Simulation and optimization of the separation of Rare Earth Elements

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Abstract

The subject of this work was to study the feasibility of the purification of REE via ion-exchange chromatography from an industrial point of view.

The decision variables were the loading volume, elution volume and gradient. The study is based on a feed stock with mainly heavy REE, dominated by Erbium and Ytterbium. The final product consisted in separated fractions of REE with a purity requirement of 99% for the element to retrieve.

It was concluded that the process is economically feasible. The production cost optimization showed eight different operation points which confirmed that the costs increased rapidly when the demand on yield increased. Retrieve Ytterbium and Thulium minimized production costs, but retrieving Holmium and Erbium was still possible if the increase in production costs is affordable.

Keywords: Rare earth elements, chromatography, simulation, optimization, benefits, production costs

Introduction

Rare Earth Elements (REE) are a group of 17 elements, 15 that belong to the chemical group lanthanides and yttrium and scandium.

REE are used nowadays in new technologies such as electronics devices and military applications.

Even though consumers do not have direct need of REE they are necessary for the production of end use products, what makes them as demanded as the final products for which they are necessary. The world demand of these elements is increasing as well as the purity requirements.

Because they have very similar chemical structures and properties REE are difficult to separate. The most common commercial separation technique is liquid-liquid extraction but for high valued products preparative ion-exchange chromatography is also used [1].

The subject of this work was to study the feasibility of the purification of REE via ion-exchange chromatography from an industrial point of view. The main objective was to optimize the separation process to provide different operation points depending on the need that the industry may have.

The decision variables were the loading and elution volumes as well as the gradient step of the eluent. The value for these variables was optimized for each objective and the other design variables had beforehand fixed values.

The final product consisted in separated fractions of REE with a purity requirement of 99% for the element to retrieve. Each different element had a different selling price and was present in a different amount in the feed.

Theory

The model used throughout the simulations in this work was a reaction dispersive model which describes the dispersion and convection in the mobile phase as well as the adsorption into the stationary phase [1].

Column model

The concentration of each component i in the mobile phase follow the equation:

$$\frac{\partial C_i}{\partial t} = D_{ax} \cdot \frac{\partial^2 C_i}{\partial z^2} - v_{lin} \cdot \frac{\partial C_i}{\partial z} - r_{ads,i} \qquad (1)$$

where C_i is the concentration of component i in the mobile phase, D_{ax} is the dispersion coefficient and $v_{lin,i}$ is the linear velocity of the mobile phase and $r_{ads,i}$ the reaction rate of component i defined as:

$$r_{ads,i} = \frac{1-\varepsilon_C}{\varepsilon_E} \cdot \frac{\partial q_i}{\partial t} \qquad (2)$$

where ε_C is the column porosity (column void), q_i the concentration of component i adsorbed onto the stationary phase and ε_E the total porosity.

For the nitric acid, which is considered to be inert, there is no reaction rate on Eq. (1).

Adsorption model

The adsorption model is based in a competitive Langmuir isotherm [2] with mobile phase modifier, which is nitric acid and affects Henry's constant thus affects the retention of the REE:

$$\frac{\partial q_i}{\partial t} = k_{kin} \cdot (H_i \cdot C_i \cdot (1 - \sum_{j}^{REE} \frac{q_j}{q_{\max,j}}) - q_i) \qquad (5)$$

where k_{kin} is the kinetic constant with an arbitrary value, $q_{max,j}$ the maximum capacity in the stationary phase for component j and H_i is the Henry's constant of component i modified by the acid as follows:

$$H_i = \frac{H_{0,i}}{C_{acid}^{\beta_i}} \qquad (6)$$

where β_i is calibrated parameter of component i, $H_{0,i}$ the calibrated constant of component i and c_{acid} the concentration of nitric acid.

A Dirichlet boundary condition describes the concentration at the inlet:

$$C_i(t,0) = C_{inlet,i} \qquad (3)$$

where $C_{inlet,i}$ is the concentration of component i at the inlet and is a given value during the loading time and zero after it.

At the outlet of the column, i.e. at z=L, where only convective transport is considered a von Neumann boundary condition is defined:

$$\frac{\partial C_i(t,L)}{\partial z} = 0 \qquad (4)$$

This model can describe adsorption and desorption at different modifier concentrations and displacements between the different components. It can also describe overloading and produce stiff peaks as results of high loading [3].

Methods

Simulation

The simulations were performed in MATLAB using the *method of lines* where space is divided into a set of grid points. The number of grid points was modified through this work between but in most of the cases was set to 50 or 100. The discretized model was solved with the *ode15s* solver in MATLAB, which is a BDF multi-step implicit method with variable order solver for stiff ordinary differential equations with a medium accuracy.

In order to speed up the code the lightest elements, present in extremely low concentrations were merged together in a pool with its characteristics equal to the heaviest of the merged elements.

The code was written following the scheme in Figure 1.

Calibration

The calibration of the model was beyond the scope of the present work even though is a necessary step for the simulation, so the different parameters such as kinetic parameters and column parameters were obtained from the previous work of [4] and [5] where linear experiments were conducted to find parameters β and H_0 and overload experiments to find the capacity of the column.
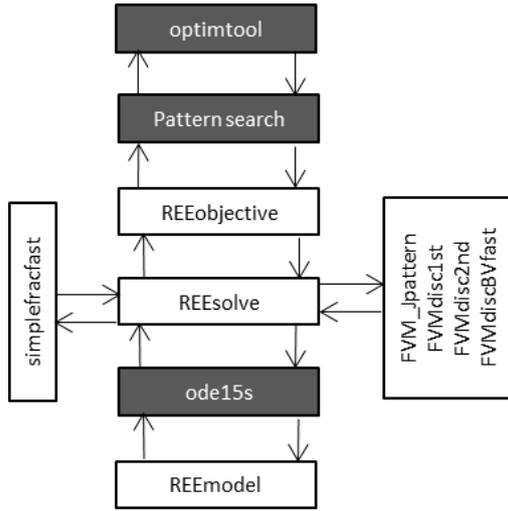
Figure 1. Structure of the code. *REEobjective* calculates the value of the objective function while *REEsolve* and *simplefracfast* calculate the amount of product with the 99% purity requirement. *REEmodel* contains system of differential equations. Auxiliary functions perform the Finite Volume Method 2-point backward discretization of the first derivative and 3-point central of the second derivative.

Optimization

The optimization method used in the present work is the *Pattern Search* algorithm due to the non-smooth characteristics of the problem. This method mainly consists on the minimization of an *objective function* through the modification of the value of a set of variables called *decision variables*. *Pattern search* is a direct search method for solving optimization problems.

Pattern Search method does not require any information about the gradient of the objective function and so they works well on non-differentiable, stochastic, and even discontinuous objective functions. Additionally *Pattern search* is also effective at finding a global minimum because of the nature of its search.

The variables are bounded for both prevent unphysical values such as negative volumes and unrealistic values.

In the present work the decision variables were loading volume, elution volume and gradient step. All the other variables were conveniently calibrated and its values known.

To study the feasibility of an industrial process several costs and revenues can be considered for the calculation of the benefits. The first objective function was defined as the annual benefits (Eq. 7).

$$B = S - FC - VC - RMC \qquad (7)$$

Where S is the annual revenue of selling the product (Eq. 8), FC are the Fixed Costs representing the investments to set up the process, such as new equipment, VC are Variable Costs meaning the costs of running the process, such as electricity, solvents and labor (Eq. 9) and RMC are the Raw Materials Costs.

$$S = n_c \cdot \sum_{i=1}^{REE} selling\ price_i \cdot prod_i \qquad (8)$$

where $prod_i$ is the amount produced of each REE and n_c the number of cycles per year.

$$VC = (SC \cdot V_e \cdot \rho_e + DC \cdot V_f \cdot C_f) \cdot n_c \qquad (9)$$

where SC is the steam cost to regenerate the eluent, V_e is the volume of eluent, ρ_e is its density, V_f is the amount of feed charged in the column and C_f is the total amount of REE in the feed.

A different approach is to evaluate the production costs for different product distribution which led to the second objective function (Eq. 10), the production costs. From this point of view the aim is to make the production as cheap as possible, deciding afterwards a proper selling price.

The advantage of this analysis is that the product distribution is much wider, allowing the successful production of more elements, which is appealing from a commercial point of view.

$$PC = \omega\left(\left(\frac{FC}{n_c} + SC \cdot V_c\right) \cdot \frac{1}{\sum_{i=1}^{REE} prod_i} + \frac{DC}{Y_G}\right) \qquad (10)$$

where FC, SC and DC are as in Eqs 7-9; V_c is the total volume used in one cycle and Y_G is the global yield. The parameter ω is introduced to force the yield to be within certain values:

$$\omega = \begin{cases} \infty & \text{if } yield < threshold \\ 1 & \text{if } yield \geq threshold \end{cases} \qquad (11)$$

In Eq. (10) fixed costs are divided per the number of cycles as it was necessary to have indirectly the time of operation taken into account on the objective function. Otherwise the optimization would lead to an analytical chromatograph, which is unfeasible for the industrial scale.

Results and discussion

Annual benefits optimization

The benefits function was optimized first for 50 grid points and then the solution refined for 100 grid points.

The optimum values for the decision variables were obtained, see Table 1. The chromatogram with the retrieved fractions can be seen in Figure 2.

Table 1 Optimized values for the decision variables

Decision variable	Value
V_{load} (CV)	0.45348
$V_{elution}$ (CV)	3.76720
step	0.18020

The results showed that the process can be implemented with positive annual benefits with the given costs and selling prices.

Due to the composition of the feed, which has a percentage of Ytterbium higher than 70%, the optimal operation points consists in overloading as much as possible the column in order to retrieve as much Ytterbium as possible without collecting any other fractions except for Thulium, see Table 2.

Table 2 Numerical results for the benefits optimization

Parameter	Value
Y_G (kg/kg)	0.6456
Y_{TM} (kg/kg)	0.5214
Y_{Yb} (kg/kg)	0.8587
PC/PC_{min}	1.0050

This is caused by several factors, Ytterbium is one of the easiest ones to collect as it is the last peak and the separation with Thulium is reasonably good, see Figure 2. The separation of Thulium on itself is also good, even though no baseline separation is achieved. Furthermore the selling price for Ytterbium is approximately on the average, which can lead to high benefits, and the selling price for Thulium is the highest one of all the REE.

It is important to notice that the optimized process does not wait for the elution of all the Ytterbium despite the last fractions of Ytterbium would consist on pure Ytterbium. This is because it is not worth to wait for the elution of low amounts, instead is more beneficial to start the following batch and perform more cycles per year.

Finally, even though the yearly benefits are maximized in this operation point it may be not wise to produce only two elements. Instead it may be more interesting for a company to have a wider product range which can modify depending on the need of the market. This idea justifies the following studies to analyze the cost of widening the product distribution.

Production costs optimization

The production costs analysis was based on the idea that the selling price was no longer beforehand known but a value that could be negotiated with the potential buyers at the time of the production.

This means that the process was optimized for different yield requirements in order to retrieve more elements than just Ytterbium and Thulium, see Table 3. Even though after the previous results it was known that the productivity would decrease following this approach, the possibility to widen the range of products was assumed to compensate the lower productivity.

The productions costs versus global yield are represented in Figure 3. Different composition of the product distribution retrieved can be seen in Figure 4.

The production costs increase almost exponentially when a higher yield was required. As expected from the results in previous sections unless REE different from
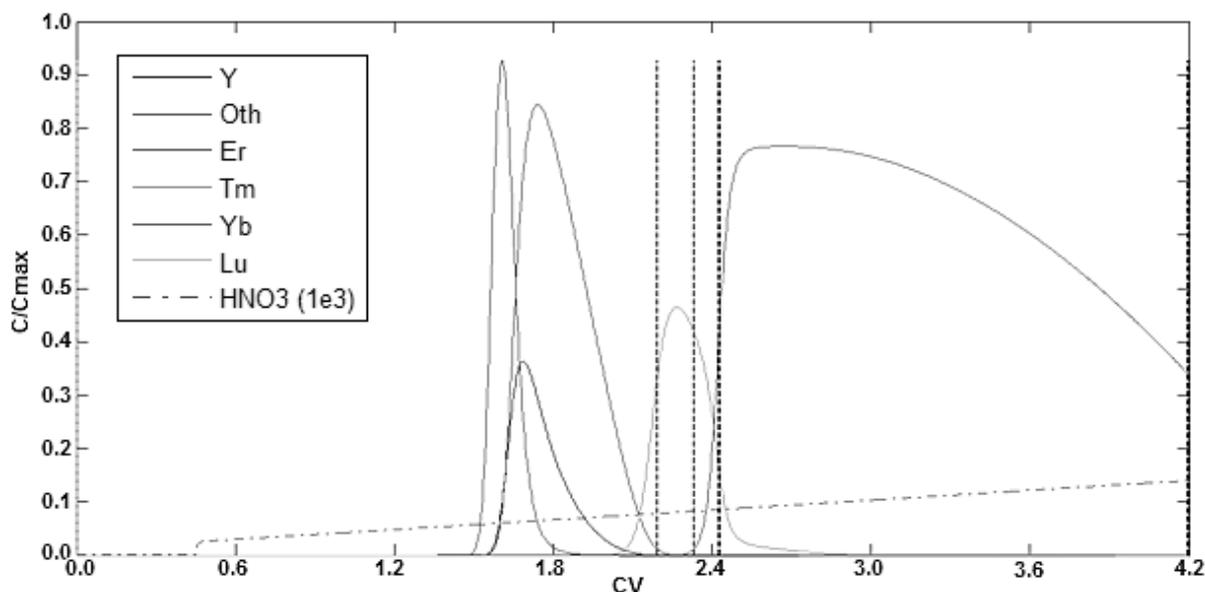
Figure 2 Retrieved fractions of the annual benefits optimum operation point. Eluent is scaled down 1000 times. Ytterbium and Thulium are successfully retrieved at a 99% purity.

Table 3 Different yield requirements for the operation points of the production costs optimization

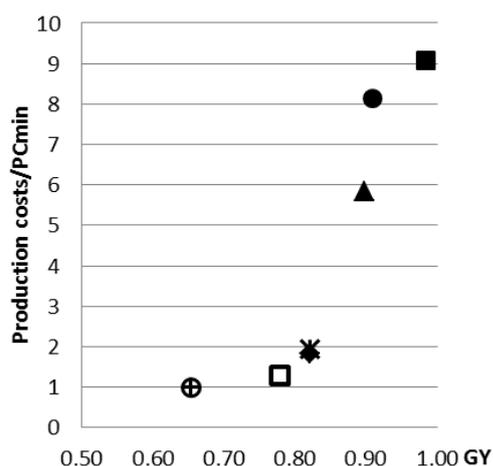| point	Ho	Er	Tm	Yb
O	-	-	-	0.85
◆	-	-	0.85	0.85
▲	0.50	-	0.85	0.85
■	0.50	0.50	0.85	0.85
□	-	-	0.50	0.85
+	-	-	-	0.50
✳	-	-	0.85	-
●	0.85	-	-	-

Figure 3 Normalized production costs vs global yield for the different operation points. Legend in Table 3.
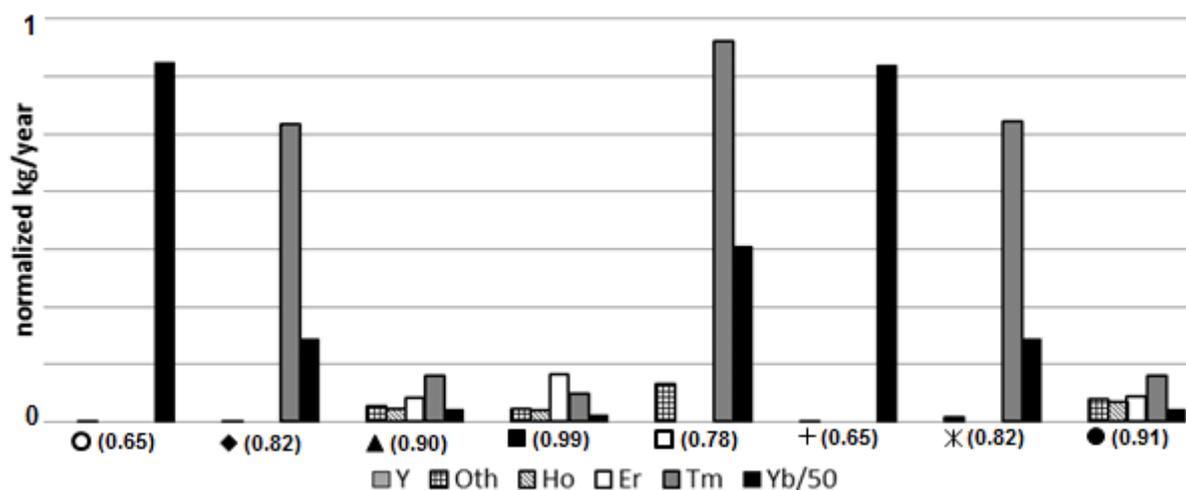

Figure 4 Normalized amount of product for each operation point. Legend in Table 3, global yield shown in brackets. The amount of Ytterbium is scaled down 50 times.

Ytterbium were explicitly required they were never retrieved in order to maintain productions costs as low as necessary.

When Thulium was required to be produced with a yield higher than 0.85, production costs increased by 81% compared to retrieving only Ytterbium.

When a different elements from Ytterbium or Thulium was required the productions costs increased by as much as 482% - 807%, depending on the requirement.

In spite of these increases on production costs most of the different operation points can be operated with benefits if proper prices are selected for the product.

Conclusions

Throughout the present work it was confirmed the feasibility of the purification of Rare Earth Elements via ion exchange chromatography from an industrial point of view.

Through different optimizations benefits and production costs have been optimized, presenting different operation points to proceed with the process.

The first conclusion was that the process is economically feasible. But the operation point for the highest annual benefits only retrieves Ytterbium and Thulium, which may not be a wide range of products enough, considering that the feed is a batch with 15 different REE.

Secondly, the production costs optimization showed eight different operation points which confirmed that the costs increased rapidly when the demand on yield increased. The option to retrieve only Ytterbium or Ytterbium and Thulium were still the most economical one, but retrieving Holmium and Erbium was still possible if the increase in production costs is affordable.

During all the optimizations it was confirmed that is extremely difficult to separate the lighter elements from Lanthanum to Dysprosium, as its separation would lead to an analytical chromatography instead of a preparative chromatography.

In conclusion this study showed that the ion exchange chromatography is a feasible separation operation on the industrial scale for the purification of REE which can be operated to retrieve a variable range of products depending on the expected revenue.

References

[1] Sato T. Liquid-liquid extraction of rare-earth elements from aqueous acid solutions by acid organophosphorus compounds. Hydrometallurgy. 1989; 22: p. 121-140.

[2] Karlsson D, Jakobsson N, Peter Axelsson J, Zacchi G, Nilsson B. Using computer simulation to assist in the robustness analysis of an ion-exchange chromatography step. 2005; 1063: p. 99-109.

[3] Karlsson D, Jakobsson N, Axelsson A, Nilsson B. Model-based optimization of a preparative ion-exchange step for antibody purification. J. Chromatogr. A. 2004; 1055: p. 29-39.

[4] Degerman M, Jakobsson N, Nilsson B. Modeling and optimization of preparative reversed-phase liquid chromatography for insulin purification. J. Chromatogr. A. 2007; 1162: p. 41-49.

[5] Max-Hansen M, Ojala F, Kifle D, Borg N, Nilsson B. Optimization of preparative chromatographic separation of multiple rare earth elements. J. Chromatogr. A. 2011; 1218: p. 9155-9161.