# **RARE EARTH EXTRACTION WITH IONQUEST 801**

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#### 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<sup>®</sup> and integrates a predictive modelling to enhance process understanding and optimization.

We conducted a screening test varying process parameters such as temperature, pH, and reagent concentrations systematically to optimize extraction efficiency. Starting PLS solution was prepared in the lab with the following rare earth element, La - Ce - Gd - Dy - Y at 0.02 M. The data obtained were used to develop empirical and mechanistic models to predict rare earth extraction yields and flowsheet.

Further tests were performed mixing specific concentration of different extractant and/or phase modifier. Our experimental results demonstrate the effectiveness of the proposed extraction methods, highlighting improvements in both yield and selectivity. The developed models successfully capture the complex relationships between process parameters and extraction efficiency, providing valuable insights for process optimization.

# 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's 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 REEs 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 1000 mixer-settlers, making piloting and plant design exceptionally complex.

### Model Construction

For a common multi-components feed, the process configuration consists of sequentially arranged units, each of them well defined by specific inputs (*e.g.*, composition g/L, pH, 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 the industrial applications (Figure 1.).



Figure 1: Global view of a typical flowsheet for metal recovery.

To improve the description of the extraction performances related to different scenarios, the experimental data need to be coupled to computing strategy. The simpler idea is starting from equilibrium parameters collected during the lab screening as input to develop a steady state model. The 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 is the best choice to estimate the mass transfer between the phases and evaluate how the extraction profile is affected to pH.

The next level consists of extending this approach on 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 the calculation of 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 rapidly proceed, not including kinetic or interfacial phenomenon.

## **EXPERIMENTAL SECTION**

A mid/heavy REE solution was chosen to evaluate IONQUEST<sup>®</sup> 801 performances (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) was prepared in HCI media (0.02 M REE as chloride). The aqueous and organic phase were kept in contact at room temperature under magnetic stirring for 15 min. HCI 20 %wt and NaOH 13%wt were used for pH adjustment. The IONQUEST<sup>®</sup> 801 profile was compared the data obtained with commercial phosphonic acid-SX.

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
Υ	303.4	0.02	1.78

### Table 1: REE feed composition (PLS).

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

$$\%Extraction = \frac{C_0 - C}{C_0} \times 100$$
[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]:

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

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

### **RESULTS AND CONCLUSIONS**

#### Solvent extraction results

The plots in Figure 2 exhibits a good trend of extraction for IONQUEST<sup>®</sup> 801. As expected for Dy and Y, the percentage of extraction is high already at low pH, similarly for Gd where the recovery gradually increases as pH increases. The lowest grouping La and Ce needs less acidic conditions to overcome the issue of co-extraction, but globally IONQUEST<sup>®</sup> 801 can achieve far better results when compared with those obtained from the commercial phosphonic acid in Figure 3.



Figure 2: IONQUEST<sup>®</sup> 801 – experimental extraction curve vs pH. 1M extractant in ESCAID 110. 0.02 rare earth metals as chloride.



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

The good trend is evidence 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<sup>®</sup> 801 distributions are much more efficient for Gd, Dy and Y when compared with commercial phosphonic acid ones. Typically, it implies a high extractability of metal ions from the

aqueous phase, in addition to separation factors ( $\beta$ ) that reflect how selectively metal can be extracted. In the Table 2 separations factors are listed for IONQUEST<sup>®</sup> 801 and commercial phosphonic acid. IONQUEST<sup>®</sup> 801 shows a remarkable selectivity for the heavy REE (Gd, Dy, Y) at the investigated pH interval. For La and Ce IONQUEST<sup>®</sup> 801 offers the same separation performances as commercial extractant but increases the percentage of extraction for the same conditions.



Figure 4: Distribution ratio experimentally calculated for IONQUEST<sup>®</sup> 801 at three different pH (0.00, 0.33, 1.00).



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

pH 0.00		IONQUEST <sup>®</sup> 801			Co	mmercial pl	nosphonic	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
рН 0.35		IONQUEST <sup>®</sup> 801			Co	mmercial pl	nosphonic	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		IONQUES	ST <sup>®</sup> 801		Co	mmercial pl	nosphonic	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

Table 2: Separation factors experimentally calculated for IONQUEST<sup>®</sup> 801 (left side) and commercial phosphonic acid (right side) at three different pH (0.00, 0.35, 1.00).

## Simulation of metal distribution

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

$$D = f(pH)$$
[4]

$$Log D = a_1(pH)^2 + a_2 pH + a_3$$
[5]

A programming tool was developed to estimate how extraction profile was affected by pH. The point was fitting 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 showed in Table 3. The correlations reveal a good agreement between two data set for the selected range of pH. 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 gives back a good representation of which are the best conditions to achieve a target REE composition.

Distribution factor – Model results						Dis	tribution	factors –	Exp res	ults
рН	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

Table 3: Laboratory data and model predictions for REE distribution with IONQUEST<sup>®</sup> 801.

### Develop of graphical interface

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

$$\nu_{\text{Org}} C_{\text{Org,n-1}}^{\text{REE}} + \nu_{\text{Aq}} C_{\text{Aq,n+1}}^{\text{REE}} = \nu_{\text{Org}} C_{\text{Org,n}}^{\text{REE}} + \nu_{\text{Aq}} C_{\text{Aq,n}}^{\text{REE}}$$
[6]

$$C_{Aq,n}^{REE} D_n = C_{Org,n}^{REE}$$
[7]



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

The programming key will be solving a set of simultaneously equations to achieve the organic and aqueous metal profile in terms of percentage of extraction. Inlet and outlet flow are characterized by some input parameters, such as flow rates volumetric ratios and pH feed (See Table 4).

The future work will be centred on the develop of an application tool, with the purpose of acquiring the metal profile specifically for a selected set of operative conditions. The interface will facilitate the user ability to sort the experimental parameters which are stored in a complete database (See Fig. 7).

	Input	Output		
Experiment	pH feed	Distribution ratio for batch scale		
	PLS composition	Efficiency for single stage		
Model	$C_{Org,n-1}^{REE}$ , $C_{Aq,n+1}^{REE}$ (Mass balance)	Distribution ratio for flowsheet process		
	$v_{\rm Org}$ , $v_{\rm Aq}$ (Flow rates)	Efficiency for <i>n</i> stages		





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

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#### REFERENCES

- 1. Aguilar, Manuel, and José Luis Cortina, eds. *Solvent extraction and liquid membranes: Fundamentals and applications in new materials*. CRC Press, 2008.
- Iloeje, Chukwunwike 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, Kevin L. Utgikar, Vivek P. Greenhalgh, Mitchell R. (2017). Dynamic Modeling for the Separation of Rare Earth Elements Using Solvent Extraction: Predicting Separation Performance Using Laboratory Equilibrium Data *Ind. Eng. Chem. Res.* 56, 4, 1048–1056 American Chemical Society.
- 4. Omelchuk, Kateryna, and Alexandre Chagnes. (2018). New cationic exchangers for the recovery of cobalt (II), nickel (II) and manganese (II) from acidic chloride solutions: Modelling of extraction curves. *Hydrometallurgy* 180, 96-103.