

## Comparative Study for Lanthanum/Praseodymium-Neodymium Separation of Egyptian Monazite using DEHPA and HEH(EHP).

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### Abstract

The present paper is concerned with a comparative solvent extraction study for La/Pr-Nd separation from Egyptian monazite using the commonly used extractants Di-2-ethylhexylphosphoric acid (DEHPA) and 2-ethylhexylphosphonic acid mono-2-ethylhexylester (HEH(EHP)) in kerosene. For this purpose, both batch extraction and stripping equilibrium experiments were performed. A complete counter current run was also studied to explore the feasibility of the HEH(EHP)/K extractant. The obtained results indicated the successful application of the latter solvent where a pure La concentrate (98%) was prepared beside pure Pr/Nd concentrate.

### 1. Introduction

The rare earth elements (REE) naturally occur together in three principal minerals; namely monazite, bastansite and xenotime. However, the high value of these elements depends mainly on their effective separation into industrial elements. Such a separation is indeed very difficult to achieve due to the very low separation factors of adjacent elements. The different methods actually used for separating individual REE from their naturally occurring mixtures utilize essentially the small difference in their basicity. The latter increases from La to Lu and results from progressive decrease in ionic radii with increasing the atomic number. The basicity

differences influence indeed the solubilities of salts, the hydrolysis of ions as well as the formation of complex species.

Several workers<sup>(1-7)</sup> have utilized these properties in achieving successful separation in individual elements; namely fractional crystallization, fractional precipitation, ion exchange and solvent extraction. To these, differences in stable valence states among some REE can also be used in their separation, where Ce, Pr and Tb can exhibit a tetravalent state while Sm, Eu and Yb can exhibit a divalent state.

In solvent extraction purposes, a REE mixture can be separated first into three groups; light rare earth group(La, Ce, Pr and Nd), a middle rare earth group(Sm, Eu and Gd) and a heavy group including Tb to Lu beside Sc and Y. This separation is favored by relatively higher separation factor of the three groups<sup>(6&8)</sup>. In this regard, several works have also been reported since 1950s to achieve this task involving different media and different extractants. The latter involve mainly di-2-ethyl hexyl phosphoric acid (DEHPA) and 2-ethylhexylphosphonic acid mono-2-ethyl hexyl ester{HEH(EHP)}<sup>(9-11)</sup> beside the natural phosphate including tri-n-butyl phosphate(TBP) and tri-n-octylphosphine oxide(TOPO)<sup>(12-14)</sup>. Also carboxylic acid derivatives<sup>(15&16)</sup>; amine<sup>(17-19)</sup>; ketones and others<sup>(18&20)</sup> have also been used.

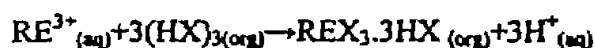
In the present work, it was decided to apply DEHPA which has extensively been used to the separation of highly pure La from Pr-Nd present in the light REE group of the Egyptian monazite. The obtained results would also be compared with those obtained by HEH(EHP). This solvent has recently been used in view of its higher separation factor beside its relatively rapid stripping properties. For both solvents, kerosene was used as the proper diluent.

The rare earth hydrous oxide cake— the feed material of the present work is produced by the digestion of Egyptian monazite concentrate with 45% NaOH solution

(Saleh,1966)<sup>(21)</sup> in Inchas Pilot Plant. This feed has actually been subjected to a proper treatment before preparing the aqueous feed solution used in the present study for the solvent extraction separation of high purity La from Pr-Nd. For this purpose, the hydrous oxide cake was dissolved in concentrated HCl solution followed by alkali fractional precipitation at a pH value of about 5.8 to precipitate admixed U and Th and the rare earth hydroxides was precipitated by increasing the pH to 8.0. The second step in preparing the aqueous feed for the present work was Ce separation using the oxidation/reduction hydrolysis technique with  $\text{KMnO}_4/\text{Na}_2\text{CO}_3$  developed by Morais et al. in 2003<sup>(22)</sup>. In this technique, the Ce filtrate of  $\text{KMnO}_4$  treatment was neutralized with  $\text{Na}_2\text{CO}_3$  solution to precipitate the RE carbonate. The latter was then dissolved in 3M HCl and was found to assay the equivalent of 16.4g/l La, 1.72g/l Pr and 6.68g/l Nd.

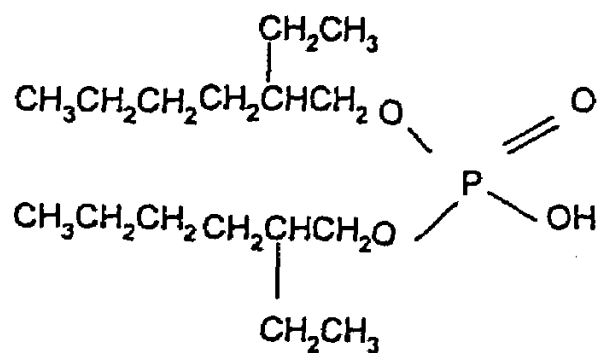
The two used extractants (Fig.1) are indeed liquid cation exchangers where the extracted metal species would exchange with the hydrogen ion in the hydroxyl group. Both extractants are prone to form dimmers through hydrogen bonding. In relatively dilute solutions, dimerization in the form of  $(\text{HX})_2$  or  $\text{H}_2\text{X}_2$  increases with decreasing the diluent polarity<sup>(23,10&24)</sup>.

According to several authors<sup>(25-29)</sup>, the extraction mechanism can be represented by the following equation

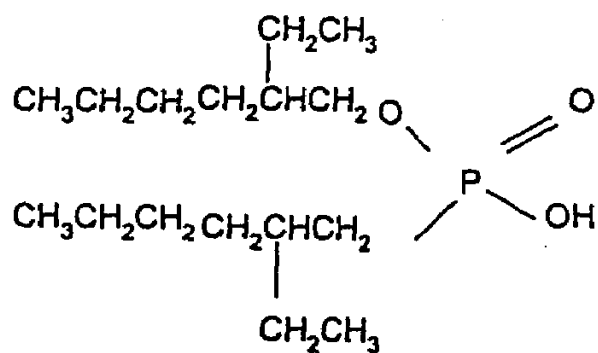


where X represents the deprotonated form

Beside such complex species, two other species are believed to be formed ( $\text{REX}_3 \cdot 2\text{HX}$  and  $\text{REX}_3$ ) when the extractant is very dilute<sup>(30,31&24)</sup>



**DEHPA**



**HEH[EHP] (Ionquest 801)**

Fig.1. Structural formula of the extractant DEHPA and HEH[EHP]

## 2. Experimental

Both batch equilibrium and counter current extraction experiments have been investigated using both DEHPA and HEH(EHP). In addition, a stripping experiment was performed from two loaded solvent samples.

### 2.1. Batch equilibration

Several batch extraction experiments have been performed for the two studied solvents using the above-mentioned prepared aqueous feed solution. The purpose was to study the effects of extractant concentration, pH of the aqueous feed solution as well as the total feed REE concentration.

In these experiments, 20 ml of the aqueous feed was contacted in an organic to aqueous ratio (O/A) 1:1 and the mixture was mechanically agitated at room temperature for 5 min. After settling, the two phases were separated in a separating funnel and the REEs were analyzed in the aqueous phase while their content in the organic phase was obtained by difference.

### 2.2. Counter current testing

A complete counter current run of the load HEH(EHP) system has been performed to obtain the relevant result. In test an acrylic mini battery mixer settler to which the feed rate of the concerned phases was adjusted by peristaltic pump. The mixing chamber of the used battery measures 13cm<sup>3</sup> while the settler volume attain 40cm<sup>3</sup>. During the test run, proper aliquot of the aqueous feed were withdrawn from each settler for analysis of their REEs content.

### 2.3. Analytical procedure

Both neodymium and praseodymium were spectrophotometrically determined using their sharp absorption bands at 522 and 444nm respectively. A Shimadzu spectrophotometer was employed and the corresponding calibration standard were prepared from pure rare earth oxides (99.9%, Aldrich)

Total REEs analysis was performed by titration against 0.03M EDTA solution using xylenol orange indicator and hexamine buffer (pH=6). On the other hand, La was determined by emission atomic absorption.

## 3. Results and Discussion

### 3.1 Study of batch extraction factors

#### 3.1.1. Effect of extractant concentration

To study the effect of the extractants concentration (DEHPA and HEH(EHP) upon La extraction, different experiments were performed using various concentrations ranging from 0.5 to 2 M of either extractant in kerosene. Other extraction conditions were kept constant at 2.4 pH value. The obtained results are shown in Table(1) and Fig(2). It is clearly shown that the extraction percent increase as the extractant concentration increases from 0.5 to 2.0 M, however with varying degrees. It is also clearly evident that the increase being relatively higher in the case of DEHPA. Extraction of Pr and Nd are quite similar for both extractants. The increase in the extraction percent from La to Nd can indeed be explained by the difference in the basicity of these elements, which increase from La to Lu. This difference is related to a systematic and smooth decrease in the ionic radii of the rare earth elements, due to the lanthanide contraction (Gschneidner, 1980 and Sundaram,

1987)<sup>(6&7)</sup>. The very low extraction of La(0.5-1.5%) with HEH(EHP) should be herein emphasized as this will help its separation from the mixture.

Table (1) Effect of HEH(EHP) and DEHPA concentration on % RE elements extraction

Extractant concentration (M)	HEH(EHP)			DEHPA		
	La <sub>2</sub> O <sub>3</sub>	Pr <sub>6</sub> O <sub>11</sub>	Nd <sub>2</sub> O <sub>3</sub>	La <sub>2</sub> O <sub>3</sub>	Pr <sub>6</sub> O <sub>11</sub>	Nd <sub>2</sub> O <sub>3</sub>
0.5	0.5	6	9	4	15	18
1.0	1.0	8	12	5	22	28
1.5	1.5	9	15	7	30	39
2.0	1.5	12	18	9	40	40

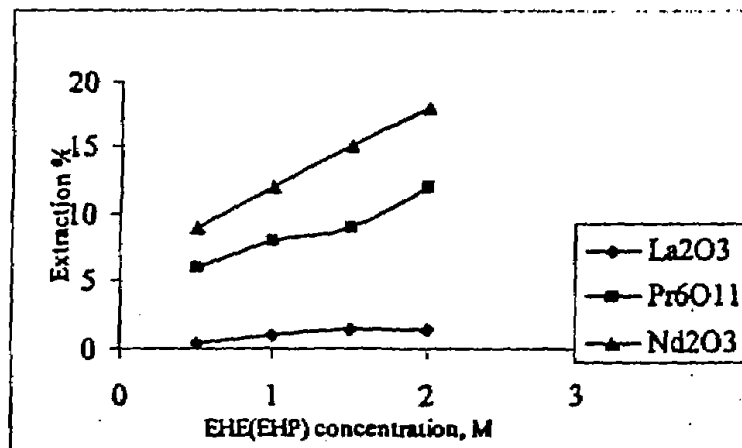


Fig (2a) Effect of HEH(EHP) concentration on RE elements extraction.

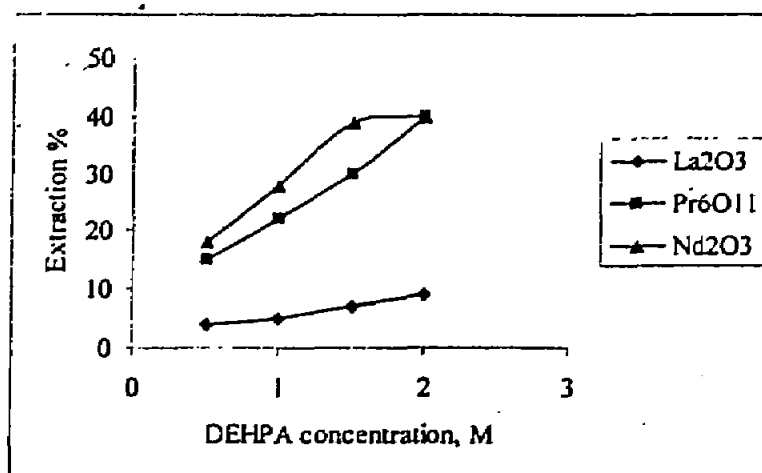


Fig (2b) Effect of DEHPA concentration on RE elements extraction.

### 3.1.2. Effect of pH

In order to study the effect of pH of the REs chloride liquor on La extraction, another series of experiments was performed using different pH values ranging from 0 to 2.5. The feed solution used assay was feed 16.4 g/La<sub>2</sub>O<sub>3</sub>, 1.72 g/l Pr<sub>6</sub>O<sub>11</sub> and 6.68 g/l Nd<sub>2</sub>O<sub>3</sub> extraction condition while using 1.0 M as the concentration of each extractant. The obtained results were summarized in Table (2) and Fig (3). It could be observed that the extraction percent increases with decrease of the acidity of the RE solution. With DEHPA extractant, the extraction percent of the studied elements increases up to pH 1 and then reaches a plateau (Fig.3b). Also, it is interesting in this regard to indicate that extraction with HEH(EHP) drops to nearly zero as the pH values decreases to 0.5 and to 0.0 for La and Nd respectively. This indicates that while the use of this reagent would require a very effective pH control during extraction, it proves greatly advantageous to keep La behind in the aqueous phase.



Table (2). Effect of acidity on the RE elements Extraction

pH	HEH(EHP)			DEHPA		
	La2O3	Pr6O11	Nd2O3	La2O3	Pr2O3	Nd2O3
0.0	0.0	0	4	2	13	15
0.5	0.0	7	9	5	26	31
1.0	0.5	8	12	4	30	35
1.5	1.0	10	15	5	30	35
2.0	1.0	12	15	5	30	37
2.5	1.0	15	19	5	32	37

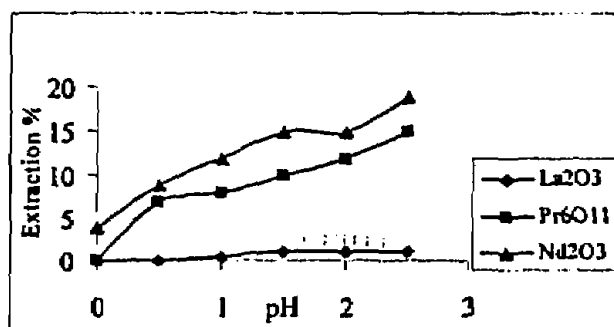


Fig (3a) Effect of chloride acidity solution on the RE elements extraction with HEH(EHP).

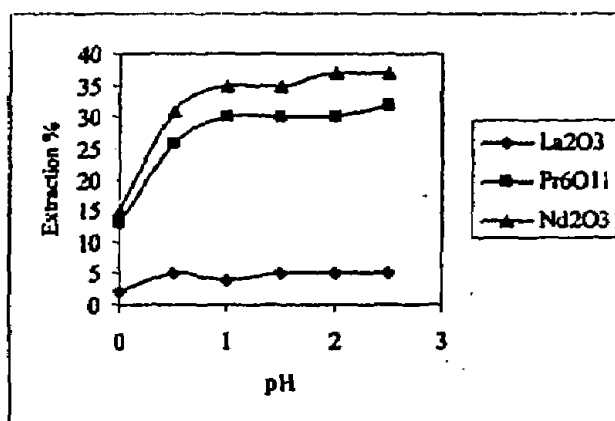
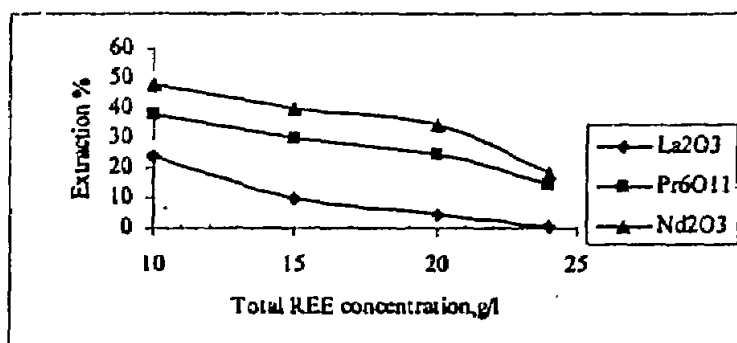


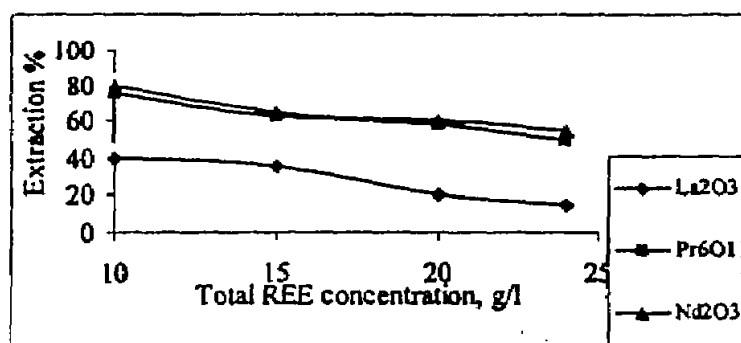
Fig (3b) Effect of chloride solution acidity on the RE elements extraction with DEHPA.

### 3.1.3. Effect of total rare earth concentration

The effect of the total rare earth concentration ( $\text{La}_2\text{O}_3 + \text{Pr}_6\text{O}_{11} + \text{Nd}_2\text{O}_3$ ) upon La, Pr and Nd extraction percent was investigated in the range from 10.0 to 24.4 g/l RE oxides prepared by proper dilution of the latter concentration. In these experiments, the other batch equilibration experimental conditions were fixed at a pH value of 2.4 and 1M as the extractant concentration. It was found that extraction percent increases as the total rare earth concentration decreases (Fig.4).



Fig(4a) Effect of the total REE concentration on the individual elements with HEH(EHP).



Fig(4b) Effect of the total REE concentration on the individual elements with DEHPA.

From the above mentioned data of the studied variable, it is quite clear that decreasing EEE concentration has the most significant influence on the indirect selectivity of La. This adverse effect on the selectivity due to the fact that the decrease in the REE concentration caused a relatively higher increase in the La extraction as compared to the increases in Pr and Nd extraction. These differences are reflected in the significant decreases in the separation factor Pr/La (Table.3). For the system HEH(EHP)-HCl, the separation factor of Pr/La decreased from 18 to 6.7, while for the system DEHPA-HCl, it varied from 6.4 to 4.4 as the total REE concentration decreases from 24.4 to 10.0 g/l.

Table(3) Extraction coefficient of La, Pr and Nd and separation factors of Pr/La and Nd/Pr

Extractant	Total RE oxides(g/l)	Extraction Coefficient			Seapration Factor	
		LaE <sub>n</sub> <sup>o</sup>	PrE <sub>n</sub> <sup>o</sup>	NdE <sub>n</sub> <sup>o</sup>	Pr/La	Nd/Pr
HEH(EHP)	24.00	0.01	0.18	0.23	18	1.3
	20.00	0.029	0.33	0.44	11.4	1.32
	15.00	0.09	0.87	1.16	9.7	1.33
	10.00	0.14	1.06	1.41	7.9	1.32
DEHPA	24.00	0.053	0.34	0.37	6.4	1.07
	20.00	0.18	0.98	1.06	5.56	1.08
	15.00	0.43	2.04	2.19	4.79	1.07
	10.00	0.66	2.94	3.2	4.38	1.1

On the other hand, the separation factor of Nd/Pr remained practically constant and equal to about 1.3, for the system HEH(EHP)-HCl, and about 1:1 for the system DEHPA-HCl. The high separation factor of Pr/La is due essentially to the absence of cerium as well as the higher acidic character of La.

From all the obtained results, it is quite evident that the extraction percent obtained with DEHPA were significantly superior to those obtained with HEH(EHP). According to the soft and hard acid/ base theory of Pearson, 1963<sup>(33)</sup> and Huheey 1992<sup>(34)</sup>, and the hydrophilic character of the different extractant, the symmetry of the four oxygen atoms around the phosphorus atom in DEHPA would be responsible for making the conjugated base of this extractant harder than in the conjugated base of HEH(EHP). In addition to this and perhaps even more relevant is the relatively higher hydrophilic nature of the phosphate group in DEHPA as compared to the phosphonic group in HEH(EHP), thus making the former more active in the organic/aqueous interface. However, this effect will be responsible for difficult stripping in DEHPA as compared to HEH(EHP).

### 3.2. Effect of HCl concentration on the REE stripping percent

In order to study the potentiality of hydrochloric acid for La, Pr and Nd stripping from the studied extractants (DEHPA and HEH(EHP)), a properly prepared loaded samples were first prepared. Loaded HEH(EHP) sample assay 2.5g/l  $\text{La}_2\text{O}_3$ , 1.62 g/l  $\text{Pr}_6\text{O}_{11}$  and 6.65 g/l  $\text{Nd}_2\text{O}_3$ , while The loaded DEHPA sample assay 5g/l  $\text{La}_2\text{O}_3$ , 1.45g/l  $\text{Pr}_6\text{O}_{11}$  and 4.5 g/l  $\text{Nd}_2\text{O}_3$ . A series of experiments was performed using HCl with different concentration varying from 0.05 to 2.0 M at an A/O phase ratio 1/2. The obtained data are shown in Table (4) and Fig(5). As mentioned above, while the extraction of the REE is higher with DEHPA compared to HEH(EHP), their stripping, is on the contrary relatively easier from the loaded HEH(EHP) as compared

to DEHPA. Thus, about 96-98% of La is stripped from HEH(EHP) with 0.2 to 0.5 M HCl solution while 1.5 M HCl was required for stripping 99% of La from DEHPA.

Table(4) Effect of HCl concentration on RE elements stripping percent from loaded HEH(EHP) and DEHPA

HCl, M	HEH(EHP)			DEHPA		
	La <sub>2</sub> O <sub>3</sub>	Pr <sub>6</sub> O <sub>11</sub>	Nd <sub>2</sub> O <sub>3</sub>	La <sub>2</sub> O <sub>3</sub>	Pr <sub>6</sub> O <sub>11</sub>	Nd <sub>2</sub> O <sub>3</sub>
0.05	35	10	5	5	0	0
0.10	60	15	10	10	0	0
0.20	96	40	35	40	15	15
0.50	98	70	60	85	35	30
1.00	98	90	80	90	60	65
1.50	99	98	97	99	90	90
2.00	99	98	97	99	99	99

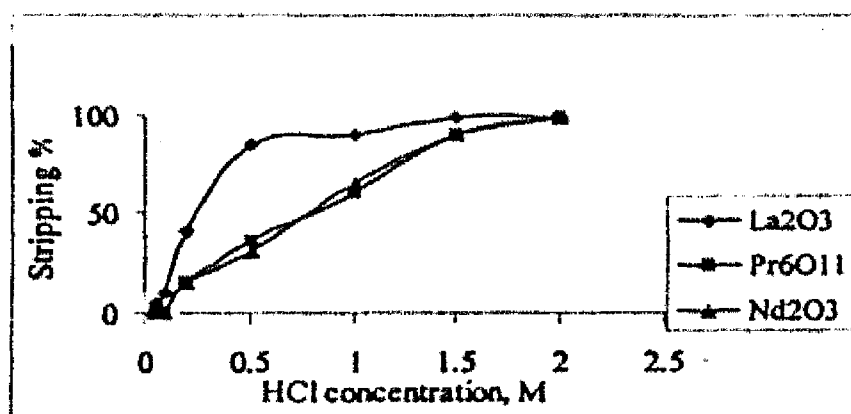


Fig (5a) Effect of the HCl concentration on the RE elements stripping from loaded HEH(EHP).

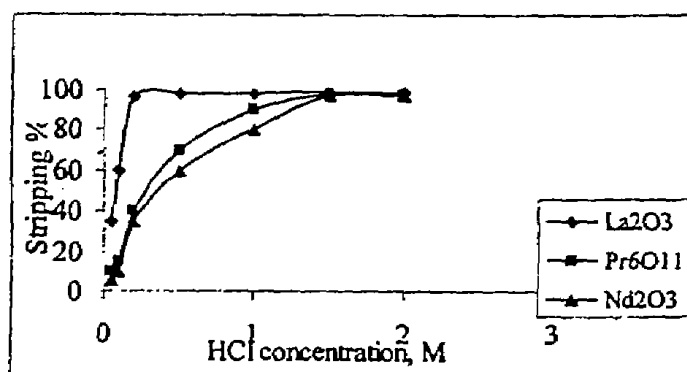


Fig (5b) Effect of the HCl concentration on the RE elements

stripping from DEHPA.

### 3.3 Counter-Current experiments for La/Pr-Nd separation

The batch experiments indicated that both Pr and Nd are much more easily extracted than La. Therefore, it was found quite necessary to design a complete extraction run. To explore the possibility of transfer of Pr and Nd to the organic phase (HEH(EHP)), while La being kept in the raffinate. Table 5 and Fig (6)

Table.5. REE concentration in the aqueous phase of the extraction section of the counter-current run.

Stage No	REE concentration, g/l		
	La <sub>2</sub> O <sub>3</sub>	Pr <sub>6</sub> O <sub>11</sub>	Nd <sub>2</sub> O <sub>3</sub>
1	5.45	nil	nil
2	8.49	nil	nil
3	7.04	nil	nil
4	11.99	nil	nil
5	12.54	nil	nil
6	13.50	nil	0.27
7	15.90	0.52	0.53
8	16.36	0.65	1.99

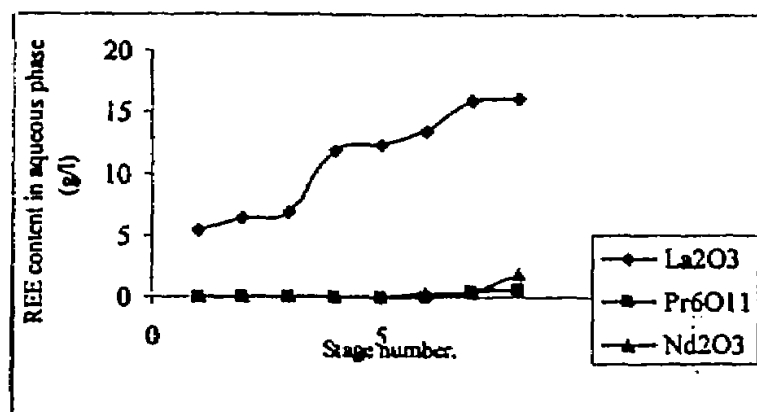


Fig (6) Profile of RE elements concentration in the aqueous phase of the extraction section of counter current run.

The extraction occurred in 8 stages where the feed solution containing 16.4 g/l La<sub>2</sub>O<sub>3</sub>, 1.72 g/l Pr<sub>6</sub>O<sub>11</sub> and 6.68 g/l Nd<sub>2</sub>O<sub>3</sub> and pH=1.2. The organic to aqueous ratio 2/1.

In the extraction circuit, the aqueous feed flow rate was adjusted at 0.8 ml/min. The obtained results are tabulated in Table.5 and Fig (6). It is clearly evident that by increasing the stage number, the concentration of La increases in the aqueous phase i.e. the extracted La in the early stage is transferred back to the aqueous phase. In stage 8, the input La concentration of 16.4 g was almost reached. However, La in the aqueous phase in this stage will be mixed both Pr and Nd. Therefore, to have 98% La purity, only 6 stages were required where the aqueous left will assay 13.5 g/l La and only 0.27g/l Nd. This effect occurs at the expense of some Pr and Nd starting from stage 7 or from stage 6-8 respectively.

#### 4. Conclusion

The performed study involved comparative data of extraction of La, Pr and Nd using the two commonly used extractants(DEHPA and HEH(EHP)). The extraction depends upon the extractant concentration, pH of the aqueous feed solution and the

total REE concentration. Also, the REE stripping percent depends upon the concentration of HCl.

A counter –current extraction run was also performed using HEH(EHP) and it was found that 6 stages would be required to obtain 98% La in the aqueous phase ( mixed with only 0.27g/l Nd. The La recovery attained 82%.

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## References

1. Topp, N.E., Editor, 1965. The Chemistry of Rare Earth Elements, Elsevier, New York, pp.112-173.
2. Kedarii, C.S., Pandit, S.S and Ramanujam, A.,1999. Studies on the in situ electrooxidation and selective permeation of cerium (IV) across a bulk liquid membrane containing tri-butyl phosphate as the ion transporter. Sep. Sc. Technol, 34, pp.1907-1923.
3. Morais, C.A. and Ciminelli, V .S.T., 1998. Recovery of europium from a rare earth chloride solution. Hydrometallurgy, 49, pp.167-177.
4. Morais, C.A. and Ciminelli, V.S.T., 2001. Recovery of europium by chemical reduction of a commercial solution of europium and gadolinium chlorides,. Hydrometallurgy, 60, pp.247-253.
5. Morais, C.A. and Ciminelli, V.S.T., 2002. A study of recovery on europium by photochemical reduction, Sep, SCI Technol, 37, 14, pp.3305-3321.
6. Gschneidner Jr., K.A.,1980. Rare earth speciality inorganic chemicals. In Symposium on speciality inorganic Chemicals, 1980, Salford Proceedings... The Royal Society of Chemistry, London, pp. 403-443.
7. Sundaram, C.V., 1987. Chemistry and metallurgy of rare earth metal extraction and applications. Trans. Indian Inst. Met, 40, pp. 457-477.
8. Qiu, L.F., Kang, X-H. and Wang, T.S.,1991. A study on photochemical separation of rare earths: the separation of europium from an industrial concentrate material of samarium, europium and gadolinium. Sep. Sci. Technol, 26, 2, pp.199-221.

9. Xu, L., Xiao, Y and Li, D., 1992. An expert system for solvent extraction of rare earths. *J. Chem. Inf. Comput. Sci*, 32, 437-442.
10. Giles, A.E., Aldrich, C and Van Devnter, J.S.J., 1996. Modeling of the rare earth solvent extraction with artificial neural nets, *Hydrometallurgy*, 43, pp. 241-255.
11. Nucciarone, D., Pagnucco, C.D., Jakovljevic, B. and Rickelton, W.A., 2001. Synergistic and antagonistic behavior in the stripping of heavy rare earth elements from solvent mixtures containing phosphonic and phosphinic acids and trialkylphosphine oxides. In. *International Solvent Extraction Conference-ISEC'99, 1999, Barcelona, Proceeding Vol.2, Society of Chemical Industry-SCI., London, pp.1133-1137.*
12. Cecconic, T. and Freiser, H., 1990. Extraction of trivalent lanthanides as hydroxide complexes with Tr-n-octylphosphine oxide. *Anal. Chem*, 62, pp. 622-625.
13. Majdan, M., 1994. The separation factors of the lanthanides in the  $\text{Ln}(\text{NO}_3)_3\text{-NH}_4\text{NO}_3\text{-TBP}$  system. Effects of change in activity coefficient. *Hydrometallurgy*, 35, pp.179-185.
14. Mathur, J.N. and Choppin, G.R., 1998. Parafin Waxx-TOPO, an extractant for actinides and lanthanides. *Solv. Extr. Ion Exch.*, 16, pp.739-479.
15. Zheng, D., Gray, N.B. and Stevens, G.W., 1991. Comparison of naphthenic acid, versatic acid and DEHPA for the separation of rare earths, *Solvent Extr. Ion Exch.*, 9, pp.82-102.
16. Du Preez, A.C. and Preston, J.S., 1992. The solvent extraction of rare-earth metals by carboxylic acids. *Solv. Extr. Ion Exch.*, 10, pp.207-230.

17. Gorski, B., Gorski, N. and Beer, M., 1991. Extraction of Sc, Y and lanthanides by quaternary ammonium salts. *Solv. Extr, Ion Exch.*, 9, pp. 623-635.
18. Hirai, T and Komazawa, I., 1991. Extraction and separation of rare earth elements by tri-*n*-octylmethylammonium nitrate and beta-diketone using water-soluble complexing agent. *J. Chem. Eng Jpn.*, 24, pp.731-736.
19. Abbruzzese, C., Fornari, P., Massidda, R. and Urbanski, T.S., 1992. Solvent extraction of lanthanum (III) and Ce(III) from aqueous chloride solutions by LX70. *Hydrometallurgy*, 28, pp. 179-190.
20. Preston, J.S., 1996. The recovery of rare earth oxides from phosphoric acid by-product: Part 4. The preparation of magnet-grade neodymium oxide from the light rare earth fractions. *Hydrometallurgy*, 42, pp. 151-167.
21. Saleh, F. 1966. Recovery of thorium, uranium and rare earth of Egyptian Monazite Sands, UARE. Int. Report/3, Cairo, Egypt.
22. Morais, C.A, Benedotto, J.S. and Ciminelli, V.S.T., 2003. A study of cerium by oxidation/ hydrolysis with  $\text{KMnO}_4\text{-Na}_2\text{CO}_3$ . In: Proceedings of 5<sup>th</sup> the International Symposium Honoring Professor Ian M. Ritchie, *Hydrometallurgy*, 2003, Vancouver Vol.2. TMS, Vancouver, pp.1773-1782.
23. Baes, Jr., C.F., 1962. The extraction of metallic species by dialkylphosphoric acids. *J. Inorg. Nucl. Chem*, 24, pp .707-720.
24. Sánchez, J.M., Hidalgo, M., Valiente, M. and Salvadó, V., 2001. Distribution of neodymium (III) between acidic aqueous nitrate solutions and organic solutions of Di(2-ethylhexyl)phosphoric acid in kerosene at

- low metal concentration. In: *International solvent extraction Conference-ISEC'99*, 1999, Barcelona, Proceeding Vol.2, Society of Chemical Industry-SCI., London, pp.1121-1125.
25. Peppard, D. F., Mason, G.W., Driscoll, W.J and Sironen, R.J., 1958. Acidic esters of orthophosphoric acid as selective extractants for metallic cation- tracer studies. *J. Inorganic Nucl. Chem.* 7, pp. 276-285.
26. Peppard, D.F., Mason, G.W. and Hucher, I., 1961. Acidic esters of phosphonic and selective extractants for metallic cations- M(III) tracer studies. *J. Inorganic. Nucl. Chem.*, 4, pp. 245-256.
27. Iglesias, M., Antico, E and masana, A.,1999. Effect of Y(III) distribution between aqueous nitrate and organic DEHPA solutions on the precipitation stripping using oxalic acid. *Solv. Extrion. Exch.*,17, pp 277-300.
28. Geist, A., Nish, W and Kim, J., 1999. On the kinetics of rare earth extraction into D2EHPA. *Chem. Eng. Sci.*, 54, pp.1903-1907.
29. Jensen, M.P and Nash, K.L., 2001. Solvent extraction separation of trivalent and actinide ions using an aqueous aminomethane-diphosphonic acid. In: *International Solvent Extraction Conference-ISEC99*, Barcelona, Proceeding, Vol.2, Society of Chemical Industry, London, pp.1089-1091.
30. Sato, T., 1989. Liquid-liquid extraction of rare-earth elements from aqueous acid solutions by acid organophosphorus compounds. *Hydrometallurgy*, 22, pp. 121-140.

31. Sánchez, J.M., Hidalgo, M. and Salvadó, V., 1999. Extraction of neodymium (III) at trace level with di(2-ethy-hexyl)phosphoric acid in hexane. *Solv. Extr. Ion. Exch.*, 17, pp. 455-474.
  
32. Pearson, R.G., 1963. Hard and Soft acids and Bases. *J. Am. Chem.*, 85, pp.3533-3539.
  
33. Huheey, J.E., Editor. 1992. Acid-base chemistry *Inorganic Chemistry: Principle of structure and reactivity*, Vol.6, Harper&Row Publishers, New York, pp 207-236.