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DEPARTMENT OF CHEMICAL ENGINEERING

Assessing the Sustainability of Electrodialysis for Rare Earth Element Recovery from  
Phosphogypsum

ALEXANDRA BRAJOVIC  
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for a baccalaureate degree  
in Chemical Engineering  
with honors in Chemical Engineering

Reviewed and approved\* by the following:

Dr. Rui Shi  
Professor of Chemical Engineering  
Thesis Supervisor

Dr. Esther Gomez  
Professor of Chemical Engineering  
Honors Adviser

\* Electronic approvals are on file.

## ABSTRACT

Electrodialysis (ED) has been sought as a method of rare earth element (REE) separation from phosphogypsum as a means to promote sustainable waste recovery and implement a circular economy. In order to handle large amounts of waste generated from mining activities, ED must be scaled up to industrial levels and evaluated as a continuous process of REE recovery, rather than as a batch or pilot-scale process, and evaluated for its environmental and financial impacts. A Life Cycle Analysis (LCA) was performed on ED using openLCA software, and the results were compared to an LCA performed on precipitation from oxalic acid. For financial impacts, a model was developed in Microsoft Excel with adjustable parameters to determine the capital and annual operating costs of an ED system that meets set production goals. Compared to precipitation from oxalic acid, ED has slightly higher global warming potential and fossil fuel consumption impacts but also displays significantly lower impacts for human and terrestrial toxicity. Financially, an ED system is economically viable; although multiple units running in parallel are required to meet production needs, the overall cost is dominated by capital costs, which scale with membrane size, which is driven by current applied to the unit. The initial investment will be made back after three years, and thus the ED system will be profitable over time.

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## Chapter 1

### Introduction

Global sustainability efforts have increasingly promoted the idea of a “circular economy,” in which less energy and fewer materials are used to make longer-lasting products and, more notably, waste is eliminated by re-entering the production process as a source of energy and materials. (1) One target of such efforts is phosphogypsum, a solid mining by-product from phosphate rock that contains rare earth elements (REEs), such as yttrium, scandium, and cerium, all of which are crucial to manufacturing electronic devices and components. (2) However, as the name implies, REEs are found only in extremely small quantities in phosphogypsum, making them difficult to separate for use in manufacturing. Given the large quantities of phosphogypsum generated from mining operations, any separation processes must be capable of handling large, industrial-scale amounts of phosphogypsum while recovering as many REEs from the waste as possible.

Research has focused on electrodialysis (ED) as a potential method to close this gap. Previously used for water desalination, ED uses an electric current to drive ion separation through a series of cation and anion exchange membranes, concentrating ions into one exit stream while leaving the other exit stream dilute and free of impurities. Along with batch desalination, ED has been proven capable of separation of REEs from waste products like coal ash and diluted wastewater. More notably, such systems prove their economic viability as well, with relatively low energy costs compared to other methods of REE separation and water purification. Most recent literature finds that capital costs contribute more to overall expense for

an ED system than annual operating costs, so an efficiently-designed ED system must minimize capital cost to be economically viable.

However, current literature on ED remains sparse and still leaves knowledge gaps to fill. Most analyses have been performed on batch or point-of-use ED systems, which are much smaller scale than required for industrial applications; the principles that apply at a batch or pilot scale may not hold when the process is made continuous, especially due to increases in capital and operating costs. Furthermore, current literature uses ED to separate REEs from waste products like wastewater and coal ash, yet few studies examine its separation from phosphogypsum specifically. Some literature also only focuses on certain REEs, like scandium, when the process's efficiency may change depending on the REE recovered.

This work aims to reinforce the findings of previous literature while expanding ED applications into REE recovery from phosphogypsum. A Life Cycle Analysis (LCA) and Technoeconomic Analysis (TEA) will each be used to quantify the environmental and financial impacts, respectively, of such a system. The LCA will compare the impacts of ED to precipitation with oxalic acid, a less complex REE separation method, while the TEA will establish the relationships between membrane area and capital cost through an Excel model and investigate the profitability of an ED system for REE recovery. Note that these analyses are considered “gate-to-gate”, so any preparation of the phosphogypsum for ED or further separation of REEs after ED will not be considered in this study.

## Chapter 2

### Literature Review

When electrodialysis (ED) emerged as a new technology for ion isolation, researchers quickly jumped to study its use in desalination and water purification. One of the first of such papers, McGovern et al., set the groundwork for designing ED systems and evaluating associated energy and capital costs in 2014. The research team performed a set of 10 batch experiments to replicate the performance of a 10-stage continuous ED system. Over the course of these stages, they would desalinate aqueous sodium chloride solutions from 195,000 parts per million (ppm) to just 240 ppm. To optimize the voltage across the ED stack, the researchers then made a model validated by the experimental results to project costs. Their numerous findings proved promising; the team claimed that energy requirements "...are similar to current ... desalination processes for feedwaters ranging between roughly 40,000-90,000 ppm TDS, but we project water costs to potentially be lower." (3) Similarly, high salinity streams produced a lower cost per unit salt removed. All results indicate that ED is economically feasible for desalination; however, as the researchers pointed out, the topic required "further investigation of robustness to fouling under field conditions." (3)

Continuing with desalination, Shah et al. further investigated capital and energy costs for batch ED systems in 2018. Modeled after existing batch systems, the research team developed a model that held feed concentration (2000 mg/L) and recovery ratio (90%) constant while altering various other parameters for different product concentrations and production requirements. Specifically, the team considered optimal geometry, flow rates, and applied voltage for minimizing total cost. Overall, the team discovered that capital costs far outweighed energy costs, so their design could maximize current density to get the best separation of ions possible.

(4) Thin channels and large membrane length-to-width aspect ratios accomplished this optimization. The team also determined optimal flow rates and voltages to meet varying production requirements, with voltage decreasing as production increased. Moreover, as feed concentration increased, overall membrane area increased to meet required product concentrations; this was also found to be more effective for higher production than increasing the number of ED cell pairs. (4) Although this paper furthered economic analyses and solidified trends for ED design, its scope is limited due to use of a batch system; any industrial application of desalination would require a continuous process.

Later research brought ED into an entirely new field: rare earth element (REE) recovery. Using the same principles as removing salt ions from water, researchers began to explore how REEs like scandium, yttrium, and other valuable ions could be separated out from waste streams for economic use. In 2020, Couto et al. applied this idea to coal ash, studying ED use for REE recovery from bituminous and anthracite coal ash. The team built a two-compartment ED cell to run different experiments. They varied the pH of the inlet solution, the current applied to the cell, and the time allotted for the process to run. Over the course of three days, with an adjusted pH and applying 50 mA of current, the ED cell recovered 70% of REEs present in the coal ash. (5) According to the study, given “the high criticality of neodymium with its high concentration in anthracite coal ash (65 ppm)” (5), the team strongly recommended implementing an ED system for REE recovery. Therefore, the results of the study are limited to coal ash; further research needed to delve deeper into other waste streams to test their viability and economic feasibility for REE recovery.

With ED gaining more ground as an established, sustainable technology, the most recent literature focused on its economic costs and its expansion into waste treatment. Some studies,

such as Generous et al., built an economic framework but still limited their scope to desalination and water purification. Devising a highly detailed and complex model, the team considered Donnan potential, boundary layer, water transport, and spacer effects. Ultimately, this determined the ED system's membrane area, which drove capital costs, while outlet concentration requirements drove energy costs. (6) Complete with sensitivity analysis, Generous et al. provided a robust economic review of an ED system for comparison to future designs and trends. (6) However, once again, the scope is limited to water desalination rather than REE recovery. At the same time, Li et al. attempted to marry these ideas, optimizing an ED design for REE recovery from diluted wastewater with some economic considerations. After rigorous testing on an ED cell with altering applied current, voltage, feed concentration, and more, the team struck gold: 99.52% recovery of scandium ions while only consuming 0.26 kWh/m<sup>3</sup> of energy. (7) Results yet again pointed to a highly efficient, environmentally-friendly process. However, once again the source only focuses on one avenue of REE recovery, with heavy emphasis on scandium in particular; the results may differ in other waste sources or with other REEs.

These sources and others typically frame ED as a method of desalination but fail to consider applications outside of water quality. Those that do focus on REE recovery fail to evaluate its costs when applied to all waste sources, not just wastewater or coal. Thus, my thesis work contributes to research ED by expanding its usage to REE recovery from phosphogypsum and evaluating the environmental and economic impacts of the process.

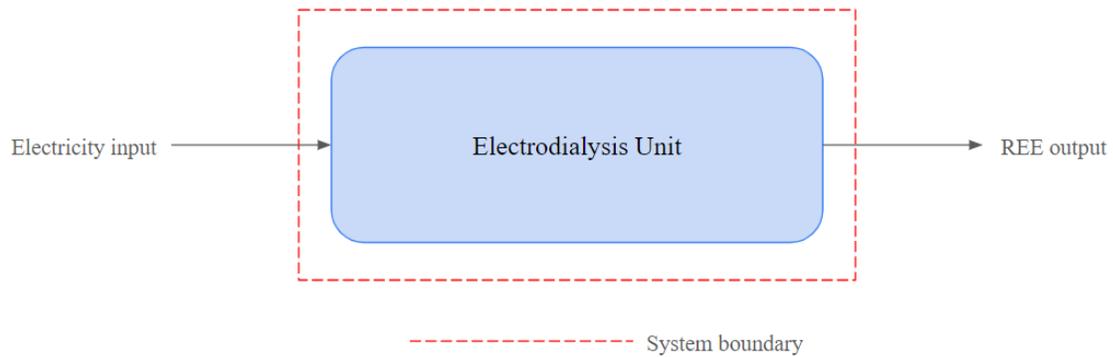
## **Chapter 3**

### **Methods**

#### **Life Cycle Analysis (LCA)**

To determine the system's environmental impacts, a Life Cycle Analysis (LCA) was performed using openLCA 1.11 and the ecoInvent 3.9.1 database. To perform the LCA and report impacts, the ReCiPe 2016 LCIA method (v1.03) was chosen for its widespread use in other LCA studies and variety of relevant impact categories, like global warming potential, fossil fuel depletion, and terrestrial ecotoxicity. The Midpoint indicator and Hierarchist perspective were used, as Midpoint indicators focus on single environmental issues, while endpoint indicators focus on higher level, aggregated issues. Midpoint indicators like global warming, water use, and fossil resources are all more appropriate for this study's scope rather than higher-level concerns, like damage to human health and ecosystems. For perspective, Hierarchist is most appropriate for this study, as it is most widely used in other LCA studies, including one used to compare LCA results (see Chapter 4 for further discussion). The Hierarchist perspective also serves as the middle and most realistic option, while the individualist perspective is overly optimistic and assumes humans will design all solutions to environmental problems, and the more conservative egalitarian perspective assumes humans will not be able to solve any environmental problems through design or proper management. Within openLCA, a new flow was created entitled "REEs" to represent the flow of REEs in and out of the system and was set as a quantitative reference as an output. The only input for the process was electricity sourced from the Southeastern U.S., specifically Florida, as the ED plant would be located there. As mentioned previously, this analysis is considered "gate-to-gate;" therefore, no processes outside

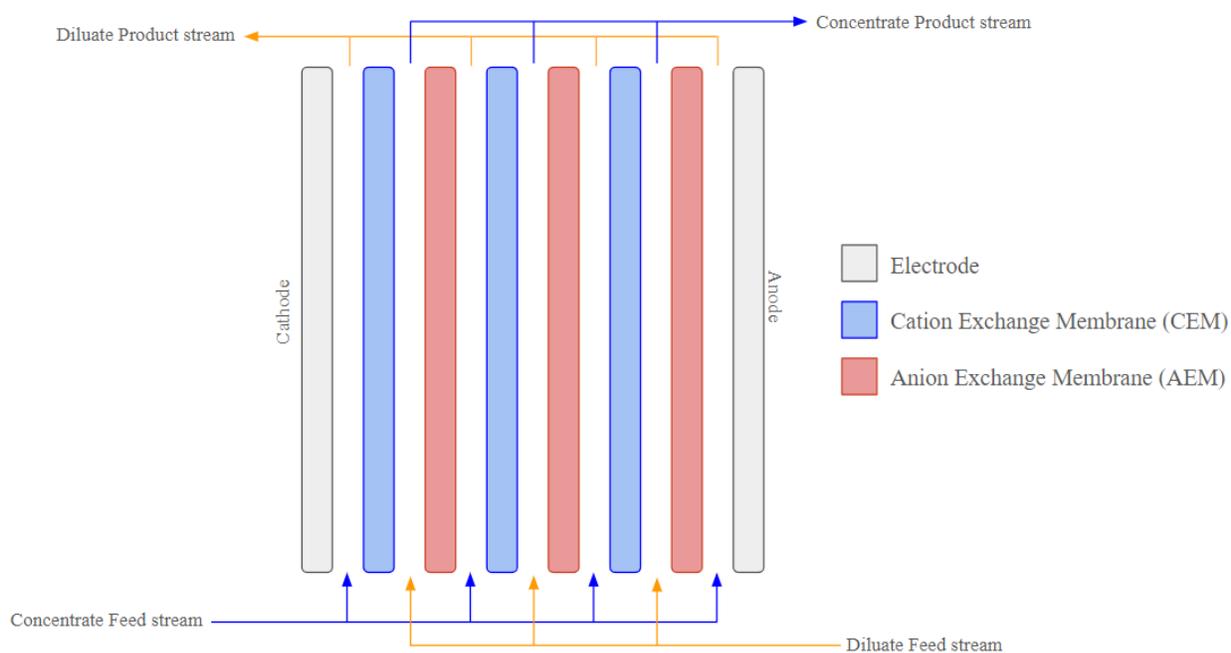
of ED will be considered for environmental impacts, such as the acquisition of phosphogypsum and its preparation for ED, or any further separation of individual REEs outside of ED. Figure 1 displays the system boundaries and the inputs and outputs considered for the LCA study.



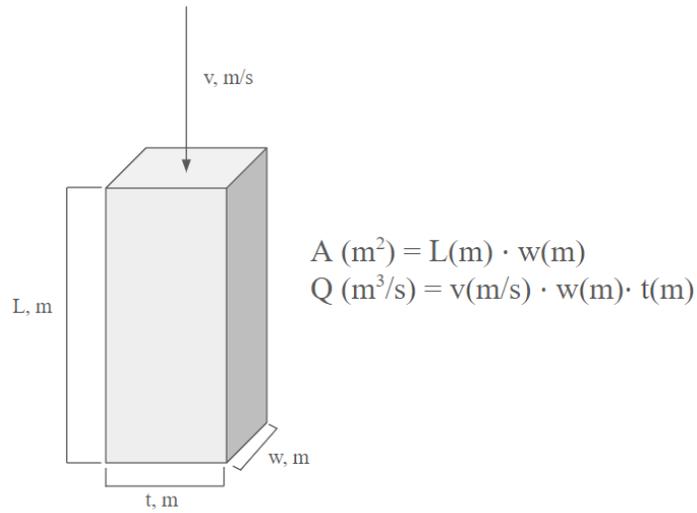
**Figure 1. The system boundary and inputs for the LCA on electrodeialysis.**

### Technoeconomic Analysis (TEA)

For the TEA, a mass balance was developed based off of the structure of an ED cell, as depicted in Figure 2, in order to determine the area of the cell membranes used and thus the capital cost of the cell. The cell contains concentrate streams, which have an elevated concentration of REEs at the exit of the cell, and diluate streams, which are expected to be free of REEs at the exit of the cell.



**Figure 2. A diagram of an ED cell. The diluate streams will have ions (REEs) at the inlet and no ions (REEs) at the outlet, while the concentrate stream will have no ions (REEs) at the inlet and be concentrated with ions at the outlet.**



**Figure 3. The diagram of an individual ED cell, or space between exchange membranes, with visual definitions of length, width, thickness, linear velocity, membrane area, and volumetric flow rate.**

Since the purpose of this ED process is to concentrate REEs for further separation and purification, the mass balance will focus on the concentrate streams. It is assumed that the system is at steady state so there is no accumulation within the ED cell due to membrane fouling. There is an inlet flow, an outlet flow, and a transport term representing the flux of ions across the membrane pair from the diluate to the concentrate stream, as given by Nemeček et al (8). Thus, the initial mass balance is given by the equation

$$n_{c,in} - n_{c,out} + n_{membrane} = 0 \quad (1)$$

in which  $n_{c,in}$  is the molar flowrate into the ED unit through the concentrate stream,  $n_{c,out}$  is the molar flowrate out of the unit through the concentrate stream, and  $n_{membrane}$  is the molar flowrate from membrane transport, all in mol/s. Rewriting the above in terms of concentration, flowrate, and other parameters (see Table 3), equation 1 then becomes

$$Q_{c,in}c_{c,in} - Q_{c,out}c_{c,out} + \frac{\eta IN_p}{zF} = 0 \quad (2)$$

where  $Q_{c,in}$  and  $Q_{c,out}$  represent volumetric flow rate in and out of the concentrate stream, respectively, in  $m^3/s$ ,  $c_{c,in}$  and  $c_{c,out}$  represent the concentration of REEs in the inlet and outlet concentrate stream, respectively, in  $mol/m^3$ ,  $\eta$  is the efficiency of the system and is unitless,  $I$  is the current through the ED unit in Amperes,  $N_p$  is the number of cell pairs,  $z$  is the atomic charge of the ions removed (assumed to be +3 as REEs are typically trivalent cations), and  $F$  is Faraday's constant, 96,500 A·s/mol. It is assumed that the volumetric flowrate in and out of the ED unit is the same, so the equation is simplified to

$$Q(c_{c,in} - c_{c,out}) + \frac{\eta IN_p}{zF} = 0 \quad (3)$$

and then modified to

$$Q(c_{c,in} - c_{c,out}) = -\frac{\eta IN_p}{zF} \quad (4)$$

The negative sign is then canceled out to get

$$Q(c_{c,out} - c_{c,in}) = \frac{\eta IN_p}{zF} \quad (5)$$

In order to further reduce the number of variables, a new parameter for the recovery of REEs into the concentrate stream,  $R$ , is introduced.  $R$  is a number between 0 and 1 governed by the equation

$$R = \frac{c_{c,out} - c_{c,in}}{c_{c,in}} \quad (6)$$

with  $c_{c,in}$  and  $c_{c,out}$  defined the same way as in equation 2. Thus, if both sides of equation 5 are divided by  $c_{c,in}$ , equation 6 may be substituted in as the recovery,  $R$ :

$$Q \frac{(c_{c,out} - c_{c,in})}{c_{c,in}} = \frac{\eta IN_p}{zF c_{c,in}} \quad (7)$$

$$QR = \frac{\eta IN_p}{zF c_{c,in}} \quad (8)$$

$$Q = \frac{\eta I N_p}{z F c_{c,in} R} \quad (9)$$

Q can then be rewritten in terms of the linear velocity of the fluid pumped through the system, v, and the cell's width, w, and thickness, t, as defined in Figure 3 and the equation

$$Q = wvt \quad (10)$$

By substituting equation 8 into equation 7 and solving for w, the area of the cell membrane can then be calculated by multiplying the cell width by an aspect ratio, L/w, defined by the operator.

$$wvt = \frac{\eta I N_p}{z F c_{c,in} R} \quad (11)$$

$$w = \frac{\eta I N_p}{z F c_{c,in} R vt} \quad (12)$$

$$A_{cell\ membrane} = w^2 \cdot \left(\frac{L}{w}\right) \quad (13)$$

From this derivation, the model was created in an Excel spreadsheet to vary current applied to the cell while holding all other parameters constant, calculating a width and therefore area from the set aspect ratio. The area was then used to determine an overall capital cost for the ED unit by using the parameters set forth by Shah et al. (5) for membrane, electrode, and spacer costs (see Table 4). The overall capital cost was multiplied by a Lang factor of 4.74 to translate the purchase cost (represented here by the overall capital cost) to a total installation cost after factoring in auxiliary equipment, like piping and fittings, as well as other expenses. For operating costs, the applied voltage was multiplied by the chosen current to obtain a power requirement in W. This was then converted to kW and multiplied by the assumed uptime of the unit in hours per year to get a kWh rating, which was then multiplied by the average electricity cost in the United States (assumed to be \$0.10 per kWh) to get an annualized operating cost. The inlet volumetric flow rate of phosphogypsum was then divided by the calculated production rate of the model, Q, from equation 10, to determine the number of units necessary to meet production goals; this

number was then multiplied by the capital and operating costs for one unit to get an overall ED capital and operating cost for the entire system. For revenue calculations, the inlet mass flow rate of phosphogypsum in kg per hour was multiplied by the weight percentage of REEs, the recovery  $R$ , and the price of REEs to determine revenue in USD per hour. This value was then multiplied by the estimated runtime of the plant in hours per year to get a yearly revenue from selling REEs. The first-year profit was then found by subtracting the sum of capital and operating costs from the revenue from REEs; for subsequent years, assuming that the ED units and membranes last longer than one year, only operating costs are subtracted from REE revenue to determine profit.

## Chapter 4

### Life Cycle Analysis (LCA) Results & Discussion

The ED process produced mostly little impact, especially in categories related to human health impacts and water consumption. The most prominent impact categories were fossil resource scarcity with 19.09 kg of oil eq per kg of REEs and global warming potential with 60.24 kg CO<sub>2</sub> eq per kg REEs. A detailed report of the process's impacts is given in Table 1.

However, in order to put the results of the LCA into further context, ED must be compared with a separate process for REE separation from phosphogypsum. In unpublished work from Smerigan et al. (9), an LCA was conducted on a process using oxalic acid to precipitate REEs from phosphogypsum using ReCiPe 2016. The results of (9) are given in Table 2. Across the board, the oxalic acid process causes more harm to human health as well as terrestrial and marine environments, with elevated levels of ecotoxicity across the latter two categories. For human non-carcinogenic toxicity, the oxalic acid process shows an impact of 36.96 kg 1,4-DCB per kg REEs, which is significantly larger than ED, which only produces 0.933 kg 1,4-DCB per kg REEs. Marine and terrestrial ecotoxicity display similarly stark contrasts, as the oxalic acid process shows impacts of 2.121 and 152.002 kg 1,4-DCB per kg REE, respectively; meanwhile, ED shows impacts of 0.919 and 0.00219 kg 1,4-DCB per kg REE to marine and terrestrial environments, respectively. ED's lower toxicity levels make sense; depending on the methods, the production of oxalic acid for precipitation requires high temperatures and the use of dangerous acids like nitric and sulfuric acid (10), both of which are highly damaging to human health and natural ecosystems. In contrast, the only sources of toxicity in ED are from electricity usage, which includes fossil fuel consumption for electricity generation.

That being said, electricity consumption also creates a noticeable difference between the processes. ED does have a higher global warming potential and more fossil resource scarcity; it has respective impacts of 60.24 kg of CO<sub>2</sub> eq per kg of REE processed for global warming potential and 19.09 kg of oil eq per kg of REE for fossil resource scarcity. Meanwhile, the oxalic acid process has impacts of only 52.11 kg CO<sub>2</sub> eq and 12 kg oil eq for per kg of REE processed. Thus, ED is the more energy-intensive process as it requires electricity consumption, so depending on the source of electricity, it could contribute more to global warming than oxalic acid production for precipitation. Even so, the scale of global warming potential and fossil resource scarcity is of a similar order of magnitude for both processes, and ED poses less of a toxicity risk to both humans and the environment than oxalic acid production. While ED may have slightly more impact on global warming and fossil fuel usage depending on its electricity source, it also avoids the use of harmful acids and high temperatures featured in the production of oxalic acid, which keeps human health intact and protects terrestrial ecosystems; if these are high-priority to the surrounding community, then ED is certainly an environmentally viable alternative for REE recovery.

**Table 1. Life Cycle Analysis Results for Electrodialysis Process.**

| <b>Impact category</b>             | <b>Reference unit</b>    | <b>Value (per kg REE)</b> |
|------------------------------------|--------------------------|---------------------------|
| Ecosystem damage – ozone formation | kg NO <sub>x</sub> eq    | 0.088134                  |
| Freshwater eutrophication          | kg P eq                  | 0.040947                  |
| Freshwater ecotoxicity             | kg 1,4-DCB               | 1.054947                  |
| Fossil resource scarcity           | kg oil eq                | 19.092292                 |
| Global warming potential           | kg CO <sub>2</sub> eq    | 60.240153                 |
| Human damage – ozone formation     | kg NO <sub>x</sub> eq    | 0.086628                  |
| Human carcinogenic toxicity        | kg 1,4-DCB               | 0.014671                  |
| Human non-carcinogenic toxicity    | kg 1,4-DCB               | 0.932557                  |
| Ionizing radiation                 | kg U235-Eq               | 0.233270                  |
| Land use                           | m <sup>2</sup> a crop eq | 0.093187                  |
| Marine eutrophication              | kg N eq                  | 0.041869                  |
| Marine ecotoxicity                 | kg 1,4-DCB               | 0.918709                  |
| Stratospheric ozone depletion      | kg CFC11 eq              | 2.10851E-06               |
| Fine particulate matter formation  | kg PM2.5 eq              | 0.055126                  |
| Mineral resource scarcity          | kg Cu eq                 | 0.017485                  |
| Terrestrial acidification          | kg SO <sub>2</sub> eq    | 0.156912                  |
| Terrestrial ecotoxicity            | kg 1,4-DCB               | 0.002185                  |
| Water consumption                  | m <sup>3</sup>           | 0.241753                  |

**Table 2. Life Cycle Analysis Results for Oxalic Acid Process.**

| <b>Impact category</b>             | <b>Reference unit</b>    | <b>Value (per kg REE)</b> |
|------------------------------------|--------------------------|---------------------------|
| Ecosystem damage – ozone formation | kg NO <sub>x</sub> eq    | 1.332412                  |
| Freshwater eutrophication          | kg P eq                  | 0.009543                  |
| Freshwater ecotoxicity             | kg 1,4-DCB               | 1.602324                  |
| Fossil resource scarcity           | kg oil eq                | 11.99514                  |
| Global warming potential           | kg CO <sub>2</sub> eq    | 52.11392                  |
| Human damage – ozone formation     | kg NO <sub>x</sub> eq    | 1.327676                  |
| Human carcinogenic toxicity        | kg 1,4-DCB               | 1.410388                  |
| Human non-carcinogenic toxicity    | kg 1,4-DCB               | 36.95604                  |
| Ionizing radiation                 | kg U235-Eq               | 0.977719                  |
| Land use                           | m <sup>2</sup> a crop eq | 0.433365                  |
| Marine eutrophication              | kg N eq                  | 0.001113                  |
| Marine ecotoxicity                 | kg 1,4-DCB               | 2.120947                  |
| Stratospheric ozone depletion      | kg CFC11 eq              | 0.000446                  |
| Fine particulate matter formation  | kg PM2.5 eq              | 0.253401                  |
| Mineral resource scarcity          | kg Cu eq                 | 0.692167                  |
| Terrestrial acidification          | kg SO <sub>2</sub> eq    | 0.794367                  |
| Terrestrial ecotoxicity            | kg 1,4-DCB               | 152.0017                  |
| Water consumption                  | m <sup>3</sup>           | 0.388642                  |

## Chapter 5

### Technoeconomic Analysis (TEA) Results & Discussion

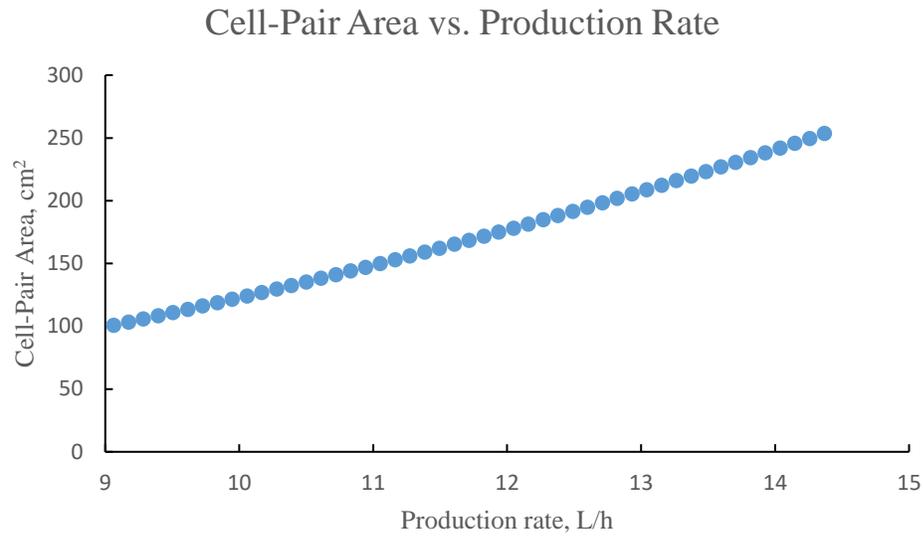
The developed mass balance was used with the parameters given in Table 3 to create an Excel spreadsheet that generates a required cell membrane area based on the current running through the ED unit. In turn, this area was used with costing parameters from Shah et al. (5) (see Table 4) to generate a capital cost for the ED unit. To determine its validity, the spreadsheet parameters (see Table 3) were modified to replicate data from (5). Specifically, the mass balance sought to replicate data for membrane area vs. production rate and capital cost vs. production rate. Production rate,  $Q$ , is defined as the volumetric flow rate exiting the ED cell, calculated from the defined thickness between membranes,  $t$ , the linear fluid velocity,  $v$ , and the calculated width of the cell,  $w$ . For further clarification, see Figure 3. Using the mass balance, the production rate was found in  $\text{m}^3/\text{s}$  and converted to  $\text{L}/\text{h}$  to scale correctly with the literature data. Figures 4 and 5 show that the model accurately replicates literature data from (5) for an exit concentration of  $300 \text{ mg}/\text{L}$  of salt, which is taken to be comparable to trivalent cations like REEs. Thus, the parameters of the model can be altered to reflect the operator's desired conditions while still accurately reflecting trends from literature.

**Table 3. TEA Parameters to Replicate Literature.**

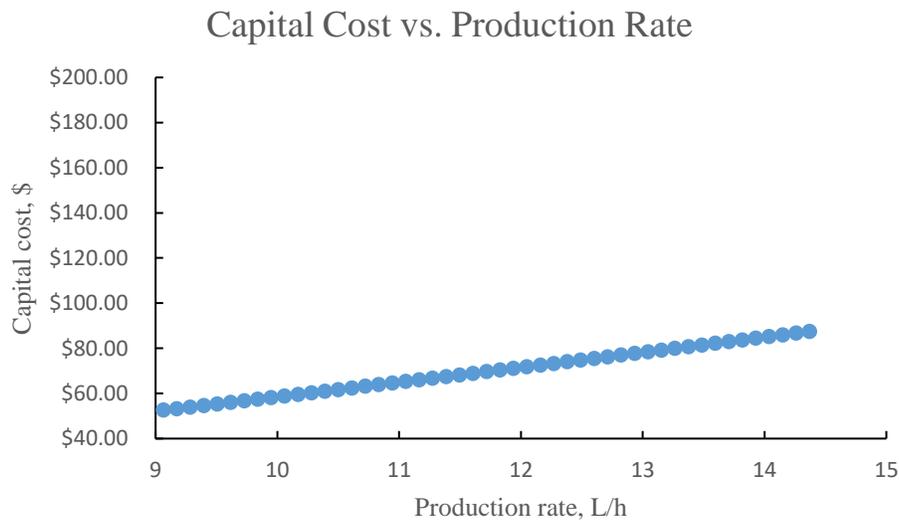
| Parameter Name                            | Variable    | Value   | Units              |
|---|-------------|---------|--------------------|
| Faraday's Constant                        | F           | 96500   | A·s/mol            |
| Recovery                                  | R           | 0.9     | Unitless           |
| Linear velocity                           | v           | 0.15    | m/s                |
| Aspect ratio                              | L/w         | 3.9     | Unitless (m/m)     |
| Efficiency                                | $\eta$      | 0.8     | Unitless           |
| Space between cells                       | t           | 0.00033 | m                  |
| Concentration of inlet concentrate stream | $C_{c, in}$ | 0.2     | mol/m <sup>3</sup> |
| Number of cell pairs                      | Np          | 20      | Unitless           |
| Charge                                    | z           | 3       | Unitless           |

**Table 4. TEA Costing Parameters to Replicate Literature.**

| Stack Component           | Value | Cost Units        |
|---------------------------|-------|-------------------|
| Electrodes                | 2000  | \$/m <sup>2</sup> |
| Cation Exchange Membranes | 45    | \$/m <sup>2</sup> |
| Anion Exchange Membranes  | 41    | \$/m <sup>2</sup> |
| Spacers                   | 3     | \$/m <sup>2</sup> |



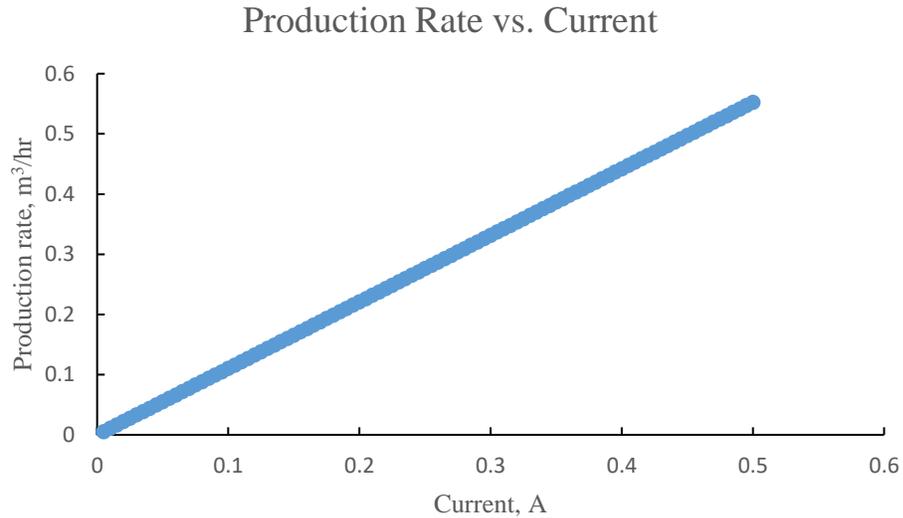
**Figure 4. Cell-Pair Area vs. Production Rate, which matches with data from (5).**



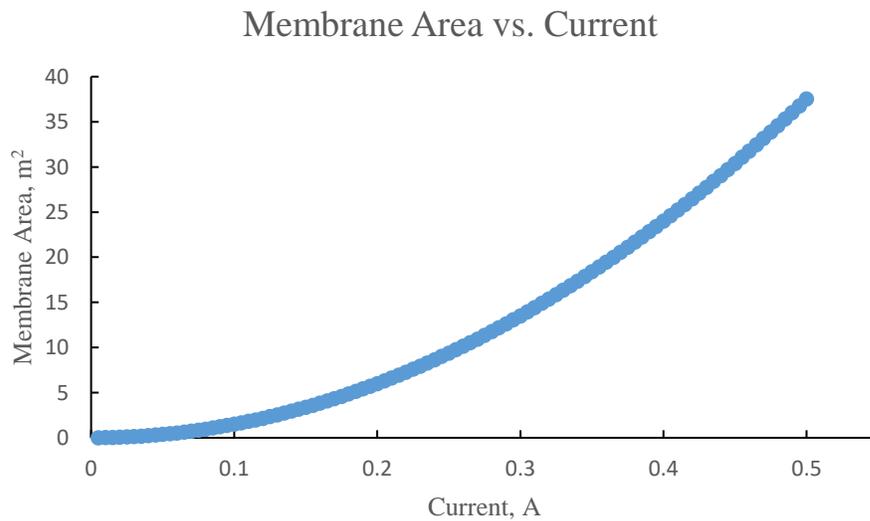
**Figure 5. Capital Cost vs. Production Rate, which matches with data from (5).**

The process for (9) requires the unit to process 2,201,706 kg per hour of leached phosphogypsum, of which 97.12% is water, 2.79% is sulfuric acid, and 0.0765% is the desired REE product by weight. Assuming the phosphogypsum flow to be the same density as water, 1000 kg/m<sup>3</sup>, this translates into a required production rate of 9,693.2 gpm. Based on the Excel model, increasing the current would drive up production rates (see Figure 6), so one ED unit

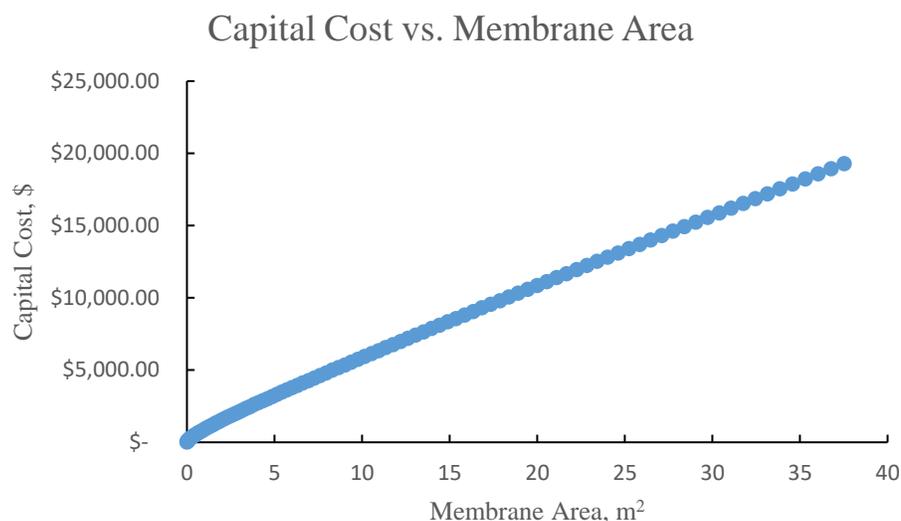
could meet production needs by running an extremely high current through the system; however, this comes at a significant capital cost, as the membranes must be large to accommodate such a current as well based on the mass balance (see Figures 7 and 8).



**Figure 6. Production Rate vs. Current for the Excel model, showing that production rate increases with current.**



**Figure 7. Membrane Area vs. Current, showing that increasing current increases the required membrane area.**



**Figure 8. Capital Cost vs. Membrane Area, showing that increasing the membrane area increases the capital cost based on parameters given in Table 4.**

Based on the parameters set by (5), multiple units must be running in parallel in order to meet production needs; for a total production rate of 9,693.2 gpm, and assuming a current of 10 A running through the ED unit (not including electricity needed for pumping fluid into the unit), approximately 200 ED units would need to run in parallel to meet production quotas. 10 A is assumed to roughly scale up current to industrial needs, as batch tests from previous literature were performed at smaller currents; while 10 A may not be the optimal current to run the ED unit, it is likely in the same order of magnitude as the optimal value to meet production rates and thus helps estimate capital costs. One unit running at 10 A would require an area of 15,005.55 m<sup>2</sup>, which would cost \$6,602,425.25 after multiplying by a Lang factor of 4.74; 200 units would then cost \$1,320,485,049.26.

For annualized costs and revenue, it is assumed that the ED plant would be running for 8000 hours a year and that the cost of electricity is about the average cost in the United States, \$0.10/kWh. Assuming 1 V supplied to the unit and 10 A of current applied, each unit will require

10 W to run; at 8000 hours a year, each unit requires 80 kWh of electricity per year, which will cost \$8.00 annually. Since 200 units are needed to meet production quotas, the annual electricity cost for this process will be \$1,600 per year. To calculate revenue, it is assumed that the price of REEs recovered will be \$51.50 per kg. R is set to 0.9, and it is therefore calculated that 1515.87 kg of REEs are in the exit stream; thus, the revenue would be \$78,067.54 per hour, or \$624,540,327.37 per year. Assuming the capital cost is a one-time expense, the plant would recover its expenses and become profitable after three years, as the operating cost is significantly lower than the capital cost, which is the trend reflected in smaller-scale ED models as well. Again, the capital and operating costs do not account for the purchase and operation of fluid pumps, nor does it account for maintenance or labor expenditures.

## Chapter 6

### Conclusions

On the whole, electrodialysis (ED) proves to be both an environmentally and financially feasible method of REE recovery from phosphogypsum at the industrial scale. Although the LCA shows that ED is inherently more electricity-intensive than precipitation using oxalic acid, which has a global warming potential of 52.11 kg CO<sub>2</sub> eq per kg REEs compared to ED's 60.24 kg CO<sub>2</sub> eq per kg REEs, it also proves that ED poses less of a toxicity concern to both human health and the surrounding land. Specifically, ED displays significantly lower impacts to human non-carcinogenic toxicity and terrestrial ecotoxicity, at 0.933 and 0.00219 kg 1,4-DCB per kg REEs, respectively, whereas oxalic acid precipitation shows impacts of 36.956 and 152.002 kg 1,4-DCB per kg REEs, respectively.

From a technoeconomic perspective, the capital costs of ED are significantly higher than annualized operating costs; driven up by increasing current to increase production rates, which in turn increases membrane area, capital investments on the unit (membranes, spacers, and electrodes) total at \$6,602,425.25, while electricity costs for the ED unit only total at \$1,600 per year assuming 10 A of current applied to the unit. In order to meet production quotas, however, multiple units must run in parallel, further increasing capital costs to \$1,320,485,049.26. Assuming an REE price of \$51.50 per kg, an inlet mass flow rate of 2,201,706 kg per hour with 0.0765 wt% REEs, a recovery ratio (R) of 0.9 and an operating time of 8000 hours per year, ED will generate \$624,540,327.37 per year, which will make back its capital investment in 3 years. Note that these costs are not optimized across all parameters, nor do they factor in other

associated costs with construction, such as pump design and operation, labor, maintenance, and any technological interfaces or additions to monitor the unit, all of which drive up costs and affect return on investment. Further investigation into the topic should seek to optimize the parameters listed in the TEA to minimize cost while maximizing REE recovery, as well as generate a more complete picture of operating costs regarding pump design and other associated expenses. On the LCA side, further comparisons should be made to other methods of REE recovery and phosphogypsum recirculation to expand the case for ED as an environmentally-conscious alternative. For now, however, this study cements the relationships between current, cell-pair area, and capital cost for electrodialysis as well as its reduced impact to human health and terrestrial ecosystems, even at the cost of global warming impact overall compared to precipitation by oxalic acid.

## Chapter 7

### Annotated Bibliography

The annotated bibliography only covers the sources discussed in the Literature Review (see Chapter 2).

- (3) McGovern, R. K.; Weiner, A. M.; Sun, L.; Chambers, C. G.; Zubair, S. M.; Lienhard V, J. H. On the Cost of Electrodialysis for the Desalination of High Salinity Feeds. *Applied Energy* **2014**, *136*, 649–661. <https://doi.org/10.1016/j.apenergy.2014.09.050>.

This paper pioneers ED in desalination and evaluates energy and equipment costs for the process. The team experimentally replicated the performance of a ten-stage ED system, developed a numerical model for said system, validated it against experimental results, and used the model to optimize voltage across the system. The researchers discovered that energy requirements for ED equaled those of current desalination processes, although the water cost decreased compared to current methods. They also found high salinity streams produced a lower cost per unit salt removed, thus pointing towards economic feasibility. This paper again demonstrates the applications of ED technology, although its narrow scope excludes the potential for REE recovery.

- (4) Shah, S. R.; Wright, N. C.; Nepsky, P. A.; Winter, A. G. Cost-Optimal Design of a Batch Electrodialysis System for Domestic Desalination of Brackish Groundwater. *Desalination* **2018**, *443*, 198–211. <https://doi.org/10.1016/j.desal.2018.05.010>.

This paper continues the electrodialysis analysis by determining parameters for a batch system that minimizes cost. The researchers altered applied voltage, flow rates, and the geometry of the cell to meet different production rate and product concentration needs. Ultimately, the research found that capital costs dominated over energy costs, so the system should use the maximum current possible; to achieve this, batch electrodialysis systems should possess thin channels and high membrane length-to-width ratios. The research also determined the optimal range of flow rates and voltages to meet production needs, and that active membrane area would increase with feed concentration. This paper, like others, demonstrates the trends expected for changing electrodialysis parameters to meet production goals; however, its scope limits its applicability to a batch system, whereas the next step would involve continuous production for REE recovery.

- (5) Couto, N.; Ferreira, A. R.; Lopes, V.; Peters, S. C.; Mateus, E. P.; Ribeiro, A. B.; Pamukcu, S. Electrodialytic Recovery of Rare Earth Elements from Coal Ashes. *Electrochimica Acta* **2020**, *359*, 136934. <https://doi.org/10.1016/j.electacta.2020.136934>.

This paper assesses the potential of using electro dialysis (ED) to recover rare earth elements (REE) from coal ash. After analyzing REE levels in bituminous and anthracite ash, the research team designed a two-compartment ED cell and ran various experiments, altering the pH of the solution fed through the cell, the current applied, and the length of time allowed for solution to run. The ED cell recovered over 70% of REEs from the coal ash using an adjusted pH, 50 mA of current, and 3 days to run the experiment. This research proves electro dialysis's effectiveness in REE recovery and provides insight into how the same technique works for other REE sources, such as phosphogypsum (PG).

- (6) Generous, M. M.; Qasem, N. A. A.; Akbar, U. A.; Zubair, S. M. Techno-Economic Assessment of Electro dialysis and Reverse Osmosis Desalination Plants. *Separation and Purification Technology* **2021**, *272*, 118875. <https://doi.org/10.1016/j.seppur.2021.118875>.

This paper determines the economic feasibility of a desalination plant that uses ED and reverse osmosis. The authors developed a model for desalination by ED that included Donnan potential, boundary layer, water transport, and spacer effects; in turn, this model created parameters for determining the plant's capital and energy costs. Based on such a model, the researchers found ED economically feasible when feed salinity fell below 7 or 9 parts per thousand. This research provides a basis for my own economic model of an ED cell and illustrates how to perform a techno-economic analysis (TEA) on a process unit, complete with sensitivity analysis. It also indicates the appropriate scale of costs based on parameters present in my model.

- (7) Li, C.; Ramasamy, D. L.; Sillanpää, M.; Repo, E. Separation and Concentration of Rare Earth Elements from Wastewater Using Electro dialysis Technology. *Separation and Purification Technology* **2021**, *254*, 117442. <https://doi.org/10.1016/j.seppur.2020.117442>.

This paper breaks ground by applying ED to separate and concentrate REEs (with an emphasis on  $\text{Sc}^{3+}$ ) from a dilute aqueous solution. Researchers once again designed an ED cell and evaluated its performance based on applied current, voltage, feed pH, feed concentration, co-ion competition and energy consumption of the process. The team analyzed recovery using chronopotentiometric and chronoamperometric technologies. Under ideal conditions, the cell recovered 99.52% of scandium ions from diluted wastewater while only consuming 0.26 kWh/m<sup>3</sup> of energy. This paper exemplifies the importance of different parameters in REE recovery and signifies how altering such parameters affects ED cell performance.

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