Polyhedron 153 (2018) 82–87

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

New insights into the separation of Nd from Pr in hydrochloric and sulfuric acid solutions

M. Sadegh Safarzadeh *, Vivek Agarwal, Luke Hayes

Department of Materials and Metallurgical Engineering, South Dakota School of Mines and Technology, 501 East Saint Joseph Street, Rapid City, SD 57701-3995, USA

ARTICLE INFO

Article history:
Received 14 March 2018
Accepted 26 June 2018
Available online 4 July 2018

Keywords:
Neodymium
Praseodymium
Cyanex 572
Taguchi
Separation factor

ABSTRACT

The solvent extraction separation of Nd from Pr with commercially available organic extractants has been studied using statistical design of experiments. In this regard, Taguchi's L_{16} ($4^4 \times 2^1$) orthogonal array was used to determine the optimum conditions for maximizing the separation factor between Nd and Pr ($\beta_{Nd/Pr}$). The effects of controllable operating experimental parameters including initial pH of the aqueous solutions (A: 2–5), concentration of rare earth element (B: 10–40 ppm), extractant type (C: DEHPA, PC88A, TOPO, and Cyanex 572), extractant concentration (D: 10–60 mM), and acid type (E: sulfuric and hydrochloric acid) on the separation performance were studied. Under selected experimental conditions Nd and Pr do not form any major chloride species, whereas both of the elements form cationic and anionic complexes in sulfate solutions ($NdSO_4^+$, $PrSO_4^+$, $Nd(SO_4)_2^-$, and $Pr(SO_4)_2^-$). The optimum operating conditions for maximizing the separation of Nd from Pr occurred at the experimental condition $A_4B_3C_1D_3E_2$, where a maximum separation factor of 2.72 was achieved, which was higher than any values reported in the literature. Analysis of variance (ANOVA) showed that pH, extractant type, and acid type had the most influential effect on the separation of Nd and Pr. DEHPA and hydrochloric acid were found to be the best organic extractant and aqueous solution, respectively. The separation performance of organic extractants followed the order DEHPA > PC88A > Cyanex 572 > TOPO, indicating that the new acidic extractant Cyanex 572 does not perform well for the separation of Nd and Pr.

1. Introduction

The separation of rare earth elements (REEs) from each other to produce pure elements or oxides of each element is a long-standing challenge that has to do with extremely similar physicochemical properties of these elements. Among these separation challenges, the separation of Nd from Pr has been a matter of intense research over the past couple of years. Solvent extraction has so far been the most versatile solution to the separation of Nd from Pr. The separation of f-block elements (lanthanides and actinides) has been extensively studied over the past years. It is well known that actinides have stronger affinity for chloride ions than lanthanides and this property has been exploited to separate actinides from lanthanides [1,2]. The cationic radii decrease across the series and this property is mainly exploited to separate individual elements of the series [3,4].

The choice of organic extractant depends on many factors, most notably the speciation of the dissolved ions in aqueous solutions. The literature indicates that the acidic organophosphorus extractants such as PC88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester), DEHPA (di-(2-ethylhexyl) phosphoric acid), and Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) have been used for the extraction of Nd and Pr, with the latter extractant being the most efficient for the separation of Nd from Pr [5].

A synergistic extractant made up of a mixture of TBP (tributylphosphate), Cyanex 272 and Alamine 336 was examined for the separation of Pr from Nd in chloride solutions [5]. An extraction synergism was observed for both Nd and Pr when TBP was added to the binary mixture of Cyanex 272 and Alamine 336, and the following solvent extraction reaction was proposed based on the observed stoichiometry:

$$(Nd^{3+} \text{ or } Pr^{3+}) + 3Cl^- + 2H_2A_2 + 2R_3N + TBP = (Nd \text{ or } Pr)ClA_2(HA)_2 \cdot TBP + 2R_3NHCl \quad (1)$$

where H_2A_2 and R_3N represent Cyanex 272 and Alamine 336. It was also found that the addition of TBP into the binary extractant mixture increased the separation factor between Nd and Pr from 1.29 to 1.59.

Banda et al. [6] reported the separation of Nd from Pr in chloride solutions using PC88A saponified with NaOH solution. While no

---

* Corresponding author. Fax: +1 605 394 3369.
E-mail address: sadegh.safarzadeh@sdsmt.edu (M.S. Safarzadeh).

https://doi.org/10.1016/j.poly.2018.06.050
0277-5387/

significant separation opportunity was found upon extraction, with the maximum separation factor of Pr over Nd of 1.5, collective extraction followed by selective scrubbing showed some promise in the separation of the metals.

Liu et al. [5] reported the extraction of Pr and Nd from chloride solutions using a mixture of Cyanex 272 and tertiary amine extractants including Alamine 336, trioctylamine (TOA), and tri-2-ethylhexyl amine (TEHA), and found that Alamine 336 showed the best synergistic effect in terms of the separation of Pr from Nd. This effect was attributed to the extraction of hydrogen ions by Alamine 336 thereby enhancing the extraction of Pr and Nd by Cyanex 272. The relative concentration of Alamine 336 and chloride ions was found to play a significant role on the extraction of Pr and Nd. The following reaction was proposed by the authors:

$$\begin{aligned}&(\mathrm{Nd}^{3+}\,\mathrm{or}\,\mathrm{Pr}^{3+}) + 3\mathrm{Cl}^- + 2\mathrm{H_2A_2} + 2\mathrm{R_3N}\\&\quad = (\mathrm{Nd\,or\,Pr})\mathrm{ClA_2(HA)_2} + 2\mathrm{R_3NHCl}\end{aligned} \tag{2}$$

It was concluded that this synergistic system did not improve the separation of metals, but rather increased the overall extraction.

In yet another study, Banda et al. [7] compared the performance of the acidic extractants DEHPA, PC88A, Cyanex 272, and Cyanex 301 diluted in Escaid 110 in the extraction of La from a chloride solution containing Nd and Pr. It was found that Cyanex 272 and saponified Cyanex 272 acted best in terms of the separation of La from Nd and Pr, and this effect was intensified by saponification of Cyanex 272.

Given this background information, it is clear that most of the commercial extractants, alone or mixed, have been examined for the separation of Nd from Pr, but promising results were not achieved. While the performance of Cyanex 272 has been compared with other acidic and neutral extractants, and it has been shown that it acts better than the other extractants in terms of the separation of Nd from Pr in hydrochloric acid solutions, the performance of Cyanex 572 and its relative performance among other extractants for the separation of Nd from Pr has not been reported in the open literature. Also, the separation of Nd from Pr in sulfuric acid solutions (arising from the acid bake leach of monazite) has not been reported. This requires a systematic statistical plan of attack to rank and quantify the performance of each extractant on the separation of Nd from Pr. In this regard, Taguchi's design was found to be most suitable approach to study the effects of initial pH (2, 3, 4, and 5), REE concentration (10, 20, 30, and 40 ppm), extractant type (tri-*n*-octylphosphine oxide (TOPO), PC88A, DEHPA, and Cyanex 572), extractant concentration (10, 20, 30, 60 mM), and acid type (hydrochloric acid and sulfuric acid) on the separation of Nd from Pr. In this regard, Taguchi's L_{16} orthogonal array composed of five factors at four levels was used to determine the optimum separation conditions. To understand the relationship between the experimental conditions and responses, analysis of variance (ANOVA) was performed and the significant experimental parameters and their contribution towards the optimum response were identified.

2. Background

The solvent extraction of Nd^{3+} and Pr^{3+} using acidic organophosphorus extractants can be expressed as:

$$(\mathrm{Nd\ or\ Pr})^{3+} + 3\,\overline{\mathrm{RH}} \rightleftarrows \overline{(\mathrm{Nd\ or\ Pr})\mathrm{R}_3} + 3\mathrm{H}^+ \tag{3}$$

where RH represents the organophosphorus extractant before dehydrogenation, and (Pr or Nd)R_3 represents the metal complex formed after extraction. The concentration-based equilibrium constant can be written as:

$$K_{\mathrm{conc}} = \frac{C_{(\mathrm{Nd}\ or\ \mathrm{Pr})\mathrm{R}_3} \cdot C^3_{\mathrm{H}^+}}{C_{(\mathrm{Nd}\ or\ \mathrm{Pr})^{3+}} \cdot C^3_{\mathrm{RH}}} \tag{4}$$

where K_{conc} represents the equilibrium constant.

Distribution coefficient (D) is the ratio of the concentration of metal in the organic phase ($C_{(\mathrm{Nd\ or\ Pr})\mathrm{R}_3}$) divided by the concentration of metal in the aqueous phase ($C_{(\mathrm{Nd\ or\ Pr})^{3+}}$), as follows:

$$D = \frac{C_{(\mathrm{Nd}\ or\ \mathrm{Pr})R_3}}{C_{(\mathrm{Nd}\ or\ \mathrm{Pr})^{3+}}} \tag{5}$$

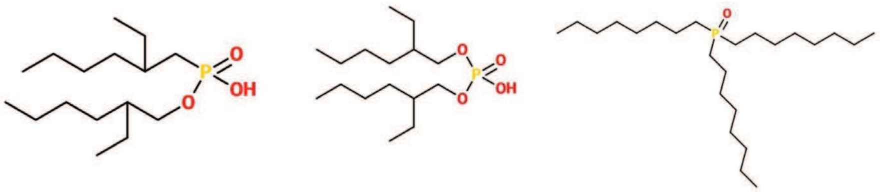
The separation factor (β) is used for measuring the effectiveness of separating two metals that is determined based on the distribution ratios. The separation factor for a binary solution can be calculated using Eq. (6).

$$\beta_{\mathrm{Nd/Pr}} = \frac{D_{\mathrm{Nd}}}{D_{\mathrm{Pr}}} \tag{6}$$

where D_{Nd} and D_{Pr} are distribution coefficients of Nd and Pr, respectively.

PC88A is an acidic ion exchange extractant and has an affinity for the lanthanide cations [8]. This reaction releases a hydrogen ion from the extractant in exchange for a metal ion [9]. PC88A is an excellent extractant and is more effective for separation purposes than other commercially available and industrially used extractants such as DEHPA. PC88A is used in the refining of REEs. It can help in cost reduction of mineral acid in the stripping and reduce the cost of alkali in neutralizing an acidic aqueous solution [10]. The structure of PC88A is shown in Fig. 1a, which shows that PC88A has a phosphonic acid structure as compared to DEHPA (Fig. 1b) which has a phosphoric acid structure.

Cyanex 572 is a novel phosphorus-based chelating extractant developed by Cytec that is mainly designed to enhance the solvent extraction efficiency and separation amongst different REEs compared to the commonly used phosphonic acid based extractants [11]. Although the composition of Cyanex 572 has not been disclosed, it is considered a mixture of phosphonic and phosphinic acids [12]. The main advantage of Cyanex 572 is in separating heavy REEs and that it requires less acid for effective stripping compared to other available phosphonic acid extractants [11]. Fig. 1c shows the structure of TOPO, which is a neutral extractant used in this study.



(a) PC88A (b) DEHPA (c) TOPO

Fig. 1. The structure of the extractants used in this study.

3. Experimental design

The Taguchi design was used as the experimental design strategy because of the distinct advantages it offers over conventional experimental design methods. In this method, orthogonal arrays are used to study a large number of variables using a smaller number of experiments. The orthogonal arrays are derived from the full factorial experiments, where each experimental variable occurs the same number of times in such a way that no experimental runs are the same [13–15]. The steps involved in Taguchi's approach are shown as a box diagram in Fig. 2. Once a target value is defined, a loss function is used to measure the performance characteristics that deviate from the target value [13–15], which is a standard tool representing the ratio of sensitivity to variability and used to optimize the process [16]. In this regard, the larger average response corresponds to the optimum response or better performance characteristic [14,15].

The experiments were performed in random order to minimize the sources of experimental noise that could affect the results. The scoping experiments revealed no significant interaction between the experimental parameters, which was further verified through confirmation experiments. The L_{16} orthogonal array that can handle five parameters, each at four levels, was selected because it was found to be the most suitable matrix for the solvent extraction experiments. Each experiment was repeated one time at different times to understand the effects of noise sources on the solvent extraction process. The L_{16} orthogonal array and the experimental levels for each parameter are shown in Table 1.

Acidity of the aqueous solution (initial pH), concentration of REEs, extractant type, extractant concentration, and acid type were chosen as experimental variables. Except for the acid type, which was varied at two levels, all other experimental parameters were varied at four levels. These levels were chosen based on the authors' experience and the preliminary experiments. Based on scoping experiments, organic to aqueous (O/A) volume ratio was fixed at 1:1. In the Taguchi design of experiments, the experiment corresponding to the optimum operating conditions might not correspond to one of the experiments listed in Table 1 in which case the experimental response corresponding to the optimum experimental conditions can be estimated by using Eq. (7).

$$Y_{opt} = \frac{T}{n} + \left(\bar{A}_i - \frac{T}{n}\right) + \left(\bar{B}_j - \frac{T}{n}\right) + \cdots \tag{7}$$

where n is the total number of experiments, T is the sum of all responses, and $\bar{A}_i, \bar{B}_j, \ldots$ are the average responses at levels i, j, etc. Also, the confidence interval at the desired error level is calculated using Eq. (8).

$$\text{C.I.} = \pm\sqrt{\frac{F(1, n_2)V_e}{N_e}} \tag{8}$$

where F is the statistical value of F at the chosen confidence level using the degrees of freedom of 1 and degrees of freedom of error (n_2), V_e is the variance of error, and N_e is the effective number of replications.

The behavior of the dissolved Nd^{3+} and Pr^{3+} aqueous species can be best represented by analyzing the speciation diagrams. At the chosen experimental conditions that represent this research (Nd and Pr concentration of 20 ppm, and chloride and sulfate concentration of 0.01 M), in the pH range of 2 to 5, the predominant species for both Nd and Pr were found to be the cationic species Nd^{3+} and Pr^{3+}, accompanied by a small fraction of the cationic species $NdCl^{2+}$ and $PrCl^{2+}$, indicating that the cationic extractants are the best choices for the extraction and separation of Nd from Pr in chloride solutions. In this pH range in chloride solutions, Nd and Pr do not show any tendency to form any complexes with chloride ions.

However, both Nd and Pr have strong tendency to form complexes with sulfate ions, but for both Nd and Pr, the cationic complexes $NdSO_4^+$ and $PrSO_4^+$ take over. Both metals form anionic complexes in sulfate solutions, $Nd(SO_4)_2^-$ and $Pr(SO_4)_2^-$. The existence of anionic complexes could result in inferior extraction of these elements using acidic extractants from sulfate solutions when compared to chloride solutions.

4. Materials and methods

Organic extractants DEHPA (≥95%), PC88A (>95%), TOPO (99%, ReagentPlus®) and Cyanex 572 were obtained from SNF Flomin, DAIHACHI Chemical (Japan), Sigma Aldrich and Cytec (now Solvay), respectively. Reagent-grade kerosene was purchased from Sigma–Aldrich and was used as the diluent for the organic extractants. Neodymium oxide (Nd_2O_3) and praseodymium oxide (Pr_2O_3), each of 99.9% purity, supplied by Alfa Aesar™, were used for the preparation of stock solutions of Nd(III) and Pr(III) in different acids. The required amounts of Pr_2O_3 and Nd_2O_3 were dissolved

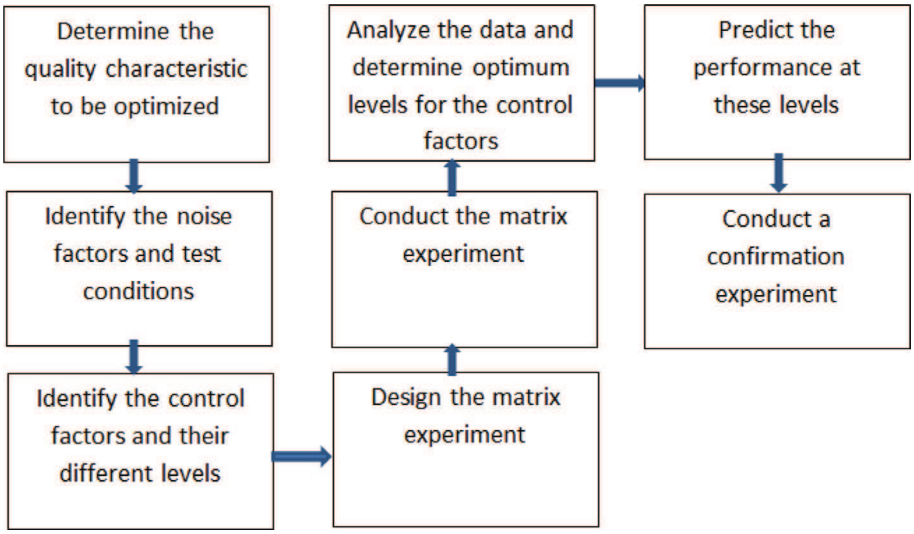


Fig. 2. Overview of the Taguchi design of experiments [16].

Table 1

L_{16} ($4^4 \times 2^1$) Taguchi matrix used in this research.

Experiment No.	Experimental parameters					Experimental results		
	pH	[REE], ppm	Extractant type	[Extractant], mM	Acid type	$\beta_{Nd/Pr}$ Run 1	$\beta_{Nd/Pr}$ Run 2	$\bar{Y}$
1	2.0	10	DEHPA	10	H_2SO_4	1.60	1.60	1.60
2	2.0	20	PC88A	20	H_2SO_4	1.11	1.17	1.14
3	2.0	30	TOPO	30	HCl	1.24	1.18	1.21
4	2.0	40	Cyanex 572	60	HCl	1.72	1.59	1.66
5	3.0	10	PC88A	30	HCl	2.11	1.99	2.05
6	3.0	20	DEHPA	60	HCl	1.00	2.20	1.60
7	3.0	30	Cyanex 572	10	H_2SO_4	1.30	1.72	1.51
8	3.0	40	TOPO	20	H_2SO_4	1.09	1.06	1.07
9	4.0	10	TOPO	60	H_2SO_4	1.09	1.10	1.10
10	4.0	20	Cyanex 572	30	H_2SO_4	1.64	1.66	1.65
11	4.0	30	DEHPA	20	HCl	2.60	2.40	2.50
12	4.0	40	PC88A	10	HCl	1.74	1.75	1.75
13	5.0	10	Cyanex 572	20	HCl	2.02	1.84	1.93
14	5.0	20	TOPO	10	HCl	2.73	1.96	2.35
15	5.0	30	PC88A	60	H_2SO_4	1.80	1.67	1.73
16	5.0	40	DEHPA	30	H_2SO_4	2.50	2.25	2.38

in each of the acids: H_2SO_4 (96.5%) and HCl (37.2% pure), all supplied by Fisher Scientific.

Adjustments to the pH were made by dropwise addition of either concentrated NaOH solution (made from 99.0% pure certified ACS NaOH pellets) or the relevant acids consistent with the aqueous matrix used. An Omega PHB-600R pH meter was used for pH measurements.

After preparation of both organic and aqueous solutions, the extraction experiments were performed at a total volume of 30 mL using 100 mL separatory funnels. The separatory funnels were shaken vigorously in an incubated shaker (Lab Companion SI-300 benchtop) for 10 min to reach equilibrium. This time was chosen based on the preliminary experiments, which showed that the equilibrium is reached practically within the first 5 min of the reaction. All experiments were performed at room temperature (25 °C). After equilibrium was reached, the funnels were removed from the shaker and were allowed to settle for two minutes. The aqueous solutions were first separated from the organic phase then diluted using 2 %vol nitric acid solution and analyzed by an inductively coupled plasma mass spectrometer (Agilent Technologies 7900 ICP-MS).

5. Results and discussion

The experimental responses (separation factors $\beta_{Nd/Pr}$) based on the L_{16} Taguchi plan of attack are listed in Table 1. The experimental data were analyzed using an EXCEL® spreadsheet and also Minitab to assess the effect of each experimental parameter on the optimization criterion, which was maximizing the separation factor. In this regard, analysis of variance (ANOVA) was used to examine the effects of the experimental parameters' variation on the average response and also to quantify the contribution of each parameter on the performance statistics. The results are shown in Table 2, where it is noted that the concentration of REE is 'pooled'. Pooling is performed when the percentage contribution of a parameter is small, in which case the sum of squares (*S*) for that parameter is merged with that for error.

The marginal mean plots are shown in Fig. 3, where the effects of controllable factors on the mean response ($\beta_{Nd/Pr}$) can be followed. According to Fig. 3, variation of the initial pH had the greatest effect on the separation of Nd from Pr, so that by increasing the initial pH, the average response significantly increased. This is further confirmed by looking at the percent contribution value (P) reported for pH in ANOVA table (Table 2). It is also noted from Table 2 that the extractant type followed by acid type had the greatest effects on the average response ($\beta_{Nd/Pr}$), which is further confirmed by performance statistics plots. For maximizing the $\beta_{Nd/Pr}$, the *F* values of pH, extractant type, and acid type factors are greater than the extracted *F* values (*F* = 3.07 for pH and extractant type and *F* = 4.32 for acid type) from the *F*-table for a 95% confidence level. This means that the variances of these factors are significant compared to the variance of error and only these factors have meaningful effects on the $\beta_{Nd/Pr}$. All of these factors affect the mechanism of the extraction reaction. The increase in separation factor as a result of increase in pH can be explained by the higher equilibrium constant of Nd extraction reaction over that for Pr represented by Eq. (1). This is consistent with the fact that increasing of pH will drive the extraction reaction to the right. Therefore, pH of 5 was chosen as optimum level for pH. Variation of concentration of REE did not affect the response significantly, indicating that there have been enough organic molecules available for the extraction. Extractant type played a significant role in the separation of Nd from Pr. The $\beta_{Nd/Pr}$ for different extractants followed the order DEHPA > PC88A > Cyanex 572 > TOPO, which shows that DEHPA acted better than the other acidic extractants PC88A and Cyanex 572 in terms of the separation of Nd from Pr. While the extraction of Nd and Pr using acidic extractants can be conveniently represented by Eq. (3), their extraction with TOPO can be written as follows:

$$(\mathrm{Nd\ or\ Pr})^{3+} + 3\mathrm{Cl}^- + m\,\overline{\mathrm{TOPO}} \leftrightarrows \overline{(\mathrm{Nd\ or\ Pr})\mathrm{Cl}_3(\mathrm{TOPO})_m} \quad (9)$$

Table 2

Analysis of variance (ANOVA) based on the average response for the separation of Nd from Pr.

Experimental parameters	*S*	*f*	*V* (*S*/*f*)	*F*	*S′*	*P*
pH (A)	2.14	3	0.71	6.52	1.81	24.73
[REE], ppm (B)	Pooled					
Extractant type (C)	1.40	3	0.47	4.26	1.07	14.59
[Extractant], mM (D)	0.47	3	0.16	1.42	0.14	1.87
Acid type (E)	1.03	1	1.03	9.36	0.92	12.49
Error/others	2.30	21	0.11	1.00		46.31
Total	7.34	31	–	–	–	100

$F = 3.07$, $F_{Acid\ Type} = 4.32$.
S: Sum of squares.
f: Degrees of freedom.
V: Mean square variance.
S′: Pure sum of squares.
P: Percentage contribution on response.

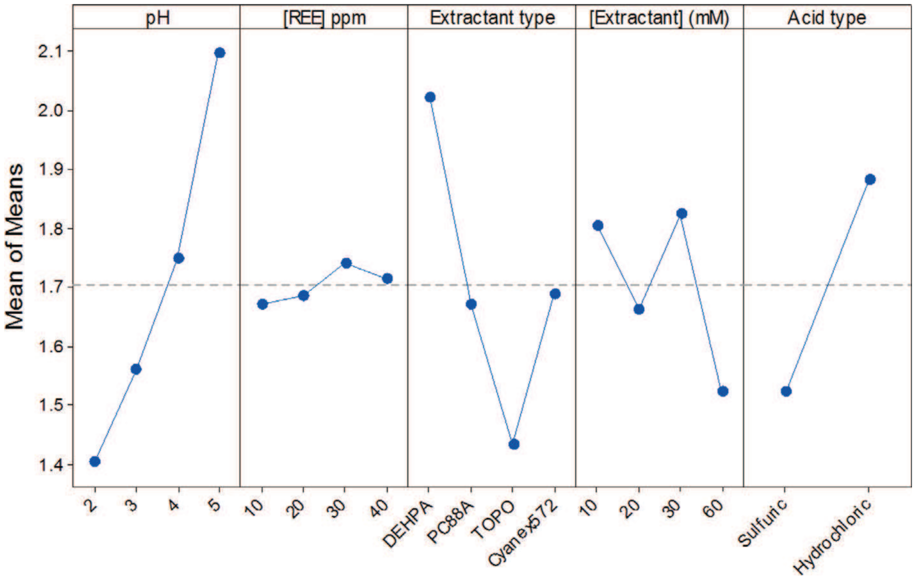


Fig. 3. The effect of controllable factors on the average separation factor ($\beta_{Nd/Pr}$).

$$(\text{Nd or Pr})^{3+} + 1.5\text{SO}_4^{2-} + m\,\overline{\text{TOPO}} \leftrightarrows \overline{(\text{Nd or Pr})(\text{SO}_4)_{1.5}(\text{TOPO})_m} \quad (10)$$

This is consistent with the fact that the extraction mechanism for both Nd and Pr is a cationic exchange mechanism. The extractant concentration had minor effect on $\beta_{Nd/Pr}$, indicating that the ratio of extractant to metal ion concentration was enough to reach maximum extraction.

Finally, acid type was another influencing factor on the separation of Nd from Pr. It is clear that hydrochloric acid acted better than sulfuric acid for separation purposes. The reason behind this might be the formation of anionic complexes in sulfuric acid explained earlier. The presence of anionic complexes would negatively affect the extraction, which is dominated by cationic exchange mechanism. This point particularly explains one of the reasons why hydrochloric acid-based solutions are preferred for the separation of REEs.

The contribution from error/others (46.31%) suggests that there should be other controllable factors influencing the separation of Nd from Pr that were not investigated in this study, including contact time, temperature, and O/A ratio. However, based on the literature it is less likely that any of the mentioned factors would have contributions greater than pH and extractant type.

Table 3
Comparison of experimental and predicted results.

Experiment	Run 1 $\beta_{Nd/Pr}$	Run 2 $\beta_{Nd/Pr}$	Average $\beta_{Nd/Pr}$	Predicted $\beta_{Nd/Pr}$
$A_4B_3C_1D_3E_2$	2.74	2.71	2.72	2.75 ± 0.58

6. Optimization of separation

After modeling the significant effects using Taguchi design, the optimum levels of exerimental parameters can be selected. The results showed that the maximum separation factor occurs

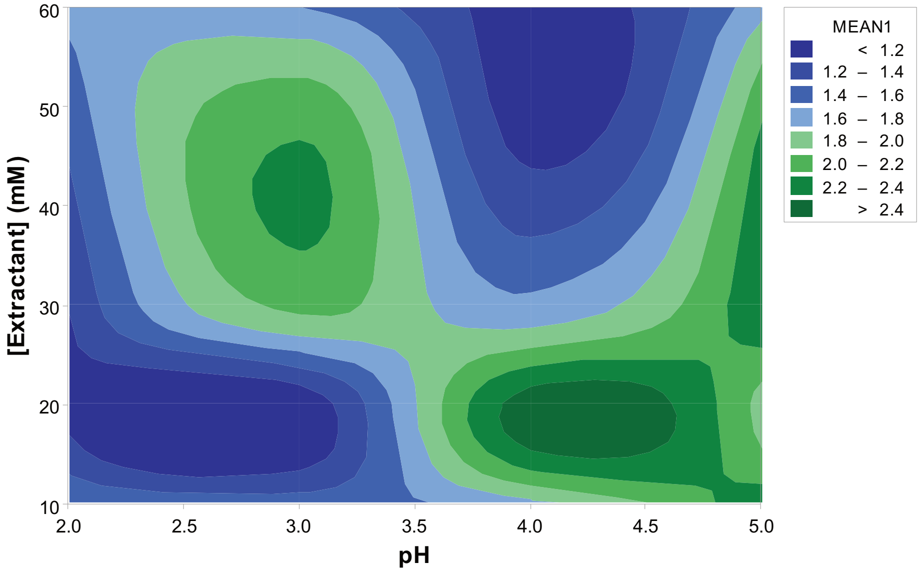


Fig. 4. Contour plots showing response surfaces for pH against extractant concentration.

through the experiment $A_4B_3C_1D_3E_2$, which is not one of the experimental runs performed in the experimental plan. Therefore the expected response ($\beta_{Nd/Pr}$) and the confidence interval were calculated based on Eqs. (7) and (8) and the results at 95% confidence level are shown in Table 3. Two confirmation experiments were performed to validate the results of optimization, and it was found that the average result was within the calculated confidence interval (Table 3). This is an indication that the interactive effects of experimental parameters were negligible and thus the design plan was a credible one [13].

Furthermore, the contour plot between extractant concentration and pH (Fig. 4) shows the areas where maximum separation of Nd from Pr can take place, which occurs in the pH range of 3.8 to 4.6 and extractant concentration range of 15 to 22 mM.

7. Conclusions

Although the separation of Nd from Pr has been a matter of research over the past years, comparing the performance of different extractants under similar experimental conditions using different aqueous media remains open to research. Also, it was the intention of this research to report on the recently available acidic extractant Cyanex 572 and its performance for the separation of Nd from Pr. This question was answered by using a statistical plan of attack, which was designed to study five experimental parameters at four levels. This included initial pH of the aqueous solutions (2–5), concentration of rare earth element (10–40 ppm), extractant type (DEHPA, PC88A, TOPO, and Cyanex 572), extractant concentration (10–60 mM), and acid type (sulfuric and hydrochloric acid). While the concentration of Nd and Pr and also the concentration of extractant had little effect on the separation of the two metals, pH, extractant type and acid type had the greatest effects on $\beta_{Nd/Pr}$. A pH of 5, DEHPA, and hydrochloric acid were found to be the best combination of the experimental parameters to achieve the maximum $\beta_{Nd/Pr}$. The better performance of hydrochloric acid for separation was attributed to the resistance of Nd and Pr to form chloride species and their tendency to form cationic and anionic complexes in sulfate solutions ($NdSO_4^+$, $PrSO_4^+$, $Nd(SO_4)_2^-$,and $Pr(SO_4)_2^-$) under the experimental conditions studied. Given the cationic exchange nature of the extraction reaction, the anionic species would not be extracted with any of the organophosphorus extractants, thereby influencing the extraction and separation in a negative way. Cyanex 572, which is supposed to be a mixture of phosphonic and phosphinic acids did not show a remarkable performance in separating Nd from Pr. The separation performance of organic extractants among the extractants studied followed the order DEHPA > PC88A > Cyanex 572 > TOPO, and the maximum separation factor achieved under optimum conditions was 2.72. This value of $\beta_{Nd/Pr}$ is higher than any other value reported in the open literature.

Acknowledgements

The authors would like to thank the National Science Foundation for providing the funds through REU Back to the Future Site DMR-1460912. Also, we are thankful to Mr. Russ Lingenfelter for running the ICP analyses.

References

[1] K. Street Jr., G.T. Seaborg, The separation of americium and curium from the rare earth elements, J. Am. Chem. Soc. 72 (6) (1950) 2790.
[2] K.L. Nash, G.R. Choppin, Separations chemistry for actinide elements: recent developments and historical perspective, Sep. Sci. Technol. 32 (1–4) (1997) 255.
[3] G.R. Choppin, Ion exchange studies of the actinide elements, J. Chem. Educ. 36 (9) (1959) 462.
[4] K.S. Pitzer, Relativistic effects on chemical properties, Acc. Chem. Res. 12 (8) (1979) 271.
[5] Y. Liu, H.S. Jeon, M.S. Lee, Solvent extraction of Pr and Nd from chloride solution by the mixtures of Cyanex 272 and amine extractants, Hydrometallurgy 150 (2014) 61.
[6] R. Banda, H.S. Jeon, M.S. Lee, Separation of Nd from mixed chloride solutions with Pr by extraction with saponified PC 88A and scrubbing, J. Ind. Eng. Chem. 21 (2015) 436.
[7] R. Banda, H.S. Jeon, M.S. Lee, Solvent extraction separation of La from chloride solution containing Pr and Nd with Cyanex 272, Hydrometallurgy 121–124 (2012) 74.
[8] M. Nilsson, P.R. Zalupski, M.R. Antonio, Supramolecular aspects of stable water-in-oil microemulsions in chemical separations. Ion exchange and solvent extraction: volume 21, Supramolecular Aspects of Solvent Extraction 197, 2013.
[9] M.-S. Lee, G.-S. Lee, J.-Y. Lee, S.-D. Kim, J.-S. Kim, Solvent extraction of Sm from chloride solution with PC88A and saponified PC88A, Mater. Trans. 46 (1) (2005) 64.
[10] A. Mukherjee, S. Kamila, V. Chakravortty, Antagonism in the extraction of uranium (VI) by the binary mixture of PC88A and benzimidazole, J. Radioanal. Nucl. Chem. 242 (3) (1999) 799.
[11] Cytec, Cyanex 572 Solvent Extraction Reagent, 2014.
[12] C. Tunsu, J.B. Lapp, C. Ekberg, T. Retegan, Selective separation of yttrium and europium using Cyanex 572 for applications in fluorescent lamp waste processing, Hydrometallurgy 166 (2016) 98.
[13] R.K. Roy, A Primer on the Taguchi Method, Van Nostrand Reinhold, New York, 1995.
[14] M.S. Safarzadeh, D. Moradkhani, M.O. Ilkhchi, Determination of the optimum conditions for the cementation of cadmium with zinc powder in sulfate medium, Chem. Eng. Process. 46 (2007) 1332.
[15] M.S. Safarzadeh, D. Moradkhani, M.O. Ilkhchi, N.H. Golshan, Determination of the optimum conditions for the leaching of Cd–Ni residues from electrolytic zinc plant using statistical design of experiments, Sep. Purif. Technol. 58 (2008) 367.
[16] N. Dhawan, M.S. Safarzadeh, J.D. Miller, M.S. Moats, M.L. Free, Understanding the agglomeration behavior of nickel laterite and gold ores using statistical design of experiments, Miner. Metall. Process. 31 (1) (2014) 21.