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Leaching of REY from Non-magnetic Coal Fly Ash with Acetic Acid

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Abstract. The escalating demand of REY in various industrial applications becomes an important issue nowadays. REY has prominent evidence to improve material properties such as high electropositive and good conductivity. In addition REY can be classified as one of renewable and clean energy resources. Due to the increasing demand of REY, exploration of alternative sources such as red mud, spent catalyst, and coal fly ash has been conducted. Coal fly ash is one of the promising alternative sources of REY in regarding to the low radioactive material concentration. The conventional method to recover REY from coal fly ash using inorganic acids produces harmful by-product to the environment. In this research, two steps experimental methods were conducted. The first step was silicate digestion which was performed using sodium hydroxide 8 M in which REY is concentrated, with solid to liquid ratio of 1:4 and temperature of 90°C for 120 minutes. The second step was leaching the REY using citric acid. The variables studied were pH, temperature and solid to liquid ratio. The optimum condition was at the temperature of 90°C, pH 1.7 and solid to liquid ratio (15%) for each element. The maximum recovery for each elements are 77.33% Lanthanum (La), 83.47 % Cerium (Ce), 88.78% Dysprosium (Dy) and 55% Neodymium (Nd). In addition, temperature does not have any significant effect at pH 3.8.

1. Introduction

Lanthanide and Scandium group referred as Ln and Sc have atomic number from 57 until 71. They are La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y. They are similar in some aspect but very different in many others[1]. Lanthanide and Scandium group commonly called as a REY group. The increasing demand of REY by various industries such as petroleum refining, batteries, metallurgical alloy, additive for optical glass, polishing agent, military defense system, medical equipment, permanent magnets, energy source and renewable energy is very noticeable[2]. Alonso et al.[3] reported that REY demand increases by 5.3% every years from 2010 until 2020 and becomes an important issue nowadays. REY has prominent evidence to improve material properties such as high electropositive and good conductivity. In addition REY can be classified as one of renewable and clean energy resources[2]. Due to escalating demand of REY, exploration of alternative sources such as red mud, spent catalyst, coal and coal fly ash has been conducted [4]–[7]. One of the most promising source is coal fly ash[8], [9]. Anggara et al.[10] recently reported that coal fly ash and bottom ash from coal power plant in Java are promising raw material for REY extraction.



Geologically the occurrence of REY in coal were influenced by mineral matter or detrital mineral such as sulphide, phosphate, quartz and clay mineral and the coal rank[11], [12]. Kashiwakura et al.[13] reported that REY concentration increases 10 times after combustion process in coal fly ash. The amount of REY in the coal fly ash will be affected by original coal type and combustion process conditions such as temperature, oxygen concentration, residence time and cooling rate of fly ash. The transition processes of REY from coal to coal fly ash divided into two types. The first transition is called as “vaporized surface and deposition process”, where REY as a semivolatile in coal are vaporized and deposited in the surface of fly ash during the combustion. The second transition type called as “accompaniment”. Due to high temperature during combustion process, REY were melted and distributed into fly ash[14], [15]. Kashiwakura et al.[13] reported that due to high temperature in combustion process, rare earth elements were melting and distributed into the fly ash such as amorphous phase, quartz(SiO_2) and mullite ($3\text{Al}_2\text{O}_3$). Due to form amorphous silicious and quartz, rare earth element was found that to be a slight enrichment in the smaller non-magnetic component of coal fly ash[16]

The mathematical formulation to estimate the REY prospect from coal fly ash has several parameters such as resource of metal, possibility of beneficiation, simplicity and hydrometallurgical recovery[17]. The minimum cut-off-grade of REY should be higher than 1000 ppm such as monazite, bastnaesite and xenotime[18]. However, due to increasing need of REY, the present price much higher than in the past. The present criterion to evaluate the REY extraction from coal fly ash based on the individual composition of the elements. They were divided into three classification such as critical (Nd, Eu, Tb, Dy, Y and Er), uncritical (La, Pr, Sm and Gd) and excessive (Ce, Ho, Tm, Yb and Lu)[18]. The ratio of the amount of critical REY in total REY to the amount of excessive REY in total REY called Outlook Coefficient (C_{out}) which is used to identify the availability of REY extraction. The minimum C_{out} index is 0.7, the higher C_{out} the more promising material for REY extraction[18]. Mathematically the equations to calculate the C_{out} is as follows (Equation 1)

$$C_{\text{out}} = \frac{((\text{Nd} + \text{Eu} + \text{Tb} + \text{Dy} + \text{Er} + \text{Y}) / \sum \text{REY})}{((\text{Ce} + \text{Ho} + \text{Tm} + \text{Yb} + \text{Lu}) / \sum \text{REY})} \quad (1)$$

Hydrometallurgy is one of the most efficient methods for extracting some metal in low concentration, because it emits small amount of gases, high recovery and consumes a little energy. Leaching is one of the hydrometallurgy processes, where acid is used to extract elements from coal fly ash. Inorganic acids such as H_2SO_4 , HCl and HNO_3 commonly used as a leaching agent[13][8]. Anyway, inorganic acids produce harmful byproducts to the environment. Nowadays, researchers have investigated the use of organic acids to substitute the inorganic acids as leaching agents such as oxalic acid, citric acid, acetic acid and nitric acid[19]–[24]. The use of organic acids called as an environmentally friendly leaching agent.

The aim of this study is to investigate the use of acetic acid as a leaching agent. Bahera and Parhi[19] have demonstrated the use of acetic acid to leach neodymium from the scrub magnetite. Furthermore, acetic acid also has been demonstrated to leach Li and Co from spent lithium-ion batteries[25]. Regarding to the mineralization of REY in the form of amorphous silicate (non-magnetic fly ash), magnetic separator was applied. Silicate digestion was conducted to decompose the amorphous silicate using sodium hydroxide. After digestion process, leaching was performed to identify the effect of variables studied (pH, temperature and solid to liquid ratio) on the REY recovery.

2. Research Methodology

2.1 Material

Coal fly ash (CFA) were collected from one of coal power plants in Java (PLTU Tuban East Java). The particle size was sieved to obtain desired particle size. The particle size less than $38 \mu\text{m}$ (- 400 mesh) were used as a raw material. Magnetic and non-magnetic components were separated using magnetic separator in Centre for Research and Technology Development of Mineral and Coal (PUSLITBANG Teknologi Mineral dan Batubara) Bandung, West Java. The non-magnetic component was analysed using ICP-MS both major elements and REY in ALS Global – Geochemistry Analytical Laboratory in North Vancouver, BC, Canada (Table 1 and Table 2).

Table 1. Major element in non-magnetic coal fly ash component[26]

Major Element	Wt (%)
SiO ₂	53.20
Al ₂ O ₃	31.90
Fe ₂ O ₃	5.58
CaO	3.08
MgO	2.11
Na ₂ O	0.90
K ₂ O	0.99

Table 2. REY concentration in non-magnetic coal fly ash[26]

REY Elements	Unit (ppm)
Ce	98,3
Dy	9,32
La	49
Nd	45,2
Y	53,2

Based on the Table 2. then the Coutlook can be calculated using equation (1) to define the material for extraction availability (another REY element not show).

$$C_{out} = \frac{((Nd + Eu + Tb + Dy + Er + Y)/\sum REY)}{((Ce + Hp + Tm + Yb + Lu)/\sum REY)}$$

The Cout is 1.068 (> 0.7). its indicated that REY content in the non-magnetic coal fly is promising to extract.

2.2 Silicate digestion condition and procedure

The silicate digestion was done using sodium hydroxide (NaOH) pro-analysis produced by Merck Inc. The digestion process was conducted in a three-necked flask by mixing 62.5 gr non-magnetic component of CFA with 250 mL of sodium hydroxide 8 M (pH 13.9). The reagent was heated using waterbath equipped with reflux condenser and with a stirrer operated at a speed 500 rpm than heated to 90 °C at atmospheric condition. They were digested for 120 minutes to decompose and breakage the amorphous silicate and form the OH⁻ bound. The solid digested were washed using distilled water (60x) based on the the dry sample weight.

2.3 Metal leaching condition and procedure

The leaching process was conducted in a three-necked flask equipped with reflux condenser which was placed on a heating mantle. The solution was agitating using an externally agitator. 250 mL of acetic acid were put in to the flask and heated until to the desired temperature. The effect of changing of three parameters were temperature (room temperature and 90 °C), pH (1.72 and 3.5) and solid to liquid ratio (5% and 15%). During the leaching experiments one of the parameters were maintained constant. The stirring speed was 500 rpm. They were leached for 240 minutes to dissolve the REY from the non-magnetic CFA.

2.4 Analysis ICP-EAS

The sample preparation was carry out by diluting 1 mL of leached sample to 20 mL (20 x dilution) using aqua for injection. The samples were filtered using a micro filter 0.22 µm to separate any suspended solid in the filtrate. The filtrate were analyzed using ICP-EAS in Indonesian Institute of Science. Reasearch Unit for Mineral Technology (Lembaga Ilmu Pengetahuan Indonesia. Balai Penelitian Teknologi Mineral. LIPI Lampung) to identify the amount of REY recovered by leaching.

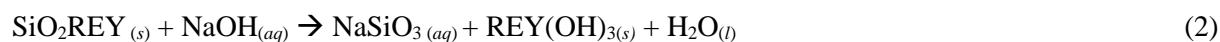
2.5 Data analysis

The data analysis were performed via MINITAB. the method used was DOE using Response Surface Method (RSM) as the basis to identify the optimum condition.

3. Result and Discussion

3.1 Silicate digestion

The non-magnetic coal fly ash was digested using sodium hydroxide due to high content of amorphous silicate. Sodium hydroxide were perform to breakage and decrease the amorphous silicate content. In addition OH^- from sodium hydroxide also change the REY bound to form REYOH. Based on the experiments result shows that amorphous silicate were decomposed up to 20-30 %. The assumption reaction in the silicate digestion can be describe as equation below.

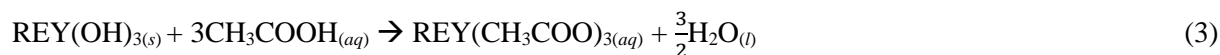


Sodium hydroxide were decomposed and breakage the amorphous silicate. This condition will open access for acid to leach the REY from nonmagnetic CFA. Alkali fusion using sodium hydroxide pellet were used to removed P from monazite and change the REE bound to REEOH. The more phosphate removed the more REE recovered[2]. The same also with silicate digestion, the more amorphous silicate decomposed, the more REY recovered by leaching.

3.2 Metal leaching

The experiment result related to acid concentration/pH, temperature and solid to liquid ratio were varied to test the optimum condition for leaching REY under defined conditions. There are four elements (REY) were compared at various leaching condition such as La, Ce, Nd and Y. The REY recovery were calculated and plot in a certain conditions. Generally, for all elements (La, Ce, Nd and Y) shows that, the higher temperature the higher metal recovery (Figure 1. and Figure 2). This phenomenon is consist with the Arrhenius rate law, which states that an increasing temperature of 10°C can increase the reaction rate twice[25] [26].

Figure 1 shows the effect of acetic concentration (pH) and temperature vs REY recovery in solid to liquid ratio 5%. The maximum REY recovery at solid to liquid ratio 5% were achieved in the higher temperature and the higher concentration (lower pH). They were 61.40 %, 64.44 %, 67.62 % and 32.49 % for La, Ce, Dy and Nd respectively. The higher concentration and the higher temperature will increase the metal solubility. However, the increasing temperature from 30°C to 90°C in the same pH (1.7) shows different effect for each metal. For La and Nd slightly increase around 3 to 3.5 % and 5 % for Dy and for Ce increase around 11.3 %. The Ce dissolution was increase simultaneously due to increasing temperature. This phenomenon exist due to different properties of each element such as solubility. Migdisov and William reported that neodymium solubility increase above 150°C in F-bearing aqueous solutions due to high stability[29]. The assumption reaction in the REY leaching can be describe as below.



This reaction shows that the REYOH bound substitute by ion H^+ from acetic acid. The more H^+ the more OH^- substitute. This reaction also similar with REE extraction from monazite, where phosphate were removed using alkali fusion to form REEOH and than acid were used as a substitution agent to replace the OH^- with ion H^+ from acid[2].

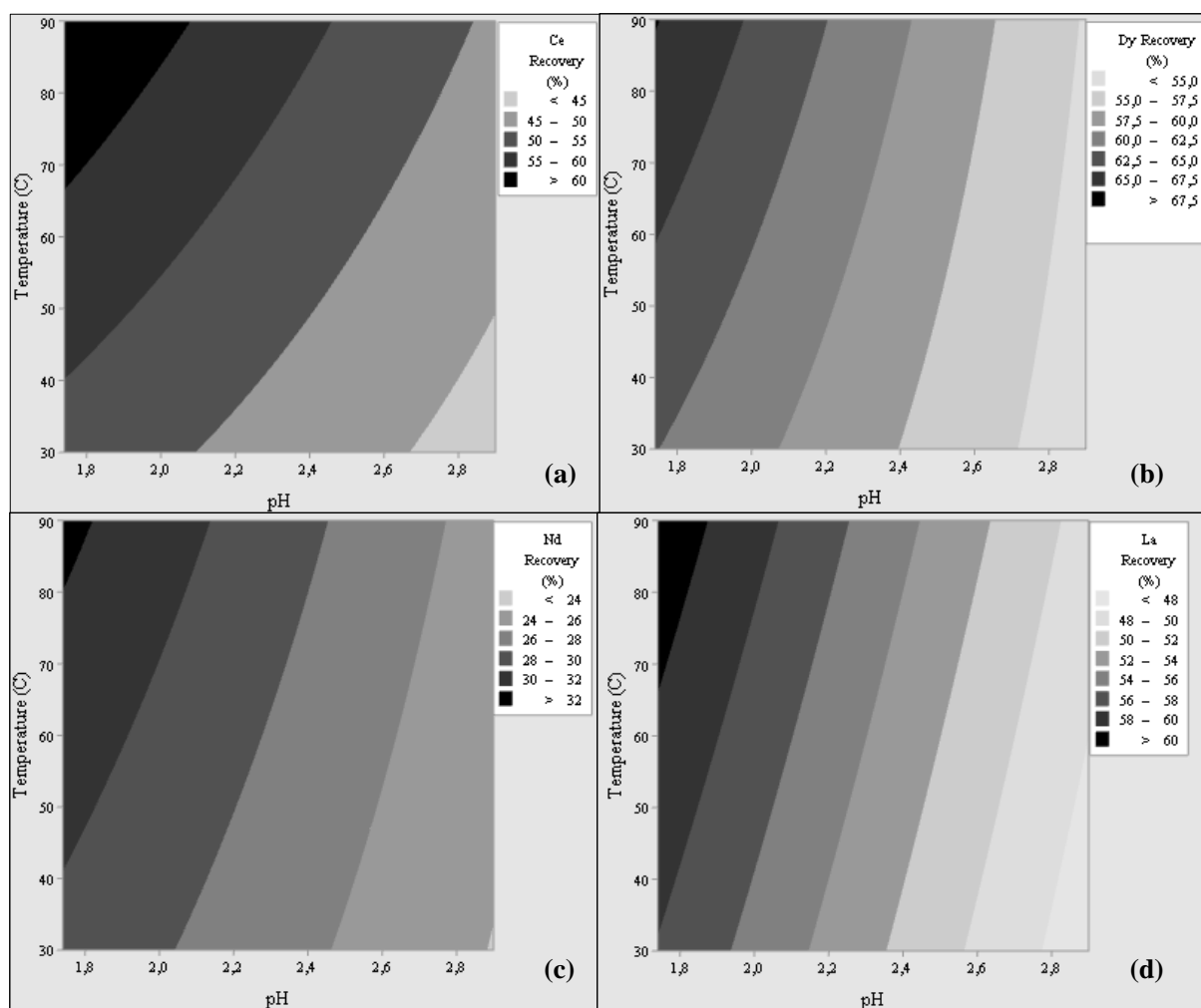


Figure 1. Contur plot of REY recovery (%) vs temperature (°C); pH at solid to liquid 5 % (a: Dy. b: La. c: Nd and d: Ce)

The experiment result related to solid to liquid ratio shows that REY recoveries were influence by solid to liquid ratio (Figure 1 and Figure 2). Generally, increasing the solid to liquid ratio increase the extraction of REY elements from the nonmagnetic coal fly ash. The increasing of solid to liquid ratio will increase the pulp density of solution. Borra et al reported that increasing solid to liquid ratio from 5% to 20% were increase the REE recovery from red mud residue. Otherwise, increasing solid to liquid ratio more than 20% does not provide any significant effect and could be decrease the REE recovery[4]. Theoretically, the higher solid to liquid ratio the lower metal recovered due to decrease the metal solubility and increase the pulp density of the solution. Lazo et.[21] al reported that the higher solid to liquid ratio the lower REE recovery using oxalic acid. However, this state influence by the reagent properties such as solubility.

The effect of leaching temperature was studied at acid concentration (pH) and solid to liquid ratio. There is no significant improvement in leaching by increasing the temperature at the pH 3.5 (Figure 1 and Figure 2). Increasing temperature from room temperature until 90 °C slightly increase the REY recovery. The REY recovery were increase for the high acid concentration simultaneously.

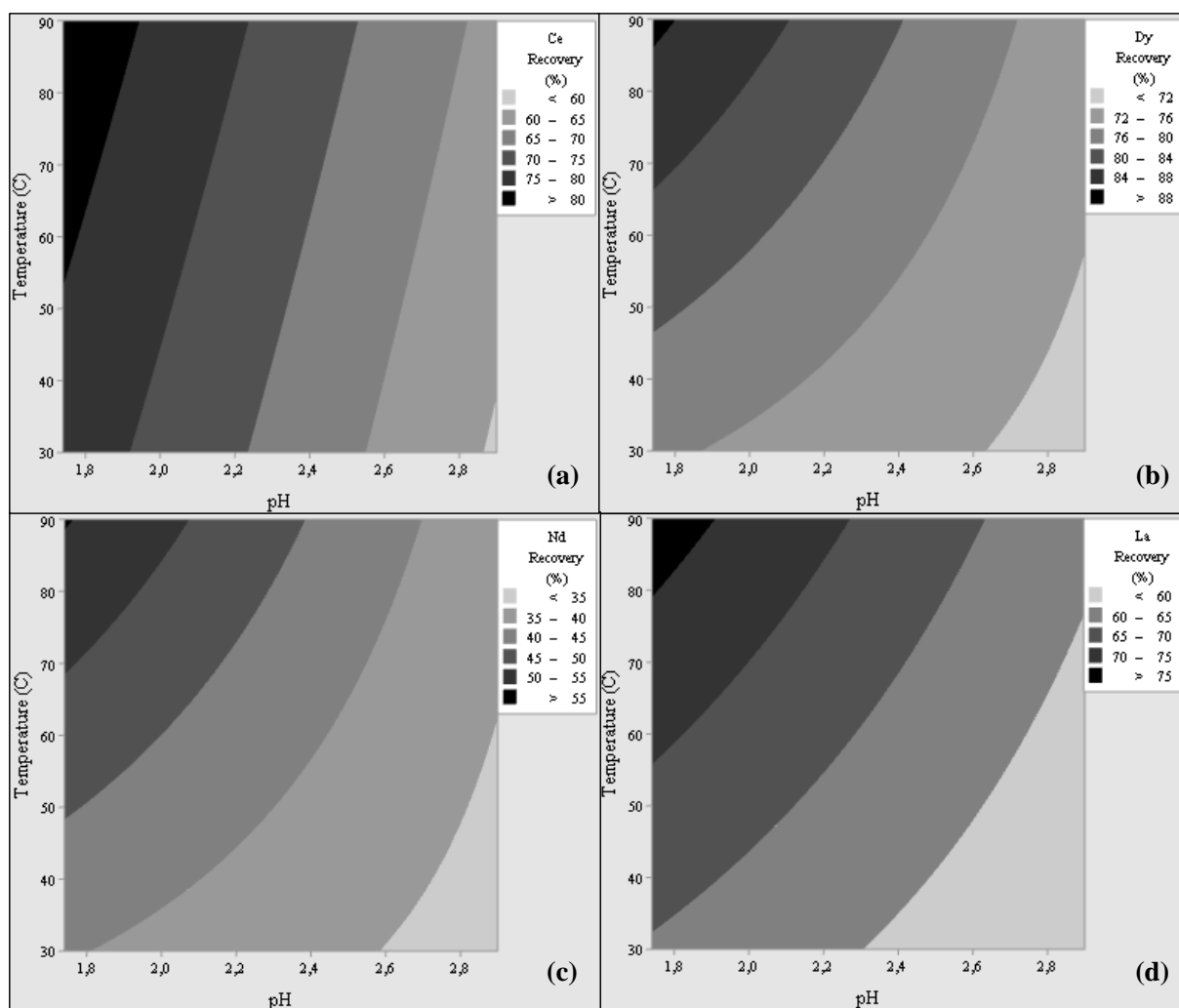


Figure 2. Contur plot of REY recovery (%) vs temperature (C); pH at solid to liquid 15 % (a: Dy. b: La. c: Nd and d: Ce)

Regarding to test the optimum condition, Figure 3 and Figure 4 shows the different recovery of REY at solid to liquid ratio 5% and 15%. The maximum REY recovery (56.7%) is achieved at temperature 90 °C and pH 1.72. The highest of REY recovery because the metal solubility were increase simultaneously.

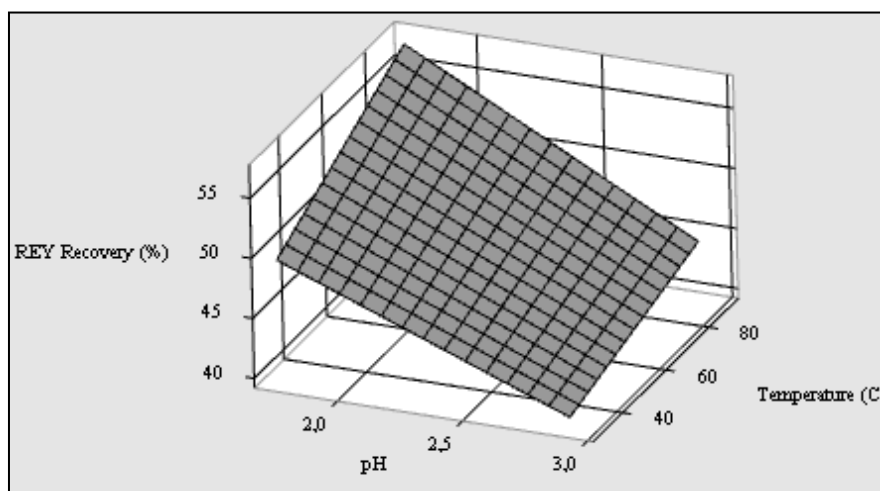


Figure 3. Surface plot of REY Recovery (%) vs Temperature (C); pH at S/L 5%

For predicting the REY recovery at solid to liquid ratio 5% of leaching have developed models and given as

$$\text{REY recovery (\%)} = 57.17 - 6.537x + 0.2055y - 0.04811xy \quad (4)$$

Figure 4 shows that the maximum REY recovery (75.95 %) is achieved at temperature temperature 90 °C and pH 1.72. The maximum recovery is achieved at the same temperature and pH for both solid to liquid ratio.

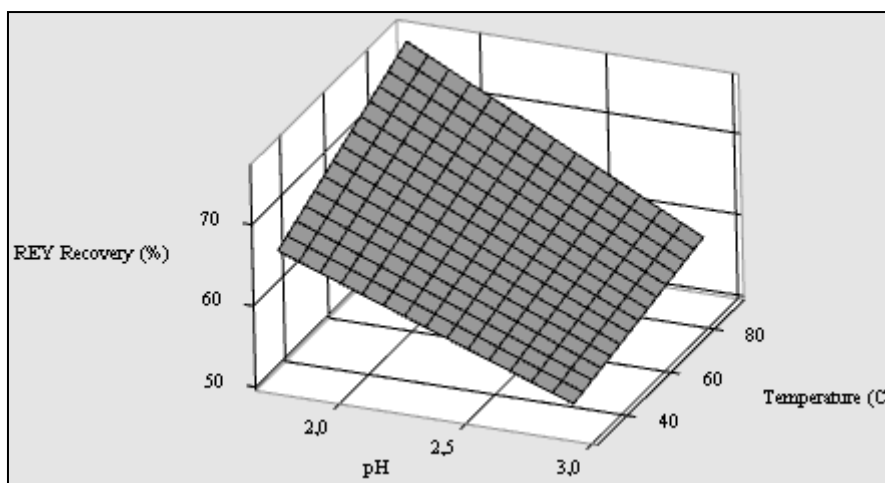


Figure 4. Surface plot of REY Recovery (%) vs Temperature (°C); pH at S/L 15%

For predicting the REY recovery (%) at solid to liquid ratio 15% leaching have developed model also and given as

$$\text{REY recovery (\%)} = 76.99 - 9.033x + 0.2950y - 0.07580xy \quad (5)$$

Where:

x is pH

y is temperature (°C).

4. Conclusion

Based on the experiments and discussion conclude that temperature, concentration and solid to liquid ratio influence the REY recovery. The optimum condition was in the higher temperature (90°C), the lower pH and the higher solid to liquid ratio (15%) for each element. They are 77.33%, 83.47 %, 88.78% and 55% achieved for La, Ce, Dy and Nd respectively. This condition is the optimum condition for leaching REY from non-magnetic coal fly ash. Otherwise, temperature does not provide any significant effect in low concentration. The optimum condition for leaching REY from nonmagnetic coal fly ash can be more than 15% solid to liquid ratio.

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