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# Economic Analysis of Lithium Recovery from Spent Lithium Ion Batteries

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April 27, 2020

 Dr. Robert Counce
CBE 488
University of Tennessee

Dear Dr. Counce:

We are submitting the attached report entitled *Economic Analysis of Lithium Recovery from Spent Lithium Ion Batteries*.

This report examines the results of designing a process and estimating the capital and manufacturing costs for the recovery of lithium from spent lithium ion batteries.

I hope you find this report satisfactory.

Sincerely,


Zoe Antonas, Makayla Hyde, Jaclyn Choate, Abby Newberry, and Madi Sherrod
Group 9


Honors Design in Green Engineering
University of Tennessee
Knoxville, Tennessee

Enclosure: Final Report

cc:

# Economic Analysis of Lithium Recovery from Spent Lithium Ion Batteries

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# Abstract

Due to rapid demand for lithium-ion batteries (LIBs) with new hybrid and electric vehicles along with modern day technologies like cell phones and computers, the supply of natural lithium-containing reserves is draining. This envisioned process could help alleviate the resource shortage and decrease the potential of environmental pollution due to improper waste disposal. The recovery of lithium hydroxide is accomplished by processing spent LIBs. The LIBs will be shredded and screened based on desirable size; this will allow separation of the different components of the spent LIB. The main components of spent LIB will be classified as the cathodic or anodic material. Other components of spent LIB like the binder and separator will be discharged as waste in the pretreatment step of the process. The spent LIBs will be acid leached with nitric acid and neutralized with sodium hydroxide. The last step of the process will be recovery which will purify the product and byproducts being sold. The main streams with byproducts and products that will be sold are from the final filtration step. Based on results of this study, the process is found to be not only economically feasible but profitable. The maximum profit was found to be around $38 million, and will remain profitable even after including the yearly equipment and operating costs.

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# 1.0 Introduction

The purpose of this report is to document the results of a study to design an industrial-sized process to recover lithium and other valuable components from lithium ion batteries (LIBs) so that these materials may be recycled. The economics of the created process will be analyzed and documented.

Due to rapid demand for LIBs with new hybrid and electric vehicles along with modern day technologies like cell phones and computers, the supply of natural lithium-containing reserves is draining. Additionally, lithium is very reactive and therefore difficult to dispose of. These problems support the need for this study. This envisioned process could help alleviate the resource shortage and decrease the potential of environmental pollution due to improper waste disposal.

The spent LIBs are assumed to be of cylindrical shape with an iron or aluminum can body (Liu et al., 2019). The design objectives for this report and process are as follows: accurately provide economic analysis for a study-level design which will be approximately +30 to -20% of projected costs, and design a process that supports a feed of 1000 kg of spent lithium batteries per hour with the composition shown in Table 1. The process is designed to be safe and environmentally friendly while producing products that are economically feasible. This report will use a late 2019 chemical engineering index value of 599.5 when referring to any economic potentials.

Table 1: Average Composition of LIBs

| Component | Weight Percent (%) |
|---|---|
| $LiCoO_2$ | 27.5 |
| Nickel Alloy (80% Nii, 20% Cr) | 24.5 |
| Copper Alloy (85% Cu, 15% Zr) | 14.5 |
| Carbon | 16 |
| Electrolyte | 3.5 |
| Polymer Casing | 14 |

[Lee and Rhee, 2002]

The recovery process is based on a process presented in Castillo et al. 2002. The process consists of isolating the cathode elements of the LIBs and selectively dissolving the materials in dilute nitric acid. These metals are then selectively precipitated to obtain the final product of separate lithium compounds. This choice of process is based on a review of literature presented later in this report. This process is sponsored by JSW Fund for Undergraduate and Graduate Research at the University of Tennessee.

# 2.0 Synthesis Information of Processes

## 2.1 Overall Process Design

The recovery of lithium hydroxide is accomplished by processing spent LIBs. Throughout the process there will be many streams so that the lithium product will be the most pure. The main streams with byproducts and products that will be sold are from the final filtration step. Figure 1 shows the general process flow diagram and begins with pretreatment of LIBs so that most of the waste from the battery will be removed. Pretreatment will include heating the LIBs to remove the polymer casing and also shredding to remove other metal components. The polymer waste will be disposed and the desired material will be sent on for further processes. The next step in the process will include acid leaching with nitric acid. The last step of the process will be recovery which will purify the product and byproducts being sold. This step will include an addition of sodium hydroxide which will be filtered to separate solid compounds from the liquid filtrate.
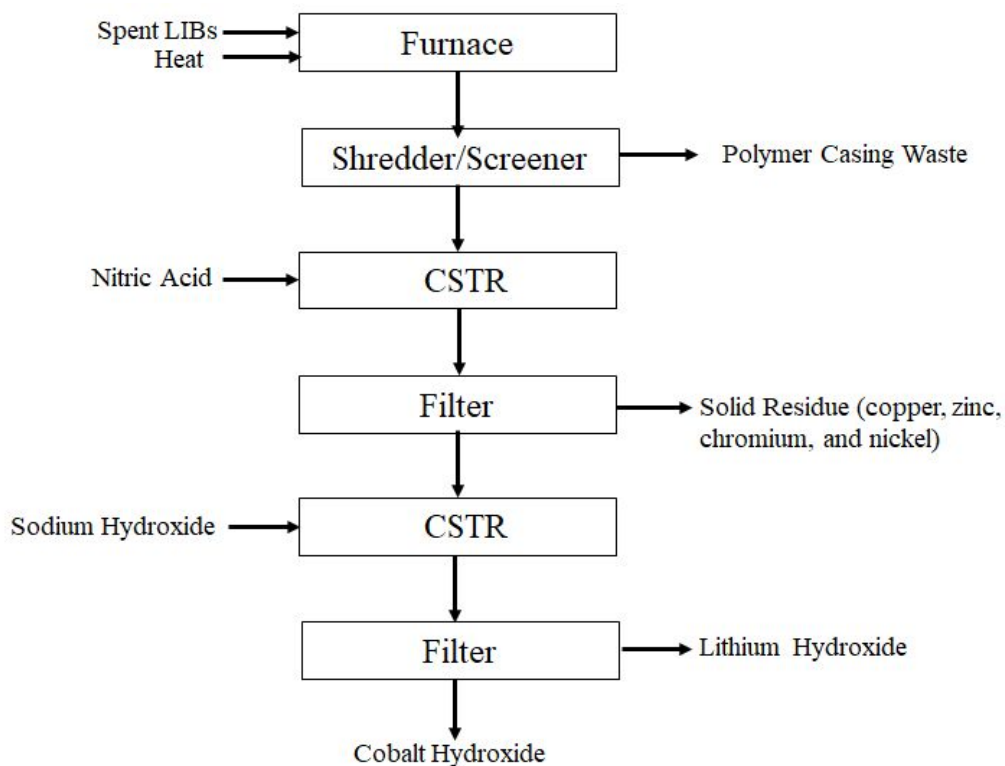
Figure 1

The proposed process does have constraints that must be met in order to design a safe environment for workers. Before processing, the spent LIBs have to be discharged to prevent short-circuiting and

self-ignition which could lead to an explosion. To discharge the spent LIBs, normally a salt-saturated solution is used. If heat is produced while shredding the batteries, refrigeration during the operation might be required. Another constraint on the overall efficiency of the process is in the problem of readily available machinery that could be used to separate the different components of LIBs. Optimal machinery may require custom design. Due to the cost of machinery, this optimal separation may be difficult to obtain.

## 2.2 Process Chemistry

The LIBs will be shredded and screened based on desirable size; this will allow separation of the different components of the spent LIB. The main components of spent LIB will be classified as the cathodic or anodic material. Other components of spent LIB like the binder and separator will be discharged as waste in the pretreatment step of the process. This classification is based on two reactions that occur inside the cell of the battery; the cathodic and anodic reactions shown in equations (1) and (2) respectively. Equation (3) represents the movement of lithium ions from cathode to anode inside the battery cell.

$$Li^{+} \ (aq) + 6 \ C(s) \ + e^{-} \leftrightarrows LiC_{6} \tag{1}$$

$$CoO_{2} \ (s) \ + \ Li^{+} \ (aq) \ + e^{-} \leftrightarrows LiCoO_{2} \tag{2}$$

$$LiCoO_{2} \leftrightarrows CoO_{2} + Li^{+} + e^{-} \tag{3}$$

When the screening has removed undesired waste material, desired material will then be sent to the acid leaching step of the process. This step is shown in equation (4), demonstrating the reaction of lithium components present in spent LIBs with nitric acid.

$$3HNO_{3} + LiCoO_{2} \ (s) \rightarrow LiNO_{3} + Co(NO_{3})_{2} + \tfrac{3}{2}H_{2}O + \tfrac{1}{4}O_{2}(g) \tag{4}$$
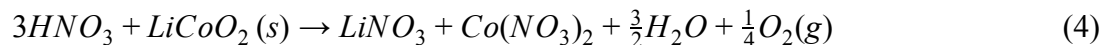
Once in solution, metals can be recovered by chemical precipitation by altering the pH of the solution. The recovery step will add NaOH to raise the pH to better purify the products. The caustic soda will bind to a metallic ion and precipitate that metal from the solution. Once the pH is raised, the metal compound, in this case cobalt hydroxide, will drop out of solution and be able to be separated by filtration. This reaction is shown in equation (5) below. NaOH is a strong base, and in an industrial scale process these steps can be controlled by using a pH sensor.

$$Co(NO_{3})_{2} + 2 \ NaOH \rightarrow Co(OH)_{2} \ (s) + 2 \ NaNO_{3} \tag{5}$$
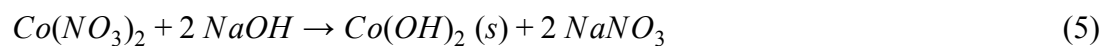
## 2.3 Literature Review

[1] *Advances in the recovery of spent lithium battery compounds [Castillo et al.]*

Various initial solubility compositions were compared to see how valorization may increase potential profits and reduce the environmental impact in comparison to the current recycling processes for spent LIBs. The initial battery cell components were identified using flame spectroscopy, and the contents were tracked over each process run. The batteries were dissolved in an acidic solution, then the resulting metal components were selectively precipitated into a hydroxyl form and removed from the solution as a byproduct. It was found that the best extraction of precipitate at 100% nickel, and a filtrate composed of 100% lithium and manganese occurs at an initial pH of 2.9 with a scale rate of 10 volume percent of NaOH added to the solution for calcination and secondary extraction. This reaction does not include organic solutes, which ensures that the environmental impact was minimized as much as possible. When comparing the acid solution, the lithium was found to dissolve best in nitric acid over hydrochloric acid in a two molar solution. The second reaction and filtration occurred by adding a base in the form of sodium hydroxide to raise the overall pH to 5.2 and precipitate out the rest of the metal impurities such as iron that is present. If the pH was allowed to increase to 10, then the manganese hydroxide will also precipitate out in a third reaction, which means only lithium ions will remain in the solution to be removed efficiently and separated into a filtrate to be collected. Valorization involves the extra step of sending manganese and metal byproducts from the first separation to a muffler furnace to be heated into a steel alloy at 500°C. This steel can then be sold to increase profits from the reaction, and remove heavy metal waste that can become a potential pollutant. Overall, valorization appears to be a reasonable avenue to take in processing the byproducts for both economical and ecological reasons.

[2] *Preparation of $LiCoO_2$ from spent lithium-ion batteries [Lee et al.]*

This paper explains a lab-scale LIB recycling process. There is an in-depth discussion of the heating process and reductive leaching. Both nitric acid and hydrogen peroxide were examined as reducing agents at different solid:liquid ratios, acid concentrations, temperatures and times. Optimal leaching conditions were determined for the lab scale process as 1M nitric acid at 75°C with a later addition of hydrogen peroxide. Conclusions drawn about the lab scale process include the benefits of shredding and results of leaching trials.

[3] *Recycling of Spent Lithium-ion Batteries in View of Lithium Recovery: A Critical Review [Liu et al.]*

This review starts by explaining how hybrid vehicles and portable electronic devices have caused greater demand for more lithium ion batteries. Not only is this demand creating a shortage of lithium in the world, but the disposal of these batteries are causing environmental and human health hazards. As a result, recycling lithium from these batteries is a major process that needs to be designed and implemented in the near future. Liu et al calls for a mild recycling process that takes

both of the good steps in the hydrometallurgy-dominant method and the pyrometallurgy-dominant method. This mild recycling method utilizes the advantages of both methods by avoiding strong acids and reducing temperatures. The review then explains in detail how both hydrometallurgy and pyrometallurgy processes work and even looks at what current industrial recycling is doing to recycle lithium. The author ends by explaining that the mild recycling process is the better process because it decreases energy consumption and avoids the application of acid.

[4] *Electrode Materials for Lithium Ion Batteries: A Review [Heidari et al.]*

This review explains the evolution of battery technology and the recent development of LIBs. It begins with an overview of past developments in battery technology as well as newer concepts and materials used for the optimization of a battery. Going into details regarding LIBs, the paper gives insight into recent trends and prospects of anode and cathode materials for optimum battery technology as well as an economic perspective for the production of the battery. Finally, the paper concludes with future prospects of LIBs and how more research must be done in order to adapt a sustainable, economically efficient battery for global use.

[5] *A Review of Processes and Technologies for the Recycling of Lithium-Ion Batteries [Xu et al.]*

This paper reviews current endeavors into the recycling of spent LIBs. Constraints are laid out, and two main processes are discussed: physical and chemical recycling. Physical processes discussed include cutting/grinding, thermal treatment, magnetic separation, and dissolution. Chemical processes include acid leaching, bio-leaching, solvent extraction, and chemical precipitation. Next, the feasibility of re-using the recycled $LiCoO_2$ was explored. Xu et al. determined that a combination of both physical and chemical recycling processes results in optimal recovery. Nine different combination recycling processes were explained with varying levels of detail. The paper ends by explaining that a practical recycling technology will both recover the useful metal resources as well as safely and sustainably dispose of harmful chemicals present in the battery such as electrode material and LIB polymer casing.

[6] *Recycling of Spent Lithium-Ion Battery: A Critical Review [Zeng et al.]*

This paper looks at each experiment that is tested in the past papers and compares and contrasts the results with respect to efficiency of lithium being recycled from LIBs. After explaining what batteries are and how important they are to today's society, Zeng et al. further explain the exact parts of a battery and the composition of each part. The major parts of the battery include the cathode, anode, separator, and a binder. It compares and contrasts the different compositions of batteries and which type of battery each experiment used. The paper explains that a general process is used to recycle lithium starting with pretreatment to secondary treatment and ending with deep recovery, looking at the differences in each step that may result in better or worse lithium recovery.

**[7]** *Leaching Study of Spent Li-ion Batteries [Wang et al.]*

This paper studies the leaching of LIBs under varying conditions. The effects of hydronium ion concentration, liquid-to-solid ratio, temperature, and time were investigated to better understand the leaching trends within the system. Wang et al. determined that the best operating conditions for leaching LIBs are 3 mol/L sulfuric acid, a 15:1 ratio of liquid-to-solid, a 0.25 mol/L concentration of sodium thiosulfate, a temperature of 90°C, and a reaction time of 3 hours. The paper briefly mentioned the reasoning behind choosing sulfuric acid but did not go into detail.

**[8]** *A Critical Review and Analysis on the Recycling of Spent Lithium-Ion Batteries [Weiguang et al.]*

This paper begins with an overview of what makes up a battery and how LIBs were developed. Next, the economical and environmental trade-offs are examined for the following processes: pre-treatment method pyro- and hydrometallurgical processes, traditional leaching, solvent extraction, and leaching resynthesis. Three current LIB recycling processes are discussed in terms of pros and cons. Ultimately, the paper summarizes that these processes have not been able to break even on an industrial scale, although they are getting closer. Additionally, the leaching process is not yet completely understood as to which chemicals are the most effective. Finally, more research into the energy use of these recycling processes must be done to best understand the cost of an LIB recycling process.

## 2.4 Basic Process Economics

In this study, the main goal was to analyze the most economical and effective way to recover lithium from spent LIBs. Many different process steps were examined from each paper that are summarized in the literature review above. The variables in the economic analysis included overall percent of lithium recovered, the individual equipment cost, and the purity of sellable byproducts. The cost information for raw materials and the price for products and byproducts are shown below in Table 2 and Table 3 respectively. Cost information for each individual component will be found in the textbook *Chemical Engineering Process Design and Economics* by Ulrich and Vasudevan [9].

<p align="center">Table 2: Cost of Raw Materials (2019)</p>

| Material | Cost/unit |
|---|---|
| Spent Lithium-ion Batteries | $1/kg |
| Nitric Acid | $300/metric ton |
| Sodium Hydroxide | $450/metric ton |
| Electricity/Fuel | $4/GJ |
| 32 barg steam | $4/GJ |

Table 3: Price of Products and Byproducts (2019)

| Material | Cost/unit |
|---|---|
| Lithium Hydroxide | $25,500/metric ton |
| Cobalt Hydroxide | $400/metric ton |
| Sodium Nitrate | $0.70/kg |
| Aluminum | $2,000/metric ton |
| Copper | $6,300/metric ton |
| Cobalt | $3,500/metric ton |
| Iron | $100/metric ton |
| Chromium | $9,400/metric ton |
| Zinc | $2.55/kg |
| Nickel | $13.90/kg |

# 3.0 Method of Approach

First, the feed of spent LIBs will be pretreated by being heated in a kiln and then sent to a grinder. The shredded pieces of LIBs will be screened based on desirable size, and the undesirable pieces will be either sold as a mixture of metals or screened based on size to separate the metals. The liquid polymer that comes off from heating the LIBs will be disposed of as waste. Then desirable size pieces will be sent to a mixing tank where nitric acid will be added to dissociate ions. This mixture will be filtered out into two streams: a solid residue composed of anodic components such as copper and carbon powder and liquid filtrate made up of lithium and cobalt. This filtrate will be sent to a mixing tank where sodium hydroxide is added to raise the pH and reduce lithium. The sodium hydroxide will also bind to cobalt ions and cause them to fall out of solution. The solution will be filtered so that cobalt hydroxide will be the solid residue and the lithium hydroxide will still be in the filtrate. The pH will be raised to around 10. Then the cobalt hydroxide compound will drop out of solution. The filtration will separate liquid lithium oxide, a stable form of the lithium, from solid cobalt hydroxide.

# 4.0 Results

All data was taken from OLI:Flowsheets and was further analyzed to see if the process was profitable or at least economically feasible. All operating conditions are manually set into OLI:Flowsheets so the simulation could provide the most accurate data specifically for this process. Final outlet streams were multiplied by their respective sell prices given in Table 3. All profit from products were discounted by 50% due to being mixed streams instead of completely pure separate product streams. Product and byproduct revenue for the process is shown below in Figure 2, which indicates which products or byproducts sell for the greatest profit.
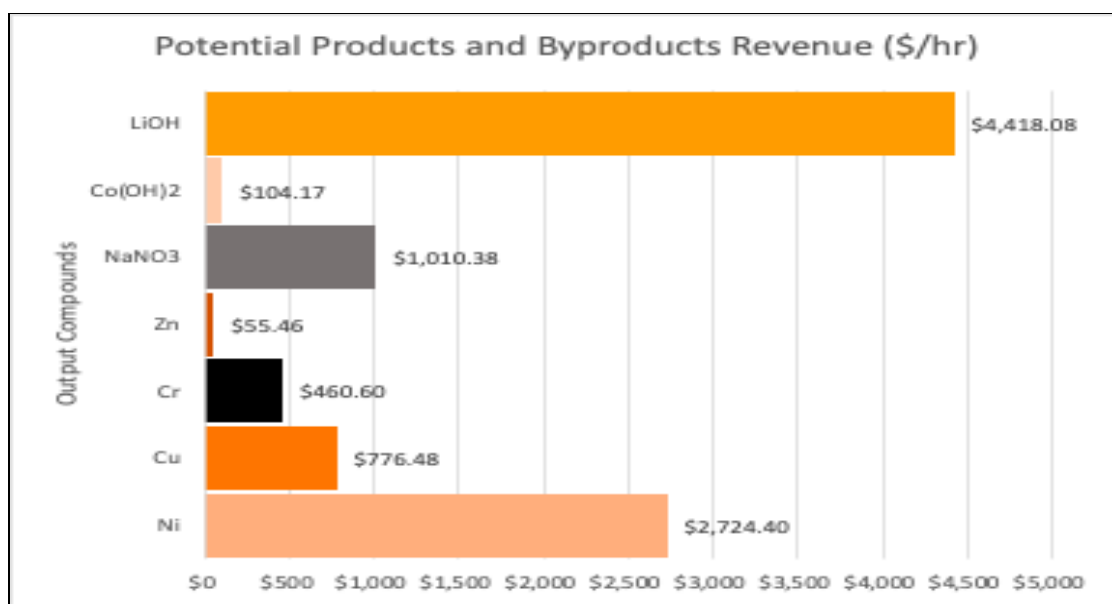


Figure 2

With a 100% recovery rate and selling all products for profit, the maximum profit was found to be $38,505,232. This profit margin did not include yearly equipment cost or operating cost. $38 million could be made solely based on product profit minus the cost of raw material. The level one economic potential is found by subtracting the cost of input compounds from the profit of output compounds, based on equation (1) in Appendix B. These prices are shown in Figure 3 and plotted based on varying amounts of product recovery.
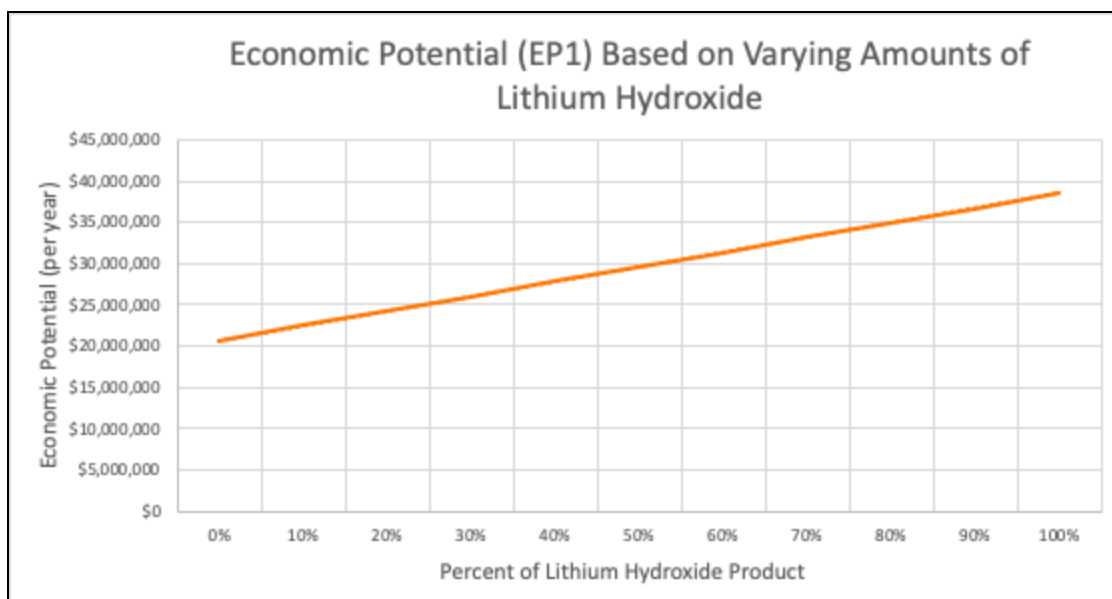
Figure 3

## 4.1 Optimization

This process was designed using our best engineering judgement, and optimization is therefore inherently built into the scaled-up design. For example, lab scale reviews shown in section 2.3 used three reactors and three filters to successfully raise the pH of the reactor throughput. As the process was scaled up, only two reactors and two filters were necessary to raise the pH to the desired level. Additionally, in this process the polymer casing is melted off right away. This allows the following unit operations to be performed at a lower temperature.

## 4.2 Process Flow Diagram

The flow diagram shown in Figure 4 starts after the spent LIBs have been heated and shredded, ensuring that no polymer casing and electrolyte in this part of the process. A thousand kilograms of liquid nitric acid are added to the spent LIB in a continuous stirred tank reactor (CSTR). The products of this reactor are then filtered to retain a liquid filtrate that contains both the lithium and cobalt compounds. The solid residue will contain nickel, copper, chromium, and zinc and these will be sold as mixed byproduct. The liquid filtrate stream named Liquid Filtration 1 will be neutralized with 800 kg of sodium hydroxide in a second CSTR. The products of this reactor called Solid Residue, are then filtered to obtain a product stream and byproduct stream. The product stream named Lithium Hydroxide will contain about 100 kg of liquid lithium hydroxide with some impurities. The byproduct stream named Cobalt Hydroxide will contain around 260 kg of cobalt hydroxide as a solid byproduct also with some impurities.

Figure 4
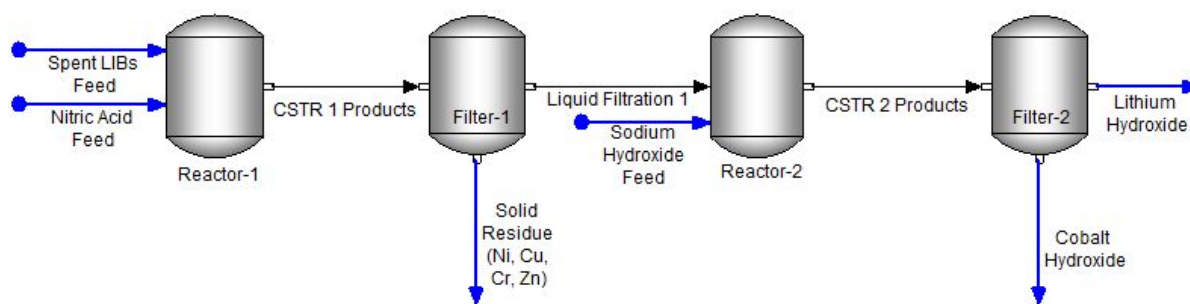
Total mass flow rates with a material balance is shown below in Table 4. Each stream name is the same as the stream name in Figure 4. Values below $10^{-4}$ of components in each stream were not included in the table below.

Table 4: Mass Flow Rate Information by Streams

| Component | MW (kg/kmole) | Streams | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Spent LIBs | Nitric Acid | CSTR 1 Products | Solid Residue | Liquid Filtration | Sodium Hydroxide | CSTR 2 Products | Cobalt Hydroxide | Lithium Hydroxide |
| Total | NA | 664.46 | 1000 | 1664.46 | 390 | 1274.46 | 800 | 2074.46 | 1329.05 | 745.411 |
| $CoO_2^{-2}$ | 90.932 | 196.159 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $Co(OH)_2$ | 92.948 | 0 | 0 | 0 | 0 | 0 | 0 | 260.434 | 260.434 | 0 |
| Cu | 63.546 | 123.25 | 0 | 123.25 | 123.25 | 0 | 0 | 0 | 0 | 0 |
| Cr | 51.996 | 49 | 0 | 49 | 49 | 0 | 0 | 0 | 0 | 0 |
| CoO | 74.933 | 48.3547 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $Co^{+2}$ | 58.933 | 0 | 0 | 165.161 | 0 | 165.161 | 0 | 0 | 0 | 0 |
| $HNO_3$ | 63.013 | 0 | 1000 | 370.665 | 0 | 370.665 | 0 | 0 | 0 | 0 |
| $H_2O$ | 18.02 | 0 | 0 | 88.128 | 0 | 88.1279 | 0 | 196.559 | 0 | 196.559 |
| $H_3O^{+1}$ | 19.023 | 0 | 0 | 1.292 | 0 | 1.292 | 0 | 0 | 0 | 0 |
| LiOH | 23.95 | 0 | 0 | 0 | 0 | | 0 | 101.629 | 0 | 101.629 |
| $Li^{+1}$ | 7 | 29.946 | 0 | 29.946 | 0 | 29.946 | 0 | 0.491 | 0 | 0.491 |
| $NO_3^{-1}$ | 62.005 | 0 | 0 | 619.266 | 0 | 619.266 | 0 | 204.435 | 0 | 204.435 |
| NaOH | 39.997 | 0 | 0 | 0 | 0 | 0 | 800 | 0.756 | 0 | 0.756 |
| $Na^{+1}$ | 22.99 | 0 | 0 | 0 | 0 | 0 | 0 | 170.349 | 0 | 170.349 |
| $NaNO_3$ | 84.995 | 0 | 0 | 0 | 0 | 0 | 0 | 1068.61 | 1068.61 | 0 |
| Ni | 58.693 | 196 | 0 | 196 | 196 | 0 | 0 | 0 | 0 | 0 |
| $OH^{-1}$ | 17.008 | 0 | 0 | 0 | 0 | 0 | 0 | 71.1382 | 0 | 71.138 |
| Zn | 65.38 | 21.75 | 0 | 21.75 | 21.75 | 0 | 0 | 0 | 0 | 0 |
| Solid Density (g/mL) | | 8.245 | | 8.54 | 8.54 | | | 2.425 | 2.435 | |
| Liquid Density (g/mL) | | 0.2 | 1.511 | 2.184 | | 2.184 | 2.13 | 1.934 | | 1.938 |
| Pressure (atm) | | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Temperature (C) | | 25 | 25 | 75 | 75 | 75 | 25 | 75 | 75 | 75 |

## 4.3 Safety, Health, and Environment Analysis

All design aspects of this plant were made while considering sustainability and environmental impact. As long as LIBs are being used, there will always be a supply of spent LIBs for the plant. If LIBs stay just as popular or become even more popular, this plant will be needed to recover the lithium because it is becoming a scarce resource. The process does produce one waste stream of polymer casing but the hope is that all of the other filtration streams will produce sellable byproducts. Since the polymer casing and undesirable metal shavings waste does not contain lithium, this will not have an environmental impact when disposing of the waste.

Another major consideration in the design of the plant was worker safety. Throughout the whole process, lithium is the largest safety concern involved in the process due to its hazardous qualities. Lithium batteries can present fire or explosion hazards. Lithium is also reactive with water so an inert gas in a commercial glove box will be used when reaction with water vapor is a concern. Dry air requirements will be met by having good vapor barriers in walls, floor, and ceiling. All equipment will be grounded, and there will be no sprinkler system that could introduce water into the dry room. Because of the arid condition of a dry room, worker safety will be monitored intensely. Personal protective equipment (PPE) will be worn at all times to account for exposure to dry powder.

The identified safety hazards and proper operating conditions are found and recorded in Table 5 as a Materials Safety Data Sheet (MSDS). It is highly recommended that operators wear corrosive resistant coverings when dealing with $HNO_3$, LiOH, and $Co(OH)_2$. Respirators may be required when dealing with the raw materials and dust created by grinding the LIBs to ensure that particles do not affect the operators' respiratory systems, as they are all considered high irritants, and some raw materials may pose as mutagenic threats.

### Table 5: Hazard Chart for All Compounds Throughout the Process

| Compound | MW | CAS No. | Melting Point (°C) | Flash Point (°C) | Boiling Point (°C) | Liquid Density (kg/m³) | Flammability | Toxicity | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | - | Deadly Poison? | Toxic? | Carcinogenic? | Mutagenic? | Irritating? | Corrosive? |
| **Inputs** | | | | | | | | | | | | | |
| LiCO2 | 97.9 | 12190-79-3 | >1000 | N/A | N/A | 4790 | 0 | Unknown | Unknown | Moderate | Unknown | High | Unknown |
| HNO3 | 63.87 | 7697-37-2 | -41.6 | N/A | 120.5 | 2500 | N/A | Unknown | Unknown | Unknown | Unknown | High | High-eyes/skin |
| LiNO3 | 68.95 | 7790-69-4 | 264 | N/A | N/A | 2380 | N/A | Unknown | Unknown | Unknown | Unknown | High | Unknown |
| Co(NO3)2 | 182.9 | 10026-22-9 | 55 | N/A | N/A | 1880 | N/A | Yes | High | Moderate | Moderate | High | Unknown |
| H2O | 18.02 | 7732-18-5 | N/A | N/A | 100 | 997 | Non-flammable | N/A | N/A | N/A | N/A | N/A | N/A |
| O2 | 32 | 7782-44-7 | -219 | N/A | -183 | 1141 | Non-flammable | N/A | N/A | N/A | N/A | N/A | N/A |
| **Outputs** | | | | | | | | | | | | | |
| NaNO3 | 85 | 7631-99-4 | 308 | N/A | 380 | 900 | N/A | Yes | Acute | N/A | Unknown | Moderate | Low |
| LiOH | 23.95 | 1310-65-2 | 450-842 | N/A | 923.9-1695 | 2013 | N/A | Unknown | Unknown | Unknown | Unknown | High | High |
| Co(OH)2 | 92.95 | 21041-93-0 | N/A | N/A | N/A | 3597 | N/A | Yes | Acute | Moderate | Moderate | High | High |

## 4.4 Capital Cost Estimates

Capital cost estimates were done for each piece of equipment necessary to the process. Sizing for each piece of equipment is shown in Table 6 and sample calculations are shown in Appendix B.

### Table 6: Design Parameters and Cost of Process Equipment

| Equipment | Number | Capacity | Equipment cost (bare material) Year 2004 | Year 2019 | Base bare module factor $F_{BM}^{C2}$ | Base bare module cost $C_{BM}^{C2}$ | Material Factor $F_M$ | Pressure Factor $F_P$ | Actual bare module factor $F_{BM}^{a}$ | Actual bare module cost $C_{BM}^{a}$ | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Reactors | | | Fig 5.23 | | | | | | | | |
| | R-200 | 7.39m³ , Stainless Steel, 1 atm | $12,000.00 | $18,000.00 | 3.0 | $54,000.00 | 7.5 | 1.0 | 7.5 | $135,000.00 | |
| | R-300 | 3.836m³ , Stainless Steel, 1 atm | $8,750.00 | $13,125.00 | 3.0 | $39,375.00 | 7.5 | 1.0 | 7.5 | $98,437.50 | |
| | | | | | | | | | | | $233,437.50 |
| Agitators/Mixers | | | Fig 5.42 | | | | | | | | |
| | M-201 | 4.95 kW, Stainless Steel , Open Tank, Mechanically-aided | $7,500.00 | $11,250.00 | 2.0 | $22,500.00 | 2.5 | 1.0 | 2.5 | $28,125.00 | |
| | M-301 | 3.836 kW, Stainless Steel, Open Tank, Mechanically-aided | $5,900.00 | $8,850.00 | 2.0 | $17,700.00 | 2.5 | 1.0 | 2.5 | $22,125.00 | |
| | | | | | | | | | | | $50,250.00 |
| Filters | | | Fig 5.57b | | | | | | | | |
| | F-202 | 0.1 m², Stainless Steel, Simple Cartridge, Continuous | $600.00 | $900.00 | 2.4 | $2,160.00 | 3.6 | 1.0 | 3.6 | $3,240.00 | |
| | F-302 | 0.129 m², Stainless Steel, Simple Cartidge, Continuous | $620.00 | $930.00 | 2.4 | $2,232.00 | 3.6 | 1.0 | 3.6 | $3,348.00 | |
| | | | | | | | | | | | $6,588.00 |
| Gas-Solid Contactors | | | Fig 5.33 | | | | | | | | |
| | B-100 | 56.75m³, Rotary kiln, Direct heating, Carbon steel | $210,000 | $315,000 | 3.75 | $1,181,250 | 3.75 | 1.0 | 3.75 | $1,181,250 | |
| | | | | | | | | | | | $1,181,250.00 |
| Conyvers | | | Fig 5.14 | | | | | | | | |
| | J-101 | 10 m Distance, 0.30 Diameter, Auger | $5,000.00 | $7,500.00 | 2.2 | $16,500.00 | 2.2 | 1.0 | 2.2 | $16,500.00 | |
| | | | | | | | | | | | $16,500.00 |
| Grinder | | | Fig 5.17 | | | | | | | | |
| | C-102 | 0.185 kg/s, Rotary Cutter, Chipper, 92.5 kW | $6,900.00 | $10,350.00 | 2.1 | $21,735.00 | 2.1 | 1.0 | 2.1 | $21,735.00 | |
| | | | | | | | | | | | $21,735.00 |

| | | | | | |
|---|---|---|---|---|---|
| Total bare module cost | | Base materials, $C_{T,BM}^{B}=\sum C_{T,BM}^{B}=$ | $1,357,452.00 | Actual Materials, $C_{T,BM}^{a}=\sum C_{T,BM}^{a}=$ | $1,509,760.50 |
| Contingency and fee | | | | | $271,756.89 |
| Total module cost | | Base materials, $C_{TM}^{C2}=1.18\times C_{T,BM}^{C2}=$ | $1,601,793.36 | $C_{TM}^{a}=$ | $1,781,517.39 |
| Auxillary facilites | | | | $C_{TM}^{C2}\times 0.30=$ | $480,538.01 |
| Grass roots capital | | | | | $2,262,055.40 |

In Figure 5, the total cost of equipment is shown and broken down by each piece of equipment.
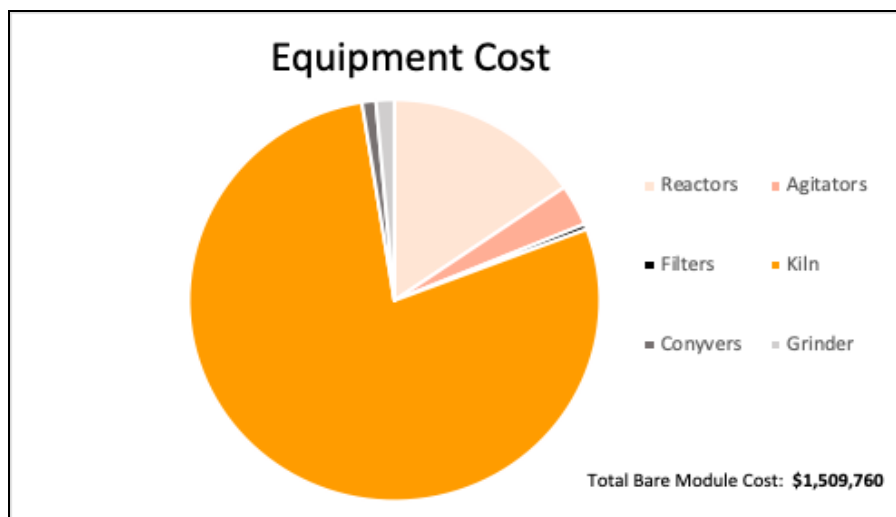


Figure 5

## 4.5 Manufacturing Cost Estimates

For our purposes, manufacturing costs, shown in Table 7, are inclusive of operating costs, but operating costs, shown in Figure 6, only encompass the operating labor and utilities cost. Equipment cost estimates were done for each piece of equipment that required some kind of utilities to run the process. Utility requirements for each piece of equipment were found; sample calculations are shown in Appendix B [9].

### Table 7: Manufacturing Costs for Designed Process

Annual Capacity= 1397153 kg/yr of Lithium Hydroxide

| Capital | | | | |
|---|---|---|---|---|
| Fixed Capital  $C_{FC}$ | $1,781,517.39 | | | |
| Working Capital $C_{WC}$ | $267,227.61 | | | |
| Total Capital Investment  $C_{TC}$ | $2,048,745.00 | | | |

| | Annual Cost $/yr | $/yr | Unit price $/kg | $/kg |
|---|---|---|---|---|
| **Manufacturing expenses** | | | | |
| **Direct** | | | | |
| Raw materials (spent LIBs @ $1/kg) | $8,064,000 | | $5.77 | |
| Byproduct credit (metal mixture @ $2,565.91 /hr) | ($16,196,292.00) | | $11.59 | |
| Catalysts and solvents | $5,322,240.00 | | $3.81 | |
| Operating labor | $567,424.20 | | $0.41 | |
| Supervisory and electrical lab | $113,484.84 | | $0.08 | |
| Utilities | | | | |
| Steam 3900 kg/hr 32 barg @ $0.029/kg | $907,594.84 | | $0.65 | |
| 6300 kg/hr 32 barg @ $0.023/kg | $1,194,425.75 | | $0.85 | |
| Electricity 8.9x10$^5$ kWh @ $0.12 kWh | $104,637.70 | | $0.07 | |
| Process water | | | | |
| Demin water | | | | |
| Cooling water | | | | |
| Waste disposal | | | | |
| Maintenance and repairs | $106,891.04 | | $0.08 | |
| Operating supplies | $16,033.66 | | $0.01 | |
| Laboratory charges | $85,113.63 | | $0.06 | |
| Patents and royalties | | | | |
| Total, $A_{DME}$ | $285,554 | $285,554 | $0.20 | $0.20 |
| **Indirect** | | | | |
| Overhead (payroll and plant), packaging, storage | $472,680.05 | | $0.34 | |
| Local taxes | $35,630.35 | | $0.03 | |
| Insurance | $17,815.17 | | $0.01 | |
| Total, $A_{IME}$ | $526,125.57 | | $0.38 | |
| Total manufacturing expense  $A_{ME} = A_{DME} + A_{IME}$ | | $811,679.22 | | $0.58 |
| **General expenses** | | | | |
| Administrative costs | $118,170.01 | | $0.08 | |
| Distribution and selling | $1,619,629.20 | | $1.16 | |
| Research and development | $809,814.60 | | $0.58 | |
| Total general expense  $A_{GE}$ | $2,547,613.81 | $2,547,613.81 | $1.82 | $1.82 |
| Depreciation $A_{BD}$ | | $178,151.74 | | $0.13 |
| Total expenses  $A_{TE}$ | | $3,537,444.77 | | $2.53 |
| Revenue from sales  $A_S$ | | ($22,308,940.26) | | $15.97 |
| Net annual profit  $A_{NP}$ | | $18,771,495.48 | | $13.44 |
| Income taxes (net annual profit x tax rate)  $A_{IT}$ | | $6,570,023 | | $4.70 |
| Net annual profit after taxes  $A_{NNP}$ | | $12,201,472.06 | | $18.14 |
| After-tax rate of return i=(1.5 $A_{NNP}$/$C_{TC}$)x100= | | 893 % | | |

*equipment is not including in the capital investment

In Figure 6, the total operating costs are shown and broken down by each piece of equipment. The kiln, grinder and conveyor belt were grouped together because of their placement in this process. For the agitators, kiln, grinder, and conveyor belt, the only required utility cost was electricity (more details shown in Appendix B). The reactor utility cost included the steam needed to heat the

jacketed CSTR. Thirty-two barg of steam was used to get the reactor at 75 ℃ and maintain this temperature. Operator cost was found using the operating factor of each piece of equipment and added together for all equipment [9].
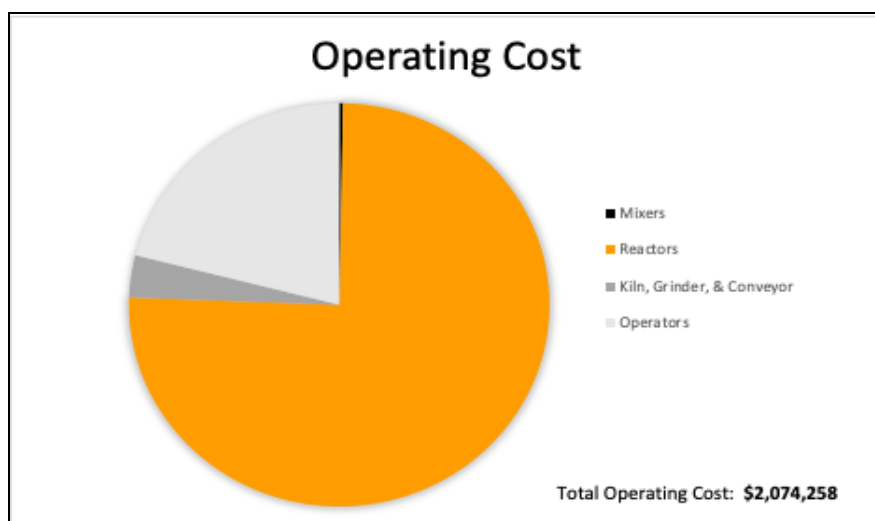


Figure 6

# 5.0 Discussion of Results

To get a better feel for the economic feasibility of the process, the second economic potential was taken. This level two analysis includes annual equipment cost along with operating cost and is shown in Figure 7. With a payback period of seven years for equipment, a max profit of the process was found to be $35,553,591. The yearly equipment cost was $254,502 and the yearly operating cost was $2,696,138. Economic potential two was found based on equation (2) from Appendix B.
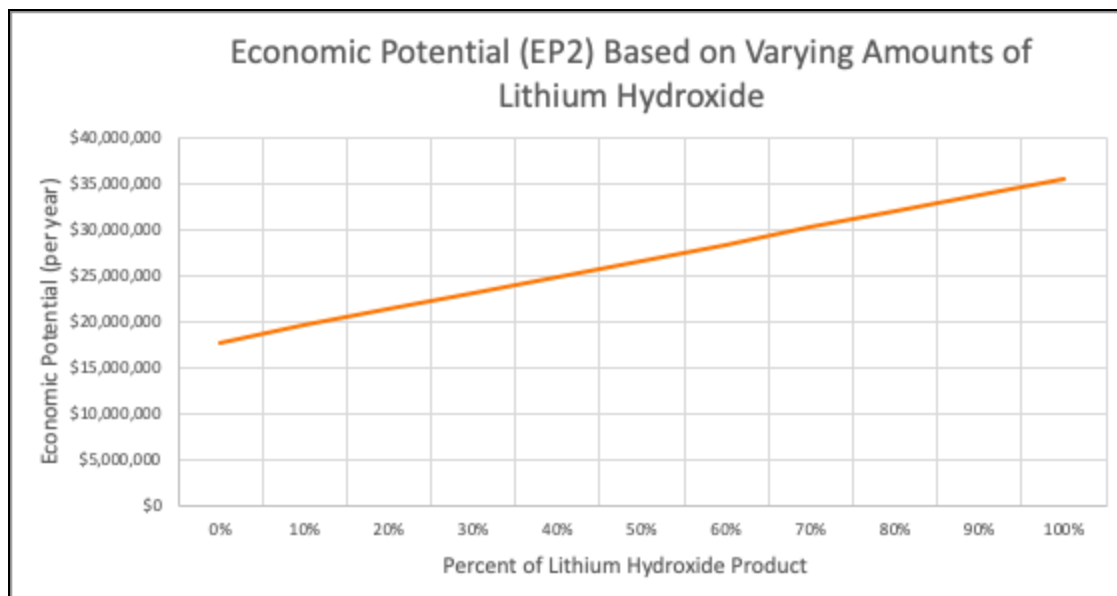


Figure 7

After a thorough evaluation of cost estimates, below is a discussion of potential optimization measures that could be taken in order to save money or produce a more efficient system. Through the equipment evaluation and costing steps of the process, other potential options were weighed, but what was thought to be the most plausible was chosen. Because there were a multitude of options for the process, such as types of equipment used or sizes of equipment, a discussion of optimization is necessary for future manipulations of the system.

## 5.1 Future Process Optimization

The rotary kiln was chosen as the most robust option to heat the LIB process feed. As seen in Figure 6, it is the most expensive unit operation, making up over 75% of the equipment expenses. More research should be done into other heating options that could reduce this high expense while still sufficiently heating the feed stream.

To design the grinder, a rotary cutter was chosen based on the assumed desired particle size of LIBs. Testing with a grinder design company would be useful to learn more about the average shredding size of LIBs. This information would help to choose the desirable size of shredded pieces as well as design the grinder to better suit our specific process needs.

The distance of the conveyor belt from the kiln to the grinder was assumed to be 7 meters. The true distance will depend on the temperature of the LIBs coming out of the grinder. The LIBs will need to cool to a temperature suitable for safety to enter the grinder. The conveyor belt length should be long enough to give the LIBs a chance to cool off if necessary. Testing on a kiln would need to be done to determine the actual temperature of LIBs leaving the kiln to decide on the exact length of the conveyor belt.

When sizing the CSTRs, stainless steel was used for both reactors due to the presence of nitric acid. Carbon steel is a lower cost material but is not suitable for the corrosivity level of nitric acid. Reactor-2 does not have any nitric acid feeds, but stainless steel was chosen in case trace amounts of acid were present in the process stream. Tests should be run in a pilot plant to determine if the nitric acid is present in trace amounts or if it is all neutralized. If neutralized, the material of Reactor-2 could be changed to carbon steel. This would allow for a cost savings of $59,000.

Both filters were priced using stainless steel for the same reason. Pilot plant tests should also be done on the filters to determine if nitric acid is present. If the acid is neutralized, Filter-2 could be priced with carbon steel to save $1,100. Additionally, simple filters were chosen for the process. Simple filters require more hands-on maintenance. Upgrading both filters from simple to automated would allow for easier operation and better yields for a cost of $13,400. Tests would need to be done to determine the difference in yield to decide if this upgrade is cost-effective.

# 6.0 Conclusions

Based on results of economic potential two shown in Figure 7, the process is found to be not only economically feasible but profitable. The maximum profit was found to be around $38 million, and will remain profitable even after including the yearly equipment and operating cost. With further analysis done in Table 7, the after-tax rate of return was found to be 893%. This analysis looks at not only the equipment and operating cost but also the indirect manufacturing cost along with general expenses and depreciation. This gives a better feel of all the expenses that will come with running this process. Table 7 goes further than just the cost to pay operators and includes administration and supervisor cost. Operating costs are expanded to include maintenance, repairs, and operating supplies. This more in depth analysis shows that the process would be economically feasible and could be extremely profitable. Since this is a study-level analysis for this process, the after-tax rate of return does have some error and will decrease with further research.

# 7.0 Recommendations

With further research, a more precise analysis can be made about the process's profitability. As discussed above in section 5.1, lab testing and a pilot plant run could be needed to obtain more accurate data. Testing can provide more accurate results than a computer simulation, and can be used to size and cost equipment to better fit the needs of the process. Data from a specific supplier of spent LIBs is necessary so a better assumption of LIB composition can be determined. Once composition is known, testing on the specific melting temperatures of the LIBs needs to be done to know exactly what kind of heating equipment would be best. The kiln that was sized for this process might be too hot for a specific composition of spent LIBs. If a different piece of equipment is used instead of a rotary kiln, this could greatly affect the profitability of the process. Testing with a grinder design company would help determine the size of grinded LIBs. This data would allow for more precise calculations for solvent flow rates and resident time for each reactor.

With more data, the process can be better laid out within a plant. With more precise equipment sizes, piping and pumps can be added to equipment cost. This will decrease the after-tax rate of return by increasing the capital investment. After more testing is done at a higher analysis level, a more accurate rate of return will decide if the process is truly profitable or not.

With a more precise analysis, the process itself does have room for improvement. The first recommendation on how to improve revenue would be to look at separating the product streams. According to Figure 2, lithium hydroxide generates the most revenue, but since it is part of a mixed product stream, the process only generates half the possible profit from lithium hydroxide. Since all product streams were mixed and were therefore discounted by 50%, this leaves room for improvement. With separate product streams, the revenue could be doubled. Before doubling the revenue, a method to separate the products in each stream must be studied for feasibility and practicality. This separation process may not be possible or economically feasible. The second recommendation would be to look at where recycling streams could be implemented throughout the process. These streams could help supply solvents back into the system and reduce the cost of continually buying new solvents.

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# Appendices

Appendix A: Project Assumptions

Table A.1: Assumptions Made Throughout the Process

| Category | Assumption | Value |
|---|---|---|
| Process | Process is continuous | |
| | Reaction time of both reactors | 3 hrs |
| Feed | All batteries are cylindrical | |
| | All batteries have a constant composition to create mass balances | |
| Equipment Sizing | Slurry viscosity | Slurry viscosity assumed to be the same as the solvent |
| | Reactor Size | Each reactor should be filled ⅔ full of reactants |
| | Belt Length | Total 10m including section into and out of kiln |
| | Kiln length to diameter ratio | L/D=15 |
| | Basic piping costs are included in the bare module price of equipment | No extra cost was accounted for piping in this process |

## Appendix B: Sample Calculations

### B.1 Economic Potentials

$$EP_1 = Value\ of\ Products\ +\ Value\ of\ Byproducts\ -\ Cost\ of\ Reactants \tag{1}$$

$$EP_2 = EP_1 - Annualized\ Equipment\ Cost\ -\ Operating\ Cost\ of\ Equipment \tag{2}$$

### B.2 Costing for Equipment

All equipment cost was found using the Chemical Engineering Process Design and Economics: a Practical Guide textbook [9].

Cost of Rotary Kiln

Table 4.10 was used for preliminary equipment selection. Based on thermal efficiency, electrical power requirements, and angle of incline, a rotary kiln was chosen. To find the kiln cost, the internal volume had to be sized first. Assuming a length-diameter ratio of 15, a diameter of 1.7 m and a length of 25 m was found. With these measurements the volume was found to be 56.75 m³. Using Figure 5.33 for rotary and vertical tower gas-solid contactors, the purchased equipment cost in 2004 dollars was found to be around $210,000. Converting this to 2019 dollars, the purchased equipment cost was found to be $315,000. To find the bare module cost, $F_{BM} = 3.75$ was used for a carbon steel rotary kiln.

$$C_{BM} = C_p \times F_{BM} \tag{3}$$
$$C_{BM} = \$315,000 \times 3.75 = \$1,181,250$$

Cost of Conveyor Belt

A conveyor belt was sized for moving material into and out of the rotary kiln. Ten meters in total distance was assumed with 3 m of belt leading up to the kiln and 7 m of belt coming out of the kiln, moving material into the grinder. Table 4.4 was used for preliminary equipment selection. Based on criteria, an auger belt with a 0.3 m auger diameter was chosen. Using Figure 5.14 for apron, auger belt and bucket conveyors, the purchase equipment cost in 2004 dollars was found to be around $5,000. Converting to 2019 dollars the equipment cost was found to be $7,500. Bare module cost using $F_{BM} = 2.2$ was used for an auger. Using equation (3) bare module cost was found to be:

$$C_{BM} = \$7,500 \times 2.2 = \$16,500$$

Cost of Grinder

To grind the spent LIBs that are coming out of the rotary kiln, a rotary cutter was chosen based on maximum feed diameter, maximum capacity and size of crushing which were described in Table

4.5a. With a feed rate of 0.185 $\frac{kg}{s}$ of spent heated LIBs, a purchased equipment cost in 2004 dollars was found to be around $6,900 from Fig 5.17. Converting to 2019 dollars, the purchased equipment cost was around $10,350. Using a $F_{BM} = 2.1$ for rotary cutter and equation (3), a bare module cost in 2019 dollars was found to be:

$$C_{BM} = \$10,350 \times 2.1 = \$21,735$$

Sample Cost of first CSTR Reactor (including agitators)

To determine reactor cost, the reactor first had to be sized. Assuming ideal mixing and additive volume, volumetric flow rate was found using OLI:flowsheets.

$$V_T \ (volumetric \ flow \ rate) = V_{Spent \ LIBs} + V_{nitric \ acid} \tag{4}$$
$$V_T = 1.1837 \ \tfrac{m^3}{hr} + 0.66162 \ \tfrac{m^3}{hr} = 1.85 \ \tfrac{m^3}{hr}$$

Once total volumetric flow rate was found, the volume of solution that filled the reactor was found based on the space time. For both reactors, we assumed a space time of 3 hrs ($\tau = 3$). To find the total reactor volume, the reactor was assumed to be ⅔ full.

$$V_{solution} = V_T \times \tau \tag{5}$$
$$V_{solution} = 1.85 \tfrac{m^3}{hr} \times 3 \ hr = 5.54 \ m^3$$
$$V_{reactor} = \tfrac{4}{3} \times V_{solution}$$
$$V_{reactor} = \tfrac{4}{3} \times 5.54 \ m^3 = 7.39 \ m^3$$

Using Figure 5.23 for a jacketed vessel the purchased equipment cost in 2004 was found to be around $12,000. Converting this to 2019 dollars, the purchased equipment cost of the vessel is $18,000. To find bare module cost $(C_{BM,vessel})$, $F_p = 1$ for pressure less than 5 barg and $F_{BM,vessel}$ =7.5 for stainless steel were used with equation (6).

$$C_{BM,vessel} = C_{P,vessel} \times F_{BM,vessel} \times F_P \tag{6}$$
$$C_{BM,vessel} = \$18,000 \times 7.5 \times 1 = \$135,000$$

To decide the agitator size, the power consumption was needed. Table 4.16 gave equation (7) which defines power consumption for a mechanically-aided agitated axial turbine with a given reactor volume.

$$P = V^{0.8} = 7.39^{0.8} = 4.95 \ kW$$

With power consumption, purchased equipment cost in 2004 dollars was found to be $7,500 from Figure 5.42. Converting to 2019 dollars, the purchased equipment cost was $11,250. Using equation (3) and an $F_{BM} = 2.5$ for stainless steel agitators, a bare module cost in 2019 dollars was found to be:

$$C_{BM} = \$11,250 \times 2.5 = \$28,125$$

Sample Cost of First Filter

Table 4.23b was used for preliminary equipment selection. Based on liquid being the continuous phase, diameter of particles, and area needed, a simple cartridge filter was chosen. To find the filter cost, the nominal filter area had to be sized first. Using equation (7) from Table 4.23b, nominal area could be found using the liquid flow rate in $m^3/s$.

$$q_l = 0.002 \times A \tag{7}$$
$$A = \frac{1.75 \times 10^{-4}}{0.002} = 0.0875 m^2 \approx 0.1 m^2$$

With this area, the filter purchasing cost can be found. Using Figure 5.57b for liquid filter, the purchased equipment cost in 2004 dollars was found to be around $600. Converting this to 2019 dollars, the purchased equipment cost was found to be $900. To find the bare module cost, equation (3) and a $F_{BM} = 3.6$ was used for a stainless steel simple cartridge filter.

$$C_{BM} = \$900 \times 3.6 = \$3,240$$

## B.3 Operating Cost

Cost of Electricity

According to the textbook, power requirements are needed for all mixers, the kiln, the conveyor belt and the grinder. The power needed for each agitator is found based on equation (8) with the volume of the reactor known.

$$P(kW) = V^{0.8} \tag{8}$$

The first reactor has a volume of $7.39\, m^3$ which requires a power of 4.95 kW of electricity. Once the power requirement is found, the cost for electricity can be used to find the annualized cost. Assuming the cost of fuel to be \$4/GJ and the plant to run 8064 hr/yr:

$$C_{(s,e,2019)} = 1.3 \times 10^{-4}(600) + 0.010(\$4/GJ)$$
$$C_{(s,e,2019)} = \$0.12/kWh$$
$$A_E = (0.94)(4.95 kW)(\$0.12/kWh)(8064\ hr/yr) = \$4,427.57/yr$$

This process was repeated to find the annualized cost of the second agitator as well. To find the power needed for the kiln, equation (9) from the textbook was used along with the internal volume of the kiln.

$$P(kW) = 0.15 \times V \tag{9}$$

Based on the length-diameter ratio of 15, a diameter of 1.7 m, a height of 25 m, the volume was found to be 56.75 m³. With this volume the power was found to be 8.5125 kW. Using this power and the cost of electricity, the annualized cost can be found.

$$A_E = (0.94)(8.5125kW)(\$0.12/kWh)(8064\ hr/yr) = \$7,614.08/\text{yr}$$

To find the power needed for the conveyor belt, equation (10) was used from the textbook along with a 10 m length and the mass flow rate.

$$P(kW) = 0.007m^{0.85} \times L \tag{10}$$

With this equation a power of 0.1668 kW was found and used with the cost of electricity to find the annualized cost.

$$A_E = (0.94)(0.1668kW)(\$0.12/kWh)(8064\ hr/yr) = \$149.20/\text{yr}$$

To find the power needed for the grinder, equation (11) was used to find a power of 92.5 kW and an annualized cost of $82,737.45/yr.

$$P(kW) = 500 \times m \tag{11}$$

Cost of Steam

Using energy given by OLI:flowsheet for both the inlet streams and the outlet streams, the difference was set equal to the energy the steam needs to supply. Using these equations below, the mass flow rate for steam can be found.

$$Q_T = Q_{outlet} - Q_{inlet} = -5.81 \times 10^9 J/hr - (-4.99 \times 10^9 J/hr) = -8.25 \times 10^8 J/hr$$
$$Q_T = -Q_{steam} = m_s C_p \Delta T$$
$$-8.25 \times 10^8 J/hr = m_s(4.184 J/g \cdot K)(348 - 298)$$
$$m_s = 3,947,703.349\ g/hr$$

Cost for steam and the annualized cost can be calculated assuming steam is supplied at 32 barg and the cost of fuel to $4/GJ.

$$C_{(s,s,2019)} = 2.7 \times 10^{-5}(m_s)^{-0.9}(600) + 0.0034(P)^{0.05}(\$4/GJ)$$
$$C_{(s,s,2019)} = \$0.029/kg$$
$$A_E = 3,947.70 kg/hr\ (\$0.029/kg)(8064\ hr/yr) = \$907,594.84$$

Cost of Operator

Each piece of equipment uses a certain amount of operator time and effort, represented by an operating factor. The operating factor for each piece of equipment is shown in the table below. Based on each piece of equipment in this process,the total operating factor is 1.7. Using this and equation (12) the annualized operating cost can be found.

Table B.3.1: Number of Operators for Each Type of Equipment

| Piece of Equipment | Operating Factor |
| --- | --- |
| Reactor w/ mixer | 0.3 |
| Filter | 0.1 |
| Kiln | 0.4 |
| Grinder | 0 |
| Conveyor | 0.5 |

$$A_E = 5 * (operating\ factor) \times \$41,600/yr\ (1.03)^{2019-2003} \tag{12}$$
$$A_E = 5 * (1.7) \times \$41,600/yr\ (1.03)^{2019-2003} = \$567,424.20/yr$$