

SEPARATION OF ADJACENT RARE EARTH ELEMENTS USING SOLVENT EXTRACTION

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Presented in Partial Fulfillment of the Requirements for the

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by

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May 2016

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## ABSTRACT

Industrial rare earth separation facilities utilize the phosphonic acid PC88A for solvent extraction processes. Separation of adjacent lanthanides using solvent extraction is especially costly and difficult due to their chemical similarities. Process improvements provide significant positive impacts on regulatory and economic challenges associated with these difficult separations.

The separation of praseodymium and neodymium has been of particular interest recently due to current and forecasted future demand for high purity neodymium. Laboratory solvent extraction testing combined with MATLAB modeling has been used to develop and test solvent extraction flowsheets to separate high purity neodymium from a 25 wt % praseodymium and 75 wt % neodymium mixture. The flowsheet chemistry is based on the current industrial extractant, PC88A. Mixer-settler flowsheet testing with PC88A has shown that greater than 99% purity neodymium can be produced with a neodymium scrub solution in a 12-stage scrubbing circuit.

An overall flowsheet concept has been designed, tested, and evaluated to simultaneously produce didymium and high purity neodymium. The methods and processes developed in this research can be applied to all of the rare earth elements (REE) in the lanthanide series to develop a modeling capability for complex separation schemes. Additionally, the modeling principles can be applied to alternative solvent systems for REE separations. The methods presented for flowsheet development and optimization provide a design capability that supports a viable domestic supply of critical materials.

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## CHAPTER 1: INTRODUCTION

### 1.1 Critical Materials

Rare earth elements (REE) are becoming commonplace materials for the manufacture of modern electronics and clean energy technologies.<sup>[1]</sup> REE are comprised of the lanthanide series (lanthanum through lutetium) and typically include yttrium and scandium. This group of elements exhibit unique properties that have proven useful for a vast range of applications. Consider the smartphone- a modern convenience that can be found in the hands or pockets of more than two-thirds of Americans, with almost 2 billion smartphone users worldwide!<sup>[2]</sup> As many as nine rare earth elements including neodymium, europium, and dysprosium are used to manufacture smartphone color screens, speakers, circuitry; even the vibration units. Smartphones are only one example of a product that relies upon the unique properties offered by REEs. Additional applications include military guidance and sonar systems, high efficiency lighting phosphors, wind turbines, electric vehicles, photovoltaic thin films, optics, lasers, and magnets.<sup>[1]</sup>

China currently produces more than 90% of the global supply of rare earth elements. Chinese domination of the supply chain was made evident beginning in 2009 when China began to impose export restrictions on rare earths, citing the needs for conservation of its exhaustible natural resources and pollution reduction related to mining operations.<sup>[3]</sup> China began to expand export restrictions and embargos in 2010. The prices of REE soared, with metals such as dysprosium increasing in price by over 9000%! The US appealed to the World Trade Organization (WTO), claiming unfair competitive advantages related to the use of rare earths in the manufacture of products such as hybrid cars, alternative energy technologies, and high efficiency lighting. The US argued that the purpose of China's export controls was not resource conservation but rather a means to promote domestic industry while hampering foreign competition. The WTO ruled against China's trade practices in March of 2014, stating that export control cannot be used to protect and nurture domestic industry.<sup>[3]</sup> Figure 1 illustrates dysprosium prices throughout the Chinese embargo and WTO dispute:

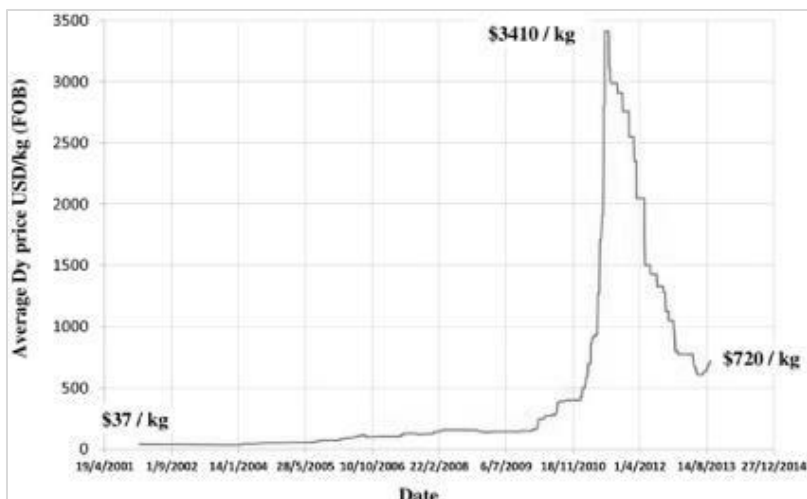


Figure 1: Historic price of dysprosium from 2001 through 2014.<sup>[4]</sup>

This drastic change in commodity pricing led to some serious questioning about the susceptibility of materials vital to US national security, technology deployment, and economic commerce. The United States subsequently published the Critical Materials Strategy in December 2011, identifying materials that are essential to clean energy technology deployment, yet are at risk for supply disruption. Five rare earth elements - dysprosium, neodymium, terbium, europium, and yttrium were listed as being critical materials. A material is defined as being critical if it is of high strategic importance for clean energy technologies *and* highly susceptible to supply chain disruption.<sup>[1]</sup> Figure 2 graphically illustrates this relationship, with the five critical rare earths depicted in black.

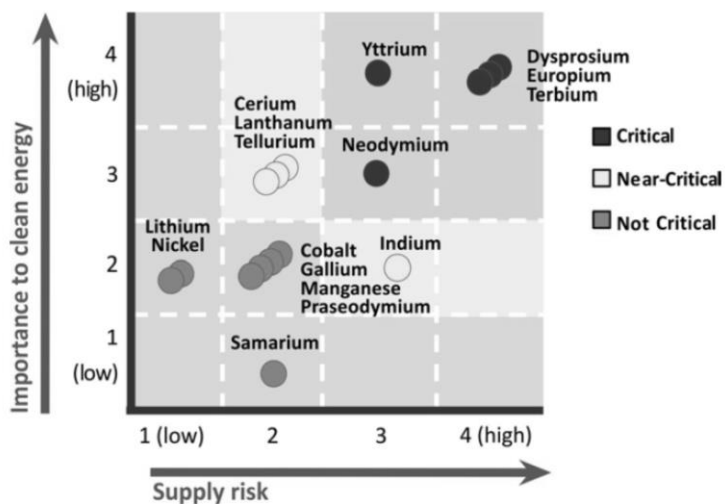


Figure 2: Medium-term (2015-2025) criticality matrix.<sup>[1]</sup>

In 2013, the Department of Energy awarded the Ames Laboratory to establish an Energy Innovation Hub to provide innovative solutions that will help ensure a viable domestic supply of critical materials. The Critical Materials Institute (CMI) was thus born, tasked with “enabling innovation in U.S. manufacturing and enhancing U.S. energy security”.<sup>[5]</sup>

The CMI is a major initiative of the US Department of Energy tasked with assuring domestic supply chain continuity for critical materials. Expansion and diversification of rare earth supply chains requires commercially viable enhancements to mining and separation processes. The rare earths are typically found in ore types such as monazite and bastnasite, and the entire lanthanide series is usually present to some extent in a given ore body (although most rare earth ore deposits primarily consist of “light” atomic weight lanthanides). The separation processes to obtain individual rare earth elements are not only complex but also notorious for being costly, inefficient, and having adverse environmental impacts. The CMI deemed separation of rare earths as a “Grand Challenge”- a problem that has the potential to cause adverse effects in a matter of months, whereas the solution could potentially take years or decades to be resolved and implemented.<sup>[5]</sup> Part of CMI’s challenge is to provide industry with practical solutions within a 5-year time frame- a daunting task considering economic, regulatory, and compliance issues.

## 1.2 Problem Statement

Separation of rare earth elements is accomplished commercially using solvent extraction. Rare earth separation processes are plagued with environmental issues relating to effluent waste streams, reagent consumption, and energy consumption. Significant reductions in reagent and water consumption at an operating facility minimizes environmental impacts and provides significant economic benefits that must be realized in order to stay competitive in the global market for critical material supply chains. For example, separation facilities in China have realized significant reductions in reagent consumption and wastewater emissions by implementing hyperlink extraction technology.<sup>[6, 15, 17]</sup>

The purpose of this thesis is to develop modeling capabilities for the design and evaluation of solvent extraction flowsheets for the separation of adjacent rare earth elements. This work is necessary for optimizing the operation of rare earth separation facilities for both economic and environmental reasons. If the United States is to secure a domestic supply chain of critical rare earths, it is essential to use advanced separation methods that are cost-competitive with foreign supply chains *and* adhere to strict US environmental regulatory requirements. If economic and

viable rare earth separation techniques are not developed, the US risks future supply disruption that will affect the production of military, commercial and consumer products. Supply chain disruption will adversely affect national and homeland security, energy security, and could prove detrimental to the US economy.

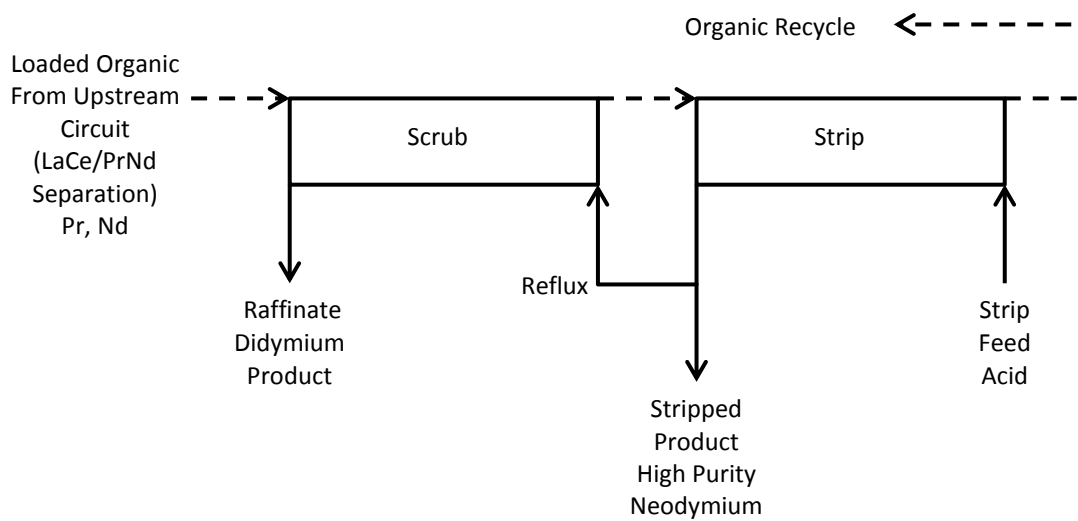
The hypothesis for this thesis is that laboratory data coupled with modeling techniques can be used to optimize and develop solvent extraction flowsheets for adjacent rare earth separations. This will result in cost effective and environmentally sound separation methods. There are four specific research subtasks required to test this hypothesis:

1. Obtain laboratory-scale solvent extraction equilibrium data
2. Develop modeling capabilities to predict the performance of solvent extraction processes
3. Design and optimize a separations flowsheet using the phosphonic acid extractant PC88A
4. Run a laboratory-scale solvent extraction flowsheet to validate modeling results predicted from laboratory equilibrium data

Separations for group lanthanides and individual lanthanides are accomplished by similar means by varying the chemical conditions in the solvent extraction circuit. Therefore, the scope of this research will focus on one specific separation. Separation of high purity neodymium from a praseodymium/neodymium (Pr/Nd) mixture has been chosen as the target separation for several reasons. First, the Pr/Nd split is one of the most challenging lanthanide separations to perform due to the remarkably similar chemical behaviors of praseodymium and neodymium. Second, the Pr/Nd split represents a typical separation that could be applied to other elements across the lanthanide series. Third, this separation is of particular interest to industry due to current and forecast demand for high purity neodymium (a critical material) for various magnet technologies. Finally, the concepts developed for this separation can be applied to any lanthanide separation by predicting the equilibrium conditions required to facilitate the separation.

Neodymium is the desirable high-value material in this separation process, so the flowsheet developed for this work will aim at producing a high-purity neodymium product to supplement an existing rare earth separation process. Neodymium used in Nd-Fe-B magnet applications ranges from 99-99.9% purity (wt%, Nd<sub>2</sub>O<sub>3</sub>) depending on the production process, with some finished magnets containing only 96 % purity neodymium.<sup>[13]</sup> Based on this range of purity requirements, the target neodymium purity for the proposed flowsheet will be 99%.

Praseodymium and neodymium are often processed together into a mixed oxide product commonly referred to as didymium. Didymium's specific UV filtering capabilities has given it several commercial applications, including safety glasses for glassblowing and photographic filters.<sup>[13]</sup> Didymium contains 25 wt%  $\text{Pr}_6\text{O}_{11}$  and 75 wt%  $\text{Nd}_2\text{O}_3$  and is produced commercially using solvent extraction. Molycorp's Mountain Pass mine located in California produced didymium as a final product at their separations facility. An opportunity exists to add an additional solvent extraction circuit that could continue production of the didymium product stream and simultaneously produce high-purity neodymium. Commercially, a loaded organic phase containing praseodymium and neodymium is stripped to recover the didymium product. Rather than stripping that loaded organic phase, an extra circuit could be added that produces both didymium and high purity neodymium. The envisioned flowsheet is shown in Figure 3.



**Figure 3: Proposed process for simultaneous production of didymium and high purity neodymium.**

The addition of the proposed solvent extraction circuit would require additional solvent extraction equipment, additional solvent inventory, and the additional strip acid to recover high purity neodymium. This is just one example of an adjacent lanthanide separation; the laboratory practices and modeling techniques developed in this work could be easily developed and applied to other rare earths, including other critical heavy rare earths. The final envisioned goal is to develop an equilibrium database coupled with a mathematical model that can be used to develop solvent extraction processes for complex mixtures of lanthanides representative of those found in processed ores such as monazite or bastnasite. This design capability will be an ongoing modeling effort at the Idaho National Laboratory (INL).

## CHAPTER 2: BACKGROUND AND LITERATURE REVIEW

### 2.1 Solvent Extraction

Historically, the lanthanides were first isolated and purified using fractional crystallization.<sup>[7]</sup> Ion exchange techniques eventually replaced fractional crystallization to produce usable quantities of high purity rare earths more effectively and efficiently. As demand for the rare earth elements increased, the low throughput and rising cost of ion exchange led to the use of solvent extraction for the industrial separation of rare earths. Solvent extraction technology is chosen for commercial production because high purity rare earths can be produced in large quantities continuously and economically. The basic principle of solvent extraction is shown in Figure 4:

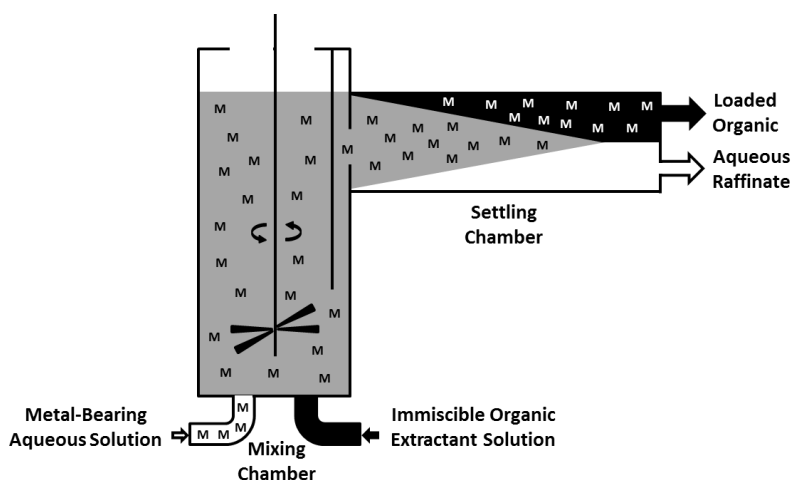


Figure 4: Solvent extraction fundamentals.<sup>[8]</sup>

Solvent extraction works on the principle of mass transfer of a desired component between two immiscible phases. An aqueous solution containing one or more solutes is intimately mixed into an emulsion with an immiscible organic solvent phase. As the two phases mix, the desired solute is selectively transferred to the organic phase from the aqueous phase. The two phases are then separated by differences in density and the desired component may be recovered by further processing of the organic phase (typically organic phase is light phase; aqueous phase is heavy phase). Solvent extraction has seen successful industrial application in the nuclear industry for nuclear fuel reprocessing, as well as a vast array of applications in the mining industry to produce metals such as copper, cobalt, nickel, molybdenum, and many more.

The organic solvent phase contains the extracting species typically diluted in a normal paraffinic hydrocarbon diluent. The extracting species is referred to as the extractant or ligand. Most

extractants are highly viscous and in some instances solid phase at room temperature; the diluent acts to dissolve solid-phase extractants, but more importantly alters the hydrodynamic properties of the organic phase. Viscous extractants exhibit poor flow characteristics and typically cause emulsion and phase disengagement issues.<sup>[10]</sup> Desirable properties of a diluent include low aqueous phase solubility, the ability to retain both complexed and un-complexed extractant species (i.e. no third phase formation) in solution, high flash point, low volatility, low surface tension, and stability.<sup>[9,20]</sup> Addition of a suitable diluent improves fluid flow properties, maintains density differences to allow proper phase disengagement, and even alters the rate or extent of extraction due to interactions between the extractant and diluent. Some aromatic based diluents such as toluene have been shown to interact with the extractant and alter the system's extraction behavior (which can be desirable in some solvent extraction systems), but extraction capability is usually increased by using diluents that have a low dielectric constant and thus limited interaction with the extracting species.<sup>[9, 20]</sup> Aliphatic long-chain hydrocarbons low in aromatic and sulfur content have low dielectric constants and have been utilized for solvent extraction processes. Additionally, if the organic solvent becomes excessively loaded with solutes, the metal-extractant complex can form a third organic phase or possibly even a solid phase. Phase modifiers can be added to the organic phase to improve solubility of the extracted metal-extractant complex. Phase modifiers such as long-chain alcohols and n-tributyl phosphate have been used to stabilize and improve the solubility of extracted complexes in some solvent systems.<sup>[9]</sup>

Several factors affect mass transfer efficiency in solvent extraction processes. Mass transfer occurs at the interface between the organic and aqueous phase, implying that increased interface surface area increases mass transfer. During emulsion formation, one phase will remain continuous and contain dispersed droplets of the other phase. An organic continuous phase with aqueous dispersed droplets provides maximum mass transfer surface area for the extraction of solutes from the aqueous phase into the organic phase.<sup>[22]</sup> Similarly, an aqueous continuous phase with droplets of dispersed organic phase promotes mass transfer for back-extraction or stripping of solutes from the organic phase into the aqueous phase. Limitations do exist- if the dispersed phase droplets become too small from intense mixing, a micro emulsion can form that will not allow droplet coalescence and the phases cannot properly disengage.

Whether operation is organic continuous or aqueous continuous is determined by the relative volume of each phase in the system. The organic to aqueous volume phase ratio, hereby referred to

as the O/A ratio, serves multiple purposes in solvent extraction systems. In the context of phase continuity, an  $O/A < 1$  will operate aqueous continuous and an  $O/A > 1$  will operate organic continuous. When the phase ratio operates near unity, the system will almost always operate aqueous continuous due to surface tension effects of the dispersed organic phase.<sup>[22]</sup>

The O/A ratio is frequently used to manipulate solute concentrations in a solvent extraction process. If an aqueous feed is highly concentrated in the desired solute for extraction, a high phase ratio provides excess organic solvent for extraction without causing loading and solubility issues. Phase ratios are also used to concentrate solutes during back-extraction and recovery. REE products are typically recovered by evaporation, precipitation, filtration, and calcination into a final rare earth oxide product. Concentrating the solutes during back extraction minimizes downstream processing costs and waste generation.

Several contact stages between aqueous and organic phases are typically required because complete solute recovery is not achieved in one stage. A single discrete solvent extraction contact constitutes an equilibrium stage, and several stages are commonly used in a continuous, counter-current cascade to efficiently produce high degrees of separation. Counter-current operation maximizes the concentration gradient driving force for mass transfer while still allowing continuous high process throughputs. A counter-current cascade is shown in Figure 5.

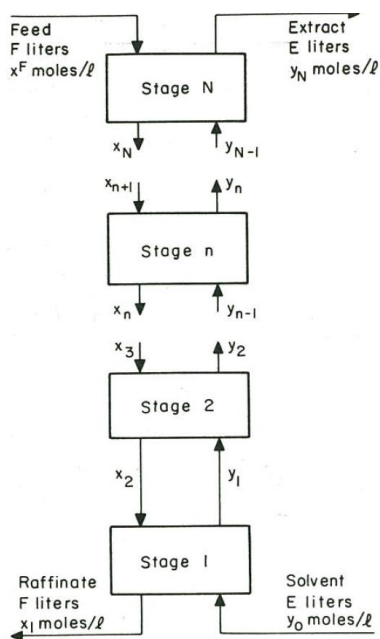
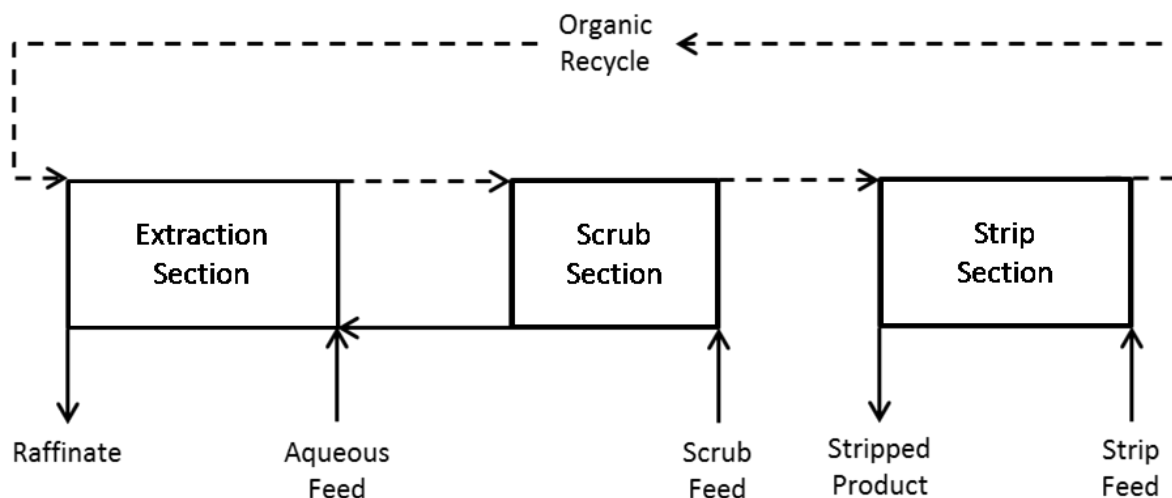


Figure 5: Principles of the counter-current solvent extraction cascade.<sup>[14]</sup>



In Figure 5, the aqueous feed enters stage N while the fresh organic solvent enters stage 1. The aqueous feed becomes depleted in solute as it moves across the cascade, and the organic solvent becomes increasingly enriched in the solute as the solvent approaches stage N. During extraction, undesirable solutes are often co-extracted into the organic phase and must be removed to produce high purity products. Several cascades will be employed for an overall flowsheet that will extract, purify, and recover target species in the process. A typical flowsheet is shown in Figure 6:



**Figure 6: Typical solvent extraction flowsheet design.**

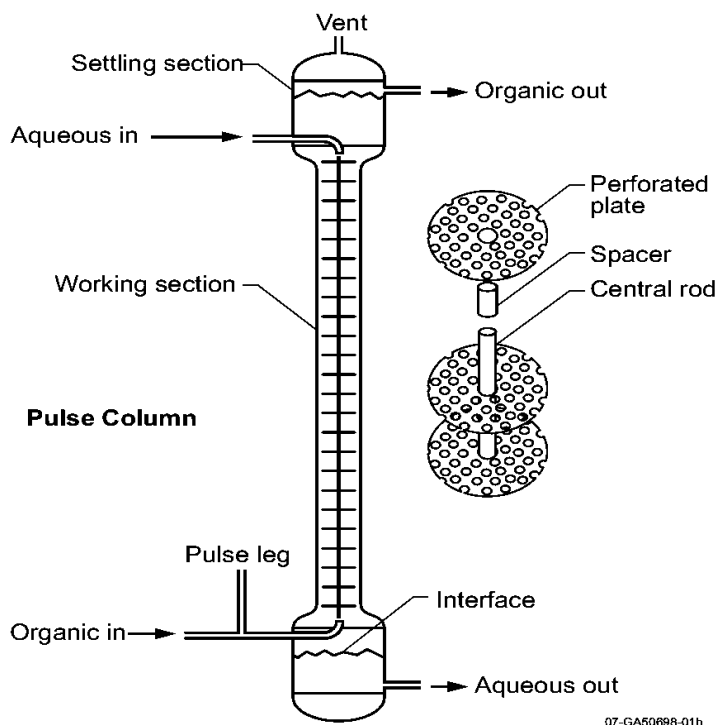
A flowsheet for a solvent extraction separation process will typically consist of an extraction section, a scrub section, and a strip section. The extraction section provides bulk separation of the desired component from the aqueous phase. REE extraction using phosphonic acids occurs at low acid concentrations. The spent aqueous phase, referred to as the raffinate, exits the extraction cascade. The organic phase, now carrying the desired component, is commonly called the “loaded solvent” or “loaded organic”. This loaded organic enters the scrub section, where impurities and undesirable components that were co-extracted in the extraction section are removed or “scrubbed” from the loaded organic phase. Scrubbing can be accomplished using a scrub feed solution with an acid concentration slightly higher than the equilibrium extraction pH or by means of metal reflux (scrubbing techniques are covered in detail in Section 2.4). Finally, the scrubbed loaded organic enters the strip section, where the desired component is recovered from the organic phase into an aqueous “stripped product” stream. Phosphonic acid-REE complexes are stripped at high acid concentrations to recover REE. The organic phase, now stripped of any solutes, is recycled to the extraction section for reuse.

## 2.2 Solvent Extraction Equipment

Solvent extraction equipment is designed to mix and separate the two immiscible phases efficiently and facilitate the mass transfer of the desired solute. Desirable attributes of solvent extraction equipment include high throughput, ease of operation, the ability to operate under a wide variety of flow rates and temperatures, high extraction efficiency, and the ability to tolerate solids suspended in aqueous solution. Standard solvent extraction equipment includes pulsed columns, centrifugal contactors, and mixer-settlers. The choice of equipment will typically depend on the facility footprint of the equipment, the process chemistry and kinetics, desired throughput and chemical compatibility.<sup>[11]</sup>

### 2.2.1 Pulsed Column

Pulsed columns are one of the most mature technologies used in solvent extraction. The heavy phase enters at the top of the column while the light phase enters from the bottom. The two phases flow countercurrent to each other due to the density differences between the heavy and light phase. The pulsed column is the only solvent extraction equipment type that employs true countercurrent flow between phases- cascades consisting of other equipment types are referred to as countercurrent simply by convention of process flow through the equipment. Mechanical energy is cyclically applied to the column through a pulse leg, typically either by means of a mechanical bellows or pressurized air. This energy creates a pulse that lifts and lowers the solution in the column. The amplitude of the pulse determines the magnitude of solution displacement in the column and the frequency at which the pulse is applied determines how quickly the solution is lifted and lowered. The column is filled with perforated plates that break up the dispersed phase into droplets. The pulsing action forces the dispersed phase through the perforations. Increasing the pulse amplitude and increasing the pulsing frequency creates smaller droplets. Smaller droplets increase available surface area and thus improve mass transfer, but if the pulse amplitude or frequency is too high the droplets may form an emulsion that will have difficulties with phase disengagement in the settling section. The actual phase disengagement and interface may be located at either the top or the bottom bulb of the pulse column, depending on whether the column is run organic continuous or aqueous continuous. If the column is run aqueous continuous, the organic phase is dispersed and the interface will be in the top bulb. If the column is run organic continuous, the interface is in the bottom bulb. The pulsed column is shown in Figure 7.



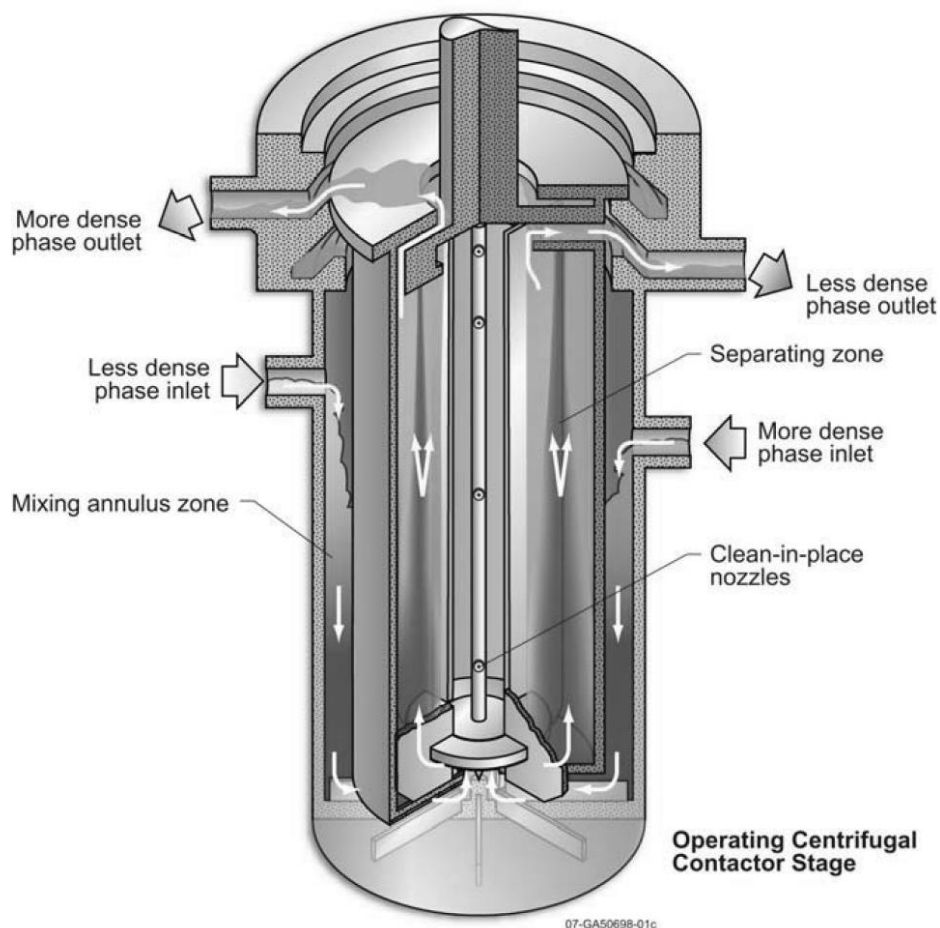
**Figure 7: Pulsed column for solvent extraction.** [11, 14]

Pulsed columns require very little maintenance because there are no moving parts in the column itself. Typically, the only item requiring maintenance is the pulsing equipment. This is one of the primary reasons pulsed columns have traditionally been used for nuclear fuel reprocessing—the column itself resides in a shielded cell and requires minimal remote maintenance, while the pulsing equipment is located outside the cell. Additionally, pulsed columns tolerate undissolved solids fairly well. The primary disadvantage of the pulsed column is their sheer size—pulsed columns require minimal floor space but can exceed 30 to 50 feet in height (or taller!). Columns do not have discrete equilibrium stages like a mixer-settler or centrifugal contactor, but rather a height equivalent to a theoretical stage (HETS). Depending on the column size and operation, an HETS typically require 1-3 feet of column height to obtain the same partitioning that could be expected in a single discrete equilibrium stage. Due to the excessive stage requirements of REE separations, pulsed columns are typically not used for this application.

### 2.2.2 Centrifugal Contactor

Centrifugal contactors are a relatively modern equipment design for solvent extraction. Each individual unit operates as a discrete equilibrium stage. The contactor utilizes a spinning rotor encased in a stationary housing to mix and separate two immiscible phases. The two phases enter

the housing and are intimately mixed due to the shearing motion of the spinning rotor. The emulsion then enters the spinning rotor, which acts as a centrifuge to separate the two phases. A weir system allows the two phases to exit the rotor into collector rings and exit the stage. The operating principles of the centrifugal contactor are shown in Figure 8.



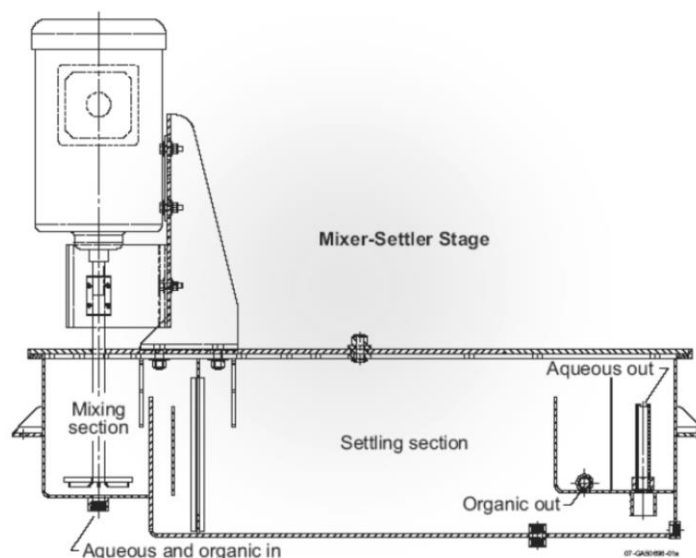
**Figure 8: Illustration of an operating centrifugal contactor.**<sup>[11]</sup>

Centrifugal contactors have extremely high efficiencies due to intense mixing and efficient phase disengagement. The equipment is compact and requires minimal facility footprint. Contactors can handle very high process throughputs with drastically lower holdup volumes relative to pulsed columns or mixer-settlers. Consequently, centrifugal contactors approach steady state very rapidly due to the low holdup and fast residence time. Fast residence times are advantageous when solvent systems are susceptible to degradation from acid hydrolysis or radiolysis, such as those conditions found in nuclear fuel reprocessing.

Centrifugal contactors have several disadvantages that have limited a more widespread use in industrial applications. First, contactors are much more expensive compared to simpler pulsed column or mixer-settler designs. Second, contactors do not tolerate process solids well due to the centrifugal forces in the rotor for phase disengagement. Third, the rotor and motor components are more likely to require increased maintenance. Many of these issues can be overcome, but the primary issue that makes centrifugal contactors unsuitable for the scope of this research is the fast residence time. The extractants of interest for this research require residence times on the order of minutes due to reaction kinetics, whereas the contactor has a residence time on the order of seconds. Centrifugal contactors have received significant attention for industrial solvent extraction processes- their benefits would reduce operating costs and increase productivity. Widespread application may be highly favorable for systems that have appropriate process chemistries.

### **2.2.3 Mixer-Settler**

Rare earth separation plants commonly use mixer-settlers and therefore this equipment will be the primary focus of this research. Mixer-settlers are chosen in the rare earth industry for several reasons: they are simple to operate, reliable, easily scalable, provide long residence times to achieve stage equilibrium, and can be re-started rapidly in the event of a process upset.<sup>[11]</sup> Additionally, laboratory data previously obtained at the INL suggests that the kinetics of phosphonic acid extractants requires a mixer residence time on the order of two to three minutes, making equipment such as centrifugal contactors non-ideal in this specific application. Primary disadvantages for mixer-settlers include large holdup volumes, floor space requirements, and a long approach to steady state. In a mixer-settler, aqueous and organic phases enter the mixing section where the two phases are mixed into an emulsion by means of an impeller. The emulsion flows from the mixing section into a settling section where the two phases disengage due to gravitational force, with the less dense light phase being on top of the dense heavy phase. The mixer-settler is illustrated in Figure 9:



**Figure 9: Illustration of a mixer-settler.**<sup>[11]</sup>

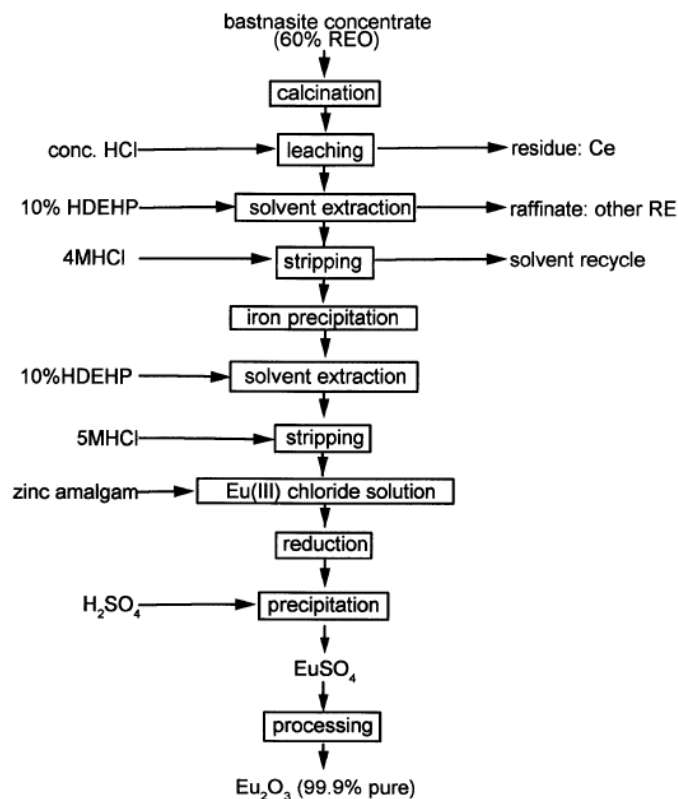
The light phase spills over an overflow weir and exits the stage, whereas the heavy phase exits through an adjustable jack-leg that allows adjustment of the interface of the two phases in the settling chamber. Interface adjustment capability is necessary because the density of both phases will change as mass transfer occurs, which can alter the interface position and potentially cause flooding if left unmitigated. Figure 9 represents just one style of mixer-settler; there are a variety of equipment designs but the operating principles are fundamentally the same.

Regardless of equipment type, process throughput will depend on the size of the equipment utilized in the process. Maximum total throughput is very important from a process perspective- if the maximum allowable throughput is exceeded, the emulsion does not have adequate time for phase disengagement. If the phases do not have adequate time to disengage, entrainment causes undesirable carryover over of one phase to the adjacent stage. Entrainment is characterized as the presence of one phase in both phase outlets. Entrainment reduces the driving force for mass transfer and thus reduces the extraction efficiency for a solvent extraction stage. Additionally, entrainment can cause issues with downstream processing of streams leaving a solvent extraction circuit such as evaporation, precipitation, calcination, etc. In worst-case scenarios, excessive entrainment can cause flooding of the equipment, characterized by little or no phase disengagement in the settling section of the equipment. Generally speaking, an organic-continuous system ( $O/A > 1.5:1$ ) will more commonly exhibit entrainment of the dispersed aqueous phase in the organic phase, while aqueous-continuous systems ( $O/A < 1:1$ ) exhibit entrainment of the dispersed

organic phase in the aqueous phase.<sup>[23]</sup> Note that entrainment can also occur due to solvent solubility losses in the aqueous phase raffinate. As the size of solvent extraction equipment increases, the maximum total throughput increases. Selection of equipment size ultimately becomes a balance of cost, desired throughput, and available floor space.

### 2.3 Lanthanide Chemistry

The lanthanide series consists of the fourteen elements on the periodic table that follow lanthanum. Yttrium and scandium are often included because of their similar chemical behavior and natural occurrence in ore deposits that contain the lanthanides. The chemistry of the rare earths is predominantly ionic and is determined by the size of the metal ion.<sup>[12]</sup> The lanthanides primarily exist as  $M^{3+}$  ion due to the valence noble gas core configuration that is achieved in this oxidation state. There are a few exceptions to the  $M^{3+}$  oxidation state due to the special stability associated with empty, half-filled, or filled f-shell electrons. Lanthanides are the first elements in the periodic table to access 4f-orbital electrons- an inner-shell orbital that can hold up to 14 electrons. For example,  $Ce^{3+}$  can be oxidized to stable  $Ce^{4+}$  (empty shell configuration) and  $Eu^{3+}$  can be reduced to stable  $Eu^{2+}$  (half-filled shell configuration). These stable oxidation states are utilized to separate pure cerium or pure europium from a mixture of rare earths. Consider Molycorp's original industrial process for producing high-purity europium oxide.<sup>[13]</sup> A europium chloride solution is produced from ore concentrate using solvent extraction. High purity europium oxide is then produced by reduction-precipitation with zinc amalgam followed by additional processing steps. The general process flowsheet is shown in Figure 10.



**Figure 10: MolyCorp process for europium oxide.**<sup>[13]</sup>

Similarly, cerium can be oxidized and separated from a mixture of rare earths by roasting the ore at high temperatures followed by iodate precipitation or solvent extraction with n-tributyl phosphate (TBP)<sup>[13]</sup>. Cerium and europium are not the only lanthanides that exhibit multiple oxidation states. Praseodymium and terbium both form complex oxides  $\text{Pr}_6\text{O}_{11}$  and  $\text{Tb}_4\text{O}_{11}$ , respectively, which are combinations of the 3+ and 4+ oxidation states of the lanthanide metal. Samarium and Ytterbium can also form stable  $\text{Sm}^{2+}$  and  $\text{Yb}^{2+}$  as this obtains the half-filled and filled f-orbital configuration, respectively. However, once these metals are dissolved in aqueous solution the trivalent oxidation state is the only observed stable state.

Inner f-shell electrons do not participate in bonding but do have some interesting effects on the element's properties. As atomic number increases across the lanthanide series, the atomic radius actually decreases. This phenomenon is quantified below in Table 1:



**Table 1: Lanthanide  $M^{3+}$  ion size.**<sup>[12]</sup>

Atomic Number	Element	$M^{3+}$ Radii (Å)
57	Lanthanum	1.061
58	Cerium	1.034
59	Praseodymium	1.013
60	Neodymium	0.995
61	Promethium	0.979
62	Samarium	0.964
63	Europium	0.950
64	Gadolinium	0.938
65	Terbium	0.923
66	Dysprosium	0.908
67	Holmium	0.894
68	Erbium	0.881
69	Thulium	0.869
70	Ytterbium	0.858
71	Lutetium	0.848
88	Yttrium	0.88

This effect is caused by imperfect shielding of one electron by another in the same subshell.<sup>[11]</sup>

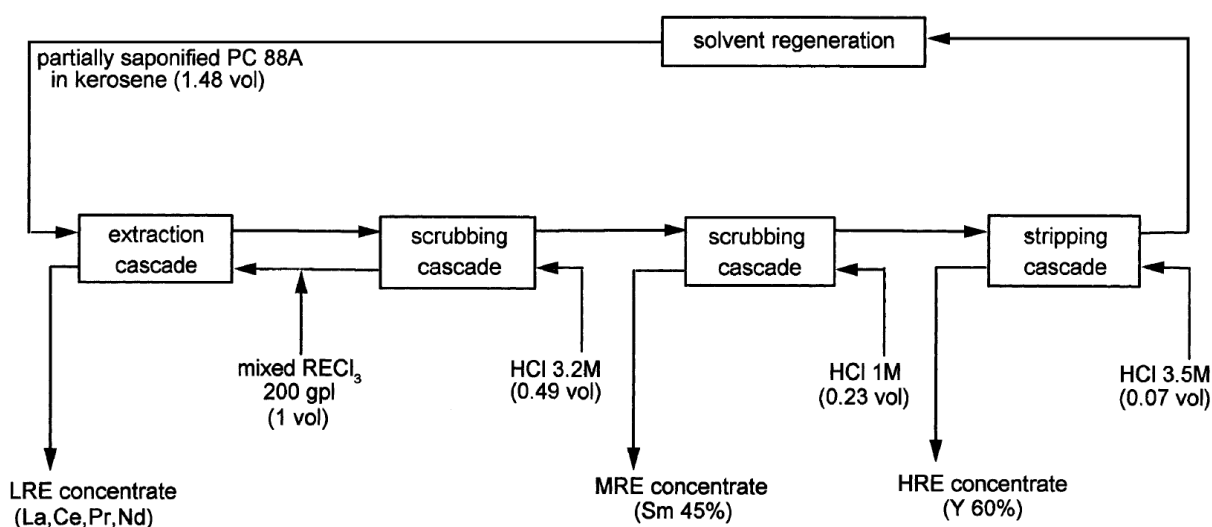
Nuclear charge increases with increasing atomic number, but electron shielding causes the effective nuclear charge to increase for f-shell electrons. The resulting effect is a decrease in atomic radius with increasing atomic number, commonly referred to as the Lanthanide Contraction.<sup>[11]</sup> The contraction alters the chemical behavior of the lanthanides because the ionization energy increases with increasing atomic number. Lanthanide ions in aqueous solution act as Lewis acids and therefore exhibit a decrease in basicity across the series. Lanthanide ions of the smallest ionic radius will form the strongest ligand complexes, allowing a means to exploit their chemical behavior for separation processes.

## 2.4 Rare Earth Separations

Separating and purifying individual rare earths has proven to be one of the most difficult separations to achieve due to the similarities in the chemical properties across the entire lanthanide series. Fortunately, as described in Section 2.3, the lanthanide series exhibits a slight decrease in the basicity of each element across the series. This small difference in basicity may be exploited to separate and purify the lanthanide elements. Phosphonic acid ligands used in solvent extraction have an increasing affinity for lanthanide extraction as the atomic number increases. Separation

factors between any two adjacent lanthanides are very low, however, since the atomic radius and subsequent difference in basicity is the only driving force for extraction affinity.

Solvent extraction flowsheets designed to separate individual elements are very complex because rare earth concentrates contain a mixture of the REE. The separation process uses multiple circuits, each comprising a large number of stages, to separate individual species. Figure 11 illustrates the complexity of a REE separations process for initial fractionation of REE from a feed solution containing all of the rare earths.<sup>[13]</sup>

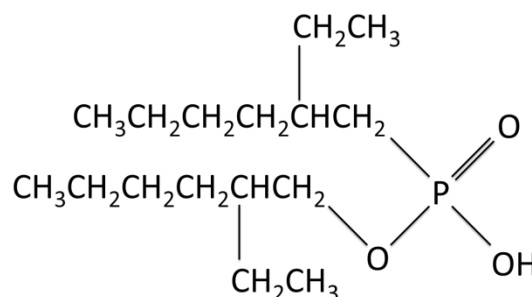


**Figure 11: Fractionation of REE concentrate into light/mid/heavy REE groups.**<sup>[13]</sup>

The circuit shown in Figure 11 only represents the first solvent extraction step to separate the rare earths. Each outlet stream contains a mixture of REE that still requires further downstream processing to obtain pure individual REE species. Each downstream step uses an additional solvent extraction circuit that requires extraction, scrubbing, and stripping at a minimum to achieve the desired separation.<sup>[13, 22]</sup> For example, the LRE concentrate produced in Figure 11 would have a downstream solvent extraction circuit to separate lanthanum and cerium from praseodymium and neodymium. If pure individual species are desired, two more downstream circuits would be required to separate cerium from lanthanum and neodymium from praseodymium. It becomes evident that a separations facility producing pure REE products would consist of hundreds of stages of solvent extraction equipment with a large number of complex, connected circuits that are highly susceptible to process transients.

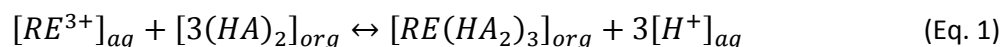
Furthermore, due to the economic competitive nature of the mining and metals industries, the actual details of plant design and operation are very closely guarded secrets. The result: there are large quantities of published information regarding extraction data and extraction chemistry, but there is very little published information about separations plant design, operation, and optimization. Additionally, published data spans such a vast variety of solvent systems and experimental conditions that it is difficult to select and support a single separation technique (especially when considering economic constraints to practical solvent extraction processes).

Various extractants have been used for industrial separation of REE, including bis (2-ethylhexyl) phosphoric acid (HDEHP), tributyl phosphate (TBP), versatic acid, versatic 10, and Aliquat 336. Lanthanide solvent extraction ligands are typically phosphoryl-based molecules, carboxylic acids, or amines. In recent years, industrial rare earth solvent extraction separations have been performed primarily with 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester, also known under the common trade names of EHEHPA, PC88A, P-507, Ionquest 801, or DS-100 (from here on it shall be referred to as PC88A, shown in Figure 12).



**Figure 12: Structure of PC88A.**

PC88A is a phosphonic acid extractant that behaves as a liquid cation exchanger according to the following equilibrium reaction:



In Equation 1, HA represents the acidic extractant molecule PC88A. Note that the extractant forms a dimer due to hydrogen bonding that occurs with the hydroxyl and double bonded oxygen groups. The metal ion is extracted into the organic phase at the ratio of 3 moles of extractant dimer to one mole of rare earth metal ion. The extent to which the metal ion is extracted is typically expressed using the distribution ratio:

$$D_{RE} = \frac{[C]_{org}}{[C]_{aq}} \quad (\text{Eq. 2})$$

The distribution ratio relates the equilibrium aqueous and organic phase metal concentrations, allowing equilibrium calculations to be conducted for stage-wise operations. Typically, a high distribution ratio implies a large extent of extraction, while a low distribution ratio indicates that extraction is limited and the metal is retained in the aqueous phase. The ratio of the distribution ratios between two extracting species A and B is defined as the separation factor:

$$\beta_{A/B} = \frac{D_A}{D_B} \quad (\text{Eq. 3})$$

The separation factor is frequently as a measure of the relative selectivity the ligand has for extracting one species over another. High separation factors indicate a higher degree of separation between the two species. One must take caution when interpreting distribution ratio and separation factor data- these parameters are nothing more than ratios of equilibrium concentrations. For example, an extraction occurring at a high O/A phase ratio may quantitatively extract a given species, but the value of the distribution ratio may appear low due to the dilution of the metal in the organic phase.

As previously mentioned, phosphonic acids behave according to a liquid cation exchange reaction. Hydrogen ion is released into the aqueous phase (3 moles of  $H^+$  per mole of metal ion). The equilibrium constant for this reaction may be expressed as:

$$K_{eq} = \frac{[RE(HA_2)_3]_{org}[H^+]_{aq}^3}{[RE^{3+}]_{aq}[(HA)_2]_{org}^3} = D_{RE} \frac{[H^+]_{aq}^3}{[(HA)_2]_{org}^3} \quad (\text{Eq. 4})$$

It becomes evident that this reaction is strongly dependent on the solution pH in the aqueous phase. Although the third-power dependency exists for the ligand concentration, flowsheets are almost always operated with excess ligand (to prevent solubility issues and third phase formation) and thus the change in free ligand concentration does not have an appreciable effect compared to the aqueous acid concentration. For PC88A, the distribution coefficient increases for low acid concentrations (high pH) and decreases for high acid concentrations (low pH). Therefore, PC88A solvent extraction flowsheets are designed such that the extraction section operates at a lower acid concentration that preferentially extracts the desired metal ion from the aqueous phase into the organic phase, and the strip section operates at a high acid concentration to shift the equilibrium such that the metal ion is transferred back into the aqueous phase.

The strong dependency on pH poses a problem- as metal ions extract, the acid concentration increases, causing an adverse effect on the extraction equilibrium. This can be mitigated by pre-neutralizing the cation extractant with a base such as sodium hydroxide or ammonium hydroxide (saponification).<sup>[16]</sup> The exchange reaction takes place between the saponified extractant and the metal ion, resulting in no net change of acid concentration. This process leads to additional issues- it is one of the largest reagent costs in a separations facility and it also causes environmental concerns due to effluent waste streams. Excessive saponification can also cause gel formation and increased solubility of the saponified extractant in the aqueous phase.<sup>[16]</sup> Saponification reagents and acid requirements for the process create some of the largest economic and environmental concerns for an operating facility.

Adjacent lanthanide separations are very difficult due to their similar ionic radii. Typical separation factors found in the literature for neodymium and praseodymium are 1.5 – 1.6, and the two typically cannot be separated from one another simply using an extraction section. The scrubbing section in a solvent extraction flowsheet provides the means of separating the two elements by exploiting the ligand's slight difference in affinity between the two metal species. For example, Section 2.3 described how ligands have a higher affinity for higher atomic weight lanthanides. Therefore, a scrub solution containing the heavier lanthanide can preferentially remove the lighter lanthanide from a loaded organic phase. This scrubbing technique is essentially a metal-metal exchange in the organic phase. This "crowding" or "preferential strip" produces a high purity loaded organic phase containing the heavier target metal of interest and recombines the spent scrub solution back into the extraction section of the flowsheet to maximize recovery. Use of REE-loaded solutions as a means for scrubbing or pH control is the basis behind the optimized hyperlink extraction technology.<sup>[17]</sup> Even though this technique has been proven to produce high purity individual rare earths, it still has the disadvantage of requiring a large number of stages to complete high purity separations.

It is not uncommon to see REE solvent extraction circuits operating at bizarre and extreme phase ratios. REE concentrate feed solutions frequently have very high metal concentrations (upwards of 200 g/L total REO), which can cause solubility issues and third phase formation in solvent extraction circuits. Chemical manufacturers recommend not exceeding 30% of the stoichiometric loading of the organic phase to avoid solubility concerns when using phosphonic acids such as PC88A and Cyanex<sup>®</sup> 572.<sup>[18]</sup> Solubility concerns are circumvented by operating with the

organic flowrate higher than the aqueous phase flow rate (increased O/A ratio). This essentially “dilutes” the metal concentration in the organic phase upon extraction. Similarly, high O/A ratios are frequently employed when stripping the organic phase for product recovery. This highly concentrates the REE product, reducing effluent waste volumes and the need for additional downstream processing.

One implication of high feed metal concentrations is that saponification is required to obtain high recovery. If the organic phase is not neutralized prior to extraction, the acid liberated during exchange will adversely affect the extraction. Once the acid concentration is too high, it does not matter how many stages are added- the phase equilibrium is determined by the acid concentration. High recoveries are only obtained if saponification is used to control pH during extraction.

Another aspect of hyperlink extraction technology involves the use REE-loaded organic as the “pre-neutralized feed” organic into a solvent extraction circuit as a means of controlling pH.<sup>[15]</sup> This technique uses the “crowding” method discussed for scrubbing and can even replace the need for saponification in certain solvent extraction circuits. For instance, a circuit separating a light and heavy lanthanide from one another would use an organic feed pre-loaded with the lighter lanthanide. The ligand has a higher affinity for the heavier lanthanide, and extracts the heavy lanthanide while scrubbing the light lanthanide with no net change in the aqueous phase pH (provided that the feed acidity equals the equilibrium acidity commensurate with that loaded organic phase). This pH control method, while promising, is not within the scope of this research because it requires a plant-wide optimization process for every solvent extraction circuit. The essential steps of flowsheet design considered in this research include:

- Develop laboratory distribution data
- Model and develop the separations flowsheet
- Laboratory flowsheet testing
- Adjustment and optimization

Overall, the design and optimization of an REE separations facility is a complex and challenging problem that requires a large number of solvent extraction stages, large amounts of reagent consumption, and extremely tight control of operating parameters such as feed concentrations and system pH. Flowsheet development requires an extensive set of empirical data coupled with modeling techniques to mitigate process startup, transients, and produce high purity products.

## CHAPTER 3: MATERIALS AND METHODS

### 3.1 Laboratory Equilibrium Distribution Data

Obtaining equilibrium distribution data is essential for the development and verification of solvent extraction flowsheet design. Extraction behavior for large multicomponent systems is complex and cannot be predicted easily from fundamental principles. Additionally, equilibrium data must be obtained to evaluate the performance of scrubbing and stripping the organic phase. Consequently, this research requires an extensive database of equilibria data to accurately model and optimize solvent extraction processes. Tests were devised to collect equilibrium data at the laboratory scale using “batch contact” solvent extraction experiments. A batch contact is performed by placing appropriate volumes of aqueous solution and organic solvent into a test tube. Solution volumes are generally less than 50 mL per phase; more commonly batch contacts involve 3-5 mL of each phase. The test tube is capped and the two phases are mixed using a vortex motion mixer, a mechanical rotary mixer, or by manual agitation for several minutes to achieve equilibrium. After mixing, the phases are separated by centrifugation or by gravity settling until phase disengagement is complete. Samples of the organic and aqueous phases are carefully taken for subsequent analysis. Analysis specific to PC88A includes determination of the aqueous phase equilibrium pH and the metal concentrations in each phase.

#### 3.1.1 Experimental Procedures

Hydrochloric acid (HCl) is used almost exclusively in the rare earth industry for solvent extraction separations; therefore HCl was chosen as the aqueous phase medium for batch contacts. The organic phase consisted of 1 M PC88A in Isopar-L. PC88A is the extracting species and Isopar-L acts as a diluent to improve the hydrodynamic properties of the organic phase such that it is fit for use in solvent extraction equipment. Isopar-L, produced by Exxon Mobile, is an aliphatic isoparaffinic hydrocarbon solvent consisting of C11-C13 isoalkanes. Isopar-L has an aqueous phase solubility that is below measurable detection limits, has a low vapor pressure (0.3 mm Hg), and contains less than 1 ppm aromatic hydrocarbons, making it a suitable diluent for laboratory scale solvent extraction processes. Industrial applications typically use a similar low-grade diluent (contains appreciable impurity aromatic and sulfur compounds) due to the increased costs associated with high purity diluents such as Isopar-L.

Aqueous feeds were prepared with 99.9% purity rare earth oxides purchased from GFS Chemical (Columbus, OH). Oxides were dissolved in excess reagent-grade HCl (37%, Sigma-Aldrich, St. Louis,

MO) and the final volume was adjusted using nano-pure water to obtain the desired metal concentration and pH. PC88A was supplied by Cytec Canada, Inc. (Niagara Falls, ON) and used without further purification. Isopar-L was purchased from chemical distributor Univar (Salt Lake City, UT) and used without further purification.

Extraction data were obtained for individual metal species as a function of acid concentration and metal concentration. Neodymium and praseodymium aqueous feeds were tested at acid concentrations varying from 0.01 M to 1 M HCl. 5 mL of aqueous feed and 5 mL organic (O/A = 1) were mixed using the batch contact method described above in Section 3.1. Specific cases of higher O/A ratios maintained 5 mL of aqueous phase and varied the organic phase volume.

Scrubbing and stripping data were obtained by contacting an organic phase containing the metal species of interest with an aqueous phase of varying acidity or metal concentration. Scrubbing contacts were aimed at producing an organic phase rich in neodymium from an organic feed that contains a mixture of praseodymium and neodymium. Strip data were obtained for individual metal species because the stripping process is the final recovery step in a flowsheet where it is expected to have high purity metal concentrations.

Data obtained from laboratory-scale batch contacts provide a means to empirically determine the partitioning behavior of each species in solution over a wide range of testing conditions. This capability can be incorporated into a mathematical model to predict transient counter-current cascade behavior and determine product purities.

### **3.1.2 Analytical Procedures**

Aqueous phase acid titrations were performed using an automatic Mettler Toledo DL50 titrator. The titrant is 0.1 M sodium hydroxide and the titrator automatically determines the equivalence point of the acid-base titration to determine the sample's acid concentration. One issue that requires mitigation during titration is the presence of metal ions in acidic aqueous solution. Hydrated metal ions in solution can act as a Bronsted acid, causing hydrolysis and lowering the pH of an aqueous solution. The observed pH of the solution will be lower than the pH that would be observed solely from the contribution of mineral acid. This phenomenon, known as metal hydrolysis, is easily mitigated by adding 5 mL of 1 M potassium oxalate to complex any metal ions in the sample solution. Addition of potassium oxalate forms an insoluble metal precipitate, allowing an accurate measurement of the solution pH. Typically oxalate precipitation is only necessary for



extremely high metal concentrations, but this method was used for all titrated samples to eliminate any uncertainty due to hydrolysis effects.

Metal concentrations were determined for organic and aqueous phases by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo iCAP 6500). Aqueous phase samples can be analyzed directly using ICP-OES, but organic-phase samples cannot be analyzed directly due to the cation complexing mechanism of the organic extractant. Any loaded metal must be stripped from the organic phase into aqueous solution for ICP analysis. This was accomplished by performing a batch contact with the organic phase sample of interest with excess concentrated hydrochloric acid. Stripped organic samples are prepared as follows:

- 500  $\mu$ L of desired organic sample
- 5 mL of 3.4 M HCl
- O/A phase ratio of 0.1
- 3-minute vortex mixing time
- Centrifuge for 3 minutes for phase disengagement
- Separate clean aqueous phase for analysis

This method has been confirmed in the laboratory to quantitatively remove extracted metals from the organic phase sample. The low O/A phase ratio dilutes the samples by an order of 10, which must be accounted for after determining the metal concentrations using ICP. Error can be introduced using this technique if the phase volumes are not accurately measured to account for dilution effects, but typically mass balances are  $\pm 5\%$  using this method. The mass balance is determined by taking a known feed solution, performing an extraction batch contact, and analyzing each phase's metal content in relation to the feed solution.

ICP-OES analysis services were performed off-site at the Center for Advanced Energy Studies (CAES). ICP-OES utilizes a plasma torch, load coil and RF power supply to sufficiently energize atoms such that they emit light. Samples are pumped through a nebulizer to produce a fine spray. The large droplets are removed by a spray chamber and the small droplets then pass through to the plasma. The plasma is formed by an intense magnetic field produced by radio frequency (RF) passing through a copper coil. The plasma generates photons of light by the excitation of atoms and ions. The emission of light which occurs as discrete lines, are separated according to their wavelength by diffractive optics using an Echelle optical design. The analytical signals are measured using a Charge Injection Device (CID) as the detector. The samples can be analyzed using either the radial or axial

plasma views depending on the sensitivity needed. Various interferences must be considered and addressed appropriately. Control of the spectrometer is provided by PC-based iTEVA software.

All samples were analyzed in radial plasma view. All wavelengths for each analyte were used during the analysis, but the reported wavelength concentration was chosen by looking at the quality control data, sensitivity and minimum spectral interference with each run. The calibration curves were generated each analysis day using NIST traceable standards from Inorganic Ventures. The calibration curve was developed using a blank and 5 concentrations ranging from 10 µg/L to 100,000 µg/L and required a linear correlation of at least 0.995. All samples were diluted 2-500X with 1% HNO<sub>3</sub> to ensure the concentration of each analyte was within the analyzed calibration range. Neodymium was analyzed with wavelengths 430.358 or 415.608 nanometers and praseodymium was analyzed with wavelengths of 417.939 or 414.311 nanometers. Each matrix type was spiked with a known concentration of analyte and recoveries were calculated and used to determine if there was any interference due to the matrix. There were no matrix interference issues with any of the samples. Duplicates were analyzed at a rate of 10%. A laboratory control standard (LCS) was analyzed prior to sample analysis to verify that the generated calibration curve was valid. The LCS was analyzed every 10 samples to ensure there was no instrument drift. A blank of the 1% HNO<sub>3</sub> used for sample dilution was analyzed every 10 samples to verify there was no contamination. The calibration standards were analyzed as samples at a rate of every 30 samples to also ensure there was no instrument drift. Detection for neodymium and praseodymium was 100 µg/L. Operating conditions of the ICP-OES are shown in Table 2.

**Table 2: ICP-OES operational conditions and instrumental standards.**

Sample flush time	75 seconds
Flush pump rate	50 rpm
Analysis pump rate	50 rpm
Pump stabilization time	5 seconds
RF power	1150 W
Auxiliary gas flow	1 L/min
Nebulizer gas flow	0.6 L/min
Coolant gas flow	12 L/min

### 3.2 Mathematical Model

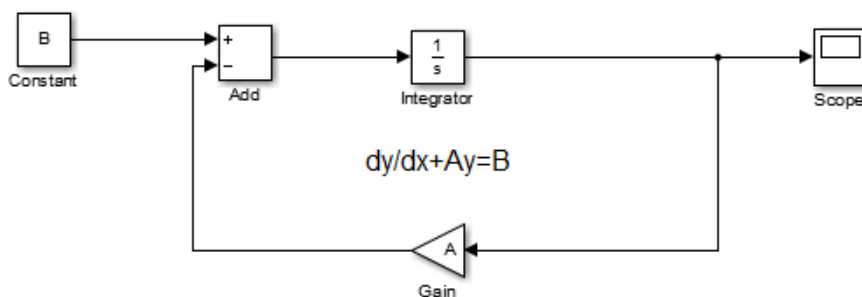
The majority of available solvent extraction models use experimentally obtained distribution data in combination with thermodynamic modelling to predict distribution coefficients for solute

partitioning.<sup>[9,24]</sup> One primary drawback to these models is that they are based on steady state material balances and therefore are only capable of predicting the steady state concentration profiles for a solvent extraction circuit. It would be desirable to have a modeling capability that predicts transient behavior for several reasons. First, an actual operating facility processes feed solutions that may vary in constituent concentrations based on the day-to-day fluctuations in upstream ore processing. Second, an operating facility is subject to process upsets and the ability to predict process transients allows improved troubleshooting and corrective actions (especially important considering the process sensitivity to pH). Third, REE separation circuits that utilize reflux require special startup conditions during the approach to steady state to avoid refluxing acid that is too concentrated for scrubbing (this adverse condition would require complete system draining, cleaning, and restart). Lastly, if a solvent extraction circuit is operated as a batch-mode campaign, the process may not achieve steady state which can alter the performance of the separation. Transient behavior is extremely important in systems that use mixer-settlers because the large holdup volumes have several adverse implications when a process upset occurs. For example, if any feed solution is abruptly changed, it can take hours for the disturbance to propagate through the circuit. These reasons provided the motivation to develop a modeling capability that can utilize equilibrium distribution data to determine transient behavior in order to optimize and understand flowsheet behavior. There are several capabilities that are desired to incorporate into the modeling effort to provide the highest degree of accuracy and flexibility. The user should have the ability to:

- model extraction, scrubbing, stripping, and solvent conditioning sections
- adjust the number of stages in each section
- select the components in the aqueous feed
- adjust the acidity and metal content of feed streams (extraction, scrubbing or stripping)
- select aqueous phase acidity conditions for startup
- select system flow rates and O/A ratios for each section
- model process upsets by allowing step changes, ramping, or intermittent changes in feed compositions or flow rates
- adjust stage efficiency to account for the performance of the solvent extraction equipment

MATLAB software was chosen for the modeling environment because of its powerful capability to simultaneously solve large systems of equations and easily integrate signal changes for transient

analysis. The MATLAB SIMULINK software package allows the user to represent differential equations in a block diagram/flowsheet representation and allows fast and easy adjustment of model input parameters. A SIMULINK representation of a first-order ordinary differential equation (ODE) is shown in Figure 13.

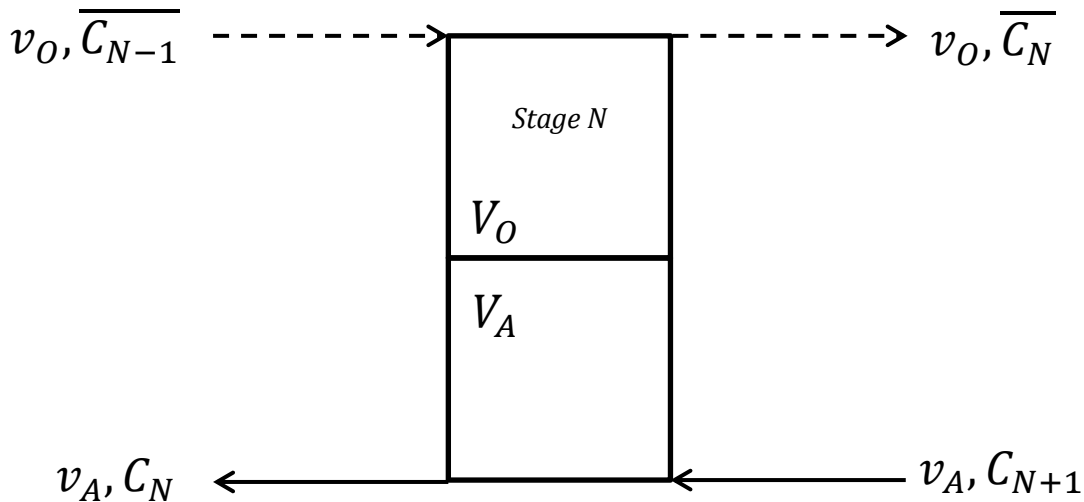


**Figure 13: SIMULINK representation of a first order ordinary differential equation.**

The governing stage balance equations must be developed prior to constructing the model in SIMULINK. The first step is to develop mass balances for each species in a single solvent extraction stage:

$$\text{Accumulation} = \text{In} - \text{Out} + \text{Generation} - \text{Consumption} \quad (\text{Eq. 5})$$

The material balance is a governing equation that is universal to any solvent extraction equipment type. A single solvent extraction stage is illustrated in Figure 14.



**Figure 14: Representation of a single solvent extraction equilibrium stage.**

Where

$\overline{C}_{N-1}$  = Organic phase metal concentration leaving stage (N – 1) and entering stage N, g/L

$\overline{C}_N$  = Equilibrium organic phase metal concentration leaving stage N, g/L

$C_{N+1}$  = Aqueous phase metal concentration leaving stage (N + 1) and entering stage N, g/L

$C_N$  = Equilibrium aqueous phase metal concentration leaving stage N, g/L

$v_O$  = Organic phase flow rate, L/min

$v_A$  = Aqueous phase flow rate, L/min

$V_O$  = Organic phase holdup in stage N, L (Assumed constant for all stages)

$V_A$  = Aqueous phase holdup in stage N, L (Assumed constant for all stages)

The holdup volumes were assumed to be constant for every stage for modeling purposes. In reality, densities of both the aqueous phase and the organic phase change as solutes transfer from one phase to the other. Changes in density change the interface position and thus the holdup within a single stage. However, testing conditions for all of the research conducted had relatively low metal concentrations and therefore minimal changes in density and subsequent holdup volumes. Additionally, the mixer-settlers have an adjustable jackleg to maintain interface position, which was used throughout the duration of flowsheet testing to maintain a consistent interface position to ensure adequate phase disengagement. The overall single-stage material balance for species N may be expressed as follows:

$$\frac{d(V_O\overline{C}_N + V_A C_N)}{dt} = v_O\overline{C}_{N-1} + v_A C_{N+1} - v_O\overline{C}_N - v_A C_N \quad (\text{Eq. 6})$$

Making the following substitutions allows separating the above equation into two ODEs:

$$\frac{v_O}{v_A} = \frac{O}{A} \quad (\text{Eq. 7})$$

$$D_N = \frac{\overline{C}_N}{C_N} \quad (\text{Eq. 8})$$

$$\frac{V_O D + V_A}{v_A} = \alpha \quad (\text{Eq. 9})$$

$$\frac{O}{A} D_N + 1 = \lambda \quad (\text{Eq. 10})$$

The ODEs represent the equilibrium species concentrations leaving stage N in the organic phase and aqueous phase, respectively.

$$\frac{d\overline{C}_N}{dt} = \frac{\frac{O}{A}D_N\overline{C}_{N-1} + D_N C_{N+1} - \overline{C}_N \lambda}{\alpha} \quad (\text{Eq. 11})$$

$$\frac{dC_N}{dt} = \frac{\frac{O}{A}C_{N-1} + C_{N+1} - C_N \lambda}{\alpha} \quad (\text{Eq. 12})$$

Note that the distribution ratio has been pulled out of the differential operator under the assumption that it does not change with time. While the measured distribution ratio does indeed change over time, it can be reasonably assumed that it is independent of time due to the short residence time of the mixing chamber compared to the extremely long approach to steady state (mixing chamber has a 3-minute residence time versus several days or weeks for the approach to steady state). Using this pseudo-steady state approximation allows the distribution ratio to be treated only as a function of feed concentrations rather than time and can therefore be pulled from the differential operators in equations 11 and 12. The distribution ratio is primarily dictated by the aqueous phase pH but also changes with REE concentrations in the aqueous and organic phases. Empirical correlations for the distribution ratio are utilized in the model to allow it to change as feed concentration changes (effectively changing the distribution ratio over time during the approach to steady state). Note that equations 11 and 12 are not independent of one another because the equilibrium organic and aqueous phase concentrations are related via the distribution coefficient. However, the modeling was performed using an ODE for each phase because it allowed for easier visualization and manipulation of the model inputs and outputs in SIMULINK.

Finally, the strong dependence on pH requires an acid material balance be written. The acid material balance is important for predicting transient equilibrium behavior because the aqueous phase acid concentration will dictate the distribution behavior of individual metal species.

$$\frac{d(v_A[H^+])}{dt} = v_A[H^+]_{N+1} - v_A[H^+]_N + 3\left(\sum_i MW_i(C_{i_{N+1}} - C_{i_N})\right) \quad (\text{Eq. 13})$$

Each stage in a solvent extraction cascade consequently solves 2 ODEs for each REE species plus an acid balance ODE that is a function of the number of species present in aqueous solution. Therefore, a system containing  $n$  number of species will result in  $2n+1$  ODEs that need to be solved per stage. Although not evident at first glance, this becomes a complex modeling problem due to the counter-current design of a solvent extraction cascade. This is one of the main reasons

SIMULINK was chosen for modeling this problem because it does not require extensive computer programming efforts to build and manipulate a counter-current simulation.

### 3.3 Flowsheet Testing

One of the most challenging aspects of this research was the interpretation and application of laboratory scale data to design a process flowsheet. The primary hurdle was the prediction of counter-current solvent extraction cascade behavior using single-contact equilibrium data that varies as a function of ligand concentration, metal concentration, and acid concentration. Laboratory data combined with the MATLAB model greatly simplified this task and allowed rapid manipulation and prediction of flowsheet parameters.

The INL recently procured a laboratory-scale 32 stage mixer-settler system that was utilized to test flowsheet designs for this research. The mixer-settlers were manufactured by MEAB Metallextraktion AB based in Sweden. The units are compact, portable, have a low holdup volume, and are constructed of materials that have superior chemical compatibility to allow a versatile testing environment for flowsheet development. The 32 stage system is shown in Figure 15.



**Figure 15: INL's 32 stage MEAB mixer-settler system.**

The mixer-settlers are constructed of Kynar (PVDF) for all wetted parts and PVDF or Teflon (PFA) connections and tubing were used in the operation of the system. Mixer speed was adjusted manually using a manual control knob. Aqueous and organic feeds to the mixer-settlers are delivered by FMI pumps from Fluid Metering, Inc. Model RHV pumps were chosen for this application because they can deliver highly accurate flow rates at the low process throughputs

required by the mixer-settlers. Table 3 lists the mixer-settler specifications provided by the manufacturer.

**Table 3: MEAB mixer-settler properties.**

Mixing chamber volume	120 mL
Settling chamber volume	480 mL
Loading surface area	0.006 m <sup>2</sup>
Maximum total throughput (combined org+ aq+ aq recycle)	10 L/hr

The loading surface area describes the total surface area of the settling section in the mixer-settler unit. The loading surface area is typically used to scale up solvent extraction processes—increased loading surface area allows higher throughputs. Scale-up works very well for solvent extraction processes because the process chemistry is unaltered, assuming phase ratios, relative flow rates and adequate mixing are maintained.

Prior to using this equipment for the Pr/Nd separation tests, several tests were performed to evaluate the mixer-settlers specifically for the 1 M PC88A/Isopar-L/HCl solvent pair. This included hydrodynamic and extraction studies to evaluate flooding, phase disengagement, efficiency, and mixing. Extraction tests were performed at various throughputs, O/A phase ratios, and mixer speeds. Proper operation requires a balance of mixing speed and throughput in order to obtain stage equilibrium and still provide adequate time for phase disengagement. As far as hydrodynamics are concerned, the equipment could obtain total throughputs of 120 mL/min for the PC88A/ Isopar-L/HCl solvent system at a mixer speed of 950 ±50 RPM as read on a portable tachometer. Mixer speeds below 900 RPM adversely affected phase dispersion and stage equilibrium due to poor mixing. Excessive mixer speeds created a micro emulsion that caused excessive carryover of the aqueous phase in the organic outlet.

The initial laboratory testing determined that the limiting parameter for operation was the reaction kinetics of extraction and stripping. A three-minute mixer residence time was required in order to achieve chemical equilibrium in a stage, which corresponds to a total throughput of 40 mL/min. Given this limitation, the range of operating conditions are within an acceptable range to avoid issues such as flooding and phase entrainment. This equipment was used for flowsheet testing to validate laboratory data and model predictions.



## CHAPTER 4: RESULTS AND DISCUSSION

### 4.1 Distribution Data

An extensive set of equilibrium data was obtained for extraction, scrub, and strip sections for praseodymium and neodymium. This data set included experiments for single metal testing as well as mixed metal testing to understand and predict complex partitioning behavior in solvent extraction systems.

#### 4.1.1 Extraction Data

A library of extraction data is necessary to determine phase distribution as a function of acid concentration and metal concentration. Table 4 reports the results from single metal batch contacts for neodymium.

**Table 4: Neodymium Extraction Data. 1 M PC88A in Isopar-L, O/A = 1.**

Feed Nd (g/L)	Feed [H <sup>+</sup> ] (M)	Equilibrium [H <sup>+</sup> ] (M)	% Extraction	D <sub>Nd</sub>
12.5	0.01	0.13	38	0.619
12.5	0.05	0.15	30	0.423
12.5	0.1	0.18	22	0.276
12.5	0.3	0.31	2	0.021
12.5	0.5	0.50	0	-
6.2	0.01	0.12	65	1.842
6.2	0.05	0.13	53	1.106
6.2	0.1	0.16	39	0.631
6.2	0.3	0.30	9	0.094
6.2	0.5	0.50	1	-
0.8	0.01	0.04	99	174.668
0.8	0.05	0.08	92	11.273
0.8	0.1	0.12	72	2.558
0.8	0.3	0.30	3	0.027
0.8	0.5	0.50	0	-

Inspection of neodymium extraction data reveals that the acid liberated from liquid cation exchange limits the extent of extraction. All neodymium feed concentrations exhibit a sharp drop in the percent extraction between 0.1 and 0.3 M feed acidity. Note that the equilibrium acid concentration resides between 0.1 and 0.2 M for feed solutions that contain an appreciable amount (> 1 g/L) of metal. As suggested in section 2.4, the extraction has a strong dependency on pH. The tests at 0.8 g/L neodymium support this claim- there is not enough metal present in the feed to

appreciably alter the acidity due to cation exchange with the ligand and hence high percentages of extraction are observed. The percent extraction does not drop significantly in this instance until the acid concentration exceeds 0.1 M.

The same approach was taken to collect extraction data for praseodymium. Experiments were conducted varying feed acidity and praseodymium concentrations. Table 5 reports the extraction results from single metal batch contacts with praseodymium.

**Table 5: Praseodymium Extraction Data. 1 M PC88A in Isopar-L, O/A = 1.**

Feed Pr (g/L)	Feed [H <sup>+</sup> ] (M)	Equilibrium [H <sup>+</sup> ] (M)	% Extraction	D <sub>Pr</sub>
13.1	0.03	0.13	29	0.418
13.1	0.05	0.14	28	0.391
13.1	0.1	0.18	14	0.161
13.1	0.3	0.30	1	0.011
13.1	0.5	0.50	0	-
6.7	0.03	0.12	50	1.003
6.7	0.05	0.13	46	0.854
6.7	0.1	0.16	26	0.359
6.7	0.3	0.30	5	0.048
6.7	0.5	0.50	0	-
0.9	0.01	0.05	99	114.332
0.9	0.05	0.08	90	8.544
0.9	0.1	0.12	65	1.821
0.9	0.3	0.30	1	0.010
0.9	0.5	0.50	0	-

Praseodymium extraction trends were very similar to the neodymium extraction results. Praseodymium has a lower atomic number and therefore is expected to have a slightly higher basicity than neodymium, which implies a lower affinity for extraction in comparison to neodymium. Like neodymium, the equilibrium acid concentration resides between 0.1 and 0.2 M with a significant drop in percent extraction for feed acid concentrations exceeding 0.3 M. Praseodymium extracts 5% less than neodymium on average for an equivalent feed acid concentration.

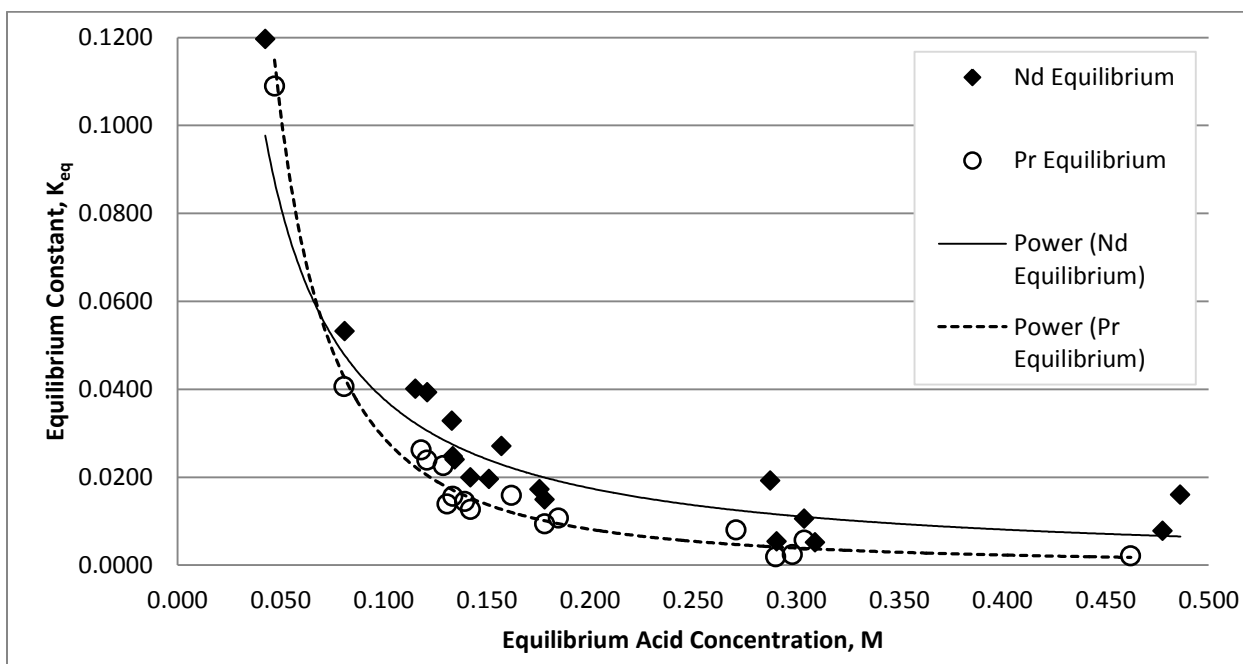
Single metal distribution data provide a strong foundation for predicting partitioning behavior, but further testing was performed to study and understand the effects of mixed metal extraction. Since it appears that acid dependency is the dominating factor for determining phase equilibria, the presence of co-extracting species will alter the distribution coefficients of other species present. Mixed metal extraction contacts were performed using a blend of praseodymium and neodymium.

The first extraction tests were performed using a 50/50 feed mixture of praseodymium and neodymium. Extraction data is shown in Table 6.

**Table 6: Mixed metal 7 g/L Pr and 7 g/L Nd feed extraction with 1 M PC88A in Isopar-L, O/A = 1.**

Feed [H <sup>+</sup> ] (M)	Equilibrium [H <sup>+</sup> ] (M)	% Nd Extraction	% Pr Extraction	$\beta$ Nd/Pr
0.02	0.13	39.7	29.4	1.581
0.05	0.14	33.8	24.5	1.574
0.1	0.18	19.6	13.3	1.586
0.3	0.30	4.3	2.3	1.860
0.5	0.49	1.7	0	-

The results of mixed metal extraction show that the percent extraction for each species does not change appreciably in comparison to the pure species extraction data. This is the result of the high ligand concentration in the extraction tests. Excess organic solvent allows both species to extract until the equilibrium is determined by the aqueous phase pH. The equilibrium constant was calculated for all of the extraction data presented in Tables 4-6 using Equation 4. Available free ligand concentration was determined by subtracting the stoichiometric amount of ligand complexed to both REE from the initial feed concentration of PC88A. Note that each data point represents a unique extraction test and the equilibrium constant was calculated for each varying feed condition. Extraction equilibria are shown in Figure 16.



**Figure 16: Extraction equilibrium constants as a function of equilibrium acidity.**

Both REE species exhibit a sharp decrease in the extraction equilibrium constant as the equilibrium pH increases. There are two important implications observed from the equilibrium constant data. First, praseodymium does indeed indicate a trend of lower equilibrium constants than neodymium for the same equilibrium acidity, but the separation factor between neodymium and praseodymium is not large enough to partition the two species using an extraction section alone (average  $\beta$  of 1.6). Second, the equilibrium constants highlight the importance of pH control during extraction. Higher amounts of metal extraction increase the equilibrium acid concentration, but Figure 16 shows that higher equilibrium acid concentrations adversely affect the equilibrium constant. Pre-neutralization of the organic ligand is necessary in order to control pH and maximize recovery of metal from the feed solution.

As previously mentioned in Section 1.2, praseodymium and neodymium are often processed together into a mixed oxide product commonly referred to as didymium. This metal ratio was chosen as the basis for mixed metal extraction experiments for a number of reasons. First, this ratio reflects the ratio produced during commercial didymium production due to the elemental abundances occurring in bastnasite ores.<sup>[13]</sup> Second, didymium could be used as the feedstock material for a separations facility that produces high purity neodymium. Third, an opportunity could potentially exist to modify an existing didymium production circuit to produce high purity neodymium in addition to didymium production. Didymium feeds were prepared by mixing a volumetric 3:1 ratio of 50 g/L neodymium solution with a 50 g/L praseodymium solution, respectively. Table 7 summarizes extraction data for high mixed metal concentrations.

**Table 7: 50 g/L Didymium feed extraction with 1 M PC88A in Isopar-L, O/A = 5.**

<b>Feed [H<sup>+</sup>] (M)</b>	<b>Equilibrium [H<sup>+</sup>] (M)</b>	<b>% Nd Extraction</b>	<b>% Pr Extraction</b>	<b><math>\beta</math> Nd/Pr</b>
0.01	0.23	24	19	1.325
0.05	0.24	20	15	1.374
0.1	0.25	17	13	1.294
0.3	0.34	6	6	1.005

The pH dependency limits the extraction once the acid concentration exceeds 0.2 M. The relative percent extracted is much lower in these experiments because the feed metal concentration is very high. The liberated acid will not allow any appreciable amount of additional extraction to take place, regardless of the number of stages utilized in the extraction circuit.

Solvent pre-neutralization (saponification), briefly mentioned in Section 2.4, provides a means for pH control in solvent extraction circuits and greatly improves the extraction of REE. Tables 6 and 7 confirm that the acid generated during extraction limits the overall extraction capability. This leads to issues with poor recovery, low raffinate purity, and overall lower circuit capacity. Saponification was tested by mixing a known volume of the organic phase with 50% sodium hydroxide on a vortex mixer until a uniform phase was formed, saponifying 16.7% of the extractant. Saponifying to 16.7% was chosen to control the pH for approximately 80% extraction of the total rare earths present in the feed solution. This allows effective pH control while minimizing erroneous observations due to washout of the saponified extractant in the presence of excess acid. The neutralized organic was contacted with the same didymium feed prepared for the contacts shown in Table 7. The results are summarized in Table 8.

**Table 8: 50 g/L Didymium feed extraction with 16.7% saponified 1 M PC88A in Isopar-L, O/A = 5.**

Feed [H <sup>+</sup> ] (M) <sup>(A)</sup>	% Nd Extraction	% Pr Extraction	$\beta$ Nd/Pr
0.01	91	87	1.533
0.05	82	75	1.505
0.1	74	65	1.507
0.3	62	52	1.492

A. Equilibrium pH is the same as the feed pH due to saponification.

The results from Table 8 show dramatically improved extraction behavior for both neodymium and praseodymium. The reduction in percent extraction is due to the overall equilibrium determined by the feed aqueous phase acidity. Saponification is necessary to control circuit pH in order to obtain high recovery from feed solutions. Note that saponification and extraction would only be necessary in a solvent extraction circuit designed to process an aqueous didymium feed stream. A pre-existing didymium production circuit would only require an additional scrub and strip section to simultaneously produce didymium and high purity neodymium, as shown in Figure 3. The separation factor,  $\beta_{Nd/Pr}$ , has an average value of 1.5 in this solvent system. The extraction data indicate that the separation factor is too low to exploit a direct partitioning separation scheme in the extraction section; further processing of the loaded organic phase is necessary to obtain high purity products.

#### 4.1.2 Scrub Data

The extraction data presented in Section 4.1.1 confirm that praseodymium and neodymium cannot be partitioned away from one another in the extraction section alone since both species co-extract with poor selectivity for neodymium. Scrubbing can be utilized to preferentially remove praseodymium from the organic phase by using a scrub solution containing neodymium. In commercial solvent extraction circuits, this is typically performed by refluxing a certain portion of the stripped product that contains high purity neodymium.<sup>[19]</sup>

Determining proper scrubbing conditions requires an understanding of the acid equilibrium and what effect it has on the distribution ratios for each species. Several experiments were performed to determine scrub conditions that preferentially remove praseodymium from the organic phase while retaining neodymium in the organic phase. High feed acid concentrations will scrub praseodymium, but consequently strip a portion of the neodymium as well. It is also undesirable to extract a large portion of neodymium from the scrub solution for several reasons. First, the driving force that scrubs praseodymium decreases as the neodymium concentration in the aqueous phase decreases. Second, the reflux ratio can be minimized if neodymium does not extract excessively. This corresponds to an increased production rate because additional product can be drawn off the circuit without refluxing it back to the scrub section. Furthermore, if the loaded organic phase is already near maximum loading, additional neodymium extraction may exceed solubility limits and form a third phase. Table 9 summarizes scrubbing contacts using neodymium feed solutions at various acidities and metal concentrations. The loaded organic in all experiments contained 3 g/L neodymium and 1 g/L praseodymium.

**Table 9: Scrubbing of Pr from a 3 g/L Nd, 1 g/L Pr loaded organic phase using pure Nd scrub solutions, O/A = 1.**

Scrub Feed Nd (g/L)	Scrub Feed [H+] (M)	Organic [Pr] <sub>final</sub> /[Pr] <sub>initial</sub>	Organic [Nd] <sub>final</sub> /[Nd] <sub>initial</sub>	Scrubbed Pr (%)
8.5	0.01	0.63	1.99	37
8.5	0.05	0.53	1.73	47
8.5	0.1	0.44	1.48	56
8.5	0.3	0.10	0.34	90
2.9	0.01	0.84	1.50	16
2.9	0.05	0.73	1.38	27
2.9	0.1	0.58	1.14	42
2.9	0.3	0.13	0.29	87

Scrubbing results indicate that praseodymium is selectively scrubbed from the organic phase in every experiment that was performed. The optimum scrubbing conditions are identified by determining the feed conditions that removes praseodymium without significantly altering the neodymium concentration in the organic phase. Regardless of the neodymium scrub feed metal concentration, the point at which the organic phase neodymium concentration does not change occurs somewhere between 0.1 and 0.3 M feed acid concentrations. This further illustrates the equilibrium dependency on acid concentration; metal-metal exchange will therefore occur without excessive extraction or stripping of neodymium if the scrub section is operated at the equilibrium acid concentration. Note that the equilibrium acid concentration in the aqueous phase may be higher or lower depending on the organic phase metal concentration (similar to the extraction results for different organic loadings observed in Tables 4-7). Based on these experiments, a scrub feed of 0.1 M acid with 10 g/L neodymium provides a promising starting point to evaluate the extent of neodymium purification that can be obtained in the scrub section.

#### 4.1.3 Strip Data

Strip data were obtained for neodymium to develop the final strip and recovery portion of the flowsheet. Stripping of the metals from the organic phase occurs at high acid concentrations. Increasing the acid concentration of the aqueous phase increases the amount of metal that is stripped from the organic phase. Similar to extraction data, an appreciable amount of metal must be present at an O/A ratio of 1 in order to observe the effect of the aqueous phase acid concentration on phase equilibria. Table 10 summarizes strip experiments performed on neodymium-loaded organic phases using various strip feed acid concentrations.

**Table 10: Neodymium strip data, O/A = 1.**

Strip [H <sup>+</sup> ] (M)	Loaded Organic Nd (g/L)	% Stripped
0.1	4.5	21
0.3	4.5	94
0.5	4.5	100
0.7	4.5	100
1	4.5	100
0.1	12.4	15
0.3	12.4	60
0.5	12.4	89
0.7	12.4	97
1	12.4	100

Strip equilibria behave as expected for changing acid and ligand-metal complex concentrations. Higher metal loading in the organic phase will strip a larger amount of metal for a given acid concentration in comparison to a lower organic loading. Similar to the extraction data, strip equilibrium depends primarily on acid concentration but is also affected by metal concentrations. Although stripping praseodymium is not required to develop this flowsheet, strip equilibrium data for praseodymium were obtained for comparison. Table 11 shows strip data for praseodymium.

**Table 11: Praseodymium strip data, O/A = 1.**

Strip [H <sup>+</sup> ] (M)	Loaded Organic Pr (g/L)	% Stripped
0.1	4	24
0.3	4	97
0.5	4	100
0.7	4	100
1	4	100

Strip equilibria for praseodymium are very similar to neodymium, an expected behavior considering the similarity in their distribution ratios for extraction. For all practical purposes the acid concentrations evaluated for neodymium will be sufficient to strip any praseodymium due to PC88A's higher affinity for neodymium.

Strip data is essential for optimizing acid consumption in a separations facility. If the metals are not fully stripped from the organic phase prior to recycling organic to the extraction section, several issues can adversely affect the separation. First, any recycled metal-ligand complexes are taking up the available ligand for extraction, effectively lowering the overall percent extraction and thus lower recovery from the feed. Excessive metal recycling can also lead to issues with third phase formation



as the ligand-metal concentration approaches the solubility limit. This condition, although less likely to occur, would require a complete system shutdown and cleanout to remove third phase organics from the system. Finally, if a solvent extraction circuit uses saponification as a means of pH control, excessive metal recycling will result in solids formation. Lanthanides form insoluble rare earth hydroxides in the presence of sodium hydroxide, and any organic recycled containing metals may react in the saponification stage. Solids formation will eventually lead to operational issues requiring system shutdown and cleanout.

Finally, the strip section requires precise optimization if the stripped product is going to be recycled as reflux into the scrub section to facilitate a separation. Excessive strip acid will adequately remove metal from the organic phase, but if the stripped product acid concentration is too high, refluxing it as a scrub solution will actually strip metals from the organic phase (this scenario was observed in Table 9 for 0.3 M acid neodymium scrub feeds). In worst-case scenarios, the acid concentration is high enough that it begins to slowly convert the scrub stages into strip stages. This leads to an irreversible condition that forces metal back into the aqueous phase and travels back towards the extraction circuit. For example, if the stripped product leaves the strip section at 1 M HCl and is refluxed as a scrub solution, the 1 M acid will quantitatively strip the neodymium and praseodymium from the organic phase (based on an  $O/A = 1$ ). The only available outlet from the flowsheet becomes the raffinate stream, and the process will either force both metals out the raffinate or cause a “pinch point” due to solubility limits and form solids or third phase. The strip section must be tuned such that the feed acid concentration and the number of stages provide a stripped product that is suitable for use as a scrub feed. Again, modeling using laboratory strip data is required to ensure flowsheet parameters are acceptable for facilitating the separation.

#### **4.2 Flowsheet Testing and Model Validation**

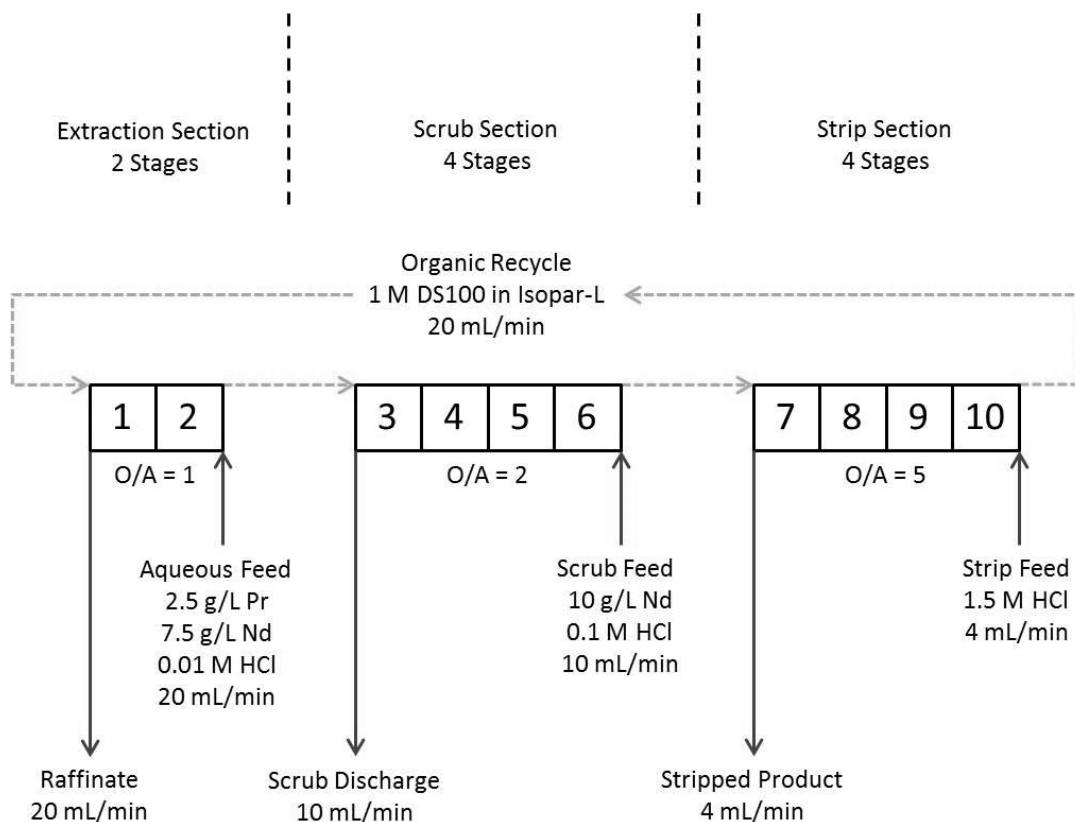
Due to the complexity of REE phase distribution behavior, a graded approach was used to develop and test solvent extraction flowsheets. Several aspects of a complete process flowsheet can convolute testing scenarios if their impacts on phase equilibrium are not fully understood and therefore simple flowsheets were initially designed and tested to evaluate specific flowsheet parameter performance.

#### 4.2.1 Simplified Flowsheet: Scrubbing Proof-of-Concept

Laboratory data from Section 4.1 indicated that the extraction equilibria for praseodymium and neodymium are too similar to exploit a direct partition separation in the extraction section. The actual separation occurs in the scrub section by exploiting the ligand's affinity for neodymium over praseodymium, albeit a small difference in selectivity. A preliminary flowsheet was designed and tested to determine if it is even feasible to produce pure neodymium by scrubbing the praseodymium from the loaded organic phase.

The purpose of the simplified scrubbing flowsheet was to load an organic phase with a mixture of 75% neodymium and 25% praseodymium and evaluate competitive REE loading using a neodymium scrub solution. It is expected and known that the conditions chosen do not provide a high recovery from the feed solution; the extraction conditions are simply chosen to produce the desired loaded organic phase. The neodymium scrub feed solution was prepared in the laboratory rather than refluxing stripped product- if the reflux acid concentration is too high, the scrub stages begin to strip REEs and can potentially form the "pinch point" discussed in Section 4.1.3. Excess acid was utilized for the strip feed to ensure that all of the REE were stripped from the organic phase prior to recycling back to the extraction section.

The scrub section was chosen to consist of 4 stages for an initial proof-of-concept test. Model predictions indicated that this is not enough stages to obtain >99% purity neodymium, but serves the purpose of validating the model and evaluating scrubbing performance. The simplified flowsheet is shown in Figure 17.



**Figure 17: Simplified scrubbing flowsheet to produce 97% purity Nd from a didymium feed.**

Fresh organic solvent contacts an aqueous feed containing 10 g/L didymium in a two stage extraction section. Scrubbing occurs in stages 3-6, where neodymium is preferentially loaded onto the organic phase and scrubs the praseodymium out into the aqueous phase. Stages 7-10 strip the organic of the neodymium product, and the organic is recycled to extraction for continuous reuse.

The model parameters were set to match the flowsheet test conditions, and constant-value distribution data were utilized from the experiments conducted in Section 4.1. Initial model conditions were set up for a system that is at hydrodynamic equilibrium but does not have any metal present in the system. Each stage therefore starts at an initial acid concentration with no metal present in preparation for the introduction of the metal feed solution. The model predictions for this flowsheet are shown in Table 12.

**Table 12: MATLAB model predictions for the 10-stage simplified flowsheet test.**

<b>Species</b>	<b>Raffinate Composition</b>	<b>Stripped Product Composition</b>
Pr g/L	0.99	0.94
Nd g/L	2.63	33.05
H <sup>+</sup> mol/L	0.14	0.80

This corresponds to a stripped product neodymium purity of 97.2%. As expected, this flowsheet does not yield a high recovery as observed by the raffinate metal concentrations. The proposed flowsheet would scrub a previously loaded organic phase from a didymium production circuit, so the recovery is not a factor under consideration here. If didymium oxide were dissolved as a feed solution for this separations flowsheet, the extraction section would require pre-neutralization of the solvent and an extended number of extraction stages to maximize product recovery.

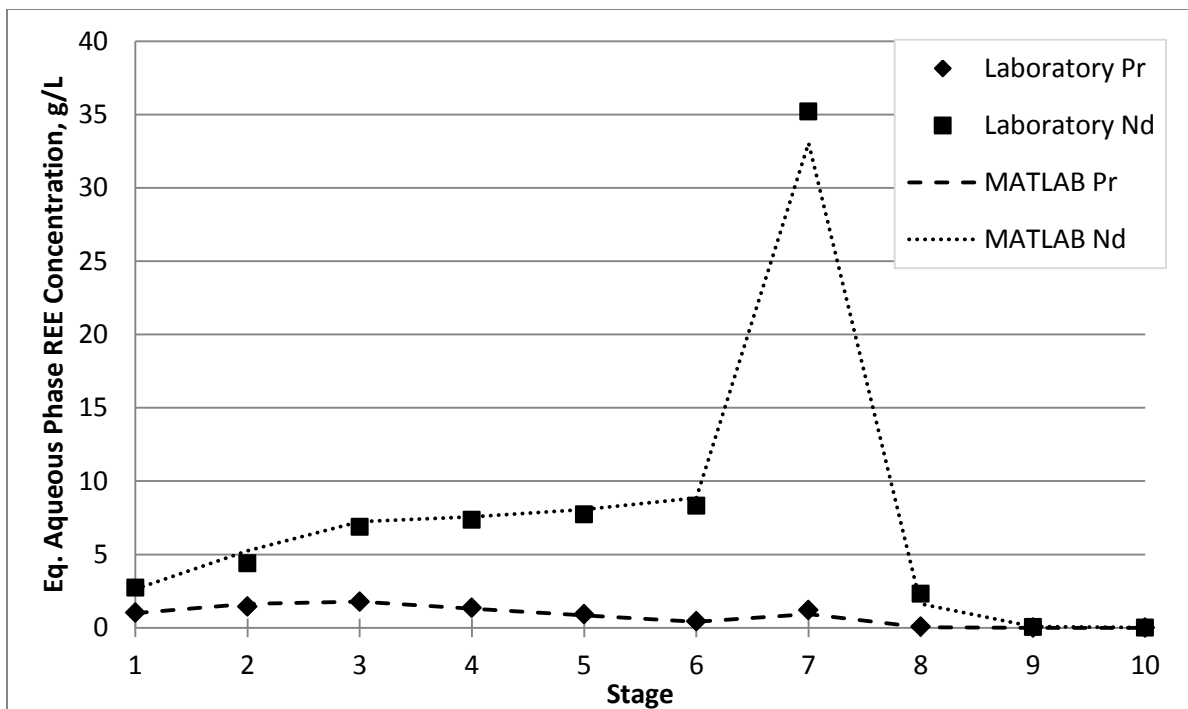
#### 4.2.2 Simplified Flowsheet Results

The flowsheet shown in Figure 17 was run continuously in the laboratory using 10 stages of MEAB mixer-settlers. The mixer-settlers were initially filled with barren acid solutions (i.e. no REEs present) and barren organic solutions and operated until hydrodynamic equilibrium was achieved. The aqueous feed was then introduced and the system operated continuously for 12 hours to achieve steady state conditions. These results are shown in Table 13.

**Table 13: Comparison of MATLAB model output and laboratory flowsheet results.**

<b>Species</b>	<b>MATLAB Predictions</b>		<b>Flowsheet Results</b>	
	<b>Raffinate</b>	<b>Stripped Product</b>	<b>Raffinate</b>	<b>Stripped Product</b>
Pr	27.3%	2.8%	27.6%	3.3%
Nd	72.7%	97.2%	72.4%	96.7%

The modeling results provide excellent agreement with the experimental data obtained for this flowsheet. Slight discrepancies can be accounted for due to error in experimental measurements such as flow rate measurements, phase ratios, or dilutions and measurements for analysis. As predicted, the four stage scrubbing circuit was not adequate to obtain neodymium purity greater than 99%. Samples were obtained for the aqueous and organic phase in each stage at the completion of the test to obtain a full concentration profile across the cascade for all species. The equilibrium aqueous phase metal concentration profiles are compared to modeling predictions in Figure 18.



**Figure 18: Equilibrium data and model predictions for aqueous phase metal profiles.**

The MATLAB model accurately predicted equilibrium aqueous phase concentrations across the cascade. The biggest error observed is the predicted neodymium concentration in the stripped product exiting stage 7. This is caused by error and fluctuations in the actual test flow rates, ultimately altering the O/A phase ratio in the mixer and affecting the final concentration. The actual flow rate was measured to be slightly less than 5 mL/min, which results in a slightly higher concentration due to the increase in the O/A ratio. The organic phase metal concentration profiles are shown in Figure 19.

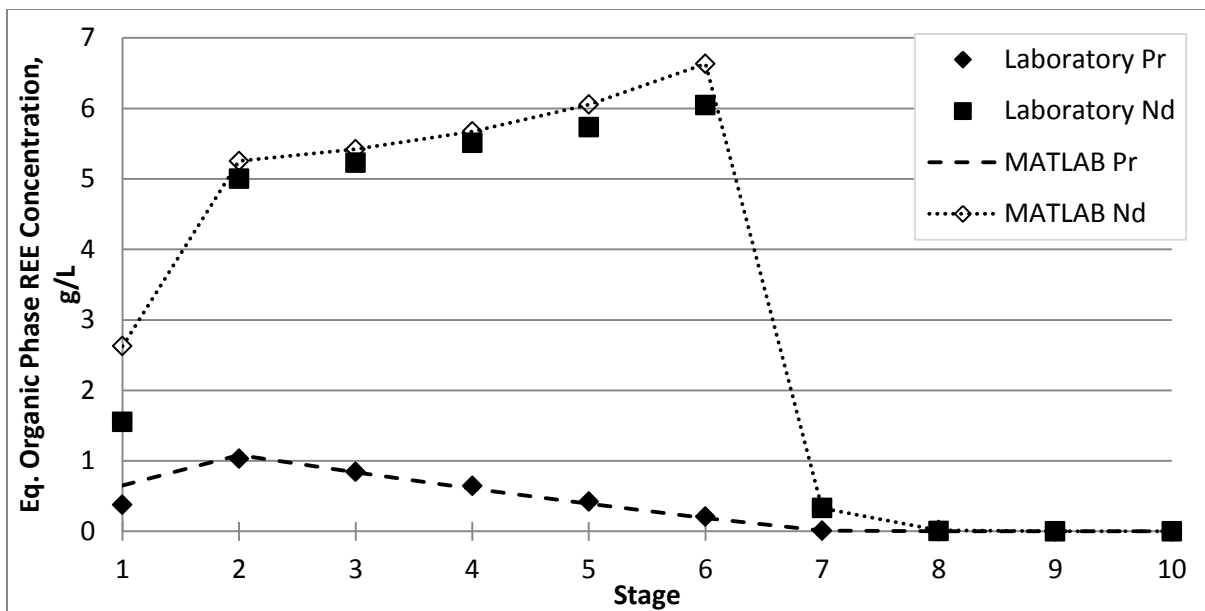


Figure 19: Equilibrium data and model predictions for organic phase metal profiles.

The loading conditions in the organic phase become rather complex from a modeling standpoint due to competing equilibrium reactions between praseodymium and neodymium. In order to facilitate understanding the competing equilibria, the equilibrium aqueous phase acidity is shown in Figure 20.

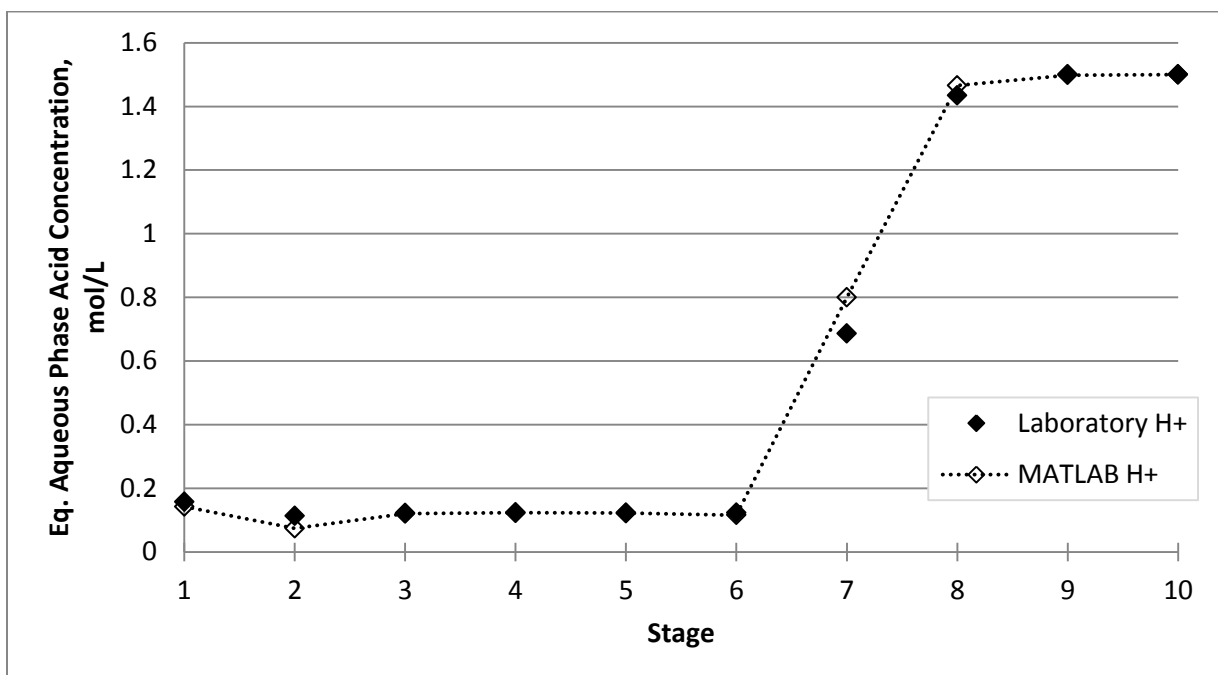
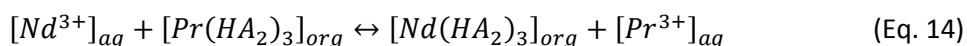


Figure 20: Equilibrium data and model predictions for aqueous acid concentration profile.

The aqueous phase acidity remains essentially constant throughout the entire scrub section of the flowsheet. Constant pH implies that the total number of moles of extracted REE does not change in the loaded organic phase. However, Figure 19 clearly shows that the praseodymium is being effectively scrubbed from the organic phase and the neodymium concentration in the organic phase is increasing across the scrub section. This suggests that the scrubbing mechanism is due to a metal-metal exchange between praseodymium and neodymium in the organic phase:<sup>[21]</sup>



The presence of excess neodymium in the scrub feed forces the equilibrium reaction to the right, scrubbing praseodymium from the loaded organic and replacing it with neodymium. In addition to constant pH, the distribution ratios for both species remained constant across the scrubbing section. This suggests that it may be reasonable to assume that both the distribution coefficient and aqueous phase pH can be assumed constant during scrubbing due to the metal-metal exchange mechanism. Table 14 shows the equilibrium parameters from the flowsheet test.

**Table 14: Equilibrium data for the simplified 10-stage flowsheet test.**

Stage	Equilibrium [H <sup>+</sup> ] (M)	D <sub>Pr</sub>	D <sub>Nd</sub>	β Nd/Pr	% Pr Scrubbed <sup>A</sup>
1	0.157	0.36	0.57	1.58	
2	0.113	0.71	1.14	1.60	
3	0.122	0.47	0.76	1.61	18%
4	0.122	0.47	0.75	1.58	23%
5	0.121	0.46	0.74	1.61	35%
6	0.123	0.47	0.73	1.56	50%
7	0.686	0.01	0.01	1.26	
8	1.434	0.03	0.002	0.07	
9	1.500	-	-	-	
10	1.500	-	-	-	

A. Pr scrubbing based on single stage material balances, not cumulative scrubbing.

The equilibrium data reveals several details about the performance of the flowsheet. First, the strip section equilibrium acidities show that there is a large amount of excess acid compared to what is required to strip the organic phase. The last two stages are not serving any purpose and could be eliminated from this flowsheet. The strip section will require additional optimization, especially if refluxing the stripped product is going to be the source of the neodymium scrub feed. The acidity of the stripped product leaving stage 7 is too high to consider for reflux in the scrub section- the equilibrium batch contact data from Section 4.1 suggests that the acidity must be approximately

0.10 M H<sup>+</sup> to avoid excessive stripping of the neodymium from the organic phase in the scrub section.

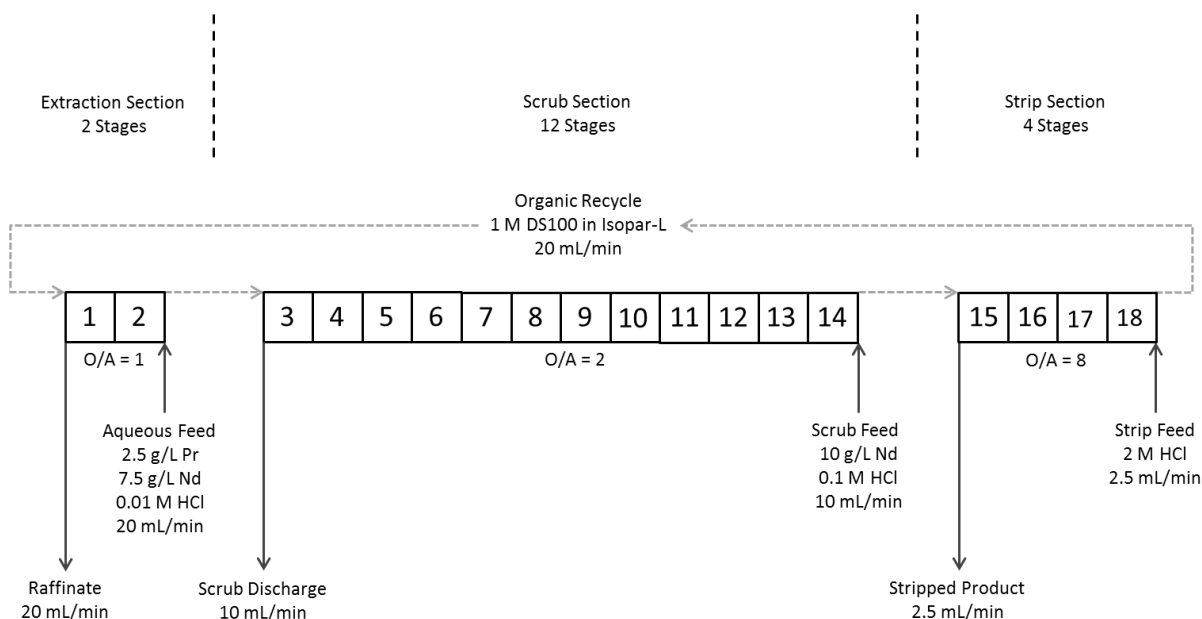
Additionally, there is a diminishing return for praseodymium scrubbing as the concentration gradient decreases across the scrub section. 50% of the praseodymium is scrubbed out in the first contact at stage 6, and the relative proportion of the remaining praseodymium scrubbed out decreases with each scrub stage. This behavior suggests that the number of stages will increase nonlinearly in order to obtain higher degrees of purity. The MATLAB model was utilized to predict product compositions for increased staging requirements in the scrub section. Table 15 highlights the effects of scrub staging.

**Table 15: Stripped product purity as a function of scrub staging.**

<b>N Scrub Stages</b>	<b>% Pr</b>	<b>% Nd</b>
4	2.8	97.20
8	1.64	98.36
12	0.96	99.04
14	0.72	99.28
20	0.47	99.53
25	0.31	99.69
30	0.22	99.79
40	0.11	99.89
50	0.06	99.94
100	0.00	100.00

As expected, the number of stages required to obtain greater than 99% purity neodymium increases dramatically. Total scrub stage numbers are often unavailable in literature for commercial processes due to proprietary concerns, but the table results appear reasonable based on the laboratory data presented in Section 4.1.2. As previously stated, the required neodymium purity for magnet applications varies from 99-99.9% and is as low as 96% in some instances. Based on this range of purity requirements, the target neodymium purity for the proposed flowsheet was chosen to be 99%. Based on the modeling results in Table 15, a second flowsheet was developed and tested to prove whether it is possible to obtain 99% purity neodymium simply by adding additional scrubbing stages. The expanded flowsheet is shown in Figure 21.





**Figure 21: Expanded flowsheet with 12 scrubbing stages to produce 99% purity neodymium.**

Note that this flowsheet still does not optimize recovery of neodymium from the aqueous feed, nor does it optimize the acid balance around the strip section. The strip section O/A ratio and feed acidity were adjusted in this test to concentrate the product and minimize highly acidic waste generation. Excess acid is still used for the purpose of completely stripping the organic phase and preventing potential complications during organic recycle.

#### 4.2.3 Expanded Flowsheet Results

The 18-stage expanded flowsheet was operated in the MEAB mixer-settlers for a period of 30 hours to obtain steady state. The results from MATLAB modeling and the flowsheet test are summarized in Table 16.

**Table 16: Expanded flowsheet test results.**

Species	MATLAB Predictions		Flowsheet Results	
	Raffinate	Stripped Product	Raffinate	Stripped Product
Pr	26.6%	0.96%	27.0%	0.3%
Nd	73.4%	99.04%	73.0%	99.7%

The flowsheet test successfully produced high purity neodymium suitable for magnet applications from a mixed feed of praseodymium and neodymium. Actual flowsheet performance was much better than predicted by the MATLAB model predictions shown in Table 16. The model

predicted 25 stages of scrub to obtain 99.7% purity neodymium- 13 stages over the actual flowsheet staging. The equilibrium parameters from the flowsheet test are shown in Table 17.

**Table 17: Equilibrium data for the expanded 18-stage flowsheet test.**

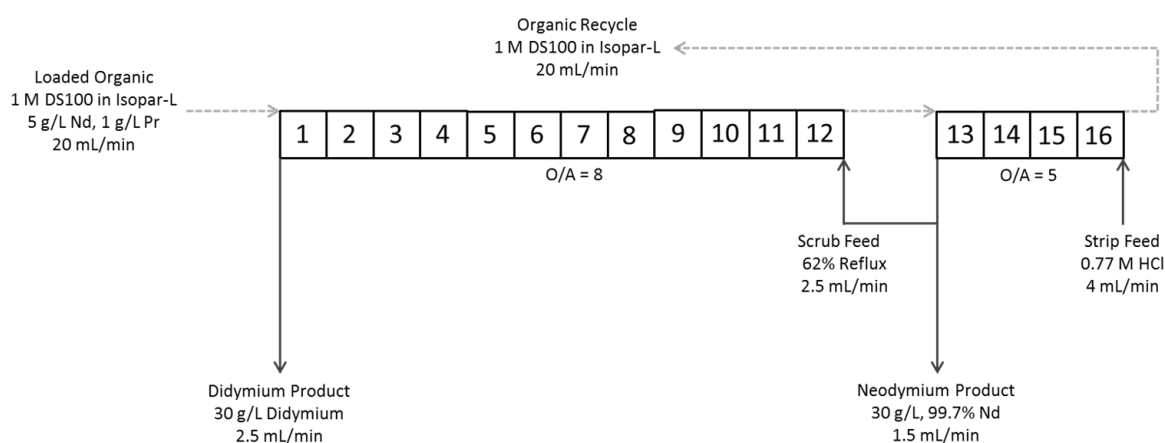
Stage	Equilibrium [H <sup>+</sup> ] (M)	D <sub>Pr</sub>	D <sub>Nd</sub>	β Nd/Pr	% Pr Scrubbed
1	0.143	0.36	0.56	1.58	
2	0.101	0.69	1.24	1.78	
3	0.116	0.38	0.67	1.77	14%
4	0.116	0.36	0.65	1.79	20%
5	0.116	0.36	0.59	1.62	18%
6	0.116	0.36	0.57	1.58	20%
7	0.118	0.35	0.60	1.73	25%
8	0.117	0.35	0.51	1.46	23%
9	0.118	0.38	0.60	1.56	20%
10	0.117	0.38	0.57	1.51	28%
11	0.118	0.36	0.56	1.55	32%
12	0.116	0.36	0.58	1.60	33%
13	0.121	0.36	0.57	1.59	41%
14	0.121	0.38	0.62	1.63	54%
15	0.886	0.00013	0.0008	0.65	
16	1.954	0.09	0.002	0.02	
17	1.987	-	-	-	
18	1.985	-	-	-	

The average separation factor between neodymium and praseodymium is 1.6 in this flowsheet. Again, we see that the scrub section operated at a near-constant acid concentration, allowing metal-metal exchange to effectively scrub praseodymium. Distribution ratios for neodymium were less than one in all of the scrub stages because the aqueous phase Nd concentration was higher than the organic phase concentration. The excess neodymium in the aqueous phase provides the driving force for metal-metal exchange and helps reduce the number of stages required to scrub praseodymium.

### 4.3 Complete Proposed Flowsheet

Flowsheet testing results indicate that high purity neodymium can be produced in a relatively small number of scrub stages using a neodymium scrub solution. An actual operating facility would reflux the stripped product as a source of high purity neodymium. The strip section requires careful monitoring and process control to ensure the acid concentration of the stripped product does not get too high. If the stripped product acidity exceeds the equilibrium acidity of the scrub section,

metal will be stripped from the organic phase and lower the overall high purity neodymium recovery in the circuit. Additionally, the number of strip stages required is altered by the strength of the strip feed acid. Excess acid was used in the simplified flowsheet testing to ensure complete stripping of the organic phase; complete stripping was obtained in two stages. Additional stages are required when using a lower acid concentration for the strip feed and ultimately obtaining the desired stripped product concentration. Laboratory testing revealed that 0.77 M strip feed adequately strips the organic phase in 4 stages at an  $O/A = 5$ . Furthermore, these strip conditions produce a stripped product suitable for reflux as a scrub feed. The final proposed flowsheet is shown in Figure 22.



**Figure 22: Final flowsheet for the simultaneous production of didymium and high purity neodymium.**

The refluxed stripped product is approximately 0.12 M HCl, which reflects the equilibrium acid conditions observed in the scrub section during flowsheet testing. This proposed circuit could potentially work more efficiently than the expanded flowsheet due to the increased neodymium concentration in the aqueous phase. Increasing the aqueous phase neodymium concentration during scrubbing increases the driving force for metal-metal exchange by shifting the equilibrium reaction shown in Equation 14. Note that any circuit utilizing reflux must first be brought to steady state using a simulated scrub feed similar to the feeds used in the 10 and 18 stage flowsheet tests. The simulant is required because the strip section acidity is too high during initial startup due to the initial absence of metals in the organic phase for stripping. The system must be brought to steady state using a scrub feed before reflux commences. Once reflux begins, the flowsheet could operate continuously in this fashion until shutdown is required due to scheduled maintenance activities.

The proposed circuit could easily be added to a pre-existing didymium production circuit simply by adding an additional 16 stages after the scrubbing section of a light REE separations flowsheet that separates praseodymium and neodymium from lanthanum and cerium (downstream fractionation of the light REE stream shown in Figure 11). The proposed circuit does not require any additional acid compared to a didymium production circuit- the same strip acid is required because the total organic metal concentration leaving the LaCe/PrNd scrub section is the same, regardless of whether it is stripped out as a didymium product or fractionated further into didymium and high purity neodymium. Complex processes have been published that are capable of producing high purity neodymium and an enriched praseodymium stream, but require significantly more stages and only produce an enriched (85%) praseodymium stream that still requires further downstream separation and polishing using ion exchange.<sup>[13]</sup> The proposed circuit does not produce a high purity praseodymium stream since praseodymium is currently not considered a critical material and market demand exists for didymium. The proposed flowsheet provides a low-risk opportunity to produce a high purity critical material with minimal disruption to current plant configurations and processes.

## CHAPTER 5: CONCLUSIONS

Separation of rare earth elements is a difficult and costly process that must be optimized in order to enable innovation in U.S. manufacturing and enhance U.S. national security. The separation of praseodymium and neodymium has been investigated in order to develop modeling capabilities for the design and evaluation of solvent extraction flowsheets.

Laboratory solvent extraction data were obtained for both praseodymium and neodymium to characterize the PC88A-HCl solvent system. Laboratory data included equilibrium partitioning behavior and equilibrium pH for extraction, scrubbing, and stripping. Analysis of the data revealed that the separation factor between neodymium and praseodymium is too low (average separation factor of 1.6) to perform a direct partition in the extraction section. Furthermore, saponification is necessary to maximize recovery and control pH during extraction. Scrubbing data suggested that PC88A's very slight selectivity for neodymium over praseodymium can be used to load the organic phase preferentially with neodymium and effectively scrub out praseodymium via a metal-metal exchange mechanism. Strip data was obtained to select appropriate conditions to recover the neodymium product and recycle the organic phase.

A mathematical model was developed using MATLAB/SIMULINK. The model uses stage-wise material balances to solve a system of ODEs for any given number of stages (extraction, scrubbing, and stripping) and to predict partitioning behavior for the specific REE species in the feed. Laboratory data were utilized to obtain an empirical fit for the distribution ratio as a function of the aqueous phase initial acidity. The MATLAB model combined with laboratory data was used to design several solvent extraction flowsheets to test and evaluate scrubbing concepts to produce high purity neodymium from a mixed feed of neodymium and praseodymium.

A 32-stage MEAB mixer-settler system was utilized to test the proposed flowsheets. Two flowsheets were designed and tested by loading an organic phase with praseodymium and neodymium from an aqueous didymium feed and subsequently scrubbing out the praseodymium using a neodymium scrub solution. A four stage scrub section produced 96.7% purity neodymium stripped product, while an 18 stage scrub section successfully produced a 99.7% purity neodymium stripped product. The MATLAB predictions were within 1% of the measured flowsheet results. The equilibrium data collected from the flowsheet tests were used to optimize model parameters for the countercurrent solvent extraction process.

The MATLAB model was utilized to design a complete solvent extraction circuit that simultaneously produces high purity neodymium and didymium. This process can easily be applied to pre-existing solvent extraction processes producing a didymium product that would traditionally be sent overseas to produce high purity neodymium. The proposed circuit utilizes 12 scrub stages, 4 strip stages, and requires 0.77 M HCl as a strip feed solution. 62% of the neodymium stripped product is recycled to the scrub section. The aqueous discharge from the scrub section contains the didymium product at a concentration of approximately 30 g/L, and the stripped product contains 99.7% purity neodymium at a concentration of approximately 30 g/L.

This proposed flowsheet produces greater than 99% purity neodymium in a relatively low number of stages and does not require any additional reagent than a pre-existing didymium production circuit (the acid required to strip a didymium product is still a molar equivalent to the acid requirements for the new proposed circuit). The proposed flowsheet provides a low-risk opportunity to produce a high purity critical material with minimal disruption to current plant configurations and processes.

The methods and processes developed in this research can be applied to all of the REE in the lanthanide series to develop a modeling capability for complex separation schemes. Additionally, the modeling principles can be applied to alternative solvent systems for REE separations. The methods presented for flowsheet development and optimization provide a framework to economically produce a domestic, viable supply of critical materials for clean energy technologies and national security in the United States.

## CHAPTER 6: RECOMMENDATIONS AND FUTURE WORK

As mentioned in Section 1.1, REE are typically found in ore types such as monazite and bastnasite, and the entire lanthanide series is usually present to some extent in a given ore body. The laboratory work and modeling efforts presented in this thesis only evaluate the separation of two adjacent rare earths, praseodymium and neodymium. This research is a stepping stone towards a much more complex separation and optimization process required in an actual industrial setting to process REE bearing ores. The primary areas recommended for additional evaluation and future work include laboratory solvent extraction data, fundamental determination of partitioning behavior, modeling improvements and integration, and alternative solvent systems.

First, laboratory solvent extraction data will be required to develop the appropriate correlations for all of the lanthanides present in a given feed solution. As previously stated, the separation principles used in this research can be applied to any adjacent pair of lanthanides by manipulating the pH conditions in the circuit. Determining the equilibrium acidities required for other lanthanide separations would greatly expand the scope and applicability of flowsheet development capabilities. Figure 11 showed that REE concentrates produced from ores are separated by fractionating a REE feed into several smaller sub-groups which are fractionated into individual REE. Laboratory data will be required to determine partitioning behavior for complex REE mixtures for a more holistic approach to plant design and optimization.

Second, it is desirable to validate laboratory solvent extraction data using a fundamental thermodynamic approach that predicts partitioning behavior for complex systems. The data collected throughout the scope of this research determined partitioning behavior by measuring the distribution coefficient and empirically correlating it to feed acid concentration. Pre-determined equilibrium curves have been the primary basis for solvent extraction modeling in industry, relying heavily on empirically determined distribution coefficients to predict countercurrent cascade behavior. A first-principles approach accounting for non-ideality, equilibria for metal-metal competitive loading, and temperature dependence would be highly desirable to reduce the dependence upon large databases of empirical equilibrium data to develop flowsheets.

Third, the solvent extraction model developed in MATLAB will be expanded to improve model reliability and user interfaces. First, the model uses laboratory-derived distribution ratios as a function of feed acidity to predict partitioning behavior. While this technique yielded reasonable results, a more robust method is desirable to predict partitioning behavior over a wide range of feed

conditions. Second, the model can evaluate the effect of transients using signal routing (ramps, step changes, etc.) but currently works as a continuous flow system. For example, if flow were disrupted to a bank of mixer-settlers, the model predicts that the REE concentrations would drop off until no REE is present in the mixer-settler. In reality, if flow were disrupted to a mixer-settler, the concentration of REE would remain constant for the solutions contained in that mixer-settler until flow is re-established. Fixing this discrepancy would provide more realistic responses to potential process upsets. Finally, the SIMULINK interface does provide an easy means to manipulate total stages, feeds, and process flows, but requires rebuilding or adjusting the SIMULINK flow diagram for each unique flowsheet simulation. Future work shall develop the capability that allows the user to specify parameters including REE concentrations in the feed, feed acid concentrations, number of extraction stages, number of scrub stages, number of strip stages, percent reflux, percent saponification, etc. Integrating this user interface would allow much more rapid evaluation, design, and optimization.

Finally, this research focused on the industrial standard extractant, PC88A. PC88A was chosen to investigate potential avenues for neodymium production for pre-existing REE separation facilities. Significant improvements to REE separation processes may be possible by investigating alternative solvent systems. Each solvent system requires its own specialized evaluation to determine operating characteristics in solvent extraction equipment and understand the process chemistry. Alternative ligands such as Cytec Solvay Group's Cyanex<sup>®</sup> 572 (a proprietary blend of phosphonic and phosphinic acids<sup>[18]</sup>) are being investigated at the INL to evaluate significant process improvements including increased separation factors, reduced chemical consumption, and reduced staging requirements. Future work with the CMI will continue to build an advanced flowsheet design capability to improve REE separation processes and ensure domestic supply chain continuity for critical materials.



## REFERENCES

1. Bauer, D. et al, "U.S. Department of Energy Critical Materials Strategy," U.S. Department of Energy Office of Policy and International Affairs, December 2011.
2. [www.emarketer.com](http://www.emarketer.com), "2 Billion Consumers to Get Smart (phones) by 2016," December 11, 2014.
3. World Trade Organization (WTO), "China- Measures Related to the Exportation of Rare Earths, Tungsten, and Molybdenum," Dispute Settlement DS431, August 2014.
4. Eggert, R.G., "Prospects for New Rare Earth Mines Outside of China," Colorado School of Mines, CMI Plenary Session Presentation, September 9, 2014.
5. <http://cmi.ameslab.gov>, "About CMI," Critical Materials Institute- An Energy Innovation Hub, December 2013.
6. Chunsheng, L., Sheng, W., Fuxiang, C., Songling, W., Yan, L., Bo, Z., and Chunhua, Y., "Clean Separation Technologies of Rare Earth Resources in China," *Journal of Rare Earths*, Volume 31, Number 4, pp. 331, April 2013.
7. Gschneider, K.A. Jr., "Rare Earths- The Fraternal Fifteen," United States Atomic Energy Commission, Division of Technical Information, December 1964.
8. Wilson, A. M. et al, "Solvent Extraction: The Coordination Chemistry Behind Extractive Metallurgy," *Chem. Soc. Rev.*, Volume 43, pp. 123-134, 2014.
9. Thakur, N. V., "Separation of Rare Earths by Solvent Extraction", *Mineral Processing and Extractive Metallurgy Review*, Volume 21, pp. 277-306, 2000.
10. Marcus, Y, Sengupta, A.K., "Ion Exchange and Solvent Extraction," Volume 17, pp. 37-83, Marcel Dekker, Inc., 2004.
11. Law, J.D., and Todd, T., "Liquid-Liquid Extraction Equipment," *Introduction to Nuclear Chemistry and Fuel Cycle Separations*, Idaho National Laboratory, 2008.
12. Cotton, F.A., and Wilkinson, G., "Advanced Inorganic Chemistry- A Comprehensive Text," 3<sup>rd</sup> Edition, John Wiley and Sons, 1972.
13. Gupta, C.K., and Krishnamurthy, N., "Extractive Metallurgy of Rare Earths", CRC Press, 2005.
14. Benedict, M., Pigford, T., and Levi, H., "Nuclear Chemical Engineering," 2<sup>nd</sup> Edition, New York: McGraw-Hill Book Company, 1981.
15. Chunhua, Y., Jiangtao, J., Chungsheng, L., Sheng, W., and Guangxian, X., "Rare Earth Separation in China," *Tsinghua Science and Technology*, Volume 11, Number 2, pp. 241-247, April 2006.

16. Lee, M.S., Lee, J.Y., Kim, J.S., and Lee, G.S., "Solvent Extraction of Neodymium Ions from Hydrochloric Acid Solution Using PC88A and Saponified PC88A," *Separation and Purification Technology*, Volume 46, pp. 72-78, 2005.
17. Liao, C. Wu, S., Cheng, F., Wang, S., Liu, Y., Zhang, B., and Yan, C., "Clean separation technologies of rare earth resources in China," *Journal of Rare Earths*, Vol. 31, No. 4, pp. 331-336, 2013.
18. Soderstrom, M.D., McCallum, T., Jakovljevic, B., and Quilodrán, A.J., "Solvent Extraction of Rare Earth Elements Using Cyanex<sup>®</sup> 572," 2014 Conference of Metallurgists Proceedings, Vancouver B.C., Canada: Canadian Institute of Mining, Metallurgy, and Petroleum, 2014.
19. Xie, F., Zhang, T.A., Dreisinger, D., and Doyle, F., "A Critical Review on Solvent Extraction of Rare Earths from Aqueous Solutions. *Minerals Engineering*, Vol. 56, pp. 10-28, 2014.
20. Bishop, M.D., Gray, L.A., Young, T.L., and Greene, M.G., "Technical Developments Leading to Modern Solvent Extraction Diluents," *Mining, Metallurgy, and Exploration, Inc., Mining Engineering*, March 1996.
21. Banda, R., Jeon, H.S., and Lee, M.S., "Separation of Nd from Mixed Chloride Solutions with Pr by Extraction with Saponified PC88A and Scrubbing," *Journal of Industrial and Engineering Chemistry*, Volume 21, pp. 436-442, January 2015.
22. Zhang, J., and Zhao, B., "Separation Hydrometallurgy of Rare Earth Elements," Springer International Publishing, Switzerland, 2016.
23. Webster, S., "Effects of O/A Ratios and Phase Continuity on Entrainment," <http://www.sxkinetics.com/entrainment.htm>, SX Kinetics, Inc, April 2014.
24. Ying, W., Huang, W., and Quan, C., "Mathematical Modelling and Simulation of Rare Earth Solvent Extraction for the System of (Gd-Tb)Cl<sub>3</sub>-HCl-HEHEHP-ShellSol D70," Beijing General Institute for Non Ferrous Metals and the Australian Nuclear Science and Technology Organization, September 1994.