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# BEHAVIOR OF DIALYSIS FOR THE RARE EARTH ELEMENTS IN CATIONIC MEMBRANES

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## ABSTRACT

In this work it is presented a dialysis process as an alternative method for the fractionation of rare earth elements. The used cell was set up with a transparent Pyrex glass cylinder with the membrane set in one extreme and using another glass chamber to collect the dialyzed solute. Cationic Membrane: Nafion® 324 manufactured by Dupont and Ionac® MC-3470XL from Sybron Chemicals were used. A series of exploratory experiments allowed concluding that there was some different behavior as function of the nature of the rare earth solutions, i.e, whether the solutions contained nitrate, sulfate or chloride.

## 1. INTRODUCTION

The separation membrane technology already reached a level for industrial application and has been important in several economical activities. Today the membrane technology reached a favorable competition with the classic techniques of separation and allows the opening of new fields, making possible processes that would not be feasible for the traditional methods.

Today, the advanced technology of membranes production and the development of separation processes as reverse osmosis, ultrafiltration, microfiltration, dialysis, electrodialysis, permeation of gases and pervaporation, make possible economical advantages that involve a minimum of energy, operational costs and maintenance. In many cases it is included a better quality of the final product with a favorable control of the environment and for the purification of different wastes [1-3].

In general, the study of the dialysis demand the knowledge of some necessary aspects for the efficient fractionation of rare earth elements (REE), such as: type of the membrane, diffusion rate of the solutes through the membrane and their properties [4].

For the rare earth ion diffusion it is convenient to know initially the separation factor between the REE solution and the solvent, using an appropriate cell. The choice of the membrane is very important for the effective separation of the chosen ions. In this work it is considered the dialysis process for the fractionation of the rare earth elements in groups and their separation and purification in the individualized form on Nafion® and Ionac® cationic membranes.

A high number of fractions was analyzed by gravimetric, atomic emission spectrometry and X-ray fluorescence methods for analytical control.

## 2. EXPERIMENTAL

### 2.1. Reagents

The REE chloride solutions were prepared from a low cerium carbonate (LCC), industrially manufactured in Brazil from the monazite sand, that was dissolved in hydrochloric acid. Other reagents were of analytical grade.

### 2.2. Membranes

Cationic Membrane: Nafion® 324, manufactured by Dupont, and Ionac® MC-3470XL, manufactured by Sybron Chemicals Inc were used.

### 2.3. The cell

The cell was made using a transparent pyrex glass cylinder, with the membrane fastened in one of its ends through sticker and with reinforcement with a plastic ring.

### 2.4 Fractionation of Rare Earths

The REE solutions (100 to 200 mL) were added into the dialyzed compartment of the cell. In the receiving compartment a known volume of deionized water (acceptor) was admitted. The liquids in both compartments can be stirred using mechanical and magnetic stirrers. During the course of the dialysis the concentration of several aliquots were analyzed in function of time. Qualitative identification of REE presence was made using oxalic acid. For identification of cerium the thiourea test was applied [5]. Periodically the solution of the receiving compartment was removed and replenished with deionized water. All experiments were run at room temperature (circa 25.C).

The total REE in each collected fraction was analyzed gravimetrically by precipitation of the oxalates which are dried and burned into an electric muffle at 900$^{o}$C for two hours, cooled and weighed.

## 3. RESULTS AND DISCUSSION

### 3.1 Dialyses using the Ionac® MC-3470XL membrane

Dialysis of the REE were worked out in hydrochloric, sulfuric and nitric acids. Experiments in hydrochloric acid were performed at pH 1 and in 4 mol $L^{-1}$ of the acid solution, whereas with sulfuric acid the expriments involved 1 mol $L^{-1}$ of the acid solution. These experiments were started with a 17.2 g $L^{-1}$ of rare earth oxide chloride solution and under stirring in the dialyzed compartment. The rare earth oxides fractions obtained from the dialyzed samples were evaluated by visual inspection of their color.

In many cases the oxide color gave reasonable indication of the fractionation. The initial fractions were more intensively colored while the last ones go to the white, according to the fractionation.

Figure 1 summarizes the results of an experiment with REE in pH=1 and 4mol $L^{-1}$ HCl, and 1mol $L^{-1}$ $H_2SO_4$, respectively, using an Ionac membrane at 25°C. Dialysis time reached over 200 hours. The amounts of REE oxides for each fraction are shown.

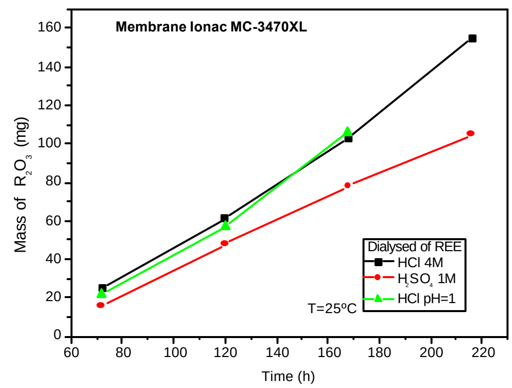


**Figure 1 – Behavior of some fractions of rare earths on Ionac membrane dialysis in hydrochloric and sulfuric media**

After 240 hours it was observed that the dialysis was finished, although some rare earths not dialyzed was still present. The pH of the final dialyzed solution was raised to 4 and the volume increased from 100 to 120mL. The results are shown in Figure 2. The analyses of the fractions in this experiment confirmed that the total amount of Er and more than 50% of La and Y were dialyzed.

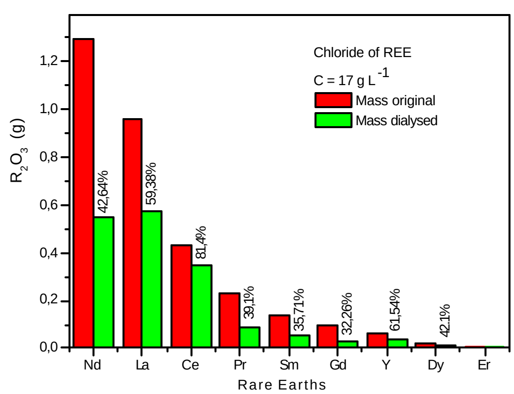


**Figure 2 – Fractionation of rare earths in pH 1, with stirring, using Ionac MC-3470XL membrane**

Some experiments were run without stirring in both compartments. It was observed a similar behavior when compared with the experiment under stirring.

## 3.2. Experiments with Nafion® - 324 membrane.

Experiments using Nafion® membrane followed the same protocol, exploring the pH and concentration effects, with and without stirring. The results are similar when compared with the Ionac membrane.

Figure 3 exhibits the results of REE dialysis at pH 1 with HCl solution and in 1mol $L^{-1}$ of $H_2SO_4$ solution on a Nafion® - 324 membrane.

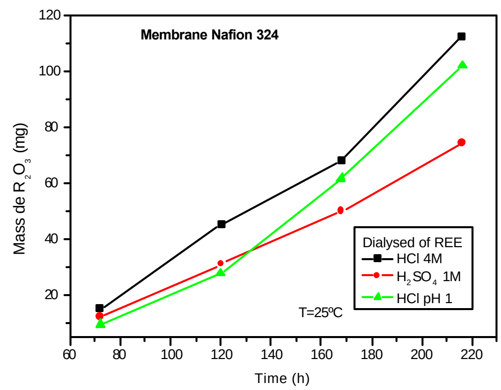


**Figure 3 - Behavior of dialysis of rare earths with Nafion membrane in hydrochloric and sulfuric media.**

The behavior of the dialysis of REE shows the corresponding oxides with different colors, coming from dark beige to white. Cerium was identified in some fractions using the blue fluorescence by the thiourea reaction [5].

Figure 4 shows the results of rare earths fractionation, without stirring the solution, using the system with Nafion – 324 membranes.

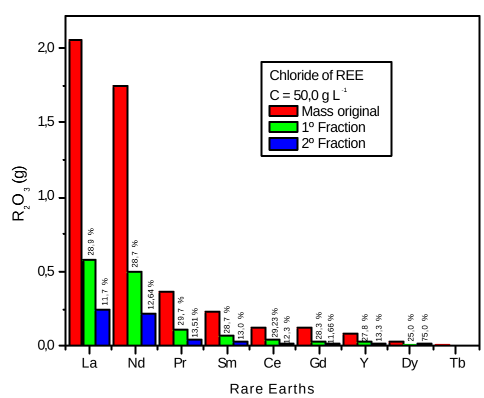


**Figure 4 – Fractionation of rare earths by dialysis at pH4, without stirring, using Nafion – 324 membranes.**

Nevertheless it was observed that the dialysis using the Nafion®-324 was slower than that one using the Ionac® MC-3470 membrane, but the profile of the individual rare earths in the dialysis with Nafion®-324 membrane at pH 1 is more efficient.

In this work it was also used nitrate medium (nitrate and nitric acid) in dialysis experiments with the above mentioned membranes, but in this system no rare earth ions dialysis occurred.

The REE cations in nitric medium are not transported across the membrane. A previous paper [6] had demonstrated this unexpected behavior.

So, for the fractionation of rare earth cations using dialysis technique hydrochloric and sulfuric acids are preferred.

### 3.3. Effect of pH

The several experiments performed in this work allowed concluding the importance of the REE pH [7].

The pH has influence over the dialysis behavior, which runs better at lower value. When pH is around 4, hydrolysis occurs starting the precipitation of rare earths and the dialysis yield is lower. Cerium, for example, has a yield of 86 % for the dialysis at pH 1, although at pH 4 it is only 5.8 %. The other REE maintain the same behavior, that is, the dialysis yield is lower for higher pH.

The results indicated that the total dialysis of some elements as cerium, neodymium and dysprosium, for instance, is about complete if the acid concentration is adequate.

## 4. CONCLUSIONS

The purpose of this paper is to describe the use of Donnan dialysis using polymeric ionic membranes. In all experiments distilled water was used as receiver and REE cations were permeated across the membranes from hydrochloric and sulfuric acids medium. It was confirmed that there was no dialysis in nitric acid medium. The results had revealed promising with the rare earths ions fractionation.

Although dialysis is a slow process, the technique is very simple, ease and inexpensive. It opens the possibility of an interesting fractionation process for the rare earth elements. It deserves more study and experimentation to improve the results as to work at higher temperature, increasing the membrane surface and controlling the pH at the dialysis compartment, since the acid is dialyzed together with the rare earths

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