



12-2019

Economic Optimizations of Phosphoric Acid Byproduct Rare Earth Element Recovery

Thomas Gaetjens

University of Tennessee, tgaetjen@vols.utk.edu

Follow this and additional works at: https://trace.tennessee.edu/utk_gradthes

Recommended Citation

Gaetjens, Thomas, "Economic Optimizations of Phosphoric Acid Byproduct Rare Earth Element Recovery." Master's Thesis, University of Tennessee, 2019.
https://trace.tennessee.edu/utk_gradthes/5522

This Thesis is brought to you for free and open access by the Graduate School at TRACE: Tennessee Research and Creative Exchange. It has been accepted for inclusion in Masters Theses by an authorized administrator of TRACE: Tennessee Research and Creative Exchange. For more information, please contact trace@utk.edu.

To the Graduate Council:

I am submitting herewith a thesis written by Thomas Gaetjens entitled "Economic Optimizations of Phosphoric Acid Byproduct Rare Earth Element Recovery." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Robert Counce, Major Professor

We have read this thesis and recommend its acceptance:

Jack Watson, Sankar Raghavan, Lawrence Heilbronn

Accepted for the Council:

Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

**Economic Optimizations of Phosphoric Acid Byproduct
Rare Earth Element Recovery**

A Thesis Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Thomas Kiefer Gaetjens
December 2019

ACKNOWLEDGEMENTS

This research is supported by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, and by a U.S. Department of Education Graduate Assistance in Areas of National Need Fellowship administered through the University of Tennessee Knoxville by Paul Frymier. Additional support was provided by the University of Tennessee Knoxville department of chemical and biomolecular engineering.

ABSTRACT

This research seeks to develop and optimize technology for the recovery of rare earth elements from waste streams originating from phosphoric acid production processes. While the technical viability of such recovery processes has previously been examined, implementation has hinged on the economic viability. The integration of these considerations – a technoeconomic analysis – results in optimized operating conditions and suggests directions for future process design.

TABLE OF CONTENTS

Introduction	1
Chapter I: Comparative Economic Analysis of Rare Earth Element Separation from Phosphoric Acid Waste Streams	2
Abstract	3
Introduction	3
Methods	4
Capital Costs: Leaching	4
Capital Costs: Solvent Extraction	6
Capital Costs: Precipitation	7
Capital Costs: Calcination	7
Operating Costs	8
Revenue and Profits	10
Cost Estimate Studies	10
Results and Discussion	11
Conclusions	13
Appendix	15
Chapter II: Economic Optimization of Rare Earth Element Leaching Kinetics from Phosphogypsum with Sulfuric Acid	20
Abstract	21
Introduction	21
Methods	24
Leaching Experiment and Analysis	24
Reactor Modeling	25
Results and Discussion	27
Conclusions	28
Appendix	30
Chapter III: Economic Optimization of Yttrium Extraction with DEHPA using Internal Recycle	35
Abstract	36
Introduction	36
Methods	37
Results and Discussion	40
Conclusions	41
Appendix	42
Conclusions and Recommendations	44
List of References	45
Vita	50

LIST OF TABLES

Table 1. Concentrations of REEs in each waste stream. [5].....	17
Table 2. Concentrations of other notable species in each waste stream. [6]	17
Table 3. Distribution coefficients for all major species at an O:A of 0.47:1. [11]	18
Table 4. Assumed raw material costs.	18
Table 5. Point estimate of process economics.	19
Table 6. Main Chemical Components and REEs in PG Sample.	33
Table 7. Summary of Kinetic Data Fit.....	34
Table 8. Summary of Optimized Costs.....	34
Table 9. Minimized Costs at each Recycle Fraction.....	43

LIST OF FIGURES

Figure 1. Mid-Level Process Flow Diagram.....	15
Figure 2. Phosphogypsum Cost Estimate Studies.	16
Figure 3. Sludge Cost Estimate Studies.....	16
Figure 4. Leaching Experiment Data Fit. Comparison of the fit of leaching data to three reaction orders.....	30
Figure 5. Diagram of Two Leaching Stages. Diagram displays two stages operating with countercurrent flow of aqueous and solid materials.	31
Figure 6. Plot of Data from Reactor Modeling. A three dimensional representation of cost data gathered at each residence time for each number of stages.	32
Figure 7. Single Stage Modeling Results. A single “cut” through the data surface in figure 6 where the number of stages is equal to one.	33
Figure 8. Diagram of the Extraction Process.	42
Figure 9. Overview of Two Constant Recycle Fraction Data Surfaces. A comparison of three dimensional cost data at the minimum and maximum values of the recycle fraction.	42
Figure 10. Cost Curves for Constant O:A = 0.1. Features the cost curves in a [DEHPA] range close to the minima.	43

INTRODUCTION

Rare earth elements (REEs) are important for the creation of a sustainable future. This statement, while broad, is difficult to assail. The current direction of green technology has long pointed innovation toward alternative energy sources, and these, whether they be wind, solar, hydroelectric or tidal, all rely on the use of REEs [1]. If the future is green, then the future likely incorporates REEs, and, to flip the syllogism, those REEs should likely also be green. Fortunately for that pursuit, domestic mining of phosphate rock produces, as a byproduct, thousands of metric tons of REEs each year [2]. If properly processed, the waste streams from domestic phosphate rock mining and phosphoric acid production facilities could provide a significant portion of the global demand for REEs [2].

**CHAPTER I: COMPARATIVE ECONOMIC ANALYSIS OF RARE
EARTH ELEMENT SEPARATION FROM PHOSPHORIC ACID
WASTE STREAMS**

A version of this chapter is being prepared for publication by Thomas Gaetjens, Robert Counce, and Jack Watson. Robert Counce and Jack Watson had an advisory role, suggesting research direction and text clarification.

Abstract

Waste streams from phosphoric acid production facilities contain a large amount of rare earth elements and represent as of yet underexplored sources of these critical materials. It was the purpose of this paper to investigate recovery of rare earth elements from phosphogypsum and sludge waste streams and report on the economic viability of such processes. A model was constructed to simulate a recovery process operating on each stream, resulting in a mixed rare earth oxide product. Output from the model indicated the possibility of a profit for the sludge stream process but not for the phosphogypsum stream process.

Introduction

There are a number of different waste streams originating from phosphoric acid processes, and the differing qualities and compositions of these streams lead to differing economic potentials. It was the goal of this paper to compare the viability of recovering REEs from two such streams and determine which of these options would be most economically attractive. This comparison was done on the basis of conceptual economic estimates. The streams considered here were the primary REE-containing waste streams of a phosphoric acid production facility: the phosphogypsum (PG) stream and the sludge stream. While it is possible to derive a rare earth product from other sources related to

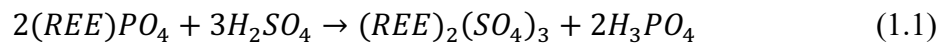
phosphoric acid production (including mine waste and process streams), the aforementioned streams were selected for study due to their high concentrations of REEs and their possibility for minimal disruption to plant operations.

Methods

The average phosphoric acid plant in the United States produces approximately 741,000 metric tons of P_2O_5 per year [3]. A phosphoric acid plant of this size produces approximately 3.63 million metric tons of PG per year and 142,000 metric tons of sludge [1][4]. These were the flow rates used in this study. A chemical engineering cost index value of 558.6 was assumed for capital cost calculation purposes.

Capital Costs: Leaching

The first step of the recovery process was the leaching and washing of the solids stream. In this step, the rare earth phosphates present in the feed reacted with sulfuric acid to form rare earth sulfates in accordance with equation 1.1 [7].



The leaching/washing section was assumed to contain six total stages featuring a countercurrent flow of aqueous to solid. Of these six stages, approximately three may be considered the leaching portion with the other three comprising the washing portion, though, in practice, their functionality would be similar. Each stage consisted of a continuously stirred tank with a residence time of two hours and a hydrocyclone filter with the exception of the final stage which featured a vacuum drum filter instead. A solid:liquid weight-based ratio of 1:3.5 was assumed to be maintained in each stage, and

the concentration of sulfuric acid in the lixiviant was assumed to be 2.5 wt%. A three stage design of this nature acting on a PG stream is known to be sufficient to leach REEs with an efficiency of 82.51% resulting in an effluent stream with a total REE concentration of 50.31 ppm [5]. Likewise, a three stage process acting on a sludge stream is known to be sufficient to leach with an efficiency of 85.40% resulting in an effluent stream with a REE concentration of 290.72 ppm [5]. It was assumed that the addition of the three washing stages would be sufficient to ensure that none of the rare earth sulfates would be removed with the solids stream.

Since the leaching process required tanks of large volume and took place at atmospheric temperature and pressure, each tank was costed as a cone roof storage tank made of concrete and lined with fluorocarbon plastic. The cost of each tank was regressed as a function of the volumetric flowrate through that stage as may be observed in equation 1.2 [8].

$$C_{Tank} = \left(\frac{C_I}{400}\right) (19.951\tau\dot{V} + 11612)(1.125 * 2.1) \quad (1.2)$$

Where C_{Tank} is the cost of the tank, C_I is the chemical engineering cost index value, τ is the residence time of the tank in hours, and \dot{V} is the volumetric flow rate of material into the tank in m^3 per hour. The initial multiplication by a ratio was used to adjust the cost estimate with respect to the inflation and changes to material costs that have occurred since the publication of the textbook from which the equation was derived. The cost function for each agitator was calculated in a similar manner [8].

$$C_{Agitator} = \left(\frac{C_I}{400}\right) (917.44\tau\dot{V} + 5830)(1.125 * 2) \quad (1.3)$$

The hydrocyclone filters consisted of clusters of subunits each of which was estimated to process a volume of 131,040 liters per hour and was costed at \$4,203 [9].

$$C_{hydrocyclone} = 4203 \left(\frac{1000\dot{V}}{36.4} \right) \quad (1.4)$$

The vacuum drum filter was assumed to feature a ratio of mass flow to area of one and an output solids composition of 61% [10][8].

$$C_{vacuum\ drum} = \left(\frac{C_I}{400} \right) (3252.7\dot{m} + 40521)(1.125 * 2.4) \quad (1.5)$$

Where \dot{m} is the mass flow rate in kilograms per second.

Capital Costs: Solvent Extraction

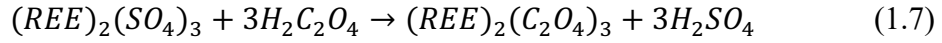
Following the leaching and washing of the solid, the effluent stream underwent solvent extraction. The solvent used was sulfuric acid, the extractant used was di-(2-ethylhexyl)phosphoric acid (HDEHP), and the stripping solution was four molar sulfuric acid. An organic to aqueous ratio (O:A) of 0.47:1 was assumed, and the process was assumed to take place using three stages of extraction and three stages of stripping [11]. The distribution coefficients used in this research were gathered for a PG sample, but, lacking suitable corresponding values from a sludge sample, they were assumed to hold for both streams. Negative distribution coefficient values indicate that stripping was quantitative.

Each stage of extraction and each stage of stripping consisted of a mixer-settler unit resulting in a total of six mixer-settler units. Where the cost of each unit was estimated according to the following equation [12].

$$C_{mixer-settler} = 5375 \left(\frac{\dot{V}}{5} \right) \quad (1.6)$$

Capital Costs: Precipitation

The next step of the process was precipitation, wherein the rare earth sulfates reacted with oxalic acid to produce insoluble rare earth oxalates in accordance with equation 1.7 [13].



The precipitator was modeled as a single vertical process vessel with an inside radius of 1.5 meters and a residence time of 20 minutes. Oxalic acid was fed at a 40% molar surplus. The reaction is known to be sufficient to successfully precipitate 99% of the REEs into the solid phase [13][8].

$$C_{precipitator} = \left(\frac{C_I}{400}\right) \left(1920 * \left(\frac{4\tau\dot{V}}{2.25\pi}\right) + 43.861\right) (1.125 * 3) \quad (1.8)$$

Before calcination, the rare earth oxalates were put through a separator, modeled as a vacuum drum filter, in order to reduce the amount of liquid in the stream, and to provide an opportunity for recovery and sale of excess sulfuric acid. The cost function used for this filter was the same as equation 1.5.

Capital Costs: Calcination

In the calciner, the rare earth oxalates were converted to rare earth oxides (REO) in accordance with equation 1.9 [14].



Where x ranges from two to ten. The calciner was modeled as an electrical resistance industrial oven with a residence time of one hour and a maximum internal temperature between 500 and 1000 degrees Celsius [8].

$$C_{calciner} = \left(\frac{C_I}{400}\right) (168.41\tau\dot{V} + 16628)(1.125 * 2) \quad (1.10)$$

Operating Costs

The operating labor for a process of this type was estimated as a function of the total production rate using the following equation and assuming an operator salary of \$45,000 per year [15].

$$C_{operating\ labor} = 45000(9.4053 \ln(24\dot{m}) - 55.621) \quad (1.11)$$

Where \dot{m} is the mass flow rate of the product stream in kilograms per hour. The supervisory and clerical labor was estimated as 15% of the operating labor.

Since the input to each process is a waste stream that would otherwise be disposed of, no cost was associated with its acquisition. It was assumed that excess sulfuric acid leaving with the aqueous waste after the precipitation step would be sold back to the plant to defray some of the cost of the sulfuric acid.

The electrical draw for each agitator was calculated according to equation 1.12 [8].

$$E_{agitator} = (\tau\dot{V})^{0.8} \quad (1.12)$$

Where τ is the residence time of the leaching tank in hours and \dot{V} is the volumetric flow rate into the leaching reactor in cubic meters per hour. The electrical consumption for each hydrocyclone was calculated according to equation 1.13 [12].

$$E_{hydrocyclone} = \frac{0.2}{3600} \dot{V} \quad (1.13)$$

The electrical consumption for each vacuum drum filter was calculated according to equation 1.14 [8].

$$E_{vacuum\ drum} = \dot{m}^{0.75} \quad (1.14)$$

Likewise, the electrical consumption for the calciner was calculated according equation 1.15 [8].

$$E_{calciner} = 0.005(\tau\dot{V})^{2/3}T_{max}^{5/3} \quad (1.15)$$

Where T_{max} is the maximum internal temperature of the calciner. The unit price for electricity was determined as a function of projected energy price and the current chemical engineering cost index assuming a fuel cost of 3.12 dollars per gigajoule [8].

$$C_{electricity} = 0.00013C_I + 0.011C_{fuel} \quad (1.16)$$

Maintenance and repair costs were estimated as 6% of the fixed capital costs, operating supplies were estimated as 15% of maintenance and repairs, and laboratory charges were estimated as an additional 15% of operating supplies [8]. The cost of disposing of the excess oxalic acid was assumed to be \$63.51 per metric ton. [16]. No cost was associated with disposal of the solid waste as it was assumed that these costs were already accounted for by the phosphoric acid production process. These costs along with the materials and labor costs comprised the direct costs.

Overhead, packaging, and storage costs were estimated as 60% of all labor plus maintenance and repairs, local taxes were estimated as 2% of the fixed capital, and insurance costs were estimated as 1% of the fixed capital [8]. These costs comprised the indirect costs. The indirect costs together with the direct costs comprised the total manufacturing expenses.

Administrative costs were estimated as 25% of the overhead, distribution costs were estimated as 2% of total expenses, and research and development costs were estimated as 1% of the total expenses [8]. Depreciation was listed as a cost and given a

value of 10% of the fixed capital cost to allow for the equipment to be replaced every 10 years.

Revenue and Profits

The product stream was a mixed REO with an approximate value of \$9.66 per kilogram [17]. A tax rate of 35% was applied to the profits from the model, and the return on investment (ROI) was calculated using the following formula:

$$ROI = 100 \left(\frac{P}{1.15C_T} \right) \quad (1.17)$$

Where P is the profit and C_T is the total of the capital costs of the process. This formula accounts for additional working capital necessary for the construction of the process.

Cost Estimate Studies

Focus was placed on the effect of the concentration of REEs in the leaching effluent stream and the effect of the extraction distribution coefficients on the profitability of the process. These design variables were adjusted and the ROI was recorded for each iteration.

In order to study the effect of the concentration of REEs in the leaching effluent stream, the ratio of water to gypsum in the leaching effluent stream was varied. It was assumed that the physical analog to this adjustment would be a change in the residence time of the aqueous stream with respect to the residence time of the waste solids stream via a change in the fraction of the aqueous stream that would be recycled into the leaching process. Leaching was assumed to take place at a constant rate [18], therefore when the effluent stream featured a residence time twice that of the solid waste stream, the concentration of REEs in the effluent stream was assumed to be twice what it was

when the residence times were equal. The effect of this ratio was studied from approximately 1:1 to 10:1 aqueous:solids.

The effect of the extraction distribution coefficients on the profitability of each process was studied by multiplying each distribution coefficient by a scalar factor. In order to maintain a constant adsorption fraction in the extraction, the ratio of organic phase to aqueous phase in the extractor was divided by the same scalar. The physical analog to this adjustment would be the use of a modified extraction system either through the use of a different extractant or through adjustment to the concentration of the extractant in solution. The effect of this increase on extraction distribution coefficient values was studied from a factor of 2 to a factor of 10.

Results and Discussion

Utilizing these cost functions, cost estimates were calculated for the two waste stream processes. A point estimate of the process economics using current literature values for leaching effluent concentration and distribution coefficients showed a marked unfavorability of the PG process and a sludge process estimate just above the breakeven point. Clearly, an economically favorable process, then, depends upon optimization of one or more design variables.

Neither increasing the residence time ratio of aqueous to solid in the leaching step, increasing the distribution coefficients, nor a combination of the two effects in the ranges studied were able to bring the PG stream to profitability. Increase in the residence time ratio corresponded to an increase in the ROI with the greatest rate of improvement

occurring between ratios of 1:1 and 4:1 aqueous:solid. The rate of improvement appeared to decrease as the ratio increased. Likewise, increase in the distribution coefficient factor resulted in an increase in the ROI with the greatest rate of improvement occurring between factors of one and two. Interestingly, almost no difference was observed between ROIs associated with factors above five. The benefits of higher distribution coefficients increased with an increase in the residence time ratio until a residence time ratio of approximately 6:1, at which point further improvements were minimal.

For the sludge stream, increase in the residence time ratio showed the same general trend as in the PG. The increase in ROI showed the greatest rate of improvement occurred between ratios of 1:1 and 3:1 aqueous:solid. A more drastic decrease in the efficacy of increasing the residence time ratio was observed in the sludge stream ROI than in the PG, but the general trend of ROI with respect to the distribution coefficient factor was similar to that of the PG. Increase in the distribution coefficient factor corresponded to an increase in the ROI, with the rate of improvement decreasing with an increase in the factor. When also increasing the residence time ratio, increase in the distribution coefficient factor was most effective around a residence time ratio of 5:1.

It should be noted that both the PG stream and the sludge stream contained small concentrations of uranium and thorium. In the PG, leaching did not cause a considerable amount of these radioactive elements to enter the effluent stream, but the sludge leaching resulted in concentrations of 1.8 ppm and 9.1 ppm of thorium and uranium respectively [6]. While the uranium did not precipitate with the REEs and therefore left the process with the aqueous waste stream [13], the thorium was present in the product. The amount

of thorium produced on a yearly basis was 216 kg using the current conditions and assumptions, and the amount of uranium in the waste was 1103 kg. Both these values significantly exceed the yearly cap of 7 kg imposed on any single process by the Nuclear Regulatory Committee [19]. This research, then, points to the necessity of a mitigatory solution for the thorium present in the sludge stream. If the waste streams of an REE recovery process can be integrated with those of the phosphoric acid plant, some of these legal issues may be resolved, but such a determination is dependent on further legal research.

Conclusions

Primarily, this research seemed to indicate that, using current technology, REE recovery from the PG waste stream was not economically viable under the process and conditions studied. Even assuming a significant amount of concentration occurred in the leaching step, and a new extraction process was developed with distribution coefficients an order of magnitude better than current values, the process was not profitable to maintain. This lack of profitability was primarily due to the low concentrations of REE present in the PG. It might be possible to attain a profitable process for the PG if residence time ratios above 10 are possible to achieve. In general, future interest in development of this process would require the demonstration of significant improvement over current technology.

The outlook for recovery efforts from the sludge stream, on the other hand, appeared to be more positive. An ROI of over 40% was attainable solely through adjustment of the residence time ratio in the leaching step. It should be borne in mind that

an extraction process of comparable distribution coefficients to the ones used in this study has yet to be demonstrated for the sludge stream, and that the concentration of contaminating metals such as iron and aluminum might inhibit the performance of extraction from such streams. However, given the relatively small volume of research dedicated to this stream, it is not unreasonable to assume that such an extraction process might exist. A significant reservation against the implementation of the sludge process is the presence of thorium in the product stream. Future interest in the development of this process would require reduction in thorium levels through some combination of more selective REE extraction, additional separation processes, differing source material, or reduced process size.

Appendix

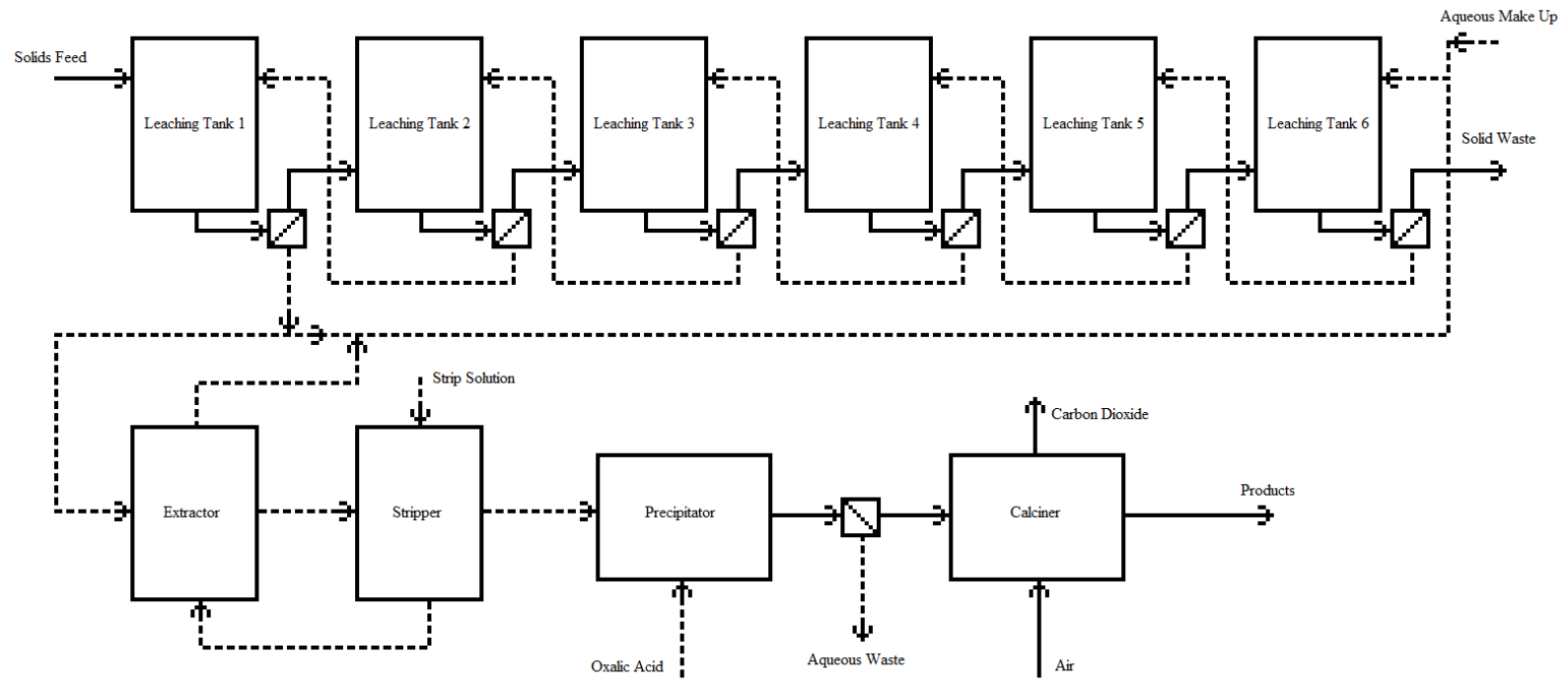


Figure 1. Mid-Level Process Flow Diagram.

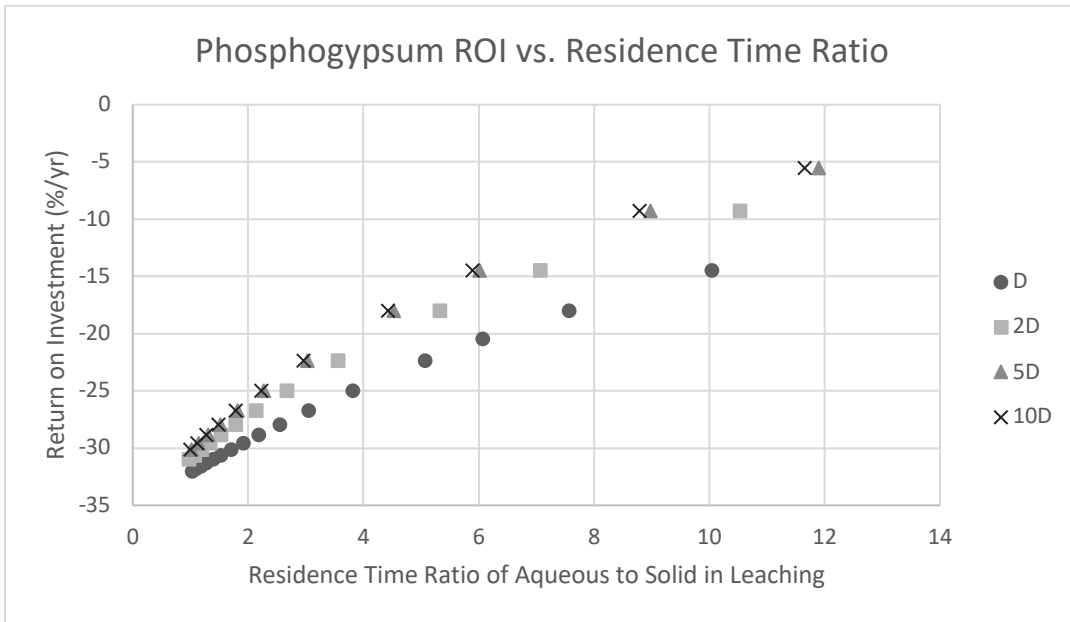


Figure 2. Phosphogypsum Cost Estimate Studies.

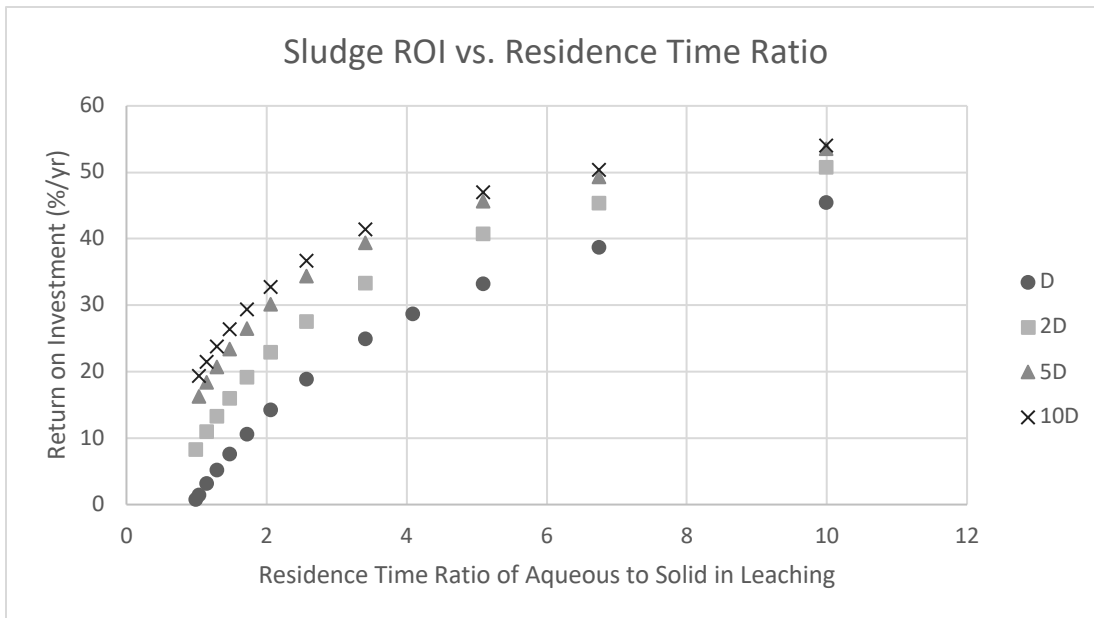


Figure 3. Sludge Cost Estimate Studies.

Table 1. Concentrations of REEs in each waste stream. [5]

	Concentration (ppm)	
	Phosphogypsum	Sludge
Pr	5.01	14.83
Eu	1.40	7.93
Tb	0.14	7.15
Dy	6.41	37.94
Ho	0.91	4.41
Er	4.35	15.03
Tm	2.26	0.85
Yb	2.02	5.67
Lu	0.00	1.63
Sc	0.34	11.82
Gd	6.87	55.95
Sm	0.00	31.58
Ce	63.84	318.96
Y	43.36	246.98
La	36.38	215.83
Nd	45.13	214.93
Total	218.42	1191.49

Table 2. Concentrations of other notable species in each waste stream. [6]

	Concentration (mass fraction)	
	Phosphogypsum	Sludge
Ca(SO₄)₂ H₂O	0.3400	0.5774
P₂O₅	0.0133	0.0896
Insol	0.4782	0.0000
CaO	0.1587	0.2160
Al₂O₃	0.0017	0.0402
Fe₂O₃	0.0015	0.0539
MgO	0.0002	0.0229

Table 3. Distribution coefficients for all major species at an O:A of 0.47:1. [11]

	Distribution Coefficient	
	Extraction	Stripping
Pr	1.37	0.33
Eu	7.99	-0.29
Tb	27.90	-0.38
Dy	91.10	-0.41
Ho	111.00	-0.33
Er	110.00	-0.11
Tm	263.00	0.42
Yb	322.00	1.53
Lu	651.00	3.02
Sc	0.60	10.20
Gd	8.20	-0.36
Sm	4.45	-0.22
Th	358.00	142.00
U	222.00	17.20
Ce	1.18	0.47
Y	221.00	-0.15
La	0.74	1.28
Nd	1.43	0.20
P₂O₅	0.09	0.03
CaO	0.00	-0.34
Fe₂O₃	6.66	0.03
Al₂O₃	0.13	0.01
MgO	0.00	0.00

Table 4. Assumed raw material costs.

	Price (\$/kg)
H₂SO₄	0.05
H₂C₂O₄	0.7
HDEHP	4

Table 5. Point estimate of process economics.

	Phosphogypsum	Sludge
[REE] in Leaching Effluent (ppm)	50.31	290.72
Fixed Capital Cost (\$)	61,518,775.63	3,843,056.13
Total Capital Investment (\$)	70,746,591.98	4,419,514.55
Annual Operating Costs (\$/yr)	27,772,521.16	1,733,228.56
Revenue (\$/yr)	5,128,321.34	1,787,519.06
Profit (\$/yr)	-22,644,199.82	35,288.83
Return on Investment (%)	-32.01	0.80

**CHAPTER II: ECONOMIC OPTIMIZATION OF RARE EARTH
ELEMENT LEACHING KINETICS FROM PHOSPHOGYPSUM
WITH SULFURIC ACID**

A version of this chapter is being prepared for publication by Thomas Gaetjens, Haijun Liang, Patrick Zhang, Ryan Moser, Haley Thomasson, Haley Dylewski, Robert Counce, and Jack Watson. Haijun Liang, Patrick Zhang, and Ryan Moser contributed to the writing of the leaching experiment and analysis section. Haley Thomasson and Haley Dylewski contributed to the writing of the introduction section. Robert Counce, and Jack Watson had an advisory role, suggesting research direction and text clarification.

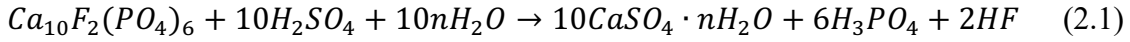
Abstract

Frequently optimizations of chemical processes are presented in terms of the maximization of fractional conversion, but the primary concern when implementing a process is much more likely to be the economic viability. These are distinct optima that tend to occur at very different points. It was the purpose of this paper to integrate leaching experimental data with cost analysis to arrive upon economically optimized leaching conditions for the recovery of rare earth elements from phosphogypsum, a water phosphate byproduct. The variables under consideration were the number of leaching reactors and the residence time of each reactor. The modeling results indicated that the optimum residence time was 270 minutes and that the optimum number of stages was one.

Introduction

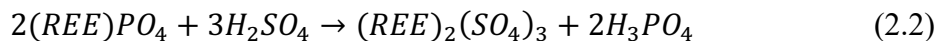
A majority of the world's phosphoric acid is produced via the "wet acid" process in which phosphate rock reacts with sulfuric acid to form phosphoric acid and calcium

sulfate. The main chemical reaction in the “wet acid” process proceeds according to the following equation [26]:



Depending on the value of n , the process may be defined as a di-hydrate ($n=2$) process, a hemi-hydrate ($n=1/2$) process, or an anhydrate process. The term $CaSO_4 \cdot nH_2O$ in the equation is commonly referred to as phosphogypsum (PG) in the industry [30]. The di-hydrate process is the most widely used process, and it is the predominant process used in the United States. Approximately 4.9 tons of PG is generated per ton of P_2O_5 produced using the di-hydrate process. Florida phosphate rock contains up to 900 ppm of REEs, and in the phosphoric acid manufacturing process, approximately 70% of the REEs eventually reports to PG [29].

Recovery of the REEs from PG hinges on a leaching reaction of the PG with an acid. While this may be performed with a number of different acids, sulfuric acid is most available on site and most easily integrated with existing infrastructure of phosphoric acid plants. Therefore, focus was placed on a sulfuric acid process in this analysis. The leaching proceeds in accordance with the following reaction [7].



Several other studies have investigated optimizing leaching PG for the recovery of REEs. In general, these studies have been concerned with the concentration of leach acid, the temperature, and the solid to liquid ratio in the reactor.

A study of a sulfuric acid system operating at a temperature of 353 K, a liquid to solid ratio of 8:1, and a residence time of 20 minutes found that at an optimum sulfuric

acid concentration of 1.5M, a maximum conversion of 33 percent was attainable [27]. Another study reported that for 2-10 percent sulfuric acid, a maximum of 56.6 percent conversion could be achieved at a liquid to solid ratio of 4:1 and a residence time of 3 hours [24].

The relatively low conversion of REEs at low sulfuric acid concentrations is thought to be due to co-crystallization with the PG by-product formed by the reaction of CaO in the feed with sulfuric acid [24]. However, these studies featuring low leaching efficiencies were all of batch systems. A study of multistage countercurrent leaching found that an efficiency of 82.51 percent was attainable using 3 stages, a sulfuric acid concentration of 2.5 percent, a liquid to solid ratio of 3.5:1, and a temperature of 298 K [22].

Conversion may be further increased by increasing the liquid to solid ratio. However, increasing this ratio at a constant solids rate decreases the concentration of both REEs and P₂O₅ in the aqueous phase, which results in an increase in the size and cost of downstream processes [23][28]. A liquid to solid ratio between 3:1 and 4:1 has been reported as an optimized value [23].

The solubility of rare earth sulfates decreases with increasing temperature [25]. High leaching temperatures have been shown to decrease efficiency for sulfuric acid systems due to increased dissolution of PG at these temperatures [27]. At temperatures between 303 and 333 K, conversion is not significantly affected by temperature [22], so it may be assumed that ambient temperature may be used.

Methods

Leaching Experiment and Analysis

Approximately 100 kilograms of representative PG were provided by the Mosaic Company. The chemical components in this PG sample are listed in Table 1. The leaching test was conducted in a 2.5L double-wall glass reactor connected with a water bath for temperature control. 300 grams of PG were used to conduct the test. A sulfuric acid concentration of 2.5 weight percent and a liquid to solid ratio of 3.5:1 were used. The leaching solution was sampled at 15 minute intervals for chemical analysis. At conclusion of leaching, the pulp was filtered and the residue was rinsed three times. Concentrations of various elements in both solution samples and the residue were analyzed using either ICP-OES or ICP-MS. The test was conducted in Florida at the Florida Industrial and Phosphate Research Institute.

The conversion of REEs in the reaction was calculated at each time interval. Conversion was defined as the ratio of the mass of REEs in solution to the initial mass of REEs in the solids. Plots were produced with the expectation that a zero, first, and second order reactions would yield linear data when concentration, the natural logarithm of concentration, and the inverse of concentration respectively were plotted vs time [20]. Furthermore, the slopes of these lines represent the kinetics constants for reactions of these orders. These plots may be found in figure 4. Note that the y axes are presented in terms of conversion instead of concentration and that the sign of the first order slope has been corrected to maintain visual consistency with the other graphs.

While all three analyses result in data that is approximately linear, the coefficient of determination (R^2) indicates the reaction most closely follows a first order model.

These values are summarized in table 2.

Assuming, therefore, a first order model, the conversion of REEs may be modeled as a function of the residence time of each leaching reactor and the total number of leaching reactors according to the following equation [20].

$$X = 1 - \frac{1}{(1+k\tau)^m} \quad (2.3)$$

Where k is the reaction kinetics constant, τ is the residence time of each reactor, and m is the total number of reactors. Other researchers have also suggested first order kinetics albeit with slightly different data fitting [27].

Reactor Modeling

Each stage of leaching was assumed to consist of a continuously stirred tank reactor and a solid liquid separation as shown in figure 5. Because the reaction didn't require elevated temperature or pressure, the leaching vessels were modeled as cone roof tanks. Due to the acidity of the contents, fluorocarbon plastic was selected as the material of production. The cost of each tank was regressed as a function of the residence time [8].

$$C_{Tank} = \left(\frac{C_1}{400}\right) (20\tau\dot{V} + 12000)(1.1 * 2.1) \quad (2.4)$$

Where C_{Tank} is the capital cost of the reactor, C_1 is the chemical engineering cost index value, τ is the residence time of the tank in hours, and \dot{V} is the total volumetric flow rate of material into the tank in m^3 per hour. A cost index value of 558.6 was used. Each

reactor was assumed to be fitted with an agitator. The capital cost for each of these was modeled in a similar manner [8].

$$C_{Agitator} = \left(\frac{C_I}{400}\right) (920\tau\dot{V} + 5800)(1.1 * 2) \quad (2.5)$$

The solid/liquid separation unit operation was modeled as a cluster of hydrocyclone subunits. Each subunit was estimated to process a volume of 131,000 liters per hour and was costed at \$4,203 [9].

$$C_{hydrocyclone} = 4203 \left(\frac{1000\dot{V}}{36.4}\right) \quad (2.6)$$

The operating costs for the process were divided into three categories: depreciation, materials, and overhead. Depreciation costs were calculated to allow for the total replacement of the capital expenditures in a ten year period in even increments of ten percent per year. Materials costs consisted of electricity costs and sulfuric acid costs. The electrical consumption of each reactor's agitator was modeled according to equation 2.7 [8].

$$E_{agitator} = (\tau\dot{V})^{0.8} \quad (2.7)$$

The electrical consumption of each hydrocyclone cluster was modeled according to equation 2.8 [12].

$$E_{hydrocyclone} = \frac{0.2}{3600} \dot{V} \quad (2.8)$$

The price of electricity was assumed to be 0.11 dollars per kilowatt-hour.

The price of sulfuric acid was assumed to be 0.13 dollars per kilogram. The concentration of sulfuric acid was set at 2.5 weight percent. The liquid to solid ratio in the reactors was set at 3.5:1.

Individual portions of the overhead of the process were determined using the capital costs. Each piece of equipment was assumed to require 0.2 operators at a yearly salary of \$45,000. Maintenance, repairs, supplies, and laboratory costs were assumed to be a total of 7 percent of capital costs, while local taxes and insurance were assumed to be a total of 3 percent of capital costs. Payroll, packaging, and storage were calculated as 60 percent of the labor costs plus the maintenance costs. Finally, distribution, sales, and research and development were assumed to cost 3 percent of the total expenditures. All of these costs were calculated as recurring, yearly expenditures [8].

Results and Discussion

The aim of the optimization was to minimize the costs per kilogram of leached REEs. The residence time per reactor was varied between 30 and 390 minutes in increments of 30 minutes, and the number of countercurrent leaching stages was varied between 1 and 10 stages. At each set of conditions, the cost per kilogram of REEs was recorded. The total volumetric flow rate of aqueous and solid material through the system was set at 251 m³ per hour [1].

The surface created by the bivariate study may be observed in figure 6. No local minima occurred. The global minimum occurred at 1 stage and a residence time of 270 minutes. The corresponding fractional conversion was 0.327 and the operating costs associated with these conditions was 4.80 dollars per kilogram per year.

At a given number of stages, costs per kilogram of REE decrease with increasing residence time until they reach an inflection point and begin to rise again. These minima

are the result of the interplay between the competing effects of the increase in costs associated with larger equipment and the decrease in costs per unit associated with leaching a higher quantity of REEs. Table 3 provides a summary of the minimum cost at each number of stages.

As may be observed from the table, the conversion of the minimum cost at one stage does not approach the maximum possible conversion of 56.6 percent found in the literature. The same is true for three stages. Thus the assumption that the concentration of REEs in the aqueous phase has minimal effect on the kinetics should not have interfered with the results of the study.

In order to more closely observe the trend in data near the global minimum, figure 7 features just the data from a single leaching stage. The minimum appears to be relatively broad, varying only 5 cents per kilogram between residence times of 180 and 360 minutes.

It is possible that the most cost-effective design for a leaching process might not be suited for a specific application if another constraint is imposed. For example, the buyer of the extracted REEs might require a purity higher than what may be obtained using a single reactor. This should be taken into account before the implementation of such a process, and the most cost-effective design producing an acceptable purity should be selected.

Conclusions

Several interesting conclusions may be drawn from the results of this modeling study that have important applications in the design of future REE recovery processes.

First, leaching PG in multiple stages does not seem to increase the cost efficacy of the process. While multiple stages may be necessary if the reactor sizing is constrained by other factors, optimal leaching may be attained with only a single stage. Second, maximum economic efficiency does not appear to occur at maximum conversion. While it would be possible to leach additional REEs from the PG, the incremental value gained by recovering the remaining REEs is not sufficient to offset the incremental costs.

Appendix

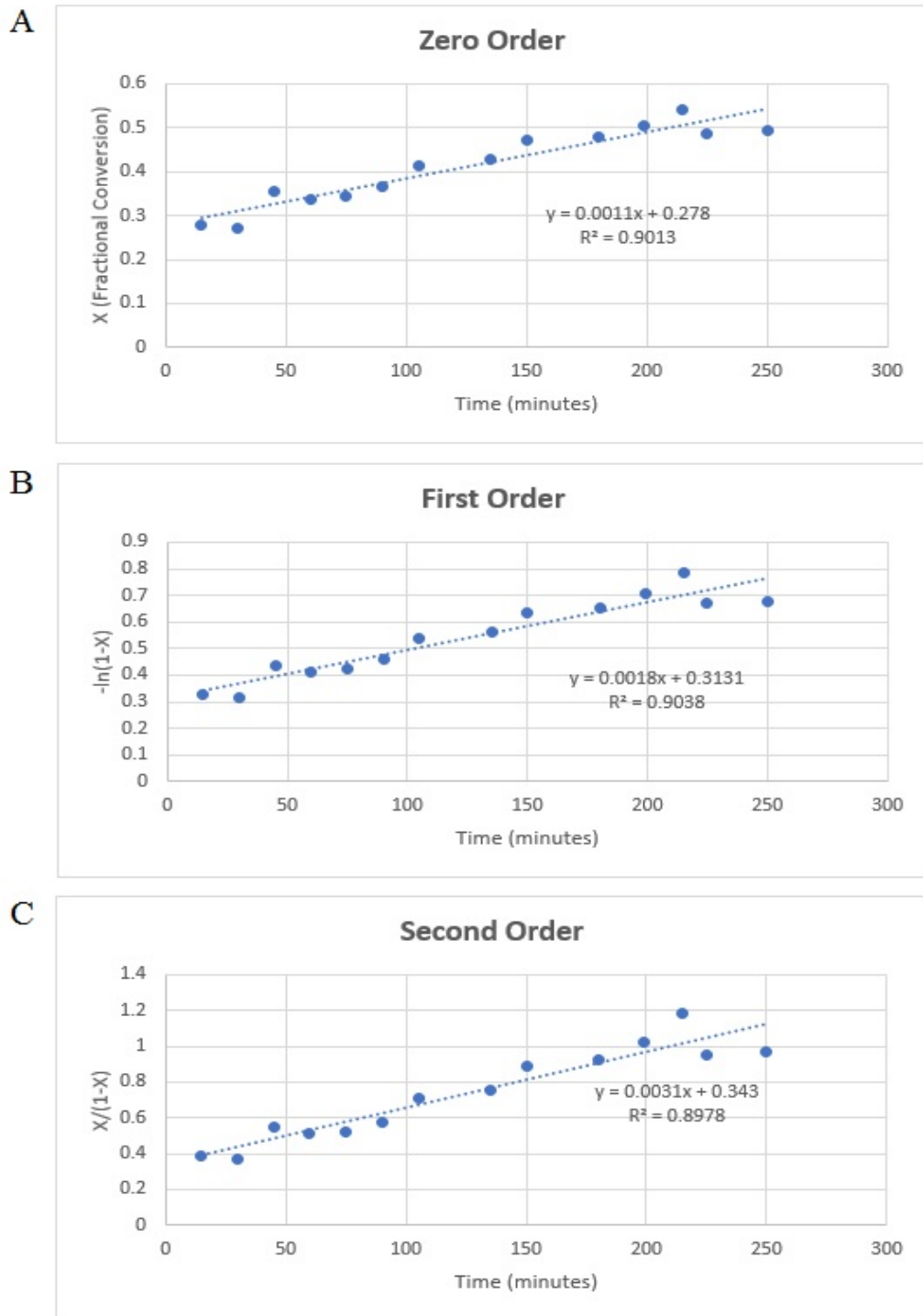


Figure 4. Leaching Experiment Data Fit. Comparison of the fit of leaching data to three reaction orders.

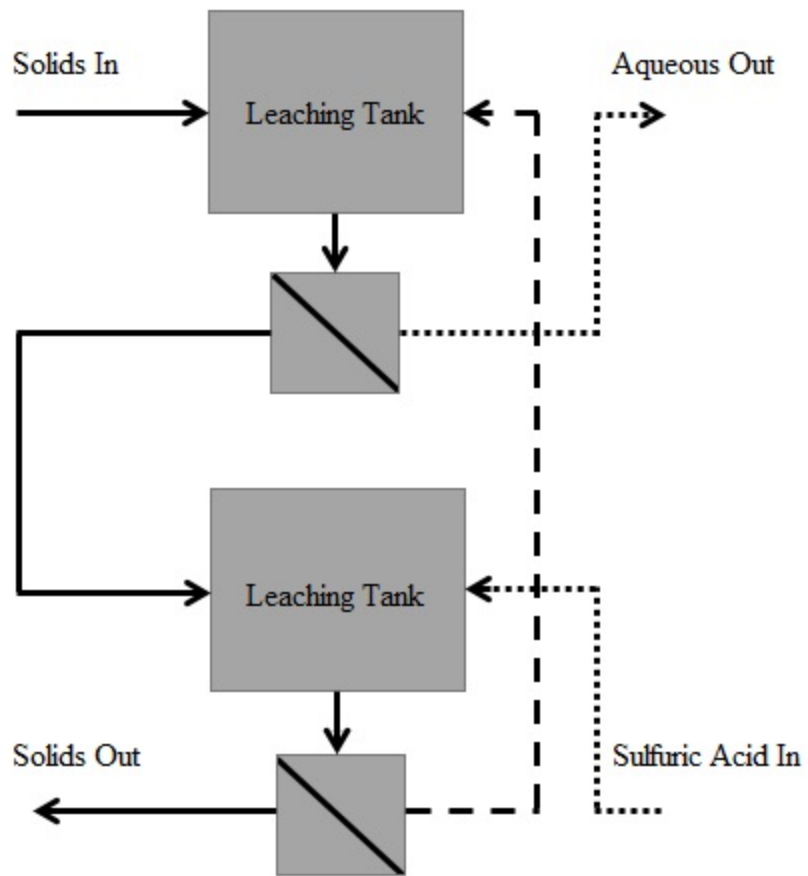


Figure 5. Diagram of Two Leaching Stages. Diagram displays two stages operating with countercurrent flow of aqueous and solid materials.

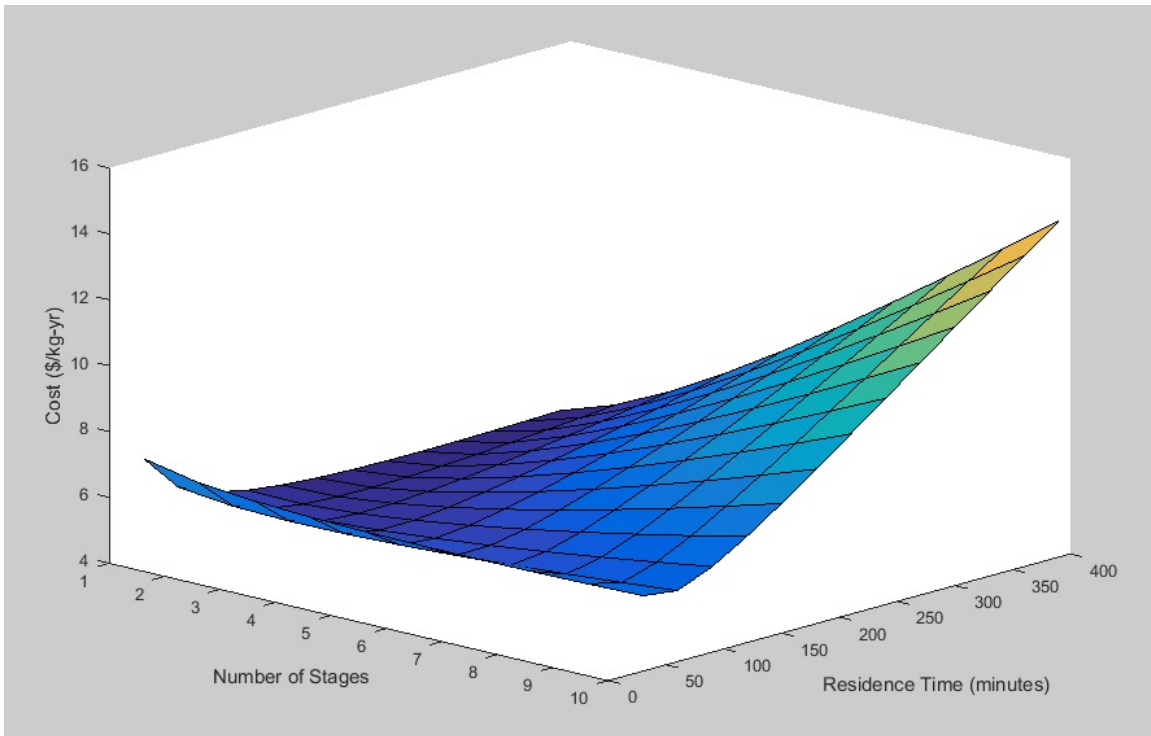


Figure 6. Plot of Data from Reactor Modeling. A three dimensional representation of cost data gathered at each residence time for each number of stages.

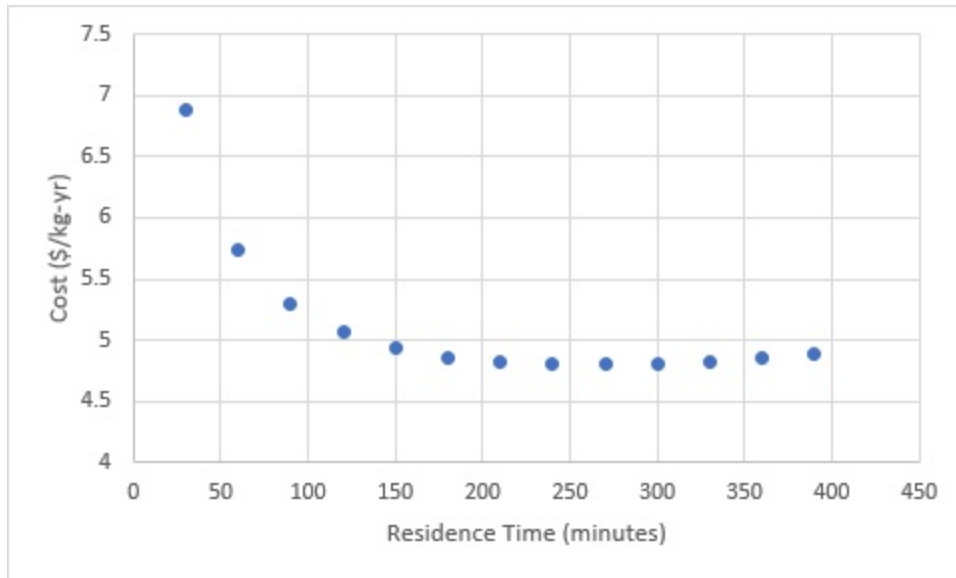


Figure 7. Single Stage Modeling Results. A single “cut” through the data surface in figure 6 where the number of stages is equal to one.

Table 6. Main Chemical Components and REEs in PG Sample.

Component	P ₂ O ₅	CaO	Fe ₂ O ₃	MgO	Al ₂ O ₃	F				
Content (%)	0.99	22.7	0.13	0.00	0.22	1.1				
Element	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Content (ppm)	0.34	43	36	64	5.0	45	0.0	1.4	6.9	0.1
Element	Dy	Ho	Er	Tm	Yb	Lu	Total REEs	U	Th	
Content (ppm)	6.4	0.91	4.4	2.3	2.0	0.0	220	32	0.1	

Table 7. Summary of Kinetic Data Fit.

Reaction Order	k	R²
0	0.0011	0.9013
1	0.0018	0.9038
2	0.0031	0.8978

Table 8. Summary of Optimized Costs.

Number of Stages	1	2	3	4	5
Residence Time (min)	270	180	120	90	90
Minimum Costs (\$/kg-yr)	4.8	4.97	5.15	5.33	5.48
Conversion	0.327	0.43	0.444	0.452	0.528

Number of Stages	6	7	8	9	10
Residence Time (min)	60	60	60	60	60
Minimum Costs (\$/kg-yr)	5.64	5.75	5.87	6.01	6.16
Conversion	0.46	0.512	0.56	0.603	0.641

**CHAPTER III: ECONOMIC OPTIMIZATION OF YTTRIUM
EXTRACTION WITH DEHPA USING INTERNAL RECYCLE**

A version of this chapter is being prepared for publication by Thomas Gaetjens, Dave DeSimone, Robert Counce, and Jack Watson. Dave DeSimone contributed to writing the methods section. Robert Counce, and Jack Watson had an advisory role, suggesting research direction and text clarification.

Abstract

This paper seeks to determine the economic favorability of implementing internal recycle in a solvent extraction process for the recovery of yttrium from phosphogypsum, a water phosphate byproduct. The variables under consideration were the concentration of extractant, the organic to aqueous phase ratio, and the fraction of the organic phase recycled. The modeling results indicated that optimum concentration of extractant was 0.48 molar, the optimum organic to aqueous ratio was 0.1, and the optimum recycle fraction was 0.0.

Introduction

One important unit operation in a process for rare earth element recovery would be some manner of selective solvent extraction. Past studies have pointed to the efficacy of di-(2-ethylhexyl)phosphoric acid (DEHPA) as a selective extractant for rare earth elements (Sato, 1989). One interesting design parameter whose effect on this process's economic has been relatively unstudied is internal recycle of extractant. While it is typical to recycle the extractant after stripping the chemical species of interest, internal recycle refers to passing unstripped extractant through the extractor multiple times to increase the efficiency of the transfer of compounds between phases.

A recent paper by DeSimone et al [31] performed an experimental study of a DEHPA extraction process on yttrium, one of the most concentrated rare earth elements in phosphogypsum, and used these experimental results to regress equations to describe the extraction behavior of yttrium at different extraction conditions. It was the goal of this paper to implement and model the effect of these equations on the costing of an extraction process from phosphogypsum.

Methods

The extraction process was modeled using spreadsheet software. The annual costs of the extraction process were divided by the mass of yttrium entering the organic phase to obtain a specific cost value. The extraction process was assumed to consist of a mixer-settler unit as depicted in figure 8.

The reaction rate constant was calculated according to the following equation [31]:

$$k_a = 0.00494V e^{(-57.15X^2 + 28.05X + 4.51Y)} \quad (3.1)$$

Where V is the volume of the mixer, X is the concentration of DEHPA in moles per liter, and Y is the organic volume fraction in the mixer. This organic volume fraction is itself a function of the fraction recycled [31].

$$Y = \frac{\dot{o}}{\dot{A}(1-r)} \quad (3.2)$$

Where r is the fraction of organic recycled. The distribution coefficient was calculated according to equation 3.3 [31]:

$$D = 3.96X - 0.28 \quad (3.3)$$

These two values are used to determine an efficiency, and then, in turn, the reaction rate [31].

$$\epsilon = \frac{\left(\frac{1+D(\frac{\dot{O}}{\dot{A}})}{\dot{O}}\right)k_a}{\left(\frac{1+D(\frac{\dot{O}}{\dot{A}})}{\dot{O}}\right)k_a+1} \quad (3.4)$$

$$R = k_a CD(1 - \epsilon) \quad (3.5)$$

Where \dot{O} is the organic phase flow rate in milliliters per minute, \dot{A} is the aqueous phase flow rate in milliliters per minute, R is the reaction rate in mg yttrium per minute and C is the concentration of yttrium in the aqueous feed stream in mg yttrium per milliliter.

The feed stream to the extractor was assumed to have a flow rate of $1.44 \cdot 10^6$ m³/yr containing $6.93 \cdot 10^4$ kg/yr of yttrium sulfate [1]. Three primary variables were selected for optimization, the concentration DEHPA, the O:A ratio, and the fraction of organic recycled. Two major sources of cost were considered, the materials costs and the depreciation costs associated with process equipment. These annual costs were divided by the mass of yttrium entering the organic phase to obtain a specific cost value.

The primary material cost for this process operation was the cost of DEHPA. DEHPA was assumed to have a price of four dollars per kilogram.

The mixer-settler unit was modeled as a horizontally oriented process vessel with an assumed residence time of twenty minutes and an inside diameter of 4 meters. The material of construction was assumed to be standard carbon steel. The volume of this vessel was calculated according to equation 3.6.

$$V = \tau \left(\dot{A} + \frac{\dot{O}}{1-r} \right) \quad (3.6)$$

Where τ is the residence time of the mixer. This volume was used to estimate the capital cost for the process vessel according to equation 3.7 [8].

$$C_{Vessel} = \left(\frac{C_I}{400}\right) \left(3100 \left(\frac{V}{16\pi}\right) + 11000\right) \quad (3.7)$$

Where C_{Vessel} is the capital cost of the mixer-settler, C_I is the chemical engineering cost index value, τ is the residence time of the mixer-settler in hours, and V is the total volume of the mixer-settler in m^3 . A cost index of 558.6 was used. The mixer settler unit was assumed to be fitted with an agitator. The capital cost for each of these was modeled in a similar manner [8].

$$C_{Agitator} = \left(\frac{C_I}{400}\right) (920V + 5800)(2.0) \quad (3.8)$$

Equipment was assumed to have a depreciation period of ten years. These capital costs were divided by the depreciation period to determine the annual costs.

The electrical requirement in kilowatts to run the agitator was calculated using equation 3.9 [8].

$$E_{agitator} = 0.3(\tau\dot{V})^{0.8} \quad (3.9)$$

The desired agitation was assumed to be between mild and vigorous, and the price of electricity was assumed to be 0.11 dollars per kilowatt-hour. The energy of agitation may be affected by the viscosity of the organic phase; however, this effect was assumed to be minimal [8].

By inspection of these equations, it may be observed that an increase in the recycle fraction leads to an increase in the fraction of organic in the mixer per equation 3.2, which leads to an increase in the reaction rate constant and, therefore, an increase in the reaction rate. However, per equation 3.6, there is also an increase in the mixer volume

which increases the capital cost of the process. These two effects form the basis of the push-pull relationship that leads to nontrivial results in the optimization.

Results and Discussion

The goal of the optimization was to minimize the operational costs per metric ton of yttrium. The concentration of DEHPA was varied between 0.12 molar and 0.6 molar in increments of 0.04, the O:A ratio was varied between 0.1 and 0.7 in increments of 0.1, and the fraction recycled was varied between 0.0 and 0.8 in increments of 0.2. At each set of conditions, the cost of the extraction per metric ton of yttrium was recorded. A series of surfaces were created, one for each fraction recycled value. Figure 9 features two of these surfaces superimposed on the same plot.

The region associated with minimized costs appears to correspond to higher concentrations of DEHPA and lower O:A ratios. Figure 10 features a cut through all of the surfaces where the O:A ratio is set to a constant value of 0.1.

For any given concentration of DEHPA less than 0.5 molar, the minimized cost is associated with a recycle fraction of 0.0, and higher recycle fractions uniformly correspond to higher costs. It is interesting to note that at higher concentrations, this trend reverses, but it should be noted that the regressions of experimental data from DeSimone (2018) are based on data in the range 0.1 to 0.4 molar DEHPA, so this trend reversal is merely an extrapolation.

Table 1 contains descriptions of the conditions for the global minimum on each recycle fraction surface. The minimum possible cost occurs at a recycle ratio of 0.0, an

O:A ratio of 0.1, and a concentration of DEHPA of 0.48 molar, and has a value of 3.1285×10^5 \$/mt.

Conclusions

The primary conclusion that may be drawn from this optimization is that, while utilizing recycle around the extraction step may increase the efficiency of the extraction, this effect is monetarily outweighed by the increase in the equipment costs due to increased mixer-settler size. Future experimental research should be conducted to verify the accuracy of the model at high extractant concentrations. Furthermore, implementation of an extraction process of this sort would indubitably require consideration of the extraction behavior of the other key rare earth elements present in phosphogypsum. Further research should be conducted to determine if other rare earth elements feature similar behavior.

Appendix

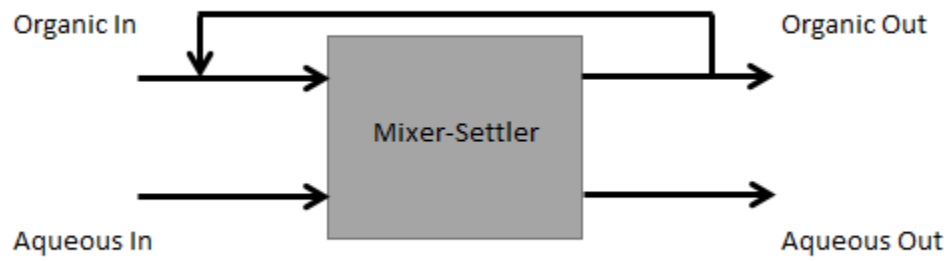


Figure 8. Diagram of the Extraction Process.

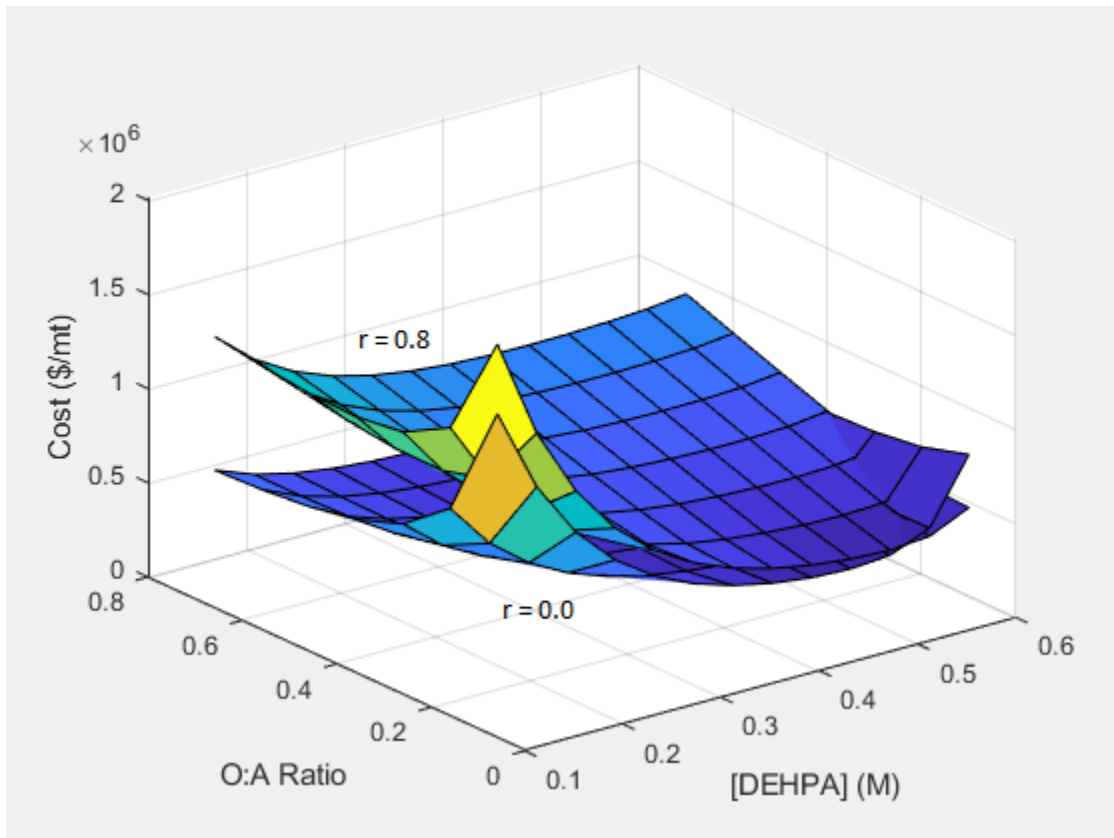


Figure 9. Overview of Two Constant Recycle Fraction Data Surfaces. A comparison of three dimensional cost data at the minimum and maximum values of the recycle fraction.

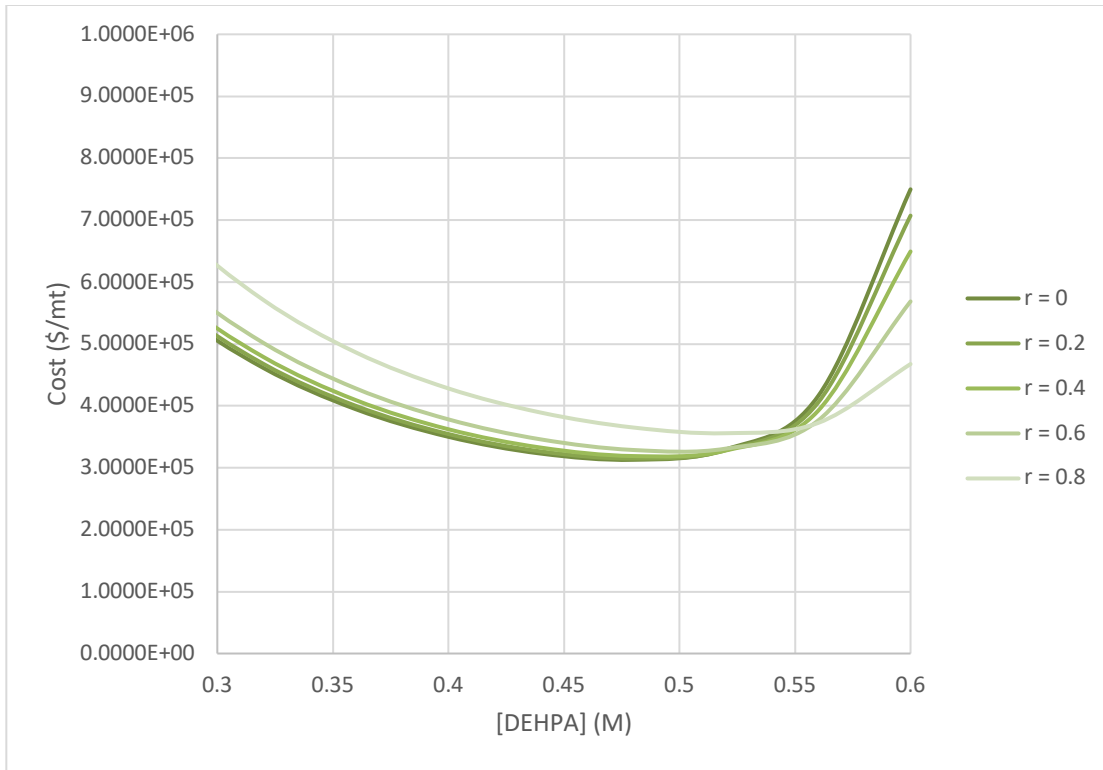


Figure 10. Cost Curves for Constant O:A = 0.1. Features the cost curves in a [DEHPA] range close to the minima.

Table 9. Minimized Costs at each Recycle Fraction.

r	O:A Ratio	[DEHPA] (M)	Cost (\$/mt)
0.0	0.1	0.48	3.1285E+05
0.2	0.1	0.48	3.1488E+05
0.4	0.1	0.48	3.1890E+05
0.6	0.1	0.48	3.2870E+05
0.8	0.1	0.52	3.5578E+05

CONCLUSIONS AND RECOMMENDATIONS

The primary conclusion resulting from this work is that, while it is chemically possible to extract REEs from phosphoric acid manufacturing waste streams, the economics for such a process are not currently advantageous. This research, therefore, may be considered “technology on a shelf” waiting for future conditions to improve the financial viability of this potential resource.

In 2011, prices of REEs soared to unprecedented levels partially due to the monopolization of the market by the Chinese mining industry [33]. Knowing that domestic mining operations have the capability to satisfy demands for REEs can be valuable information to have even if there are minimal incentives to make use of that capacity in the short term future.

For this reason, it may be advisable to continue to investigate technology for this extraction process in the event that some combination of the movements of the markets and the development of different extractants and techniques might unlock the significant potential of this resource.

LIST OF REFERENCES

1. Zhang, P. (2014) Comprehensive Recovery and Sustainable Development of Phosphate Resources. *Procedia Engineering*, 83: 37-51.
2. DePaoli, D.; Delmau, L.; Heathman, C.; Reynolds, C.; Zhang, P.; Jin, Z. (2014) Recovery of rare earth elements and uranium from phosphate ore processing. Presentation.
3. International Fertilizer Development Center. (2014) Worldwide Phosphoric Acid Capacity Listing by Plant. 1-2.
4. Counce, R. (2016) University of Tennessee, Knoxville. Personal Communication.
5. Liang, H.; Zhang, P.; DePaoli, D.; Medley, A.; Jin, Z.; Kucera, P.; Whitt, G.; Bidinger, E. (2016) Beneficiation and Leaching of Phosphate Process Stream for REE Recovery. Florida Industrial and Phosphate Research Institute. Presentation.
6. Zhang, P. (2016) Florida Industrial and Phosphate Research Institute. Personal Communication.
7. Zhu, Z.; Pranolo, Y.; Cheng, C. (2015) Separation of uranium and thorium from rare earths for rare earth production - A review. *Minerals Engineering*. 77: 185-196.
8. Ulrich, G.; Vasudevan, P. (2004) *Chemical engineering process design and economics : a practical guide*, 2nd Ed.; ProcessPub.:Durham, NH, USA.
9. Gomez, C. (2016) Weir Minerals. Personal Communication.
10. Sivakumar, T.; Vijayaraghavan, G.; Vimal Kumar, A. (2011) Enhancing the Performance of Rotary Vacuum Drum Filter. *Int. J. Adv. Eng. Tech.* 2(4): 41-47.

11. DeSimone, D.; Counce, R. (2016) Project Area 1.1.2 2016 Q1 Quarterly Report. Critical Materials Institute.
12. Soderstrom, M. (2015) Cytec Industries Inc. Personal Communication.
13. Amer, T.; Abdella, W.; Abdel Wahab, G.; El-Sheikh, E. (2013) A suggested alternative procedure for processing of monazite mineral concentrate. *Int. J. Mineral Processing*. 125: 106-111.
14. Wang, N.; Zhang, X.; Qiu, G.; Sun, H.; Liu, Q.; Mi, X.; Wang, X. (2010) Synthesis of La³⁺ and Nd³⁺ co-doped yttria nanopowder for transparent ceramics by oxalate precipitation method. *J. Rare Earths*. 28(2): 232-236.
15. Peters, M.; Timmerhaus, K.; West, R. (2003) *Plant Design and Economics for Chemical Engineers*, 5thEd.; McGraw Hill: New York, NY, USA.
16. Waste Management (2014) Simi Valley Landfill and Recycling Center Service and Fee Schedule.
17. Shanghai Metals Market. (2016) Rare Earth Prices.
18. Moser, R., Zhang, P. (2016) Unpublished Manuscript.
19. Nuclear Regulatory Committee. (2015) Code of Federal Regulations. Title 10, Chapter I, Section 40.22.
20. Fogler, Scott. *Elements of Chemical Reaction Engineering* 4th edition. Upper Saddle River, NJ: Prentice Hall, 2005.
21. Jin, Yanya; Kim, Junbeum; Guillaume, Bertrand; 2016. Review of critical material studies. *Resources, Conservation and Recycling* 113, 77-87.

22. Liang, Haijun. "Beneficiation and Leaching of Phosphate Process Stream for REE Recovery." Presentation at Critical Materials Institute Workshop on Rare Earths and Uranium from Phosphate Ore, Florida Industrial and Phosphate Research Institute, Bartow, FL, January 19, 2016.
23. Liang, H.; Zhang, P.; Jin, Z.; DePaoli, D.; 2017. Rare Earths Recovery and Gypsum Upgrade from Florida Phosphogypsum. Accepted for publication in Minerals and Metallurgical Processing.
24. Lokshin, E. P.; O. A. Tareeva; and I.R. Elizarov; 2016. Agitation Leaching of Rare Earth Elements from Phosphogypsum by Weak Sulfuric Solutions. Theoretical Foundations of Chemical Engineering 50, 857-862.
25. Molycorp Inc. *A Lanthanide Lanthology, Part II, M-Z*. Mountain Pass, CA: Molycorp Inc., 1997.
26. United Nations Industrial Development Organization (UNIDO) and International Fertilizer Development Center (IFDC). *Fertilizer Manual*. Dordrecht, the Netherlands: Kluwer Academic Publishers, 1998.
27. Walawalkar, Mugdha; Connie K. Nichol; and Gisele Azimi; 2016. Process Investigation of the Acid Leaching of Rare Earth Elements from Phosphogypsum Using HCl, HNO₃, and H₂SO₄. Hydrometallurgy 166, 195-504.
28. Wang, Liangshi; Long, Zhiqi; Huang, Xuiowei; Cui, Dali; Zhang, Guocheng; 2009. Recovery of rare earths from wet -process phosphoric acid. Hydrometallurgy 101, 41-47.

29. Zhang, Patrick. "Recovery of Critical Elements from Florida Phosphate Phase 1: Characterization of Rare Earths." Presentation at ECI International Conference: Rare Earth Minerals /Metals – Sustainable Technologies for the Future, San Diego, CA, August 13, 2012.
30. Zhang, P.; and Stana, R.; 2012. Phosphogypsum management and Utilization: A Review of Research and Industry Practices. Beneficiation of Phosphates – New Thought, New technology, New Development, pp 309-322, Zhang et al., editors. Society for Mining, Metallurgy, and Exploration, Inc. (SME), Englewood, Colorado.
31. DeSimone, D.; Ghezawi, N.; Gaetjens, T.; Counce, R.; Watson, J. 2018. Modeling the rate constant for yttrium extraction – a designed experiment employing internal recycle. Manuscript.
32. Sato, T. 1989. Liquid-liquid extraction of rare-earth elements from aqueous acid solutions by acid organophosphorus compounds. *Hydrometallurgy* 22. 121-140.
33. Bradsher, K. 2011. Supplies Squeezed, Rare Earth Prices Surge. *New York Times*. May 2, 2011.

VITA

Thomas Gaetjens received a Bachelor of Science in Chemical Engineering from the University of Tennessee Knoxville in 2016. He is the recipient of the 2017 Jack S. Watson Graduate Award for Excellence in Separation Research and a Chancellors Citation for Outstanding Professional Promise. He is a member of the Tau Beta Pi National Engineering Honor Society. He is a Graduate Assistance in Areas of National Need fellow.