

# MODELING AND SIMULATION OF SOLVENT EXTRACTION OF THE RARE EARTH ELEMENTS USED IN PERMANENT MAGNET MANUFACTURE

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*ABSTRACT - Separating rare earth elements is one of the most challenging hydrometallurgical processes due to their chemical similarities. In this work, we modeled and simulated the separation of neodymium, praseodymium, and lanthanum through an empirical pseudo-equilibrium model. First, we simulated the partition in an in-house computer program to define a solvent extraction circuit. Next, we characterized the pseudo-equilibrium state, and finally, we proposed a circuit based on the pseudo-equilibrium model. Our findings suggested the power law pseudo-equilibrium model can predict the organic recovery of the three elements with good agreement between observed and predicted data. We believe the evidence presented here will contribute to the establishment of an REE separation facility in Brazil.*

## 1 INTRODUCTION

Rare earth elements (REE) are paramount for the achievement of the sustainable development goals (SDG) posed by the United Nations (UN), and the didymium (neodymium and praseodymium), currently used to generate electricity in electric vehicles, plays an essential role due to their unique magnetic properties. However, they are regarded as critical minerals due to the risk of geological or geopolitical supply shortages. Brazil has the second-largest REE deposit in the world, but the country does not produce REE oxides due to technological and cost issues. Moreover, due to their chemical similarities, REE refining is one of the most difficult hydrometallurgical operations, which demands hundreds of mixer settlers to achieve the desired purity. One way to design such separations is to model the solvent extraction (SX) process.

Previous researchers have analyzed thermodynamic (PAVÓN et al., 2019), semi-empirical (REDDY et al., 1992), and empirical (SANTOS et al., 1999) approaches to model REE separation. In the first study, some mechanisms were proposed to separate Y/Eu/Ce through the liquid cation exchange reaction by selecting a model with the least residual mean square ( $MS_{res}$ ). The second study investigated the relationship between the equilibrium acidity and the Nd partition coefficient to define an SX circuit. Finally, the authors suggested several empirical equations to model the Sm/Gd separation process in the last work. The empirical models had many parameters, the equations were highly nonlinear, and the continuous extraction was done in separatory funnels, i.e., complete mass transfer was attained in each stage. Although the authors reached a good agreement between the model and observed values, incomplete mass transfer is expected in continuous processes (AZEVEDO; ALVES, 2013). So, we tried to describe the process inefficiencies through empirical modeling. We sought simpler models to predict the REE

organic recovery in a counter-current extraction through a pseudo-equilibrium (PSE) empirical model.

Hence, we aimed to model and simulate the Nd, Pr, and La extraction with PSE models. First, we conducted a batch experiment to obtain equilibrium data and relate the organic metal concentration to the aqueous metal concentration. Then we used our in-house software to simulate the extraction process and design an SX circuit. Finally, we compared the predicted values from the models to the observed extraction values, selecting the model with the least  $MS_{res}$ . These findings can help establish a REE separation process in Brazil.

## 2 EXPERIMENTAL

### 2.1 Materials

All organic reagents were used without any purification. To develop Pr/La separation, we used D2EHPA - 92% wt. (Di(2-Ethylhexyl) phosphoric acid) supplied by Luoyang Aoda Chemicals (China), and n-isoparaffin purchased from Ypiranga (Brazil) to use as diluent. All assays were done without pH control.

We simulated an aqueous stream from a previous separation (Sm/Nd) in an REE refining site. The feed liquor had  $10.8 \text{ gL}^{-1} \text{ Nd}_2\text{O}_3$ ,  $4.2 \text{ gL}^{-1} \text{ Pr}_6\text{O}_{11}$ , and  $36.0 \text{ gL}^{-1} \text{ La}_2\text{O}_3$ . All batch experiments were performed in deionized water, chloride media, and at room temperature.

The counter-current continuous extraction experiments were conducted on a mini-pilot scale in several mixer settlers, which have 240 mL mixer chamber volume and 240 mL settling capacity. Peristaltic pumps introduced the streams in the SX circuit (Cole Palmer).

### 2.2 Batch extraction: isotherm

We conducted a batch extraction experiment to determine the REE partition between the aqueous phase and extractant. The phase variation method was employed to gather equilibrium data; details have been described elsewhere (KISLIK, 2012). Briefly, an aqueous organic amount was placed inside a separatory funnel, and the system was agitated at 300 rpm for 30 min. The mixture was left at rest until complete phase disengagement, after which the raffinate was analyzed by UV spectroscopy, complexometric metal titration, and neutralization titration to determine the equilibrium metal aqueous concentration and acidity. Finally, the organic metal concentration was calculated by mass balance.

### 2.3 Solvent extraction plant design: modeling and simulation

To select an SX circuit, we simulated the solvent extraction process. For this purpose, we built a simulator in an open-source language (*Python*) to solve the mass balance (Eqn. 1):

$$\bar{C}_i - \bar{C}_{i-1} - R \cdot (C_{i+1} - C_i) = 0 \quad (1)$$

coupled with the isotherm equation (Section 2.2). In Eqn. (1), the subscript  $i$  denotes the  $i$ -th stage. Also, we aimed for 99.0% Pr organic recovery (first criterion) and 99% La aqueous purity (second criterion).

The SX circuit selection involved a general factorial design with the number of stages and

the aqueous-organic ratio as independent variables. We tested the range of 2-12 stages with step increments of 2 and 0.3 - 1.0 A/O ratio with step 0.1. The response variables were the Pr organic recovery and La aqueous purity. We selected a configuration that met project specifications for further validation.

## 2.4 Continuous extraction: model validation

A continuous counter-current experiment was carried out in mixer-settler extraction cells to validate the simulation. The raffinate was monitored through UV-Vis spectrophotometry and titration with EDTA until constant metal concentration values. When the steady state was reached, 30 mL of the aqueous phase was removed from each stage for chemical analysis, and the organic metal concentration was calculated by mass balance (Eqn. 1). To select the model describing the steady state, we chose the model with the least residual mean square (MONTGOMERY; PECK; VINING, 2012) (Eqn. 2):

$$MS_{res} = \frac{\sum_i^n (y_{i,obs} - y_{i,pred})^2}{n - p} \quad (2)$$

where  $y_{obs}$  is the observed (extraction) values;  $y_{pred}$ , the predicted (extraction) values from the isotherm model;  $n$ , the number of stages; and  $p$ , the number of parameters in the equilibrium model.

## 3 RESULTS AND DISCUSSION

### 3.1 Batch extraction: isotherm

To develop an empirical model, we first performed tests to determine the equilibrium isotherm. The results showed a similar extraction profile of the three elements (Figure 1). Conversely, a comparison of the distribution coefficient of the elements (Table 1) indicated that neodymium had the highest partition coefficient while La had the lowest value. Hence, we concluded that the acid organophosphorus extractants had more affinity for the heavier REE (Nd > Pr > La), which was in line with Pearson's hard-soft acid-base theory (PEARSON, 1966) and lanthanide contraction (GUPTA; KRISHNAMURTHY, 2015).

The organic stream was contaminated with La, so we could not generate pure didymium (Nd + Pr) with an extraction circuit. Therefore, the organic stream needs a scrubbing stage to produce pure didymium, and future research should be conducted to model both circuits.

Table 1: Calculated model coefficients from the least squares fit of isotherm models.

Model	Neodymium	Praseodymium	Lanthanum
Constant D	0.75	0.58	0.19
Linear isotherm	(0.95; -0.006)	(0.73; -0.002)	(0.22; -0.01)
Power law	(1053.83; 3.16)	(6875.55; 3.20)	(36.17; 4.17)
Parabolic	(38.38; -0.59; 0.001)	(73.96; -0.46; 0)	(2.43; -0.27; 0)
Cubic	(1657.97; -65.17; 0.97; 0)	(9121.81; -156.77; 0.94; 0)	(41.39; -12.07; 0.97; 0)

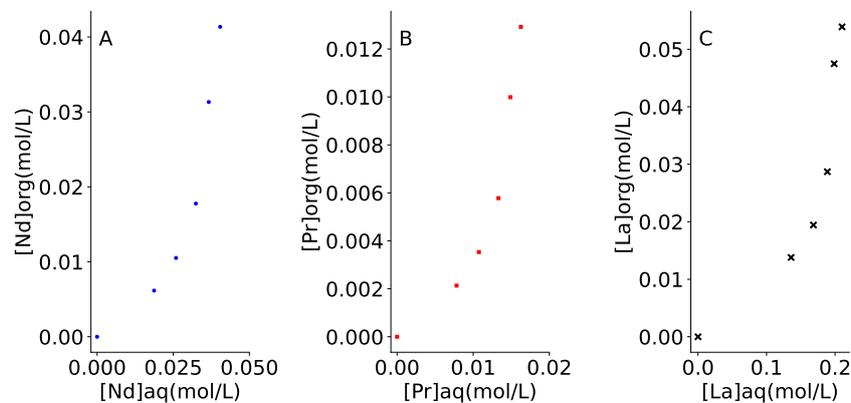


Figure 1: Equilibrium isotherm for Neodymium (A), Praseodymium (B), and Lanthanum (C).

### 3.2 Solvent extraction plant design: modeling and simulation

We designed an extraction plant with ten stages and A/O 0.3 to recover at least 99% of Pr in an organic stream. Using our simulator, we evaluated 48 separation scenarios and selected the only four that met our first criterion (99% Pr organic recovery). All four circuits satisfied our second criterion (99% La aqueous purity), so we chose a plant with ten stages and A/O 0.3 to validate the model predictions. Due to its simplicity, we used the "Constant D" model to design the SX plant. Then, we compared the observed values with all the equilibrium isotherms (Table 1) to select the one with the least  $MS_{res}$ .

### 3.3 Continuous extraction: model validation

The power law equilibrium model for Nd and La and the cubic model for Pr presented the least  $MS_{res}$  values (Table 2). However, they could not accurately predict the organic recovery of REE (Figure 2), indicating that the batch models were insufficient to explain the continuous operation. The continuous extraction might not operate at equilibrium conditions due to poor phase separation and incomplete mass transfer in each stage (AZEVEDO; ALVES, 2013). Also, competitive extraction might exist, so the prediction would require measuring the actual equilibria (KISLIK, 2012) in a continuous experiment. The similarity in isotherm shape for the three elements (Figure 1) and the liquid cation exchange reaction support this theory.

In light of this, we formulated a PSE isotherm based on the continuous counter-current experiment. First, new coefficients were estimated from the least squares fit of the equations

Table 2: The residual mean square of equilibrium models.

Model Nd	$MS_{res}$ Nd	Model Pr	$MS_{res}$ Pr	Model La	$MS_{res}$ La
Power law	0.0540	Cubic	0.0180	Power law	0.0015
Linear isotherm	0.0740	Power law	0.0400	Parabolic	0.0018
Parabolic	0.1260	Linear isotherm	0.0530	Cubic	0.0049
Cubic	0.1410	Constant D	0.0670	Constant D	0.0138
Constant D	0.1430	Parabolic	0.0810	Linear isotherm	0.0154

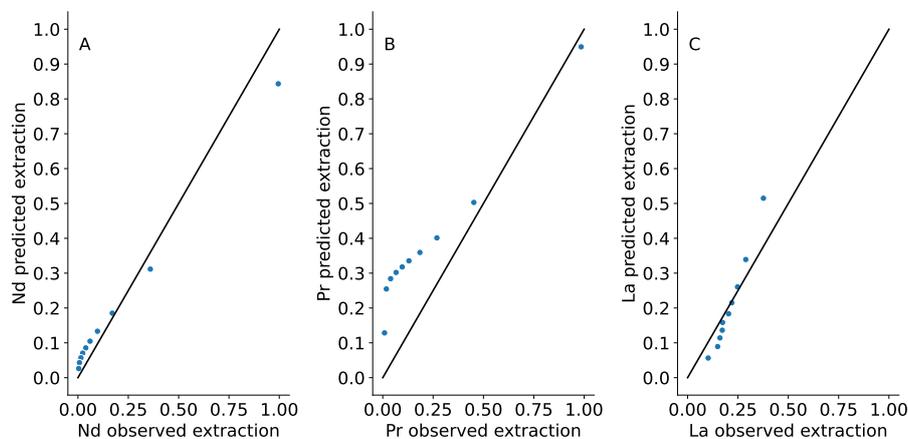


Figure 2: The predicted and observed extraction values for Nd (A), Pr (B), and La (C) using the least  $MS_{res}$  models for each element in each stage of the first SX circuit ( $N = 10$  stages,  $A/O = 0.30$ ).

shown in Table 1. Then an SX circuit with eleven stages and  $A/O$  0.50 was proposed to validate the model predictions. Finally, we compared the predicted and observed values of the three elements and calculated the  $MS_{res}$  to decide which empirical model was suitable for SX REE separation design.

The power law PSE model for all elements had the least  $MS_{res}$  (Table 3), and we could predict the REE organic recovery in a continuous extraction (Table 4). We achieved good agreement between the PSE model and the observed values.

Table 3: The residual mean square of PSE models.

Model Nd	$MS_{res}$ Nd	Model Pr	$MS_{res}$ Pr	Model La	$MS_{res}$ La
Power law	0.0540	Power law	0.0252	Power law	0.0004
Linear isotherm	0.0596	Parabolic	0.0295	Linear isotherm	0.0005
Parabolic	0.0755	Linear isotherm	0.0363	Cubic	0.0009
Cubic	0.0808	Cubic	0.0365	Constant D	0.0018
Constant D	0.1922	Constant D	0.0497	Parabolic	$2.0 \cdot 10^9$

Table 4: Predicted and observed purities and recoveries with power law PSE model.

Property	$Nd_2O_3$		$Pr_6O_{11}$		$La_2O_3$	
	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.
Aqueous composition	1.1%	1.0%	1.1%	1.0%	97.8%	98.0%
Organic composition	41.4%	45.1%	15.0%	16.3%	43.6%	38.6%
Aqueous recovery	2.5%	2.4%	6.7%	6.6%	69.0%	74.7%
Organic recovery	97.5%	97.6%	93.3%	93.4%	31.0%	25.3%

## 4 CONCLUSION

Using a pseudo-equilibrium model, we have successfully demonstrated the potential for predicting the recovery of rare earth elements (REE). Our findings revealed the pseudo-equilibrium power law model to be a promising predictor for organic recovery in continuous counter-current extraction of REE. Furthermore, the model's predictions agreed with experimental results by describing the pseudo-equilibrium state in a new SX circuit. Our results provide compelling evidence for establishing a REE separation facility in Brazil to ensure the production of essential permanent magnets, which are vital for achieving the SDG of the UN.

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