Conceptual Design Optimization of Solvent Extraction Processes for REE/CM Recovery

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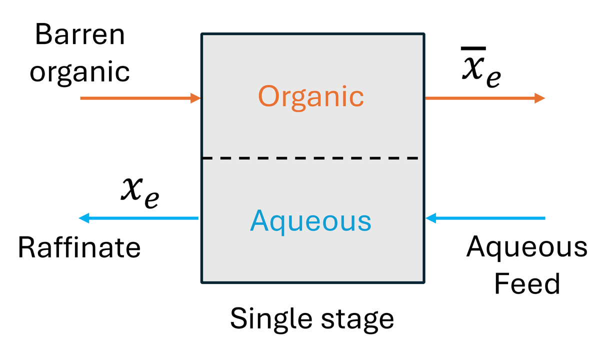
Motivations

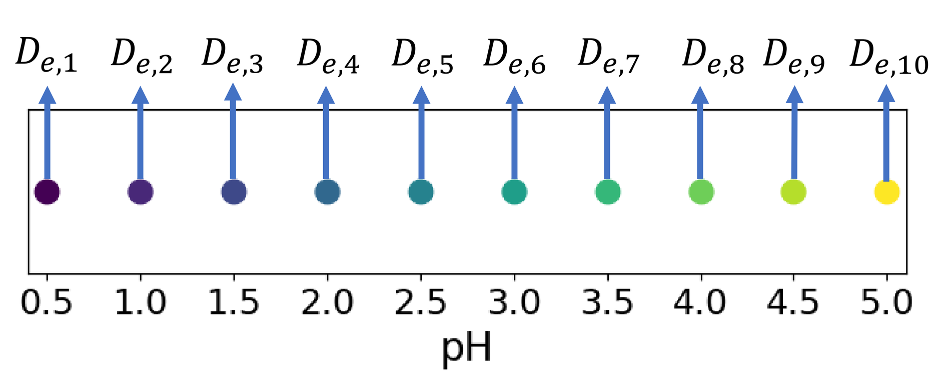
- **Rare Earth Elements (REEs)** underpin the clean energy technologies that are central to our climate change initiatives, particularly in applications such as electric vehicles and energy storage [1].
- The current U.S. supply chain is insufficient for projected growth, and we must consider **alternative feedstocks** [2].
- Solvent extraction allows efficient separation of REEs with relatively low operational cost, but they are challenging to design because of the highly combinatorial options [3].

Distribution Coefficient Model



$$D_e = \frac{\bar{x}_e}{x_e} \Rightarrow D_e x_e = \bar{x}_e$$

$$D_e = 10^{Q_e \times \text{pH} + C_e}$$



Future work: precipitation model

Formulation - MIQCP

$$\min \sum_{q\in Q}\sum_{s\in S_q} y_{q,s} - \sum_{q\in Q}\sum_{s\in S_q}\sum_{j\in J_{qs}} \left(\alpha(\text{PH}_v)(z_{q,v,j})\right)$$

Minimize the total number of stages; include a cost term for acid usage (pH)

$$\bar{x}^{out}_{q,s,e} = \bar{x}^{in}_{q,s+1,e}$$
$$x^{in}_{q,s-1,e} = x^{out}_{q,s,e}$$

Connect the stages

$$\bar{F}_q \bar{x}^{in}_{q,s,e} + F_q x^{in}_{q,s,e} = \bar{F}_q \bar{x}^{in}_{q,s,e} + F_q x^{in}_{q,s,e}$$

Stagewise material balances

$$\bar{F}_L \bar{x}^{out}_{L,N,e} = \bar{F}_S \bar{x}^{in}_{S,1,e}$$
$$F_L x^{in}_{L,N,e} = F_S x^{out}_{S,1,e} + F_{Feed} x_{Feed,e}$$

Connect the sections

$$\sum_{v\in V_q}\sum_{j\in J_q} z_{q,v,j} = 1, \forall\, q \in Q$$

Select only one pH per section

$$\tilde{x}_{q,s,e} = \sum_{v\in V_q} (D_{q,v,e,j}\, z_{q,v,j}) x^{out}_{q,s,e}$$
$$\bar{x}^{out}_{q,s,e} = \tilde{x}_{q,s,e} y_{q,s,j} + (1 - y_{q,s,j})\ \bar{x}^{in}_{q,s,e}$$

Stage existence and equilibrium

$$y_{q,s-1} \geq y_{q,s}$$

Stage existence ordering

$$\sum_{v\in V_q} z_{L,v,j} = \sum_{v\in V_q} z_{S,v,j}\ \forall\, j \in J$$

Select the same extractant for both sections

$$\bar{F}_S \bar{x}^{out}_{S,N,O_{key}} \geq R_{min} F_{Feed} x_{Feed,O_{key}}$$
$$F_L x^{out}_{L,1,A_{key}} \geq R_{min} F_{Feed} x_{Feed,A_{key}}$$

Minimum recovery on the outlet concentration of key components

$Q = \{\text{Load, Strip}\}$, $S = \{1,\ldots, N_{max}\}$, $J=\{J_1, \ldots, J_4\}$, $E=\{\text{REE}\}$

$z_{q,v,j}, y_{q,s} = \{0,1\}$, $\tilde{x}_{q,s,e}, \bar{x}_{q,s,e}, x_{q,s,e} \in \mathbb{R}$

Conclusions

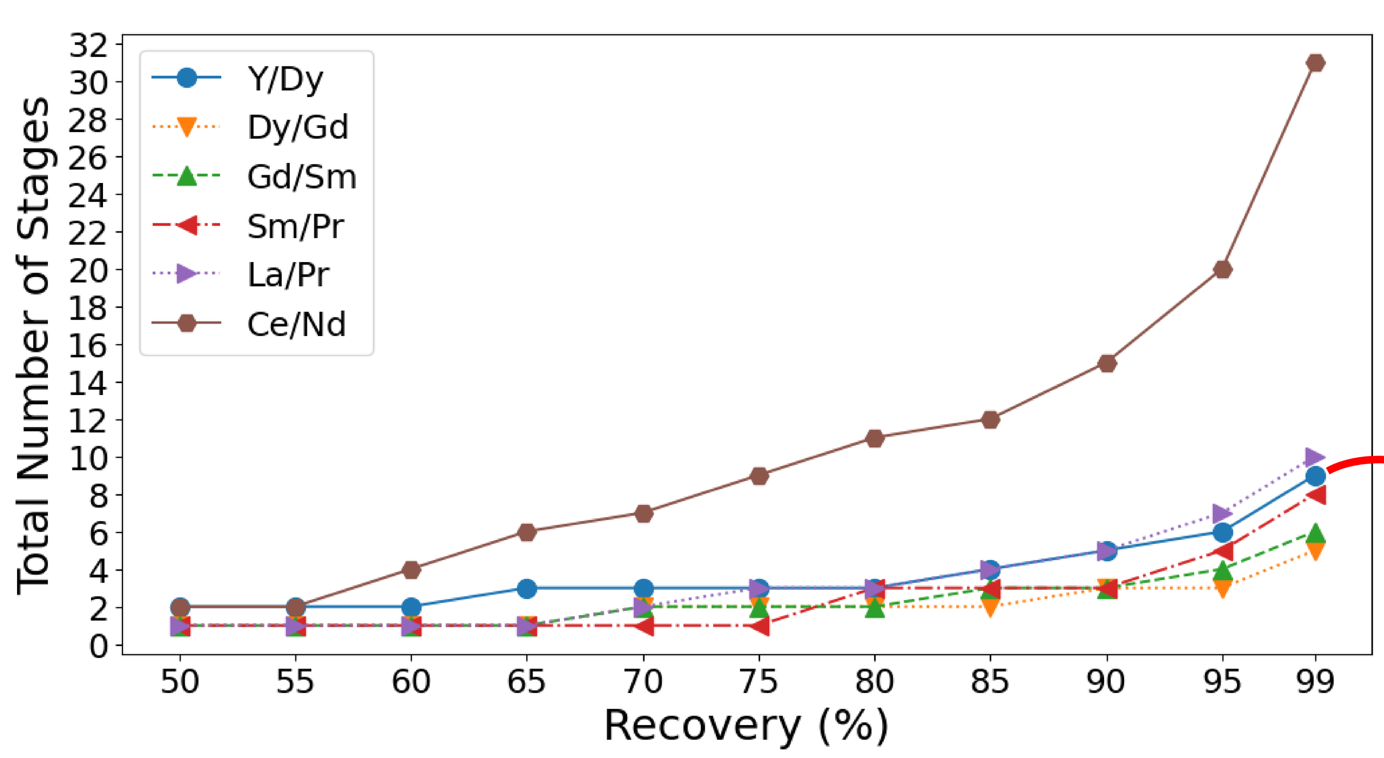
- This work demonstrates the applicability of superstructure optimization in the conceptual design of a solvent extraction process
- Discretizing the pH removes the nonlinearity in the distribution coefficient relation and improves the model tractability
- The optimization formulation can be used to determine the optimal design for different key components
- The formulation includes the ability to optimally select the number of stages, the pH, and the extracting.

Future Work

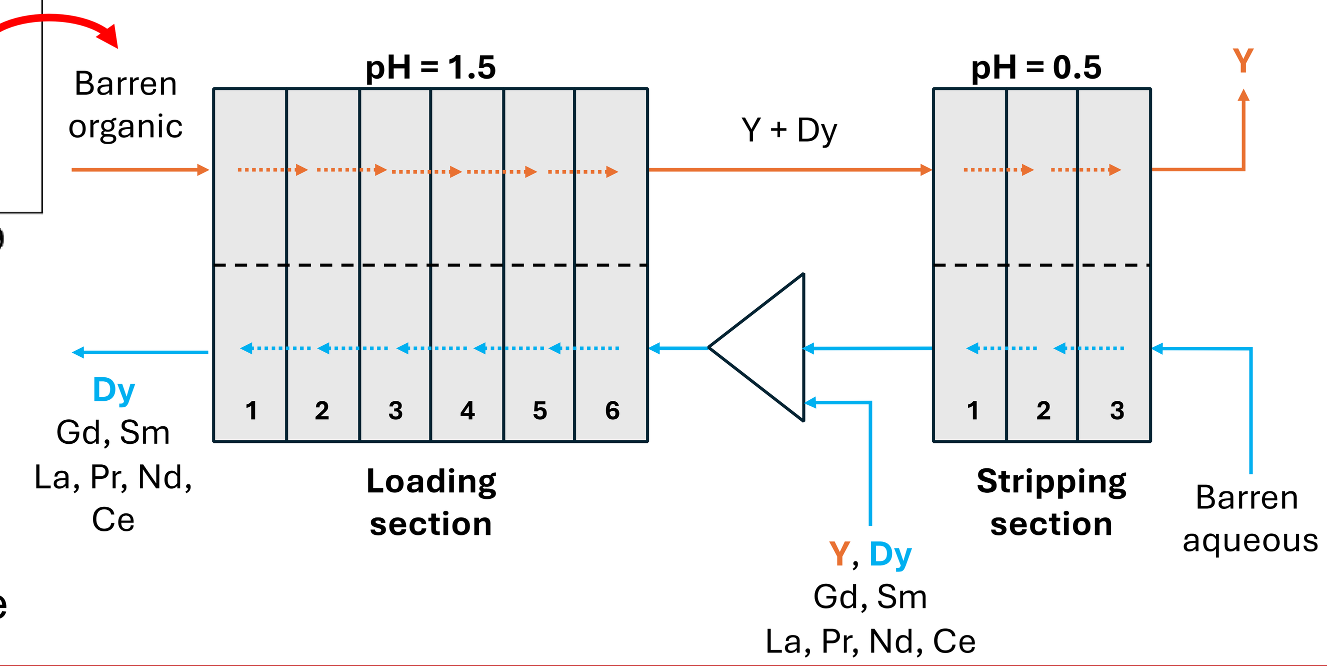
- Introducing precipitation constraints to increase the model fidelity
- Converting the current equilibrium model into a rate-based model for potential equipment sizing
- Include extractant cost to improve cost estimates in the optimal design formulation
- Extend the formulation to determine the optimal separation sequence with product selection

Results

Optimal Design for Sharp Separation with 5% DEPHA 10% TBP



Cerium (Ce) – Neodymium (Nd) Separation	
85%	7 L.Stages at pH 5.0, 5 S.Stage at pH 2.5
90%	10 L.Stages at pH 5.0, 5 S.Stage at pH 2.0
95%	16 L.Stages at pH 5.0, 4 S.Stage at pH 0.5
99%	14 L.Stages at pH 5.0, 17 S.Stages at pH 3.0

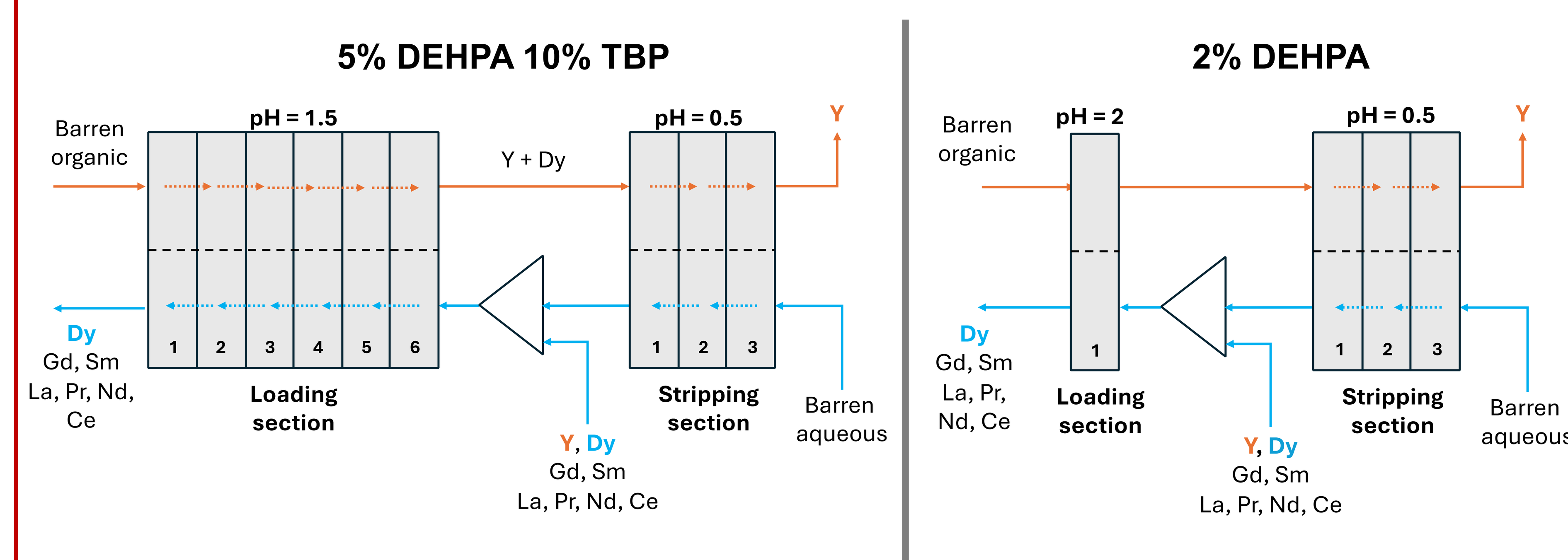


80	Binary variables
2386	Continuous variables
2448	Constraints

Solved to global optimality with average runtime of 20 s per node

Solvent Selection Influences on the Optimal Design

Sharp Separation (99%) of Yttrium (Y) and Dysprosium (Dy)



- Introduces 4 different solvent mixtures choices that affect the distribution coefficient:
  - *5% DEHPA 10% TBP | 2% DEHPA 10% TBP | 2% DEHPA | 2% Cyanex*
- Changing the solvent mixture reduces the total number of stages from 9 to 3
- Slightly increases the pH gap from 1 to 1.5
- Significant increase in runtime from 20 seconds to 8.4 minutes

References

[1] – IEA (2021), The Role of Critical Minerals in Clean Energy Transitions, IEA, Paris

[2] – Rick Honaker et al. "Pilot-Scale Testing of an Integrated Circuit for the Extraction of Rare Earth Minerals and Elements from Coal and Coal Byproducts Using Advanced Separation Technologies"

[3] - Feng Xie et al. "A critical review on solvent extraction of rare earths from aqueous solutions". In: Minerals Engineering 56 (2014)

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