Korean J. Chem. Eng., **28**(2), 557-562 (2011)
DOI: 10.1007/s11814-010-0383-4

Rare earth elements leaching from Chadormalu apatite concentrate: Laboratory studies and regression predictions

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(*Received 21 December 2009 • accepted 20 July 2010*)

Abstract−The extraction of rare earth elements from apatite concentrate of Chadormalu plant of Iran was studied with the dissolution of ore in nitric acid. The parameters of acidity: 60%, solid to liquid ratio: 30%, leaching time: 30 minute, agitation rate: 200 rpm, temperature: 60 °C and particle size (d_{80}): 50 microns were determined as the optimum operational conditions. The recoveries of lanthanum, cerium, neodymium and yttrium were achieved at 74, 59, 72 and 73%, respectively, in the optimized conditions. Multivariable regression was used to predict La, Ce, Nd, Y and total REEs (Y+Nd+Ce+La) leaching recoveries, using experimental data from laboratory studies. It was achieved quite satisfactory correlations of 0.93, 0.98, 0.99, 0.97 and 0.99 for the prediction of Y, Nd, Ce, La and total REEs recoveries, respectively. It was shown that the proposed equations accurately reproduce the effects of operational variables on the different REEs recoveries, and can be used to optimize the REEs leaching plant.

Key words: Leaching, Apatite, Rare Earth Elements, Regression

INTRODUCTION

Rare earth elements (REEs) are a group of elements with atomic numbers 57 through 71. Yttrium with atomic number 39 is included with the rare earth elements because it often occurs with them in nature and has similar chemical properties [1]. The most common rare earth elements containing minerals are apatite, monazite and, more rarely, xenotime. The general formula for apatite is $Ca_{10}(PO_4)_6X_2$, X being a fluorine, chlorine ion or an hydroxyl group [2]. Apatite containing average 0.1-0.8% rare earth oxides is the main source of phosphate fertilizers and phosphoric acid [3].

The REEs have a high application interest in many fields. For instance, Y and Sm have an interesting application in the field of nuclear technology due to the low cross-section for neutron capture and high temperature stability of their oxides. Cerium oxide is uniquely suited as a polishing agent for glass. Permanent magnet technology has been revolutionized by alloys containing Nd, Sm, Gd, Dy, or Pr [4,5].

La, Y, Sm, and Nd oxides find application in the ceramic industry for coloring glass and as glazers. Gadolinium is useful in nuclear technology in fuel element fabrication and as control rods, and as refractory material and in ceramic industries. Yttrium is used in many applications, as in the manufacture of superconductors, in the composition of phosphors, in super alloys of nickel and cobalt as well, and in electronic materials and solid oxide fuel cells [4,5]. Lanthanum continues to be used in the fabrication of mischmetal alloy, in the composition of special glasses [4] and, more recently, into catalyst zeolite for use in the cracking of petroleum.

Iran is a REEs importer country. One of the by-products of Chadormalu iron ore concentrator plant is apatite concentrate which is rich in rare earth elements [6]. The Chadormalu iron deposit is located in Yazd province in the center of Iran and the ore is being exploited in an open pit operation. The feed of plant consists of magnetite, hematite, martite, quartz, apatite, gypsum, biotite and anhydrite minerals. The plant concentrates are iron ores, hematite and magnetite, and apatite is a by- product [7].

The objectives of the present work are (a) to optimize the operating variables in the leaching of REEs from apatite concentrate; and (b) to determine the multivariable relationship between REEs leaching recovery and operational variables as leaching time, pulp density, leaching agent concentration, agitation rate, with the use of experimental data from laboratory studies. In this work, for the first time in the literature, regression was introduced as an efficient tool for the prediction of REEs recoveries in the leaching process.

REES LEACHING FROM APATITE

Nitric, sulfuric and hydrochloride acids have been used as leaching reagents for extracting of REEs from apatite. The recovery of REEs and the type of products which are yielded in the leaching process does vary dependent on leaching agent [8,9].

REEs could be extracted as a by product of manufacturing phosphoric acid. Phosphoric acid is conventionally produced from the reaction of phosphate ore with sulfuric acid in the so-called wet processes according to following reaction.

$$Ca_{10}(PO_4)_6F_2+10H_2SO_4 \rightarrow 6H_3PO_4+10CaSO_4.xH_2O+2HF \quad (1)$$

In the above-mentioned reaction most of the REEs contribute in the gypsum by-product and it must be followed by gypsum leaching in order to extract REEs [8-13]. REEs could also be recovered from phosphoric acid sludge [14,15].

Once nitric acid is used as leaching agent for the extraction of REEs, most of REEs substituted in the apatite lattice for calcium

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Table 1. Assay of light REEs in apatite concentrate

Light rare earth elements	La	Ce	Pr	Nd	Sm	Eu	Total
Assay (ppm)	1514	4204	455	1738	293	24.5	8228.5
Assay distribution (%)	18.39	51.1	5.52	21.12	3.58	0.29	100

Table 2. Assay of heavy REEs in apatite concentrate

Heavy rare earth elements	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Total
Assay (ppm)	233	28.9	145	24.2	63.2	7.76	40.9	4.94	855	1402.9
Assay distribution (%)	16.61	2.07	10.34	1.73	4.51	0.55	2.9	0.35	60.94	100

ion would be recovered [3,8,16-22].

$$Ca_{10}(PO_4)_6F_2+20\ HNO_3 \rightarrow 6H_3PO_4+10\ Ca\ (NO_3)_2+2\ HF \qquad (2)$$

Hydrochloride acid is scarcely used for extracting of REEs from apatite in laboratory scale but it has not found industrial application [8].

Despite the popularity of REEs extraction from phosphate fertilizer industry, it includes some disadvantages as follows [23].

a- Generation of large amount of gypsum that is likely to be radioactive and it represents storage and environmental problems.

b- Extensive material handling problems.

Although nitric acid is expensive in comparison with sulfuric acid, the gypsum problems could be eliminated by using it. Considering above-mentioned considerations, nitric acid was used as leaching agent to extract REEs from apatite concentrate.

EXPERIMENTAL METHODS

1. Sampling

Different samples were prepared from apatite concentrate during different working shifts of the Chadormalu plant and representative samples were prepared by conning and quartering methods. The representative samples with d_{80}:50 microns were used for characterization and leaching studies without any further size reduction.

2. Analytical Methods

Although there are many analytical techniques used for determination of REEs in geological samples, inductive coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are the most popular ones [24]. In this study the REEs were detected by means of ICP-MS in ACME analytical laboratories in Canada (for apatite concentrate) also ICP-AES of geological survey of Iran (for pregnant liquors). The Brunker diffraction unit from geological survey of Iran was used in order to identify the mineral constituents of the samples.

3. Leaching Studies

The leaching experiments were carried out using nitric acid with concentrations of 20, 35, 50 and 60%, reaction times of 10, 20, 30 and 40 minutes, particle size (d_{80}) of 50 micron, solid to liquid ratios of 30, 40 and 50%, agitation rates of 100, 150 and 200 rpm and temperature of 60 °C. Following the reaction, the reactor was cooled and the pulp filtered to recover the pregnant liquor. The filtrate was washed with hot water, and the pregnant liquor was analyzed for REEs by ICP-AES. The chemical reagents were obtained from the Merck manufacturer.

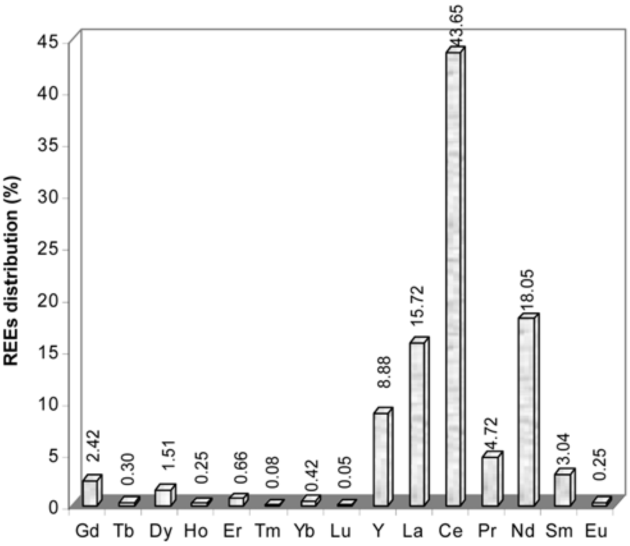

Fig. 1. Distribution of different REEs in apatite concentrate.

RESULTS AND DISCUSSIONS

1. Characterization of Apatite Concentrate

The assays of each light and heavy REEs in apatite concentrate are shown in Tables 1 and 2, respectively. As it can be seen from Tables 1 and 2, total of light and heavy REEs are 8228.5 and 1402.9 ppm respectively. Cerium and yttrium, with 51.1 and 60.94%, are predominant forms of light and heavy REEs, respectively, on apatite concentrate.

The REEs distribution in apatite concentrate in comparison to each other is shown in Fig. 1 as well. It is understood from this figure that cerium with distribution of 43.65% is the predominant form of REEs in apatite concentrate. The ICP-MS studies also revealed the absence of radioactive elements (Uranium and Thorium) in the apatite concentrate. This considerably simplifies and cheapens the technology of obtaining the commodity REE products because the REEs extracted from apatite are also not radioactive and hence, do not require decontamination or question about burying the radioactive wastes.

According to the XRD analysis fluorapatite, ankerite and calcite are the mineral phases of apatite concentrate of which the fluorapatite is the dominant one.

2. Effect of Pulp Density and Acidity

In the first stage of experiment, nine leaching tests were con-

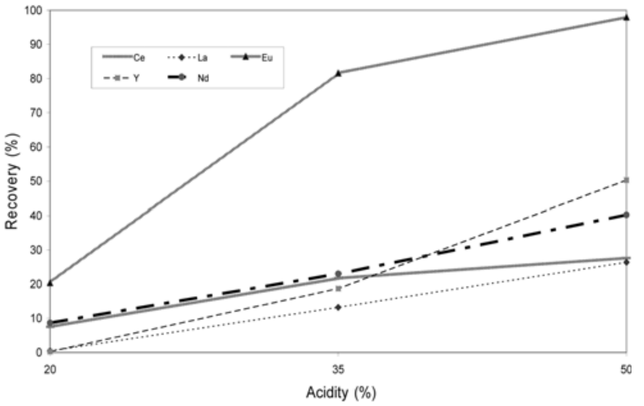

Fig. 2. The influence of acidity on REEs recovery (S/*l*: 0.3, leaching time: 10 min, agitation rate: 150 rpm).

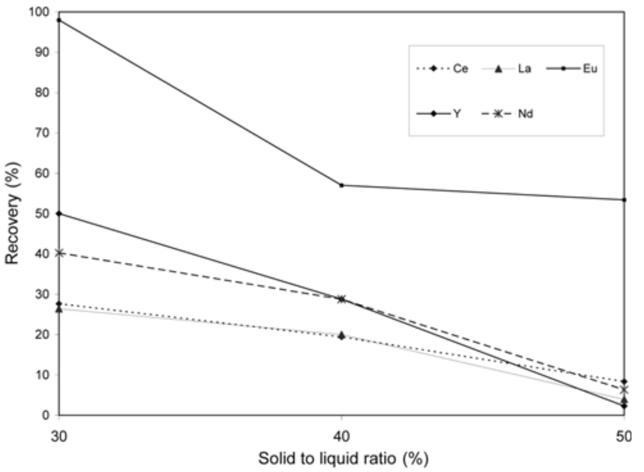

Fig. 3. The influence of solid to liquid ratio on REEs recovery (acidity: 50%, leaching time: 10 min, agitation rate: 150 rpm).

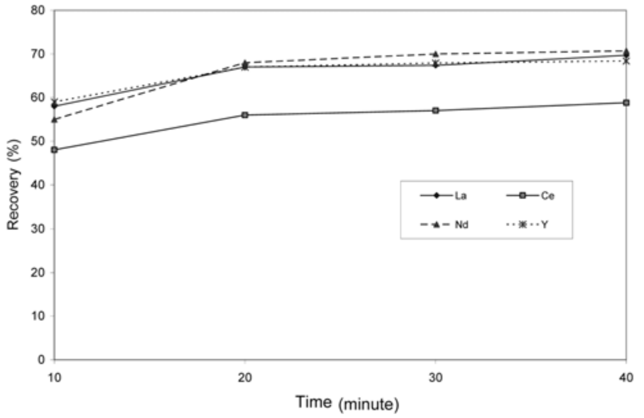

Fig. 4. The influence of leaching time on REEs recovery (S/*l*: 0.3, agitation rate: 100 rpm, acidity: 60%).

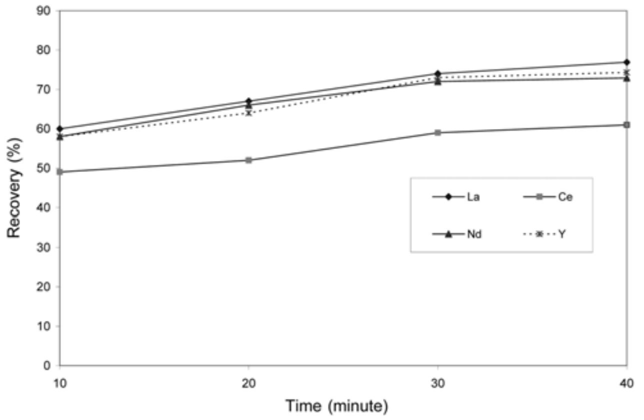

Fig. 5. The influence of leaching time on REEs recovery (S/*l*: 0.3, agitation rate: 200 rpm, acidity: 60%).

ducted, three different acidities (v/v) (20, 35 and 50) were used for three solid to liquid ratios (w/w) (30, 40, and 50), and temperature, leaching time, agitation rate and particle size were 60 °C, 10 min, 150 rpm and less than 50 micron (d_{80}), respectively. The temperature does not influence the leaching efficiency of rare earths, but higher temperature is advantageous to the volatilization of S and F [3].

Fig. 2 illustrates the effect of acidity on recovery of REEs for solid to liquid ratio 0.3. It is evident that recovery of REEs is enhanced by an increase in the acidity.

Fig. 3 indicates the effect of solid to liquid ratio on recovery of REEs for acidity=50% (v/v); it can be seen that recovery of REEs decreases by an increase of solid to liquid ratio.

3. Effect of Agitation Rate and Leaching Time

To assess whether or not REEs recovery enhances by increasing acidity more than 50%, nitric acid concentration of 60% (v/v) was used in the second stage of experiment. To investigate the effect of leaching time and agitation rate on REEs recovery, 8 leaching tests were performed which four different leaching times (10, 20, 30, and 40 minutes) were used for two different agitation rate (100, 200 rpm) and solid to liquid ratio and acidity were kept 30% (w/w) and 60% (v/v) respectively.

Figs. 4 and 5 illustrate the influence of leaching time and agitation rates of 100 and 200 rpm on REEs recovery, respectively. It can be seen from Fig. 4 that once agitation rate was kept at 100 rpm, with increasing of leaching time from 10 to 20 minute, recoveries of La, Ce, Nd and Y increased from 58, 48, 55 and 59% to 67, 56, 68 and 67%, respectively. After the mentioned time, the REEs recovery was not changed substantially.

As it can be seen from Fig. 5, in agitation rate of 200 rpm, likewise agitation rate equal to 100 rpm, the recovery of REEs increased with increasing of leaching time from 10 to 30 minutes and it does not change substantially after 30 minutes. Subsequently, the conditions of acidity--60%, solid to liquid ratio: 30%, leaching time: 30 minute, agitation rate: 200 rpm and temperature: 60 °C--were selected as optimum operating conditions for REEs extraction. In these conditions the recoveries of La, Ce, Nd, Y and Eu were achieved 74, 59, 72, 73, and 98%, respectively. The leaching test on optimized conditions was performed in duplicate to evaluate of experimental reproducibility.

4. Regression Prediction of REEs Recoveries

Modeling by regression has many applications in chemical engineering methods [25-27]. In this study, by least square mathematical method, the correlation coefficients of La, Ce, Nd, Y and total

Table 3. The correlation coefficients of La, Ce, Nd, Y and total rare earth elements leaching recoveries with operational variables

Variables	Total recovery	Time	S/L	Acidity	RPM
Total recovery	1	0.74	−0.73	0.89	−0.001
La recovery	0.97	0.75	−0.64	0.87	0.046
Ce recovery	0.99	0.74	−0.75	0.88	0.004
Nd recovery	0.99	0.74	−0.77	0.88	0.016
Y recovery	0.97	0.71	−0.7	0.86	0.021

rare earth elements (La+Ce+Nd+Y) leaching recoveries with operational variables of leaching time (min), solid to liquid (%), acidity (%) and agitation rate (rpm) were determined and are shown in Table 3. It can be seen that the higher leaching time and acidity can result in higher rare earth elements recovery. The results also show that the increase of the solid to liquid ratio can achieve lower recovery for the mentioned rare earth elements.

The best correlated equations between the various mentioned parameters with La, Ce, Nd, Y and total rare earth elements leaching recoveries, can be shown as follows:

$$\textbf{Lanthanum recovery}\ (\%)=418.242+0.466\ \text{Time}-0.167\text{S/L}+3.282\text{Acidity}-6.248\text{RPM}-0.039\ \text{Acidity}^2+0.021\text{RPM}^2\ R^2=0.97 \quad (3)$$

$$\textbf{Cerium recovery}\ (\%)=207.241+0.382\ \text{Time}-0.717\text{S/L}+1.106\text{Acidity}-2.642\text{RPM}-0.009\ \text{Acidity}^2+0.009\ \text{RPM}^2\ R^2=0.99 \quad (4)$$

$$\textbf{Neodymium recovery}\ (\%)=159.463+0.499\ \text{Time}-1.08\text{S/L}+0.421\text{Acidity}-1.713\ \text{RPM}-0.004\ \text{Acidity}^2+0.006\text{RPM}^2\ R^2=0.98 \quad (5)$$

$$\textbf{Yttrium recovery}\ (\%)=218.406+0.435\ \text{Time}-0.757\text{S/L}+2.541\text{Acidity}-0.024\text{RPM}-0.004\ \text{Acidity}^2+0.01\text{RPM}^2\ R^2=0.936 \quad (6)$$

$$\textbf{Total recovery}\ (\%)=242.282+0.343\ \text{Time}-0.665\ \text{S/L}+1.129\ \text{Acidity}-3.151\ \text{RPM}-0.007\ \text{Acidity}^2+0.011\text{RPM}^2\ R^2=0.99 \quad (7)$$

The regression estimated Nd, La, Y, Ce and total recoveries (Eqs. (3) to (7)) versus actual determined ones are shown in Figs. 6 to 10 with satisfactory correlations of 0.98, 0.97, 0.93, 0.99 and 0.99, re-

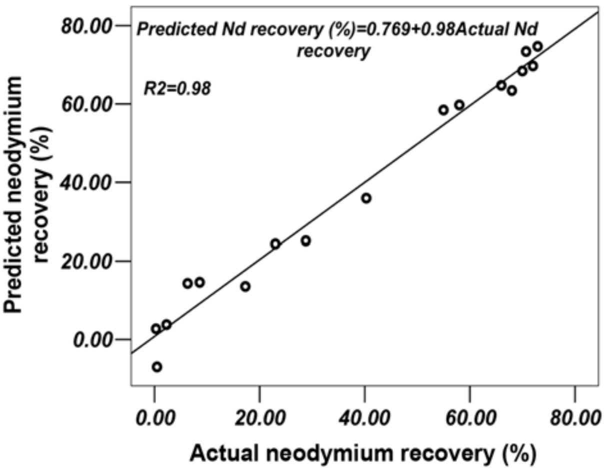

Fig. 6. Regression estimated Neodymium recovery versus actual determined in laboratory.

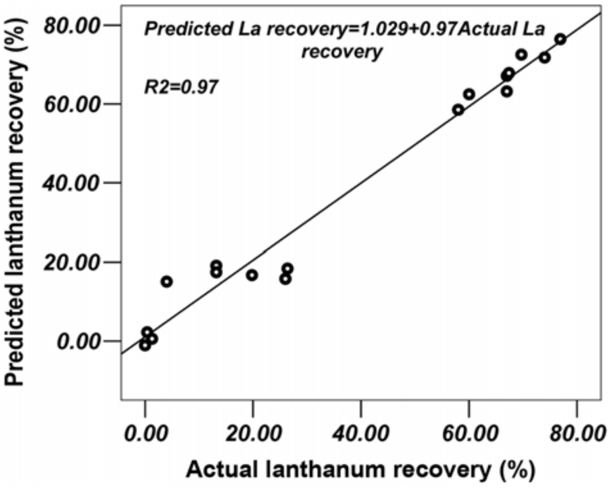

Fig. 7. Regression estimated Lanthanum recovery versus actual determined in laboratory.

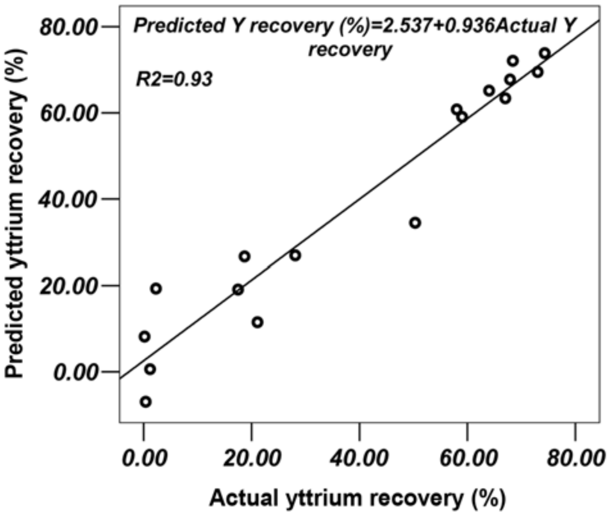

Fig. 8. Regression estimated Yttrium recovery versus actual determined in laboratory.

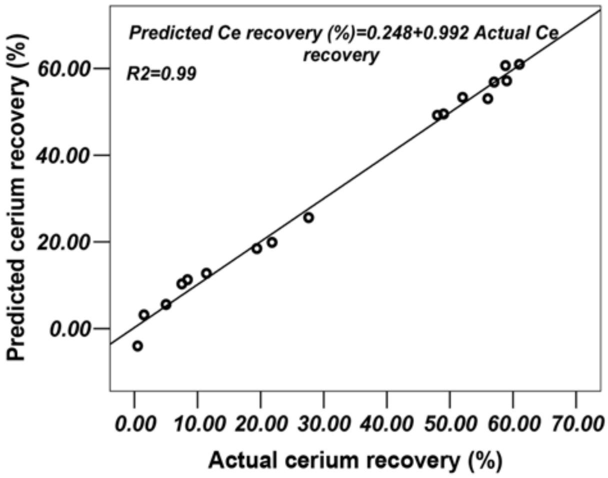

Fig. 9. Regression estimated Cerium recovery versus actual determined in laboratory.

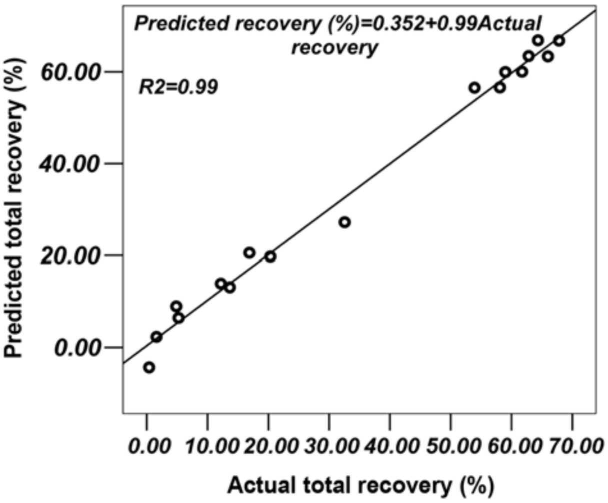

Fig. 10. Regression estimated total recovery versus actual determined in laboratory.

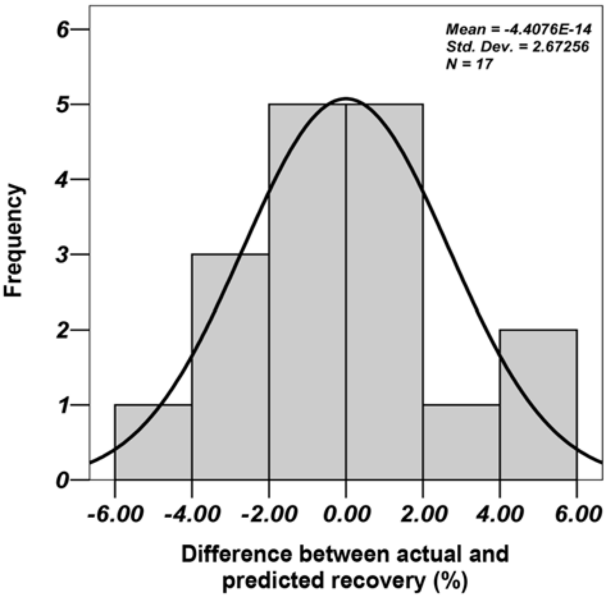

Fig. 11. The frequency of differences between actual and predicted total recovery.

spectively. The frequencies of differences between actual and predicted total recoveries are shown in Fig. 11. According to the above-mentioned significant results, it could be concluded that the proposed equations yield significant predictions of REEs recoveries and can be used for process optimization in the REEs leaching plant.

CONCLUSIONS

The conclusions drawn from this study are as follows:

- The REEs characterization studies show that the assay of predominant forms of rare earth elements, La, Ce, Nd and Y also total REEs in apatite concentrate are 1,514, 4,204, 1,738, 855 and 9,631 ppm, respectively, and cerium and yttrium, with 51.1 and 60.94%, were predominant forms of light and heavy REEs, respectively on apatite concentrate.
- Nitric acid was used as leaching agent; the influence of acidity, solid to liquid ratio, leaching time, and agitation rate on REEs extraction was investigated. The recovery of REEs enhances by increasing the acidity from 20 to 60% and decreased by increasing of solid to liquid ratio from 30 to 50%.
- The conditions of acidity: 60%, solid to liquid ratio: 30%, leaching time: 30 minute, agitation rate: 200 rpm and temperature: 60 °C– were selected as optimum operational conditions for REEs extraction. In the optimized conditions, the recoveries of La, Ce, Nd, Y and Eu were achieved 74, 59, 72, 73 and 98%, respectively.
- The correlations between REEs recoveries and individual operational variables illustrate that the increase of leaching time and acidity can result in higher rare earth elements recovery; the increase of the solid to liquid ratio also can bring about lower recovery for the mentioned rare earth elements.
- The proposed multivariable equations for prediction of La, Ce, Nd, Y and total rare earth elements recoveries were achieved R^2= 0.97, 0.99, 0.98, 0.936 and 0.99, respectively, which are quite satisfactory.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support provided by Science and Research Branch of Islamic Azad University.

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