Rare Earth Extraction with Ionquest® 801
initial modelling development

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Dates:
Received: 29 May 2024
Published: October 2024

How to cite:
Carrozza, C.F., Dutoy, F., Stella, M.B. 2024. Rare Earth Extraction with Ionquest® 801 initial modelling development. *Journal of the Southern African Institute of Mining and Metallurgy*, vol. 124, no.10 pp. 555–558

DOI ID:
http://dx.doi.org/10.17159/2411-9717/689/2024

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This paper is based on a presentation given at the Southern African Rare Earths 2nd International Conference 2024, 19-20 June 2024, Swakopmund Hotel and Entertainment Centre, Swakopmund, Namibia

Abstract

Rare earth elements (REEs) are indispensable components in the manufacturing of high-tech devices, renewable energy technologies, and defence applications. As global demand for these elements continues to rise, there is a pressing need to optimize extraction processes for both efficiency and environmental sustainability. This study explores approaches to rare earth extraction using Ionquest® 801 and integrates a predictive modelling to enhance process understanding and optimization.

We conducted a screening test varying pH process to evaluate the best extraction efficiency. Starting pregnant leach solution (PLS), solution was prepared in the lab with the following rare earth elements: La, Ce, Gd, Dy, and Y, at 0.02 M for each element. The data obtained were used to develop empirical and mechanistic models to predict rare earth extraction yields and flowsheet. Further tests were performed by mixing specific concentrations of different extractant and/or phase modifier. Our experimental results demonstrated the effectiveness of the proposed extraction methods, highlighting improvements in both yield and selectivity. The developed models successfully captured the complex relationships between process parameters and extraction efficiency, providing valuable insights for process optimization.

Keywords

rare earth elements, phosphonic acid-SX, distribution ratio, modeling development

Introduction

Rare earth elements (REEs) constitute a family of 15 elements crucial for various high-tech applications, including wind turbines, electric motors, catalysts, and batteries. The surge in REE prices in 2010, triggered by China's decision to reduce exports, underscored the need for countries to secure their own REE supplies. As a result, there has been a growing interest in exploiting REE resources domestically and through recycling.

The majority of REE production comes from mining ore bodies, where the elements are clustered in minerals like bastnasite and monazite. Extracting REE from these ores requires separating and precipitating them into individual rare earths, a process typically accomplished through solvent extraction (SX) in mixer-settlers.

Unlike the more commonly used SX processes for metals like copper or uranium, REE extraction poses unique challenges due to the chemical similarities among the elements and the need for extensive separation steps. While conventional SX circuits may involve fewer than 10 units, REE separation circuits can require over 1 000 mixer-settlers, making piloting and plant design exceptionally complex.

Model construction

For a common multi-component feed, the process configuration consists of sequentially arranged units, each of them well defined by specific inputs e.g., composition in g/L, pH, and mass balance between inlet and outlet. The outcomes should be able to solve the requirements of stage extraction efficiencies, considering all the experimental variables. The complexity of the system increases from bench to pilot scale and as a result, the output profile requires a large data set for obtaining an accurate representation. In addition, this challenge is directly linked to the optimization of design flowsheet, especially for industrial applications (Figure 1).

To improve the description of the extraction performances related to different scenarios, the experimental data need to be coupled with computing strategy. The simpler idea is starting from equilibrium parameters collected during the lab screening as input to develop a steady state model. The

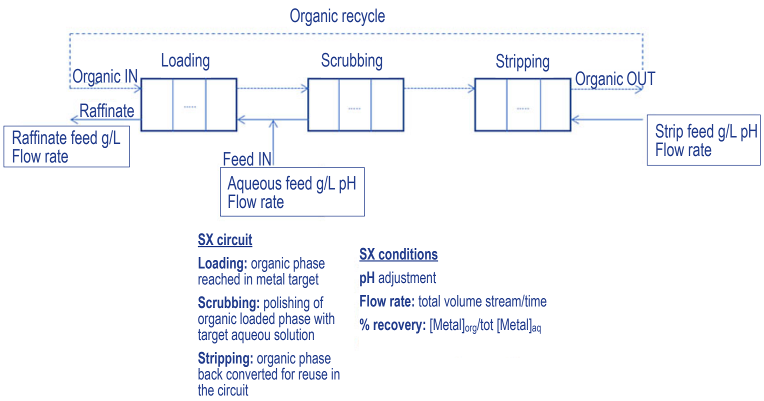

Figure 1—Global view of a typical flowsheet for metal recovery

equilibrium concentrations of the target REE are calculated under fixed conditions of temperature and pH. Those data are used to construct a curve fitting based on distribution ratio, this being the best choice to estimate the mass transfer between the phases and evaluate how the extraction profile is affected by pH.

The next level consists of extending this approach on a counter-current separation model to include the description of multi-stage extraction. The D-ratios can be included in a set of equations, which define the mass balance for each REE in the mixer unit. The goal is to calculate the metal amount in every stage by setting some known parameters, such as the total number of stages, the organic and aqueous flow rate, and the selected equilibrium pH. This approach works under the assumption that the steady-state variables are reasonable for a good representation of reactions that rapidly proceed, not including kinetic or interfacial phenomenon.

Experimental section

A mid/heavy REE solution was chosen to evaluate Ionquest® 801 performance: 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester and 0.3 M in aliphatic diluent ESCAID 110 provided by Exxon Mobil. The primary purpose was to find the operating conditions in terms of pH, as REE recovery occurs at remarkable acidic range. The pregnant leach solution (PLS, Table I) was prepared in HCl media (0.02 M REE as chloride). The aqueous and organic phases were kept in contact at room temperature under magnetic stirring for 15 min. HCl 20% wt and NaOH 13% wt were used for pH adjustment. Ratio A/O was 1 for all the lab work. The Ionquest® 801 profile was compared published data obtained from commercial phosphonic acid-SX.

The metal ion concentration was determined by ICP-OES. The extraction efficiency can be calculated according to Equation [1]:

Table I

REE feed composition (PLS)

REE	MW salt	Molarity REE	g/l REE
La	371.4	0.02	2.78
Ce	372.6	0.02	2.80
Gd	263.6	0.02	3.15
Dy	377.0	0.02	3.25
Y	303.4	0.02	1.78

$$\%\text{Extraction} = \frac{C_0 - C}{C_0} \times 100 \qquad [1]$$

The distribution ratio and the separation factor are introduced to evaluate and quantify the performance of extractant. For the metals A and B, they are respectively expressed as Equations [2] and [3]:

$$D_A = \frac{\text{Concentration of metal A (organic)}}{\text{Concentration of metal A (aqueous)}} \qquad [2]$$

$$\beta_{AB} = \frac{D_A}{D_B} \qquad [3]$$

Results and conclusions

Solvent extraction results

The plots in Figure 2 exhibit a good trend of extraction for Ionquest® 801. As expected for Dy and Y, the percentage of extraction is high already at low pH. For Gd the recovery gradually increases as pH increases. The light REE grouping La and Ce needs less acidic conditions to overcome the issue of co-extraction of other rare earth elements, but Ionquest® 801 can achieve far better results when compared with those obtained from a commercial phosphonic acid reagent, as demonstrated in Figure 3.

The good trend is evident when distribution ratios are calculated for each REE. Three values of pH are selected to achieve a description of extraction capability. As depicted in Figures 4 and 5, the Ionquest® 801 distributions are more efficient for Gd, Dy, and Y when compared with commercial phosphonic acid extractants. Typically, it implies a high extractability of metal ions from the aqueous phase, in addition to separation factors (β) that reflect how selectively metal can be extracted. In Table II separation factors are listed for Ionquest® 801 and a commercial phosphonic

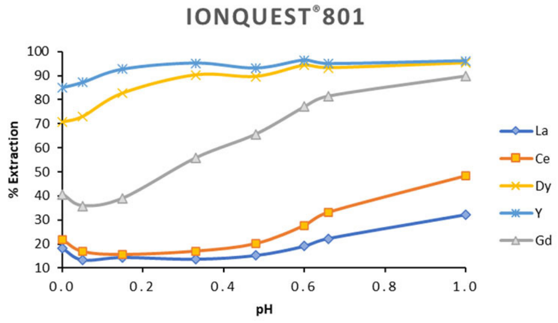

Figure 2—Ionquest® 801 – experimental extraction curve vs pH. 1M extractant in ESCAID 110. 0.02 rare earth metals as chloride

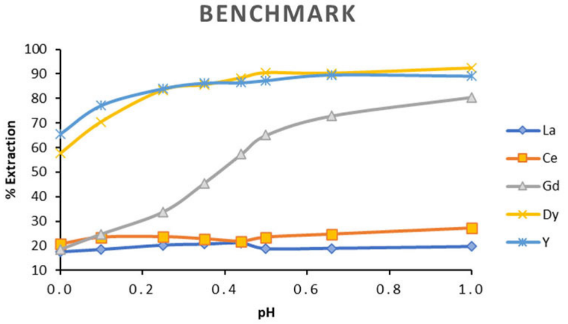

Figure 3—Commercial phosphonic acid SX reagent – experimental extraction curve vs. pH. 1M extractant in ESCAID 110. 0.02M rare earth metals as chloride

acid extractant. ionquest® 801 shows a remarkable selectivity for the heavy REE (Gd, Dy, Y) at the investigated pH interval. For La and Ce Ionquest® 801 offers the same separation performances as commercial extractant but increases the percentage of extraction under the same conditions.

Simulation of metal distribution

The distribution ratios that were experimentally determined were used to validate the fitting curves resulting from the simulations. The approach was to functionalize empirical correlations with parameters known to affect equilibrium distribution. An intuitive strategy is proposed in the Equations [4] and [5]: D-ratios can be expressed as a function of pH and then predicted from a polynomial fitting. Note that the polynomial grade is directly related to stoichiometric coefficients of proton in the equilibrium reaction and, consequently, to ionic state of metal in the aqueous phase.

$$D = f(\mathrm{pH}) \qquad [4]$$

$$\mathrm{Log}\,D = a_1(\mathrm{pH})^2 + a_2\,\mathrm{pH} + a_3 \qquad [5]$$

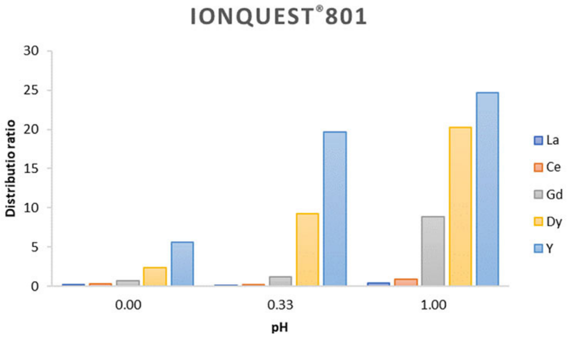

Figure 4—Distribution ratio experimentally calculated for Ionquest® 801 at three different pH values (0.00, 0.33, 1.00)

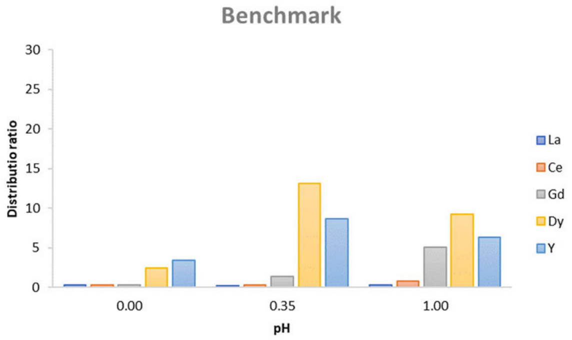

Figure 5—Distribution ratio experimentally calculated for commercial phosphonic acid SX at three different pH values (0.00, 0.33, 1.00)

A programming tool was developed to estimate how the extraction profile was affected by pH. The objective was to fit the experimental D-ratio by minimizing the sum of the squares of the deviations of the data from the model (least-squares fit). The results are demonstrated in Table III. The correlations reveal a good agreement between the two data sets for the selected range of pH.

Table II

Separation factors experimentally calculated for Ionquest® 801 (left side) and a commercial phosphonic acid (right side) at three different pH values (0.00, 0.33, 1.00)

pH 0.00	**Ionquest® 801**				**Commercial phosphonic acid**			
	Ce	**Gd**	**Dy**	**Y**	**Ce**	**Gd**	**Dy**	**Y**
La	1.25	3.08	10.77	25.37	1.20	1.30	9.40	13.33
Ce		2.47	8.63	20.33		1.08	7.82	11.08
Gd			3.50	8.24			7.25	10.28
Dy				2.36				1.42
pH 0.35	**Ionquest® 801**				**Commercial phosphonic acid**			
	Ce	**Gd**	**Dy**	**Y**	**Ce**	**Gd**	**Dy**	**Y**
La	1.28	7.87	58.03	123.06	1.31	1.31	62.07	40.61
Ce		6.13	45.21	95.87		4.82	47.22	30.90
Gd			7.37	15.64			9.81	6.42
Dy				2.12				0.65
pH 1.00	**Ionquest® 801**				**Commercial phosphonic acid**			
	Ce	**Gd**	**Dy**	**Y**	**Ce**	**Gd**	**Dy**	**Y**
La	1.98	18.88	42.93	52.41	2.51	16.62	30.29	20.69
Ce		9.54	21.68	26.47		6.61	12.05	8.23
Gd			2.27	2.78			1.82	1.24
Dy				1.22				0.68

The threshold for the error estimation is below 5%, but some small discrepancies can be corrected by changing the grade of polynomial fitting. In other words, the model provides a good representation of which are the best conditions to achieve a target REE extraction.

Future development

The next challenge is to successfully implement the D-ratio model into a model for a counter-current extraction flowsheet. The first step consists of including the experimental data in the species mass balance equations (Equation [6] and [7]). In accordance with mass transfer, as schematized in Figure 6, the objective is determining the REE composition at stage n for each unit as present in the entire flowsheet.

$$\nu_{Org}\ C^{REE}_{Org,n-1} + \nu_{Aq}\ C^{REE}_{Aq,n+1} = \nu_{Org}\ C^{REE}_{Org,n} + \nu_{Aq}\ C^{REE}_{Aq,n} \qquad [6]$$

$$C^{REE}_{Aq,n}\ D_n = C^{REE}_{Org,n} \qquad [7]$$

The programming key will be simultaneously solving a set of equations to achieve the organic and aqueous metal profile in terms of percentage of extraction (Figure 7). Inlet and outlet flow are characterized by some input parameters, such as flow rates, volumetric ratios, and pH of the feed (See Table IV).

Acknowledegements

This work, in particular related to the modelling development, is supported by the IPCEI Eu-Batin project. We thank all people included for their hard work and collaboration.

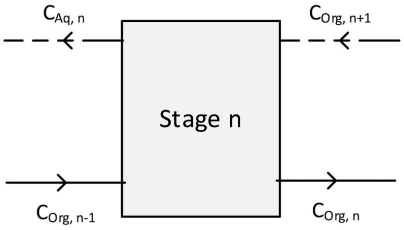

Figure 6—Mass balance diagram illustration for a single unit in a current-current extraction process

Table IV

Parameters set up for counter-current simulation flowsheet

	Input	Output
Experiment	pH feed PLS composition	Distribution ratio for batch scale Efficiency for single stage
Model	$C^{REE}_{Org,n-1}$, $C^{REE}_{Aq,n+1}$ (mass balance) Flow rate	Distribution ratio for flowsheet process Efficiency for *n* stages

References

Aguilar, M., Cortina, J.S. 2008 eds. *Solvent extraction and liquid membranes: Fundamentals and applications in new materials.* CRC Press.

Iloeje, C.O. 2020. Modeling Liquid–Liquid Extraction for Critical Elements Separations: An Overview Multidisciplinary Advances in Efficient Separation Processes. *ACS Symposium Series* American Chemical Society. pp 335–365.

Lyon, K.L., Utgikar, V.P., Greenhalgh, M.R. 2017. Dynamic Modeling for the Separation of Rare Earth Elements Using Solvent Extraction: Predicting Separation Performance Using Laboratory Equilibrium Data *Industrial & Engineering Chemistry Research.*,vol. 56, no. 4, pp. 1048–1056 American Chemical Society.

Omelchuk, K., Chagnes, A. 2018. New cationic exchangers for the recovery of cobalt (II), nickel (II) and manganese (II) from acidic chloride solutions: Modelling of extraction curves. *Hydrometallurgy* vol. 180, pp. 96–103.

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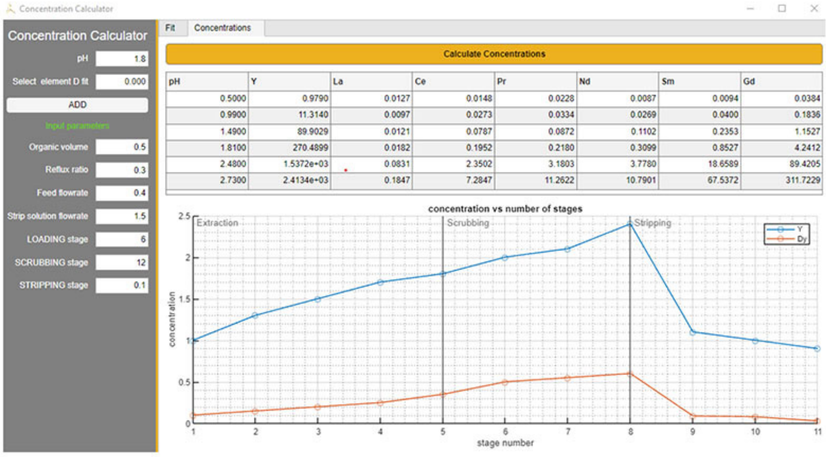
Table III

Laboratory data and model predictions for REE distribution with Ionquest® 801

pH	Distribution factor – Model results					Distribution factors – Exp results				
	La	Ce	Gd	Dy	Y	La	Ce	Gd	Dy	Y
0.00	0.19	0.22	0.53	2.43	6.41	0.22	0.28	0.69	2.41	5.67
0.33	0.18	0.24	1.36	7.69	14.99	0.16	0.21	1.26	9.28	19.69
1.00	0.50	1.03	9.82	19.71	23.15	0.47	0.93	8.90	20.23	24.70



pH 1.8
Select element D fit 0.000
Organic volume 0.5
Reflux ratio 0.3
Feed flowrate 0.4
Strip solution flowrate 1.5
LOADING stage 6
SCRUBBING stage 12
STRIPPING stage 0.1

pH	Y	La	Ce	Pr	Nd	Sm	Gd
0.5000	0.9790	0.0127	0.0148	0.0228	0.0087	0.0094	0.0384
0.9900	11.3140	0.0097	0.0273	0.0334	0.0269	0.0400	0.1836
1.4900	89.9029	0.0121	0.0787	0.0872	0.1102	0.2353	1.1527
1.8100	270.4899	0.0182	0.1952	0.2180	0.3099	0.8527	4.2412
2.4800	1.5372e+03	0.0831	2.3502	3.1803	3.7780	18.6589	89.4205
2.7300	2.4134e+03	0.1847	7.2847	11.2622	10.7901	67.5372	311.7229

Figure 7—Application interface for D-ratio model. Example of REE calculated profile using equilibrium parameters