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To Whom It May Concern:

This paper was generated via request by Dr. Robert Counce to create an economic analysis of the extraction of rare earth elements (REEs) from clay waste stream. The analysis was conducted by creating a flowsheet REE extraction process, and providing capital and operating cost estimates according to process specifications. All calculations were done in Microsoft Excel.

As stated in the paper, there was an annual net profit after taxes of \$13,613,558.65. This profit comes from the sale of REEs and H_3PO_4 , and recycle of H_2SO_4 . The majority of expenses came from the cost of the extractant: neutral ligand and ISOPAR. We concluded the extraction of REEs would make a return of investment in 2 years and 36 days. Improvements can be made through optimization and the refinement of removal of uranium and thorium to meet radioactivity regulations.

Sincerely,

Marti Bell, Melanie Lindsey, and Mary McBride

An Economic Analysis of the Extraction of Rare Earth Elements from Clay Waste Stream

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Group 1

CBE 488: Honors Design in Green Engineering

Professor: Dr. Counce

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1.0 Introduction

The purpose of this manuscript is to show the process of extracting rare earth elements (REEs). In addition, the manuscript will provide capital and manufacturing costs in 2017 U.S. dollars of processing the clay waste stream from the wet process of phosphoric acid production.

Rare earth elements (REEs) are found in ores mined to produce H_3PO_4 . These REEs are largely discharged in various waste streams of the wet process of phosphoric acid production. The State of Florida has several large wet process production sites for H_3PO_4 , and waste streams for these processes are attractive options as REE sources. The process will use sulfuric acid to leach out the REEs and to hydrolyze phosphate salts through extraction.

After the phosphoric acid production, traces of REEs are left in the clay waste stream. By leaving the REEs in these waste streams, the revenue that could be generated is lost. Though there are only trace amounts of each REE in the waste stream, collectively they become valuable due to their high value. Overall, REEs are of strategic importance to the U.S. They are found in apatite ores in significant quantities all together that are mined for phosphoric acid production.

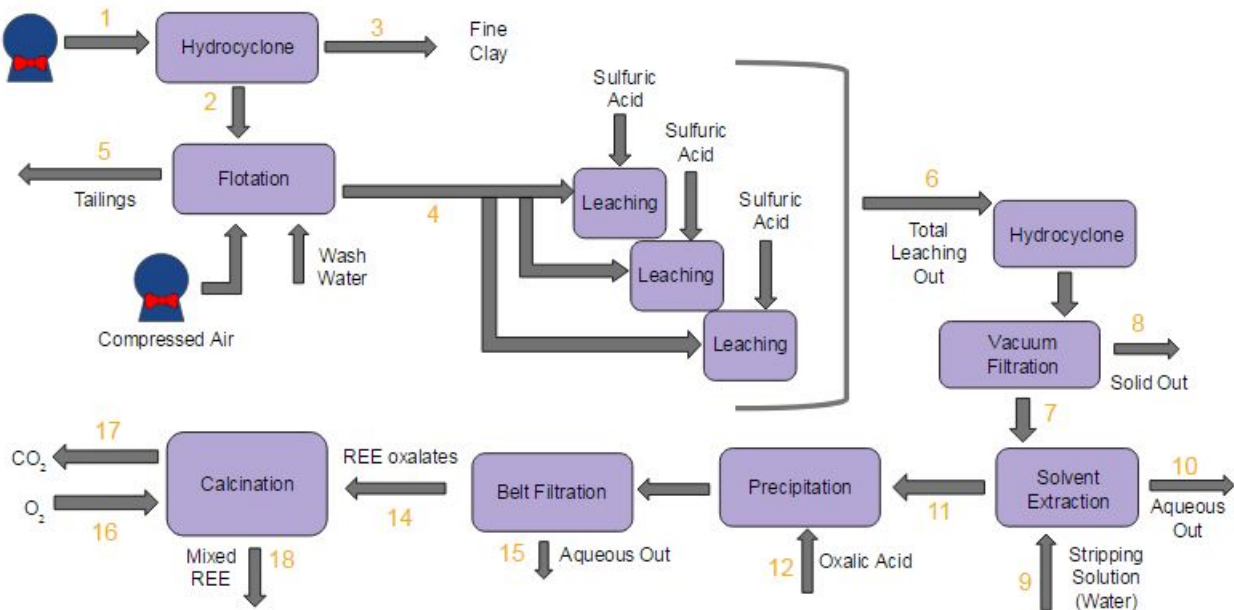
The project focus is to create a flowsheet and economic estimation of the clay waste stream from mining operations for phosphate ores as a source of REEs. A typical clay waste stream is 4 million metric tons per year with about 300 parts per million (ppm) of REEs and 6 wt% of P_2O_5 . 40% of the clay waste stream will be used in this analysis. The product should be solid and must be greater than 50 weight percent (wt%) of REE concentration. The product must be at an acceptable level of radioactivity. The value of the mixed REEs is approximately \$10 / kg of elemental REE. All costs, including manufacturing, capital, and other costs, will be in 2017 U.S. dollars.

Important contributors are Critical Materials Institute (CMI; a US Department of Energy (DOE) innovation hub), Oak Ridge National Laboratory (ORNL), University of Tennessee (UT), Idaho National Laboratory (INL), and the phosphoric acid industry, with support from Dr. Patrick Zhang of the Florida Industrial and Phosphate Research (FIPR) Institute through providing data regarding the typical analytical results of the clay stream.

The manuscript will include supporting information, sample calculations, process flowsheet, estimated capital investment, and manufacturing costs.

2.0 Synthesis Information for Processes

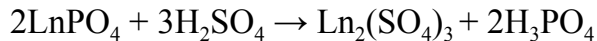
2.1 Overall Process Schematic



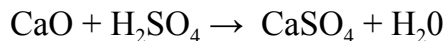
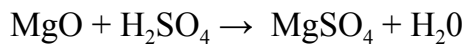
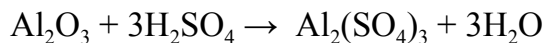
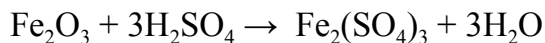
2.2 Chemical Equations

Leaching:

REEs react with sulfuric acid to become highly soluble sulfates

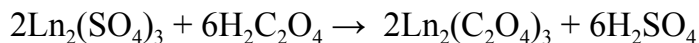


Additional metals react with sulfuric acid

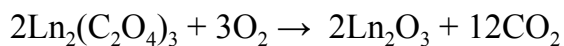


Oxide REE Production:

REE sulfate to make REE oxalate



REE oxalate to REE oxide (PRODUCT)



2.3 Literature Summary

According to the Florida Industrial and Phosphate Research Institute (FIPR), the hydrocyclone performance should have 12 to 15 weight percent of solids in the underflow of the coarse clay stream. Additionally, up to 35 to 40 weight percent of solids should be recovered in the underflow of the hydrocyclone. FIPR also notes that the leaching performance should have over 30 percent recovery of solids in the concentrate, over 70 percent rare earth elements recovery in the concentrate, and over 80 percent P₂O₅ recovery in the concentrate. FIPR recommends using a 90 percent REE recovery, 95 percent P₂O₅ recovery, 35 percent Al leaching, 20 percent Mg leaching, and 10 percent Fe leaching. They also suggest performing the leaching process at 75 degrees celsius and with a ratio of sulfuric acid to calcium oxide of 4.

The goal of precipitation is to solidify the target oxides, which in this case is rare earth element oxalates, to allow for separation from the supernatants, which in this process is sulfuric acid. Oxalic acid is colorless, transparent, strongly acidic and is soluble in water or alcohol. It is used in other processes such as white cloth printing, manufacturing straw hats, cleaning brass and copper pieces as well as wooden surfaces, and bleaching powder in removing writing from paper. Upon heating with sulfuric acid, it will split into CO₂, CO, and water. Oxalic acid has a pH of 1.3 which is optimal for maximum recovery and purest precipitate. Approximately 40 percent excess oxalic acid is required to obtain 90 to 95 percent recovery due to the loss of acid to consumption by iron, aluminum, magnesium and calcium.

2.4 Tables of Product, By-Product, Energy, and Raw Material Costs

Raw Material (Industrial Grade) and Product Costs (approximate 2017 U.S. \$)

H ₂ SO ₄	\$0.05/kg
H ₃ PO ₄	\$0.50/kg
H ₂ C ₂ O ₄	\$0.70/kg
REEs (Ln ₂ O ₃) [mixed]	\$10.00/kg elemental REE
ISOPAR Solvent	\$2.00/kg
Neutral Ligand A	\$60.00/kg (MW = 600 g/mol)

2.5 Chemical Properties

Compound	MW (g/mol)	MP (°C)	BP (°C)	Hf (kJ/mol)	Solubility	Safety
P_2O_5	7.34	340	360	-2984	yes	Cancerous
MgO	40.3	2800	3600	-601.8	slightly	Irritant
Fe_2O_3	159.7	1565	Decomposes	-823.2	no	Irritant
Al_2O_3	101.96	2072	2980	-1669.8	no	Irritant
CaO	56.1	2572	2850	-635.5	slightly	Irritant
$LnPO_4$	233.88	-	-	-296.2	no	Irritant
$Ln_2(SO_4)_3$	566	-	-	-1443	-	Irritant
H_2O	18.015	0	100	-285.8	-	-
H_2SO_4	98.08	-35	270	-811.3	yes	Strong Irritant, cancerous
H_3PO_4	97	21	158	-1288	yes	Strong Irritant
SO_3	80.06	16.8	45	-	violently	Irritant, Cancerous
$MgSO_4$	120.38	-	-	-1278.2	yes	Irritant
$Fe_2(SO_4)_3$	400	decomposes, 480	-	-653.3	-	Irritant
$Al_2(SO_4)_3$	342	-	-	-3771.9	yes	Irritant, reproductive toxin
$CaSO_4$	136	1450	-	-1432.7	slightly	Irritant
$H_2C_2O_4$	90	Decomposes, 189.5	-	-821.7	yes	Irritant, toxic, combustible
O_2	32	-218.8	-183	-	yes	-
$Ln_2(C_2O_4)_3$	541.87	-	-	-1269	yes	Irritant
CO_2	46	-56.6	-78.5	-393.5	slightly	Irritant
Ln_2O_3	325.81	2315	4200	-1675.7	no	Irritant

2.6 Base Cases

Below is data from Dr. Zhang from FIPR and is the head samples. This data will be used as a base case and is what will be improved upon during this project.

	CMI 1-1-2 WC (Waste Clay)	CMI 1-1-2 WC (Waste Clay) Dup	Waste Clay Average	wt%	Flow Rate (kg/yr)	kg/s	MW (g/mol)	mol/s
P2O5 wt%	6.10	5.89	5.99	5.991716115	239668644.6			
P2O5 wt%	5.64	5.55	5.60	5.595406741	223816269.7			
P2O5 avg wt%	5.87	5.72	5.79	5.793561428	231742457.1	7.343475332	283.89	25.86732654
Insol wt%	51.04	51.75	51.39	51.39403911	2055761564	65.14315297	273	238.619608
MgO wt%	2.33	2.13	2.23	2.232851531	89314061.22	2.830191815	40.3044	70.220418
Fe2O3 wt%	2.16	1.86	2.01	2.010500442	80420017.68	2.548356582	159.688	15.95834742
Al2O3 wt%	7.84	6.48	7.16	7.15819033	286327613.2	9.073174551	101.96	88.98758877
CaO wt%	9.55	9.40	9.48	9.47537645	379015058	12.01026244	56.0774	214.1729545
Pr ppm	2.55	2.63	2.59	0.000258664	10346.54092	0.000328087	140.91	0.002328342
Eu ppm	1.92	1.82	1.87	0.000187255	7490.200804	0.000237513	151.97	0.001562892
Tb ppm	1.02	0.95	0.98	9.81907E-05	3927.626444	0.000124544	158.93	0.000783642
Dy ppm	7.26	7.11	7.19	0.000718747	28749.88988	0.000911653	162.5	0.005610172
Ho ppm	0.55	0.80	0.68	6.78172E-05	2712.687874	8.60188E-05	164.93	0.000521547
Er ppm	4.77	4.49	4.63	0.000462927	18517.06707	0.000587172	167.26	0.003510537
Tm ppm	0.60	0.52	0.56	5.64015E-05	2256.061969	7.15393E-05	168.93	0.000423485
Yb ppm	4.41	4.27	4.34	0.000433852	17354.08457	0.000550294	173.04	0.003180157
Lu ppm	0.84	0.79	0.81	8.11855E-05	3247.420469	0.000102975	174.97	0.00058853
Sc ppm	6.05	6.16	6.10	0.000610481	24419.23669	0.000774329	44.96	0.017222618
Gd ppm	10.42	9.82	10.12	0.001011776	40471.04896	0.001283329	157.25	0.008161072
Sm ppm	6.07	6.47	6.27	0.000626684	25067.37305	0.000794881	150.36	0.00528652
Th ppm	5.24	6.61	5.92	0.000592313	23692.5291	0.000751285	232.04	0.00323774
U ppm	37.12	37.49	37.31	0.003730609	149224.3702	0.004731874	238.03	0.019879317
Ce ppm	85.65	86.28	85.97	0.008596711	343868.436	0.010903997	140.12	0.077818988
Y ppm	61.00	59.35	60.18	0.006017574	240702.965	0.007632641	88.91	0.085846822
La ppm	42.02	41.30	41.66	0.004165969	166638.7667	0.005284081	138.91	0.038039599
Nd ppm	54.16	53.19	53.67	0.005367289	214691.5545	0.006807825	144.24	0.047197896
ΣREE	289.30	285.93	287.62	0.028761524	1150460.961	0.036480878		0.321199875

2.7 Design Variables

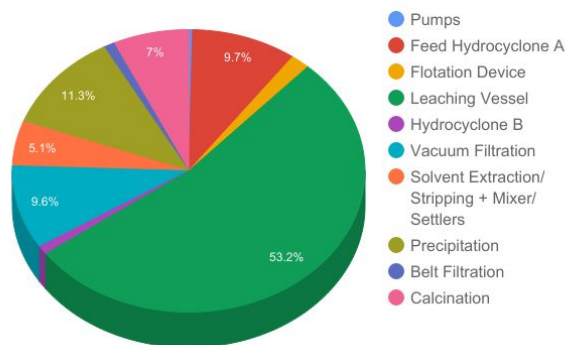
In designing the process to extract REEs from the clay waste stream, several variables were of concern. These consist of temperature, acidity, volume capacity, and radioactivity. Temperature is a concern due to the heat generated in the leaching, precipitation, and calcination reactions. Materials for the equipment and piping must be able to handle temperatures from 25 °C to 150 °C. The consideration of adding a heat exchanger must also be considered if the temperature reaches over 100 °C. Acidity is also a concern when selecting materials for use in equipment design since concentrated H₂SO₄ and H₂C₂O₄ will be added to the process in order to drive the reactions throughout. Volume capacity should also be taken into consideration as with any other plant design. Maximum diameter will be chosen in all equipment design to insure capability of handling the capacity of the inlet stream and any slight variability that may occur. Additionally, radioactivity of the product stream must be considered due to uranium and thorium being in the group of targeted REEs to be extracted. The nuclear regulatory committee determines that the radioactivity that is permissible is 7 kg/yr.

2.8 Cost Information

The cost and/or profit amount per compound is listed in part 2.4, Tables of Product, Byproduct, Energy, and Raw Material Costs. This cost information will be utilized along with installation, manufacturing, and capitals costs according to equipment design and flow rates. Below are the total costs for each equipment. The detailed calculation follows in part 4.1.4, Capital Cost Summaries.

Equipment	Material	Size	Bare Module Cost
Feed Pump	Cast Iron	6.74 kW Shaft Power	\$ 37,668.75
Feed Hydrocyclone A	Carbon Steel	91 Hydrocyclones	\$ 1,726,624.19
Air Pump	Cast Iron	2.80 kW Shaft Power	\$ 26,368.13
Flotation Device with Sieve Trays	Carbon Steel	8.64 m ² H/D of 11	\$317,106.30
Leaching Vessel with Mixer	Stainless Steel	273.33 m ³ each	\$9,492,525.00
Hydrocyclone B	Stainless Steel	2 Hydrocyclones	\$ 179,130.28
Vacuum Filtration	Stainless Steel	1.5 m ²	\$ 1,704,780.00
Solvent Extraction/Stripping +Mixer/Settlers	Stainless Steel, Polymeric Packing	0.39 m ²	\$ 913,295.00
Precipitation	Stainless Steel	0.195 m ³	\$2,023,350.00
Belt Filtration	Stainless Steel	1.054 m ²	\$175,644.00
Calcination	Stainless Steel	19.75 m ³ , 2.96 kW	\$1,248,450.00

Distribution of Equipment Costs



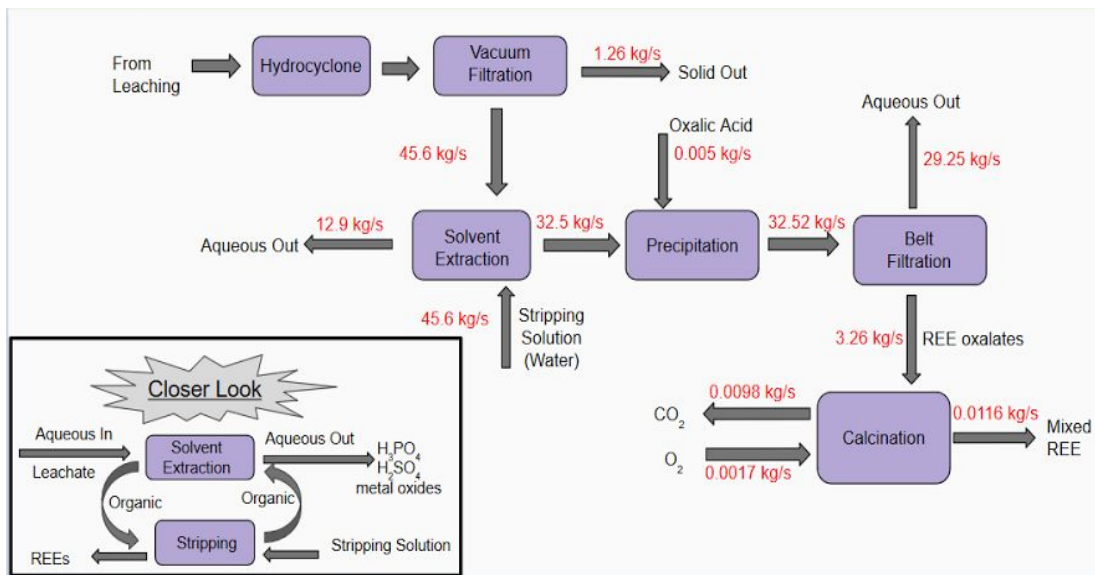
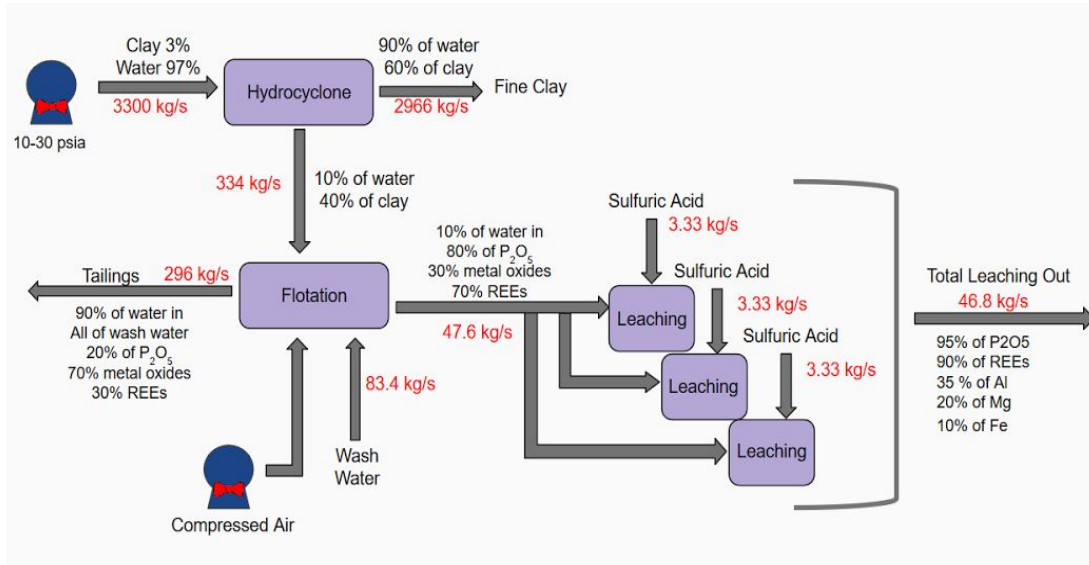
3.0 Method of Approach

The method of approach is based on design steps and collective assumptions. The objective and goal of the process was studied to ensure understanding of the steps needed. Also research of each step was taken on by each peer consultant group to ensure further detailed understanding. Based on each step in the process, a flowsheet was assembled through deciding general equipment types (i.e. vessel, hydrocyclone, filter, etc.) and stream information. Starting with an initial flow rate of 3300 kg/s with a composition of 3% clay and 97% water, a material balance analysis was performed. Stream splitting information was given for the hydrocyclone, flotation step, and the leaching step by the Florida Industrial and Phosphate Research Institute. After performing a material balance on each component in the process, an energy balance was done on the leaching, precipitation, and calcination steps. Heats of reaction along with molar flow rates were found to calculate the inlet and outlet temperatures. It was then insured that the process did not need a cooling mechanism after leaching because the outlet temperature was below 100°C, which is the guideline for the vacuum filter that comes after the second hydrocyclone where this would be an issue. Once mass and volumetric flow rates were known, specific equipment types were chosen. Considerations included temperature, acidic content, and volume. Equipment material and sizing are listed in the Appendix. Most equipment was made out of stainless steel to protect against high temperatures and the sulfuric acid content. Sizing of the equipment followed maximum diameters, lengths, and flow rates for insurance. After deciding on equipment material and size, the equipment was costed. Cost includes all equipment related to each specific step. For example, the cost of the leaching step includes a jacketed vessel and a mixer. Once equipment costs were found, the extractant cost initial inventory was calculated along with its cost. This was included in the total fixed capital cost. Capital costs and manufacturing costs were established and shown in detail in part 4.1.4 and 4.2.1, respectively. The overall cost of the process and return of investment was determined from the manufacturing cost sheet provided by Dr. Ulrich from “Chemical Engineering, Process Design and Economics: A Practical Guide.”

4.0 Results

4.1 Capital Cost Estimates

4.1.1 Schematic Flow Sheets



4.1.2 Final Mass Flow Rate Information by Streams

	Stream 1	total parts (kg/s)	98.99058							
		water (kg/s)	3200.695							
	Clay In		3299.686							
	Stream 2	Stream 3		Stream 4		Stream 5		Stream 6		
	Hydrocyclone Course Continue / Flotation In	Hydrocyclone Fine Out		Flotation Continue / Leaching In		Flotation Out (Tailings)		Leaching Continue / Hydrocyclone In		
	kg/s	mol/s	kg/s	mol/s	kg/s	mol/s	kg/s	mol/s	kg/s	mol/s
P2O5 avg wt%	2.937390133	10.34693	4.406085	15.5204	2.349912	8.277544	0.587478	3.104079	0.117496	0.413877
Insol wt%			65.14315	238.6196						
MgO wt%	1.132076726	28.08817	1.698115	42.13225	0.339623	8.42645	0.792454	19.66172	0.271698	6.74116
Fe2O3 wt%	1.019342633	6.383339	1.529014	9.575008	0.305803	1.915002	0.71354	4.468337	0.275223	1.723502
Al2O3 wt%	3.62926982	35.59504	5.443905	53.39255	1.088781	10.67851	2.540489	24.91652	0.707708	6.941032
CaO wt%	4.804104976	85.66918	7.206157	128.5038	1.441231	25.70075	3.362873	59.96843		
Pr ppm	0.000131235	0.000931	0.000197	0.001397	9.19E-05	0.000652	3.94E-05	0.000279	9.19E-06	6.52E-05
Eu ppm	9.50051E-05	0.000625	0.000143	0.000938	6.65E-05	0.000438	2.85E-05	0.000188	6.65E-06	4.38E-05
Tb ppm	4.98177E-05	0.000313	7.47E-05	0.00047	3.49E-05	0.000219	1.49E-05	9.4E-05	3.49E-06	2.19E-05
Dy ppm	0.000364661	0.002244	0.000547	0.003366	0.000255	0.001571	0.000109	0.000673	2.55E-05	0.000157
Ho ppm	3.44075E-05	0.000209	5.16E-05	0.000313	2.41E-05	0.000146	1.03E-05	6.26E-05	2.41E-06	1.46E-05
Er ppm	0.000234869	0.001404	0.000352	0.002106	0.000164	0.000983	7.05E-05	0.000421	1.64E-05	9.83E-05
Tm ppm	2.86157E-05	0.000169	4.29E-05	0.000254	2E-05	0.000119	8.58E-06	5.08E-05	2E-06	1.19E-05
Yb ppm	0.000220118	0.001272	0.00033	0.001908	0.000154	0.00089	6.6E-05	0.000382	1.54E-05	8.9E-05
Lu ppm	4.119E-05	0.000235	6.18E-05	0.000353	2.88E-05	0.000165	1.24E-05	7.06E-05	2.88E-06	1.65E-05
Sc ppm	0.000309732	0.006889	0.000465	0.010334	0.000217	0.004822	9.29E-05	0.002067	2.17E-05	0.000482
Gd ppm	0.000513331	0.003264	0.00077	0.004897	0.000359	0.002285	0.000154	0.000979	3.59E-05	0.000229
Sm ppm	0.000317952	0.002115	0.000477	0.003172	0.000223	0.00148	9.54E-05	0.000634	2.23E-05	0.000148
Th ppm	0.000300514	0.001295	0.000451	0.001943	0.00021	0.000907	9.02E-05	0.000389	2.1E-05	9.07E-05
U ppm	0.001892749	0.007952	0.002839	0.011928	0.001325	0.005566	0.000568	0.002386	0.000132	0.000557
Ce ppm	0.004361599	0.031128	0.006542	0.046691	0.003053	0.021789	0.001308	0.009338	0.000305	0.002179
Y ppm	0.003053056	0.034339	0.00458	0.051508	0.002137	0.024037	0.000916	0.010302	0.000214	0.002404
La ppm	0.002113632	0.015216	0.00317	0.022824	0.00148	0.010651	0.000634	0.004565	0.000148	0.001065
Nd ppm	0.00272313	0.018879	0.004085	0.028319	0.001906	0.013215	0.000817	0.005664	0.000191	0.001322
ZREE					0.01175	0.089936				0.008994
REE2(SO4)3									0.022907	0.040471
H2O	320.0695347	17766.84	2880.626	159901.5	32.00695	1776.684	288.0626	15990.15	32.5038	1804.263
H2SO4					10.08282	102.803			6.266426	63.89162
H3PO4									1.533403	15.80828
SO3										23.591
MG(SO4)									0.20274	1.68529
FE2(SO4)3									0.0766	0.1915
AL2(SO4)3									1.278218	3.737479
CASO4									3.495303	25.70076
H2C2O4										
O2										
REE2(C2O4)3										
CO2										
REE2O3										
Total Flow For This Stream	333.6085046		2966.077		47.62687	1934.575	296.0594	16102.27	40.14235	1954.738

Table 1: Flowsheet Streams 1-6

4.1.3 Equipment

- Pumps: feed and air
- Hydrocyclones: A at beginning and B after leaching
- Process Vessels: Flotation device, solvent extraction/stripping - mixer/settler, and precipitation
- Jacketed Vessel: Leaching vessel
- Filters: Vacuum filtration and belt filtration
- Calcination

4.1.4 Capital Cost Summary

Job Title: Economic Analysis of the Extraction of Rare Earth Elements from Clay Waster Stream				Location: University of Tennessee							
				Cost Index Type: 574							
		Purchased equipment cost									
Equipment Identification	Capacity or Size Specifications	Year 2004 or 2016	Year 2017	F _{BM} ^{CS}	C _{BM} ^{CS}	F _M	F _P	F _{BM} ^a	C _{BM} ^a		
Feed Pump	Cast Iron, 6.74kW shaft power	\$ 7,500.00	\$ 10,762.50	1	\$ 10,762.50	1	1	3.5	\$ 37,668.75		
Hydrocyclone A	Carbon steel, 91 hydroclones	\$ 544,458.15	\$ 575,541.40	1	\$ 575,541.40	-	-	3	\$ 1,726,624.19		
Air Pump	cast iron, 2.80kW shaft power	\$ 5,250.00	\$ 7,533.75	1	\$ 7,533.75	1	1	3.5	\$ 26,368.13		
Flotation Device	carbon steel, 8.64 m2, 11 H/D	\$ 51,000.00	\$ 73,185.00	1	\$ 73,185.00	1	1	4.1	\$ 300,058.50		
Leaching Vessel	Sieve Trays, 2 trays and 3 Fq	\$ 5,400.00	\$ 7,749.00	1	\$ 7,749.00			2.2	\$ 17,047.80		
	Stainless steel, 273.33 m3	\$ 330,000.00	\$ 473,550.00	1	\$ 473,550.00	-	2.4	7.5	\$ 8,523,900.00		
	Mixer	\$ 270,000.00	\$ 387,450.00	1	\$ 387,450.00	-	-	2.5	\$ 968,625.00		
Hydrocyclone B	Stainless steel, 2 hydroclones	\$ 42,364.00	\$ 44,782.57	1	\$ 44,782.57	-	-	4	\$ 179,130.28		
Vacuum Filtration	Stainless steel, 1.5 m2	\$ 330,000.00	\$ 473,550.00	1	\$ 473,550.00	-	-	3.6	\$ 1,704,780.00		
Solvent Extraction/Stripping	Stainless steel, polymetric packing, .39 m3	\$ 35,000.00	\$ 50,225.00	1	\$ 50,225.00	4	1	9.4	\$ 472,115.00		
	Packing	\$ 5,000.00	\$ 7,175.00	1	\$ 7,175.00	-	-	1	\$ 7,175.00		
	Neutral Ligand Inventory	\$ 5,909,760.00	\$ 5,909,760.00	1	\$ 5,909,760.00	-	-	1	\$ 5,909,760.00		
Precipitation	Isopar Inventory	\$ 1,074,427.20	\$ 1,074,427.20	1	\$ 1,074,427.20	-	-	1	\$ 1,074,427.20		
	Mixer/Settler	\$ 88,236.00	\$ 441,180.00	1	\$ 441,180.00	-	-	1	\$ 441,180.00		
	Stainless steel, .195 m3	\$ 150,000.00	\$ 215,250.00	1	\$ 215,250.00	4	1	9.4	\$ 2,023,350.00		
Belt Filtration	Stainless steel, 1.054 m2	\$ 34,000.00	\$ 48,790.00	1	\$ 48,790.00	-	-	3.6	\$ 175,644.00		
Calcination	Stainless steel, 19.75 m3, 2.96 kW	\$ 145,000.00	\$ 208,075.00	1	\$ 208,075.00	4	1	6	\$ 1,248,450.00		
Total									\$ 24,836,303.85		

Table 4: Capital Cost Summary

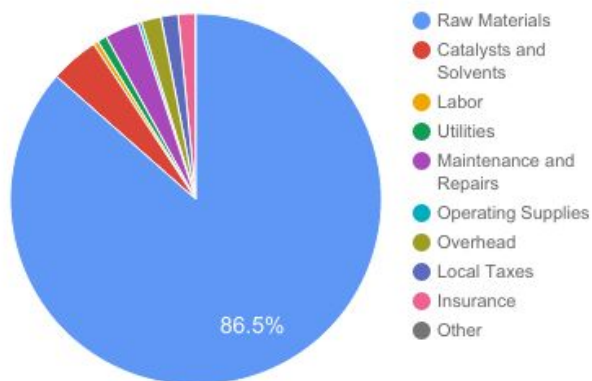
4.2 Operating Cost Estimates

Below is the breakdown of the manufacturing/operating expenses of the process.

Lab charges are noted as other in the chart. Further calculation of the costs are shown in

4.2.1, Operating Cost Summary.

Operating/Manufacturing Costs



4.2.1 Operating Cost Summary

Manufacturing Cost Summary			Page 1 of 1		
			By: Bell, McBride, and Lindsey		
			Date: April 26th, 2017		
Job Title: An Economic Analysis of the Extraction of Rare Earth Elements from the Clay Waste Stream					
Location: University of Tennessee, Knoxville			Annual capacity (kg/yr): 3,600,000,000		
Date: April 26th, 2017			Cost index type: 2016		
			Cost index value: 574		
Capital			Operating factor: N/A		
Fixed Capital, C_{FC}		\$	24,836,303.85		
Working Capital (10 to 20% of fixed capital), C_{WC}		\$	3,725,445.58		
Total Capital Investment, C_{TC}		\$	28,561,749.42		
			Annual cost		\$/s
Manufacturing Expenses			\$/yr	\$/yr	fo 0.9 by-product 0.315237 input 0.5075141
Direct					
Raw Materials		\$	14,414,333.87		
By-product credits		\$	(8,936,968.95)		
Catalysts and solvents		\$	704,545.20		
Operating labor		\$	72,800.00	31557600	
Supervisory and clerical labor (10 to 30% of operating labor)		\$	7,280.00		
Utilities					
Steam ____ kg/y ____ barg @ ____ \$/kg		\$	-		
____ kg/y ____ barg @ ____ \$/kg		\$	-		
Electricity ____ kWh @ ____ \$/kWh		\$	56.94		
Process water ____ m ³ @ ____ \$/m ³		\$	-		
Demin water ____ m ³ @ ____ \$/m ³		\$	-		
Cooling water ____ m ³ @ ____ \$/m ³		\$	134,839.31		
Waste Disposal ____ kg @ ____ \$/kg		\$	-		
Maintenance and repairs (2 to 10% of fixed capital)		\$	496,726.08		
Operating supplies (10 to 20% of maint. & repairs)		\$	49,672.61		
Laboratory charges (10 to 20% of operating labor)		\$	7,280.00		
Patents and royalties (0 to 6% of total expense)		\$	-		
Total, A_{DME}		\$	6,950,565.06		
Indirect					
Overhead (payroll and plant), packaging, storage (50 to 70% of op. labor, supervision, and		\$	288,403.04		
Local taxes (1 to 3% of fixed capital)		\$	248,363.04		
Insurance (1 to 2% of fixed capital)		\$	248,363.04		
Total, A_{IME}		\$	785,129.12		
Total manufacturing expense, $A_{ME} = A_{DME} + A_{IME}$		\$	7,735,694.18		
General expenses					
Administrative costs (25% of overhead)		\$	72,100.76		
Distribution and selling (10% of fixed cost)		\$	1,210,757.32		
Research and development (5% of fixed cost)		\$	605,378.09		
Total general expense, A_{GE}		\$	1,888,236.17		
Depreciation (approx. 10% of fixed capital), A_{BD}		\$	2,483,630.38		
Total expenses, A_{TE}		\$	12,107,560.73		
Revenue from sales (____ kg/yr @ ____ \$/kg), A_S		\$	29,124,509.04		
Net Annual Profit, A_{NP}		\$	17,016,948.31		
Income taxes (net annual profit x tax rate), A_{IT}		\$	3,403,389.66		
Net annual profit after taxes ($A_{NP} - A_{IT}$), A_{NNP}		\$	13,613,558.65		
After-tax rate of return, $i = (1.5 A_{NNP}/C_{TC}) \times 100 =$				20 %	

Table 5: Manufacturing Cost Summary

5.0 Discussion of Results

After evaluating the objectives of the project, the process schematic as provided in 4.1.1 was determined to be the most sensible and cost-effective design. The significant modification from the initial design in 2.1 was changing the leaching process. Because of volume constraints,

three jacketed vessels had to be used for leaching instead of one. After calculating flow rates for each stream using a material and energy balance, the solid REE production was calculated to be 0.011587 kg/s. Temperature changes were then taken into consideration for the determination of equipment type and material, and the final equipment list is shown in 4.1.3. From this point, a capital cost summary could be made and the total cost was projected to be just under \$25,000,000. A pie chart in 4.2 gives a visual breakdown of the costs, and shows that the raw materials cost is the biggest expense each year. After completing the manufacturing cost summary, the net annual profit after taxes was calculated to be \$13,613,558.65, indicating that this design proves to be profitable each year of operation.

6.0 Conclusions

The current design for the extraction of REEs from the clay waste stream is economically favorable. The current net annual profit after taxes is about \$13.6 million, and the return on investment will be made in two years and 36 days. This time period is reasonable for the process. The major factors that add to both capital and annual costs are the cost of the extractant and the cost of sulfuric acid. Optimizing the amount of the replacement amount needed for the neutral ligand and ISOPAR could bring down annual costs. Water was used as the stripping agent to lessen the cost of sulfuric acid yearly. There are many different assumptions made that could be optimized to make a greater profit overall. Future work includes optimization to maximize REE extraction amount and refinement of the removal of uranium and thorium.

7.0 Recommendations

7.1 Sustainability

REEs are included in the clay waste stream of the manufacturing of phosphoric acid. By using this stream, we are not creating new waste. In addition, phosphate is required by plants and animals, so the production of phosphoric acid is useful.

7.2 Product Quality

Mixed REE_2O_3 is a marketable product. However, The radioactivity content of the product is 54958.14 kg of U and Th in one year. This is above the acceptable limit of 7 kg/yr, so it would take more work to refine the product to lessen the radioactivity.

	Uranium	Thorium	Total
Original (kg/s)	0.004732	0.000751	0.036481
	13%	2%	
Final (kg/s)	1.5E-05	2.39E-06	0.011587
1 year (kg)	474.2795	75.30191	549.5814

Table 6: Amounts of Thorium and Uranium

7.3 Financial

- Product profit: \$ 29,124,509.04
- By-product profit: \$ 8,936,968.95
- Net profit after taxes: \$ 13,613,558.65
- Estimated time until return on investment: 2 years and 36 days (about 25 months)

7.4 Environmental

The waste stream of the phosphoric acid process is being used as our initial feed. Since this process is established, the chemicals are already in common use in H_3PO_4 manufacturing. Therefore, environmental considerations are already in place.

7.5 Worker Safety and Health

Safety policies are already in place for phosphoric acid production, and the same materials and similar processes are used in this system. Therefore, worker safety and health information can be shared.

8.0 Acknowledgements

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Mr. Dave DeSimone, Ph.D. student in Chemical Engineering at the University of Tennessee

Peer Consultants, groups of students in CBE 488 class that researched and presented on particular aspects of process

9.0 References

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10.0 Appendix

Equations for Extent of Reaction Calculations

REEs Equation (1)
$2(\text{REEPO}_4) + 3(\text{H}_2\text{SO}_4) \rightarrow \text{REE}_2(\text{SO}_4)_3 + 2(\text{H}_3\text{PO}_4)$
P₂O₅ Equation (2)
$\text{P}_2\text{O}_5 + 3 (\text{H}_2\text{O}) \rightarrow 2(\text{H}_3\text{PO}_4)$
MgO Equation (3)
$\text{H}_2\text{SO}_4 + \text{MgO} \rightarrow \text{Mg}(\text{SO}_4) + \text{H}_2\text{O}$
Fe₂O₃ Equation (4)
$\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$
Al₂O₃ Equation (5)
$\text{Al}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O}$
CaO Equation (6)
$\text{H}_2\text{SO}_4 + \text{CaO} \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$
REE Sulfate Equation (7)
$\text{REE}_2(\text{SO}_4)_3 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow 10\text{H}_2\text{O} + \text{REE}_2(\text{C}_2\text{O}_4)_3 + 3\text{H}_2\text{SO}_4$
REE Oxalate Equation (8)
$\text{REE}_2(\text{C}_2\text{O}_4)_3 + 1.5\text{O}_2 \rightarrow \text{REE}_2\text{O}_3 + 6\text{CO}_2$

Calculation of Extent of Reaction

Extent of Reactions				90% REE Recovery -> multiplied REE coming in by .9 to get REE going out											
nequilibrium = extent * Vi + ni				10% Fe		95% P2O5 Recovery									
H2SO4 REEs				20% Mg		35% Al									
REEs Equation (1)				Species						Equations					
2(REEPO4) + 3(H2SO4) -> REE2(SO4)3 + 2(H3PO4)				REEPO4	na	0.089936	0.0089936	0.0809424	nai - 2 ^{na}	0.04047	7.86367	1.68529	0.1915	3.73748	25.70076
				H2SO4	nb	102.80302	63.891623	38.911395	nbi - 3 ^{nb} - n ^{na} - 3 ^{nb} - n ^{nb}						
P2O5 Equation (2)				REE2(SO4)3	nc	0	0.0404712	-0.040471	ncl + n ^{na}						
P2O5 + 3 (H2O) -> 2(H3PO4)				H3PO4	nd	0	15.808277	-15.80828	ndi + 2 nd + 2 nd						
				P2O5	ne	8.2775445	0.4138772	7.8636673	nel - n ^{na}						
MgO Equation (3)				SO3	nf	0	0	0	nfi						
H2SO4 + MgO -> Mg(SO4) + H2O				MgO	ng	8.4264502	6.7411602	1.68529	ngi - n ^{na}						
				Mg(SO4)	nh	0	1.68529	-1.68529	nhi + n ^{na}						
Fe2O3 Equation (4)				H2O	ni	1776.7	1803.4944	-26.79442	nii + n ^{na} + 3 ^{na} + 6 ^{na} + n ^{na} - 3 ^{na}						
Fe2O3 + 3H2SO4 -> Fe2(SO4)3 + 3H2O				Fe2O3	nj	1.9150017	1.7235015	0.1915002	nji - n ^{na}						
				Fe2(SO4)3	nk	0	0.1915002	-0.1915	nki + n ^{na}						
Al2O3 Equation (5)				Al2O3	nl	10.678511	6.9410322	3.7374789	nli - n ^{na}						
Al2O3 + 3H2SO4 -> Al2(SO4)3 + 6H2O				Al2(SO4)3	nm	0	3.7374789	-3.737479	nmi + n ^{na}						
				CaO	nn	25.700755	0	25.700755	nni - n ^{na}						
CaO Equation (6)				CaSO4	no	0	25.700755	-25.70076	noi + n ^{na}						
H2SO4 + CaO -> CaSO4 + H2O															
REE sulfate equation (7)															
REE2(SO4)3 + H2C2O4 -> 10H2O + REE2(C2O4)3 + 3H2SO4				H2C2O4	In	Out	Change								
					0.0576715	0.0221074	0.0355641								
REE Carbonate equation (8)															
REE2(C2O4)3 + 1.5O2 -> REE2O3 + 6CO2				O2	0.0533461	0	0.0533461								

Solvent Extraction Distribution Coefficients

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U		
1	Acidified Clay																						
2	~0.2 M Technical Grade Neutral Ligand 20 mM Trioctylamine 30% v/v Exsal-13 in Isoparl																						
3																							
4			45Sc	89Y	139La	140Ce	141Pr	146Nd	147Sm	153Eu	157Gd	159Tb	163Dy	165Ho	166Er	169Tm	172Yb	175Lu	232Th	238U			
5		Extrn D	9.98082	1027.28	1.5959	4.30643	9.69326	26.5159	-440	270.833	229.634	146.1	504.95	252.6	1711.2	1411	2638.5	-2127	419.741	0.93397			
6		error	0.40084	877.255	0.09438	0.21595	1.05182	6.89599	-1066.84	383.141	71.7051	289.317	785.723	428.748	1452.88	1996.11	1867.38	-3008.8	66.6265	0.06012			
7																							
8		Strip D	0.27927	0.43814	0.14032	0.17012	0.14781	0.14591	0.17378	0.16906	0.17248	0.19852	0.2847	0.4239	0.6416	0.81596	1.05371	1.40611	0.38503	0.28507			
9		error	0.04943	0.06766	0.06368	0.04984	0.05115	0.04906	0.04223	0.04236	0.0395	0.0484	0.0522	0.07218	0.10081	0.15758	0.16062	0.20793	0.0313	0.07968			
10																							
11																							

Heats of Reactions Calculations

REEs Equation (1)			Heats of Reaction			Leaching		
2(REEPO4) + 3(H2SO4) -> REE2(SO4)3 + 2(H3PO4)						REEPO4 = GdPO4 REE2(SO4)3 = CeSO4		
	Mr			-992.7 kJ/mol				
	Mt			0.0809424 mol/s				
	Cp			1955 mol/s				
	Delta T			75.52 J/mol/k				
				-0.544233607 K				
P2O5 Equation (2)								
P2O5 + 3 (H2SO4) -> 2(H3PO4) + 3(SO3)								
	Mr			1588.1 kJ/mol				
	Mt			7.863667275 mol/s				
	Cp			1955 mol/s				
	Delta T			75.52 J/mol/k				
				84.58517111 K				
MgO Equation (3)								
H2SO4 + MgO -> Mg(SO4) + H2O								
	Mr			-151.1 kJ/mol				
	Mt			1.68529004 mol/s				
	Cp			1955 mol/s				
	Delta T			75.52 J/mol/k				
				-1.724766767 K				
Fe2O3 Equation (4)								
Fe2O3 + 3H2SO4 -> Fe2(SO4)3 + 3H2O								
	Mr			1745.4 kJ/mol				
	Mt			0.19150017 mol/s				
	Cp			1955 mol/s				
	Delta T			75.52 J/mol/k				
				2.263896372 K				
Al2O3 Equation (5)								
Al2O3 + 3H2SO4 -> Al2(SO4)3 + 6H2O								
	Mr			-1383 kJ/mol				
	Mt			3.73747885 mol/s				
	Cp			1955 mol/s				
	Delta T			75.52 J/mol/k				
				-35.01000565 K				
CaO Equation (6)								
H2SO4 + CaO -> CaSO4 + H2O								
	Mr			-271.7 kJ/mol		Delta T	-82.3114 K	T in 75
	Mt			25.700755 mol/s		Hrxn	535 kJ/mol	T out 157.311
	Cp			1955 mol/s				
	Delta T			75.52 J/mol/k				

Costing the Flotation Device

$$333.61 \text{ kg/s} \rightarrow 0.33361 \text{ m}^3/\text{s}$$

$$\tau = 3 \text{ min} * (0.33361 \text{ m}^3/\text{s}) * 60 \text{ s/min} = 60.0498 \text{ m}^3$$

$$L/D = 3 \text{ (needs to be between 2-6)}$$

$$V = \pi * (D^2/4) * L$$

$$L = 3D$$

$$V = \pi * (D^2 3D)/4$$

$$D = 2.94 \text{ m} \rightarrow 3 \text{ m}$$

$$L = 9 \text{ m}$$

$$C_p = \$51,000$$

$$F_p = 1.0$$

$$F_m = 1.0$$

$$F_{bm} = 4.1$$

$$C_{BM} = (574/400)(4.1)(51,000) = \$300058.50$$

Sieve trays:

$$C_{BM} = C_{pss} * F_{BM} * N_{art} * f_q$$

$$C_{p,ss} = 900$$

$$F_{BM} = 2.2$$

$$N_{art} = 2$$

$$F_q = 3$$

$$C_{BM} = (900)(2.2)(3)(2)(574/400) = \$17047.80$$

$$\text{TOTAL } C_{BM} = \$300058.50 + \$17047.80 = \$317,106.30$$

Costing the Leaching Vessel

$$\tau = 240 \text{ min} * (.057 \text{ m}^3/\text{s}) * 60 \text{ s/min} = 820.8 \text{ m}^3$$

3 leaching vessels

$$\text{Jacketed vessel, Volume} = 273.33 \text{ m}^3 \text{ each}$$

$$C_p = \$110,000$$

$$F_{bm} = 7.5$$

$$F_p = 2.4$$

$$C_{bm} = \$1,980,000 (574/400) = \$2841300$$

$$\text{Total (3)} = \$8,523,900$$

Mixer, Agitator, Mechanical Seal

$$\text{Power consumption} = 1.1V^{0.95}$$

$$1.1(273.33 \text{ m}^3)^{0.95} = 226 \text{ kW}$$

$$C_p = \$270,000$$

$$F_{BM} = 2.5$$

$$C_{BM} = \$675,000 (574/400) = \$968,625$$

$$\text{Total } C_{BM} \text{ jacket plus mixer} = \$9,492,525$$

Costing Hydrocyclone B

$$46.8 \text{ kg/s} = 0.0468 \text{ m}^3/\text{s}$$

$$\text{One hydrocyclone} = 36.4 \text{ L/s} = 0.0364 \text{ m}^3/\text{s}$$

$$0.0468/0.0361 = 2 \text{ hydrocyclones}$$

$$C_{p,H} (2016) = 185,000(46.8 \text{ L/s} / 546 \text{ L/s})^{0.6} = \$42,364.00$$

$$F_{BM} = 4$$

$$C_p (2017) = (\$42,364.00)(4)(574/543) = \$179,130.28$$

Costing Vacuum Filtration

$$46.8 \text{ kg/s}$$

$$1 \times 10^{-3} \text{ A}$$

$$L = 1.5 \text{ m}$$

$$D = 1 \text{ m}$$

$$C_p = \$330,000$$

$$F_{BM} = 3.6$$

$$C_{BM} = (\$330,000)(3.6)(574/400) = \$1,704,780.00$$

Costing Solvent Extraction/Stripping

$$91.2 \text{ kg/s} \rightarrow 0.0912 \text{ m}^3/\text{s}$$

$$\tau = 30 \text{ min} * (0.0912 \text{ m}^3/\text{s}) * 60 \text{ s/min} = 164.16 \text{ m}^3$$

$$L/D = 6 \text{ (needs to be between 2-6)}$$

$$V = \pi * (D^2/4) * L$$

$$L = 6D$$

$$V = \pi * (D^2 6D)/4$$

$$D = 2.0 \text{ m}$$

$$L = 12 \text{ m}$$

$$C_p = 35,000$$

$$F_p = 1.0$$

$$F_m = 4.0$$

$$F_{BM} = 9.4$$

$$C_{BM} = (574/400)(9.4)(35,000) = \$472,115.00$$

Mixer Settlers:

5 stages

$$82.08 \text{ m}^3/\text{stage} / 5 \text{ m}^2 = 16.416 \text{ m}$$

$$16.416 \text{ m} * 5375 = \$88,236 \text{ per mixer settlers}$$

$$\$88,236 * 5 = \$441,180.00$$

$$\text{TOTAL } C_{\text{BM}} = \$ 913,295.00$$

Extractant:

At 15 min/stage

Flow rate aqueous in = 45.6 kg/s

Density 1000 kg/m³

$$45.6 / 1000 = .0456 \text{ m}^3/\text{s} * 60 \text{ s} = 2.736 \text{ m}^3/\text{min}$$

Organic flow = 2.736 m³/min bc 1:1

$$\text{Extractant total} = 5.472 \text{ m}^3/\text{min}$$

$$\text{Per extractor stage} = 5.472 (15 \text{ min}) = 82.08 \text{ m}^3/\text{stage}$$

$$\text{At 5 stages, } 82.08 * 5 = 410.4 \text{ m}^3 \text{ (extractor volume)}$$

$$\text{Stripper volume approx. same} = 410.4 \text{ m}^3$$

$$\text{Total volume} = 820.8 \text{ m}^3$$

$$\text{Double for piping, tankage, etc.} = 1641.6 \text{ m}^3$$

$$\text{Volume of organic} = 820.8 \text{ m}^3 = \text{inventory of organic}$$

Composition .2 M neutral ligand A, the rest is isopar

$$.2 \text{ kmol/m}^3 (820.8 \text{ m}^3) = 164.16 \text{ kmol}$$

$$164.16 \text{ kmol} * (600 \text{ kg/kmol}) = 98496 \text{ kg neutral ligand A} * (\$60) = \underline{\$5,909,760 \text{ Neutral}}$$

Ligand A:

$$98496 / (800 \text{ kg/m}^3) = 123.12 \text{ m}^3 \text{ volume of nlA}$$

$$820.8 - 123.12 = 697.68 \text{ m}^3 \text{ volume of isopar}$$

$$\text{Density isopar} = 770 \text{ kg/m}^3$$

$$697.68 * 770 = 537213.6 \text{ kg isopar} * (\$2) = \underline{\$1,074,427.2 \text{ isopar}}$$

Replacement:

$$.1 * 820.8 = 82.80 \text{ m}^3/\text{yr}$$

$$0.01 * 820.8 = 8.280 \text{ m}^3/\text{yr}$$

$$.2 \text{ kmol/m}^3 (82.80 \text{ m}^3/\text{yr}) = 16.56 \text{ kmol}$$

$$16.56 \text{ kmol} * (600 \text{ kg/kmol}) = 9936 \text{ kg neutral ligand A} * (\$60) = \underline{\$596,160/\text{year Neutral}}$$

Ligand A:

$$9936 / (800 \text{ kg/m}^3) = 12.42 \text{ m}^3 \text{ volume of nlA}$$

$$82.8 - 12.42 = 70.38 \text{ m}^3 \text{ volume of isopar}$$

$$\text{Density isopar} = 770 \text{ kg/m}^3$$

$$70.38 * 770 = 54192.6 \text{ kg isopar} * (\$2) = \underline{\$108,385.2/\text{year isopar}}$$

Costing Precipitation

$$32.505 \text{ kg/s} \rightarrow 0.195 \text{ m}^3/\text{s}$$

$$\tau = 30 \text{ min} * (0.195 \text{ m}^3/\text{s}) * 60 \text{ s/min} = 351 \text{ m}^3$$

$$L/D = 4 \text{ (needs to be between 2-6)}$$

$$V = \pi * (D^2/4) * L$$

$$L = 6D$$

$$V = \pi * (D^2 6D)/4$$

$$D = 4.2 \text{ m} \rightarrow 4.0 \text{ m}$$

$$L = 24 \text{ m}$$

$$C_p = \$150,000$$

$$F_p = 1.0$$

$$F_m = 4.0$$

$$F_{BM} = 9.4$$

$$C_{BM} = (574/400)(9.4)(150,000) = \$2,023,350$$

Costing Belt Filtration

Liquid-solid process filter

$$0.011A = 0.0116 \text{ kg/s}$$

$$A = 1.054 \text{ m}^2$$

$$L = 1 \text{ m}$$

$$D = 1.054 \text{ m}$$

$$C_p = \$34,000$$

$$F_{BM} = 3.6$$

$$C_{BM} = (\$34,000)(3.6)(574/400) = \$175,644.00$$

Costing Calcination

$$3.26 \text{ kg/s} \rightarrow 0.0503 \text{ m}^3/\text{s}$$

With density of 3890 kg/m^3 (Al_2O_3)

$$\tau = 1759.9 * (0.0503 \text{ m}^3/\text{s}) = 88.523 \text{ m}^3$$

$$L/D = 4 \text{ (needs to be between 2-6)}$$

$$V = \pi * (D^2/4) * L$$

$$L = 4D$$

$$V = \pi * (D^2 4D)/4$$

$$D = 3.0 \text{ m}$$

$$L = 12 \text{ m}$$

$$C_p = \$52,000$$

$$F_p = 1.0$$

$$F_m = 4.0$$

$$F_{BM} = 9.4$$

$$C_{BM} = (574/400)(9.4)(52,000) = \$701,428.00$$