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Leaching kinetic of Nd. Y, Pr and Sm in rare earth hydroxide (REOH) use nitric acid

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Leaching kinetic of Nd. Y, Pr and Sm in rare earth hydroxide (REOH) use nitric acid

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Abstract. The purpose of this study were to determine the order of reaction, rate reaction constant and activation energy of reaction $Y(OH)_3$, $Nd(OH)_3$, $Pr(OH)_3$ and $Sm(OH)_3$ with HNO_3. The rate reaction constant is necessary to determine the residence time in the design of continuously stirred tank reactor (CSTR). The studied parameters were leaching temperature ($60 - 90\ ^oC$) and leaching time (0-15 minutes). From the resulting data can be concluded that the leaching process were strongly influenced by the time and temperature process. Leaching rare earth hydroxide (REOH) using nitric acid follows second order. At leaching 10 grams of REOH using 40 ml HNO_3 0.0576 mol were obtained maximum conversion at 90 ^oC and leaching time 15 minutes for Y was 0.95 (leaching efficiency was 95%), for Nd was 0.97 (leaching efficiency was 97%), for Pr was 0.94 (leaching efficiency was 94%) and for Sm was 0.94 (leaching efficiency was 94%). The largest activation energy was Y of 23.34 kJ /mol followed by Pr of 20.00 kJ /mol, Sm of 17.94 kJ /mol and the smallest was Nd of 16.39 kJ /mol. The relationship between the rate constant of the reaction with T for Y was $k_Y = 338.26\ e^{-23,34/RT}$, for Nd was $k_{Nd} = 33.69\ e^{-16,39/RT}$, for Pr was $k_{Pr} = 102.04\ e^{-20/RT}$ and for Sm adalah was $k_{Sm} = 50.16\ e^{-17,94/RT}$

Keywords: REOH, HNO_3, leaching

1. Introduction

The rare earth elements (REEs) are a unique group of metals regarded as being among the most critical elements that are highly valued for their specialwased applications in many modern technologies. In the recent years, REEs have become a significant topic of interest in the metals industry due to a global supply shortage and strengthening demand[1] This has led many companies to develop processing techniques for extracting REEs from less common rare earth bearing deposits[2] and reclaiming REEs from end-of-life products by recycling (urban mining) spent batteries. phosphors and permanent magnets[3]. One of such examples was the apatite group of minerals (mainly fluorapatite) which are commonly mined for the production of phosphoric acid in the fertilwaser industry[4,5,6]. The monazite ores are known to contain significant quantities of REEs and therefore processing of monazite ores for REEs has become more prominent recently[7]. In the processing of monazite deposits however, often require a pre-leach stage prior to the acid bake stage at elevated temperature where the latter converts REE-phosphates to water soluble REE-sulphates[8].The purpose of the pre-leach stage of the ore / concentrate was to remove the disturbing calcium during the REE manufacturing stage.

Rare earths hydroxide (REOH) was a monazite process products containing REE elements namely Ce, La, Nd, Pr, Y, Sm and Gd[9]. For the separation of each of those elements. REOH should be leached, so that the solution was formed. The leaching reaction that occurs could be between the base with an acid and a base with an acid. The base will react with the acidic solution to form salt and water[10]. K. Stonea et al., who studied comparison of H_3PO_4, HCl, $HClO_4$ and HNO_3 usage leading to the leaching[11]. Leaching with HNO_3 also for laterite leaching[12]. Use of HNO_3, resulting in the greatest leaching efficiency. In general, leaching of REOH using HNO_3, because in addition of HNO_3 to easy and strong in leaching, it was also an oxidizer that will form Ce of III valence to Ce of IV valence[13]. Thus Ce will have different properties from other REE elements that have double valences of II and III, so Ce could be separated from other REE elements. Rare earth elements that are easily soluble or are leached are Y, Nd, Pr and Sm while Ce will dissolve later.

In this work, REOH was prepared from monazite sand. The leaching of REOH using HNO_3 0.0576 moles, the parameters were leaching temperature (60 – 90 ^{o}C) and leaching time (0-15 minutes). The solution product of leaching are analyzed by XRF.

The purpose of this study were to determine the order of reaction, rate reaction constant and activation energy of reaction $Y(OH)_3$, $Nd(OH)_3$, $Pr(OH)_3$ and $Sm(OH)_3$ with HNO_3. The rate reaction constant is necessary to determine the residence time in the design of continuously stirred tank reactor (CSTR).

2. Theory

The reaction rate represents the molarity of the solute in the reaction produced each reaction time[14].

$$A + B \rightarrow C$$

$$\text{The reaction rate } = r_A = -\frac{\Delta [A]}{\Delta t} = -\frac{\Delta [B]}{\Delta t} \tag{1}$$

The factors affecting the rate of reaction: temperature, catalyst, molarity and reactant concentration and factors affecting the constant or constant rate of reaction was temperature[15,16,17]. Determination of the constant and leaching reaction rate at the optimum condition of the use of the reactant ratio of REOH with HNO_3. The parameters studied were the variation of leaching time and temperature. The reactions that occurred between REOH and HNO_3 were as follows

$$RE(OH)_{3(s)} + 3HNO_{3(a)} \rightarrow RE(NO_3)_{3(a)} + 3H_2O_{(a)}[18] \tag{2}$$
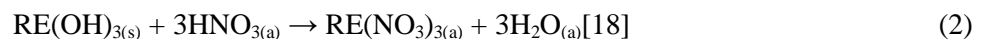
s : solid, a : solution
RE : Y, Pr, Nd, Sm

$$-r_A = k_1.C_A^n.C_B = (k1\ C_B)\ C_A^n = k\ C_A^n[19] \tag{3}$$

n = reaction order
k = the overall reaction rate constant
C_A = concentration (mol) RE
C_B = concentration (mol) HNO_3

In the initial state or t_0, the number of reagents A or NA_0 and at time t of NA, the conversion of A (X_A) at a constant volume system was[14]:

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{C_A}{C_{A0}} \tag{4}$$

$$dX_A = \frac{dC_A}{C_{A0}}$$

(5)

Data analisys was by integral begins by selecting a certain rate equation to be tested in an integral way and comparing the approximate C-curve relationship with C data to t from the experiment. If they do not match, other estimates are then tested.

First Order Reaction

In general, the first order reaction can be represented by the following reaction equation:

A → product
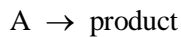
If the first order reaction, then the equation of reaction rate was[20]:

$$- r_A = \frac{dC_A}{dt} = kC_A$$

(6)

The integration of equation (7) becomes:

$$- \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k\int_0^t dt$$

(7)

$$- ln\frac{C_A}{C_{A0}} = kt$$

(8)

C_{A0} = RE concentration in the feed

C_A = RE concentration after reaction

If expressed in terms of conversion, the equation of rate reaction becomes (9):
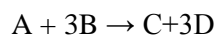
$$\frac{dX_A}{dt} = k(1 - X_A) \text{ [21]}$$

(9)

$$- ln\,(1-X_A) = kt \text{ [22]}$$

(10)

If the graph of the relationship ln (1-X_A) or ln (C_A / C_{A0}) to t was a linear line then the reaction which we observe was correct, following the first order reaction[23].

Second Order Reaction

For the second order reaction with the constant rate of reaction referring to the overall reaction rate constant, could use the following equation::

A + 3B → C+3D

$$-r_A = -C_{A0}\frac{dX_A}{dt} = -\frac{dC_B}{dt} = kC_AC_B^3 = k(C_{A0} - C_{A0}X_A)(C_{B0} - C_{A0}X_A)$$

(11)

$$- r_A = -C_{A0}\frac{dX_A}{dt} = kC_{A0}^2(1 - X_A)(M - 3X_A)$$

(12)

If it was integrated into [24,26,27]

$$\ln\frac{M-3X_A}{M(1-X_A)} = \ln\frac{C_BC_{A0}}{C_{B0}C_A} = \ln\frac{C_B}{MC_A} = = C_{A0}(M-2)kt = (C_{B0} - C_{A0})kt$$

(13)

M = comparison (mole B / mol A) start = C_{B0} / C_{A0} = mole of initial HNO_3 / mole RE

The experimental variables in equation (13) are made in the form of a $\ln\dfrac{(M - 3X_A)}{M(1 - X_A)}$ vs-t

relationship. If a linear line was obtained then the asummption of second order was correct and the C_{A0} slope (M-2) k. The value of the reaction rate constant was the slope of the linear line divided by C_{A0} (M-2).

The k relation as a function of temperature by refering to the Arrhenius equation,

$$k = e^{Ea/R.T} [28]$$

(14)

Han Wang[29], states the relationship between k and T was formulated in the equation

$$\ln k = \ln A - \left(\frac{Exp}{R}\right)\left(\frac{1}{T}\right)$$

(15)

A was the frequency factor or pre - exponential factor, R was the universal gas constant = 8.314J / gmol ^{0}K and T was the absolute temperature, ^{0}K, Ea = activation energy, J / gmole.

The equations for the determination of the reaction order may be used for the reaction of aqueous solids such as Na Thiosulfate with methyl iodide [14] so these equations may be used in the determination of REOH reaction with HNO_3.

3. Methodology

Materials

The materials used were REOH of the processed monazite sand which Ce and La was taken partly (2 times fractionation), technical HNO_3, water, filter paper, Nd_2O_3, Sm_2O_3, Pr_5O_{11}, Y_2O_3 Merck as analyswas standard materials.

Equipments

Glass equipments, analytic scales, Ikamag heater stirrers, thermometers, ovens, x-ray spectrometers (XRF)

Methods

Nitric acid (HNO_3) with the molarity of 14.4 M as much as 4 ml was put in the glass beaker added water up to 10 ml plus REOH of 10 grams, heated to a certain temperature of 60 ^{o}C while stirring. The heating time varied 3, 6, 9, 12 and 15 minutes. After each process, the residue was filtered. The leaching solution was taken as 1 ml diluted with water to 5 ml analyzed using XRF. The remaining solids or residues, dried and weighed. The work was repeated for temperatures of 70, 80 and 90 ^{o}C.

Measurable quantities
- The element content (%) in the REOH feed used XRF
- Concentrations of Y, Pr, Nd and Sm (ppm) elements in the leached solution

4. Results and discussion

The results of the composition analysis of REOH (Feed) using XRF were presented in Table 1. In general the largest element content in REOH was Nd, followed by Nd and La. In this research REOH used as the feed was REOH which was partly taken its Ce and La (fractination 2 times), so that the Nd content increases, La and Ce content decreases.

Table 1. The composition analysis of REOH (feed) using XRF

No	Component	Elements concentration %	Atomic Weight	Molecular Weight	Compound Concentration %
1	Y (OH)$_3$	5.36	89	140	8.43
2	Ce(OH)$_3$	19.07	140	191	26.01
3	La(OH)$_3$	6.36	139	190	8.69
4	Nd(OH)$_3$	20.68	144	195	28.00
5	Sm(OH)$_3$	13.18	150	201	17.66
6	Pr(OH)$_3$	4.26	141	192	5.80
7	Dy(OH)$_3$	0.94	162	213	1.24

| 8 | Gd(OH)$_3$ | 3.14 | 157 | 208 | 4.16 |
| | Total | | | | 100.00 |

Effects Temperature and Leaching Time on The Leaching Conversion

From the analysis result of REOH and leaching product solution could be determined or the leaching conversion (X) could be calculated at various time and temperature.

$$\text{Element conversion (X)} = \frac{weight\ of\ element\ in\ the\ feed\ -weight\ of\ element\ in\ the\ solution}{weight\ of\ element\ in\ the\ feed} \quad (16)$$

Weight of element in the feed = concentration of element x weight of REOH
Weight of element in the solution= concentration of element x volume of solution

The effect of time and leaching temperature on the conversion was shown in Figure 1a to Figure 1d. The longer time and the higher leaching temperature, the leaching conversion would be greater. In general reaction, reaction rate one of which was very influenced by temperature and the completely reaction was influenced by reaction time duration
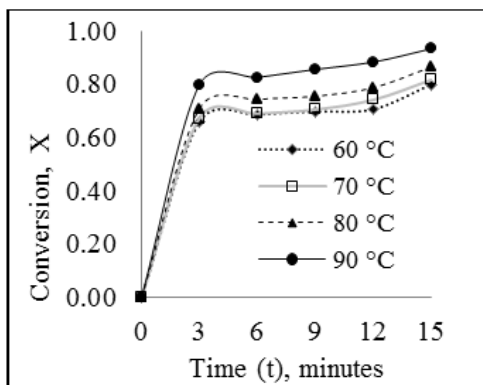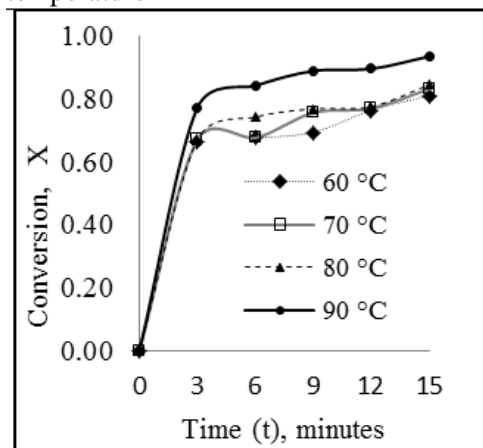

Figure 1a. Correlation between Y leaching time and conversion at various temperature
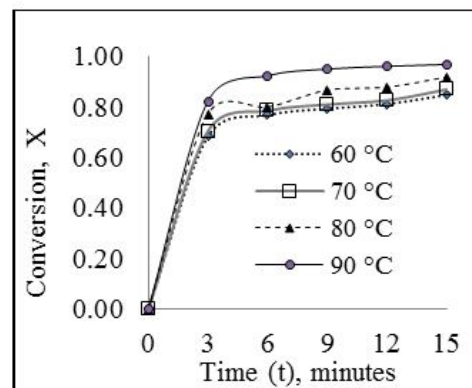
Figure 1b. Correlation between Nd leaching time and conversion at various temperature
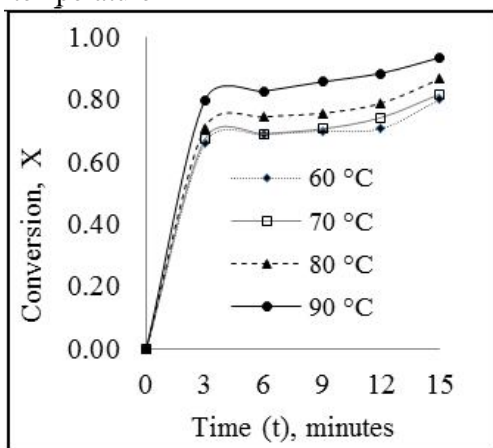
Figure 1c. Correlation between Pr leaching time and conversion at various temperature


Figure 1d. Correlation between Sm leaching time and conversion at various temperature

The conversion value of Y was in the range of 0.00 - 0.95, the Nd conversion values were in the range of 0.00 - 0.97, Pr conversion value were in the range of 0.00 - 0.94 and Sm conversion value were in the range of 0.00 - 0.94.

**Reaction order and rate reaction constant determination**

First Order Reaction

In the calculation of reaction rate constant with first order reaction , it was needed the graph of time correlation with –ln (1-X) where X was conversion (mole). Based on the equation (13), first order reaction was experimented for finding the reaction constants. The reaction rate was the overall reaction rate constant with the assumption that the concentration of HNO_3 was constant because its amount tends to approach 1, therefore it could be mentioned that the occuring reaction was first order. The calculation results could be seen in Figure 2a to 2d and Table 2
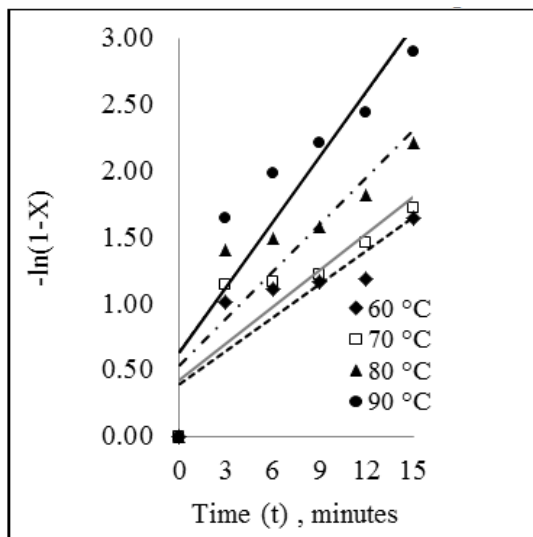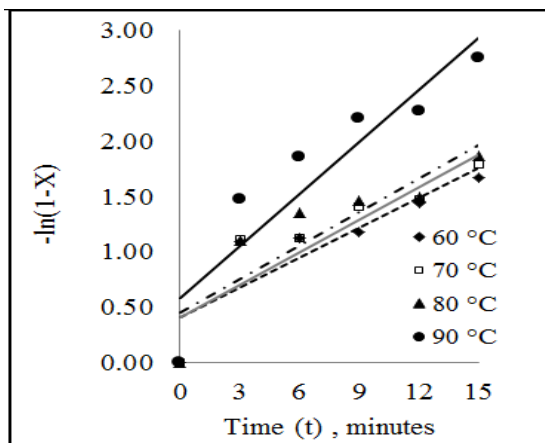

Figure 2a. Correlation between time and -ln(1-X) for determining of k value and linearity of first order reaction for Y element
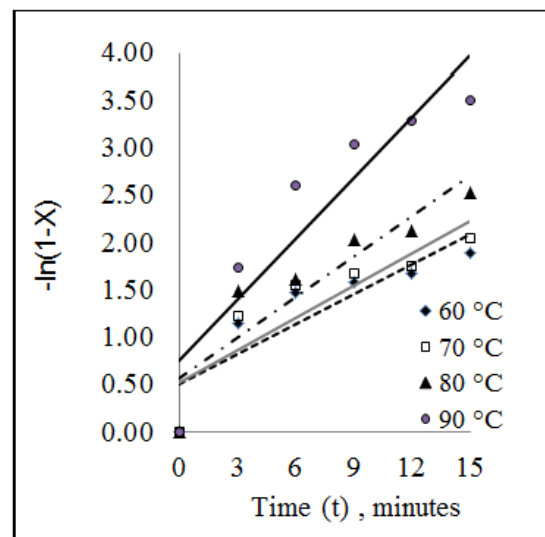
Figure 2b. Correlation between time and -ln(1-X) for determining k value and linearity of first order reaction for Nd element
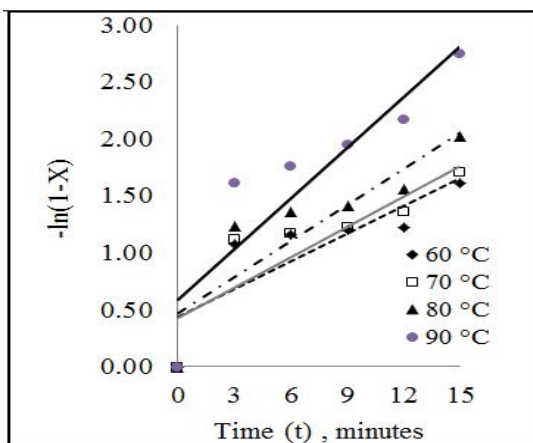
Figure 2c. Correlation between time and -ln(1-X) for determining k value and linearity of first order reaction for for Pr element

Figure 2d. Correlation between time and -ln(1-X) for determining k value and linearity of first order reaction for Sm element

Linear regression values were obtained from square root of R^2 of Y, Nd, Pr and Sm elements at various temperature as shown in Table 2.

Table 2. The equation and the value of linearity (R^2) in the first order reaction

	Temperature 60 °C	Temperature 70 °C	Temperature 80 °C	Temperature 90 °C
Y	y60 = 0.0835x + 0.394 R^2 = 0.7396 .	y70 = 0.0914x + 0.4322 R^2 = 0.7557	y80 = 0.1182x + 0.5317 R^2 = 0.7753	y90 = 0.1631x + 0.6384 R^2 = 0.8278
Nd	y60 = 0.1061x + 0.4993 R^2 = 0.7675	y70= 0.1139x + 0.5192 R^2 = 0.778	y80 = 0.1425x + 0.5606 R^2 = 0.8231	y90 = 0.2152x + 0.7458 R^2 = 0.8453
Pr	y60 = 0.0886x + 0.4336 R^2 = 0.7414	y70 = 0.0886x + 0.4336 R^2 = 0.7414	y80 = 0.1056x + 0.4739 R^2 = 0.7685	y90 = 0.1485x + 0.5911 R^2 = 0.8126
Sm	y60 = 0.0901x + 0.4123 R^2 = 0.7693	y70 = 0.0959x + 0.4728 R^2 = 0.7467	y80 = 0.1021x + 0.4366 R^2 = 0.7955	y90 = 0.1569x + 0.5837 R^2 = 0.8382

Second Order Reaction

Calculation of the second order reaction rate constant required the time-versus $\ln \dfrac{(M - 3X_A)}{M(1 - X_A)}$ correlation graph. To find the value of M, the number of Y, Nd, Pr and Sm moles in REOH and HNO_3 were initially calculated.

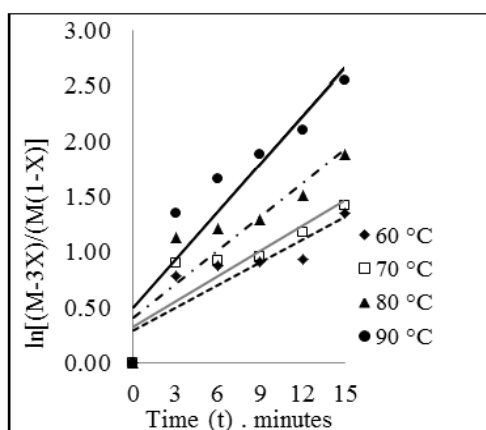M = mol HNO_3 (C_{B0}) / mol C_{A0} (Y, Nd, Pr and Sm) hydroxide

Mol HNO_3 = 0.0576 and moles Y, Nd, Pr and Sm are seen in Table 3. Table 3 presents the M values for Y, Nd, Pr and Sm elements.

Table 3. M value for Y,Nd, Pr and Sm

M Y	M Pr	M Nd	M Sm
9.5624	19.056	4.01	6,5559

The results of second order reaction could be seen in Figures 3a– 3d and Table 4.

Figure 3a. Correlation between time and $\ln \dfrac{(M - 3X_A)}{M(1 - X_A)}$ for determining k value linearity of second order of Y element
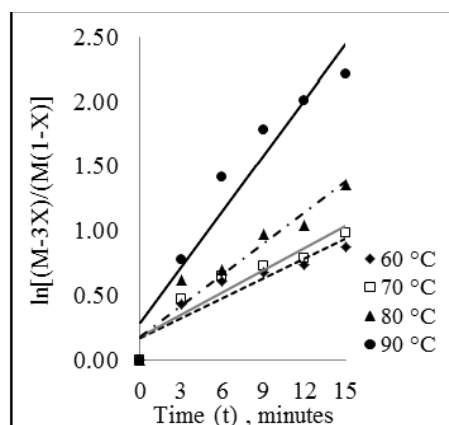
Figure 3b. Correlation between time and $\ln \dfrac{(M - 3X_A)}{M(1 - X_A)}$ for determining k value linearity of second order of Nd element

Figure 3c. Correlation between time and $\ln\dfrac{(M-3X_A)}{M(1-X_A)}$ for determining k value linearity of second order of Pr element

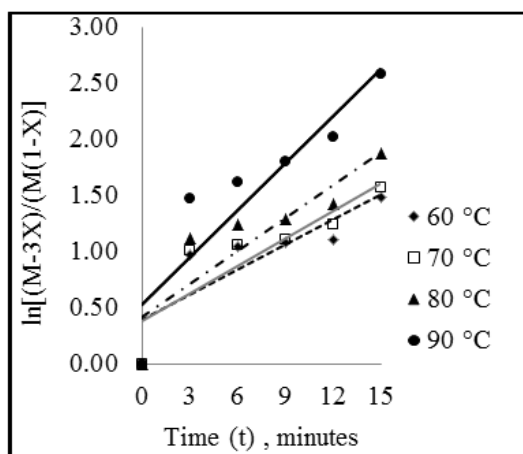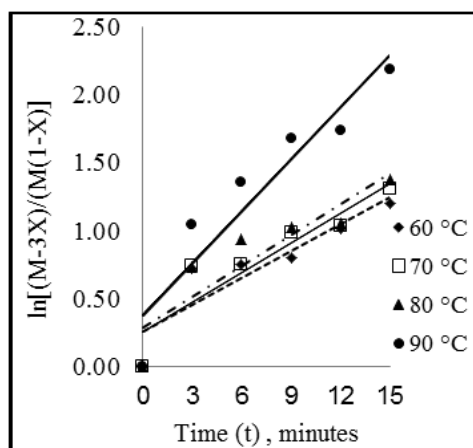**Figure 3d.** Correlation between time and $\ln\dfrac{(M-3X_A)}{M(1-X_A)}$ for determining k value linearity of second order of Sm element

The linear regression value obtained from the square root of R^2 in the second order reaction of elements Y, Nd, Pr and Sm at various temperatures was presented in Table 4.

Table 4. The equation and the value of linearity (R^2) in the second order reaction

	Temperature 60 ^{o}C	Temperature 70 ^{o}C	Temperature 80 ^{o}C	Temperature 90 ^{o}C
Y	y60 = 0.0791x + 0.3636 R^2 = 0.7463	y70 = 0.0868x + 0.4 R^2 = 0.7637	y80 = 0.1132x + 0.495 R^2 = 0.7837	y90 = 0.1578x + 0.5976 R^2 = 0.8365
Nd	y60 = 0.0936x + 0.4124 R^2 = 0.7892	y70 = 0.1011x + 0.4296 R^2 = 0.8001	y80 = 0.1289x + 0.4641 R^2 = 0.8456	y90 = 0.2007x + 0.6357 R^2 = 0.8638
Pr	y60 = 0.0794x + 0.4217 R^2 = 0.7052	y70 = 0.0864x + 0.4178 R^2 = 0.7451	y80 = 0.1033x + 0.457 R^2 = 0.7723	y90 = 0.146x + 0.5717 R^2 = 0.8167
Sm	y60 = 0.0833x + 0.366 R^2 = 0.7814	y70 = 0.0889x + 0.423 R^2 = 0.7587	y80 = 0.0949x + 0.3883 R^2 = 0.808	y90 = 0.1489x + 0.5256 R^2 = 0.8509

Linearity values (R^2) of first order reaction (Table 2) were smaller compared to the linearity values(R^2) second order reaction (Table 4), so it could be stated that the reaction was second order.

In general, the determinant of the reaction rate was the phase with the smallest rate, especially for the chemical reactor design [30].

The list of k values of the 2nd order reaction at various temperatures can be arranged in Table 5.

Table 5. The k values of 2nd order reaction at various temperature

	Temperature, ^{o}C	T, ^{o}K	k , liter/mole.time	1/T	ln k	- ln k
Y	60	333	0.0791	0.0030	-2.537	2.537
	70	343	0.0868	0.0029	-2.444	2.444
	80	353	0.1132	0.0028	-2.179	2.179
	90	363	0.1578	0.0028	-1.846	1.846
Pr	60	333	0.0794	0.0030	-2.533	2.533

	70	343	0.0864	0.0029	-2.449	2.449
	80	353	0.1033	0.0028	-2.270	2.270
	90	363	0.0794	0.0028	-1.924	1.924
Nd	60	333	0.0936	0.0030	-2.369	2.369
	70	343	0.1011	0.0029	-2.292	2.292
	80	353	0.1289	0.0028	-2.049	2.049
	90	363	0.1489	0.0028	-1.904	1.904
Sm	60	333	0.0833	0.0030	-2.485	2.485
	70	343	0.0889	0.0029	-2.420	2.420
	80	353	0.0949	0.0028	-2.355	2.355
	90	363	0.1489	0.0028	-1.904	1.904

After obtaining the element's reaction rate constants of second order reaction at each temperature, the correlation of the reaction rate constant k as a function of temperature by referring to the Arrhenius equation, ln k = ln A - Ea /RT. (equation 15).

The calculation results are expressed in the linear line graph between ln k as ordinate and 1 / T as the abscissa for Y. Nd, Pr and Sm element could be observed in Figure 4. From Figure 4, the relationship between 1 / T and ln k, line alignment was expressed by R^2, the slope obtained was the activation energy and the intercept was the frequency factor.
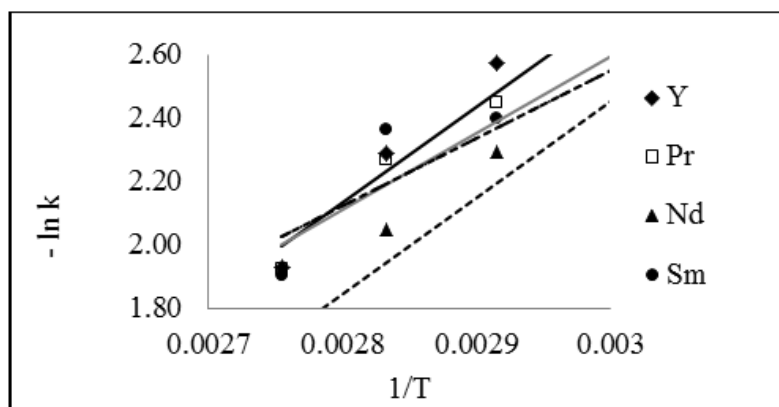
Figure 4a. Correlation between 1/T and -ln k for Y, Pr, Nd and Sm element

The linear equation of the correlation between 1/T (x) and -ln K (y) could be seen inTable 6. The activation energy was defined as the energy that must be exceeded so that chemical reactions can occur. Frequency factor (A) depends on the weight and molecular structure. frequency and position of collisions between molecules. The value of the frequency factor (A) could be determined from the intercept and the activation energy (E) was the value of the slope multiplied by R (gas constant 8.314 J/mole.°K). The calculation results of A and E values could be observed also in Table 6. From Table 6 it could be seen that the largest activation energy was Y of 23.34 kJ/mole followed by Pr of 20.00 kJ/mole. Sm of 17.94 kJ/mole and the smallest one was Nd of 16.39 kJ/mole

Table 6. Activation energy (E) and Frequency factors (A) values

Element	Y	Pr	Nd	Sm
Equation	y = 2807.3x - 5.8238	y = 1971.4x - 3.5173	y = 2157.6x - 3.9152	y = 2157.6x - 3.9152
Linearity	R^2 = 0.9063	R^2 = 0.9063	R^2 = 0.9612	R^2 = 0.7663
E/R	2807.3	2405.5	1971.4	2157.6
E, KJ	23.34	20.00	16.39	17.94
ln A	5.8238	4.6254	3.5173	3.9152
A	338.255	102.044	33.693	50.159
Arhenius Equation	$k_Y = 338.26\,e^{-23.34/RT}$	$k_{Pr} = 102.04\,e^{-20/RT}$	$k_{Nd} = 33.69\,e^{-16.39/RT}$	$k_{Sm} = 50.16\,e^{-17.94/RT}$

Ferdowsi et al, did and optimizing and kinetics of leaching process of cerium, lanthanum and neodymium elements of apatite using nitric acid. The maximum leaching efficiency of which were 66.1%, 56.8% and 51.7% respectively for Ce, La and Nd, achieved under the optimum leaching conditions with nitric acid concentration of 18%, 0.06 ratio of solid to liquid and leaching time of 38 minutes, the activation energy of Ce of 6.54 kJ / mole[20]

5. Conclusion

The leaching process was strongly influenced by the temperature and time of process. Leaching of REOH using nitric acid follows second order reaction. In leaching 10 g of REOH using 40 ml of HNO_3 0.0576 moles were obtained maximum conversion at 90 ^{0}C and leaching time of 15 minutes for Y was 0.95 (leaching efficiency of 95%). for Nd was 0.97 (leaching efficiency of 97%). for Pr was 0.94 (leaching efficiency of 94%) and for Sm was 0.94 (leaching efficiency of 94%). The largest activation energy was Y of 23.34 kJ / mole followed by Pr of 20.00 kJ/ mole, Sm of 17.94 kJ / mole and the smallest was Nd of 16.39 kJ / mole. The correlation between the reaction rate constant with T for Y was $kY = 338.26\,e^{-23.34/RT}$. for Nd was $kNd = 33.69\,e^{-16.39/RT}$, for Pr was $kPr = 102.04\,e^{-20/RT}$ and for Sm was $kSm = 50.16\,e^{-17.94/RT}$

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