Gibbs energy minimization model for solvent extraction with application to rare earths recovery

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ABSTRACT

The emergence of technologies in which rare earth elements provide critical functionality has increased the demand for these materials, with important implications for supply security. Recycling provides an option for mitigating supply risk and creating economic value from the resale of recovered materials. While solvent extraction is a proven technology for rare earth recovery and separation, its application often requires extensive trial-and-error experimentation. We describe a modeling strategy based on Gibbs energy minimization that incorporates parameter estimation for required thermodynamic properties as well as process design for solvent extraction and illustrate its applicability to rare earths separation. Visualization analysis during parameter estimation revealed a linear relationship between the standard enthalpies of the extractant and respective organo-metal complexes, analogous to the additivity principle for predicting molar volumes of organic compounds. Establishing this relationship reduced the size of the parameter estimation problem and yielded good agreement between model predictions and reported equilibrium extraction data, validating the property estimates for the organic phase species. Design exploration and optimization results map out the space of feasible solvent extraction column configurations and identify the set of optimal design parameter values that meet recovery and purity targets.

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S0-A: Input (xml) data


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Co.,Ltd 2008-->

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refit of Holmes, H.F., Busey, J.M., Simonson, J.M., Mesmer, R.E., Archer, D.G., and Wood, R.H., 1987, The enthalpy of dilution of HCl(aq) to 648 K and 4p MPa. Thermodynamic properties, Journal of Chemical Thermodynamics, v. 19, p. 863-890.

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ref: Shock and Helgeson (1998), Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: corellation algorithms for ionic species and equation of state to 5kb and 1000C Geochimica et Cosmochimica Acta, Vol 52. pp 2009 – 2036


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ref: Shock and Helgeson (1998), Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: corellation algorithms for ionic species and equation of state to 5kb and 1000C Geochimica et Cosmochimica Acta, Vol 52. pp 2009 – 2036


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ref: Shock and Helgeson (1998), Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: corellation algorithms for ionic species and equation of state to 5kb and 1000C Geochimica et Cosmochimica Acta, Vol 52. pp 2009 – 2036

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ref: Shock and Helgeson (1998), Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: corellation algorithms for ionic species and equation of state to 5kb and 1000C Geochimica et Cosmochimica Acta, Vol 52. pp 2009 – 2036

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ref: Shock and Helgeson (1998), Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: corellation algorithms for ionic species and equation of state to 5kb and 1000C Geochimica et Cosmochimica Acta, Vol 52. pp 2009 – 2036


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ref: Shock and Helgeson (1998), Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: corellation algorithms for ionic species and equation of state to 5kb and 1000C Geochimica et Cosmochimica Acta, Vol 52. pp 2009 – 2036


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            2036
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S0-B: Data sources for extraction equilibrium isotherms

In this study, we used the single component data from Li (1987) in the visualization step to discover the linear relationship between the extractant standard property and those of the organo-metal complexes, then used multicomponent data from other sources for the least squares fitting. There is no need to use more than one equilibrium dataset for the least square fit, as long as the reported equilibrium data considered a range of values for pH, rare earth concentration and extractant fraction. Our decision to combine different sources for this study reflects our uncertainty about the (mostly unreported) measurement errors in the different equilibrium data sources. Table 1 summarizes the different data sources.

Table 1: Data sources

Single component data		Multi-component data	
Rare earth	Source	Rare earth	Source
Nd	Lee(2005)[1], Li(1987)[2], Lyon(2016) [3]	Nd, Pr	Liu(2014), Lyon(2016, 2017)[3,4]
Pr	Li(1987)[2], Lyon(2016)[3]	Nd, Pr, La	Banda(2014)[5]
Ce	Li(1987)[2]	Nd, Pr, Ce, La	Formiga(2016)[6], Kim(2012)[7]
La	Li(1987)[2]		

S1-A: Additional Parameter fit plots

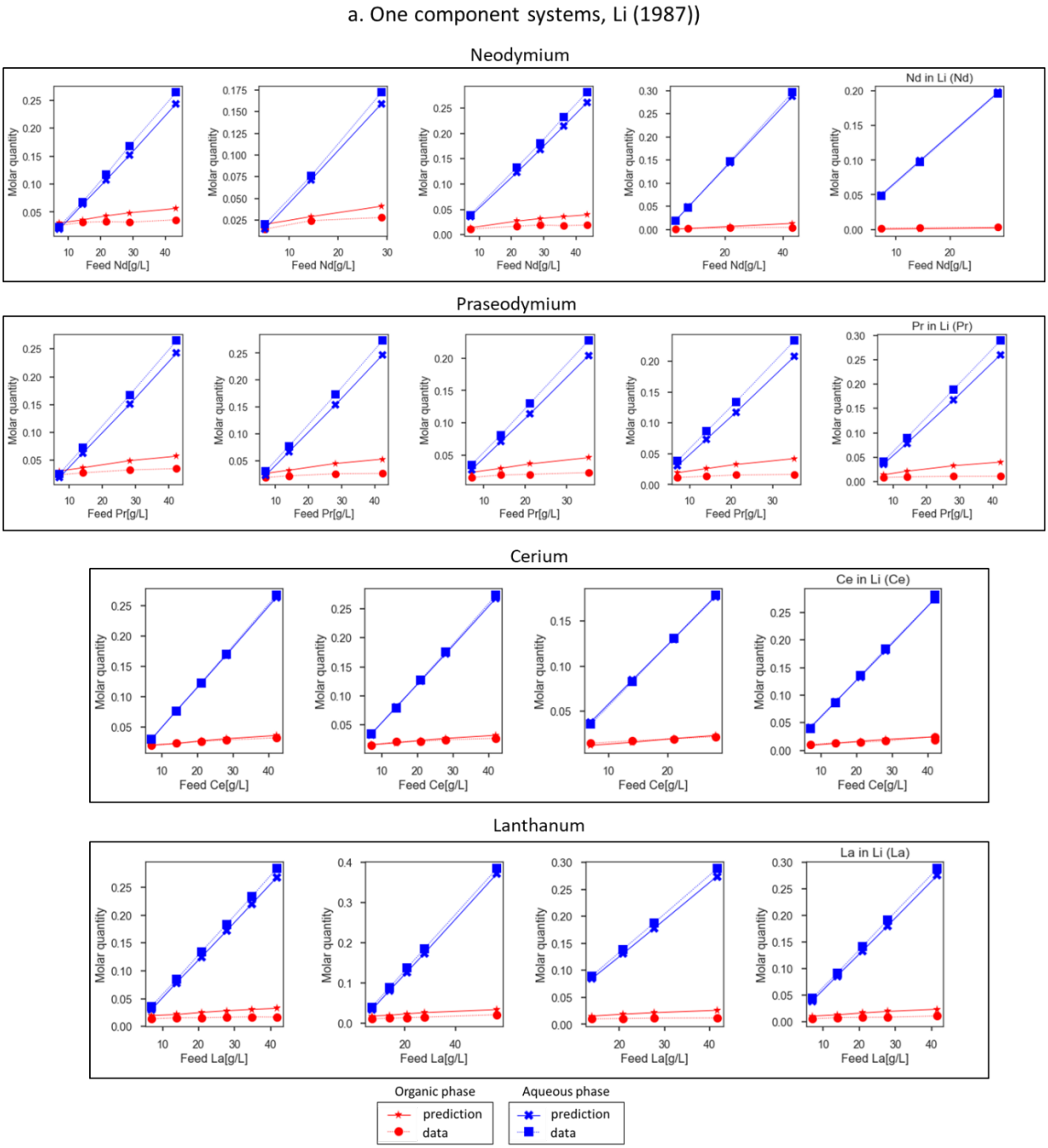

Fig. 1: Additional parameter estimation validation results comparing predicted and reported equilibrium molar compositions in both the aqueous and organic phases with individual rare earth equilibrium data from Li et al[2].

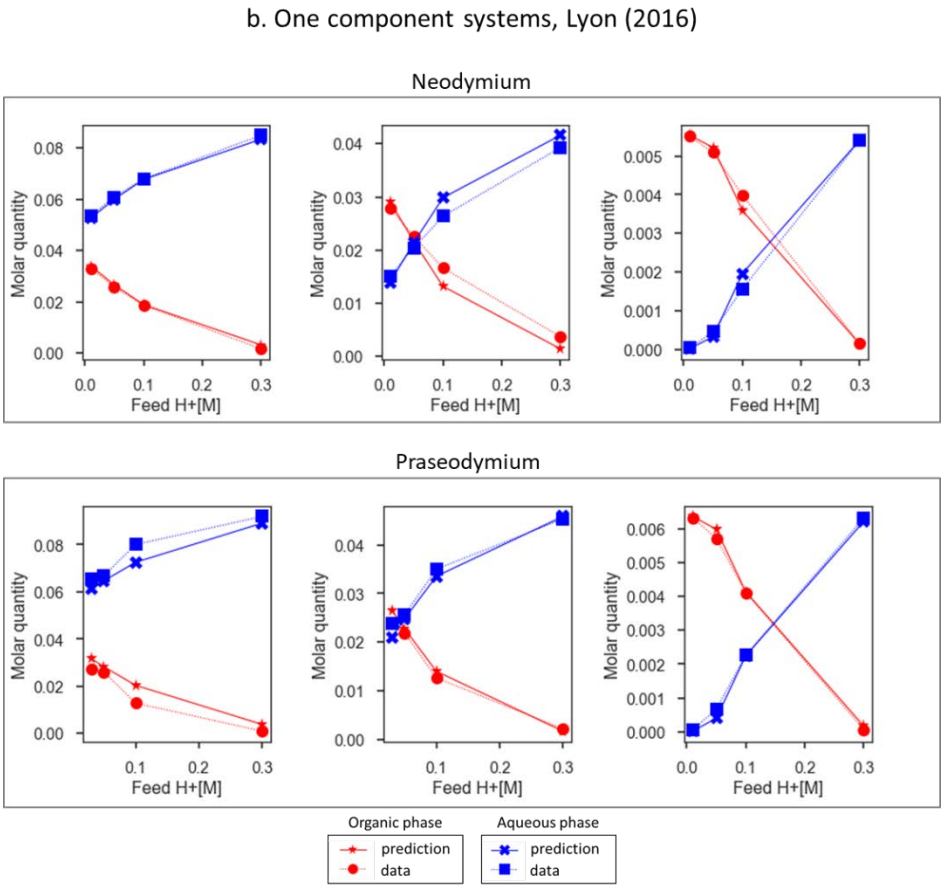

Fig. 2: Additional parameter estimation validation results comparing predicted and reported equilibrium molar compositions in both the aqueous and organic phases with individual rare earth equilibrium data from Lyon et al[3].

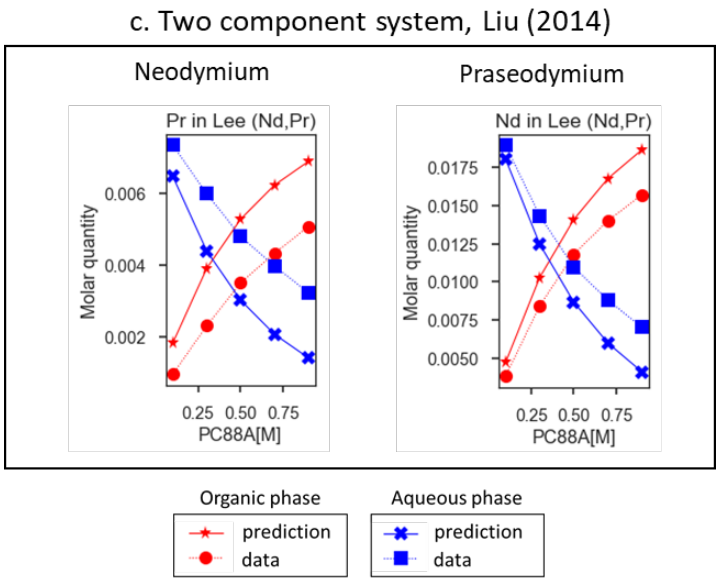

Fig. 3: Additional parameter estimation validation results comparing predicted and reported equilibrium molar compositions (Neodymium, Nd, and Praseodymium, Pr) in both the aqueous and organic phases with individual rare earth equilibrium data from Liu et al[8].

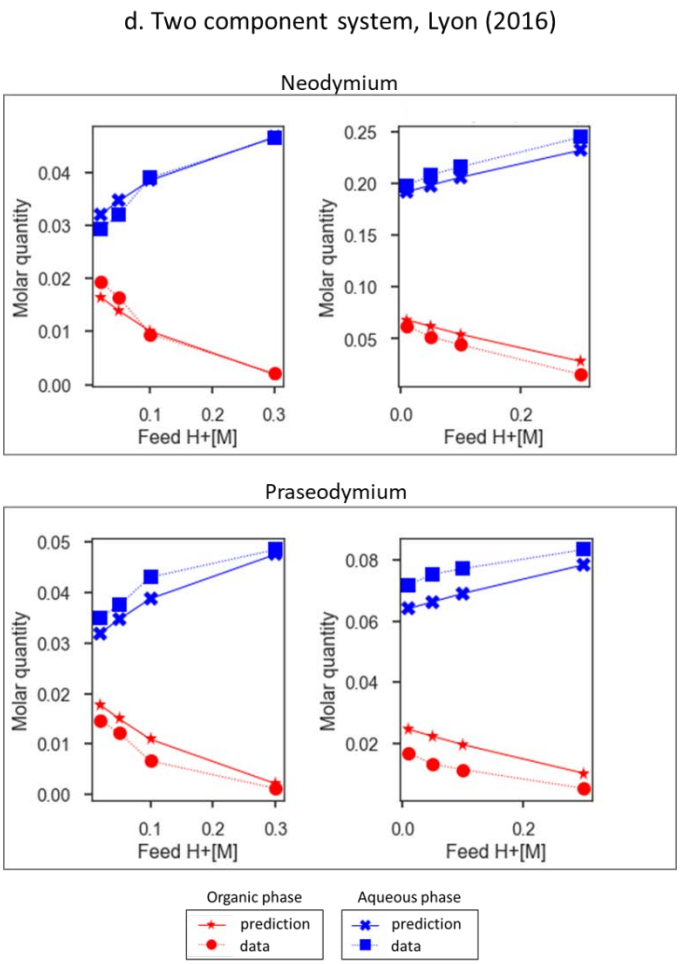

Fig. 4: Additional parameter estimation validation results comparing predicted and reported equilibrium molar compositions in both the aqueous and organic phases with individual rare earth equilibrium data from Lyon et al[3].

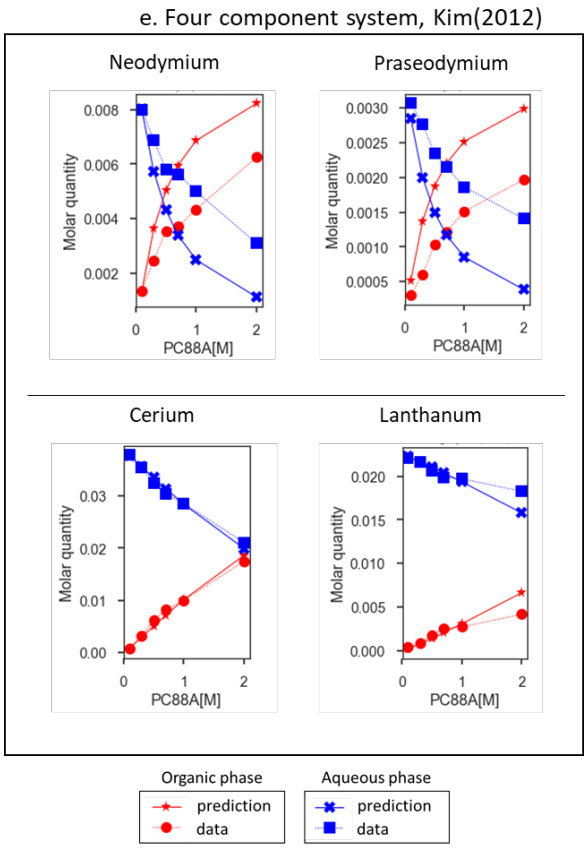

Fig. 5: Additional parameter estimation validation results comparing predicted and reported equilibrium molar compositions in both the aqueous and organic phases with mixture data from Kim et al.[7]. Although the deviation for Nd and Pr seem pronounced, the absolute values are very small.

S2-A: Solvent extraction process model

Process simulation: Each solvent extraction column is composed of a combination of individual stages, which are the basic functional units of the solvent extraction process. The Gibbs minimization model simulates equilibrium for each stage, taking as input the output streams from adjacent stages. Fig. 6 represents the software flowchart for implementing the solvent extraction model. Step 1 loads process parameters and system specifications, which include aqueous and organic feed compositions, y_j^0, number of stages per column, N_j, and organic-to-aqueous phase ratios for each column, $(\mathrm{O/A})_j$. These parameters stay fixed for design simulations but can become variables for optimization runs. Step 2 creates and initializes a vector of stage compositions, Y_j, for each column, j. The size of Y_j is $(N_j + 1) \times (n_{aq} + n_{org})$, where n_{aq}, n_{org} are the number of species in the aqueous and organic phases in each stage, respectively. Y combines Y_j from all three columns to form a vector of all stage compositions. Step 3 minimizes Gibbs to predict a new set of equilibrium compositions, Y', for each stage. Step 4 evaluates the residual from a difference function of the two vectors, Y and Y'. Step 5 tests the convergence criteria and ends the simulation if met; otherwise, step 6 updates Y and repeats steps 3–5. The combined steps 3–6 are a root-finding problem, which can be solved using a number of methods. We found reliable performance with the modified Powell's algorithm.[9–11]

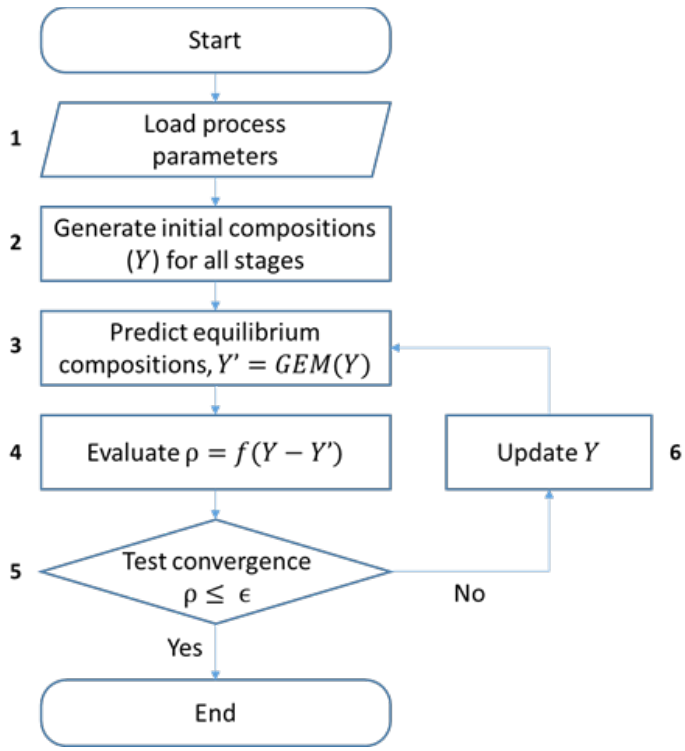

Fig. 6: Flowchart for simulating solvent extraction system

S3-A: Design Exploration – method details

Parameter sweep: The set of design and operating parameters that define column performance include compositions of aqueous and organic process streams for the extraction, scrub, and strip columns; the relative volumetric flow rates of the different streams; and the number of stages in each column. Designing for both high recovery and high purity becomes an exercise in tuning these parameters, recognizing the nonlinear nature of their coupled interactions. To gain insight into the best combinations for these parameters, we use parameter sweeps to explore and understand the solution space of recovery and purity predictions. We split the parameters into two groups: operating and design parameters. For each operating parameter, we define select representative low,

medium, and high values (Table 2), and use these values to generate a combinatorial table of operating parameter sets.

Table 2: Solvent extraction column operating parameter levels for sweep analysis

Levels	Extractant fraction	H+ concentration (M)		
		Extraction column	Scrub column	Strip column
Low	0.2	0.001	0.001	0.001
Medium	0.4	0.03	0.03	0.03
High	0.6	1	1	1
Levels	*O/A ratio			Recycle fraction
	Extraction column	Scrub column	Strip column	
Low	0.5	0.5	0.5	0
Medium	3.25	3.25	3.25	0.6
High	6	6	6	1.2**

*O/A: Organic-to-aqueous phase volumetric ratio.
**Recycle is defined relative to the molar quantity in the feed stream

For the design parameters (number of stages per column), we define a bounded series of integer values representing the total number of stages and, for each item in this set, generate combinations of extraction, scrub, and strip stages whose sums equal its value. We further streamline the combinations by excluding those in which the maximum difference between the number of extraction, scrub, and strip stages in each combination exceeds six. This constraint balances the distribution of design cases across the different stage totals and reduces the fraction of cases with infeasible combinations. Then we combine the two datasets by mapping each design case with the table of operating parameter combinations and set it up for three separation scenarios: scenario 1, Nd, Pr from Ce, La; scenario 2, Nd

from Pr; scenario 3, Ce from La. Then for each case of the combined dataset, we run simulations to predict the corresponding recovery and purity performance.

S4-A: Process optimization – method details

In the previous section, we described a method for implementing multi-parameter sweeps for exploring the space of feasible column configurations. Here, we add directionality to the design exploration, with the objective of finding optimal process designs. Then we use parametric analysis to understand the sensitivity of the optimized designs to parameter peturbations and evaluate the effect of uncertainty in feed composition on the distribution of optimal solutions.

Formulation: Eqn. 1 summarizes the problem formulation for optimizing the solvent extraction system.

$$
\begin{aligned}
&Minimize\ f(x_i, y_j) \\
&s.t. \\
&h(x_i, y_j) = 0 \\
&g(x_i, y_j) \leq 0 \\
&y_{min} \leq y_j \leq y_{max} \\
&x_{min} \leq x_i \leq x_{max}
\end{aligned} \tag{1}
$$

Here, x_i represents a vector of design and operating variable parameters, and y_j is the vector of stagewise stream compositions. Since the scope of this study excludes economics, we keep things simple and set the the objective function, $f(x_i, y_j)$ as the total number of equilibrium stages, a surrogate for the required equipment capital outlay. The equality constraint, $h(x_i, y_j)$, comprises the set of Gibbs minimization equations, embedded in the

solvent extraction column simulation model (Fig. 6) with implicit mass, species, elemental, and charge balances. The inequality constraints, $g(x_i, y_j)$, include process targets (e.g., recovery, purity, as well as constraints on maximum number of stages). Table 3 summarizes the resulting optimization specifications and bounds.

Table 3: Optimization variable parameter bounds

Parameter	Lower bound	Upper bound
Operating parameters		
Extractant fraction	0.25	0.65
O/A, extraction*	1	6
O/A scrub*	1	6
O/A, strip*	1	6
Recycle fraction**	0.0	0.9
pH Extraction/Scrub	3	5
pH Strip	0	0.3
Design parameters		
Number of extraction stages	1	12
Number of scrub stages	1	12
Number of strip stages	1	12

*O/A = organic/aqueous phase volumetric ratio.
**Recycle is defined relative to the molar quantity of target solute(s) in the feed stream

The resulting optimization problem is mixed integer nonlinear: the numbers of extraction, scrub. and strip stages compose the integer variables. Since we have embedded a design simulation – that expresses the underlying physics – within the optimization problem, we

relied on a derivative-free technique to implement the optimization. Specifically, we use the RBFOpt toolbox, an open-source library for simulation-based optimization,[12] which allows us to specify different algorithmic schemes to deal with mixed-integer decision variables (in this case, Ipopt[13] and Bonmin[14] as the respective nonlinear and mixed-integer subsolvers). The python interface for this framework was provided via the Pyomo platform.[15,16] Table 4 summarizes the results.

Table 4: Solvent extraction process optimization results.

Parameter	Module 1: Nd, Pr from Ce, La	Module 2: Nd from Pr	Module 3: Ce from La
Extractant fraction	0.65	0.4	0.57
O/A, extraction	5.9	6	6
O/A scrub	1.2	1	1
O/A, strip	1.6	4	1
Recycle	0.86	0.89	0.89
extraction stages	6	1	4
scrub stages	6	8	9
strip stages	4	2	2
Total stages	16	9	15
Recovery (%)	97%	86%	91%
Purity (%)	99.8%	99%	99.5%

Note that changing the optimization constraints and bounds will lead to a different set of results. For instance, the low strip O/A ratios for modules 1 and 3 imply that relatively dilute raffinate streams are sent to the precipitation tanks, which is not desirable. One way to fix this is to reset

the O/A bounds to no more than 2 for extraction, and no less than 4 for scrub and strip columns. A sample run with these new specifications yielded a design with only third of the previous extractant loading, and delivers scrub (strip) raffinate at three (four) times the previous concentration. However, it requires about 50% more stages and only manages 85% recovery.

References

(1) Lee, M.-S.; Lee, J.-Y.; Kim, J.-S.; Lee, G.-S. Solvent Extraction of Neodymium Ions from Hydrochloric Acid Solution Using PC88A and Saponified PC88A. *Sep. Purif. Technol.* **2005**, *46* (1), 72–78. https://doi.org/10.1016/j.seppur.2005.04.014.

(2) Li, H.; Chen, Z.; Meng, S. Extraction Equilibria of Individual Rare Earth in HEH(EHP)-Kerosene-HCl-RECl3 System. *J. Chin. Rare Earth Soc.* **1987**, *5* (3), 71–74.

(3) Lyon, K. Separation of Adjacent Rare Earth Elements Using Solvent Extraction. Thesis, University of Idaho: Idaho, 2016.

(4) Lyon, K. L.; Utgikar, V. P.; Greenhalgh, M. R. Dynamic Modeling for the Separation of Rare Earth Elements Using Solvent Extraction: Predicting Separation Performance Using Laboratory Equilibrium Data. *Ind. Eng. Chem. Res.* **2017**, *56* (4), 1048–1056. https://doi.org/10.1021/acs.iecr.6b04009.

(5) Banda, R.; Jeon, H. S.; Lee, M. S. Separation of Ce and La from Synthetic Chloride Leach Solution of Monazite Sand by Precipitation and Solvent Extraction. *Metall. Mater. Trans. B* **2014**, *45* (6), 2009–2017. https://doi.org/10.1007/s11663-014-0124-x.

(6) Formiga, T. S.; de Morias, C. A. Cerium Separation from Light Rare Earth Concentrate by Liquid-Liquid Extraction. *World J. Eng. Technol.* **2016**, *4* (3), 129–137.

(7) Soo Kim, J.; Nagaphani Kumar, B.; Lee, J. Y.; Lakshmi Kantam, M.; Ramachandra Reddy, B. Separation and Recovery of Light Rare-Earths from Chloride Solutions Using Organophosphorus Based Extractants. *Sep. Sci. Technol.* **2012**, *47* (11), 1644–1650. https://doi.org/10.1080/01496395.2011.654170.

(8) Liu, Y.; Jeon, H. S.; Lee, M. S. Solvent Extraction of Pr and Nd from Chloride Solution by the Mixtures of Cyanex 272 and Amine Extractants. *Hydrometallurgy* **2014**, *150*, 61–67. https://doi.org/10.1016/j.hydromet.2014.09.015.

(9) More, J.; Garbow, B.; Hillstrom, K. *User Guide for MINPACK-1*; Technical Report ANL-80-74; Argonne National Laboratory: Lemont, Illinois, 1980.

(10) Oliphant, T. E. Python for Scientific Computing. *Comput. Sci. Eng.* **2007**, *9*, 10–20.

(11) Millman, K. J.; Aivazis, M. Python for Scientists and Engineers. *Comput. Sci. Eng. 13*, 9–12.

(12) Costa, A.; Nannicini, G. RBFOpt: An Open-Source Library for Black-Box Optimization with Costly Function Evaluations. *Math. Program. Comput.* **2018**, *10* (4), 597–629. https://doi.org/10.1007/s12532-018-0144-7.

(13) Wächter, A.; Biegler, L. T. On the Implementation of an Interior-Point Filter Line-Search Algorithm for Large-Scale Nonlinear Programming. *Math. Program.* **2006**, *106* (1), 25–57. https://doi.org/10.1007/s10107-004-0559-y.

(14) Bonami, P.; Biegler, L. T.; Conn, A. R.; Cornuéjols, G.; Grossmann, I. E.; Laird, C. D.; Lee, J.; Lodi, A.; Margot, F.; Sawaya, N.; et al. An Algorithmic Framework for Convex Mixed Integer Nonlinear Programs. *Mem. George B Dantzig* **2008**, *5* (2), 186–204. https://doi.org/10.1016/j.disopt.2006.10.011.

(15) Hart, W. E.; Laird, C. D.; Watson, J.-P.; Woodruff, D. L.; Hackebeil, G. A.; Nicholson, B. L.; Siirola, J. D. *Pyomo–Optimization Modeling in Python*, Second.; Springer Science & Business Media, 2017; Vol. 67.

(16) Hart, W. E.; Watson, J.-P.; Woodruff, D. L. Pyomo: Modeling and Solving Mathematical Programs in Python. *Math. Program. Comput.* **2011**, *3* (3), 219–260.