Amorphous Silicate Decomposition from Non-Magnetic Coal Fly Ash using Sodium Hydroxide

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Abstract. In five years, from 2015 to 2020, the need of coal in Indonesia is doubled to 166.2 million tonnes and increasing up to 2050 as stated in the Indonesian Energy Mix policy. Generally, coal is used in the coal-fired power plan. After the combustion, there are some residual materials such as mineral matter, fly ash and bottom ash (FABA) listed as hazardous materials due to the toxicity and metal contents. Referring to the amount of coal consumption in 2020, the fly ash and bottom ash will be of about 19.92 million tonnes. The utilization of FABA is then become a must thing to do. One of the alternatives is rare earth element (REE) extraction. Indonesian coal contains sufficient amount of REE to extract that is concentrated in the FABA to the value of more than 400 ppm. Regarding to the REE mode of occurrence that is mostly concentrated in the glass form or amorphous silicate, this study was conducted in order to observe the effect of sodium hydroxide to breakage the amorphous silicate structure. In order to obtain the amorphous silicate, magnetic separator was applied. Based on the XRF analysis, the non-magnetic fly ash (amorphous silicate of glass form) contained major elements of SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO and the rest were minor and trace elements such as Na₂O, K₂O, Cr₂O₃, MnO, SrO and P₂O₅. The particle size of the amorphous silicate is less than < 38 µm (-400 mesh). To run the experiments, sodium hydroxide was used as the reagent with varied concentrations of 6 M, 8 M and 10 M. Other variables were temperature of 28°C (room temperature), 60°C and 90°C and residence time of 2, 4, and 6 hour. Based on the results analysis, the amorphous silicate was decomposed to the most of about 22% at 90°C of temperature, 10 M of sodium hydroxide concentration, and 6 hour of residence time.

1. Introduction
Coal is one of the main energy resource in the world. Indonesia is listed as a top ten of coal producer in the world. In 2019, Indonesia has 50,763.52 million tonnes of resources and 39,890.95 million tonnes of coal reserves[1]. Indonesian coal mostly in medium rank until low rank due to high content of impurities such as mineral matter, moisture content, ash and sulfur content[2]. In five years, from 2015 to 2020, the need of coal in Indonesia is doubled to 166.2 million tonnes and increasing up to 2050 as stated in the Indonesian Energy Mix policy. Generally, coal is used in the coal-fired power plan. After the combustion, there are some residual materials such as mineral matter, fly ash and bottom ash (FABA) listed as hazardous materials due to the toxicity and metal contents. Referring to the amount of coal consumption in 2020, the fly ash and bottom ash will be of about 19.92 million tonnes[3]. The utilization of FABA is then become a must thing to do. Coal fly ash were listed as a one of alternative resource of
rare earth element (REE)[4]–[6]. Ferian et al[7] recently reported that fly ash and bottom ash from coal power plant in Java are promising raw material for rare earth element extraction.

The existence of rare earth element in coal fly ash were influenced by the coal rank and mineral matter such as quartz, clay mineral, sulphide and phosphate[8]. Kashiwakura et al[9] reported that due to high temperature in combustion process, rare earth element were melting and distributed into the fly ash such as amorphous phase, quartz (SiO$_2$) and mullite (3Al$_2$O$_3$). Due to form amorphous silicious and quartz, rare earth element was found that to be a slight enrichment in the samaller non-magnetic component of coal fly ash[10].

Indonesian coal contains sufficient amount of REE to extract that is concentrated in the FABA to the value of more than 400 ppm[6], [7]. Regarding to the REE mode of occurrence that is mostly concentrated in the glass form or amorphous silicate, this study was conducted in order to observe the effect of sodium hydroxide to breakage the amorphous silicate structure. In order to obtain the amorphous silicate, magnetic separator was applied.

The aim of this study is to identify the optimum condition of sodium hydroxide to breakage the amorphous silicate. The variable studied were reagent concentration, residence time and temperature. In addition sodium hydroxide not only decomposed the amorphous silicate but also to change the REE bound to from REEOH.

2. Research methodology

2.1. Material

Coal fly ash were collected from PLTU Tuban East java. Each particle size were separated using sieve. The particle size less than 38 µm (-400 mesh) were used as a raw material. In order to obtain non-magnetic component (amorphous silicate), wet magnetic separator was applied in Centre for Research and Technology Development of Mineral and Coal (PUSLITBANG TekMIRA) Bandung, West Java. XRF analysis were applied for raw material characterization to identify the major and minor component. ICP-MS also were done to identify the rare earth element concentration in ALS Global – Geochemistry Analytical Laboratory in North Vancouver, BC, Canada.

| Mineral | 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  |

2.2. Silicate digestion procedure

Silicate digestion process was conducted in a erlenmeyer 100 mL which was placed on a water bath equipped with shaking equipment. 10 gr sample with 50 mL sodium hydroxide (solid-to-liquid 20 %) and heated until to desired temperature. The variable studied were reagent concentration (6M, 8M and 10 M), temperature (30°C (room temperature), 60°C and 90°C), and residence times(2 hour, 4 hour and 6 hour). The solid digested were washed using destilated water (60x) based on dry weight sample in 30 minutes and stirred using magnetic stirrer.

2.3. Data analysis and calculation

The data analysis for this experiment were performed via MINITAB. The method used was DOE using Response Surface Method as the basis to find the optimum condition.
3. Result and discussion

3.1. Material characterization

The major elements concentration in the form of oxide as given in Table 1. Silicate oxide is the major oxide in the non-magnetic coal fly ash followed by alumina oxide, iron oxide, calcium oxide, magnesium oxide, sodium oxide and kalium oxide. The concentration of Rare Earth Element and Yittrium (REY) in raw CFA around 260.38 ppm and REY concentration in non-magnetic CFA around 314.15 ppm. It was enriched around 20.65% after magnetic separator. The amount of each rare earth element can be seen as in Figure 1.

![Figure 1](image-url). Rare earth and Yittrium concentration in raw CFA and non-magnetic CFA

Figure 1 shows that rare earth and yittrium concentrations were slightly increase from raw CFA after physical separation using magnetic separator. to non-magnetic CFA component. Blisset et al[10] also reported that, rare earth element was found to be enrichment in the non-magnetic coal fly ash. The enrichment processes consist due to mineralization of REY in the coal fly ash after combustion process and than distributed to amorphous mineral such as silicious, clay mineral, mullite[9], [12], [13].

3.2. Silicate digestion

The experiment result related to silicate digestion at various reagent concentration, temperature and residence time are shown in Figure 2 and Figure 3. Sodium hydroxide were used to decrease and breakage the amorphous silicate content. Generally, the higher concentration the higher SiO2 decomposed, thin consist in all residence time and all temperature. The maximum SiO2 decomposed around 21% at temperature 90 ºC, sodium hydroxide concentration 10M and residence time 6 hours. Based on the coal fly ash characterization shows that REY were distributed in the amorphous mineral, than the chemical formulation can be wrote as SiO2.REY. Na+ and OH- from sodium hydroxide will react with SiO2.REY, the assumption reaction can be Describe as equation 1 below.

\[
\text{SiO}_2\text{REY}^{(s)} + \text{NaOH}^{(aq)} \rightarrow \text{NaSiO}_3^{(aq)} + \text{REY(OH)}_3^{(s)} + \text{H}_2\text{O}^{(l)}
\]  

(1)

Equation 1 shows that Na+ from sodium hydroxide react with SiO2 and form NaSiO3 in aqueous phase. In addition, OH- from sodium hydroxide were modify the REY bound to form REY(OH)3 in the solid phase. Figure 2 shows the amount of SiO2 were decomposed in the various temperature and concentration at 6 hour residence time.
Figure 2 shows that temperature and concentration influence the amount of SiO$_2$ decomposed. In this part, residence time at 2 hour and 4 hours are not shown due to the similar phenomenon with 6 hours residence time. For predicting the SiO$_2$ decomposed at 2, 4 and 6 hours residence time of silicate digestions have developed models and given as Equaiton 2, Equation 3 and Equation 4 below.

For 2 hour residence time

\[
\text{SiO}_2 \text{ Decomposed (\%)} = 27.29 - 2.90x - 0.4935y + 0.109x^2 + 0.004491 y^2 + 0.02240 xy \\
R\text{-sq} = 99.32 \%
\]  
(2)

For 4 hour residence time

\[
\text{SiO}_2 \text{ Decomposed (\%)} = 20.3 - 3.43x - 0.091y + 0.224x^2 + 0.00272y^2 + 0.0048xy \\
R\text{-sq} = 93.23 \%
\]  
(3)

For 6 hour residence time

\[
\text{SiO}_2 \text{ Decomposed (\%)} = 9.3 - 0.01x - 0.229y + 0.042x^2 + 0.002379y^2 + 0.02087xy \\
R\text{-sq} = 96.82 \%
\]  
(4)

Where:
- $x$ = concentration (M)
- $y$ = temperature (°C).

Based on the Equation 2, 3 and 4 shows that intercept for each residence times were different, they were 27.29 (2 hour), 20.3 (4 hour) and 9.3 (6 hour).
Figure 3 show the surface plot of SiO$_2$ decomposed at various temperature and concentration. The influence of temperature on the SiO$_2$ decomposed shows that increasing temperature from room temperature to 60 °C and 90 °C were increase the SiO$_2$ decomposed. This is consist with Arrhennius rate law, which states that, reaction rate will increase twice when increasing temperature 10°C[14], [15]. This data also shows that, the solubility of amorphous silicate were increase simultaneously during increasing temperature until 90 °C.

The influence of residence times on SiO$_2$ decomposed shows that, residence times were influence the SiO$_2$ decomposed. Increasing residence time were increase the SiO$_2$ solube. The maximum SiO$_2$ decomposed 15,16%, 17,4% and 22,01% were achieved at 2, 4 and 6 hour residence time respectively at temperature 90 °C and concentration 10 M.

The influence of concentration on SiO$_2$ decomposed shows that (Figure 2 and Figure 3), there were no significant effect of sodium hydroxide concentration in room temperature reaction. Increasing temperature from room temperature to 60 °C where increase the SiO$_2$ decomposed from 9% to 15%. Increasing temperature until 90 °C shows that, there were significant effect to SiO$_2$ decomposed, where SiO$_2$ decomposed were increase from 15 to 21%. This phenomenon consist with thermodynamic rule which states that, reaction rate (k) is a function of temperature[16]. However, in the highest temperature (90°C), concentration were slightly influence the SiO$_2$ decomposed, where the higher concentration the more SiO$_2$ dissolve.

4. Conclusion
The experiment results in this work conclude that physical separation using magnetic separator was increase the REY concentration around 20.65 %. While the silicate digestion is strongly affected by temperature, concentration and residence time. The maximum decomposition of SiO$_2$ (21%) was achieved at temperature of 90 °C, sodium hydroxide concentration of 10 M and residence time of 6 hour. The increasing concentration of sodium hydroxide from 6 M up to 10 M does not provide any significant effect for decreasing SiO$_2$ content. However, only temperature that strongly affect the rate of silicate decomposition. Increasing residence time more than 2 hour slightly increases the rate of silicate decomposition.

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