Optimal Membrane Cascade Design for Critical Mineral Recovery Through Logic-based Superstructure Optimization

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ABSTRACT

Critical minerals and rare earth elements play an important role in our climate change initiatives, particularly in applications related with energy storage. Here, we use discrete optimization approaches to design a process for the recovery of Lithium and Cobalt from battery recycling, through membrane separation. Our contribution involves proposing a Generalized Disjunctive Programming (GDP) model for the optimal design of a multistage diafiltration cascade for Li-Co separation. By solving the resulting nonconvex mixed-integer nonlinear program model to global optimality, we investigated scalability and solution quality variations with changes in the number of stages and elements per stage. Results demonstrate the computational tractability of the nonlinear GDP formulation for design of membrane separation processes while opening the door for decomposition strategies for multicomponent separation cascades. Future work aims to extend the GDP formulation to account for stage installation and explore various decomposition techniques to enhance solution efficiency.

Keywords: Critical Minerals, Lithium Recovery, Diafiltration Cascade, Superstructure Optimization, Generalized Disjunctive Programming, Mixed-Integer Nonlinear Programming.

INTRODUCTION AND RELATED WORK

The U.S. relies on the import of rare earth elements (REE) and critical minerals (CM) which are central to our climate change initiatives, particularly in applications such as electric vehicles and energy storage [1]. With an increasing demand for REE and CM, restrictions by competitors on exports have disrupted the U.S. supply chain and pose a risk to the national economy [2]. Projections by the IEA indicate a staggering 60% surge in renewable energy power capacity from 2020 to 2026 [3]. As a result, recycling REE and CM has become one of the main objectives of the Department of Energy (DOE) since 2014 [1].

One potential source of Lithium recovery is Lithium-ion battery recycling [4]. This process addresses the lack of domestic CM production [5], as it can recover battery-grade Lithium and Cobalt for a fraction of the materials extracted from either brine or ores [6]. However, concerns arise from improper recycling, which affects human health and the environment [7], prompting opportunities to employ energy efficient processes with minimal environmental impact like membrane separation.

Diafiltration membranes offer significant advantages in the efficiency of recycling CM over existing battery recycling pathways, reducing energy needs and chemical use and cost. In a diafiltration membrane, the process employs a dilute solution, called diafiltrate, to reduce the solubility limit effect that leads to fouling. This approach allows the staging of membrane units into cascades, facilitating the extraction of lithium and cobalt from leach liquors.

There is a growing interest in utilizing membranes for the recovery and extraction of CM, as evident in recent literature. A comprehensive review and feasibility assessment for membrane-based technology in lithium recovery were provided by Li et al. [8]. Similarly, Alvarez et al. [9] demonstrated the potential to enhance water security by utilizing membranes to filter out metals during water treatment. In the realm of lithium recovery

methods, Bae et al. [10] conducted a study that investigated and compared various proposed techniques, including chemical extraction and selective membrane processes, with a focus on quantitative efficiency and purity based on existing literature. Razmjou et al. [11] delved into the physical construction of a nanofiltration membrane for lithium recovery, proposing design principles to enhance selectivity. The prevailing trend in the current literature emphasizes a primary understanding and performance evaluation of membrane processes, while rigorous mathematical optimization is less commonly addressed.

In a prior study conducted by Wamble et al. [12], a superstructure formulation was introduced to determine the optimal configuration of a membrane cascade. This superstructure selects design variables (e.g., flow, concentration, stage length) while maximizing Cobalt recovery and adhering to a minimum Lithium recovery fraction, employing the epsilon constraint approach. This superstructure was posed as a nonlinear program (NLP), which was solved using IPOPT.

In the earlier method, the determination of stream connectivity was performed continuously, allowing for the division of feed, diafiltrate, and refluxed streams. However, the authors noted that this continuous approach failed to consistently generate "physically sensible cascade designs" [12]. To address this issue, the authors introduced a second optimization step. In our proposed extension of this approach, we suggest modeling stream connectivity as a discrete decision, ensuring the singular allocation of side streams. As the model incorporates bilinear mixing and nonlinear performance constraints, the proposed method requires solving a nonconvex mixed-integer nonlinear programming (MINLP) problem. Additionally, we propose formulating the MINLP superstructure as a Generalized Disjunctive Program (GDP), a widely employed approach in the literature for superstructure optimization. The motivation behind this is the fact that GDP effectively avoids singularities in nonlinear expressions, particularly when variables become zero, a phenomenon recognized in the literature as zero-flow issues [13]. This approach allows for the identification of the globally optimal superstructure and facilitates future extensions for the optimal determination of the number of separation stages.

Generalized Disjunctive Programming

Generalized Disjunctive Programming (GDP) corresponds to a mathematical optimization framework designed for modeling and solving problems characterized by embedded logic. Within GDP, the feasible region is represented by the intersection of disjunctions of sets, employing Boolean variables as indicators for each set. In this context, a $True$ value for a Boolean variable indicates that the solution resides within the corresponding set

[14]. The general formulation of a GDP is as follows:

$$\min \ f(x)$$

$$s.t. \quad g(x) \leq 0$$

$$\bigvee_{i \in D_k} \begin{bmatrix} Y_{ik} \\ r_{ik}(x) \leq 0 \end{bmatrix}, \qquad k \in K$$

$$\Omega(Y_{i,k}) = \text{True}$$

$$x \in \mathbb{R}^n$$

$$Y_{ik} \in \{\text{True}, \text{False}\}, i \in D_k , k \in K$$

where, an objective function $f(x)$ is to be minimized over a set of continuous real variables x subject to a set of global constraints $g(x) \leq 0$. Boolean variable Y_{ik} acts as the indicator for the set implied by constraints $r_{ik} \leq 0$, standing for the ith disjunct set of the kth disjunction. Each of the K disjunctions are related with an exclusive OR operator ($\veebar$), which can be interpreted as an *exactly-One* operator when $|D_k| > 2$. The set of logical propositions Ω is composed of logical clauses connected with logical operators such as AND ($\wedge$), OR ($\vee$), XOR ($\veebar$), negation ($\neg$), implication ($\Rightarrow$), and equivalence ($\Leftrightarrow$). Here, Ω is required to be $True$ to indicate that all the propositions must be satisfied.

GDP offers a dual advantage by providing an intuitive means to model the logic inherent in problems and presenting a diverse array of solution methods that can be broadly categorized in two groups. One major category involves reformulating the GDP as a mixed-integer (non)linear program through various transformations. These transformations translate the logical structure of the problem into a mathematical formulation suitable for traditional MINLP optimization algorithms. Examples of such transformations include Big-M [15], Hull [16], and Hybrid Planes [17], among others. The second category encompasses logic-based decomposition methods that directly operate on the logical structure of the problem. Tailored methods within this category include Logic-based Outer Approximation [18], Logic-based Branch and Bound [16], and the Logic-based Discrete-Steepest Descent Algorithm [19], providing specialized approaches to address the unique complexities associated with the logic of the problem at hand.

PROBLEM STATEMENT

Given is the following information for the optimization of a multistage diafiltration cascade aimed at separating Lithium from Cobalt. The provided parameters include the predetermined number of separation stages and the number of discretization elements per stage. Additionally, the model involves the flows and concentrations associated with both the feed and diafiltrate streams. Relevant membrane parameters, such as the stage width, solvent flux across the membrane, and the
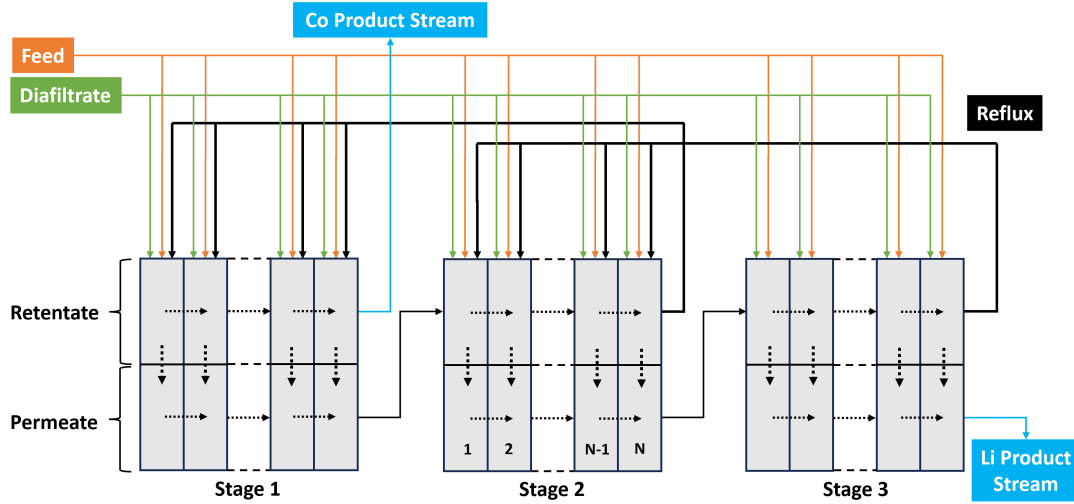
Figure 1: Superstructure sketch for a three-stage ($|K| = 3$) diafiltration membrane cascade.
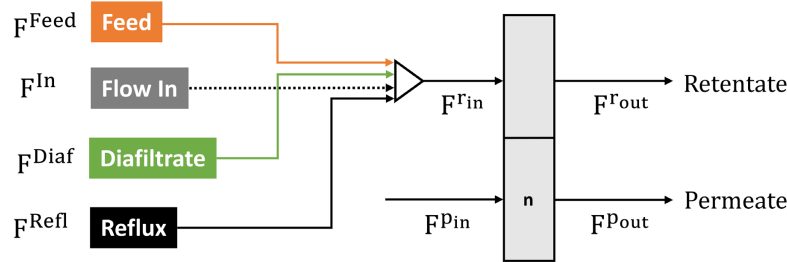

Figure 2: Skecth of the flow structure of a single discretized element.

sieving coefficients for both components, are also specified. Furthermore, the model includes the performance relationships that govern the system's behaviour as provided in Wable et al. [12].

Design variables that specify the optimal diafiltration membrane cascade superstructure need to be determined. Firstly, the optimal stream connections within the superstructure must be established. This involves identifying the position (in terms of stage and discretized element) for the feed, the diafiltrate, and the recycle from upstream stages. Additionally, the length of each stage in the diafiltration cascade needs to be determined to achieve an efficient separation process. Moreover, comprehensive determination of all flows and concentrations in regard to both components (Lithium and Cobalt) throughout the entire system must be determined. This comprehensive set of determinations forms the basis for configuring an optimized and well-functioning multistage diafiltration system for the separation of Lithium and Cobalt.

The primary objective of the optimization model is to maximize the recovery of Cobalt within a Cobalt-rich stream extracted from the retentate flow of the initial stage in the diafiltration cascade. This goal is set against the constraint of ensuring a minimum recovery of Lithium

within a Lithium-rich stream exiting the permeate flow of the final stage. In essence, the goal is to manage the inherit multi-objective nature of recovering both Lithium and Cobalt. In this work, we consider the system to be isotropic, meaning that all stages share identical lengths. The configuration of the superstructure is presented in Figure 1.

PROPOSED GDP SUPERSTRUCTURE

In this section, we illustrate the modifications made to the original model, primarily focusing on incorporating the necessary logic into the GDP framework to represent installing a singular position for the feed (F^{Feed}), diafiltrate (F^{Diaf}), and reflux per stage (F_n^{Refl}). To accomplish this objective, we model each discrete element individually, as illustrated in Figure 2, wherein the incoming side flows are handled in a disaggregated manner. Through this approach, the following disjunctions are implemented, allowing for the activation or deactivation of incoming streams, thereby determining the existence of an incoming side stream. Here, the Boolean variables Y_{nk}^{Feed}, Y_{nk}^{Diaf}, and Y_{nk}^{Refl} indicate the existence of a feed, diafiltrate or reflux in a particular position respectively.

$$\begin{bmatrix} Y_{nk}^{Feed} \\ F_{nk}^{Feed} = \hat{F}^{Feed} \\ x_{cnk}^{Feed} = \hat{x}_c^{\ Feed} \ \forall c \in C \end{bmatrix} \vee \begin{bmatrix} \neg Y_{nk}^{Feed} \\ F_{nk}^{Feed} = 0 \\ x_{cnk}^{Feed} = 0 \ \forall c \in C \end{bmatrix},$$
$$\forall n \in N, \ k \in K$$
$$(1)$$

$$\begin{bmatrix} Y_{nk}^{Diaf} \\ F_{nk}^{Diaf} = \hat{F}^{Diaf} \\ x_{cnk}^{Diaf} = \hat{x}_c^{\ Diaf} \ \forall c \in C \end{bmatrix} \vee \begin{bmatrix} \neg Y_{nk}^{Diaf} \\ F_{nk}^{Diaf} = 0 \\ x_{cnk}^{Diaf} = 0 \ \forall c \in C \end{bmatrix},$$
$$\forall n \in N, \ k \in K$$
$$(2)$$

$$\begin{bmatrix} Y_{nk}^{Refl} \\ F_{nk}^{Refl} = F_{|N|,\{k+1\}}^{r_{out}} \\ x_{cnk}^{Refl} = x_{c,|N|,\{k+1\}}^{r_{out}} \ \forall c \in C \end{bmatrix} \vee \begin{bmatrix} \neg Y_{nk}^{Refl} \\ F_{nk}^{Refl} = 0 \\ x_{cnk}^{Refl} = 0 \ \forall c \in C \end{bmatrix},$$
$$\forall n \in N, \ k \in K \backslash \{|K|\}$$
$$(3)$$

where $\hat{F}^j$ and $\hat{x}^j$ represent the known flow and composition of the incoming side stream $j \in \{Feed, Diaf\}$. The first two disjunctions establish connections between the incoming stream and known parameter values. In contrast, the third disjunction, which models the recycle, links a discretized element to the stream coming from the retentate of the subsequent stage. While these disjunctions exclusively represent the presence of a stream at a given position, we also ensure a singular feed and diafiltrate throughout the entire structure, as well as a singular recycle per stage. To account for this logic, the following cardinality clauses are introduced.

$$exactlyOne([Y_{nk}^{Feed} \ \forall n \in N, \ k \in K]) \qquad (4)$$

$$exactlyOne([Y_{nk}^{Diaf} \ \forall n \in N, \ k \in K]) \qquad (5)$$

$$exactlyOne([Y_{nk}^{Refl} \ \forall n \in N]), \quad k \in K \backslash \{|K|\} \qquad (6)$$

Equations (1-6) represent the modeling logic of the superstructure. Next, with the introduced side stream disaggregation, the per-element mass balances are outlined as follows:

$$F_{nk}^{In} + F_{nk}^{Feed} + F_{nk}^{Diaf} + F_{nk}^{Refl} = F_{nk}^{r_{in}}, \ \forall n \in N, \ k \in K \quad (7)$$

$$F_{nk}^{In}x_{cnk}^{In} + F_{nk}^{Feed}x_{cnk}^{Feed} + F_{nk}^{Diaf}x_{cnk}^{Diaf} + F_{nk}^{Refl}x_{cnk}^{Refl} = F_{nk}^{r_{in}}x_{cnk}^{r_{in}}, \ \forall c \in C, \ n \in N, \ k \in K$$
$$(8)$$

$$F_{nk}^{r_{in}} + F_{nk}^{p_{in}} = F_{nk}^{r_{out}} + F_{nk}^{p_{out}}, \ \forall n \in N, \ k \in K$$
$$(9)$$

$$F_{nk}^{r_{in}}x_{cnk}^{r_{in}} + F_{nk}^{p_{in}}x_{cnk}^{p_{in}} = F_{nk}^{r_{out}}x_{cnk}^{r_{out}} + F_{nk}^{p_{out}}x_{cnk}^{p_{out}}, \ \forall c \in C,$$
$$n \in N, \ k \in K \qquad (10)$$

The permeate mass balance is a function of the membrane flux (J), the width of the stage (w) and the element length ($\hat{L}$) as:

$$F_{nk}^{p_{in}} + Jw\hat{L}_{nk} = F_{nk}^{p_{out}}, \ \forall n \in N, \ k \in K$$
$$(11)$$

In the previous study, the performance equation was examined in terms of a log transform. However, we suggest maintaining the equation in its exponential form and rearrange the expression to remove the fraction. This reformulation ensures a well-defined expression within the domain of our variables, mitigating the risk of evaluation errors and contributing to the overall stability and well-behaved nature of the NLP formulation. The resulting expression where, S is the sieving coefficient per component is as follows:

$$x_{cnk}^{r_{out}} = x_{cnk}^{r_{in}} \left(\frac{F_{nk}^{r_{out}}}{F_{nk}^{r_{in}}} \right)^{S_c - 1}, \forall c \in C, \ n \in N, \ k \in K \qquad (12)$$

The elements can now be interconnected to create stages, where the key concept is to establish connections between the flow and composition exiting the permeate of one stage with the retentate entering the subsequent stage. These connections can be expressed as:

$$F_{n\{k-1\}}^{p_{out}} = F_{nk}^{In}, \qquad \forall n \in N, \ k \in K \backslash \{1\} \qquad (13)$$

$$x_{cn\{k-1\}}^{p_{out}} = x_{cnk}^{In}, \quad \forall c \in C, \ n \in N, \ k \in K \backslash \{1\} \qquad (14)$$

Moreover, the permeate and the flow-in entering the first element of each membrane are both assigned a value of zero. Similarly, in the last stage, there is no recycle entering.

$$F_{1k}^{p_{in}} = F_{1,1}^{In} = 0, \qquad \forall k \in K$$
$$(15)$$

$$x_{c1k}^{p_{in}} = x_{c1k}^{In} = 0, \quad \forall c \in C, \ k \in K$$
$$(16)$$

$$F_{n|K|}^{Refl} = 0, \qquad \forall n \in N$$
$$(17)$$

$$x_{cn|K|}^{Refl} = 0, \qquad \forall c \in C, \ k \in K$$
$$(18)$$

A minimum Lithium recovery ($R_{\min}^{Li}$) from the lithium-rich stream in the permeate exiting the last stage must be satisfied.

$$F_{|N||K|}^{p_{out}}x_{Li,|N||K|}^{p_{out}} \geq R_{\min}^{Li} \left(\hat{F}^{Feed}\hat{x}_{Li}^{\ Feed} + \hat{F}^{Diaf}\hat{x}_{Li}^{\ Diaf} \right)$$
$$(19)$$

The objective function is to maximize the recovery of Cobalt in the Cobalt-rich stream exiting the permeate of the first stage. Considering that the cobalt entering the system remains constant, it suffices to maximize the following expression:

$$\max \ F_{|N|,1}^{r_{out}}x_{Co,|N|,1}^{r_{out}} \qquad (20)$$

For the remaining aspects of the model formulation and parameter values along with a deeper understanding of the system's physical intuition, we direct the readers to Wamble et al. [12].

RESULTS

The proposed GDP superstructure model was transformed into a nonconvex MINLP problem via a Big-M transformation. To solve this MINLP, the solver SCIP v8.0 was used, implemented through GAMS 40.4.0. The computation was performed on a Linux machine featuring 8 Intel Xeon Gold 6234 CPUs operating at 3.30 GHz, with a single hardware thread, and equipped with 1 TB of RAM, all within the Ubuntu environment. It is worth mentioning that we attempted solving the same problem using BARON v22.7.23 but the solver, incorrectly, found the problem to be infeasible.

We conducted a study of the scalability and solution quality of the proposed superstructure. For this, we opted for a three-stage ($|K| = 3$) membrane cascade superstructure, varying the number of discretized elements. All superstructures were solved to global optimality (up to 0.001% gap). Figure 3 encapsulates the outcomes, specifically summarizing the results for the case where a minimum Lithium recovery ($R_{\min}^{Li}$) of 60% was required.
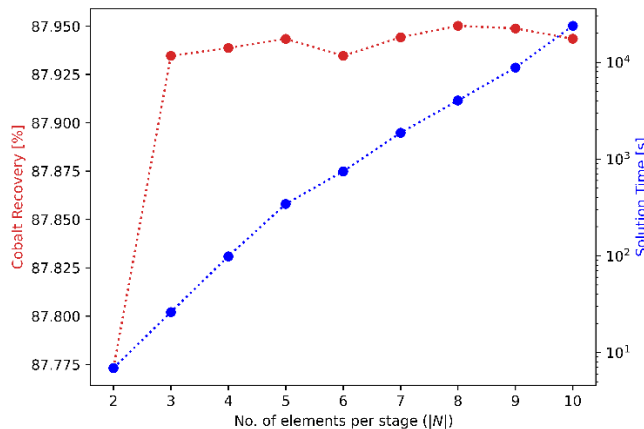

Figure 3: Cobalt recovery and solution time of a three-stage superstructure with a minumum Lithium recovery of 60% for different number of discretized elements per stage.
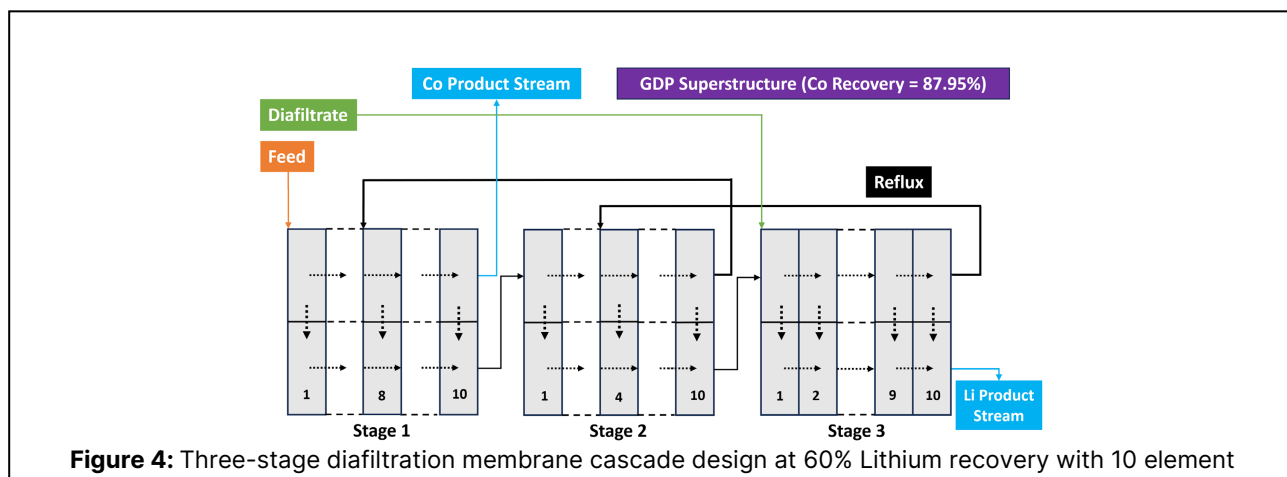
As anticipated, the solution time exhibits rapid growth with the increasing size of the superstructure, as a larger number of elements results in a larger model. This poses a significant limitation when compared to the previous methodology that could solve large superstructures within seconds. The challenge arises from the fact that achieving global optimality in solving a nonconvex

MINLP is computationally much more demanding than solving an NLP to local optimality. However, despite this computational complexity, the proposed approach demonstrates a slightly better solution compared to the previous methods. Figure 4 shows the resulting three-stage superstructure (with $|N| = 10$) for a lithium recovery of 60%. It is noteworthy that the locally optimal superstructure obtained by Wamble et al. [12] exhibits the feed stream split at two different locations, while our superstructure is characterized by a single side stream allocation. Nevertheless, our approach yields a similar Cobalt recovery (0.25% increase) while also ensuring the construction of a physically sensible membrane cascade. Considering that we are dealing with a membrane design problem that requires a one-time solution, it may be preferable to tackle the problem to achieve global optimality. Furthermore, we want to extend this approach to use GDP methods for multicomponent cascade recycling.

We proceed to assess the scalability of the number of stages, opting for a discretization of only two elements per stage. This choice was informed by the examination of objective values presented in Figure 3, revealing a relatively stable Cobalt recovery. Notably, this value does not exhibit a monotonic trend in relation to the number of discretized elements. Therefore, for this specific membrane system and its performance equations, the resolution achieved by increasing the number of discretization elements does not substantially impact the objective. Consequently, a coarser discretization can be employed. The outcomes of this scalability analysis can be found in Figure 5.

As expected, the Cobalt recovery rises as we include more stages. Interestingly, and in contrast to the scenario where discrete elements were added, an increase in the number of stages leads to a substantial rise in the recovery. It can be appreciated that the recovery values almost double when progressing from 2 stages to 12. This captures the trade-off between the profit of recovering Cobalt in kg/hr and the expense associated with installing an additional membrane stage. Although current solution approaches cannot easily address this problem, within the GDP framework, tackling this trade-off is straightforward. To achieve this, a Boolean variable can be introduced to represent the presence or absence of a stage. When the Boolean variable is $True$, the performance equations for the stage are considered. Conversely, when the Boolean variable is False, the stage operates as a bypass, and no side streams can be installed.

Regarding the solution time, it is evident that reducing the number of discretized elements has diminished the model's size, enabling the solution of larger structures. Although this reduction may lead to a loss in resolution, potentially impacting the quality of the solution, as discussed earlier, we anticipate the recovery values to remain within a similar order for a higher discretization.

Figure 4: Three-stage diafiltration membrane cascade design at 60% Lithium recovery with 10 element

Furthermore, the application of decomposition strategies will be investigated to tackle large-scale conceptual design problems.
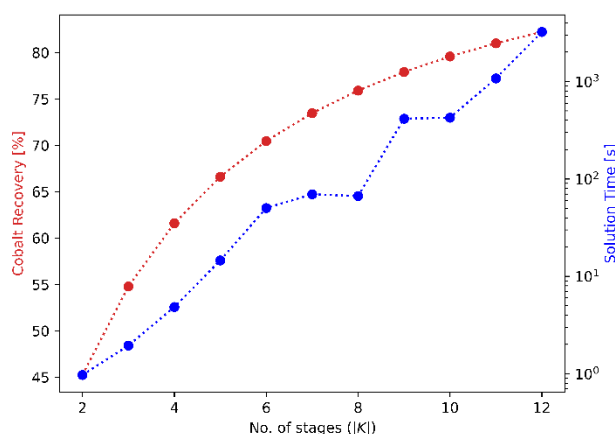

Figure 5: Cobalt recovery and solution time for a superstructure with a minumum Lithium recovery of 95% for different number of stages.

CONCLUSIONS

This study introduces a Generalized Disjunctive Programming formulation for optimizing the superstructure design of a multi-stage diafiltration cascade aimed at separating Lithium and Cobalt. The proposed superstructure ensures a unique side stream allocation for the feed, fresh diafiltrate, and recycle streams. We successfully solved the model to global optimality and investigated how the solution time and Cobalt recovery varied with different numbers of stages and discretized elements per stage. The results demonstrate the value of pursuing solutions with global optimality and highlight a trade-off between capitalizing on recovered Cobalt and the installation of additional membranes. Future research directions include expanding the GDP formulation to account for stage existence, addressing the aforementioned trade-off. Moreover, given the computational expense of solving the superstructure directly, exploration of decomposition techniques to improve solution time is warranted. In this context, the Logic-based Steepest-Descent Algorithm (LD-SDA) [19] emerges as a promising alternative, particularly due to its suitability for handling spatially ordered Boolean decisions inherent in the membrane superstructure.

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DISCLAIMER

REFERENCES

1. Critical Minerals and Materials Program. National Energy Technology Laboratory (2021)
2. Lee Y, Dacass T. Reducing the United States' risks of dependency on China in the rare earth market. Resources Policy 77 (2022)
3. IEA. The role of critical minerals in clean energy transitions. OECD. (2021)
4. Zhang, X., Li, L., Fan, E., Xue, Q., Bian, Y., Wu, F., & Chen, R. Toward sustainable and systematic recycling of spent rechargeable batteries. Chemical Society Reviews, 47(19), (2018)
5. Rankin WJ. Minerals, metals and sustainability: meeting future material needs. CSIRO publishing (2011)
6. National Blueprint for Lithium Batteries. Office of Energy Efficiency and Renewable Energy (2021)
7. Kang DH, Chen M, Ogunseitan OA. Potential environmental and human health impacts of rechargeable lithium batteries in electronic waste. Environmental science & technology 47.10 (2013)
8. Li X, Mo Y, Qing W, Shao S, Tang CY, Li J. Membrane-based technologies for lithium recovery from water lithium resources: A review. Journal of Membrane Science (2019)
9. Alvarez PJ, Chan CK, Elimelech M, Halas NJ, Villagrán D. Emerging opportunities for nanotechnology to enhance water security. Nature nanotechnology 13.8 (2018)
10. Bae H, Kim Y. Technologies of lithium recycling from waste lithium ion batteries: a review. Materials advances 2.10 (2021).
11. Razmjou A, Asadnia M, Hosseini E, Habibnejad Korayem A, Chen V. Design principles of ion selective nanostructured membranes for the extraction of lithium ions. Nature communications 10.1 (2019)
12. Wamble NP, Eugene EA, Phillip WA, Dowling AW. Optimal diafiltration membrane cascades enable green recycling of spent lithium-ion batteries. ACS Sustainable Chemistry & Engineering 10.37 (2022)
13. Chen Q, Liu Y, Seastream G, Siirola JD, Grossmann IE. Pyosyn: a new framework for conceptual design modeling and optimization. Computers & Chemical Engineering 153 (2021)
14. Grossmann IE, Trespalacios F. Systematic modeling of discrete-continuous optimization models through generalized disjunctive programming. AIChE Journal 59.9 (2013)
15. Raman R, Grossmann IE. Modelling and computational techniques for logic based integer programming. Computers & Chemical Engineering 18.7 (1994)
16. Lee S, Grossmann IE. New algorithms for nonlinear generalized disjunctive programming. Computers & Chemical Engineering 24.9-10 (2000)
17. Sawaya NW, Grossmann IE. A cutting plane method for solving linear generalized disjunctive programming problems. Computers & chemical engineering 29.9 (2005)
18. Türkay M, Grossmann IE. Logic-based MINLP algorithms for the optimal synthesis of process networks. Computers & Chemical Engineering 20.8 (1996)
19. Bernal, D.E., Ovalle, D., Liñán, D.A., Ricardez-Sandoval, L.A., Gómez, J.M. and Grossmann, I.E. Process Superstructure Optimization through Discrete Steepest Descent Optimization: a GDP Analysis and Applications in Process Intensification. Computer Aided Chemical Engineering. Vol. 49. Elsevier, (2022)