of binary REE mixtures. The verified rate model simulations can be used to replace a large number of time-consuming experiments for designing or developing LAD processes. The verified rate model simulations also enabled us to elucidate the separation mechanism of a binary REE mixture in LAD and the transition from the transient-pattern to the formation of a constantpattern isotachic train. The results showed that fast complexation reactions between the ligand and the presaturant, which has higher affinity for the ligand than REEs, drives a CPIT in LAD. The complexation of the ligand with a high-affinity REE (or REE1) results in the development of a relatively pure REE1 band (or a "box car") following the desorption wave of the presaturant. Since the ligand prefers REE1 to REE2, eventually the REE2 band lags behind and separates from the REE1 band to form an isotachic train. The apparent separation of a mixture and the formation of a constant-pattern isotachic train are similar to those in conventional displacement chromatography (without ligand), where the displacer with the highest affinity for the sorbent displaces the most strongly adsorbed species in the feed mixture. The strongly adsorbed solute in turn displaces the solute with a lower affinity. The chain displacement of a lower affinity solute by a high-affinity solute eventually results in sharp boundaries between the bands at the constant-pattern state. The species with the lowest affinity with the sorbent elutes first. By contrast, the sharp boundaries in LAD result from the complexation reactions of the ligand with the feed components and the presaturant. The species with the highest affinity for the ligand elutes the first.

Development of a constant-pattern isotachic train is important for producing high-purity products with high yields in LAD. The minimum column length for the formation of an isotachic train for binary system for an ideal system can be calculated from the local equilibrium theory (Appendix B). However, the general conditions for the formation of an isotachic train in non-ideal systems are unknown from the literature. The formation of a constant-pattern shock layer in conventional displacement of a low affinity species by a high affinity species for non-ideal systems is well known form the literature. The shock layer thickness in binary systems can be estimated from the effective sorbent selectivity between the two species and the overall mass transfer coefficients. However, the shock layer theory does not address the question about the column length or the general conditions which are required to reach the constant-pattern state.

In this study, the key dimensionless groups controlling the formation of constant-pattern shock layer were first derived from the effective sorbent selectivity α^e , nonlinear distribution coefficient K_d, and the dimensionless overall mass transfer coefficient k_f^* . The multiple parameters were combined into dimensionless groups to reduce the number of variables. Rate model

simulations for the separation of a binary REE mixture were then designed to verify the literature solutions of the constant-pattern shock layer thickness. They were also designed to obtain the transient mass transfer zone lengths and the minimum column lengths to reach the constant patternstate with various loading fraction L_f . The minimum column lengths for the formation of an isotachic train in an ideal system were obtained from the wave interference theory and used as the characteristic lengths to obtain various dimensionless column lengths ϕ and ϕ_{min} . The dimensionless groups for constant-pattern shock layer were modified to incorporate the loading fraction. The feed length for an ideal system instead of the column length was used as the characteristic length for the transient and the constant-pattern mass transfer zone lengths. The dimensionless column length points with the same loading fractions are connected to form the constant ϕ lines, which intersect with the constant-pattern line (diagonal) at ϕ_{min} . The minimum dimensionless column length curve (ϕ_{min} curve) was found by plotting the intersection points of the constant ϕ lines with the CP line in Figure 3.14a versus the function related to the RHS of Eq. (3.18). The values of ϕ_{min} obtained from the simulations were plotted against the strategically formulated new dimensionless group to generate a map, which clearly separates the parameter space into the constant-pattern state and the transient state. This ϕ_{min} curve obtained from simulations was further verified using five experiments for the separation of Nd and Pr.

The minimum required conditions to reach the constant-pattern state is shown as the ϕ_{min} curve on the map. The minimum column length to reach the constant pattern state (L_{iso-nid}) is controlled by the effective sorbent selectivity, loading fraction, and dimensionless overall mass transfer coefficient. As dimensionless overall mass transfer coefficient and effective sorbent selectivity increase, the minimum column length to reach the constant-pattern state for a nonideal system (L_{iso-nid}) approaches that for an ideal system. High effective sorbent selectivity and large

dimensionless overall mass transfer coefficient reduce the constant-pattern mass transfer zone length $L_{MTZ,CP}$ as well as the minimum column to reach the constant-pattern state $L_{iso-nid}$. If the intrinsic material and operating parameters are known for a given LAD system, this map can tell whether the system is in the constant-pattern region or in the transient-pattern region. If the material properties, intrinsic parameters, operating velocity, and feed composition and feed volume are given, the ϕ_{min} curve in the general map can be used to predict, without simulations, the minimum column length which is required to reach the constant-pattern state. Alternatively, if column length is fixed, one can determine the maximum loading volume to reach the constantpattern state. The general map is useful for designing efficient LAD system for separating binary mixtures of REEs with high purity and high yield.

CHAPTER 4. CONSTANT-PATTERN DESIGN METHOD FOR THE SEPARATION OF TERNARY MIXTURES OF RARE EARTH ELEMENTS USING LIGAND-ASSISTED DISPLACEMENT CHROMATOGRAPHY

4.1 Introduction

Ligand-assisted displacement chromatography (LAD) method that has also shown promise for the separation of a multicomponent mixture of REEs. An example of the dynamic column profiles for the separation of a ternary mixture is shown in Figure 4.1. For ideal ligand-assisted displacement systems, h-transformation theory can be used to find the minimum column length required to develop an isotachic train [74]. However, h-transformation theory does not apply for nonideal systems, which have wave spreading due to mass transfer effects. Although analytical solutions for the mass transfer zone length of nonideal systems have been derived, they are limited to systems that have reached a constant-pattern state [72,73]. Without a method to determine the minimum column length required for a nonideal system to reach a constant-pattern state, no design and optimization method for multicomponent separations for nonideal systems was available.

In Chapter 3, a general map was developed for LAD. This map showed how key dimensionless groups affect the dimensionless minimum column length to reach a constant-pattern state [29]. The key dimensionless groups are the effective sorbent selectivity, loading fraction, and overall mass transfer coefficient. This map can be used to determine if a pair of components will reach a constant-pattern state under a specific set of operating conditions. However, the map does not tell the yields of the components for a target product purity and a given set of operating conditions.



Figure 4.1 Simulated dynamic column profiles for the separation of a ternary mixture of Sm, Nd, and Pr in LAD. The simulation parameters are discussed in the Theory section.

In this chapter, a method to design the separations of ternary mixtures using LAD was developed. The use of the general map is extended for ternary systems, and an equation for the yield of each component is derived in terms of dimensionless groups. The yield equations allow for the specific yield of a single component or the minimum target yields for multiple components to be achieved in the design. The specific objectives of this study are (1) to develop a constant-pattern design method for ternary separation with high purity, high yield, and high productivity, (2) to verify the design method experimentally, and (3) to understand the effects of material properties, intrinsic parameters, and operating parameters on the yield and the productivity for LAD process for ternary separations.

An overview of the research approach for the development of the constant-pattern design method is shown in Figure 4.2. First, the general map based on dimensionless group analysis and rate model simulations was extended for the separation of ternary mixtures. Next, an equation for the yield of a given component in LAD in terms of dimensionless groups was derived from shock layer theory and dimensionless group analysis. The map and the yield equations were used to obtain the operating conditions required to achieve a target yield of a single component or minimum target yields of two or three components in a ternary mixture. The developed method was tested in lab scale experiments for different yields, ligand concentrations, and feed compositions. The key factors controlling the product yield and productivity were found from the derived yield and productivity equations. The effects of the key dimensionless groups on the yield, productivity, and design were examined using experiments and rate model simulations.

The highlights of this study are as follows. A robust and scalable design method was developed for the separation of ternary mixtures for nonideal systems. The development of a constant-pattern state is limited by the lowest selectivity weighted composition factor. Longer columns and higher ligand concentrations result in higher productivity for the target yields and required purity. Multiple variables are optimized without any simulations to achieve a separation with the desired yield and purity. The results show that the constant-pattern design method enables 839 times higher total productivity than literature values.



Figure 4.2 Research approach to develop constant-pattern design method for ternary separation.

4.2 Theory

4.2.1 Maximum loading fraction to develop an isotachic train for a ternary mixture in ideal systems

Key components of the design of ideal LAD systems are the effective sorbent selectivity and feed length (L_{feed}). The effective sorbent selectivity is the sorbent selectivity relative to the ligand selectivity, as defined in Eq. (3.1). The feed length is defined as the length of the column in an ideal system that is saturated with the solutes after the feed is loaded (Eq. (3.3)).

Helfferich and James developed wave interference theory to determine the minimum column length relative to the feed length (L_{iso-id}/L_{feed}) that was required to form an isotachic train in ideal, multi-component systems [33,75,87]. While in binary ideal systems L_{iso-id} is only a function of the effective sorbent selectivity, in ternary ideal systems, L_{iso-id} is a function of both the effective sorbent selectivity and the feed composition. A separation of an equimolar mixture of three components using LAD is illustrated in Figure 4.3. The column length required to separate three components of a ternary mixture (z_{ij}) are shown in Eq. (4.1) [74]:

$$\frac{z_{13}}{L_{feed}} = \frac{\alpha_{1,3}^e}{\alpha_{1,3}^e - 1}$$
(4.1a)

$$\frac{z_{12}}{L_{feed}} = \frac{\alpha_{1,2}^e \alpha_{1,3}^e(h_2 - 1)}{h_2(\alpha_{1,2}^e - 1)(\alpha_{1,3}^e - 1)}$$
(4.1b)

$$\frac{z_{23}}{L_{feed}} = 1 + \frac{\alpha_{1,3}^e(\alpha_{1,3}^e - h_1)}{h_1(\alpha_{1,3}^e - 1)(\alpha_{1,3}^e - \alpha_{1,2}^e)}$$
(4.1c)

where h_i is the non-trivial roots of the H-function of component "*i*". To separate all three components, the largest length calculated from Eq. (4.1) should be used for the value of the dimensionless minimum column length for an ideal system L_{iso-id}/L_{feed} (Eq. (4.2a)). The inverse of that ratio is the maximum loading fraction for an ideal system to develop an isotachic train (Eq. (4.2b)).

$$\frac{L_{iso-id}}{L_{feed}} = \max\left(\frac{z_{13}}{L_{feed}}, \frac{z_{12}}{L_{feed}}, \frac{z_{23}}{L_{feed}}\right)$$
(4.2a)

$$L_{f,max,id} = \frac{L_{feed}}{L_{iso-id}}$$
(4.2b)



Figure 4.3 (a) Separation of three components by loading a displacer and (b) corresponding band migrations on a distance-time diagram.

4.2.2 Constant-pattern mass transfer zone length for ternary nonideal systems

The length of the mass transfer zone (L_{MTZ}) is the key to determining the yield of a nonideal displacement process. The lengths of the mass transfer zones in ternary systems are illustrated with respect to the length in the column or the elution time in Figure 4.4a and 4.4b, respectively. In the

constant-pattern state, Eq. (3.17) can be applicable to the length or time of the mass transfer zone at constant-pattern ($L_{MTZ,CP}$ or $t_{MTZ,CP}$).



Figure 4.4 Definition of mass transfer zone length: (a) L_{MTZ} in column length and (b) t_{MTZ} in effluent histories. The shaded regions are the lengths of the mass transfer zones for a specific cut θ .

As in binary nonideal systems, the column length required to develop a constant-pattern isotachic train in ternary nonideal systems is longer than the minimum column length for an ideal system L_{iso-id} with the same selectivity. It is useful to define a dimensionless column length (ϕ), which is defined in Eq. (3.22) [29].

For a constant-pattern isotachic train to form in a ternary system, all the mass transfer zones between each pair of components in the train must reach a constant-pattern state. Because the operating conditions of the column are the same for all the components in a ternary mixture, the lowest selectivity pair will require the longest column length to reach a constant-pattern. Therefore, the overall lowest value of α^e in a ternary system should be used to determine the minimum column length required to form a constant-pattern isotachic train when designing ternary separations. Because this is the most conservative value, all other components will also have sufficient column length to reach a constant-pattern state to form an isotachic train. This assumption was verified using rate model simulations and an example is shown in Figure 4.1. The simulation parameters of this figure are based on Design 2A in Table 4.1.

An example of the general design map with several points from experiments in this study are shown in Figure 4.5a [29]. This map divides the constant-pattern region from the transient region by the ϕ_{min} curve. The ϕ_{min} is the minimum required column length to form a constantpattern isotachic train in non-ideal systems ($L_{iso-nid}$) non-dimensionalized by the minimum column length to form an isotachic train in a corresponding ideal system. This ϕ_{min} is also the dimensionless maximum loading fraction of a non-ideal system to reach a constant-pattern state, Eq. (4.3)

$$\phi_{min} = \frac{L_{iso-nid}}{L_{iso-id}} = \frac{L_{iso-nid}/L_{feed}}{L_{iso-id}/L_{feed}} = \frac{L_{f,max}}{L_{f,max,id}}$$
(4.3)

The ϕ_{min} curve shown in Figure 4.5a has been correlated as a function of $L_f k_f^*$ and the minimum α^e among all the selectivity pairs for a binary system (Eq. (3.27)) [29]. In this study, we verified that the ϕ_{min} curve is applicable for ternary systems if the lowest effective sorbent selectivity between the target components and their adjacent components is used in this equation.



Figure 4.5 General map identifying constant-pattern and transient pattern regions and (b) Effects of Y_i and θ on $L_f k_f^*$ values and corresponding ϕ values. The designed experiments (Design 1~4) are marked along the ϕ_{min} curve in (a).

4.2.3 Derivation of the yield equation for a given component in a ternary nonideal system

While the general map can determine if a separation train has reached a constant-pattern state, it cannot determine the yield of the separation. Therefore, an expression for the yield is needed for the design of effective LAD systems. The yield for component i is defined as the ratio of the amount of product i collected in the effluent and the total amount of component i in the feed as illustrated in Figure 4.6. This can be expressed mathematically as:

$$Y_i = \frac{c_d V_x}{c_{f,i} V_f} \tag{4.4}$$

where c_d is the ligand concentration and V_x is the elution volume of a product which can be expressed as:

$$V_x = V_i - \frac{1}{2} (t_{MTZ,1} + t_{MTZ,2}) \varepsilon_b u_0 A_c$$
(4.5)

where V_i is the volume of solution eluted between the adsorption wave center and desorption wave center. For an ideal system (without any wave spreading), then this elution volume would contain all the loaded component in the feed.

If Eq. (3.17b), which is the effluent time corresponding to the mass transfer zone length, and Eq. (4.5) are substituted into Eq. (4.4), the yield is derived in terms of dimensionless groups (Eq. (4.6a)). To further simplify this expression, the effective sorbent selectivity and mole fraction in the feed (x_i) were combined into a selectivity weighted composition factor (γ) in Eq. (4.6b). Eq. (4.6b) can be rearranged to express a function $f(Y_i, \beta)$ in Eq. (4.6c).

$$Y_{i} = 1 - \frac{\beta}{2x_{i}L_{f}k_{f}^{*}} \left(\frac{\alpha_{i-1,i}^{e} + 1}{\alpha_{i-1,i}^{e} - 1} + \frac{\alpha_{i,i+1}^{e} + 1}{\alpha_{i,i+1}^{e} - 1} \right)$$
(4.6a)

$$Y_i = 1 - \frac{\beta}{2\gamma_i L_f k_f^*} \tag{4.6b}$$

$$f(Y_i,\beta) = (1 - Y_i)2\gamma_i L_f k_f^* - \beta = 0$$
(4.6c)

$$L_f k_f^* = \frac{\beta}{(1-Y_i)2\gamma} \tag{4.6d}$$

$$\gamma_i = x_i \left(\frac{\alpha_{i-1,i}^e + 1}{\alpha_{i-1,i}^e - 1} + \frac{\alpha_{i,i+1}^e + 1}{\alpha_{i,i+1}^e - 1} \right)^{-1}$$
(4.7)

where L_f is the loading fraction, or the total amount loaded divided by the total column capacity. This equation allows for the design to achieve a target yield for the component of interest. If the yields of more than one component are of interest, then the yield equation for the component with the lowest γ should be used in the design for finding the maximum loading volume and mobile phase velocity for the given column length. If the yield for the component with the lowest γ is achieved, all the other components will have a higher yield. Thus, the component with the lowest γ value is defined as the controlling component. This strategy ensures that all components of interest meet the target minimum yield requirement.



Figure 4.6 Yield of a middle component from an isotachic band in (a) an ideal system and (b) a nonideal system

When the function in Eq. (4.6b) is plotted as a 3-D surface for the middle component in a ternary mixture ($\theta = 0.05$), the result is shown in Figure 4.7. As evidence by the figure, the selectivity weighted composition factor γ plays an important role in the operating conditions (loading fraction L_f and dimensionless overall mass transfer coefficient k_f^*) required to reach a target yield. For a fixed γ , a larger value of $L_f k_f^*$ is needed to achieve a higher yield. As γ increases, the same value of $L_f k_f^*$ can be used to achieve a higher yield. It is also evident from Eq. (4.6b) that as γ increases, lower values of $L_f k_f^*$ can be used to achieve the same yield. This means that higher flowrates can be used, and higher productivities can be achieved.



Figure 4.7 Yield correlation with combined dimensionless groups $L_f k_f^*$ and selectivity weighted composition factor γ as shown in Eq. (4.6b).

4.2.4 Constant-Pattern Design Method

An overview of the design method is given in Figure 4.8. Given a minimum target yield of a key component, a breakthrough cut value (θ), feed composition, selectivities, intraparticle diffusivities, particle size, and void fractions, a value of γ_i can be calculated from Eq. (4.7) for all components. If there are multiple products of interest, this process is done for the component with the lowest γ to give the most conservative design. The most conservative design should achieve or exceed the target minimum yield for all components. Next, based on the controlling component, which has the lowest γ , a value of $L_f k_f^*$ can be calculated from the yield equation (Eq. (4.6)). Since the lowest α^e between target components and adjacent components determines the constantpattern state, the lowest α^e and a $L_f k_f^*$ value can be applied in Eq. (3.27) to solve for the ϕ_{min} value for a non-ideal system. Then wave interference theory can be used to calculate the minimum column length to achieve the constant-pattern state for the corresponding ideal system, L_{iso-id} , Eq. (4.2a) and $L_{f,max,id}$, Eq. (4.2b). Once ϕ_{min} is calculated from the general map, then the maximum loading fraction for a non-ideal system ($L_{f,max}$) can be calculated from ϕ_{min} and $L_{f,max,id}$ in Eq. (4.2b). One can then solve for k_f^* from $L_{f,max}$ using Eq. (4.6d).

To optimize the operating conditions in the algorithm, a wide range of column lengths and their corresponding linear velocities were calculated based on the obtained k_f^* using Eqs. (3.13-14). The operating velocity can be found from Eq. (3.14a) or (3.14b) if film resistance is negligible. The resulting operating velocity gives the target yield of the component of interest. The calculation loop continues until the pressure drop of each condition is limited by the maximum pressure drop limit (Eq. (4.15)). Next, one can choose optimal conditions for the maximum productivity, which has maximum column length and corresponding u₀, or find operating conditions for a specific column length. The loading amount used in the design is calculated based on $L_{f,max}$ and the adjusted column capacity, which takes into account ligand efficiency [29]. The maximum ligand concentration for the band width limit is calculated based on the loading amount and given conditions.



Figure 4.8 Scheme of constant-pattern design method for ternary separations

4.2.4.1 Productivity in LAD

Productivity is an important design variable that can determine the size and number of columns required for a separation. Productivity is defined in this study as the amount of product produced per column volume per unit time.

$$P_{R,i} = \frac{C_{f,i}V_fY_i}{V_C t_{cycle}} \tag{4.8}$$

where t_{cycle} is the total cycle time. Because the elution time (t_{elute}) is much longer than the time required for loading and regeneration, the cycle time can be approximated as the elution time.

$$t_{cycle} \approx t_{elute} \tag{4.9}$$

where

$$t_{elute} = \frac{L_c(1+K_d)}{u_0} \approx \frac{L_c K_d}{u_0}$$
(4.10)

If Eq. (20), Eq. (23), and the expressions for the feed volume and column volume are substituted into Eq. (21), the resulting productivity equation is as follows:

$$P_{R,i} \approx \frac{\varepsilon_b x_i C_d u_0 L_f}{L_c} \left(1 - \frac{\beta}{2\gamma_i L_f k_f^*} \right) \tag{4.11}$$

4.2.4.2 Assumptions and limits for the Design Method

While Eq. (4.11) would suggest that raising the ligand concentration will increase the productivity without decreasing yield, there are some physical limitations to the ligand concentration that can be used. One important limit is the solubility limit of the ligand in solution. If the concentration is too close to the solubility limit, then clogging of pipes or in the column can stop flow or cause high pressures.

Another concentration limit is based on the length of the mass transfer zone. The assumption made in this analysis is that the components will form bands with flat tops. If the concentration of the ligand is sufficiently high, the elution band becomes too narrow to maintain a flat top in the presence of mass transfer spreading, then the analysis is no longer valid. Formally this maximum ligand concentration can be found using mass balance and the mass transfer zone length as follows. The input of component "j" into the column is equal to the volume of the column occupied by component "j" in an ideal system:

$$C_{f,j}V_f = L_j A_c q_{max} + \varepsilon_t C_d A_c L_j \qquad (j = 1,2,3)$$

$$(4.12)$$

Eq. (25) means that:

$$L_{j} = \frac{c_{f,j} v_{f}}{A_{c}(q_{max} + \varepsilon_{t} c_{d})} \qquad (j = 1, 2, 3)$$
(4.13)

where L_j is the length of the component "j" band in an ideal system, ε_t is the total porosity. If this length is shorter than one half of the sum of the two mass transfer zone lengths, then the assumed shape of the bands is not valid, and the design will be inaccurate. This condition should be checked for all components of interest.

$$L_{j} = \frac{C_{f,j}V_{f}}{A_{c}(q_{max} + \varepsilon_{t}C_{d})} \ge \frac{1}{2} \left(L_{MTZ,ij} + L_{MTZ,jk} \right) \qquad (j = 1,2,3)$$
(4.14)

When q_{max} is large compared to $\varepsilon_t C_d$, the ligand concentration limit calculated by Eq. (4.14) is much higher than the solubility limit. Therefore, the ligand concentration is limited by solubility rather than band width.

The pressure limit is another limiting factor in this design method. For Reynold's numbers less than 1, the simplified Ergun equation gives the pressure drop.

$$\Delta P = L_c \left[150 \frac{P^2 \mu u_0}{4R_p^2} \right]$$
(4.15)

In the design, the pressure limit is checked. For a specified maximum pressure drop (ΔP_{max}) the maximum column length ($L_{c,max}$) for a given particle radius and velocity can be calculated [88].

$$L_{c,max} = \frac{\Delta P_{max} R_p^2}{37.5 P^2 \mu u_0}$$
(4.16)

4.2.4.3 Breakthrough cut and yield on the minimum column length ϕ_{min} and productivity

The selected cut (θ) can affect both the designed loading fraction and the operating velocity for a given system. Additionally, using lower θ values will increase the purity of the products in a
LAD system, as expected from Figure 4.6, but result in a larger value of $\beta (= ln \left| \frac{1-\theta}{\theta} \right|)$. It is clear from Eq. (4.11) that lower θ values (or higher β) will give a smaller productivity, indicating a trade-off between product purity and productivity.

Figure 4.5a shows that when the x-axis value is 34 or greater, $\phi_{\min}=1$, or $L_{f,\max}=L_{f,\max,id}$. For a fixed yield, Eq. (4.6d) indicates the value of k_f^* is proportional to the value of β , meaning that smaller θ values require larger k_f^* values to achieve the same yield. Because larger k_f^* values correspond to longer columns and slower flowrates, lower productivities are achieved. This means that if yield is fixed, there is a tradeoff between product purity and productivity in the region where $\phi_{\min}=1$.

In the design method, the yield and the cut are fixed. The function $f(Y_i, \beta)$ in Eq. (4.6c) plotted versus $L_f k_f^*$ is a straight line. An example is shown in Figure 4.5b. The $L_f k_f^*$ value that satisfies Eq. (4.6c) for a specified yield and β is the intercept of this straight line on the x-axis. The absolute value of the intercept of this straight line on the y-axis is the β specified in the design. The slope of the straight line is proportional to $(1-Y_i)$ and γ . As the specified yield increases or γ decreases, the slope decreases, and the $L_f k_f^*$ value increases. As the cut decreases, the β value increases, and the straight line shifts downward, resulting in a larger $L_f k_f^*$ required in the design. Figure 4.5b shows qualitatively how the key dimensionless groups affect the key design variables.

4.3 Material and Methods

4.3.1 Separation of REEs using ligand-assisted displacement chromatography

Two Millipore columns were connected in series. The packed column sizes were 1.16 cm $(ID) \times 39$ cm (L_c) , and 1.16 cm $(ID) \times 44$ cm (L_c) , respectively. The column void fractions were then characterized by pulse tests. Prior to REEs separation, the columns were pre-equilibrated with

 Cu^{2+} by loading 0.1 M CuSO₄ solution (5 mL/min) until the Cu breakthrough curve appeared. Excessive copper ions in the mobile phase were removed by flushing the columns with DDW until the conductivity of effluent dropped to below 0.005 mS/cm.

To validate the design method, three experiments targeting different yields (70%, 80%, 95%) for the middle component (Nd) were carried out. The feed for the ligand-assisted displacement chromatography experiments were a synthetic mixture of Pr³⁺, Nd³⁺, and Sm³⁺ (0.06 M each). The loading volume and linear interstitial velocity for Design 95%, 80%, and 70% were 115 mL and 1.7 cm/min, 115 mL and 8.7 cm/min, and 102 mL and 10.6 cm/min, respectively. The ligand solution (EDTA-Na) was prepared by dissolving a stoichiometric amount of EDTA in DDW, titrating using sodium hydroxide solution to pH 8.4 and diluting to a final concentration of 0.03 M.

To investigate the effects of ligand concentration on the yield and productivity, another LAD experiment targeting 80% yield for the middle component (Nd) was carried out using the same conditions except the ligand concentration was raised to 0.06 M. To investigate the effects of feed composition on the yield and productivity, a 66 mL of feed mixture with concentrations of 0.0467 M Sm³⁺, 0.1267 M Nd³⁺, and 0.06 M Pr³⁺ was loaded on the column. Then, REEs were eluted out by loading 0.03 M EDTA-Na (pH 8.4) with interstitial velocity 10.5 cm/min.

After all the REEs were eluting out in each LAD experiments, the column was saturated with Na^+ . To regenerate the column, the column was washed by DDW first to remove all the ligand solution in the mobile phase and then pre-equilibrated by Cu^{2+} .

4.4 Results and Discussion

4.4.1 Experimental verification of the design method for the separation of equimolar mixtures with target yields for all three components

The constant-pattern design method was verified for the separation of three equimolar REEs with three experiments. A summary of the design procedure utilized is shown in Figure 4.8 for specific column length of 83 cm. The film resistance was assumed to be negligible (Eq. (3.14b)). The method was tested by targeting minimum yields of 70%, 80%, and 95% for all three components in an equimolar mixture of Sm, Nd, and Pr. The minimum purity requirement was 99%. To achieve the purity requirements, a θ value of 0.05 was tested. Under the experimental conditions in this investigation, a θ value of 0.05 was sufficient to achieve purities >99%. In the equimolar case, Nd was the element with the lowest value of γ (Table 4.1). For this reason, Nd was the controlling component for the design method. The yield equation for Nd was used in the design to solve for the linear velocity. The lowest overall selectivity pair in this separation was between Nd and Pr ($\alpha_{min}^e = 1.8$). The effective sorbent selectivity for the pair of Nd and Pr was used to calculate ϕ_{min} using the general map because it gave the most conservative estimate. The calculated values of $L_f k_f^*$ for each design case were marked in Figure 4.7 as well as on the general map in Figure 4.5a. The parameters used for the design and simulations are listed in Table 4.1. The selectivities and diffusivities for each component were estimated experimentally and verified in the previous study [29].

A summary of the experimental yield, purity, and productivity for the three runs is shown in Table 4.2 and the resulting chromatograms are shown in Figures 4.9a-c. All the designed separations reached a constant-pattern state. The simulated dynamic profiles for Design 2A are shown in Figure 4.1 as an example. The purity of all three components was higher than 99% when the breakthrough cut is 0.05 in all the designs. In all cases, the experimental yields of the controlling component, Nd, were achieved within experimental error (2%), demonstrating the effectiveness of the design method. Because Nd had the lowest γ , all other components had even higher yields than the target yields. By selecting the operating conditions based on the controlling component, which has the lowest γ , the yields of all other components are ensured.

In Figure 4.9d, the yields and productivities of Sm, Nd, and Pr from the experimental results were compared with the yield-productivity curve of Nd calculated from the design method. Since the yields of Sm and Pr were higher than that of Nd in the same train, the productivities of Sm and Pr were higher than that of Nd in each case. The yields and productivities of Nd from the experimental results were close to the yield-productivity curve (dotted line in Figure 4.9d). Both experimental results and the theoretical curve show a trade-off between yield and productivity.

The reason for the trade-off relationship is that increasing the minimum target yield requires a reduction in the mass transfer zone lengths. The mass transfer zone length in Figure 4.9a is smaller than those in Figures 4.9b and 4.9c. The required value of k_f^* for Figure 4.9a is larger than those for Figures 4.9b and 4.9c (Table 4.2). Increasing k_f^* reduces the flow rate, which results in a lower productivity of all component.

The productivity results based on the constant-pattern design method were compared with those in the literature in Figure 4.9d. For the similar purity and yields of Sm, Nd, and Pr, the experimental productivities based on the constant-pattern design method are two orders of magnitude higher ($\times 200 \sim 400$) than those in the literature [30].

System and operating parameters												
L _c (cm)	ID (cm)	R _p (μm)	DV ε _b (mL)			ε _p	q _{max} (meq./mL BV)		C _{f,i} (N)			
83	1.16 56		7.6 0.3		5	0.34	1.45		0.18			
	Design 1		Design 2	A/2B	Ι	Design 3		Design 4				
Feed volume (mL)	115		115			.02		66				
u ₀ (cm/min)	1.7	8.7	7 10.6				10.5	.5				
Mass transfer parameters												
Component	Brow diffusiv (cm ² /2	nian ity, D _b min)	Po diffus D (cm ² /	ore sivity,) _p /min)	Axial dispersion coefficient, E _b (cm ² /min)			Film mass transfer coefficient, k _f (cm/min)				
All species	4×10 ⁻⁴	9×10 ⁻⁵			(\	Chung and Wen (1968)			Wilson and Geankoplis (1966)			
Isotherm parameters (Constant separation factor isotherm)												
Component	Cu (ref)		Sm	Ν	Nd		Pr		EDTA-Na			
α _{i,ref}	1		5		16		28.8 1		144			
Numerical parameters (unit: N)												
Axial element	Step size (L/u ₀)	Col	Collocation points			Tolerance		e				
		Axia	Axial Particle			Absolute		Relative				
100	0.01	4	4 2			1x10 ⁻⁴		1x10 ⁻⁴				

Table 4.1 Parameters for design and rate model simulations



Figure 4.9 LAD separation experiments designed for the minimum target yield (a) 95%, (b) 80%, and (c) 70%, respectively, for (>99%) purity (θ: 0.05); and (d) comparison of the yield and productivity of the middle component (Nd) (dashed line) estimated from the design method with experimental results and literature data; Sm (round), Nd (triangle), Pr (square); Solid lines are effluent histories and dashed lines are simulation results. Literature data obtained from [30] is enlarged at the corner.

Table 4.2 Yield, purity, and productivity obtained from experimental results. Designs 1-3 are based on the minimum target yields for recovering all components, while Design 4 is for the recovery of only the major component, Nd, with a minimum target yield. The designs did not consider film resistance and were based on 0.8 minimum target yield. The unit of productivity (P_R) is kilogram per bed volume (m^3) per day.

Design		1	2A	3	2B	4	
I.		0.49	0.49	0.43	0.49	0.36	
Lf		975.1	243.8	202.4	243.8	203.7	
γ _{Sm}		0.097	0.097	0.097	0.097	0.159	
Yna		0.061	0.061	0.061	0.061	0.1	
γ_{Pr}		0.066	0.066	0.066	0.066	0.109	
Sm	Yield (%)	97	90	81	86	63	
	Purity (%)	99.9	99.1	99.7	99.8	99.5	
	P _R	2.8	15.2	20.4	31.9	8.3	
Nd	Yield (%)	95	82	70	80	80	
	Purity (%)	99.9	99.7	99.3	99.4	99.6	
P _R		2.8	14.1	16.8	28.3	27.5	
Pr	Yield (%)	95	84	76	86	67	
	Purity (%)	99.9	99.9	99.4	99.7	99	
	P _R	2.8	15	18	29.8	10.6	
Total P _R		8.4	44.3	55.2	90	46.4	

4.4.2 Effects of effective ligand concentration on the yield and productivity

According to Eq. (4.6), the operating conditions required to achieve a target yield are independent of the ligand concentration unless the solubility limit or band width limit is reached. Therefore, higher ligand concentrations can be used without penalty to the yield of a system. To verify that the yield is independent of the ligand concentration, an additional experiment with a minimum target yield 80% for >99% product purity was tested. Operating conditions were the same as those used for Design 2A (Figure 4.9b), with the exception that the ligand concentration was doubled. The resulting chromatogram is shown in Figure 4.10a and a summary of the results can be found in Table 4.2. The chromatogram showed that the system reached a constant-pattern state with doubled band concentrations compared to Figure 4.9b. The minimum target yield for the controlling component, Nd, was reached within 1% and the yields of the other two components exceeded 80%. Also, the purity of all components was >99% in Figure 4.10a.

The productivity of Nd was nearly doubled as a result of the reduced elution time, as predicted in the yield-productivity curve in Figure 4.10b. Additionally, the productivities of Nd, Sm, and Pr for similar yields were much higher (×600~800) than those in the literature by utilizing a high ligand concentration. Both the theory and the experimental data suggest that using a higher ligand concentration results in more concentrated products and increases productivities without a penalty to yield. However, for designing a separation process, one should consider the ligand solubility limit and the maximum ligand concentration that can result in flat-top bands, Eq. (4.13), in the constant–pattern state.

Additionally, the total productivity of Nd, Sm, and Pr for the same purity and similar yields was 839 times higher than those in the literature [30]. This large improvement in productivity is a result of the cumulative effects of the following design differences: (1) a more efficient ligand

EDTA and a higher ligand concentration resulted in 6 times higher productivity, (2) about 5 times smaller sorbent particle size resulted in about 25 times higher productivity, (3) about 13 % higher loading fraction, and (4) about 5 times higher linear velocity results in 5 times higher productivity. The improvement in these key design parameters result in the huge improvement in productivity. Such an improvement is unlikely using a trial and error approach. Each experimental trial may take days or weeks. This example explains clearly why the design method is essential for designing processes for large scale production. The 839 times increase in sorbent productivity indicates that the column volume can be 839 times smaller, resulting in significant reduction in footprint, capital expenditure, chemical costs, and solvent costs.

The productivity of liquid-liquid extraction was estimated to be 3 kg REE/m³/day [12]. The productivity in LAD (90 kg REEs/m³/day) was estimated to be 30 times higher productivity and 25 times lower amounts of extractants. Most of the ligand and water can be recycled [10,89]. Hundreds to thousands of mixer-settler units can be replaced by a few chromatography columns, resulting in an order of magnitude smaller footprint and capital cost.



Figure 4.10 (a) LAD chromatograms using doubled ligand concentration for the same target yield as Design 2A (Fig. 9b) and (b) Comparison of the yield and productivity for different ligand concentrations; Sm (round), Nd (triangle), Pr (square); Solid lines are effluent histories and dashed lines are simulation results. Literature data obtained from [30] is enlarged at the corner.

4.4.3 Constant-pattern design to recover for a single component

One special case of ternary separation is the separation of one component from two impurities. To demonstrate the viability of the design method in this scenario, a different feed composition of Sm, Nd, and Pr, similar to one mineral source of REEs (1:2.7:1.3), was tested in Design 4 case with the same target yield and purity of Nd as Design 2A case [19]. With this new composition, Nd had the highest value of γ , however the goal in this scenario was to separate Nd from the other two components, thus it was treated as the target component. The resulting chromatogram is shown in Figure 4.11a.

To maintain the same target yield of Nd, for a larger value of x_i compared to the equimolar case (Design 2A), lower values of L_f and k_f^* were required. Thus, a higher flowrate was used than that in the equimolar case, resulting in a higher productivity of Nd (Figure 4.11b). However, the minor components, Sm and Pr, had lower yield and productivity than those of Nd. Therefore, a single component can be targeted with the design method to successfully reach a target yield, at the expense of the recovery of the other components. They are either collected as waste or must be sent to a secondary separation process.



Figure 4.11 (a) LAD chromatograms using different feed composition (Sm:Nd:Pr = 1:2.7:1.3) when designed a process for target yield of 80% for Nd with >99% purity (Design 4), (b) Yield-productivity plot comparing different feed composition with equimolar composition feed mixture

4.4.4 Effects of pressure drop limit and band concentration limit on the productivity for the target yield

Although the design method is scalable using dimensionless groups, for a minimum target yield and purity requirement, using a long column length and high ligand concentration is beneficial for improving productivity. Figure 4.12a is based on Design 2A and Figure 4.12b is based on Design 4. In Figure 4.12, the productivity of Nd for a given yield (80%) is plotted as a function of column length and effective ligand concentration according to Eq. (4.11).

As illustrated in Figure 4.11 the productivity curves rapidly increase in a short column, but they level off as column length increases. Since the value of k_f^* is a constant for a target yield and purity, using a longer column length requires a higher flowrate to keep the same k_f^* value. According to Eq. (3.14a), the Pe_b term is independent of the linear velocity so that the linear velocity will be raised at a slightly higher rate than the column length to maintain the same k_f^* . Since productivity is affected by column length and linear velocity as seen in Eq. (4.11), the productivity for the given yield increases slightly as the column length increases. Eventually the column length and velocity increase to the point of the maximum allowable pressure. The maximum productivity is achieved at the maximum column length (Eq. (4.16)) when the pressure drop limit is reached.

As shown in Figure 4.12, the productivity for the target yield and purity is proportional to the effective ligand concentration if the shapes of constant-pattern isotachic bands are maintained according to Eq. (4.14). Depending on the feed composition, it is possible to reach the solubility limits of a system before the band width limit is reached. It is recommended that the highest possible ligand concentration should be used, as there is no penalty to yield for high ligand concentrations as long as the model assumptions are true.



Figure 4.12 Productivity plot versus column length and effective ligand concentration for the target yield (80%) of the middle component (a) in Design 2A and (b) in Design 4, the different feed composition case (1:2.7:1.3).

4.4.5 Effects of the lowest effective sorbent selectivity on the productivity for the target yield

For Design 2A, if x_i , $\alpha_{i,j}^e$, Y_i , β are fixed, the values of L_f , k_f^* and ϕ_{min} are affected by the lowest effective sorbent selectivity. Thus, the lowest α^e pair determines the operating conditions to reach constant-pattern and limits the productivity for the given yield and purity. Figure 4.13 shows the effects of the lowest α^e on L_f , k_f^* , and the productivity for a minimum target yield of 80% if the lowest α^e is varied from 1.3 to 2.8. When the lowest α^e increases, the feed is more easily separated so that the maximum loading fraction increases. For a given yield and purity, the value of $L_f k_f^*$ decreases as the lowest α^e increases. Because the loading fraction increases when the value of the lowest α^e increases, the value of k_f^* decreases as a result (Figure 4.13a). Thus, when the lowest α^e increases, the productivity for the target yield is increased by reducing k_f^* and increasing L_f as illustrated in Figure 4.13b.



Figure 4.13 (a) Effects of the lowest sorbent selectivity on the loading fraction (L_f) and dimensionless overall mass transfer coefficient (k_f^*) for the target yield of 80% for Nd with >99% purity (Design 2A case) and (b) Effects of the lowest sorbent selectivity on the on the productivity for target yield (80%).

4.4.6 Effects of feed composition on the yield and productivity

While the separation of equimolar mixtures was useful for the development and verification of the design method, many natural mixtures of REEs have varied compositions that include both major and minor components. In the previous section, a range of γ (0.061~0.159) were studied. In this section, a wider range of γ and k_f^* values were studied. The effects of the feed mixture composition were investigated in three cases using rate model simulations. Studies on low selectivity or small γ cases showed that film resistances in the high k_f^* region (e.g. Case A) are no longer negligible. For this reason, the design method including film resistances (Eq. (3.14a)) was used in the case studies in this section. Parameters used for design and simulations are listed in Table 4.3. In all cases, the total feed concentration was 0.5 N.

In Case A, all three components of a mixture were targeted as desired products. In Case B, only the two major components of a ternary mixture are targeted as products and the minor impurity is collected as waste. In Case C, a single major component is purified from two minor components. A summary of the results of the case study can be found in Table 4.3.

In Case A, mixtures with ratios of Sm:Nd:Pr of 1:5:5, 5:1:5, 5:5:1, and 10:1:1 were separated. The minimum target yield for this case study was 80%, and the rest of the simulation parameters can be found in Table 4.3. Because the effects of composition are considered in the γ term in the design method, the design algorithm can be used with no modifications for the separation of both equimolar and non-equimolar mixtures. The low values of γ caused by the minor components in the mixtures lead to large values of k_f^* . As shown in Table 4.4, all target yields were achieved or exceeded in Case A, demonstrating that the design method is effective regardless of the composition of the feed mixture. The total productivity correlates well with a

higher value of the controlling γ value because the most difficult separation determines the velocity and loading fraction.

System and operating parameters											
L _c	ID	R _p	DV Eb		ε _p	q_{max}	C _{f,i}				
(cm)	(cm)	(µm)	(mL)		(meq		mL (N)				
						BV)					
83	1.16	56	7.6	0.35	0.34	1.45	0.18				
	Case A		Case B	Case B							
	(A1/A2	/A3/A4)	(B1/B2/B3	3)	(C1/C2/C3))					
Feed	115/115	5/125/165	97/104/10	7	112/71/71						
volume (mL)											
u ₀ (cm/min)	2.7/1.5/	1.9/2.2	8.3/9.8/9.2		30.4/11.9/12	2.5					
Mass transfer parameters											
Component	Brownian diffusivity, D _b (cm ² /min)		Pore diffusivity, D _p (cm ² /min)		Axial dispersion coefficient, E _b (cm ² /min)		Film mass transfer coefficient, k _f (cm/min)				
All species	4×10 ⁻⁴		9×10 ⁻⁵		Chung and Wen (1968)		Wilson and Geankoplis (1966)				
Isotherm parameters (Constant separation factor isotherm)											
Component	Cu (ref)	Sm]	Nd	Pr		EDTA-Na				
α _{i,ref}	1	5	16		28.8		144				
Numerical parameters (unit: N)											
Axial element	Step size Coll		location points		Т	Colerance	ce				
	(L/u_0)	Axia	l Partic	ele	Absolute		Relative				
250	0.01	4	2		1x10 ⁻⁴		1x10 ⁻⁴				

Table 4.3 Parameters for design and rate model simulations

In Case A, the controlling γ for each case was always a minor component of the mixture because of its small mole fraction (Eq. (4.7)). If the minor component is not desired as a product, the minor component can be ignored in the design. By ignoring the smallest γ , the corresponding value of $L_f k_f^*$ is decreased. The lower values of k_f^* correspond with higher productivities. In other words, by sacrificing the minor component, the overall productivity of the system is increased significantly. This is demonstrated in Case B. In Case B, mixtures of Sm, Nd, and Pr with composition ratios of 1:5:5, 5:1:5, and 5:5:1, respectively, were separated while ignoring the minor component. The minimum target yields were reached and exceeded by the design method for the two components of interest. The total productivities in Case B were more than double the total productivity in the Case A with the same composition. This confirms that the productivity is limited by the component with the smallest γ .

Another alternative case is the separation of a single major component from two impurities. In this case, the controlling γ and the minimum α^e correspond to the only target component. This case is demonstrated in Case C in Table 4.4. The minimum target yield is reached only for the target component. The other components are collected as a waste. By sacrificing the minor components, the total productivity of the system is increased in a similarly as in Case B. Both Case A4 and Case C1 show the separation of a feed mixture with a composition of Sm, Nd, and Pr of 10:1:1. The total productivity is much higher in Case C1 where only Sm is targeted. This suggests that there is a significant productivity sacrifice to separate minor components with very small γ values. Table 4.4 Yield, purity, and productivity of each component obtained from rate model simulations for different feed composition cases. The parameters used for the design and simulations were listed in Table 2. Total feed concentration in all cases was 0.5 N. Dead volume in all cases was 2% of column volume. The unit of productivity (P_R) is kilogram per bed volume (m³) per day.

Composition Target Sm:Nd:Pr Yield (%		Target Controlling Field (%) Component	Controlling γ	L _f	k_f^*	Sm			Nd			Pr			
	Target Yield (%)					Yield (%)	Purity (%)	P_R	Yield (%)	Purity (%)	P_R	Yield (%)	Purity (%)	P_R	Total P _R
Case A. Target All 3 Components with Minimum Target Yield 0.8															
A1 (1:5:5)	80	Sm	0.027	0.45	613	80	99.6	1.6	94	99.9	9.8	95	99.9	9.1	20.5
A2 (5:1:5)	80	Nd	0.017	0.45	973	97	99.96	7.0	81	99.5	1.2	98	99.9	6.7	14.9
A3 (5:5:1)	80	Pr	0.018	0.49	821	96	99.98	7.2	96	99.9	7.4	85	99.6	1.2	15.8
A4 (10:1:1)	80	Nd	0.015	0.65	730	99	99.98	21.0	81	99.6	1.8	85	99.7	1.7	24.5
Case B. Target 2 of 3 Components with Minimum Target Yield 0.8															
B1 (1:5:5)	80	Nd	0.084	0.38	230	-	-	-	81	99.6	26.9	82	99.6	25.0	51.9
B2 (5:1:5)	80	Pr	0.091	0.41	198	88	99.8	29.2	-	-	-	81	99.6	25.4	54.6
B3 (5:5:1)	80	Nd	0.084	0.42	210	88	99.8	28.0	81	99.6	26.3	-	-	-	54.3
Case C. Target Only 1 Major Component with Minimum Target Yield 0.8															
C1 (10:1:1)	80	Sm	0.24	0.44	68	81	99.6	161.0	-	-	-	-	-	-	161.0
C2 (1:10:1)	80	Nd	0.15	0.29	166	-	-	-	81	99.6	43.4	-	-	-	43.4
C3 (1:1:10)	80	Pr	0.17	0.28	158	-	-	-	-	-	-	81	99.6	40.9	40.9

4.5 Conclusions

The feasibility of ligand-assisted displacement chromatography (LAD) to separate mixtures of are earth elements into pure fractions has been shown since the 1950s. However, the literature processes were designed using trial and error and typically had low yield and low productivity. In this study, the constant-pattern design method for separating ternary mixtures of REEs using LAD was developed for nonideal systems. The general correlation for the minimum column length required to achieve the constant–pattern state for binary separations from our previous work was extended to ternary separations. Additionally, an equation for the yield of a target component as a function of 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 ensures the yields and the constant–pattern state for the target components. The design method minimizes the column length and improves the productivity, while also guaranteeing target

yields and high product purities (>99%). Given material properties, intrinsic parameters, and a minimum target yield, the design method provides the optimal operating conditions without trial and error. Because the design method uses intrinsic parameters and dimensionless groups, the designs are robust and scalable.

The design method was verified experimentally by separating ternary mixtures of REEs with different minimum target yields, ligand concentrations, and feed compositions. The minimum target yields of the controlling components were achieved within experimental errors (~2%), and the minimum target yields of all other target components were exceeded. The experimental product purity exceeded 99% in all cases using a breakthrough cut of 0.05. The productivities based on the constant-pattern design method were two orders of magnitude higher than the literature results with similar yields and purities.

The productivity of LAD systems can be improved by using higher ligand concentrations or longer columns. The maximum productivity for the given yield is achieved when a system reaches the pressure drop limit. Higher ligand concentrations also provide higher productivities with no penalty to the yield or purity of the system. The lowest effective sorbent selectivity α^e among the target components controls the minimum column length required to achieve the constant pattern state for the target components. For a fixed yield, systems with higher α^e values can have higher loading fractions and higher velocities, thus leading to higher total productivities. A selectivity weighted composition factor (γ) was developed to allow the design method to specify a minimum target yield for one or multiple components. The productivity of a LAD system is most strongly limited by the controlling component, which has the lowest γ value due to the lowest selectivity or the smallest composition among the target components. In mixtures with both major and minor components, a minor component can be the limiting component, even if its selectivity is not the lowest. The productivity was significantly reduced if both the major and the minor components need to be recovered. The total productivity of a system can be significantly increased by sacrificing minor components with very small γ values. Ignoring the minor components led to total productivities that were significantly higher than the case for recovering all the components. These feed composition studies demonstrate the versatility of the design method in a variety of separation cases.

CHAPTER 5. CONCLUSION AND RECOMMENDATION

5.1 Conclusions

In this dissertation, the methods to recover REEs and other compounds from coal fly ash and the constant-pattern design method for REEs purification using ligand-assisted displacement chromatography were developed.

In Chapter 2, the sequential separation process was developed to extract REEs from class F coal fly ash and to separate REEs from other components. Since most of the REEs were trapped in the aluminosilicate glassy matrix, the NaOH digestion process was conducted to remove the glassy matrix. In the NaOH digestion step, 48% of silica was dissolved and aluminosilicates formed sodalite structures. In the subsequent acid dissolution step, REEs, aluminosilicate, iron oxide, and calcium oxide were easily dissolved in the hydrochloric acid. On average 74% of the REEs were extracted while 44% of SiO₂, 74% of Al₂O₃, 24% Fe₂O₃, and 65% of CaO were extracted in the acid solution.

More than 99% of the extracted REEs, Fe, Al, and Ca were effectively captured in a strong cation exchange column. Nonadsorbing Si species were eluted out with water washing. By eluting with 2 M NaCl, >99% of Al and 88% of Fe were eluted but REEs and Ca remained in the column. By using a DTPA ligand, almost all (>99%) REEs were collected at the first breakthrough curve with DTPA-Fe. Compared with the major components, the normalized total REEs concentration was increased 226 times in the recovered fractions. The feasibility of the REEs concentration step at large scale was demonstrated using a synthetic mixture of DTPA-Fe and DPTA-Nd. In order to make a profitable process, high purity (98-99.9%) SiO₂ gel was produced by changing the pH or temperature. Also, by using precipitation methods, the extracted

Fe and Al were produced as Fe(OH)₃ and Al(OH)₃, with the purity of >95% and >99%, respectively.

In Chapter 3, a rate model and simulations were developed for ligand-assisted displacement chromatography. The parameters were estimated from experimental data and verified with literature and experimental data. Rate model simulations showed that a presaturant having lower effective sorbent selectivity drives the isotachic train in LAD. For a nonideal system, the constant-pattern isotachic train is formed in LAD. The required column length to develop a constant-pattern isotachic train was longer than that for an ideal system.

The formation of a constant-pattern isotachic train in nonideal LAD systems were investigated using rate model simulations. Key parameters controlling a constant-pattern state were found from the h-transformation theory for an ideal system and the shock layer theory for a nonideal system. The effective sorbent selectivity (α^e), the overall dimensionless mass transfer coefficient (k_f^*), the loading fraction (L_f), and the dimensionless column length (ϕ) were key dimensionless groups. The transition from transient-pattern to constant-pattern was found using rate model simulations. The strategically formulated dimensionless groups developed a general map. The map shows a general correlation between the combined dimensionless groups ($L_f k_f^* \left(\frac{\alpha^e - 1}{\alpha^e + 1}\right)$) and the dimensionless column length ϕ to reach a constant-pattern state. The minimum required conditions to develop a constant-pattern state in binary LAD systems were shown in the map as a ϕ_{min} curve. The correlations between key dimensionless groups and the ϕ_{min} curve were empirically found and verified with experiments. One can tell the constantpattern state of LAD or design a LAD process to develop a constant-pattern based on the general map without trial and error. In Chapter 4, a scalable constant-pattern design method was developed for ternary separations in LAD based on the general map and the key dimensionless groups. The design method requires the intrinsic parameters, material properties, target purity, and the minimum target yields for one or multicomponent. By solving the yield and ϕ_{min} equations, the design method provides operating conditions to develop a constant-pattern state using a minimum column length. Ternary separations of Sm, Nd, and Pr were tested and the experimental results have met the minimum target yields within 2% experimental errors with the purity of >99% in all cases. The productivities were two orders of magnitude higher than the literature data with similar yields and purities.

According to the yield equation and the design procedure, the productivity of LAD can be improved by using higher ligand concentrations or longer column length. The maximum productivities can be achieved when a system reaches the pressure drop. When target components have the high effective sorbent selectivities, high productivities were achieved. However, for a feed source with a varied REEs composition, the selectivity weighted composition factor (γ) can have significant impacts on the yields and productivity. When the minimum target yield is required for all components, the total productivity of LAD was limited by a component having the lowest γ . Even if a component has high effective sorbent selectivities between adjacent pairs, a minor component reduces the total productivity significantly. Ignoring minor components that have low γ values leads to having a higher total productivity, compared to a case where all components are to be recovered.

5.2 Recommendations

The study of the extraction and capture process for recovering REEs is still in early development stage. The extraction mechanisms of REEs and other compounds need to be further studied to improve the extraction yields. Specifically, it is recommended to remove Ca at an early step to improve the separation processes. The residual solids need to be recycled or further treated to reduce the waste. Also, a process focusing on the recovery rate of Sc will increase the economic viability of the whole process. Additionally, more efficient recycling methods using inexpensive chemicals or different leaching conditions need to be explored. Also, the capture process needs to be further optimized. Design and optimization of a process using rate model simulations and dimensionless group analyses is recommended.

The constant-pattern design method was developed for LAD nonideal systems for the first time. However, the yields of products did not reach >99% in the batch processes because of the mixed band regions in the mass transfer zone. Thus, it is recommended to design continuous LAD systems to improve the yields and productivities. Additionally, since we have performed experiments using a synthetic mixture of REEs, it is highly recommended to perform LAD separations using an actual REEs feed. As actual REEs sources have varied compositions, there can be several options for separating multicomponent REEs. The development of strategic splitting methods for multi-zone LAD systems is in need.

REFERENCES

- P. Rozelle, A. Khadilkar, N. Pulati, N. Soundarrajan, M. Klima, M. Mosser, C. Miller, S. Pisupati, A Study on Removal of Rare Earth Elements from U.S. Coal Byproducts by Ion Exchange, Metall. Mater. Trans. E. 3E (2016) 6–17. doi:10.1007/s40553-015-0064-7.
- [2] N. Haque, A. Hughes, S. Lim, C. Vernon, Rare Earth Elements: Overview of Mining, Mineralogy, Uses, Sustainability and Environmental Impact, Resources. 3 (2014) 614–635. doi:10.3390/resources3040614.
- [3] B.C. McLellan, G.D. Corder, A. Golev, S.H. Ali, Sustainability of the Rare Earths Industry, Procedia Environ. Sci. 20 (2014) 280–287. doi:10.1016/j.proenv.2014.03.035.
- [4] D.S. Abraham, The elements of power : Gadgets, guns, and the struggle for a sustainable future in the rare metal age, Yale University Press, 2015.
- [5] A. Jordens, Y.P. Cheng, K.E. Waters, A review of the beneficiation of rare earth element bearing minerals, Miner. Eng. 41 (2013) 97–114. doi:10.1016/j.mineng.2012.10.017.
- [6] J. Lucas, P. Lucas, T. Le Mercier, A. Rollat, W. Davenport, Rare Earths Science, Technology, Production and Use, Elsevier, Amsterdam, 2015. doi:https://doi.org/10.1016/B978-0-444-62735-3.00001-2.
- [7] USGS, Annual Mineral Commodity Summaries Rare Earths, n.d. https://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/.
- [8] R.K. Taggart, J.C. Hower, G.S. Dwyer, H. Hsu-Kim, Trends in the Rare Earth Element Content of U.S.-Based Coal Combustion Fly Ashes, Environ. Sci. Technol. 50 (2016) acs.est.6b00085. doi:10.1021/acs.est.6b00085.
- [9] E. Vahidi, F. Zhao, Environmental life cycle assessment on the separation of rare earth oxides through solvent extraction, J. Environ. Manage. 203 (2017) 255–263. doi:10.1016/j.jenvman.2017.07.076.
- [10] L. Ling, N.-H.L. Wang, Ligand-assisted Elution Chromatography for Separation of Lanthanides, J. Chromatogr. A. 1389 (2015) 28–38. doi:10.1016/j.chroma.2015.02.004.
- [11] F. Xie, T.A. Zhang, D. Dreisinger, F. Doyle, A critical review on solvent extraction of rare earths from aqueous solutions, Miner. Eng. 56 (2014) 10–28. doi:10.1016/j.mineng.2013.10.021.
- [12] J. Zhang, B. Zhao, B. Schreiner, Separation hydrometallurgy of rare earth elements, Springer, 2016. doi:10.1007/978-3-319-28235-0.
- [13] British Geological Survey, Rare Earth Elements, 2010. http://www.bgs.ac.uk/downloads/start.cfm?id=1638.

- [14] C. Liao, S. Wu, F. Cheng, S. Wang, Y. Liu, B. Zhang, C. Yan, Clean separation technologies of rare earth resources in China, J. Rare Earths. 31 (2013) 331–336. doi:10.1016/S1002-0721(12)60281-6.
- [15] J. Wise, Stephen A., Robert. L Watters, NIST Certificate of Analysis Standard Reference Material 1633c - Trace Elements in Coal Fly Ash, 2011.
- [16] J.M. Ekmann, Rare Earth Elements in Coal Deposits a Prospectivity Analysis *, NETL Rep. 80270 (2012) 22–26.
- [17] A. Kolker, C. Scott, J.C. Hower, J.A. Vazquez, C.L. Lopano, S. Dai, Distribution of rare earth elements in coal combustion fly ash, determined by SHRIMP-RG ion microprobe, Int. J. Coal Geol. 184 (2017) 1–10. doi:10.1016/J.COAL.2017.10.002.
- [18] J.C. Hower, J.G. Groppo, P. Joshi, S. Dai, D.P. Moecher, M.N. Johnston, Location of Cerium in Coal-Combustion Fly Ashes : Implications for Recovery of Lanthanides, Coal Combust. Gasif. Prod. 5 (2013) 73–78. doi:10.4177/CCGP-D-13-00007.1.
- [19] J.C. Hower, Shifeng Dai, Vladimir V. Seredin, Lei Zhao, I.J. Kostova, L.F.O. Silva, S.M. Mardon, G. Gurdal, A Note on the Occurrence of Yttrium and Rare Earth Elements in Coal Combustion Products, Coal Combust. Gasif. Prod. 5 (2013) 39–47. doi:10.4177/CCGP-D-13-00001.1.
- [20] C.K.K. Gupta, N. Krishnamurthy, Extractive metallurgy of rare earths, 1992. doi:10.1179/imr.1992.37.1.197.
- [21] M. Ahmaruzzaman, A review on the utilization of fly ash, Prog. Energy Combust. Sci. 36 (2010) 327–363. doi:http://dx.doi.org/10.1016/j.pecs.2009.11.003.
- [22] Committee on Mine Placement of Coal Combustion Wastes Board on Earth Sciences and Resources, D. on E. and L. Studies, Managing Coal Combustion Residues in Mines, THE NATIONAL ACADEMIES PRESS, 2006.
- [23] American Coal Ash Association, An American Recycling Success Story: Beneficial Use of Coal Combustion Products, (2016). https://www.acaausa.org/Portals/9/Files/PDFs/ACAA-Brochure-Web.pdf (accessed December 7, 2016).
- [24] J.F. King, R.K. Taggart, R.C. Smith, J.C. Hower, H. Hsu-Kim, Aqueous acid and alkaline extraction of rare earth elements from coal combustion ash, Int. J. Coal Geol. 195 (2018) 75–83. doi:10.1016/J.COAL.2018.05.009.
- [25] C.-J. Kim, H.-S. Yoon, K.W. Chung, J.-Y. Lee, S.-D. Kim, S.M. Shin, S.-J. Lee, A.-R. Joe, S.-I. Lee, S.-J. Yoo, S.-H. Kim, Leaching kinetics of lanthanum in sulfuric acid from rare earth element (REE) slag, Hydrometallurgy. 146 (2014) 133–137. doi:10.1016/j.hydromet.2014.04.003.

- [26] S. Kashiwakura, Y. Kumagai, H. Kubo, K. Wagatsuma, Dissolution of Rare Earth Elements from Coal Fly Ash Particles in a Dilute H₂SO₄ Solvent, Open J. Phys. Chem. 03 (2013) 69– 75. doi:10.4236/ojpc.2013.32009.
- [27] P.B. Joshi, D. V Preda, D.A. Skyler, A. Scherer, D. Green, W.J. Marinelli, Recovery of rare earth elements and compounds from coal ash, 2013. doi:US20130287653 A1.
- [28] R.S. Lanigan, T.A. Yamarik, F.A. Andersen, Final report on the safety assessment of EDTA, calcium disodium EDTA, diammonium EDTA, dipotassium EDTA, disodium EDTA, TEA-EDTA, tetrasodium EDTA, tripotassium EDTA, trisodium EDTA, HEDTA, and trisodium HEDTA, Int. J. Toxicol. (2002). doi:10.1080/10915810290096522.
- [29] H. Choi, D. Harvey, D. Yi, N.L. Wang, Key parameters controlling the development of constant-pattern isotachic trains of two rare earth elements in ligand-assisted displacement chromatography, J. Chromatogr. A. 1563 (2018) 47–61. doi:10.1016/j.chroma.2018.05.057.
- [30] F.H. Spedding, E.I. Fulmer, J.E. Powell, T.A. Butler, The Separation of Rare Earths by Ion Exchange. V. Investigations with One-tenth Per Cent. Citric Acid-Ammonium Citrate Solutions 1, J. Am. Chem. Soc. 72 (1950) 2354–2361. doi:10.1021/ja01162a004.
- [31] F.H. Spedding, E.I. Fulmer, T.A. Butler, E.M. Gladrow, M. Gobush, P.E. Porter, J.E. Powell, J.M. Wright, The Separation of Rare Earths by Ion Exchange1. III. Pilot Plant Scale Separations, J. Am. Chem. Soc. 61 (1947) 2812–2818.
- [32] F.H. Spedding, J.E. Powell, The Separation of Rare Earths by Ion Exchange. VIII. Quantitative Theory of the Mechanism Involved in Elution by Dilute Citrate Solutions, J. Am. Chem. Soc. 76 (1954) 2550–2557. doi:10.1021/ja01638a074.
- [33] D.B. James, J.E. Powell, F.H. Spedding, Cation-exchange elution sequences—I Divalent and rare-earth cations with EDTA, hedta and citrate, J. Inorg. Nucl. Chem. 19 (1961) 133– 141. doi:10.1016/0022-1902(61)80055-9.
- [34] F.H. Spedding, A.F. Voigt, E.M. Gladrow, N.R. Sleight, J.E. Powell, J.M. Wright, T.A. Butler, P. Figard, The Separation of Rare Earths by Ion Exchange. II. Neodymium and Praseodymium, J. Am. Chem. Soc. 69 (1947) 2786–2792. doi:10.1021/ja01203a060.
- [35] R.E. Lindstrom, Separation of rare-earth elements in bastnasite by ion exchange, U.S. Dept. of the Interior, Bureau of Mines, Washington D.C., 1959.
- [36] J.O. Winget, R.E. Lindstrom, Amino Acids as Retaining Agents in Displacement Chromatography of the Rare-Earth Elements, Sep. Sci. 4 (1969) 209–216. doi:10.1080/01496396908052252.
- [37] B.W. Moore, L.J. Froisland, A.E. Petersen, Rapid separation of heavy rare-earth elements, U.S. Dept. of the Interior, Bureau of Mines, 1995. https://search.library.wisc.edu/catalog/999776393902121.

- [38] F.H. Spedding, E.I. Fulmer, J.E. Powerll, T.A. Butler, I.S. Yaffe, The Separation of Rare Earths by Ion Exchange. VI. Conditions for Effecting Sepearations with Nalcite HCR and Onte-tenth Per Cent. Citric Acid-Ammonium Citrate Solutions, J. Am. Chem. Soc. 73 (1951) 4840–4847. doi:10.1021/ja01154a110.
- [39] D. Kołodyńska, Z. Hubicki, Investigation of Sorption and Separation of Lanthanides on the Ion Exchangers of Various Types , Ion Exch. Technol. (2012) 376. doi:10.5772/2925.
- [40] R. Lin, M. Stuckman, B.H. Howard, T.L. Bank, E.A. Roth, M.K. Macala, C. Lopano, Y. Soong, E.J. Granite, Application of sequential extraction and hydrothermal treatment for characterization and enrichment of rare earth elements from coal fly ash, Fuel. 232 (2018) 124–133. doi:10.1016/J.FUEL.2018.05.141.
- [41] R. Lin, B.H. Howard, E.A. Roth, T.L. Bank, E.J. Granite, Y. Soong, Enrichment of rare earth elements from coal and coal by-products by physical separations, Fuel. 200 (2017) 506–520. doi:10.1016/J.FUEL.2017.03.096.
- [42] R.C. Merrill, R.W. Spencer, Gelation of sodium silicate Effect of Sulfuric Acid, Hydrochloric Acid, Ammonium Sulfate, and Sodium Aluminate, J. Phys. Chem. (1950). doi:10.1021/j150480a009.
- [43] A.M. Mustafa Al Bakri, H. Kamarudin, M. Bnhussain, I.K. Nizar, W.I.W. Mastura, Mechanism and Chemical Reaction of Fly Ash Geopolymer Cement- A Review, J. Chem. Inf. Model. 53 (2013) 1689–1699. doi:10.1017/CBO9781107415324.004.
- [44] W.-H. Shih, H.-L. Chang, Conversion of fly ash into zeolites for ion-exchange applications, Mater. Lett. 28 (1996) 263–268. doi:10.1016/0167-577X(96)00064-X.
- [45] ASTM International, ASTM C618-17a, Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, West Conshohocken, PA, 2017. doi:10.1520/C0618-17A.
- [46] H. Yu, J. Shen, J. Li, X. Sun, W. Han, X. Liu, L. Wang, Preparation, characterization and adsorption properties of sodalite pellets, Mater. Lett. 132 (2014) 259–262. doi:10.1016/J.MATLET.2014.06.089.
- [47] J. Ding, S. Ma, S. Zheng, Y. Zhang, Z. Xie, S. Shen, Z. Liu, Study of extracting alumina from high-alumina PC fly ash by a hydro-chemical process, Hydrometallurgy. 161 (2016) 58–64. doi:10.1016/j.hydromet.2016.01.025.
- [48] J.B. Zhang, S.P. Li, H.Q. Li, M.M. He, Acid activation for pre-desilicated high-alumina fly ash, Fuel Process. Technol. (2016). doi:10.1016/j.fuproc.2016.05.036.
- [49] Z. Liu, C. Shi, D. Wu, S. He, B. Ren, A Simple Method of Preparation of High Silica Zeolite Y and Its Performance in the Catalytic Cracking of Cumene, J. Nanotechnol. 2016 (2016) 1–6. doi:10.1155/2016/1486107.

- [50] L. Ling, N.L. Wang, Analysis of Dynamic Phenomena in Liquid Chromatographic Systems with Reactions in the Mobile Phase, in: G. Eli, G. Nelu (Eds.), Adv. Chromatogr., 52nd ed., CRC PRESS, 2014: pp. 169–246. https://www.crcpress.com/Advances-in-Chromatography-Volume-52/Grushka-Grinberg/9781482223507.
- [51] E.A. Gorrepati, P. Wongthahan, S. Raha, H.S. Fogler, Silica precipitation in acidic solutions: mechanism, pH effect, and salt effect., Langmuir. 26 (2010) 10467–74. doi:10.1021/la904685x.
- [52] U. Zulfiqar, T. Subhani, S.W. Husain, Synthesis and characterization of silica nanoparticles from clay, J. Asian Ceram. Soc. (2016). doi:10.1016/j.jascer.2015.12.001.
- [53] I.A. Rahman, V. Padavettan, Synthesis of Silica nanoparticles by Sol-Gel: Size-dependent properties, surface modification, and applications in silica-polymer nanocompositesa review, J. Nanomater. (2012). doi:10.1155/2012/132424.
- [54] M.V.J. Ernest, R.D. Whitley, Z. Ma, N.-H.L. Wang, Effects of Mass Action Equilibria on Fixed-Bed Multicomponent Ion-Exchange Dynamics, Ind. Eng. Chem. Res. 36 (1997) 212– 226. doi:10.1021/ie960167u.
- [55] F.W.E. Strelow, P.F.S. Jackson, Determination of Trace and Ultratrace Quantities of Rare Earth Elements by Ion Exchange Chromatography-Mass Spectrography, Anal. Chem. 46 (1974) 1481–1486. doi:10.1021/ac60347a018.
- [56] F.W.E. Strelow, R. Rethemeyer, C.J.C. Bothma, Ion Exchange Selectivity Scales for Cations in Nitric Acid and Sulfuric Acid Media with a Sulfonated Polystyrene Resin, Anal. Chem. 37 (1965) 106–111. doi:10.1021/ac60220a027.
- [57] S.S. Rath, H. Sahoo, N. Dhawan, D.S. Rao, B. Das, B.K. Mishra, Optimal Recovery of Iron Values from a Low Grade Iron Ore using Reduction Roasting and Magnetic Separation, Sep. Sci. Technol. (2014). doi:10.1080/01496395.2014.903280.
- [58] C. Brinker, G. Scherer, Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing, Adv. Mater. (1990). doi:10.1186/1471-2105-8-444.
- [59] C.J. Brinker, Hydrolysis and condensation of silicates: Effects on structure, J. Non. Cryst. Solids. 100 (1988) 31–50. doi:10.1016/0022-3093(88)90005-1.
- [60] L. Wang, X. Huang, Y. Yu, L. Zhao, C. Wang, Z. Feng, D. Cui, Z. Long, Towards cleaner production of rare earth elements from bastnaesite in China, J. Clean. Prod. 165 (2017) 231– 242. doi:10.1016/j.jclepro.2017.07.107.
- [61] P.N. Nesterenko, P. Jones, Isocratic separation of lanthanides and yttrium by highperformance chelation ion chromatography on iminodiacetic acid bonded to silica, in: J. Chromatogr. A, 1998. doi:10.1016/S0021-9673(97)01272-7.

- [62] H.K. Knutson, M. Max-Hansen, C. Jönsson, N. Borg, B. Nilsson, Experimental productivity rate optimization of rare earth element separation through preparative solid phase extraction chromatography, J. Chromatogr. A. 1348 (2014) 47–51. doi:10.1016/j.chroma.2014.04.085.
- [63] N. McGillicuddy, E.P. Nesterenko, P.N. Nesterenko, E.M. Stack, J.O. Omamogho, J.D. Glennon, B. Paull, A new N-hydroxyethyliminodiacetic acid modified core-shell silica phase for chelation ion chromatography of alkaline earth, transition and rare earth elements, J. Chromatogr. A. (2013). doi:10.1016/j.chroma.2013.10.057.
- [64] R.S. Dybczyński, K. Kulisa, M. Pyszynska, A. Bojanowska-Czajka, New reversed phasehigh performance liquid chromatographic method for selective separation of yttrium from all rare earth elements employing nitrilotriacetate complexes in anion exchange mode., J. Chromatogr. A. 1386 (2015) 74–80. doi:10.1016/j.chroma.2015.01.091.
- [65] D.B. James, J.E. Powell, F.H. Spedding, CATION-EXCHANGE ELUTION SEQUENCES--I Divalent and Rare-earth Cations with EDTA, HEDTA and Citrate, J. Inorg. Nucl. Chem. 19 (1961) 133–141.
- [66] D.B. James, J.E. Powell, H.R. Burkholder, Displacement ion-exchange separation of ternary rare earth mixtures with chelating eluants, J. Chromatogr. 35 (1968) 423–429. doi:10.1016/S0021-9673(01)82404-3.
- [67] J.E. Powell, H.R. Burkholder, K. Gonda, Experimental determination of elution requirements in displacement ion exchange, J. Chromatogr. A. 54 (1971) 259–267. doi:10.1016/S0021-9673(01)80273-9.
- [68] F.D. Antia, C. Horváth, Analysis of isotachic patterns in displacement chromatography, J. Chromatogr. A. 556 (1991) 119–143. doi:10.1016/S0021-9673(01)96216-8.
- [69] C. Horváth, A. Nahum, J.H. Frenz, High-performance displacement chromatography, J. Chromatogr. A. 218 (1981) 365–393. doi:10.1016/S0021-9673(00)82066-X.
- [70] J. Zhu, Z. Ma, G. Guiochon, The thickness of shock layers in liquid chromatography, Biotechnol. Prog. 9 (1993) 421–428. doi:10.1021/bp00022a009.
- [71] V. Natarajan, B. Wayne Bequette, S.M. Cramer, Optimization of ion-exchange displacement separations, J. Chromatogr. A. 876 (2000) 51–62. doi:10.1016/S0021-9673(00)00138-2.
- [72] H.-K. Rhee, N.R. Amundson, Shock layer in two solute chromatography: effect of axial dispersion and mass transfer, Chem. Eng. Sci. 29 (1974) 2049–2060. doi:10.1016/0009-2509(74)80219-8.
- J. Zhu, G. Guiochon, Shock layer thickness and optimum linear velocity in displacement chromatography, J. Chromatogr. A. 659 (1994) 15–25. doi:10.1016/0021-9673(94)85003-8.

- [74] F. Helfferich, D.B. James, An equilibrium theory for rare-earth separation by displacement development, J. Chromatogr. 46 (1970) 1–28. doi:10.1016/S0021-9673(00)83961-8.
- [75] F. Helfferich, D.B. James, An equilibrium theory for rare-earth separation by displacement development, J. Chromatogr. A. 46 (1970) 1–28. doi:10.1016/S0021-9673(00)83961-8.
- [76] D.R. Garg, D.M. Ruthven, Linear driving force approximations for diffusion controlled adsorption in molecular sieve columns, AIChE J. 21 (1975) 200–202. doi:10.1002/aic.690210137.
- [77] D.R. Garg, D.M. Ruthven, Theoretical prediction of breakthrough curves for molecular sieve adsorption columns—I Asymptotic solutions, Chem. Eng. Sci. 28 (1973) 791–798. doi:10.1016/0009-2509(77)80013-4.
- [78] L. Ling, L.-W. Kao, N.-H.L. Wang, A New General Method for Designing Affinity Chromatography Processes, J. Chromatogr. A. 1355 (2014) 86–99. doi:10.1016/j.chroma.2014.05.081.
- [79] S.F. Chung, C.Y. Wen, Longitudinal dispersion of liquid flowing through fixed and fluidized beds, AIChE J. 14 (1968) 857–866. doi:10.1002/aic.690140608.
- [80] J.A. Berninger, R.D. Whitley, X. Zhang, N.-H.L. Wang, A versatile model for simulation of reaction and nonequilibrium dynamics in multicomponent fixed-bed adsorption processes, Comput. Chem. Eng. 15 (1991) 749–768. doi:10.1016/0098-1354(91)85020-U.
- [81] E.J. Wilson, C.J. Geankoplis, Liquid Mass Transfer at Very Low Reynolds Numbers in Packed Beds, Ind. Eng. Chem. Fundam. 5 (1966) 9–14. doi:10.1021/i160017a002.
- [82] G. Klein, D. Tondeur, T. Vermeulen, Multicomponent ion exchange in fixed beds: General Properties of Equilibrium Systems, Ind. Eng. Chem. Fundam. 6 (1967) 339–351. doi:10.1021/i160023a004.
- [83] L. Ling, P.L. Chung, A. Youker, D.C. Stepinski, G.F. Vandegrift, N.H.L. Wang, Capture Chromatography for Mo-99 Recovery from Uranyl Sulfate Solutions: Minimum-Columnvolume Design Method, J. Chromatogr. A. 1309 (2013) 1–14. doi:10.1016/j.chroma.2013.08.023.
- [84] E.J. Wheelwright, F.H. Spedding, G. Schwarzenbach, The Stability of the Rare Earth Complexes with Ethylenediaminetetraacetic Acid, J. Am. Chem. Soc. 75 (1953) 4196–4201. doi:10.1021/ja01113a020.
- [85] T. V Ternovaya, V.P. Shelest, N. V Gerasimenko, E.L. Il'nitskaya, Structure of ethylenediaminetetraacetates of rare-earth elements in crystals and solutions, Theor. Exp. Chem. 21 (1985) 418–428. doi:10.1007/BF01004513.
- [86] P.C. Wankat, Rate-Controlled Separtions, Springer netherlands, 1994. doi:10.1007/978-94-011-1342-7.

- [87] Z. Hagiwara, H. Oki, Theoritical treatment of the elution system of rare-earth with dilute H.E.D.T.A eluant, J. Inorg. Nucl. Chem. 32 (1970) 291–307. doi:10.1016/0022-1902(70)80472-9.
- [88] S. Ergun, Fluid flow through packed columns, American Institute of Chemical Engineers, 1952.
- [89] R.E. Lindstrom, J.O. Winget, Process for recovering ethylenediamine-tetraacetic acid (EDTA) from copper-EDTA-ion exchange effluent solutions, US 3,138,637, 1964.

APPENDIX A. SCALE UP AND ECONOMIC FEASIBILITY OF THE OVERALL PROCESS

For a large scale process, CaO removal process was added before NaOH digestion. It was noticed that cenosphere, which is hollow particles of alumina and silica, can be collected from the washed solution as shown in Figure A1. Using filtration, 0.5 wt.% of total ash was collected as cenosphere, which could be a valuable byproduct in large scale production.

A flowchart of the large scale processes is shown in Figure A2 with water balance. The detailed scheme of the overall process in Figure A2 is represented in Figure A3. Based on the Figure A3, the required equipment size, type, and estimated cost are shown in Table A1. The estimated total equipment cost was about \$1.4 million for 1 ton ash/day capacity. The capital cost was calculated by multiplying a ratio factor (x5) to the total equipment cost to consider the installment of solid-fluid processing [1].

Economic analysis of the overall process was shown in Table A2 based on 2,000 ton/day capacity. The capital equipment investment was calculated based on the six-tenth rule [1]. It should be mentioned that the chemical cost and product revenue are highly dependent on chemical compositions of coal ash as well as the price of acid, base, and REEs. Based on the used coal fly ash, the major cost is chemical cost, \$496/ton ash and the potential profit is about \$182/ton. However, assuming that the separation processes are repeated for the nonmagnetic residual solids and thus most of Al, Si, and Fe are extracted, the potential profit can be increased to \$366/ton because of the significant increase in product revenue compared to processing cost. Thus, in large scale, the recycling process for the residual solids is worth to be considered in order to reduce waste and to increase profits. In Table A3, a business case study of the process

with recycling residual solids indicated that the break-even point is slightly lower than 100 ton/day capacity. At 3,000 ton/day capacity, return on investment (ROI) is about 2.4 year.

Overall, the economic analysis indicates the economic feasibility of the overall process and potential profits at large scale, higher than 100 ton/day capacity by considering recycle processes of residual solids. It should be pointed out that the results can be changed in different feed compositions since the major chemical revenue comes from byproducts. Also, the chemical revenue can be fluctuated by the yield of the REEs which have high market values such as Sc, Tb, and Dy.


Figure A. 1 SEM-EDS image of cenosphere collected in CaO removal process.



Figure A. 2 Flowchart of the large scale separation processes with water balance.



Figure A. 3 Detailed flowchart of the large scale processes

Process	Туре	Unit	Equipment size	Area, m ²	Unit price	Total
Reactor1	Reactor equipped with heater	1	5,000 L	4	\$20,000	\$20,000
Ash	Storage tank	1	1,000 L	1.4	\$500	\$500
HCl tank	Storage tank	1		2.8	-	
CO ₂	Tank	1		1	\$20	\$20
Ca(OH) ₂ tank	Storage tank	1	1,000 L	1.4	\$500	\$500
Water tank1 for Reactor 1	Storage tank	1	10,000 L	5	\$5,000	\$5,000
NaOH tank	Storage tank	1	1,000 L	1.4	\$500	\$500
NaOH recycle tank	Storage tank	1	5,000 L	4	\$3,000	\$3,000
Water tank 2 for washing	Storage tank	1	10,000 L	5	\$5,000	\$5,000
SiO ₂ gelation reactor 1	Stirred reactor	1	3,000 L	2	\$15,000	\$15,000
SiO ₂ gelation tank 1	Storage tank	1	1,000 L	1.4	\$500	\$500
Calcination	Storage tank	1	1,000 L	1.4	\$40,000	\$40,000
Magnetite separator	Separator	1	10-20 ton/hr	4	\$5,000	\$5,000
Magnetic fraction	Storage tank	1	500 L	1.4	\$500	\$500
Nonmagnetic fraction	Storage tank	1	500 L	1.4	\$500	\$500
Nonmagnetic fraction	Stirred reactor	1	500 L	1.4	\$1,000	\$1,000
Pumps	Pumps	21		10	\$1,000	\$21,000
SiO ₂ gelation reactor 2	Stirred reactor	1	5,000 L	4	\$10,000	\$10,000
Dryer for Al & Fe products	Rotary dryer	5		20	\$5,000	\$25,000
Filtration for Al&Fe products	Filter press	1		4	\$5,000	\$10,000
Conveyer belt		8		1	\$500	\$4,000
Centrifugal separator	Separator	9		10	\$15,000	\$135,000
Capture column	Column (ID 1m, L _c 1m)	3	785 L	5	\$5,000	\$15,000
Chromatography equipment	Column parts	1		1	\$500,000	\$500,000
Concentration column	Column (ID 0.1m, L _c 1m)	1	28 L	1	\$1,000	\$1,000
Resins	Column parts	1	2,383 L		\$18/L	\$42,894
Water tank 3 for elution	Storage tank	1	50,000 L	25	\$8,000	\$8,000
NaOH tank	Storage tank	1	100 L	1	\$500	\$500
NaCl tank 1	Storage tank	1	40,000 L	20	\$7,000	\$7,000
NaCl tank 2	Storage tank	1	20,000 L	7.5	\$6,000	\$5,000
Fe & Al PPT reactor	Stirred reactor	2	3,000 L	4.2	\$5,000	\$10,000
Fe & Al PPT storage tank	Storage tank	2	100 L /200 L	4	\$500	\$1,000
Waste storage	Storage tank	1	5,000 L	4	\$3,000	\$3,000
R/O purification		1	800 L/hr	10	\$30,000	\$30,000
ED		1	1000 L/hr	10	\$30,000	\$30,000
Evaporator		1	0.5 kg/hr	20	\$20,000	\$40,000
DTPA tank	Storage tank	1	12,000 L	12	\$5,000	\$5,000
DTPA recycle reactor	Stirred reactor	1	1,000 L	1.4	\$500	\$1,000
Total 215.5						\$1,003,414
Total (tax + shipping: 1.5 times)						\$1,505,121
Total capital cost (ratio factors: 5 times)						\$7,525,605
Depreciation 10 years per day						\$2,351.75

Table A. 1 Estimated equipment list, size, and cost for 1 ton ash/day capacity (The estimated cost was referred from vendors in Alibaba (https://www.alibaba.com/)

Component	Price/Ton	Purity	Amount (Ton)	Price (\$)	
Ash	\$10	-	1	\$0.00	
NaOH	\$350	99%	1.20	\$212.1(
NaOH	79% Recycled		-0.59	\$212.10	
	\$50	99%	7.03		
NaCl	>99% recycle from NaCl			\$0.00	
	effluents		-7.03		
HCl	\$150	37%	1.75	\$262.95	
CO ₂ gas	\$15	100%	0.24	\$3.60	
Ca(OII)	\$100	100%	0.54	\$0.00	
	Recycle by CaCO ₃ calcination		-0.54	\$0.00	
	\$0.40		55.30		
Water	Recycle water		-42.00	\$5.32	
	\$0.44		13.00	\$5.72	
	\$4,500	99%	0.069	¢0.21	
DIFA	Recycle rate 99.9%		0.069	\$0.31	
$CuSO_4$	\$2,000	99%	0.0002	\$0.40	
A. Major Chemical Costs/ton	\$495.95				
B. Major Chemical Costs/ton	\$575.30				
Energy Cost (2,000 ton/day; \$	0.07/kWh)			\$22.92	
Equipment Cost (2,000 ton/da	\$113.00				
Silica Gel	\$1,000	99.9%	0.405	\$405.00	
Al(OH) ₃	\$1,000	99%	0.234	\$234.00	
Fe(OH) ₃ (pigment)	\$1,500	95-99%	0.068	\$102.00	
Fe-riched solids (ore grade)	\$50	(Fe >56%)	0.115	\$5.75	
REEs	\$35,000	99.9%	0.0005~0.001	\$17.50 ~ 35.00	
Cenosphere	\$1,000		0.005	\$5.00	
NaCl	\$50	99%	0.89	\$44.5	
A. Major Chemical Revenue/	\$813.75~\$831.25				
B. Major Chemical Revenue/	\$1,098~\$1,115				
A. Potential Profit/ton ash (2	\$181.8~\$199.38				
B. Potential Profit/ton ash (2	\$366.12~\$400.24				

Table A. 2 Economic analysis based on the chemical cost and processing cost (2,000 ton ash/day)

A. Without Recycling Residual Solids								
Capacity	1 kg/day	1 ton/day	100	1,000	2,000	3,000		
			ton/day	ton/day	ton/day	ton/day		
Capital Investment* (\$ M)								
	0.5	7.5	119	475	720	918		
Annualized Unit Equipment Cost								
(\$/ton ash; 10 year Depreciation)	1,563	2,351	373	148	113	96		
Energy Cost (\$/ton ash)								
	23	23	23	23	23	23		
Chemical Cost (\$/ton)	406	406	406	406	406	406		
Major Process Cost (\$/ton ash)	490	490	490	490	490	490		
	2.082	2.870	892	667	632	615		
Potential Revenue (\$/ton ash)	,	,						
	814	814	814	814	814	814		
Potential Profit (\$/ton/day)								
	(1,268)	(2,056)	(78)	147	182	199		
Return on investment			(0.02)	0.10	0.16	0.21		
Payback Daried (year)			(0.02)	0.10	0.10	0.21		
rayback renou (year)				10.1	6.2	4.8		
B. With Recycling Residual Solids								
Capacity	1 kg/day	1 ton/day	100	1,000	2,000	3,000		
			ton/day	ton/day	ton/day	ton/day		
Capital Investment* (\$ M)								
	0.5	7.5	119	475	720	918		
Annualized Capital Cost	1,563	2,351	373	148	113	96		
(\$/ton ash; 10 year Depreciation)	27	27	27	27	27	27		
Energy Cost (\$/ton asn)	27	27	27	27	27	27		
Chemical Cost (\$/ton)	575	575	575	575	575	575		
Major Process Cost (\$/ton ash)	2,165	2,953	975	751	715	698		
Potential Revenue (\$/ton ash)	1,098	1,098	1,098	1,098	1,098	1,098		
Potential Profit (\$/ton/day)	(1,067)	(1,855)	123	347	383	400		
Return on investment			0.03	0.23	0.34	0.42		
Payback Period (year)				4.3	2.9	2.4		

Table A. 3 Business case for large scale production

*Use Six-tenth rule for scale up capital equipment investment *Capital investment = 5 x (equipment cost)

References

[1] Peters, M. S., K. D. Timmerhaus, and R. West, *Plant Design and Economics for Chemical Engineers*, Fifth Edition, McGraw-Hill, 2003

APPENDIX B. MINIMUM COLUMN LENGTH TO FORM AN ISOTACHIC TRAIN FOR BINARY SEPARATION IN DISPLACEMENT CHROMATOGRAPHY FOR AN IDEAL SYSTEM

In an ideal conventional displacement system, two feed components (A and B) are loaded on the column. Then, the components are displaced by a high affinity displacer. The components A and B adsorb on the top of the column showing L_{feed} in Figure A1. The band movements of both components are shown on a distance-time diagram in Figure B1(b). Two shock waves, u_A and u_B , are shown as the slopes of the boundary between a mixed zone (A+B) and pure zones (either A or B) before two components are fully separated ($t_2 - t_4$). The two shock waves meet when two components are fully separated forming an isotachic train (t_4). At t_4 , an isotachic train is formed and the corresponding column position is the minimum column length to develop an isotachic train for an ideal system (L_{iso-id}).



Figure B. 1(a) Separation of two feed components by loading a displacer and (b) corresponding band movements on a distance-time diagram. Component A has lower sorbent affinity than Component B.

According to wave movement theory, the shock wave velocity can be expressed as below.

$$u_A = \frac{u_0}{1 + P\varepsilon_p + \frac{\Delta q_A}{\varepsilon_b \Delta c_A}} \tag{B1a}$$

$$u_B = \frac{u_0}{1 + P\varepsilon_p + \frac{\Delta q_B}{\varepsilon_b \Delta c_B}} \tag{B1b}$$

where u_0 is interstitial velocity, Δq_A or Δq_B are the change in the stationary phase concentration, which is based on bed volume, Δc_A or Δc_B are the change in the mobile phase concentration, P is the phase ratio(= $(1 - \varepsilon_b)/\varepsilon_b$), ε_p is the particle porosity, ε_b is the bed void fraction.

If we assume that components, A and B, are exchanged one-to-one as in an ion exchange system, the concentration change occurs between only two components at the boundary (u_A or u_B).

$$x_A + x_B = 1 \tag{B2a}$$

$$y_A + y_B = 1 \tag{B2b}$$

where x_A or x_B are the equivalent fraction of component A or B in the mobile phase, respectively; y_A or y_B are the equivalent fraction of component A or B in the stationary phase, respectively.

At boundary between the pure band of A and the mixed zone, the concentration change of component B is from zero to c_B and q_B , respectively. On the other hand, at boundary between the pure band B and the mixed zone, the concentration change of component A is from c_A to zero. Thus, the concentration change in the stationary phase relative to that in the mobile phase can be calculated.

$$\frac{\Delta q_A}{\Delta c_A} = \frac{q_{max}(0-y_A)}{0-x_A} = \frac{q_{max}y_A}{x_A}$$
(B3a)

$$\frac{\Delta q_B}{\Delta c_B} = \frac{q_{max}(y_B - 0)}{x_B - 0} = \frac{q_{max}y_B}{x_B}$$
(B3b)

where q_{max} is the column capacity per bed volume.

Therefore, Eq. (B1) can be rearranged to Eq. (B4).

$$u_A = \frac{u_0}{1 + P\varepsilon_p + \frac{q_{max}y_A}{\varepsilon_b x_A}} \tag{B4a}$$

$$u_B = \frac{u_0}{1 + P\varepsilon_p + \frac{q_{max}y_B}{\varepsilon_b x_B}} \tag{B4b}$$

The slope of u_A and u_B are calculated from Figure B1.

$$u_A = \frac{L_{iso-id}}{t_4} \tag{B5a}$$

$$u_B = \frac{L_{iso-id} - L_{feed}}{t_4} \tag{B5b}$$

Eq. (B5) can be combined in terms of t₄.

$$t_4 = \frac{L_{iso-id}}{u_A} = \frac{L_{iso-id} - L_{feed}}{u_B} \tag{A6}$$

By rearranging Eq. (B6), L_{iso-id}/L_{feed} can be shown.

$$L_{iso-id}\left(\frac{1}{u_B} - \frac{1}{u_A}\right) = \frac{L_{feed}}{u_B} \tag{B7a}$$

$$\frac{L_{iso-id}}{L_{feed}} = \frac{\frac{1}{u_B}}{\left(\frac{1}{u_B} - \frac{1}{u_A}\right)} = \frac{1}{1 - \frac{u_B}{u_A}}$$
(B7b)

Eq. (B4) can be substituted into Eq. (B7).

$$\frac{L_{iso-id}}{L_{feed}} = \frac{1}{1 - \frac{1 + P\varepsilon_p + \frac{q_{max}y_A}{\varepsilon_b x_A}}{1 - \frac{1 + P\varepsilon_p + \frac{q_{max}y_B}{\varepsilon_b x_B}}}}$$
(B8)

In general, the retention factor is very large so the term, $(1 + P\varepsilon_p)$, is much smaller than the last term $(\frac{q_A}{\varepsilon_b c_A} \text{ or } \frac{q_B}{\varepsilon_b c_B})$, which is usually 40~200. This assumption leads to the simplification of Eq.

(B8) into Eq. (B9) by ignoring the term $(1 + P\varepsilon_p)$.

$$\frac{L_{iso-id}}{L_{feed}} = \frac{1}{1 - \frac{y_A x_B}{x_A y_B}} \tag{B9}$$

When component B displaces component A, the effective sorbent selectivity (α_{BA}^{e}) between the two components is defined as follows.

$$\alpha_{BA}^e = \frac{y_B x_A}{x_B y_A} \tag{B10}$$

By using Eq. (B10), Eq. (B9) can be expressed as a function of α_{BA}^{e} .

$$\frac{L_{iso-id}}{L_{feed}} = \frac{1}{1 - \frac{1}{\alpha_{BA}^e}} = \frac{\alpha_{BA}^e}{\alpha_{BA}^e - 1}$$
(B11)

Eq. (B11) shows that the minimum column length to form an isotachic train (L_{iso-id}) is a function of selectivity between two components but independent of the feed composition.

APPENDIX C. CONSTANT-PATTERN MASS TRANSFER ZONE LENGTH (L_{MTZ,CP}) FOR A NONIDEAL SYSTEM

The overall mass transfer coefficient ($k_{f,overall}$) correlation was found in the linear driving force model based on the concentration difference in the mobile phase (c) [24].

$$\frac{1}{k_{f,overall}} = \frac{R_p}{3k_f} + \frac{E_b(1-\varepsilon_b)}{\varepsilon_b u_0^2} + \frac{R_p^2}{15\varepsilon_p D_p}$$
(C1)

The phase ratio and convection time were factored out front of the right-hand side (RHS) of Eq. (C1) to give Eq. (C2). Then, the RHS of Eq. (C2) was expressed with the dimensionless groups defined in Eq. (3.14) yielding Eq. (3.13).

$$\frac{1}{k_{f,overall}} = \frac{(1-\varepsilon_b)L_c}{\varepsilon_b u_0} \left(\frac{\varepsilon_b u_0 R_p}{3(1-\varepsilon_b)L_c k_f} + \frac{E_b}{u_0 L_c} + \frac{\varepsilon_b u_0 R_p^2}{15(1-\varepsilon_b)\varepsilon_p D_p L_c} \right) = \left(\frac{PL_c}{u_0}\right) \left(\frac{1}{N_f} + \frac{1}{Pe_b} + \frac{1}{15N_D}\right)$$
(C2)

When the constant-pattern is formed, the following conditions are valid.

$$\frac{c}{c_d} = \frac{q_p}{q_{d,p}} \tag{C3}$$

where c and q_p are the mobile and particle phase concentrations, respectively. The equilibrium concentration in the mobile phase (c_d) is the isotachic band concentration in LAD and $q_{d,p}$ is the corresponding equilibrium concentration in the particle phase (= $q_d/(1 - \varepsilon_b)$). Thus, K_f can be expressed in terms of $k_{f,overall}$ as shown in Eq. (3.12).

The lumped mass transfer coefficient K_f in Eq. (3.9) considers film mass transfer and intraparticle diffusion but axial dispersion is shown separately as Pe_b. Therefore, the K_f in Eq. (3.9) can be expressed by substituting Eq. (C2) into Eq. (3.12) and ignoring the axial dispersion term yielding Eq. (C4).

$$\frac{1}{K_f} = \frac{q_{d,p}}{c_d} \frac{(1-\varepsilon_b)L_c}{\varepsilon_b u_0} \left(\frac{1}{N_f} + \frac{1}{15N_D}\right) \tag{C4}$$

By substituting Eq. (3.8) into Eq. (C4) and assuming that the term, $P\varepsilon_p$, is much smaller than the last term $(\frac{q_d}{\varepsilon_b c_d})$ in Eq. (3.8), Eq. (C4) can be further simplified to Eq. (C5).

$$\frac{1}{K_f} = \left(K_d - P\varepsilon_p\right) \frac{L_c}{u_0} \left(\frac{1}{N_f} + \frac{1}{15N_D}\right) \approx \frac{K_d L_c}{u_0} \left(\frac{1}{N_f} + \frac{1}{15N_D}\right)$$
(C5)

When the Eq. (C5) is substituted into Eq. (3.9), the $L_{MTZ,CP}$ and $t_{MTZ,CP}$ can be expressed in terms of dimensionless groups.

$$\frac{L_{MTZ,CP}}{L_c} = \left[\frac{1+K_d}{K_d P e_b} + \frac{K_d}{1+K_d} \left(\frac{1}{15N_D} + \frac{1}{N_f}\right)\right] \left(\frac{\alpha+1}{\alpha-1}\right) ln \left|\frac{1-\theta}{\theta}\right|$$
(C6a)

$$\frac{t_{\text{MTZ,CP}} u_0}{L_c} = \left[\frac{(1+K_d)^2}{K_d P e_b} + K_d \left(\frac{1}{15N_D} + \frac{1}{N_f} \right) \right] \left(\frac{\alpha+1}{\alpha-1} \right) ln \left| \frac{1-\theta}{\theta} \right|$$
(C6b)

In LAD, K_d is very large ($K_d \gg 1$) and the sorbent selectivity (α) is replaced with the effective sorbent selectivity (α^e) so Eq. (C6) can be simplified to Eq. (3.15).

In most preparative chromatography, film mass transfer resistance is relatively small, resulting in negligible $1/N_f$. When Pe_b is much higher than $15N_D$ in Eq. (C2), a diffusion-controlled system is developed. Usually, if N_D/Pe_b is less than 0.001, the axial dispersion is negligible and thus intraparticle diffusion controls the mass transfer zone length. Then, Eq. (3.15a) can be simplified for diffusion controlled systems.

$$\frac{L_{MTZ,CP}}{L_c} = \frac{1}{15N_D} \left(\frac{\alpha^e + 1}{\alpha^e - 1} \right) ln \left| \frac{1 - \theta}{\theta} \right|$$
(C7)

Note that if Eq. (C7) is converted to the single component breakthrough curve for the diffusion controlled system as expressed in Eq. (C8), it is consistent with the expression of constant-pattern $L_{MTZ,CP}$ for affinity chromatography [76].

$$\frac{L_{MTZ,CP}}{L_c} = \frac{1}{15N_D} \frac{2+bC_f}{bC_f} \ln \left| \frac{1-\theta}{\theta} \right|$$
(C8)

where bC_f is the dimensionless group used in Langmuir isotherm.

APPENDIX D. ESTIMATION OF MODEL PARAMETERS

As shown in Figure D1a, the measured $q_{max,Cu}$ was 1.68 eq./L bed volume. When copper was stripped from the column using 0.03 M EDTA, a band concentration of 0.039 M copper resulted as illustrated in Figure D1b. This result indicates that EDTA binds with copper in a molar ratio of roughtly 1:1.3, resultin in the ligand binding efficiency difference between the copper and the REE bands.



Figure D. 1(a) Breakthrough curve of Cu^{2+} (0.2N) on a column (i.d. 1 cm x Lc 9 cm) and (b) elution curve of Cu^{2+} eluted by 0.03 M EDTA-Na (pH 8.4) solution.

APPENDIX E. PROCEDURE TO CALCULATE THE MINIMUM COLUMN LENGTH FOR A NONIDEAL SYSTEM

A procedure to calculate the minimum column length for a nonideal system is described in Figure E1. If the feed composition, intrinsic parameters, and material properties are known, one can choose a feed loading volume and a linear velocity. Then, the feed length (L_{feed}) and the minimum column length to develop an isotachic train for an ideal system (L_{iso-id}) can be calculated using Eq. (3.2) and (3.3), respectively. Next, based on the definition of the dimensionless groups in Eq. (3.13), (3.14), and (3.19), the value of combined dimensionless groups $L_f k_f^* \left(\frac{\alpha^e - 1}{\alpha^e + 1} \right)$ can be calculated because the column length is cancelled in the combined dimensionless groups. The value of $L_f k_f^* \left(\frac{\alpha^e - 1}{\alpha^e + 1} \right)$ gives the corresponding minimum dimensionless column length ϕ_{min} using the general map or using Eq. (3.27). One can calculate the minimum column length for a non-ideal system from the ϕ_{min} value and Eq. (3.24).

For Figures 3.6a-e, one needs to calculate the maximum feed loading and flowrate for the given column length, particle size, intrinsic parameters and feed compositions (Table 3.2), and the specific ϕ_{min} values. First, the minimum dimensionless column length to develop an isotachic train for an ideal system (L_{iso-id}/L_{feed}) was calculated using Eq. (3.1-3). Since the column length is fixed, L_{iso-id} and the maximum loading fraction (L_{fmax}) were calculated using Eq. (3.26) for each different ϕ_{min} value. Next, the corresponding value of the combined dimensionless groups $L_f k_f^*(\alpha^e - 1)/(\alpha^e + 1)$ for the given ϕ_{min} value was calculated using Eq. (3.27). Since L_f and α^e was calculated, the value of the dimensionless overall mass transfer coefficient k_f^* was calculated. Assuming N_f is very large and Pe_b follows Chung and Wen correlation, one can obtain N_D for the given ϕ_{min} from the calculated k_f^* using Eq. (3.14) and (3.16). The linear velocity was

calculated from the obtained N_D value using Eq. (3.14c). The feed loading volume (V_f) was calculated from the loading fraction and feed length using Eq. (3.3) and (3.19). The designed operating conditions were carried out using the same ligand conditions as used in Figure 3.5.



Figure E. 1 Procedure to calculate the minimum column length for a nonideal system using the general map

VITA

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