

An Economic Analysis of the Extraction of Rare Earth Elements from WPPA Sand Tailings Waste Stream

CBE 488: Honors Design in Green Engineering

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1.0 Introduction

The purpose of this manuscript is to document the development and economic analysis of processes for the recovery of rare earth elements (REEs) from the wet process of phosphoric acid production (abbreviated WPPA). Each year around 220 million tons of phosphate rock is processed annually, with China and the US producing a combined 121 million tons. The phosphates extracted are used primarily as a fertilizer in the agricultural sector for commercial farming operations. In this project, we develop and compare flow sheets, capital cost, and operating cost estimates for the recovery of REEs from sand (amine tails), a side waste stream of phosphoric acid processing, and the produced phosphoric acid stream (typically of approximately 30 wt % H_3PO_4) of the wet phosphoric acid process. The basis for our stream flow rates is a process to handle 3 million tons of phosphate rock (10 million tons of extracted ore) per year, a sand flow rate of about 4 million ton/yr and a produced total acid stream of about 1.6 ton/yr. The composition of these streams is presented in Table 1.

Table 1. Composition (ppm) of rare earth elements in sand (amine tails) waste stream and in produced acid stream.

REE	Amine Tails	Acid
Y	36.05	31.0
La	29.35	3.28
Ce	65.75	15.5
Pr	5.705	0
Nd	39.65	9.61
Sm	4.925	0
Eu	0.955	0
Gd	3.95	0.91
Tb	0.205	0
Dy	4.745	0.54
Ho	1.09	0.11
Er	2.815	1.92
Tm	0.495	0.57
Yb	2.265	3.18
Lu	0.075	0.56
Th	6.54	6.21
U	24.8	212.0
Total	229	

The final report will document the results of this study. A Chemical Engineering Index of 574 will be used in the economic calculations of the current report. Supporting information and advice is provided by Dr. Watson and Dr. DePaoli of Oak Ridge National Research Laboratories located in Oak Ridge, TN and Dr. Patrick Zhang of the Florida Industrial and Phosphate Research Institute.

2.0 Synthesis Information for Processes

Rare earth elements are present in small quantities in ore mined for production of H_3PO_4 . These REEs are present in the product H_3PO_4 and in waste streams from the wet process, a common process for H_3PO_4 production. In the current activity, waste streams and the product stream from H_3PO_4 production in central Florida are considered as sources of REEs. The production of H_3PO_4 in central Florida begins with the mining of apatite, $\text{Ca}_5(\text{PO}_4)\text{X}$, where X may include OH, F, Cl or Br. In the apatite formations are small concentrations of rare earth elements, iron, aluminum, uranium, thorium and other elements. In the manufacturing of H_3PO_4 the ore is first separated into fractions of phosphate rock, sand, and clay, with each fraction containing impurities such as phosphates and rare earth elements. The sand and clay fractions are currently discarded as waste materials while the phosphate rock is used for production of H_3PO_4 . Another waste stream is the phosphogypsum stream from the dissolution of phosphate rock by aqueous H_2SO_4 . Yet another waste stream of interest is the sludge stream from H_3PO_4 concentration operations.

2.1 Process Schematics

Figure 1. Conceptual Process for Recovery of REEs from Sand (Amine Tails)

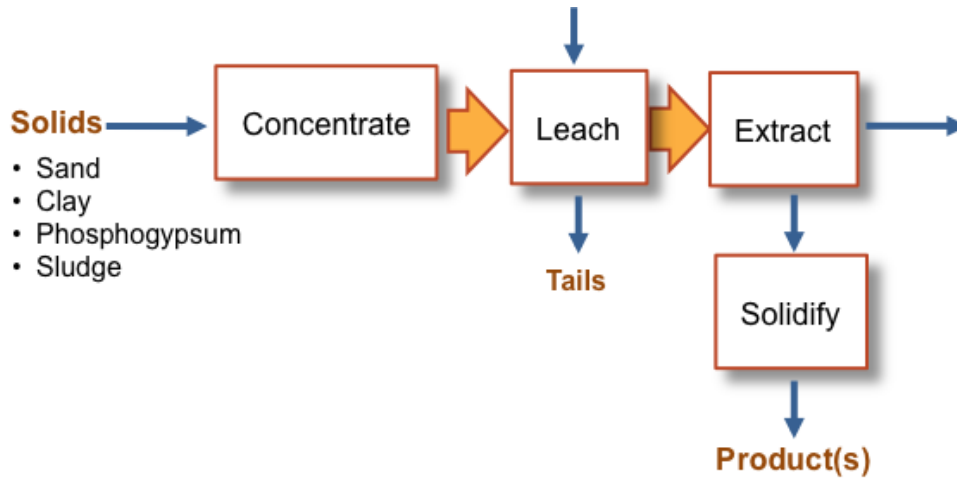
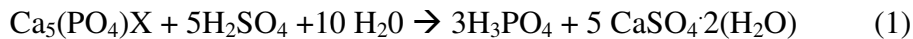


Figure 2. Conceptual Process for Recovery of REEs from Initial Produced Acid Stream



2.2 Chemical Equations

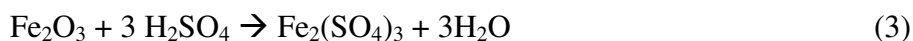
In the wet process for production of H_3PO_4 , the phosphate rock fraction is contacted with concentrated H_2SO_4 resulting in production of CaSO_4 , a highly insoluble compound, and H_3PO_4 .



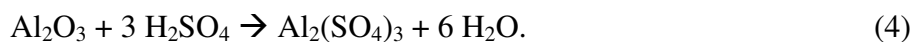
The REEs, present as impurities in the ore, react similarly, illustrated here with YPO_4 and a soluble sulfate product.



Other metals present as impurities in the ore such as Fe_2O_3 and Al_2O_3 also react with H_2SO_4 , resulting in reactions illustrated here as sulfates of varying solubility in water.



and



In the current activity REEs are recovered purified to produce a product concentration of > 50 % mixed REEs.

2.3 Literature Summary

Rare earth elements are a set of fifteen elements that are usually considered difficult to extract and refine to their purest form, because of their low concentrations. Despite their low demand in industry in terms of weight, specific REEs can serve an evolving array of high-technology applications, many of which are in the green energy sector. It is for this reason they are often referred to as the ‘seeds of technology’¹. Most of these elements are not as uncommon as the name suggest; they are simply uncommon in commercially viable concentrations. Cerium, for instance, is more abundant in the earth’s crust than copper or lead. Such elements make for strong magnets commonly used in electric motors to produce greater power and torque due to their strong magnetic abilities. These electric motors are an essential component in hybrid vehicles. This is one of many examples of REE-dependent technology that is becoming increasingly popular in the automobile industry, soon to become abundant on roads across the world.

In a world of increasing technological innovations, REEs also serve as components of efficient lighting and display panels. The popularity of such applications leads to an increase in demand for europium, terbium, and yttrium, those being the main REEs for these applications². Lanthanum is another example of an REE used in rechargeable batteries. It is used in a mix of metal alloy that makes the anode of the most utilized battery system, NiOH.

Element	Symbol	Atomic Number	Upper Crust Abundance, ppm [*]	Chondrite Abundance, ppm [†]
Yttrium	Y	39	22	na [‡]
Lanthanum	La	57	30	0.34
Cerium	Ce	58	64	0.91
Praseodymium	Pr	59	7.1	0.121
Neodymium	Nd	60	26	0.64
Promethium	Pm	61	na	na
Samarium	Sm	62	4.5	0.195
Europium	Eu	63	0.88	0.073
Gadolinium	Gd	64	3.8	0.26
Terbium	Tb	65	0.64	0.047
Dysprosium	Dy	66	3.5	0.30
Holmium	Ho	67	0.80	0.078
Erbium	Er	68	2.3	0.20
Thulium	Tm	69	0.33	0.032
Ytterbium	Yb	70	2.2	0.22
Lutetium	Lu	71	0.32	0.034

Table 2. Rare Earth Elements with respective abundance in ppm.

Currently, China accounts for 94% of global production while other countries make up for the rest, which leaves the US 100% dependent on foreign exports³. The growing demand for REEs causes a deficit in supply due to worldwide limitations. For this reason, several projects are projected to overcome this deficit. Such projects include finding viable economic means to recover REEs from sand, clay, sludge, phosphogypsum and phosphoric acid.

3.0 Method of Approach

By using a basis of 10 million metric tonnes of phosphate ore, the corresponding mass of sand tailings to be processed is 4 million metric tonnes based on existing phosphoric acid production processes. Amine sand tailings, which are the focus of the process, account for approximately 297,000 tonnes of the 4 million tonnes of tailings, according to the beneficiation mass balance given in Table 3 below.

Beneficiation Mass Flows (given values, in tonnes)			
Stream	Coarse Feed	Fine Feed	Total
Feed	785000	4510000	5295000
FA Tails	478000	3420000	3898000
Amine Tails	70110	227000	297110
Concentrate	236890	863000	1099890

Table 3. Incoming mass flows from beneficiation process.

Once the mass of amine sand tailings had been established, the object was to design an industrial process that would maximize extraction of rare earth elements from the tailings while minimizing cost and waste products. The method of approach for the design of the process began by researching existing extraction and stripping processes and equipment, and carrying out preliminary calculations to test the viability of these processes in REE extraction. Research and calculations yielded a number of process steps that were chosen to be included in the industrial design, and the next task was to put the steps in an order that was most effective for extraction. The results of these first tasks and the final design flowsheet are summarized later in Section 4.1.

The next task was to construct a mass balance of the overall process. This task involved gathering large amounts of raw data from small-scale experimental results, and implementing this data in extensive calculations. Key data sets included step-by-step REE concentration estimations; percent recovery values of overall mass and REE mass; extraction and stripping distribution coefficients varied by extraction and stripping agent concentration; and solid-liquid contact ratios. The results of the overall mass balance are summarized in various tables throughout this report, as well as a comprehensive summary included in the Appendix.

For the next task in the design process, the mass balance was to be used to size and cost the equipment. The mass of the streams to be processed in each step of the design directly correlate to the minimum equipment size that can efficiently carry out the processes. The size of

the equipment then subsequently determines the cost. Many literary sources had to be consulted to accurately cost the equipment, and the results of this task are summarized in Section 4.2.

The final task, a corollary to the previous one, is to analyze the finalized design to estimate operating cost and total economic potential of the process. Up-to-date pricing estimates of input energy and raw materials needed to be gathered for this task, as well as current market prices of rare earth elements. The final results of this task are summarized in Section 4.3.

4.0 Results

4.1 Flowsheets

4.1.1 Recovery of REES from Amine Tails (Sand) Waste Stream

From the separation of phosphate ore, the amine tails in the sand waste effluent are sent through a separate extraction process to recover the REEs. The incoming amine tail feed stream is initially sent through a gravity separator in order to remove the larger sand components. From a mass balance, a 56% recovery of REEs from the gravity separation unit is expected. This process has two product streams that include a large sand component waste stream and a stream containing the REE's and finer sand particles, which is fed into a flotation unit. In the flotation step, any remaining sand components are physically separated from the REEs and sent out as a waste stream, with an estimated 89% REE recovery. The concentrated REEs are fed into a mixing tank and reacted with aqueous 93%-weight sulfuric acid to produce REE-sulfates. At this point in the process, the stream of interest should contain primarily REE-sulfates, sulfuric acid, and water with minimal sand particle and phosphoric acid components. The stream is then sent to an extraction unit to separate the REEs via the use of Isopar-L diluent, a commercial solvent with properties similar to kerosene. Using an estimated 5 extraction stages followed by 5 scrubbing stages, our calculations estimate this extraction unit can reach 31% recovery. The sulfuric acid product stream is sent off as waste (potential recovery possible), and the REE-carrier stream is fed into a stripping unit. In this step, very dilute sulfuric acid is introduced as a stripping agent to remove the REEs from the Isopar-L. The solvent stream is recycled back to the extraction unit and the REE/Stripping agent stream is fed into a mixing tank, where it is reacted with ammonium carbonate. From the tank, the components are separated physically

through a settling unit in which the precipitate REE-carbonates are removed and the liquid stripping agent/ammonium stream is sent out as waste (potential recovery possible). After this final step, the REE-carbonates are in a marketable form and can be sold to a potential customer.

Should the calculations show a low REE recovery from this process, a calcination step may need to be introduced after the carbonation precipitation. This will concentrate the REEs in a higher weight percent, and can provide for cheaper transportation costs in our cost estimations.

4.2 Capital Cost Estimates

Equipment Identification	Number	Total
Process Vessels		
Extraction Unit	U-100	498.89125
Stripping Unit	U-101	765.1297085
Scrubbing Unit	U-102	627.975
Calcinator	U-103	5802.489
Total Vessels		\$7,694,485
Mixers		
Leaching Agitator	M-100	17.44375
Leaching Tank	M-101	59.30875
Carbonation M/S Agitator	M-102	13.955
Carbonation M/S Tank	M-103	17.44375
Total Mixers		\$108,151
Separators		
Shaking Table	F-110	310.49875
Flotation Unit	F-122	713.1005
Total Separators		\$1,023,599
Pump		
Pump 1	P-100	12.9825
Pump 2	P-101	12.9825
Pump 3	P-102	12.9825
Pump 4	P-103	12.9825
Pump 5	P-104	12.9825
Total Pumps		\$64,913
Total bare module cost		\$8,826,235
Contingency and fee		\$1,588,722
Total module cost		\$10,414,958
Auxiliary (offsite) Facilities		\$3,124,487
Grass Roots capital		\$13,539,445

Table 4. Capital costs of process equipment used recovering Rare Earths.

4.3 Operating Cost Estimate for Recovery of REES from Amine Tails

Operating Costs	Total (\$/yr)
Solvent (Isopar-L)	
Initial Inventory (Depreciated 10yrs)	\$ 9,215,300.00
Annual Cost	\$ 9,215,300.00
Total Solvent	\$ 18,430,600.00
Sulfuric Acid	\$ 4,000,000
Ammonium Carbonate	\$ 28,000
Labor	\$ 500,000
Electricity	\$ 200,000
Water	\$ 550,000
Total Annual Operating Costs	\$23,708,600

Table 5. Annual operating costs of recovery of Rare Earths. Cost of capital is spread over 10-year operational life of equipment. Individual mass flow rates and related costs are located in Appendix A.

5.0 Discussion of Results

Based on the equipment design proposed in this study, approximately 68.15 tonnes of REE's can be processed annually with a 13% recovery rate. The estimated capital costs are around \$13,600,000 with a yearly operating cost of \$23,710,000. The bulk of the operating costs stem from the use of Isopar-L as the primary solvent, with an initial inventory charge of over \$92,000,000. This cost was depreciated over 10 years and combined with a 10% expected operational loss. The following shows an annual balance sheet.

Operating Costs (\$/yr)	Total (\$/yr)
Revenue	
REE Recovery	\$ 662,046.00
Total Revenue	\$ 662,046.00
Capital Costs	
10-Yr Straightline Depreciation	\$ 1,360,000.00
Total Capital Equipment	\$ 1,360,000.00
Operating Costs	
Solvent (Isopar-L)	\$ 18,430,600.00
Sulfuric Acid	\$ 4,000,000.00
Ammonium Carbonate	\$ 28,000.00
Labor	\$ 500,000.00
Electricity	\$ 200,000.00
Water	\$ 550,000.00
Total Operating Costs	\$ 23,708,600.00
Total Annual Revenue	-\$24,406,554

Table 6. Balance sheet providing estimates on yearly revenue, expenses, and operating profit in recovery of rare earths from sand tailings.

6.0 Conclusions

As seen from the results, the process does not seem to be economically viable under the current design parameters. However, several variables can be worked on to improve the economic profitability of the process, some of which include reducing solvent cost, using a centrifugal contractor at the extraction step, and finding alternative cheaper equipment than the ones used in this design. These variables prove to show great promise in reducing overall expense, making the economic design of the process worthwhile.

7.0 Recommendations

An initial recommendation is to incorporate a centrifugal contact separator to the equipment design. In turn, this would lower the unit residence time to about 20 seconds (factor of 30), reducing the initial solvent inventory proportionately and the annual solvent loss by a factor of 10. The combined effect on annual solvent cost is a 300X reduction and a total savings

of over \$18 Million per year relative to our initial design. This is represented in the following table.

Operating Costs (\$/yr)	Total (\$/yr)
Revenue	
REE Recovery	\$ 662,046.00
Total Revenue	\$ 662,046.00
Capital Costs	
10-Yr Straightline Depreciation	\$ 1,360,000.00
Total Capital Equipment	\$ 1,360,000.00
Operating Costs	
Solvent (Isopar-L)	\$ 337,817.00
Sulfuric Acid	\$ 4,000,000.00
Ammonium Carbonate	\$ 28,000.00
Labor	\$ 500,000.00
Electricity	\$ 200,000.00
Water	\$ 550,000.00
Total Operating Costs	\$ 5,615,817.00
Total Annual Revenue	-\$6,313,771

Table 7. Balance sheet providing estimates on yearly revenue, expenses, and operating profit in recovery of rare earths from sand tailings with addition of centrifugal contactors.

After the addition of centrifugal contactors, the costs for sulfuric acid remain one of the largest opportunities for improvement. Sulfuric acid is a major component in the leaching and stripping steps of the process, and further explorations must be made for ways to recycle and maximize its use. It has also been proposed to investigate a range of acid concentrations to see which are the most effective in both processes and give the largest return on our investment.

Additional cost savings could potentially be found in the choice of equipment and more efficient use of utilities and labor to accompany. For example, further study may find that more effective means exist than the gravity separation step paired with a flotation unit featured in this design. The alternative methods may provide savings in initial capital purchases as well as the energy and resources needed in operation.

Finally, society in general must find more ways to increase the demand of REEs and, thus, the price in order to generate a substantial revenue for this process. As noted in Appendix A, the market price of bulk rare earths would need to rise to almost \$1,800 per kilogram to reach

a 10% profit from the initial design. Even with the implementation of the contactors and potential savings aforementioned, the current \$4/kg bulk rate will likely not be enough to overcome the high capital and operating costs of this process. More research is necessary to find ways to reduce costs, increase revenue, and make rare earth processes a reality here in the United States of America.

References:

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3. Humphries, Marc. *Rare Earth Elements: The Global Supply Chain* (n.d.): n. pag. *Federation of American Scientists*. Congressional Research Service, 16 Dec. 2013. Web. <<http://fas.org/sgp/crs/natsec/R41347.pdf>>.

Appendix A. Comprehensive Mass Balance

- All mass values are in metric tons, taken on a yearly basis
- Given values are taken from small-scale laboratory testing done by FIPR and/or the Critical Materials Institute research group at ORNL
- Critical REEs (those with significant economic value) are highlighted in yellow, undesirable radioactive elements (Thorium and Uranium) are highlighted in red

Benification Mass Flows (given values, in tonnes)			
Stream	Coarse Feed	Fine Feed	Total
Feed	785000	4510000	5295000
FA Tails	478000	3420000	3898000
Amine Tails	70110	227000	297110
Concentrate	236890	863000	1099890

Gravity Separation	REE Mass (tonnes) before Gravity Separation	REE Concentration (ppm) before Gravity Separation	REE Concentration (ppm) after Gravity Separation
REE			
Y	10.7108	36.05	87.20
La	8.7202	29.35	57.23
Ce	19.5350	65.75	128.21
Pr	1.6950	5.705	11.12
Nd	11.7804	39.65	105.00
Sm	1.4633	4.925	9.60
Eu	0.2837	0.955	1.86
Gd	1.1736	3.95	7.70
Tb	0.0609	0.205	0.40
Dy	1.4098	4.745	9.25
Ho	0.3238	1.09	2.13
Er	0.8364	2.815	5.49
Tm	0.1471	0.495	0.97
Yb	0.6730	2.265	4.42
Lu	0.0223	0.075	0.15
Th	1.9431	6.54	12.75
U	7.3683	24.8	48.36
Total (given)		229	487
Total (calculated)	68.15	229.365	491.85
% Recovery			56%
Total mass (tons)	68.15	68.15	38.16

Flotation Mass Flows	
NA ₂ SiO ₃ dosage = 0.55 kg/kg total feed	
<u>Stream</u>	<u>Mass</u>
Amine Tails	77589.44
NA ₂ SiO ₃	94831.54

Flotation	REE Mass (tonnes) after Gravity Separation	REE Concentration (ppm) after Flotation
REE		
Y	6.7658	191.84
La	4.4406	125.91
Ce	9.9479	282.07
Pr	0.8632	24.47
Nd	8.1469	231.00
Sm	0.7451	21.13
Eu	0.1445	4.10
Gd	0.5976	16.95
Tb	0.0310	0.88
Dy	0.7179	20.36
Ho	0.1649	4.68
Er	0.4259	12.08
Tm	0.0749	2.12
Yb	0.3427	9.72
Lu	0.0113	0.32
Th	0.9895	28.06
U	3.7522	106.39
Total (given)		1080
Total (calculated)	38.16	1082.06
% Recovery		89%
Total Mass (tons)	38.16	33.96

Leaching Mass Flows	
Solid-Liq Ratio = 0.7	
<u>Stream</u>	<u>Mass</u>
Concentrate	31388.46
Sulfuric Acid (93 wt%)	13452.20

Leaching	REE Mass (tonnes) after Flotation	REE Mass (tonnes) after Leaching	REE Concentration (ppm) after Leaching
REE			
Y	6.0216	5.7205	424.31
La	3.9522	3.7150	275.56
Ce	8.8537	8.4995	630.45
Pr	0.7682	0.6530	48.43
Nd	7.2507	5.5106	408.74
Sm	0.6632	0.5040	37.39
Eu	0.1286	0.0977	7.25
Gd	0.5319	0.4042	29.98
Tb	0.0276	0.0210	1.56
Dy	0.6389	0.4856	36.02
Ho	0.1468	0.1115	8.27
Er	0.3791	0.2881	21.37
Tm	0.0667	0.0507	3.76
Yb	0.3050	0.2318	17.19
Lu	0.0101	0.0077	0.57
Th	0.8807	0.6693	49.64
U	3.3395	2.5380	188.26
Total (given)			
Total (calculated)	33.96	29.55	2188.76
% Recovery		87%	
Total Mass (tons)	33.96	29.55	29.55

Extraction Mass Flows	
Extractor O/A Ratio = 0.1	
Ligand Concentration in O = 187 g/L	
<u>Stream</u>	<u>Mass</u>
Feed (Leach Acid + Scrub Acid + REE)	21483.70
Extractant Fluid, O	2148.37

<u>Extraction</u>	Distribution Coefficient (from correlations)	Mass flow entering feed stage	Mass fraction in feed	Extraction Factor
REE				
Y	45.2231	6.2315	2.90E-04	4.5223
La	0.0643	3.7390	1.74E-04	0.0064
Ce	0.1638	8.6415	4.02E-04	0.0164
Pr	0.4101	0.6810	3.17E-05	0.0410
Nd	1.0106	6.1296	2.85E-04	0.1011
Sm	10.5806	0.7190	3.35E-05	1.0581
Eu	1.7819	0.1187	5.53E-06	0.1782
Gd	3.1389	0.5612	2.61E-05	0.3139
Tb	13.1164	0.0280	1.30E-06	1.3116
Dy	64.7921	0.5146	2.40E-05	6.4792
Ho	7.2635	0.1685	7.85E-06	0.7264
Er	16.0694	0.3701	1.72E-05	1.6069
Tm	31.3393	0.0577	2.68E-06	3.1339
Yb	63.1937	0.2458	1.14E-05	6.3194
Lu	23.5679	0.0087	4.04E-07	2.3568
Th	0.4114	0.6983	3.25E-05	0.0411
U	0.0186	2.5430	1.18E-04	0.0019

- Number of stages was increased until percent recovery of critical REEs did not change significantly

Extraction	# of stages				
	1	2	3	4	5
REE	Fraction of REE extracted				
Y	0.8189	0.9615	0.9916	0.9981	0.9996
La	0.0064	0.0064	0.0064	0.0064	0.0064
Ce	0.0161	0.0164	0.0164	0.0164	0.0164
Pr	0.0394	0.0409	0.0410	0.0410	0.0410
Nd	0.0918	0.1001	0.1010	0.1010	0.1011
Sm	0.5141	0.6853	0.7708	0.8219	0.8559
Eu	0.1512	0.1735	0.1774	0.1780	0.1782
Gd	0.2389	0.2920	0.3072	0.3118	0.3132
Tb	0.5674	0.7520	0.8410	0.8919	0.9238
Dy	0.8663	0.9798	0.9969	0.9995	0.9999
Ho	0.4207	0.5563	0.6208	0.6570	0.6792
Er	0.6164	0.8073	0.8929	0.9375	0.9626
Tm	0.7581	0.9283	0.9776	0.9929	0.9977
Yb	0.8634	0.9788	0.9967	0.9995	0.9999
Lu	0.7021	0.8878	0.9545	0.9811	0.9920
Th	0.0395	0.0411	0.0411	0.0411	0.0411
U	0.0019	0.0019	0.0019	0.0019	0.0019
REE	Fraction of REE not extracted				
Y	0.1811	0.0385	0.0084	0.0019	0.0004
La	0.9936	0.9936	0.9936	0.9936	0.9936
Ce	0.9839	0.9836	0.9836	0.9836	0.9836
Pr	0.9606	0.9591	0.9590	0.9590	0.9590
Nd	0.9082	0.8999	0.8990	0.8990	0.8989
Sm	0.4859	0.3147	0.2292	0.1781	0.1441
Eu	0.8488	0.8265	0.8226	0.8220	0.8218
Gd	0.7611	0.7080	0.6928	0.6882	0.6868
Tb	0.4326	0.2480	0.1590	0.1081	0.0762
Dy	0.1337	0.0202	0.0031	0.0005	0.0001
Ho	0.5793	0.4437	0.3792	0.3430	0.3208
Er	0.3836	0.1927	0.1071	0.0625	0.0374
Tm	0.2419	0.0717	0.0224	0.0071	0.0023
Yb	0.1366	0.0212	0.0033	0.0005	0.0001
Lu	0.2979	0.1122	0.0455	0.0189	0.0080
Th	0.9605	0.9589	0.9589	0.9589	0.9589
U	0.9981	0.9981	0.9981	0.9981	0.9981

Extraction	# of stages				
	1	2	3	4	5
REE	Mass flow in extract after N stages				
Y	5.1031	5.9916	6.1789	6.2199	6.2289
La	0.0239	0.0240	0.0240	0.0240	0.0240
Ce	0.1392	0.1415	0.1415	0.1415	0.1415
Pr	0.0268	0.0279	0.0279	0.0279	0.0279
Nd	0.5626	0.6138	0.6189	0.6194	0.6194
Sm	0.3697	0.4927	0.5542	0.5910	0.6154
Eu	0.0180	0.0206	0.0211	0.0211	0.0212
Gd	0.1341	0.1639	0.1724	0.1750	0.1758
Tb	0.0159	0.0210	0.0235	0.0250	0.0258
Dy	0.4458	0.5042	0.5130	0.5144	0.5146
Ho	0.0709	0.0938	0.1046	0.1107	0.1145
Er	0.2281	0.2988	0.3305	0.3470	0.3562
Tm	0.0437	0.0535	0.0564	0.0572	0.0575
Yb	0.2122	0.2406	0.2450	0.2457	0.2458
Lu	0.0061	0.0077	0.0083	0.0085	0.0086
Th	0.0276	0.0287	0.0287	0.0287	0.0287
U	0.0047	0.0047	0.0047	0.0047	0.0047
Total Mass	7.4323	8.7289	9.0536	9.1617	9.2107
REE	Percent Extraction				
Y	81.89%	96.15%	99.16%	99.81%	99.96%
La	0.64%	0.64%	0.64%	0.64%	0.64%
Ce	1.61%	1.64%	1.64%	1.64%	1.64%
Pr	3.94%	4.09%	4.10%	4.10%	4.10%
Nd	9.18%	10.01%	10.10%	10.10%	10.11%
Sm	51.41%	68.53%	77.08%	82.19%	85.59%
Eu	15.12%	17.35%	17.74%	17.80%	17.82%
Gd	23.89%	29.20%	30.72%	31.18%	31.32%
Tb	56.74%	75.20%	84.10%	89.19%	92.38%
Dy	86.63%	97.98%	99.69%	99.95%	99.99%
Ho	42.07%	55.63%	62.08%	65.70%	67.92%
Er	61.64%	80.73%	89.29%	93.75%	96.26%
Tm	75.81%	92.83%	97.76%	99.29%	99.77%
Yb	86.34%	97.88%	99.67%	99.95%	99.99%
Lu	70.21%	88.78%	95.45%	98.11%	99.20%
Th	3.95%	4.11%	4.11%	4.11%	4.11%
U	0.19%	0.19%	0.19%	0.19%	0.19%
Total	25.19%	29.58%	30.68%	31.05%	31.21%
Critical REEs	47.19%	54.91%	56.48%	56.82%	56.90%
U & Th	1.00%	1.03%	1.03%	1.03%	1.03%

<u>Scrubber Mass Flows</u>	
Scrubber S/O Ratio = 3.71	
<u>Stream</u>	<u>Mass</u>
Feed (O + REE)	2157.58
Scrub Acid (4M Sulfuric Acid)	8000

<u>Scrubber</u>	Distribution Coefficient	Mass flow entering feed stage	Scrubbing Factor
REE			
Y	45.2231	6.2289	0.0820
La	0.0643	0.0240	57.7063
Ce	0.1638	0.1415	22.6401
Pr	0.4101	0.0279	9.0410
Nd	1.0106	0.6194	3.6690
Sm	10.5806	0.6154	0.3504
Eu	1.7819	0.0212	2.0809
Gd	3.1389	0.1758	1.1813
Tb	13.1164	0.0258	0.2827
Dy	64.7921	0.5146	0.0572
Ho	7.2635	0.1145	0.5105
Er	16.0694	0.3562	0.2307
Tm	31.3393	0.0575	0.1183
Yb	63.1937	0.2458	0.0587
Lu	23.5679	0.0086	0.1573
Th	0.4114	0.0287	9.0117
U	0.0186	0.0047	199.5246

5-Stage Scrubber			
Scrubber	Fraction of REE not scrubbed	Fraction of REE scrubbed	Mass REE In Scrub Acid after 5 stages
REE			
Y	0.91801	0.081990	0.5107
La	1.54E-09	1.000000	0.0240
Ce	1.61E-07	1.000000	0.1415
Pr	1.47E-05	0.999985	0.0279
Nd	0.00109	0.998905	0.6188
Sm	0.65077	0.349232	0.2149
Eu	0.01348	0.986521	0.0209
Gd	0.10557	0.894428	0.1572
Tb	0.71768	0.282323	0.0073
Dy	0.94277	0.057227	0.0294
Ho	0.49834	0.501659	0.0574
Er	0.76938	0.230624	0.0822
Tm	0.88169	0.118311	0.0068
Yb	0.94133	0.058674	0.0144
Lu	0.84269	0.157314	0.0014
Th	1.50E-05	0.999985	0.0287
U	3.15E-12	1.000000	0.0047
Mass of Scrub Acid sent to Extractor (Scrub Acid In + Scrubbed REE)			8001.9484

REE	Mass REE added to leach solution from scrubber	Mass REE sent to stripper (REE extracted - REE scrubbed)
Y	0.5107	5.7182
La	0.0240	3.69E-11
Ce	0.1415	2.27E-08
Pr	0.0279	4.11E-07
Nd	0.6188	6.78E-04
Sm	0.2149	0.4005
Eu	0.0209	2.85E-04
Gd	0.1572	0.0186
Tb	0.0073	0.0186
Dy	0.0294	0.4851
Ho	0.0574	0.0571
Er	0.0822	0.2741
Tm	0.0068	0.0507
Yb	0.0144	0.2314
Lu	0.0014	0.0073
Th	0.0287	4.30E-07
U	0.0047	1.49E-14
Total Mass	1.9484	7.2624
	(U+Th)/Total U & Th ppm	5.92E-08
		0.05917889

Stripping Mass Flows	
Stripper S/O Ratio = 1.0	
<u>Stream</u>	<u>Mass</u>
Feed (Extractant Fluid + REEs)	2155.63
Stripping Agent (dilute H ₂ SO ₄)	2155.63

<u>Stripping</u>	Distribution Coefficient	Mass flow entering feed stage	Mass fraction in feed	Stripping Factor
REE				
Y	0.01	5.7182	2.65E-03	100
La	0.01	3.69E-11	1.71E-14	100
Ce	0.01	2.27E-08	1.06E-11	100
Pr	0.01	4.11E-07	1.91E-10	100
Nd	0.01	6.78E-04	3.15E-07	100
Sm	0.01	0.4005	1.86E-04	100
Eu	0.01	2.85E-04	1.32E-07	100
Gd	0.01	0.0186	8.61E-06	100
Tb	0.01	0.0186	8.61E-06	100
Dy	0.01	0.4851	2.25E-04	100
Ho	0.01	0.0571	2.65E-05	100
Er	0.01	0.2741	1.27E-04	100
Tm	0.01	0.0507	2.35E-05	100
Yb	0.01	0.2314	1.07E-04	100
Lu	0.01	0.0073	3.36E-06	100
Th	0.01	4.30E-07	1.99E-10	100
U	0.01	1.49E-14	6.90E-18	100

<u>Stripping</u>	Fraction of REE not stripped	Fraction of REE stripped	Mass flow in stripping agent	Mass flow in recycled organic
REE				
Y	0.009901	0.990099	5.6616	0.0566
La	0.009901	0.990099	3.65E-11	3.65E-13
Ce	0.009901	0.990099	2.25E-08	2.25E-10
Pr	0.009901	0.990099	4.07E-07	4.07E-09
Nd	0.009901	0.990099	6.71E-04	6.71E-06
Sm	0.009901	0.990099	0.3965	3.97E-03
Eu	0.009901	0.990099	2.82E-04	2.82E-06
Gd	0.009901	0.990099	0.0184	1.84E-04
Tb	0.009901	0.990099	0.0184	1.84E-04
Dy	0.009901	0.990099	0.4803	4.80E-03
Ho	0.009901	0.990099	0.0565	5.65E-04
Er	0.009901	0.990099	0.2714	2.71E-03
Tm	0.009901	0.990099	0.0502	5.02E-04
Yb	0.009901	0.990099	0.2291	2.29E-03
Lu	0.009901	0.990099	7.18E-03	7.18E-05
Th	0.009901	0.990099	4.26E-07	4.26E-09
U	0.009901	0.990099	1.47E-14	1.47E-16
Total Mass			7.1905	0.0719

REE Recovery Flows	
Reaction Stoichiometry = 1:3::1:3	
<u>Stream</u>	<u>Mass</u>
Stripping Agent (H ₂ SO ₄ + REEs)	2162.82
Ammonium Carbonate	2162.82

Precipitation	Mass flow entering	Mol flow entering	Percent reacted	(REE) ₂ (CO ₃) ₃ mol flow leaving	(REE) ₂ (CO ₃) ₃ mass flow leaving
REE					
Y	5.6616	63684.9463	100%	31842.4731	11.3942
La	3.65E-11	2.63E-07	100%	1.31E-07	6.02E-11
Ce	2.25E-08	1.61E-04	100%	8.04E-05	3.70E-08
Pr	4.07E-07	2.89E-03	100%	1.44E-03	6.67E-07
Nd	6.71E-04	4.6539	100%	2.3270	1.09E-03
Sm	0.3965	2637.2691	100%	1318.6346	0.6339
Eu	2.82E-04	1.8578	100%	0.9289	4.50E-04
Gd	0.0184	116.8557	100%	58.4278	0.0289
Tb	0.0184	115.5901	100%	57.7950	0.0288
Dy	0.4803	2955.7557	100%	1477.8778	0.7464
Ho	0.0565	342.5001	100%	171.2500	0.0873
Er	0.2714	1622.0747	100%	811.0374	0.4174
Tm	0.0502	297.3321	100%	148.6661	0.0770
Yb	0.2291	1323.7728	100%	661.8864	0.3482
Lu	7.18E-03	41.0399	100%	20.5200	0.0109
Th	4.26E-07	1.83E-03	100%	9.17E-04	5.91E-07
U	1.47E-14	6.19E-11	100%	3.09E-11	2.03E-14

Calcination	(REE) ₂ O ₃ Mol Flow	(REE) ₂ O ₃ Mass Flow
REE		
Y	31842.4731	7.1900
La	1.31E-07	4.28E-11
Ce	8.04E-05	2.64E-08
Pr	1.44E-03	4.76E-07
Nd	2.3270	7.83E-04
Sm	1318.6346	0.4598
Eu	0.9289	3.27E-04
Gd	58.4278	0.0212
Tb	57.7950	0.0211
Dy	1477.8778	0.5512
Ho	171.2500	0.0647
Er	811.0374	0.3103
Tm	148.6661	0.0574
Yb	661.8864	0.2608
Lu	20.5200	8.17E-03
Th	9.17E-04	4.70E-07
U	3.09E-11	1.62E-14
Total	36571.8265	8.9459
Critical REEs	33381.4019	7.7635
(U+Th)/Total		5.25E-08
U&Th ppm		0.052486

- Molar mass (g/mol) of recovery step reaction streams for reference

REE	MW REE	MW R-Carb	MW R-Oxide
Y	88.9	357.83	225.8
La	138.9	457.83	325.8
Ce	140.116	460.262	328.232
Pr	140.9	461.83	329.8
Nd	144.242	468.514	336.484
Sm	150.36	480.75	348.72
Eu	151.964	483.958	351.928
Gd	157.25	494.53	362.5
Tb	158.9	497.83	365.8
Dy	162.5	505.03	373
Ho	164.93	509.89	377.86
Er	167.295	514.62	382.59
Tm	168.9	517.83	385.8
Yb	173.04	526.11	394.08
Lu	174.967	529.964	397.934
Th	232.038	644.106	512.076
U	238.029	656.088	524.058

Appendix B. Cost Information

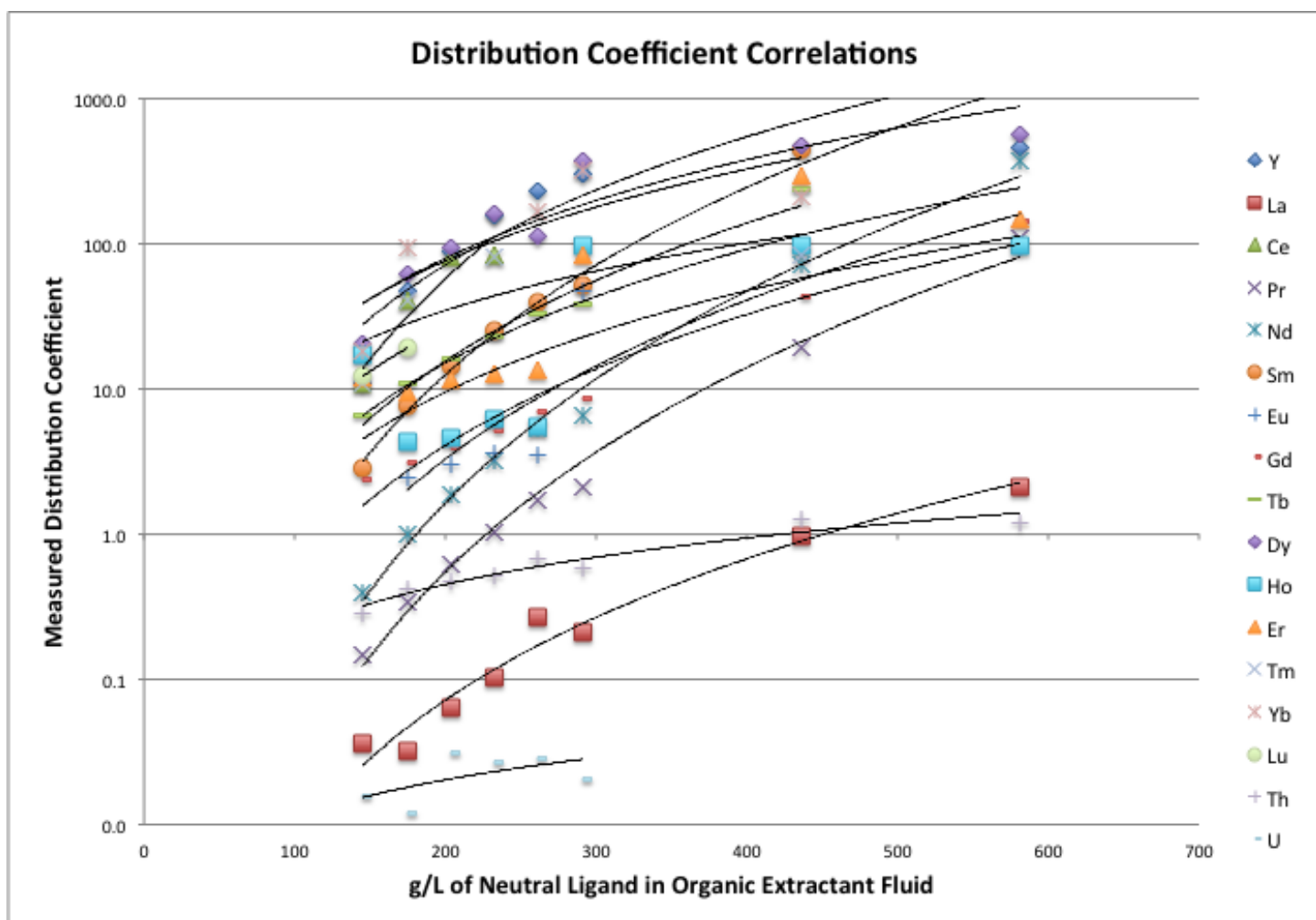
Revenue Analysis	REO Mass Flow (kg)	REO Distribution Ratio	Average \$/kg REO	Maximum Potential Revenue	% of Revenue
REE					
Y	7190.0304	0.3067	\$61.50	\$442,186.87	66.79%
La	negligible	1.83E-12	n/a	n/a	
Ce	negligible	1.12E-09	n/a	n/a	
Pr	negligible	2.03E-08	n/a	n/a	
Nd	0.7830	3.34E-05	\$81.00	\$63.42	0.01%
Sm	459.8342	1.96E-02	\$34.00	\$15,634.36	2.36%
Eu	0.3269	1.39E-05	\$595.00	\$194.51	0.03%
Gd	21.1801	9.03E-04	\$44.50	\$942.51	0.14%
Tb	21.1414	9.02E-04	\$605.00	\$12,790.56	1.93%
Dy	551.2484	2.35E-02	\$295.00	\$162,618.29	24.56%
Ho	64.7085	2.76E-03	unknown	n/a	
Er	310.2948	1.32E-02	\$89.00	\$27,616.24	4.17%
Tm	57.3554	2.45E-03	unknown	n/a	
Yb	260.8362	1.11E-02	unknown	n/a	
Lu	8.1656	3.48E-04	unknown	n/a	
Total	8945.91	0.3816		\$662,046.76	

Stream	Mass	Cost per Unit	Annual Cost	Initial Cost	Notes
Strong Sulfuric Acid	12510 tonnes	317 \$/tonne	\$3,971,539	\$3,971,539	none recycled
Weak Sulfuric Acid	108 tonnes	317 \$/tonne	\$3,422.20	\$34,222	recycled with 10% loss per year
Organic Solvent	2148 tonnes	43 \$/kg	\$9,215,300	\$92,153,000	recycled with 10% loss per year
Ammonium Carbonate	75000 kg	0.37 \$/kg	\$27,778	\$27,778	100% reacted
Total Cost			\$13,218,039		

Sand Group		
Sulfuric acid	\$	4,000,000
Water	\$	550,000
Organic solvent annual	\$	9,215,000
Ammonium Carbonate	\$	27,777
Utilities	\$	200,000
Labor	\$	500,000
Total Yearly Cost	\$	14,492,777
Capital costs		
Solvent	\$	92,153,757
Plant Equipment	\$	13,600,000
Total Capital	\$	105,753,757
Expected mixed REE Yield		8945.91 kg/yr
Price of REE for 10% annual profit	\$	1,782.05 \$/kg

Appendix C. Miscellaneous Tables and Figures

- Distribution Coefficient Raw Laboratory Data



- Distribution Coefficient Power Law Models based on raw data

Power Law Models		D for various g/L N				
		10 g/L	50 g/L	150 g/L	180 g/L	187 g/L
Y	$y = 1E-05x^{2.9295}$	8.50E-03	9.49E-01	23.7061	40.4409	45.2231
La	$y = 3E-09x^{3.2268}$	5.06E-06	9.11E-04	0.0315	0.0568	0.0643
Ce	$y = 6E-11x^{4.1535}$	8.54E-07	6.84E-04	0.0655	0.1398	0.1638
Pr	$y = 1E-11x^{4.6715}$	4.69E-07	8.64E-04	0.1464	0.3432	0.4101
Nd	$y = 1E-11x^{4.8435}$	6.98E-07	1.70E-03	0.3474	0.8401	1.0106
Sm	$y = 2E-09x^{4.28}$	3.81E-05	3.74E-02	4.1181	8.9866	10.5806
Eu	$y = 1E-08x^{3.6318}$	4.28E-05	1.48E-02	0.8001	1.5513	1.7819
Gd	$y = 5E-07x^{2.9922}$	4.91E-04	6.06E-02	1.6228	2.8002	3.1389
Tb	$y = 9E-07x^{3.1532}$	1.28E-03	2.05E-01	6.5448	11.6297	13.1164
Dy	$y = 0.0005x^{2.2504}$	8.90E-02	3.3291	39.4499	59.4614	64.7921
Ho	$y = 4E-05x^{2.3149}$	8.26E-03	3.43E-01	4.3601	6.6495	7.2635
Er	$y = 2E-05x^{2.5992}$	7.95E-03	5.21E-01	9.0600	14.5524	16.0694
Tm	$y = 0.0099x^{1.5408}$	3.44E-01	4.1059	22.3129	29.5501	31.3393
Yb	$y = 0.0011x^{2.0949}$	1.37E-01	3.9863	39.8186	58.3395	63.1937
Lu	$y = 8E-05x^{2.4074}$	2.04E-02	9.84E-01	13.8616	21.4997	23.5679
Th	$y = 0.0016x^{1.0609}$	1.84E-02	1.02E-01	0.3256	0.3951	0.4114
U	$y = 0.0002x^{0.8663}$	1.47E-03	5.93E-03	0.0154	0.0180	0.0186

- Capital Cost Summary

TABLE 5-5 CAPITAL COST SUMMARY**

Date to which estimate applies: 04/24/2015

Page 1 of 1

Job title: Amine REE Recovery Process

Location: University of Tennessee

Capacity: _____

By: Group 1

Date: 04/24/2015

CHE Ind = 558.2

Equipment Identification		Number	Equipment Specifications	Purchased Equipment Cost (base material)		Base Bare Module Factor, F _{BM}	Base Bare Module Cost, C _{BM} (\$k)	Material Factor, F _M	Pressure or other Factors, F _p	Actual Bare Module Factor, F _{BM}	Actual Bare Module Cost, C _{BM} (\$k)	Total	
				Year 2004 (\$k)	Target Year*(\$k)								
Process Vessels													
Extraction Unit	U-100	Vertically Oriented, 2.7 m Length, 1.55 m Diameter		\$143.0	\$199.56	2.5	498.9	1.0	1.0	2.5	\$498.9	\$7,694,485	
Stripping Unit	U-101	Vertically Oriented, 0.93 m Length, 1.63 m Diameter		\$219.3	\$306.05	2.5	765.1	1.0	1.0	2.5	\$765.1		
Scrubbing Unit	U-102	Vertically Oriented, 0.78 m Length, 1.22 m Diameter		\$180.0	\$251.19	2.5	628.0	1.0	1.0	2.5	\$628.0		
Calcinator	U-103	Heat Duty = 45,096 kJ/s		\$1,980.0	\$2,763.09	2.1	5802.5	1.0	1.0	2.1	\$5,802.5		
Tower Total													
Mixers													
Leaching Agitator	M-100	Intense Mixing, Open Tank, 2 kW/hr		\$5.0	\$6.98	2.5	17.4	1.0	1.0	2.5	\$17.4	\$108,151	
Leaching Tank	M-101	Vertically Oriented, 3.1 m Length, 1.77 m Diameter		\$17.0	\$23.72	2.5	59.3	1.0	1.0	2.5	\$59.3		
Carbonation M/S Agitator	M-102	Intense Mixing, Open Tank, 0.3 kW/hr		\$4.0	\$5.58	2.5	14.0	1.0	1.0	2.5	\$14.0		
Carbonation M/S Tank	M-103	Vertically Oriented, 1.5 m Length, 0.86 m Diameter		\$5.0	\$6.98	2.5	17.4	1.0	1.0	2.5	\$17.4		
Total Mixers													
Separators													
Shaking Table	F-110	Process 600 m-ton/hr		\$89.0	\$124.20	2.5	310.5	1.0	1.0	2.5	\$310.50	\$1,023,599	
Flotation Unit	F-122	Process 19.7 m-ton/hr		\$146.0	\$203.74	3.5	713.1	1.0	1.0	3.5	\$713.10		
Total Separators													
Pump													
Pump 1	P-100	Carbon Steel, 10 kW, Centrifugal		\$9.0	\$12.98	1.0	13.0	1.0	1.0	1.0	\$12.98	\$64,913	
Pump 2	P-101	Carbon Steel, 10 kW, Centrifugal		\$9.0	\$12.98	1.0	13.0	1.0	1.0	1.0	\$12.98		
Pump 3	P-102	Carbon Steel, 10 kW, Centrifugal		\$9.0	\$12.98	1.0	13.0	1.0	1.0	1.0	\$12.98		
Pump 4	P-103	Carbon Steel, 10 kW, Centrifugal		\$9.0	\$12.98	1.0	13.0	1.0	1.0	1.0	\$12.98		
Pump 5	P-104	Carbon Steel, 10 kW, Centrifugal		\$9.0	\$12.98	1.0	13.0	1.0	1.0	1.0	\$12.98		
Total Pumps													
Total bare module cost				Base materials, C _{TBM} = Σ C _{BM} =				\$3,024					\$8,826,235
Contingency and fee				Total Module Costs =				\$1,885					\$1,588,722
Total module cost													\$10,414,958
Auxiliary (offsite) Facilities													\$3,124,487
Grass Roots capital													\$13,539,445