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Extraction of ThO₂ From Monazite Ore

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April 24, 2019

Dr. Robert Counce

CBE 488

University of Tennessee

Dear Dr. Counce,

We have attached a report entitled *Production of Thorium Oxide from Extracted Monazite Ore* that we will be submitted accordingly.

Our report investigates both the capital cost and the manufacturing cost of a process involving the production of thorium oxide from monazite ore extracts through a study-level process design.

Sincerely,

Group 9 (Brian Grim, Kevin Harricharran, Sidharth Mahajan, and Maggie Mann)

Honors Design in Green Engineering

University of Tennessee

Knoxville, Tennessee

Enclosure: Final Report

Draft Report on:

Production of Thorium Oxide from Extracted Monazite Ore

Submitted to:

Dr. R. M. Counce

Department of Chemical Engineering

University of Tennessee

Prepared by:

Brian Grim, Kevin Harricharran, Sidharth Mahajan, Maggie Mann

CBE 488: Honors Design Internship in Green Engineering

Submitted:

April 24, 2019

Chemical and Biomolecular Engineering Department

University of Tennessee

Dougherty Engineering Building

1331 Circle Park Drive SW, Knoxville, TN, 37916

Summary:

Process Goals:

The primary objective of our study level process design was to devise a method for the production of thorium oxide from monazite ore extracts while also accommodating environmental and safety considerations. Primary concerns for safety included process operation conditions such as temperature, pressure, and pH. For environmental conditions, dangerous wastewater conditions were mitigated as much as possible, and radioactive material was separated during processing.

Capital Cost:

After considering the sizing, material, and type of equipment for our process, we calculated a capital cost of approximately **\$17,033,000**. This estimate includes both equipment and wastewater treatment costs.

Manufacturing Cost:

Due to the significant profitability of the rare earth element oxide byproducts, the total manufacturing expense was calculated at an estimated **-\$21,550,000** (meaning an annual earnings of \$20.4 million). The calculated net annual profit after taxes was **\$46,920,000**, and the calculated after tax rate of return was **359.28%**.

Conclusion:

Overall, these numbers show significant promise for a profitable thorium oxide production process that takes both safety and environmental factors into consideration. Throughout the flowsheet construction and design process, high process temperatures and high steam pressures were minimized to limit hazardous conditions. However low stream pH values present a challenge to operator and engineer safety. Regardless, given the rudimentary nature of a study-level process design, significant progress has been made in determining a process that meets all of the previously stated goals.

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1.0 Introduction

In the following report the study level design of extracting thorium oxide from monazite ore was explored. This was accomplished using the simulation software of OLI Flowsheet. An acid catalyzed method was used in which monazite ore was treated with sulfuric acid. Once the monazite ore is treated with sulfuric acid, thorium was processed, using various process equipments, into its most economically viable form of thorium oxide. Thorium oxide is a valuable product that has applications in areas such as nuclear fuels, catalysis, and glass manufacturing. Rare earth elements from the monazite ore such as Neodymium, Lanthanum, and Cerium were also processed into their subsequent oxide forms to maximize process production value.

For this design project, we fed 1000 kilograms per hour of monazite ore, and our objective was to recover 90% by mass of thorium oxide while focusing on pollution prevention and process safety. The general goal of the manuscript is to provide baseline information regarding processing challenges, safety considerations, and intermediate economic analysis. A ChE index of 616 was used in doing all economic analysis calculations.

Contributions to this study level design were made by the department of Chemical and Biomolecular Engineering at the University of Tennessee, Knoxville and Electric Power Research Institute.

2.0 Synthesis Information for Processes

2.1 Overall Process Schematic

Thorium oxide production was achieved by separation and purification from mined monazite ore. Once the monazite ore is mined, it is leached with sulfuric acid to

break apart thorium and REE's into their respective phosphates. In order to mitigate extreme temperatures, the stream is flashed and cooled. After continuous filtration to remove the solid thorium sulfate and silicon dioxide, two separate processes occur to recover thorium oxide and REE oxides. As can be seen in Figure 2.1, the thorium oxide recovery process is as follows: (1) React thorium sulfate/silicon dioxide mixture with ammonium hydroxide to produce thorium oxide. (2) Filter out waste water and ammonium from reaction. (3) Solubilize silicon dioxide with sodium hydroxide. (4) Filter out silicon dioxide. Additionally, the REE recovery process is as follows: (1) React REE sulfates with sodium hydroxide to add hydroxyl groups. (2) Filter out waste water and excess sodium hydroxide. (3) Calcine REE hydroxides to produce REE oxides. The 2 processes are outlined below:

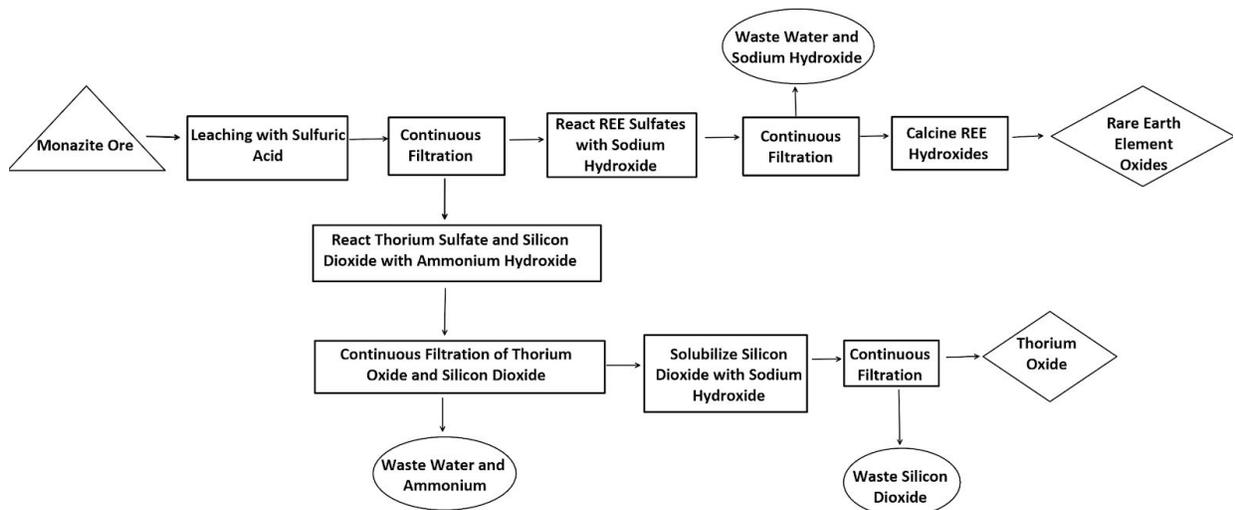
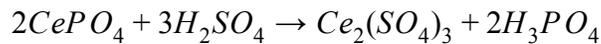
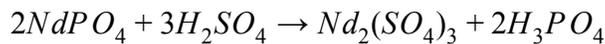
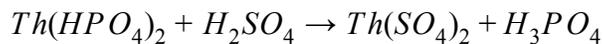
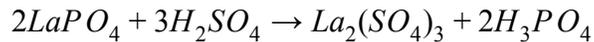


Figure 2.1: Thorium Oxide and REE Oxide Recovery Process

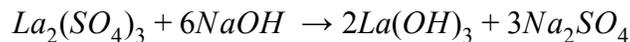
2.2 Process Chemistry

The process for producing thorium oxide and rare earth oxides from monazite ore is described through the reactions below. The process begins by thorium phosphate and the rare earth phosphates from the monazite ore reacting with sulfuric acid to produce thorium sulfate and rare earth sulfates. Thorium sulfate is then reacted with ammonium hydroxide to form thorium hydroxide and the rare earth silicates are reacted with sodium hydroxide to form rare earth hydroxides. Thorium hydroxide and the rare earth hydroxides are then calcined to complete the process where thorium oxide and the rare earth oxides are formed.

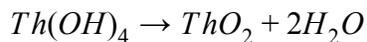
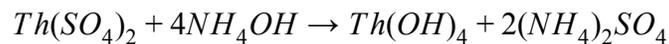
Reactor 1



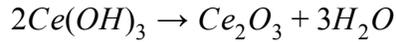
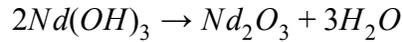
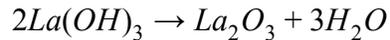
Reactor 2/ Reactor 4



Reactor 3



Calciner



2.3 Literature Summary

Isyatun Rodliyah, S. R., Tatang Wahyudi. (2015). Extraction of Rare Earth Metals from Monazite Mineral Using Acid Method. *Indonesian Mining Journal*, 18, 39-45.

The purpose of this study was to determine the extent to which rare earth elements could be extracted from monazite using the acid method. In the experiment, monazite was first leached with sulfuric acid under pressure. Thorium was then precipitated out using ice. The remaining rare earth elements were treated with sodium hydroxide to convert them to the hydroxide form. They were then run through a calciner to convert them into rare earth oxides. During the experiment, leaching temperature, solvent concentration, and length of dissolving time were all varied. The study found that the greatest rare earth element extraction occurred when the volume ratio of sulfur acid to water was 1 to 2. It was also found that the extraction was greatest when the leaching temperature was 220 C and the leaching duration was 150 minutes.

John Demol, E. H., Gamini Senanayake. (2018). Sulfuric acid baking and leaching of rare earth elements, thorium and phosphate from a monazite concentrate: Effect of bake temperature from 200 to 800 °C. *Hydrometallurgy*, 179, 254-267.

The purpose of this study is to gain a further understanding of the chemistry that occurs during the sulfuric acid baking of monazite and how baking temperature affects the dissolution of rare earth elements during leaching. The acid bake experiments were

performed in a furnace, and the temperature ranged from 200 and 800 degrees Celsius. The weight of monazite used was 20 grams, and the amount of sulfuric acid was kept constant at 250% of the stoichiometric amount needed. The baked monazite samples were then cooled and ground before leaching. Monazite was leached with sulfuric acid at a ratio of 40 to 1 sulfuric acid to monazite. The study found that between 200 and 300 degrees Celsius that the leaching of rare earth elements was maximized. Between 400 and 500 degrees Celsius, the extraction of rare earth elements decreased, and between 600 and 800 degrees Celsius, the monazite started to reform. It was also found that the reaction between sulfuric acid and monazite was complete after two hours at 250 C.

Loren Berry, Vivek Agarwal, Jennifer Galvin & M. Sadegh Safarzadeh (2018) Decomposition of monazite concentrate in sulphuric acid. *Canadian Metallurgical Quarterly*, 57(4), 422-433.

The goal of this study was to examine the bake-leach process of monazite with sulfuric acid and the effects baking on the extraction of rare earth elements, uranium and thorium from monazite during leaching. Five grams of monazite were used in the baking experiments, and baking was carried out in a muffle furnace. The temperature and duration of baking were varied along with the ratio of sulfuric acid to monazite concentrate. After baking, the monazite was then leached in a 500 mL beaker. The temperature and duration of leaching were kept constant at 70 C and 30 min. The study found that nearly full extraction of rare earth elements, uranium, and thorium was possible at a bake temperature of 250 C and a bake duration of four hours with a sulfuric acid to monazite concentrate ratio of 4 to 1. Changes in temperature between 180 and 250 C had a minimal effect on the extraction of rare earth elements. However,

it was also found that the amount of thorium and uranium extracted from monazite decreased with increasing bake temperatures.

Barry Perlmutter. Comparison of Gypsum Dewatering Technologies at Flue gas Desulfurization Plants. *Presented at the 45th ISA Power Industry Division (POWID) Conference San Diego, California on June 2-7, 2002.*

This paper provides a review of three possible filtration techniques for the filtration of gypsum in flue gas desulfurization plants. The review includes analysis of utilities and maintenance required for each technique as well as analysis of performance. There are two types of vacuum filtrations: continuous belt filters (CBF) and continuous-indexing belt filters (CI-BF). One of the main differences between CBF and CI-BF is that CBF requires a rubber belt, which must be cooled continuously with water. This increases the water needed in the plant. The CI-BF has a longer filter cloth life than CBF, and CI-BF uses pneumatics instead of a motor, so it requires less energy. Another big difference between CBF and CI-BF is that CBF uses continuous washing, while CI-BF uses intermittent washing that is controlled by a residence time. The benefits of intermittent washing are that the residence time can be altered, and a smaller amount of water is required. The other technique used in filtration is vertical basket centrifuges. This technique runs on a batch basis with a typical batch time at 8 to 10 minutes. A major benefit of vertical basket centrifuges is that it produces a dry cake. However, it requires high maintenance due to rotation speeds. The review study found that out of the three techniques, CI-BF is the best option because it requires the least maintenance and the least amount of water.

Farzaneh Sadri, F. R., Ahmad Amini (2017). Hydrometallurgical digestion and leaching of Iranian monazite concentrate containing rare earth elements Th, Ce, La and Nd. *International Journal of Mineral Processing*, 159, 7-15.

This paper examines the effects of temperature and time on a three step procedure for the removal of rare earth elements from monazite. The three steps outlined in this paper are acidic digestion, leaching, and precipitation. The acidic digestion was done using sulfuric acid and 3 grams of monazite. The temperature of digestion was varied at 200, 225, and 250 C. The ratio of sulfuric acid to monazite was varied between 1, 1.75, and 2.5. Lastly, the length of acid digestion was varied between 1, 3.5, and 6 hours. The acid digestion experiments found that the optimal conditions for digestion are a temperature of 225 C, a sulfuric acid to monazite ratio of 2.5, and a duration of 3.5 hours. Leaching was also performed under three temperatures of 25, 50, and 75 C. The duration of leaching was varied between 5, 10, and 15 hours, and the ratio of water to solid was varied between 5, 7.5, and 10. The experiment found that the optimal conditions for leaching are a temperature of 75 C, a duration of 15 hours, and a water to solid ratio of 7.5. All precipitation was done for 30 minutes using oxalic acid at an acid to solid ratio of 1 to 1. The precipitate was then run through a calciner at 800 C for 1 hour. The final purity of the rare earth oxides was 84%.

2.4 Basic Process Economics

One objective of this study is to determine the economic potential of removing rare earth elements from monazite ore and converting them to oxides. The economic analysis performed takes into account the cost of products, byproducts and raw

materials as well as equipment and operational costs. The costing information used for products, raw materials, and energy is shown in Table 2.1 below.

Cost Assumptions	
Material	Cost/Unit
Monazite Concentrate	\$1.00/kg
H ₂ SO ₄	\$0.04/kg
HNO ₃	\$0.4/kg
ThO ₂	\$80.00/kg
La ₂ O ₃	\$2.00/kg
CeO ₂	\$2.00/kg
Nd ₂ O ₃	\$60.00/kg
NaOH	\$0.35/kg
NH ₄ OH	\$0.2/kg
Natural Gas	\$4.40 /GJ

Table 2.1: Cost of Materials

3.0 Method of Approach

3.1 Sustainability, Environmental, and Worker Safety

The major reason for thorium oxide production stems from the necessity of a fertile alternative to uranium alone for nuclear power. When reacted in conjunction with uranium in a thermal breeder reactor, the excess neutrons produced can be reused in the initial fuel mixture. This significantly reduces the amount of fuel required for nuclear energy production. Additionally, thorium is a much more abundant resource than uranium. Although thermal breeder reactors are a developing technology, their potential as a more sustainable method for nuclear energy extraction demands a viable method for thorium oxide extraction. Regarding environmental safety, the most concerning aspect of nuclear energy production involves the production of atoms larger than uranium (also known as transuranic atoms). Thorium oxide processing in thermal

breeder reactors avoids transuranic atom production altogether. Regarding the process of thorium oxide extraction from monazite ore, there is a significant environmental and worker safety risk associated with the radioactivity of thorium. The rare earth elements are toxic to humans, and the strong acids and bases utilized throughout the process (like sulfuric acid and sodium hydroxide) can significantly irritate and even burn workers if they aren't wearing proper personal protective equipment. Furthermore, plant design should be optimized for worker safety. A more comprehensive outline of the hazards of the raw materials are presented in the stream hazards chart in Appendix F. The design has been optimized by allowing extra space in the equipment to prevent splashing as well as having sturdy materials of construction that can handle the high levels of corrosivity. There is also comprehensive tertiary treatment wastewater plant that will keep harmful waste from the environment and the workers. There is also endothermic flaring and flue gas cleaning on the vapor outlet of the flash tank such that harmful vapors are not released to the environment. Worker safety will also depend on safety training modules and simulation training that will be mandated for all employees.

3.2 Product Quality

A main objective in designing the process was to recover at least 90% by mass of thorium oxide. The process was designed in order to maximize the product quality of thorium oxide as well as the byproduct quality of REE oxides. Achieving this level of product quality allows us to use the values for thorium oxide and REE oxides cited in Table 2.1. This constraint affected the design of the flowsheet and choice of equipment.

4.0 Results

4.1 Capital Cost Estimates

The design of each piece of equipment used in the process is detailed in Appendix E. The equipment was sized based on the mass balance of the process given by OLI Flowsheet. All mass flow rates from OLI Flowsheet are presented Appendix C. These pieces of equipment were given 25 percent more volume than the minimum volume to contain the material. This was done a safety measure to protect against minor fluctuations in time throughout the process. The costs of these pieces of equipment were estimated using the capital cost estimation charts in Ulrich. The total capital cost for this grass root plant is \$17.03 million as can be seen in Capital Cost Summary in Figure D.1 in Appendix D . Example costing calculations for each type of equipment can be found in Appendix B. The distribution of these costs are shown in Figure 4.1.

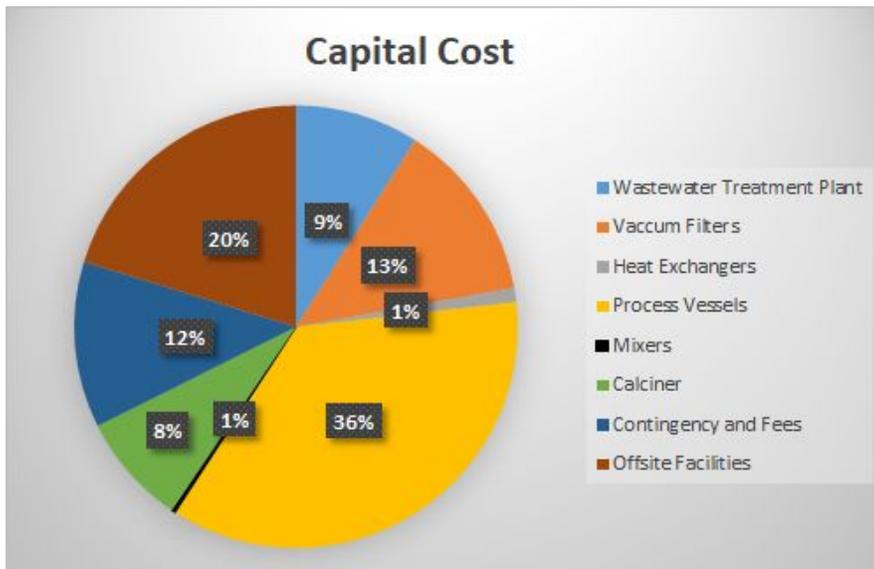


Figure 4.1: Capital Cost Distribution

4.2 Manufacturing Cost Estimates

Manufacturing costs were calculated using equations provided by Ulrich. Overall general expenses were not included in Figure 4.2 because the value was negative (indicating net monetary gain as opposed to expense). In a similar fashion, the total manufacturing cost was determined to be -\$20,459,064.63. The negative magnitude is emblematic of a manufacturing process that earns approximately 20 million dollars annually after counting expenses alone. The primary reason for this negative value is based on byproducts credits earned from selling rare earth element oxide byproducts in addition to thorium oxide. These byproducts alone generate over 40 million dollars of revenue annually. The revenue generated from the sales of thorium oxide alone is \$37.84 M a year. Combining the total revenue from sales as well as the total manufacturing expenses gives a net profit of \$46.92 M per year. The calculations for manufacturing costs are shown in Figure D.2 in Appendix D.

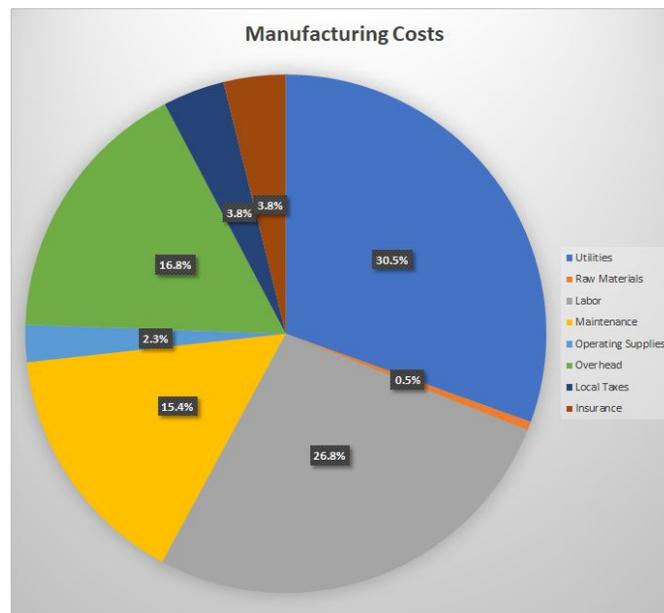


Figure 4.2: Annual Manufacturing Expense Distribution

5.0 Discussion of Results

The extraction of thorium oxide and rare earth oxides seems to be very profitable as determined by this study level analysis. The total profit of the process on a yearly basis is \$46.92 M a year while only having \$17.03 M in capital costs. This gives an net annual rate of return after taxes of 359%. This level of economic prosperity may not be entirely accurate given the scope and assumptions of the analysis, however the economic potential of this process seems to be very favorable.

6.0 Conclusion

Overall, these economic numbers show significant promise for a profitable thorium oxide production process with an annual rate of return after taxes of 359 %. This design also takes both safety and environmental factors into consideration by effective wastewater treatment and proper equipment design. Throughout the flowsheet construction and design process, high process temperatures and high steam pressures were minimized to limit hazardous conditions in order to promote worker safety. However, low and high stream pH values present a challenge to operator and engineer safety. This study level design is rudimentary in nature, however; significant progress has been made in determining a potential process that meets all of the previously stated goals.

7.0 Recommendations

The scope of this study level design with all of the given assumptions, are a beginning to understanding the feasibility of this process. However, the assumptions listed in Appendix A require that this design deviates from reality. In order to further progress the study of this potential process, these assumptions need to be more closely related to reality. The filtration system must further be studied to have a more accurate efficiency and not a perfect 100 percent. The heat exchangers must be studied more closely with heat transfer coefficients that more closely resemble the actual heat transfer coefficient of the fluids involved with the process. There must also be a closer look into the amount of operators needed to run this potential plant in an efficient manner. There must also be more rigorous estimations of the amount of downtime that will inevitably occur in the plant as equipment fails. Another major factor that needs to further studied is the kinetic parameters of the system. This design was created using OLI Flowsheet which calculates an equilibrium for each piece of equipment. The kinetics for each piece of equipment may drastically influence the design of this process and thus needs more rigorous study. The kinetic and thermodynamic parameters of the calciner must also be further analyzed because this piece of equipment was not available in OLI. This further level of analysis can be accomplished by further laboratory work as well as in the future building a small pilot plant.

The pH of this process must also be tempered in order to ensure process safety. One proposed method is to use a specific type of biological catalyst (enzyme) that is capable of removing phosphate groups. These enzymes are called phosphatases, and

although no known phosphatase is capable of carrying out the dephosphorylation reaction of monazite ore components, designing one could result in a significant increase in productivity and safety. Lower pH streams would be eradicated since they would no longer be necessary to remove phosphate groups from thorium and rare earth elements.

8.0 References

1. Ulrich, G. D. (2004). *Chemical Engineering Process Design and Economics: A Practical Guide* (Second ed.). Durham, New Hampshire: Process Publishing. Print.
2. John Demol, E. H., Gamini Senanayake. (2018). Sulfuric acid baking and leaching of rare earth elements, thorium and phosphate from a monazite concentrate: Effect of bake temperature from 200 to 800 °C. *Hydrometallurgy*, 179, 254-267.
3. Loren Berry, Vivek Agarwal, Jennifer Galvin & M. Sadegh Safarzadeh (2018) Decomposition of monazite concentrate in sulphuric acid. *Canadian Metallurgical Quarterly*, 57(4), 422-433.
4. Farzaneh Sadri, F. R., Ahmad Amini (2017). Hydrometallurgical digestion and leaching of Iranian monazite concentrate containing rare earth elements Th, Ce, La and Nd. *International Journal of Mineral Processing*, 159, 7-15.
5. Barry Perlmutter. Comparison of Gypsum Dewatering Technologies at Flue gas Desulfurization Plants. *Presented at the 45th ISA Power Industry Division (POWID) Conference San Diego, California on June 2-7, 2002.*

Appendix A: Project Assumptions

- Filtration was assumed in which the efficiency of all filters is thought to be 100%
- Liquid on the cold of the heat exchangers have a similar overall heat transfer coefficient to water and brines
- 5 operators are needed to run a piece of equipment continuously but only needs to have a third of their attention
- Operator of salary increases by 3% every year
- The reactions all have enough time to reach equilibrium for each piece of equipment
- The rare earth hydroxides react completely in C-230 giving only the respective rare earth oxides as well as water
- Production process has a 24/7/365 runtime (no downtime)

Appendix B: Sample Calculations

B.1: Reactor Costing Sample Calculations

Reactor 2:

From OLI Flowsheet : $Q = 7.2563 \text{ m}^3/\text{hr}$

$\tau = 3 \text{ hr}$

$V = Q * \tau * 1.25 = (7.2563 \text{ m}^3/\text{hr})(3 \text{ hr})(1.25) = 27.2111 \text{ m}^3$

$D = (V/\pi)^{1/3} = (27.2111 \text{ m}^3/\pi)^{1/3} = 2.05 \text{ m}$

$L = 4 * D = 4 * 2.05 \text{ m} = 8.21 \text{ m}$

From Ulrich 2004 Figure 5.44 : $C_p = \$65,161$

From Ulrich 2004 Figure 5.45 ($p = 1 \text{ barg}$) : $F_p = 1$

For Carbon Steel Base with PTFE lining : $F_m = 5$

$F_m * F_p = 5 * 1 = 5$

From Ulrich 2004 Figure 5.46 (vertical orientation) : $F_{BM}^a = 11$

$C_{BM} =$

$F_{BM}^a * C_p * (\text{ChE Index 2018}/\text{ChE Index 2004}) = 11 * \$65,161 * (616/400) = \$1,087,699$

B.2: Mixers Costing Sample Calculations

Mixer 2:

From OLI Flowsheet : $Q = .157 \text{ m}^3/\text{hr}$

$\tau = 3 \text{ hr}$

$V = Q * \tau * 1.25 = (.157 \text{ m}^3/\text{hr})(3 \text{ hr})(1.25) = .58875 \text{ m}^3$

$D = (V/\pi)^{1/3} = (.58875 \text{ m}^3/\pi)^{1/3} = .5722 \text{ m}$

From Ulrich 2004 Figure 5.41 : $C_p = \$75,000$

From Ulrich 2004 Figure 5.41 (Stainless Steel) : $F_{Bm} = 2.9$

$C_{BM} =$

$$F_{Bm} * C_p * (ChE Index 2018/ChE Index 2004) = 2.9 * \$75,000 * (616/400) = \$33,005$$

B.3: Flash Tank Costing Sample Calculations

From OLI Flowsheet : $Q = 749.7 \text{ m}^3/\text{hr}$

$\tau = .01 \text{ hr}$

$$V = Q * \tau * 1.25 = (749.7 \text{ m}^3/\text{hr})(.01 \text{ hr})(1.25) = 9.37 \text{ m}^3$$

$$D = ((4/5)(V/\pi))^{1/3} = ((4/5)(9.37 \text{ m}^3/\pi))^{1/3} = 2.866 \text{ m}$$

$$L = 5 * D = 5 * 2.866 \text{ m} = 14.33 \text{ m}$$

From Ulrich 2004 Figure 5.44 : $C_p = \$88,387$

From Ulrich 2004 Figure 5.45 ($p = 1 \text{ barg}$) : $F_p = 1$

For Carbon Steel Base with PTFE lining : $F_m = 5$

$$F_m * F_p = 5 * 1 = 5$$

From Ulrich 2004 Figure 5.46 (vertical orientation) : $F_{BM}^a = 11$

$C_{BM} =$

$$F_{BM}^a * C_p * (ChE Index 2018/ChE Index 2004) = 11 * \$88,387 * (616/400) = \$1,497,275$$

B.4 Heat Exchanger Costing Sample Calculations:

Heat Exchanger 1:

From OLI Flowsheet : $Q = \text{Amount of heat generated} = 5.18 * 10^8 \text{ cal/hr}$

$$(5.18 * 10^8 \text{ cal/hr})(4.18 \text{ J/cal}) = 2.16 * 10^9 \text{ J/hr}$$

From OLI Flowsheet : $\Delta T = 115 \text{ K}$

From Ulrich 2004 Figure 4.15a Water + Brine Cold Side : $U = 900 \text{ J/m}^2 - \text{K}$

$$Q = UA\Delta T$$

$$A = Q/UA\Delta T = (2.16 * 10^9 \text{ J/hr})/(900 \text{ J/m}^2 - \text{K})(115 \text{ K}) = 5.42 \text{ m}^2$$

From Ulrich 2004 Figure 5.36 (Multiple double - pipe) : $C_p = \$6,478$

From Ulrich 2004 Figure 5.36 (Titanium) : $F_m = 12$

From Ulrich 2004 Figure 5.37 ($p = 1 \text{ barg}$) : $F_p = 1$

$$F_p * F_m = 1 * 12 = 12$$

From Ulrich 2004 Figure 5.38 : $F_{BM}^a = 17.5$

$$C_{BM} =$$

$$F_{BM}^a * C_p * (\text{ChE Index 2018/ChE Index 2004}) = 17.5 * \$6,478 * (616/400) = \$172,031$$

B.5 Filter Costing Calculations

Filter 1:

Solids Handling Rate from Coulson and Richardson's Chemical Engineering Vol. 2 = .03 kg dry solids per m²-s

Stream Mass Flow Rate entering filter = 101.67 kg/hr = .0282 kg/s

$$A = \text{Stream Mass Flow Rate entering filter} / \text{Solids Handling Rate} = .0282 \text{ kg/s} / .03 \text{ kg/m}^2 - \text{s} = .941 \text{ m}^2$$

From Ulrich 2004 Figure 5.57b (Vacuum) : $C_p = \$57,000$

For Carbon Steel Base with PTFE Lining : $F_m = 5$

$$C_{BM} = F_m * C_p * (\text{ChE Index 2018/ChE Index 2004}) = 5 * \$57,000 * (616/400) = \$438,900$$

B.6 Wastewater Manufacturing Treatment Calculations

Waste 2 Stream: From OLI Flowsheet : $q = 6,268,380 \text{ g/hr} = 0.002014 \text{ m}^3/\text{s}$

$$C_{s,u} = a * ChE Plant Cost Index 2018 + b * C_{s,f}$$

$$C_{s,f} = Price of Fuel (\$/GJ) = 4.4 \$/GJ$$

$$From Ulrich 2004 Table 6.3 : a = 0.001 + 2 * 10^{-4} * q^{-0.6} \quad b = 0.1$$

$$a = 0.001 + 2 * 10^{-4} * 0.002014^{-0.6} = 0.009291$$

$$C_{s,u} = 0.009291 * 616 + 0.1 * 4.4 = 6.16 \$/m^3 = 391,429.716 \$/year$$

B.7 Wastewater Plant Calculations

$$From OLI Flowsheet : q_{total} = .00413 m^3/s$$

$$From Ulrich 2004 Figure 5.12 : CBM (2004) = \$1,000,000$$

$$CBM (2018) = CBM (2004) * ChE Index 2018/ChE Index 2004 = \$1,000,000 * (616/400) = \$1,540,000$$

Appendix C: Mass and Energy Balance

Material	MW (kg/kmole)	Monazite Stream (kg/hr)	Acid Stream (kg/hr)	Stream 1 (kg/hr)	Stream 2 (kg/hr)	Stream 3 (kg/hr)	Th/Sr-1	Th/Sr-2	Th/Sr-3	Th/Sr-4	NH4OH-1	Solids
H2O	18.02	1000	3000	4348.86	361.37	364.95	0	315.5422	315.422	16.2138	300	0
LaPO4	236.899	241.981	0	59.3308	241.981	241.981	0	0	0	0	0	0
CePO4	235.0874	480.142	0	21.074	288.203	480.142	0	0	0	0	0	0
NdPO4	239.21	195.504	0	13.052	187.778	195.504	0	0	0	0	0	0
Th(HPO4)2	423.99	86.7073	0	0	0	0	0	0	0	0	0	0
U3(PO4)4	1093.97	0	0	0	0	0	0	0	0	0	0	0
H2SO4	98.07	0	2375	0	0	0	0	0	0	0	0	0
SrO2	60.08	15.5	0	15.5	15.5	15.5	14.93	14.93	14.93	14.83	0	14.83
NH4OH	35.04	0	0	0	0	0	0	0	0	0	30	0
ThO2	264.03	0	0	0	0	0	0	53.9955	53.9955	53.9955	0	53.9955
U(HPO4)2	429.98	0	0	0	0	0	0	0	0	0	0	0
UO2	270.02	1.44	0	0	0	1.44	0	0	0	0	0	0
O2	31.99	0	0	0	0	0	0	0	0	0	0	0
NaOH	39.99	0	0	0	0	0	0	0	0	0	11.9992	0
HNO3	63.01	0	400	400	343.75	343.75	0	0	0	0	0	0
C2H2O4	122.09	0	0	0	0	0	0	0	0	0	0	0
SrO	80.06	0	0	1796.73	1921.53	1922.38	0	32.7463	32.7463	0	0	0
Ce2(SO4)3	568.41	0	0	289.896	0	0	0	0	0	0	0	0
CePO4.2H2O	271.1274	0	0	252.885	221.356	0	0	0	0	0	0	0
LaPO4.2H2O	272.939	0	0	210.79	0	0	0	0	0	0	0	0
NdPO4.2H2O	275.25	0	0	209.934	8.891	0	0	0	0	0	0	0
P2O5	141.94	0	0	86.905	14.5138	14.5138	0	0	0	0	0	0
Th(SO4)2	424.16	0	0	86.7414	86.7417	86.7418	0	0	0	0	0	0
U(SO4)2	430.15	0	0	2.294	2.286	0	0	0	0	0	0	0
NH3	17.03	0	0	0	0	0	0	14.5785	14.5785	0	0	0
Ce(OH)3	191.13	0	0	0	0	0	0	0	0	0	0	0
La(OH)3	189.92	0	0	0	0	0	0	0	0	0	0	0
Nd(OH)3	195.264	0	0	0	0	0	0	0	0	0	0	0
Total:		2021.2743	5775	7796.9922	6943.9005	6943.9005	101.6718	431.7925	431.6723	97.0385	330	68.8255

Material	MW (kg/kmole)	NaOH	NaOH-1	NaOH-2	REE	REE-1A	REE-1B	REE-2A	REE-2B	REE-3A	REE-3B	REE-Final
H2O	18.02	4500	0	16.2138	1820.97	1820.97	1820.97	6268.38	6268.38	0	0	0
LaPO4	236.899	0	0	0	241.981	120.991	120.991	0	0	0	0	0
CePO4	235.0874	0	0	0	480.142	240.071	240.071	0	0	0	0	0
NdPO4	239.21	0	0	0	195.504	97.7522	97.7522	0.208978	0.208978	0	0	0
Th(HPO4)2	423.99	0	0	0	0	0	0	0	0	0	0	0
U3(PO4)4	1093.97	0	0	0	0	0	0	0	0	0	0	0
H2SO4	98.07	0	0	0	0	0	0	0	0	0	0	0
SrO2	60.08	0	0	0	0.57	0.285	0.285	0.285	0.285	0	0	0
NH4OH	35.04	0	0	0	0	0	0	0	0	0	0	0
ThO2	264.03	0	0	0	0	0	0	0	0	0	0	0
U(HPO4)2	429.98	0	0	0	0	0	0	0	0	0	0	0
UO2	270.02	0	0	0	1.44	0.72	0.72	0.72	0.72	0.716648	0.716648	1.43329
O2	31.99	0	0	0	0	0	0	0	0	0	0	0
NaOH	39.99	1500	0	11.9992	0	0	0	1500	1500	0	0	0
HNO3	63.01	0	0	0	343.75	171.875	171.875	171.875	171.875	0	0	0
C2H2O4	122.09	0	0	0	0	0	0	0	0	0	0	0
SrO	80.06	0	0	0	192.238	96.1192	96.1192	96.1192	96.1192	0	0	0
Ce2(SO4)3	568.41	0	0	0	0	0	0	0	0	0	0	0
CePO4.2H2O	271.1274	0	0	0	0	0	0	0	0	0	0	0
LaPO4.2H2O	272.939	0	0	0	0	0	0	0	0	0	0	0
NdPO4.2H2O	275.25	0	0	0	0	0	0	0	0	0	0	0
P2O5	141.94	0	0	0	14.5138	7.25691	7.25691	7.25691	7.25691	7.25691	7.25691	14.5138
Th(SO4)2	424.16	0	0	0	0	0	0	0	0	0	0	0
U(SO4)2	430.15	0	0	0	0	0	0	0	0	0	0	0
NH3	17.03	0	0	0	0	0	0	0	0	0	0	0
Ce(OH)3	191.13	0	0	0	0	0	0	0	0	0	0	0
La(OH)3	189.92	0	0	0	0	0	0	0	0	0	0	0
Nd(OH)3	195.264	0	0	0	0	0	0	0	0	0	0	0
Total:		6000	6000	28.213	6842.2368	3421.1311	3421.1311	9421.11578	9421.11578	373.780246	373.780246	7475.6129

Material	MW (kg/kmole)	Waste-1 (kg/hr)	Waste-2	Waste-3	Waste-4	Waste-5	ThO2
H2O	18.02	796.136	6268.38	6268.38	315.422	16.2138	0
LaPO4	236.899	0	0	0	0	0	0
CePO4	235.0874	0	0	0	0	0	0
NdPO4	239.21	0	0.208978	0.208978	0	0	0
Th(HPO4)2	423.99	0	0	0	0	0	0
U3(PO4)4	1093.97	0	0	0	0	0	0
H2SO4	98.07	0	0	0	0	0	0
SiO2	60.08	0	0.285226	0.285226	0.093	14.83	0
NH4OH	35.04	0	0	0	0	0	0
ThO2	264.03	0	0	0	0	0	53.9955
U(HPO4)2	429.98	0	0	0	0	0	0
UO2	270.02	0	0	0	0	0	0
O2	31.99	0	0	0	0	0	0
NaOH	39.99	0	1500	1500	0	11.9992	0
HNO3	63.01	56.25	171.875	171.875	0	0	0
C2H2O4	122.09	0	0	0	0	0	0
SO3	80.06	0	961.192	961.192	32.7463	0	0
Ce2(SO4)3	568.41	0	0	0	0	0	0
CePO4.2H2O	271.1274	0	0	0	0	0	0
LaPO4.2H2O	272.939	0	0	0	0	0	0
NdPO4.2H2O	275.25	0	0	0	0	0	0
P2O5	141.94	0	145.387	145.387	0	0	0
Th(SO4)2	424.16	0	0	0	0	0	0
U(SO4)2	430.15	0	0	0	0	0	0
NH3	17.03	0	0	0	14.5785	0	0
Ce(OH)3	191.13	0	0	0	0	0	0
La(OH)3	189.92	0	0	0	0	0	0
Nd(OH)3	195.264	0	0	0	0	0	0
Total:		852.386	9047.328204	9047.328204	362.8398	43.043	53.9955

Figure C.1: Stream Table

Appendix D: Capital Cost and Manufacturing Cost

TABLE 5-5 CAPITAL COST SUMMARY**				Date to which estimate applies Dec. 2018		Page 1 of 1			
Job title: <u>Monazite Extraction</u>		Location: <u>India</u>		By <u>Group 9</u>					
(Flow Sheet Page Number: 1)		Cost Index Type <u>CE Plant Cost Index</u>		Cost Index Value <u>616</u>		Date <u>April 28th 2019</u>			
Equipment Identification	Number	Capacity or Size Specifications	Purchased Equipment Cost (base material)		Material Factor, F_M	Pressure or other Factors, F_P	Actual Bare Module Factor, F_{BM}	Actual Bare Module Cost, C_{BM}	Total
			Year 2004	Target Year*					
Auxiliary Facilities									
	A-240	Waste Water, Tertiary Treatment	1 M	1.54 M	-	-	-	1.54 M	
	A*								
Total Auxiliary Facilities									1.54 M
Separators									
	H-140	Carbon Steel Base with PTFE Lining, 1 atm, .94 m ²	57 k	87 k	5.00	-	-	434 k	
	H-170	Carbon Steel Base with PTFE Lining, 1 atm, .637 m ²	50 k	77 k	5.00	-	-	385 k	
	H-210a	Carbon Steel Base with PTFE Lining, 1 atm, 3.46 m ²	70 k	108 k	5.00	-	-	539 k	
	H-210b	Carbon Steel Base with PTFE Lining, 1 atm, 3.46 m ²	70 k	108 k	5.00	-	-	539 k	
	H-190	Carbon Steel Base with PTFE Lining, 1 atm, .499 m ²	45k	69 k	5.00	-	-	347 k	
Total Heat Exchangers									2.24 M
Heat Exchangers									
	E-120	5.4 m ² , Titanium, Double Pipe, 1 atm	6.5 k	10 k	12.0	1.0	17.5	175 k	
	E-160	.4 m ² , Titanium, double pipe, 1 atm	1.5 k	2.3 k	12.0	1.0	17.5	40.4 k	
Total Heat Exchangers									175 k
(Other items as taken from the equipment list)									
Process Vessels									
	R-100	Carbon Steel Base with PTFE Lining, 30 atm, 8.7 m ³	58.4 k	89.9 k	5.0	2.8	27.0	2.4 M	
	R-200a	Carbon Steel Base with PTFE Lining, 1 atm, 9.1 m ³	65.1 k	100 k	5.0	1.0	11.0	1.1 M	
	R-150	Stainless Steel, 1 atm, 0.5 m ³	7.5 k	11.6 k	4.0	1.2	11.0	128 k	
	R-200b	Carbon Steel Base with PTFE Lining, 1 atm, 9.1 m ³	65.1 k	100 k	5.0	1.0	11.0	1.1 M	
	R-110	Carbon Steel Base with PTFE Lining, 2 atm, 9.3 m ³	88k	135 k	5.0	1.0	11.0	1.4 M	
Tower Total									6.126 M
Mixer									
	M-180	Stainless Steel, 1 atm, .05 m ³	2.9 k	4.4 k	-	-	2.9	13 k	
	M-220	Stainless Steel, 1 atm, .157 m ³	7.5 k	11.5 k	-	-	2.9	33 k	
Total Pumps									46 k
Gas Solid Contactor									
	C-230	Nickel Alloy, 1 atm, 0.7 m ³	100 k	154 k	-	-	9.0	1.39 M	
Total Storage Vessels									1.39 M
Total bare module cost							Actual materials, $C_{BM} = \sum C_{BM} =$		11.51 M
Contingency and fee							$C_C + C_F = C_{TM} \times 0.18 =$		2.07 M
Total module cost							$C_{TM} =$		13.58 M
Auxiliary (offsite) Facilities							$C_{TM} \times 0.30 =$		3.45 M
Grass Roots capital							$C_{GR} =$		17.03 M

Figure D.1: Capital Cost Summary

MANUFACTURING COST SUMMARY		Page 1 of 1	
		by CBE 488 Group 3	
		Date 25 Apr. 2019	
Job Title <u>Thorium Extraction from Monazite Ore</u>			
Location <u>Knoxville, TN</u>		Capacity: <u>8,760,000 kg /yr Monazite</u>	
Effective Date to Which Estimate Applies <u>2019</u>		Cost Index Type <u>CE Plant Cost Index</u>	
		Cost Index Value <u>616</u>	
Capital			
Fixed capital, C_{FC}			\$17,033 k
Working capital (15% of fixed capital), C_{WC}			\$2,555 k
Total capital investment, C_{IC}			\$19,588 k
Manufacturing Expenses			
Direct			
Raw materials			\$ 0.04
By-product credits			\$ (40.44)
Catalysts and solvents			\$ 12.98
Operating labor			\$ 1.78
Supervisory and clerical labor (15% of operating labor)			\$ 0.27
Utilities			
Process water	891,302 m ³ @	1.1 \$/m ³	\$ 0.98
Wastewater Treatment			\$ 0.90
Natural Gas	33,482.88 GJ @	4.4 \$/GJ	\$ 0.15 \$ 2.03
Maintenance and repairs (6% of fixed capital)			\$ 1.02
Operating supplies (15% of maintenance & repairs)			\$ 0.15
Laboratory charges (15% of operating labor)			\$ 0.02
Patents and royalties (5% of total expense)			\$ 0.06
Total, A_{DME}			\$ (22.08) \$ (22.08)
Indirect			
Overhead (Payroll and Plant), Packaging, and Storage (60% of Operating Labor, Supervision, and Maintenance)			\$ 1.11
Local taxes (1.5% of fixed capital)			\$ 0.26
Insurance (1.5% of fixed capital)			\$ 0.26
Total, A_{IME}			\$ 1.62 \$ 1.62
Total manufacturing expense, $A_{ME}=A_{DME}+A_{IME}$			\$ (20.46)
General Expenses			
Administrative costs (25% of overhead)			\$ 0.28
Distribution and selling (10% of total expense)			\$ (2.05)
Research and development (5% of total expense)			\$ (1.02)
Total general expense, A_{GE}			\$ (2.79) \$ (2.79)
Depreciation (approximately 10% of fixed capital), A_{DP}			\$ 1.70
Total Expenses, A_{TE}			\$ (21.55)
Revenue from Sales	473040 kg/yr @	80 \$/kg, A_s	\$ 37.84
Net annual profit, A_{NP}			\$ 59.39
Income taxes (net annual profit times the tax rate), A_{IT}			\$ 12.47
Net annual profit after taxes ($A_{NP}-A_{IT}$), A_{NPA}			\$ 46.92
			After tax rate of return, $I = (1.5 A_{NPA}/C_{IC}) \times 100 = 359.28\%$

Figure D.2: Manufacturing Cost Summary

Appendix E: Equipment Design

R-100: In reactor R-100, monazite ore is leached with sulfuric acid in order to turn phosphates into sulfates. R-100 is at a temperature of 220 degrees celsius, a pressure of 30 atm, and the volume of the reactor is 8.7 cubic meters. The material that is used for R-100 is a carbon steel base with PTFE lining. This material is chosen because PTFE lining can handle acidic process conditions and can handle temperatures up to 220 degrees celsius. Carbon steel was the most economical base material to use.

R-110: In the flash tank, R-110, the effluent of R-100's at a pressure of 30 atm is dropped to a pressure of 2 atm where filtration is possible. The temperature of the flash tank is 135 degrees celsius. The volume of the flash tank is 0.5 cubic meters. The material that is used for R-110 is carbon steel base with PTFE lining. This material is chosen because PTFE lining can handle acidic process conditions up to 220 degrees celsius. Carbon steel was the most economical base material to use.

E-120: In heat exchanger E-120, the liquid stream coming out of R-110 is cooled from 135 degrees Celsius to 20 degrees Celsius at a pressure of 2 atm. This is done in order to be able to precipitate out Thorium Sulfate from solution as well as allowing efficient filtration in the next stage of the plant. The heat exchanger area is 5.4 m². The material used is Titanium due to its resistance to degradation at the acidic inlet conditions at 135 degrees Celsius.

H-140: In filter H-140, the liquid process stream coming out of E-120 at 20 degrees Celsius and 2 atm is fed to a continuous belt vacuum filter in order to separate thorium sulfate and SiO₂ from the rest of the solubilized rare earth sulfates. This filter has an area of .94 m². A continuous belt vacuum filtration allows for efficient operational use. The material used is carbon steel base with a PTFE lining. The PTFE lining allows for resistance due to degradation from the acidic conditions at the inlet of the filter. The carbon steel base is used as it is the most economically base to use.

R-150: In reactor R-150, thorium sulfate is converted to thorium oxide by treating it with ammonium hydroxide. The reactor is at a pressure of 1 atm and the volume of the reactor is 0.5 cubic meters. Stainless steel is used as the material of the reactor because it is the economical choice of material that can handle basic process condition that comes with using ammonium hydroxide.

E-160: In heat exchanger E-160, the effluent of R-150 is cooled from 90 degrees Celsius to 80 degrees Celsius at 1 atm. This is done in order to have efficient filtration in the next stage of the plant. This double pipe heat exchanger area is .4 m² with the material of construction being titanium. This material was used as precautionary safety

measure that could easily withstand the process conditions while also not being very expensive due to the small area of the exchanger.

H-170: In filter H-170, continuous belt vacuum filtration is used to separate solid thorium oxide and silicon dioxide from the liquids coming from R-150. The filter is at a pressure of 1 atm and has an area of .637 square meters. The material for the filter is a carbon steel base with PTFE lining. This material is used because it allows for efficient continuous filtration and allows for precautionary measures against possible corrosion.

M-180: In mixer M-180, ThO₂ and SiO₂ are mixed with NaOH at a temperature of 80 degrees Celsius and 1 atm. The basic conditions created by mixing NaOH allows for the solubilization of SiO₂ while ThO₂ stays as a solid. The volume of this mixer is .05 m³. The material of construction used is stainless steel. This material was chosen because it is the cheapest material that can be used that can withstand the basic condition created by NaOH at 80 degrees Celsius.

H-190: In filter H-190, using continuous belt vacuum filtration thorium oxide is separated from silicon dioxide and the rest of the aqueous solution. The filter is at a pressure of 1 atm and a temperature of 80 degrees Celsius with an area of .499 square meters. The material for the filter is a carbon steel base with PTFE lining. This material is used because it allows for efficient continuous filtration and it will stand up to the basic process conditions.

R-200a/200b: In reactors R-200a and R-200b, the liquid streams containing rare earth sulfates are reacted with NaOH in order to transform the sulfates into their respective rare earth hydroxides. These identical reactors have volumes of 9.1 m³ and are operated at a temperature of 50 degrees Celsius and a pressure of 1 atm. The material of construction is PTFE lining with a carbon steel base. This is used in order to be able to handle the extremely acidic and basic solutions entering and existing the reactors.

H-210a/210b: In continuous belt vacuum filters H-210a and H-210b, The rare earth hydroxide solids are isolated from the effluents from R-200a and R-200b. The identical filter have an solids handling area of 3.46 m² and are operated at pressure of 1 atm and a temperature of 50 degrees Celsius. The material of construction used is a carbon steel base with PTFE lining. This material was chosen due to its ability to withstand the basic conditions of the process while also using the most economic base material of carbon steel.

M-220: In mixer M-220, two streams or rare earth oxides are mixed into one stream that can be fed to a calciner to complete the process. The mixer is at a pressure of 1 atm and has a volume of .157 cubic meters. The material that is used is stainless steel. Stainless steel is used as precautionary safety measure to ensure minimal corrosion.

C-230: In calciner C-230, rare earth hydroxides are converted rare earth hydroxides by exposing them to a temperature of 850 degrees Celsius. Nickel alloy is used as the material because it can handle very high temperatures at which structural damage is possible. The pressure at the calciner is 1 atm and it has a volume of 0.7 cubic meters.

A-240: In wastewater treatment plant A-240: 14.9 m³ an hour of process liquid must be treated before release to the environment or fed back to the plant. Some streams are very basic so a comprehensive tertiary treatment must be used. This includes filtration, activated sludge, and chemical processing in order to neutralize and clean the streams to an acceptable regulated level.

Appendix E.1: Flowsheet Design

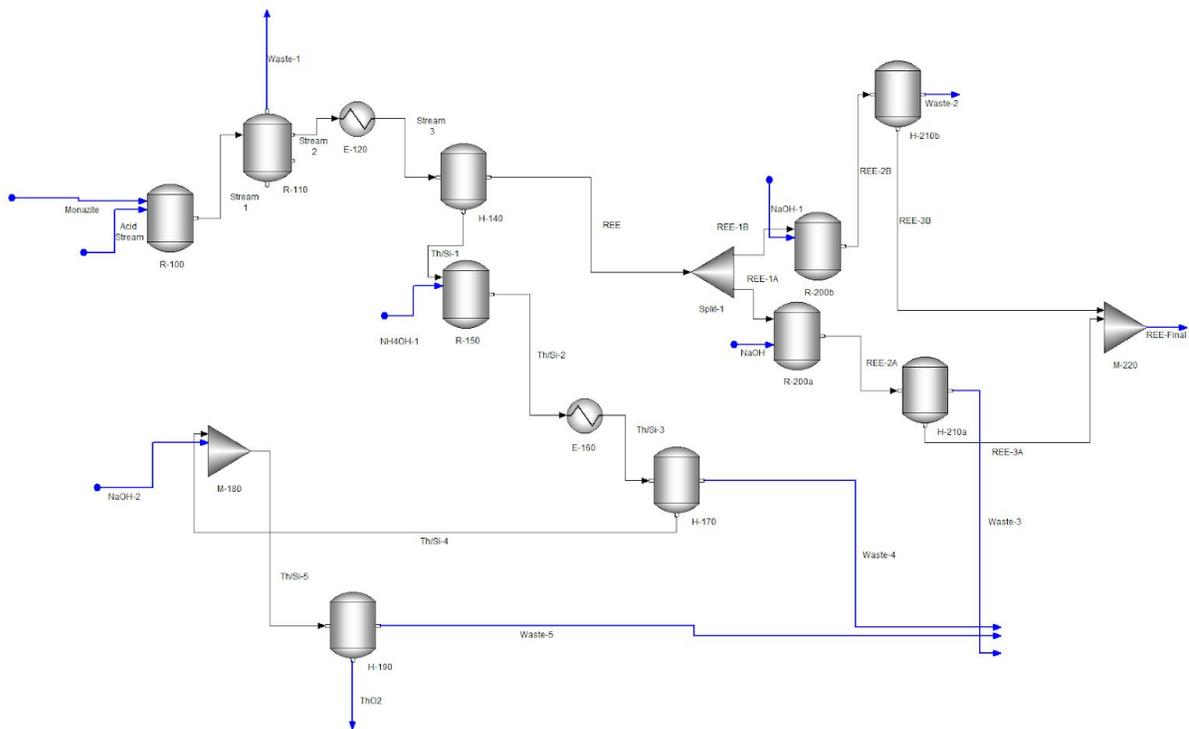


Figure E.1: OLI Flowsheet Design

Appendix F: Stream Hazards

Stream Hazard Chart							Flammability	Toxicity					Corrosive?
Compound	mw	CAS No.	Melting Point (°C)	Flash Point (°C)	Boiling Point (°C)	Liquid Density (kg/m ³)	High	Deadly Poison?	Toxin?	Carcinogenic?	Mutagenic?	Irritating?	Corrosive?
H ₂ O	18	7732-18-5	0	Non-flammable	100	1000	Non-flammable	no	no	no	no	no	no
SiO ₂	60.08	7631-86-9	1710	Non-flammable	2230	2650	Non-flammable	no	no	yes	yes	yes	no
La ₂ O ₃	325.81	1312-81-8	2315	Non-flammable	4200	6510	Non-flammable	no	no	no	no	yes	no
Nd ₂ O ₃	336.8	1313-97-9	2233	Non-flammable	3760	7240	Non-flammable	no	yes	no	no	yes	no
Ce ₂ O ₃	328.24	1345-13-7	2177	Non-flammable	3730	6200	Non-flammable	no	yes	no	no	no	no
H ₂ SO ₄	98.079	7664-93-9	10	Non-flammable	337	1840	powerful oxidant	no	yes	yes	no	strongly	strongly
ThO ₂	264.04	1314-20-1	3390	Non-flammable	4400	10000	Non-flammable	no	no	yes	yes	yes	no
H ₃ PO ₄	98	7664-38-2	42	Non-flammable	158	2030	Non-flammable	no	no	no	no	yes	yes
Monazite	-	-	2000	Non-flammable	-	5100	Non-flammable	no	yes	yes	no	yes	no
HNO ₃	63.012	7697-32	-42	Non-flammable	83	1510	Non-flammable	no	yes	no	no	yes	yes
NaOH	39.9971	1310-73-2	318	Non-flammable	1388	2130	Non-flammable	no	yes	no	no	yes	yes
NH ₄ OH	35.04	1336-21-6	-57.5	Non-flammable	37.7	910	Non-flammable	no	yes	no	no	yes	yes

Figure F.1: Stream Hazards Chart