

## Organophosphorous compounds and the synergistic effect of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone in europium and gadolinium extraction behavior

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**ABSTRACT:** A few articles report the separation of Eu/Gd pair using solvent extraction, emphasizing the importance of this study. Therefore, the present study has the aim of evaluating the separation of Gd and Eu by solvent extraction, using organophosphorous extractants, with a pyrazolone as the chelating agent. Gd and Eu chloride solutions were prepared from a Gd and Eu carbonate provided by Indústrias Nucleares do Brasil (INB). Different variables were evaluated, such as extractant nature, molar ratio of pyrazolone and pH variation. The quantitative chemical analyses of the rare earth elements were conducted by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP). The results show the effect of the mixtures and the working pH values on extraction percentages and synergistic coefficient values. The study of the synergistic effect indicates possible alterations that may occur in the extraction mechanism, favoring the extraction of the lighter element, Europium.

**Keywords:** Europium, gadolinium, pyrazolone, solvent extraction.

Date of Submission: 22-08-2017

Date of acceptance: 05-09-2017

### I. INTRODUCTION

Rare earth elements (REE) constitute a group of elements with atomic number between 57 and 71 belonging to the lanthanoid group (previously and still called lanthanides), including Yttrium (Y) and Scandium (Sc). The name "earth" is due to their earthy appearance, although the term "rare" is a misnomer, since they are relatively abundant in the earth's crust [1]. However, they are typically dispersed and only rarely occur in concentrated mineral deposits with exploratory economic potential.

These elements can be classified according to their atomic number and the chemical properties of each group, thus separating them into heavy (Gd-Lu) elements, also known as Yttrium group, and light (La-Eu), also known as Cerium group. Some authors also classify some elements as medium (Sm-Gd) [1,2,3].

One of the main REE characteristics, responsible for most of their physical and chemical properties, is the presence of electrons in the f orbital of the fourth energy level. The remarkable uniformity of REE chemical properties is attributed to the internal filling of the 4f layer. The property changes that can occur within the family are due to the filling order of the electronic layers from one element to another [1,4].

Many minerals are rich in these elements and, currently, about 200 REE minerals are known, distributed in several classes, including as halides, carbonates, oxides, phosphates and silicates, among others [5]. Among minerals of commercial interest, we can cite gadolinite, alanite, euxenite, apatite, monazite, bastnaesite and xenotime [6]. The largest bastnaesite reserves are located in China and in the United States. Considerable bastnaesite in carbonatites reserves are located in the Mountain Pass, California. Several other bastnaesite deposits are found in the Sichuan Province, China, as well as in the massive deposit at Bayan Obo, inland Mongolia, China [3].

REE occur in monazite and sands containing heavy minerals in Brazil, India, South Africa, Thailand, Sri Lanka, Malaysia and the United States and China [7,8]. According to the Brazilian Department of Mineral Production - DNPM, the main REE occurrences in Brazil are located in Catalão (GO), Araxá (MG), Itapirapuã Paulista (SP), São Francisco de Itabapoana (RJ), Vale do Sapucaí (MG), Poços de Caldas (MG) and Pitinga

(AM), the latter being a xenotime, not monazite, deposit, thus being rich in heavy REE, not light, among others [7].

Since 2010, when an increase in international REE prices and decreases of export quotas imposed by China occurred, a worldwide discussion began on new REE-related projects. The decline in these export quotas by China, which were implemented at the end of 2010, led to higher international prices throughout 2011 and increased interest in mineral exploration and REE production in other countries, such as USA, Canada, Australia, Vietnam, South Africa, including the reactivation of the Mountain Pass mine in 2012 [9]. The high REE prices during 2011 decreased in the following year (2012) and have steadily decreased since then, but some oxides, such as dysprosium oxide, for example, remains costlier than previous prices practiced by the protectionist chinese policy [10,11].

According to the latest Mineral Summary published in 2015, Brazil ranks second in relation to the reserves of these elements (17%), only behind China, that owns about 44%. Australia comes in third, with 2.5% of world reserves. China is also the leader in world production, with 85.2% of REE oxides produced in 2014 (86.6% in 2013) [7]. Brazil has decreased its production, with no records for 2014 and 2015 [7,11]. In addition to leading world production, China also consumes 64% of the world's REE production, followed by Japan (15%), the USA (10%) and the European Union (7%). Although much research on the subject is available, there are no efficient substitutes for the various uses of REE [7].

Solvent extraction is the most used hydrometallurgical technique to produce REE, and synergism between extractants is traditionally studied. Numerous research is available involving the study of the synergistic effect on the extraction of metal ions, including REE, drawing attention to the use of chelating extracts [12]. Chelating extracts are compounds possessing groups capable of forming complexes with metal ions. This occurs through a mechanism similar to that of cationic extractants, where an  $H^+$  exchange with the metal of interest occurs. Variations of oximes and hydroxyquinolines are used as chelating agents, as well as some pyrazolones [13]. These extractants have been used in the extraction of europium in nitric media and cerium and lanthanum in hydrochloric media. Numerous studies have applied this type of extractant to the separation and purification of copper, mainly using oximes [14].

Due to the aforementioned economic factors, in addition to the numerous applications of REE, especially europium and gadolinium, this study proposes the evaluation of europium and gadolinium through solvent extraction using organophosphorus extractants and a type of pyrazolone.

## II. LITERATURE REVIEW

Solvent extraction is a unitary operation of hydrometallurgy, consisting of efficiently and selectively extracting a metal from an aqueous solution using an insoluble organic extractant, thus forming two phases. In general, this extractant displays high viscosity, hindering its direct use in the extraction process. Thus, the extractant is usually previously diluted in an organic solvent, which should not interfere with the extraction process [15].

The metal of interest reacts with the extractant to form a compound more soluble in the organic phase, which is then extracted [15,18]. The first solvent extraction operation was carried out in 1872, but the first REE solvent extraction occurred only in 1930. Since then, research related to solvent extraction has advanced significantly, through the study of new extractants and through changes in reaction parameters that may favor the extraction of a specific metal [14,17].

Solvent extraction for REE separation displays many advantages, one of which is the possibility of using high concentrations of REE in a robust extraction system, such as the integration of mixer-settlers [17].

Numerous published studies are available applying solvent extraction for both metal separation and purification. However, regarding REE, many studies only address REE separation into groups (light, medium and heavy), such as the study conducted by Preston et al. [18] that evaluated separation of medium and light REE using di-(2-ethylhexyl) phosphoric acid (D2EHPA) in a nitric medium.

Morais et al. [19] investigated the separation of the Eu/Gd pair using different acidic and basic extracts, such as D2EHPA, P507 and Alamine 336, among others. The acid extracts were investigated in a hydrochloric medium, while the basic extracts were investigated in nitric and sulfuric media. Despite the great difficulties described by the authors in separating Eu/Gd, the study was considered satisfactory, since separation factors higher than 2.0 were observed using the basic extractants.

The synergistic effect has been studied since the middle of the last century. Numerous papers have been published in the literature in this regard applying solvent extraction and different metals, including REE. This effect consists in extraction behavior with an organic solution composed of two or more extractants, which may be of the same nature, such as two organophosphorous acids, or the combination of two different types, such as an organophosphorous acid and a chelating agent, like a pyrazolone. Generally, these studies are performed comparing the results to those obtained in the presence of only one of the extractants. Not only can synergistic extraction improve extraction efficiency, but it may also improve selectivity [12,20].

In the beginning, studies on the synergistic effect on solvent extractions were mostly conducted in the nuclear field. From the 1970s, other metals were studied [14]. Lakshmanan et al. [21] for example, performed a synergistic study regarding cobalt extraction using Kelex 100 and Versic Acid 911, while Kandil et al. [22] studied europium extraction applying a mixture of P507 and TBP. Several studies using different extractant mixtures have been conducted, but the chemistry involving synergistic effect is complex. What is known is that the synergistic effect, in many cases, displays a different way of extracting the metal by increasing extraction levels and element separation [14].

The extractant 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP), applied herein, is a chelating-type extractant, widely used in the study of the synergistic effect alongside extractants of different natures, such as those displaying cationic, anionic and solvation processes, for the extraction of transition metal elements. Atanassova et al. [23] studied the synergistic effect on lanthanide extraction using HPMBP and two different crown ethers in a dichloroethane medium. The effects of pH and extractant concentrations were evaluated, and not only was an increase in the percentage of lanthanide extraction observed, but also an improvement in selectivity.

Dukov et al. [24] carried out a study on the synergistic behavior of an extractive system containing HPMPB and different primary ammonium salts in the extraction of Pr, Gd and Yb. The evaluated extractant system improved the Gd/Pr separation factor from 11 to 18.2, but decreased the Yb/Gd pair separation factor from 8.1 to 1.4, indicating HPMBP preference for lighter elements.

### III. MATERIAL AND METHODS

Three variables were investigated herein regarding Eu and Gd solvent extraction, namely, pH, the concentrations of the aqueous and organic solutions and the molar fraction of one type of pyrazolone. All assays were performed in triplicate.

#### 3.1 Liquor preparation

A stock solution of Eu and Gd chloride at  $0.5 \text{ mol L}^{-1}$  ( $[\text{Eu}] = 2.0 \times 10^{-2} \text{ mol L}^{-1}$  and  $[\text{Gd}] = 0.49 \text{ mol L}^{-1}$ ) was prepared for subsequent dilutions, according to each assay. A Gd and Eu carbonate sample, a by-product of the hydrometallurgical processing of a monazite concentrate, provided by INB (Indústrias Nucleares do Brasil), was used. The chemical analysis of the carbonate as starting material was performed by X-Ray Fluorescence (Shimadzu XRF-800HS) and is displayed in Table 1.

Table 1- Chemical composition of the Gd and Eu carbonate sample.

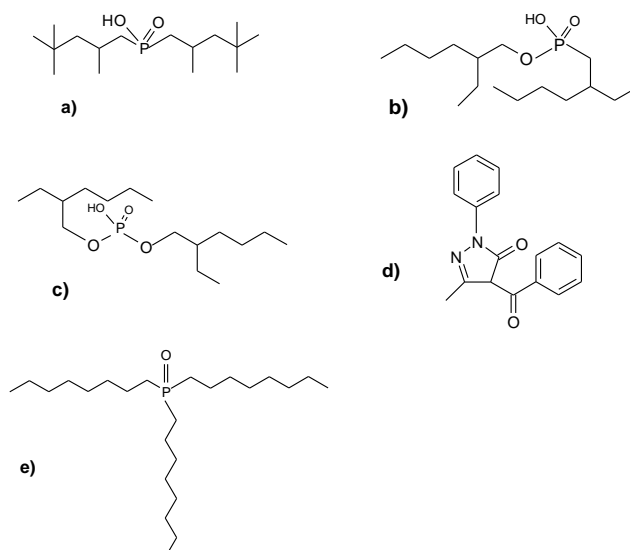
| Fe       | K       | Na     | La     | Ce    | Pr    | Nd     | Sm    | Gd    | Eu   |
|----------|---------|--------|--------|-------|-------|--------|-------|-------|------|
| <0.10ppm | 28.8ppm | 747ppm | <10ppm | <8ppm | <8ppm | <16ppm | 0.17% | 49.3% | 1.9% |
| Tb       | Dy      | Ho     | Er     | Yb    | Y     | Th     | U     | Sc    |      |
| 0,21%    | <2ppm   | 0.16%  | 575ppm | 24ppm | 0.12% | <24ppm | 28ppm | <2ppm |      |

The chloride solution was prepared by heating and dissolving the Gd and Eu carbonate by the addition of a 10% stoichiometric excess HCl. The formed chloride, according to Equation (1), was then transferred to a volumetric flask and made up with distilled water.



#### 3.2 Preparation of the organic solution

All extractant solutions were prepared by diluting them as received, in Solvesso, an aromatic hydrocarbon provided by QUIMESP, according to the concentration required for each assay. The following were extractants used: D2EHPA (di-(2-ethylhexyl) phosphoric acid) were supplied by RHODIA, Cyanex 272 (di-2,4,4-trimethylpentyl phosphinic acid), Cyanex 923 (trioctylphosphine oxide), both were supplied by Cytec, P507 (2-ethyl hexylphosphic mono 2-ethyl hexyl ester) were supplied by Louyang Inc and the chelating agent HPMBP (1-phenyl-3-methyl-4-benzoyl-5-pyrazolone) were supplied by Interprise Instrumentos Analíticos Ltda. The extractant structures are displayed in Figure 1.



**Fig. 1**— Extractant structures: (a) CYANEX 272; (b) P507; (c) D2EHPA; (d) HPMBP; (e) CYANEX 923

D2EHPA, Cyanex 272 and P507 are cation extractants. In this case, the extraction reaction occurs by exchanging the cation from the aqueous solution with  $H^+$ . Cyanex 923 is a solvating extractant, while HPMBP is a chelating-type extractant.

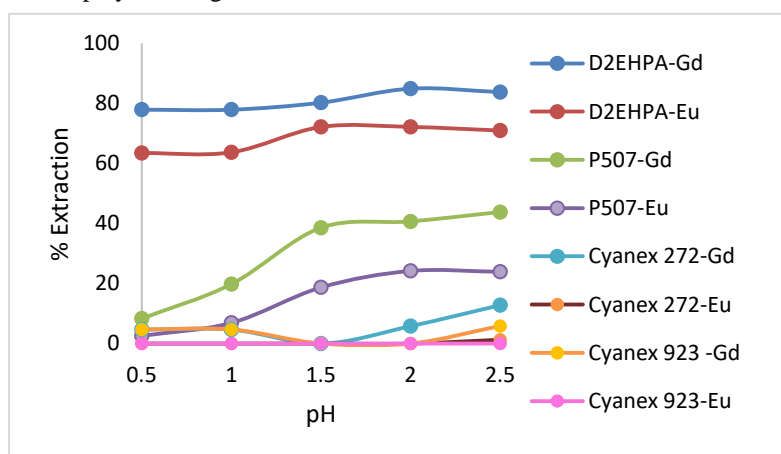
### 3.3 Extraction assays

The extraction assays were performed in 150 mL separation funnels using 25 mL of each solution. The systems were shaken on a bench shaker (IKA, model H5501), for 15 minutes at room temperature. Subsequently, the solutions were allowed to stand for 40 minutes and the phases were then separated. The raffinate (aqueous phase) was filtered through blue band quantitative paper to remove organic waste. After filtration, the raffinate was analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-OES) for the quantitative determination of Gd and Eu. Gd and Eu concentrations in the organic phases were determined by mass balance in relation to the aqueous feed.

## IV. RESULTS AND DISCUSSION

### 4.1 Exploratory assays

Initially, assays were performed using D2EHPA, Cyanex 272, Cyanex 923 and P507 and varying the pH and organic concentrations. These exploratory tests aimed to evaluate the extractive systems for later study of the synergistic or antagonistic effects with HPMBP. To evaluate pH effects on extraction percentage and separation factors, five tests were performed for each extractant, with the pH of the initial liquor ranging from 0.5 to 2.5. The concentration of the aqueous feed solution was of  $6.4 \times 10^{-2} \text{ mol L}^{-1}$  (Gd + Eu), prepared by diluting the stock solution. The pH of the liquor was adjusted to each value by adding a  $6 \text{ mol L}^{-1}$  HCl aqueous solution. The results are displayed in Figure 2.



**Fig. 2**- Percentages of Eu and Gd extractions at different pH values (aqueous solution (A)  $6.4 \times 10^{-2} \text{ mol L}^{-1}$ , organic solution (O) =  $0.3 \text{ mol L}^{-1}$ , 1: 1 ratio A/O)

An increase in extraction percentages was observed with increases in the initial pH for most of the extractive systems. For the D2EHPA extractant system, extractions already began at high percentages, of about 63% for Eu and 78% for Gd, respectively, reaching 71 % and 83% at pH 2.5. A clear preference of this extractant system for Gd, with a higher atomic number, was observed.

For P507, the extraction preference for Gd was also evidenced in every tested pH range. However, the effect of the initial pH on the extraction percentages is more evident for this extractant system, beginning at 5 and 9% for Eu and Gd, reaching 24 and 44%, respectively. This can be explained by the chemical nature of these compounds (Figure 1). Since they are stronger acids than the other organophosphates, the increase in initial pH favors the equilibrium represented in Equation (2), in the direction of the formation of the organometallic complex, thus increasing extraction percentages. In equilibrium,  $M^{n+}_{(aq)}$  represents the molar concentration of free Eu and Gd in the aqueous phase,  $RH_{(org)}$  represents the molar concentration of the organic phase extracting system,  $MR_{n(org)}$  represents the formed organometallic complex and  $nH^+_{(aq)}$  represents n protons released during the extraction process.

The same behavior was not so evident for the other extraction systems, that maintained extraction percentages below 15% over the entire tested pH range. Cyanex 272 displays the lowest acid character among the evaluated cationic extractants, while Cyanex 923 is considered a solvation extractant, which confers a lower extractive power compared to the cationic extracts. Thus, the preference order as a function of extraction percentage for Eu and Gd was D2EHPA > P507 > Cyanex272 ≥ Cyanex 923.

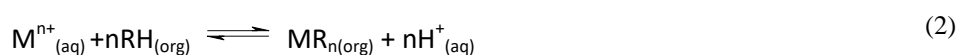
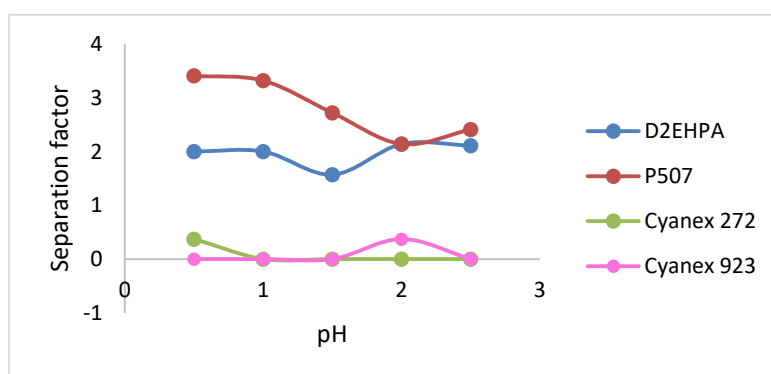


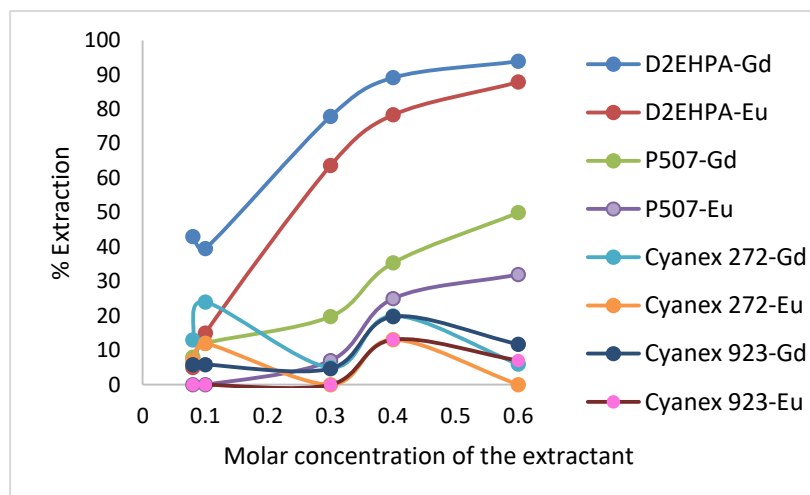
Figure 3 displays the separation factors for all the evaluated extraction systems.



**Figure 3-** Influence of pH on the separation factors all the evaluated extraction systems

The Gd/Eu separation factors were studied at different pH values and were consistent with the literature [17]. P507 presents a higher selective behavior compared to D2EHPA at pH values below 2, expected when taking into account the extraction force of the two compounds. From pH 2, the two extracts present similar behaviors. The separation factors obtained using Cyanex 272 and Cyanex 923 were significantly lower with the increase in pH when compared to those obtained with D2EHPA and P507. This behavior is also expected, due to the lower extraction force of these extracts, even at higher pH values.

The extract concentration effects on the organic solution ( $0.08 \text{ mol L}^{-1}$ ,  $0.1 \text{ mol L}^{-1}$ ,  $0.3 \text{ mol L}^{-1}$ ,  $0.4 \text{ mol L}^{-1}$  and  $0.6 \text{ mol L}^{-1}$ ) were determined by varying the concentration of each extractant, to identify its influence on the two studied elements. Five assays were performed for each of the four extractants. The results are displayed in Figure 4.



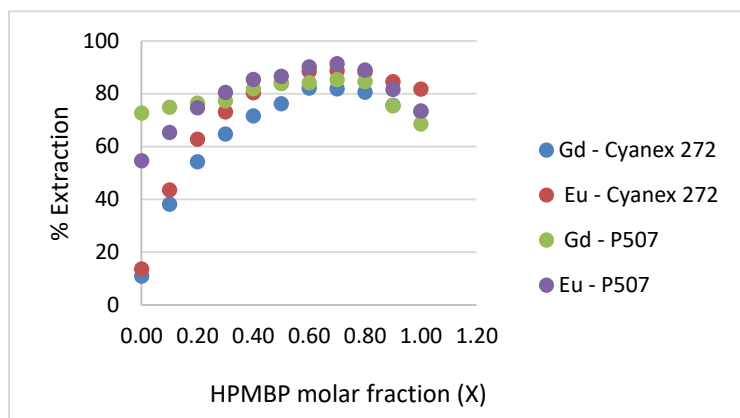
**Fig. 4-** Influence of extractant concentrations on Eu and Gd extraction (aqueous solution (A) =  $6.4 \times 10^{-2}$  mol L<sup>-1</sup>, pH 1.0, 1: 1 ratio A/O)

An increase in extraction percentages with increases of the extractant concentrations was observed. Again, this increase was much more pronounced with the most acidic cationic extractants (D2EHPA and P507). However, when using D2EHPA, the increases in Eu and Gd extraction percentages decreased selectivity, since the extraction percentages of both were very close. This indicates a decrease of the separation factor and, consequently, of selectivity. The same behavior was not observed using P507, where a greater difference in the extraction percentages at 0.6 mol L<sup>-1</sup> organic phase (32% of Eu of 50% of Gd) was observed. The extraction percentages using Cyanex 272 and Cyanex 923 were lower than 20% at all studied concentrations.

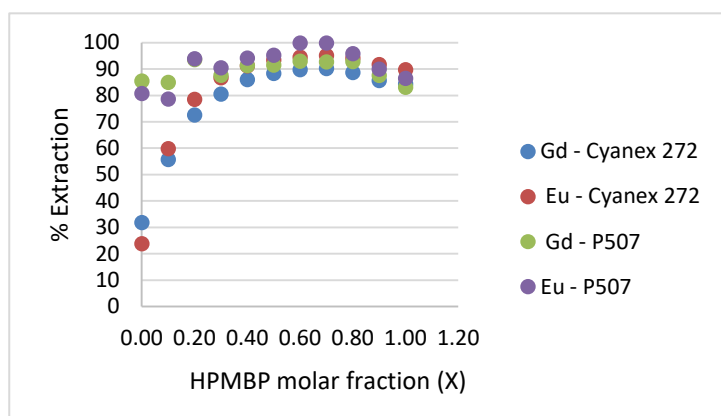
#### 4.2 Analysis of the synergistic effect

The preliminary tests indicated that increases in extractant concentrations, alongside increases in pH, culminate in an increase in extraction percentages, but with an undesired decrease in selectivity. Thus, a study of the mixture of P507 and Cyanex 272, both cationic organophosphorous extractants, alongside a pyrazolone, HPMBP was conducted. These extractants were chosen because they presented intermediate behaviors among the four extractants with regard to acid extraction force. D2EHPA was not studied at this stage because it is a very strong extractant, displaying high extraction percentages, which would probably make it difficult to perceive HPMBP effects regarding extraction percentages and separation factors. Cyanex 923 was also discarded from this study, since it presented insignificant values regarding REE extraction percentages.

HPMBP effects were evaluated by varying its molar fraction (X), from 0 to 1, at two different pH values (2.5 and 3.0). In addition to pH 2.5, we opted to perform a study at pH 3.0, higher than the pH values discussed in the preliminary tests, since pH is a favorable variable to increase extraction percentages. The results of the Eu and Gd extraction percentages obtained at pH 2.5 and 3.0 for both extraction systems, HPMBP + P507 and HPMBP + Cyanex272, are displayed in Figures 5 and 6.



**Fig. 5-** Extraction percentages applying different HPMBP molar fractions (aqueous solution(A)=  $5.0 \times 10^{-3}$  mol L<sup>-1</sup>, organic solution (O)= 0.1 mol L<sup>-1</sup>, pH 2.5, A/O 1: 1).



**Figure 6-** Extraction percentages applying different HPMBP molar fractions (aqueous solution (A) =  $5.0 \times 10^{-3} \text{ mol L}^{-1}$ , organic solution (O) =  $0.1 \text{ mol L}^{-1}$ , pH 3.0; A/O 1: 1).

As observed in the preliminary results, extractants P507 and Cyanex 272, when alone ( $X = 0$ ), present well differentiated extraction behaviors. In this condition, P507 again exhibits higher acid strength, leading to higher Eu and Gd extraction percentages when compared to Cyanex 272. Some selectivity when using P507 regarding Gd is observed (Figure 5), with extraction values around 72%, while the extraction percentage for Eu was around 55%. At pH 3.0, loss of the selectivity when using P507 is observed (Figure 6), attributed to the increase in pH, with an extraction percentage for both elements close to 85%. The separation factors  $F_{\text{Gd/Eu}}$  when using P507 at both pH values were of, respectively, 2.22 at pH 2.5 and 1.42 at pH 3.0. Cyanex 272, on the other hand, presented very close extraction values for both elements, at both pH values, showing a slight selectivity for Gd. The separation factors of this extractant system were 1.79 at pH 2.5 and 1.42 at pH 3.0.

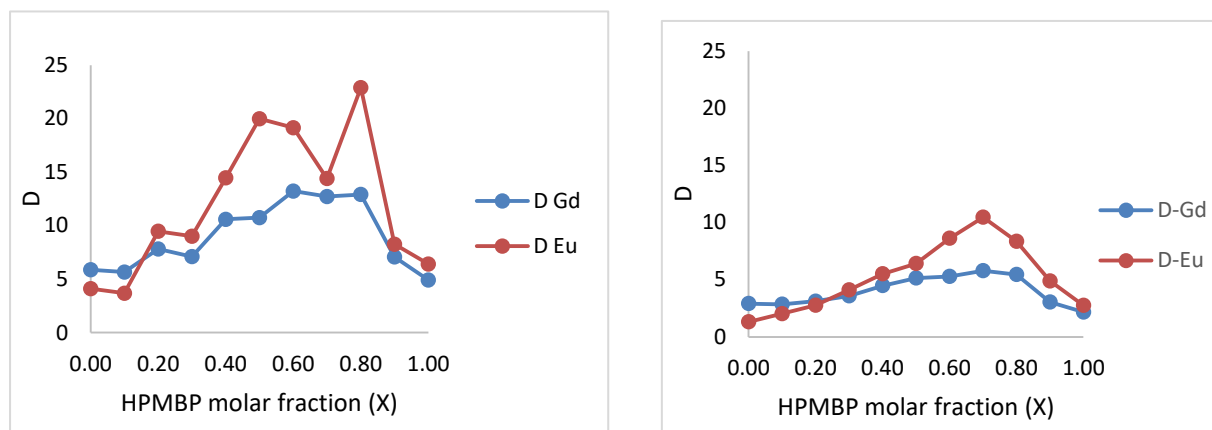
By increasing the molar fraction of HPMBP in the two extractive systems, a reversal of the curves at the two pH values was observed. A clear extraction preference for Eu compared to Gd with increases of the HPMBP molar fraction was verified, an interesting effect of this reagent. The lighter Eu is preferably extracted during the first HPMBP addition ( $X = 0.1$ ) in the Cyanex 272 system and, from  $X = 0.3$  in the P507 system, at both pH values. These observations are presented and confirmed in Figures 7.a, 7.b, 8.a and 8.b, which display the distribution coefficients of both elements in both extraction systems at the evaluated pH values. A greater influence of the HPMBP fraction on Eu was observed in all cases. This did not occur with pure organophosphorous extractants ( $X = 0$ ), where the extraction preference was always for Gd, corroborating reports in the literature [14]. Another observation displayed in Figures 5 and 6 is that the extraction percentages increase and approach each other from  $X = 0.4$ . The difference in the ionization force between the tested organophosphorous extractants is less clear along the HPMBP additions. Regarding HPMBP, Roy et al. [25] indicate similar organophosphate behaviors in REE extraction, of an HPMBP preference for heavier ions, forming an organometallic  $\text{LnP}_3$ -type complex. The present study, however, reports the contrary.

According to these results, a possible alteration in the extraction mechanism is, thus, postulated and discussed. According to Dukov et al. [24], Atanassova et al. [26], Tong et al. [12] and Atanassova, et al. [26], HPMBP can form  $\text{LnP}_3\cdot\text{HP}$  species, where HP represents the solvated HPMBP molecule and P represents its anionic species formed by the release of the proton  $\text{H}^+$ . These compounds are also called "self-adducts." Self-adducts would be formed in two steps, first forming  $\text{LnP}_3$  by the cation exchange mechanism, followed by the solvation of this compound by HPMBP itself, leading to the formation of a  $\text{LnP}_3\cdot\text{HP}$  species.

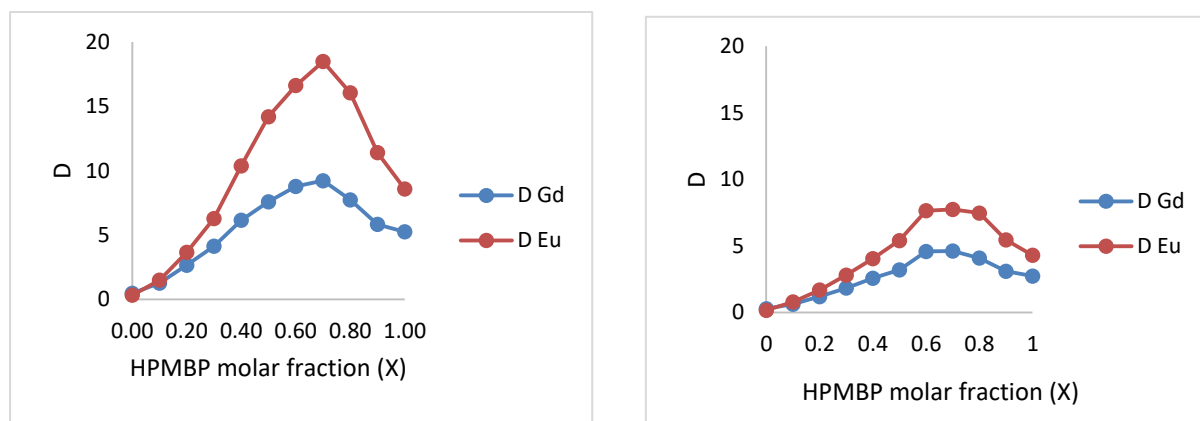
According to these authors, this subsequent solvation mechanism is very effective, and occurs preferentially with lighter REE elements, probably due to steric hindrance in the formation of heavier REE species, caused by retraction of the ionic radius. The authors suggest that the  $\text{LnP}_3$  chelate receives an extra HPMBP molecule by replacing a water molecule in its coordination sphere, thus originating the  $\text{LnP}_3\cdot\text{HP}$  species. This phenomenon is then considered to be self-synergistic, since solvation by the HPMBP molecule would facilitate the transfer of the lighter REE ion to the organic phase. Atanassova et al. [27] also cite the existence of a competition between cation exchange, ion-molecule bonding and solvation mechanisms in the interaction of the HPMBP molecule with the hydration sphere of the ionic species. Decreases in extraction percentages in  $X$  between 0.8 and 1 are observed in all curves displayed Figures 5 and 6.

Indications of synergy favoring the increase of extraction percentages when combining HPMBP and the organophosphorous extractants in specific molar fractions were observed. For all cases, extraction percentages were lower when  $X = 1$ , that is, only HPMBP effects.

The distribution coefficients displayed in Figures 7 and 8 further illustrate the understanding of the two phenomena discussed herein, of an extraction preference for Eu, with a lower atomic number element, and the synergistic effect of the extractive systems. Higher D values for the P507 system compared to the Cyanex 272 system at both pH and for both Eu and Gd were also observed. On the other hand, increases in the molar fraction led to clear increases in the Eu distribution coefficient compared to Gd in all extractive systems and pH values. However, the values of the distribution coefficients fall in X values ranging from 0.8 and 1.0. In other words, the role of the organophosphorous HPMBP + extractant in the extraction of Gd and Eu is noteworthy.



**Fig. 8** - Distribution coefficients (aqueous solution (A)=  $5.0 \times 10^3 \text{ mol L}^{-1}$ , P507 + HPMBP =  $0.1 \text{ mol L}^{-1}$ ; A/O 1: 1) a) pH 3.0 b) pH2.5



**Figure 7** - Distribution coefficients (aqueous solution (A)=  $5.0 \times 10^3 \text{ mol L}^{-1}$ , Cyanex 272 + HPMBP =  $0.1 \text{ mol L}^{-1}$ , 1: 1 A/O) a) pH 3.0 b) pH 2.5.

From the determined distribution coefficients, an analysis of the separation factors was conducted (Figure 9), emphasizing that F Eu/Gd occurs, since Eu is the preferential element of the evaluated extractant systems.

The addition of HPMBP directly influenced selectivity, favoring Eu against Gd. The highest Eu/Gd values were observed at pH 3.0 for both the P507 and Cyanex 272 systems. For the P507 system, the best separation factor,  $F_{\text{Eu/Gd}} = 1.81$ , was observed at  $X = 0.7$ , while in the Cyanex 272 system this occurred at  $X = 0.8$ , with  $F_{\text{Eu/Gd}} = 2.08$ . A greater influence of HPMBP was observed with Cyanex272, since  $F_{\text{Eu/Gd}}$  was higher in this system for all tests, inverting selectivity as follows: (Cyanex 272+ HPMBP) > (P507 + HPMBP).



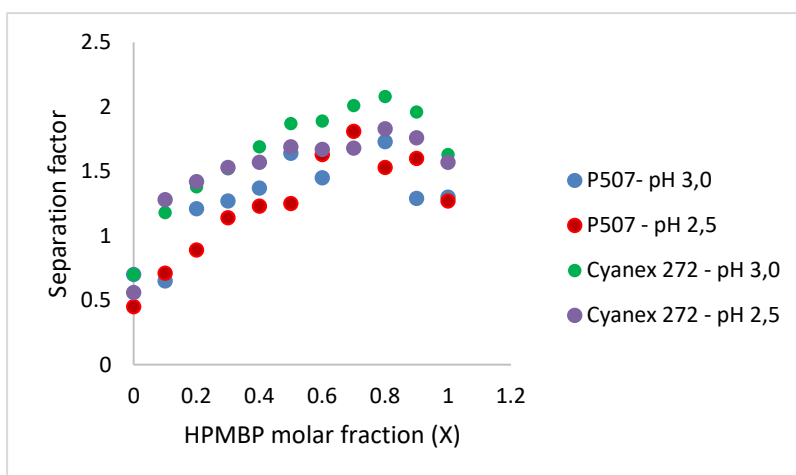


Fig. 9- Eu/Gd separation factors as a function of HPMBP molar fraction with P507 and Cyanex 272 at pH 2.5 and 3.0.

The synergistic or antagonistic effect evaluates whether a mixture of extractants may, in terms of extraction percentage or distribution coefficient, be more effective or not. In this regard, in addition to selectivity, we attempted to evaluate if the extractant mixtures with HPMBP could also be effective with regard to the coefficients of distribution of Eu and Gd. According to Tong et al.[12] the synergistic or antagonistic effect on metal extraction can be evaluated by the R coefficient, displayed in Equation (3), where this effect is considered positive (or synergic) when  $R \geq 1$ . With A and B are the extractants of interest, the equation is:

$$R = \frac{D_{mixture}}{D_A + D_B} \tag{3}$$

The R values obtained from Equation 3 were then plotted and are displayed in Figures 10 and 11, comparing the P507 and Cyanex272 extractant systems at pH 2.5 and 3.0 as a function of HPMBP molar fractions.

R values greater than or equal to 1, in other words, synergistic behavior, was observed in a wide range, from X = 0.3 for pH 2.5 and X = 0.4 for pH 3.0. This can be easily understood, since higher pH values lead to better performance of cationic extractants in capturing Eu and Gd, thus requiring a greater amount of HPMBP to compensate for this effect through its solvating behavior. The synergic effect is always higher for Eu compared to Gd in all extractive systems, as discussed previously and attributed to the greater tendency of Eu to form  $LnP_3 \cdot HP$ . It is known that organophosphorous extractants tend to preferentially extract lanthanides with a greater atomic mass, in this case Gd [14] Again, reference is made to a possible alteration in the extraction preference of evaluated systems. Therefore, the use of extractants displaying other extraction mechanisms, such as anionic compounds, like amines and their salts [14] is suggested for future studies in the search for synergistic effects on the extraction of Gd and Eu with the use of HPMBP.

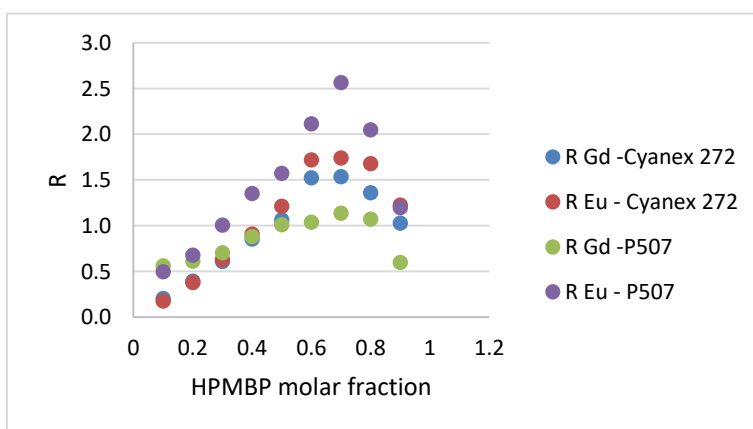


Fig. 10- Evaluation of the synergistic coefficient at pH 2.5.

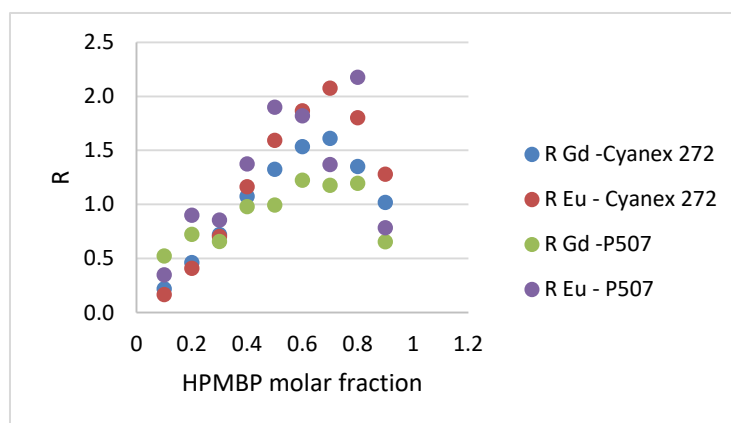


Fig. 11-Evaluation of the synergistic coefficient at pH 3.0.

## V. CONCLUSIONS

Eu and Gd extraction studies were performed for organophosphate extractive systems. These compounds showed an extraction preference for Gd in all cases. The extraction force follows the acidic character of the evaluated extractive molecules, as follows: D2EHPA > P507 > Cyanex 272 ≥ Cyanex 923. Increases in pH and extractant phase concentrations favored increase in the extraction of Gd and Eu for cationic-type extractants. Cyanex 923, as a solvating extractant, showed no effect after pH modifications. Higher extraction percentages were accompanied by a decrease in the separation factors, which impaired selectivity between Gd and Eu.

The presence of HPMBP, a chelating extractant, included as an integral part of the P507 and Cyanex272 extraction systems, resulted in higher extraction percentages for both Gd and Eu. With increases in the HPMBP fraction, the percentage differences became imperceptible for the both extractive systems.

HPMBP creates a preference for increased Eu extraction, reversing its position in relation to Gd, verified herein by the extraction percentages, distribution coefficients, separation factors and synergistic coefficient results. Thus, alterations in the reaction mechanism for this process are a possibility. The selective behavior regarding Eu by HPMBP is discussed as two possible extraction mechanism effects: a cationic mechanism followed by a solvation mechanism, which, in this case, seems to be the determinant for the change in extraction behavior.

## REFERENCES

- [1]. D. Shriver, P. Atkins, Química Inorgânica (Porto Alegre: Bookman, 2008).
- [2]. E.V. Vieira, F.F Lins., Concentração de minérios de Terras-Raras: uma revisão (Rio de Janeiro: Série Tecnológica Mineral-CETEM, 1997).
- [3]. F. Xie, T.A Zhang, D. Dreisinger, , F. Doyle, A critical review on solvent extraction of rare earths from aqueous, Solutions.Minerals Engineering. 56, 2014,10–28.
- [4]. J.B. Russel, Química Geral, v.I e II.( São Paulo:Pearson Makron Books, 1994).
- [5]. Y. Kanazawa, M. Kamitani, Rare earth minerals and resources in the world, Journal of Alloys and Compounds. 408–412, 2006, 1339–1343.
- [6]. A. Abrão, Química e tecnologia de Terras-Raras (Rio de Janeiro: Série de Tecnologia Mineral- CETEM, 1994).
- [7]. R.H.P.,Andrade, Sumário Mineral 2015 (Departamento Nacional de Produção Mineral, 2015).
- [8]. R. Yang., W. Wang, X Zhang, L. Liu, H. Wei., M. Bao J. Wang, A new type of rare earth elements deposit in weathering crust of Permian basalt in western Guizhou,NW China Journal of Rare Earths. 26, 2008, 753-759.
- [9]. R.H.P. Andrade, Sumário Mineral 2012 (Departamento Nacional de Produção Mineral, 2012).
- [10]. J. Peganine, S. Guedes, J.C. Teixeira, Terras -Raras: Estratégia para o futuro. Revista em Discussão: Revista de audiências públicas do Senado Federal, 4 (17), 2013, 35.
- [11]. USGS-United State Geological Survey (Mineral commodity summaries 2016).
- [12]. S. Tong, N. Song, Q. Jia, W. Zhou, W. Liao, Solvent extraction of rare earths from chloride medium with mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 and sec-octylphenoxyacetic acid, Separation and Purification Technology. 69, 2009, 97–101.
- [13]. A. Jyothi, G.N. Rao, Solvent extraction behavior of lanthanum(III), cerium(III), europium(III), thorium(IV) and uranium(VI) with 3-phenyl-4-benzoyl-5-isoxazolone, Talanta, 37,1990, 431-433.
- [14]. G.M. Ritcey, A.W. Ashbrook, Solvent Extraction – Principles and applications to process metallurgy. v. I e II (Elsevier Science Publishers, 1984).
- [15]. C.K. Gupta, T.K. Mukherjee Hydrometallurgy in Extraction Processes v. I e II (CRC Press, 1990).
- [16]. L. Alders, Liquid-liquid extraction, theory and laboratory experiments (Netherlands:Elsevier Publishing Company, 1955).
- [17]. C.K. Gupta, N. Krishnamurthy.,Extractive Metallurgy of Rare Earths (Florida: CRC PRESS, 2004).
- [18]. J.S. Preston, A.C. Du Preez, P.M. Cole, M.H. Fox, The recovery of rare earth oxides from a phosphoric acid by-product. Part 3. The separation of the middle and light rare earth fractions and the preparation of pure europium oxide, Hydrometallurgy, 42, 1996, 131-149.

- [19]. C.A Morais, V.S.T. Ciminelle, Selection of solvent extraction reagent for the separation of europium(III) and gadolinium(III), *Minerals Engineering*. 20, 2007, 747–752.
- [20]. M. Atanassova, I.L. Dukov, Synergistic solvent extraction and separation of trivalent lanthanide metals with mixtures of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one and aliquat 336, *Separation and Purification Technology*, 40, 2004, 171–176.
- [21]. V. I., Lakshmanan, G. J. Lawson, Extraction of cobalt by KELEX 100 and KELEX100/VERSATIC 911 mixtures. *J. Inorg. Nucl. Chem.* 35, 1973, 4285-4294.
- [22]. A.T. Kandil, K.N Farah, The solvent extraction of terbium and europium by di-(2-ethylhexyl)-phosphoric acid and various organophosphorous compounds. *J. Inorg. Nucl. Chem.* 32,1979, 277-280.
- [23]. M. Atanassova, I.L. Dukov, Synergistic Solvent Extraction of Trivalent Lanthanoids with Mixtures of 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone and Crown Ethers, *Acta Chim. Slov.*, 53, 2006, 457–463.
- [24]. I.L. Dukov, V.M. Jordanov, Synergistic solvent extraction of lanthanides with mixtures of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and primary ammonium salts. *Hydrometallurgy*. 48,1998, 145–151.
- [25]. A. Roy, K. Nag, Solvent extraction behavior of rare earth ions with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone. *Journal of Inorganic and Nuclear Chemistry*. 40, 1978, 331-334.
- [26]. M. Atanassova, V. Kurteva, I. Dukov, The interaction of extractants during synergistic solvent extraction of metals. Is it an important reaction? *RSC Adv.* 6, 2016, 81250–81265.

B.S.M. Valverde. “Organophosphorous compounds and the synergistic effect of 1-Phenyl-3-Methyl-4-Benzoyl-5-Pyrazolone in europium and gadolinium extraction behavior.” *American Journal of Engineering Research (AJER)*, vol. 6, no. 9, 2017, pp. 19–29.