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Extraction of Aluminium (Al) Metal from Coal Fly Ash of PLTU-Paiton with NaOH Solvent

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Abstract: Fly ash, a solid waste product from the coal combustion process at the Paiton PLTU, contains 14.52-23.78% alumina (Al_2O_3). This can be extracted using NaOH for further utilization. The $Al(OH)_3$ precipitate was obtained using a 4 M HCl solution with pH variations of 6 and 6.5. Meanwhile, Al metal was obtained using a reduction temperature variation of 600-700 ºC with an interval of 50 ºC using Mg metal reductant for 2.5 hours. The aluminum metal obtained was subjected to qualitative analysis by UV-Vis spectrophotometer and quantitative analysis by AAS. The $Al(OH)_3$ precipitate obtained at a pH of 6.001 weighed 1.581 grams, with a yield of 61.83%, while at a pH of 6.5 it weighed 1.688 grams, with a yield of 66.02%. Applying a specific reagent for Al metal, alizarin, to qualitative analysis resulted in a maximum wavelength of 495 nm. A quantitative study was conducted utilizing the atomic absorption spectrophotometer (AAS) at a wavelength of 309.3 nm. The alumina content in fly ash was determined to be 14.52%, with an Al metal yield of 8.67% at a pH of 6 and 9.01% at a pH of 6.5, at an optimal reduction temperature of 650°C.

Keywords: Fly ash, NaOH solvent extraction, Al metal.

INTRODUCTION

Fly ash is a solid waste material produced by burning coal in the furnace at the PLTU. This is then captured using an electrostatic precipitator [1]. Fly ash is generally stored temporarily in PLTU and finally disposed of in landfills [2]. Fly Ash has a detrimental effect on human health, particularly on the respiratory system and the integumentary system. Consequently, as per the provisions stipulated in PP85/1999, fly ash waste is designated as B3 (Toxic and Hazardous Material) waste. The utilization of fly ash waste can be achieved on the condition of prior knowledge of its physical and chemical properties, thus ensuring optimal utilization [3]. Fly ash has been found to contain SiO_2 in the range of 30.25-36.83%, Al_2O_3 in the range of 14.52-23.78%, Fe_2O_3 in the range of 13.46-19.94%, CaO in the range of 1.40-16.57%, MgO in the range of 5.360-8.110%, and other materials [4]. Aluminum is the second most abundant element in the composition of the aggregate, with a percentage of 25.82%, surpassed only by silica. Aluminum has a multitude of applications due to its combination of lightweight, corrosion-resistant, and strong properties.

A plethora of studies have previously been conducted on the utilization of fly ash. One such study, which was carried out by [3], examined the effect of NaOH, a solvent used in solid-liquid extraction, on the extraction of Al_2O_3 and SiO_2 from fly ash for use in geopolymer production. The optimum result to extract alumina and silica for use as geopolymer is 10 M NaOH. In another study, [5] examined the synthesis of ultrafine aluminum hydroxide from coal fly ash through an alkaline dissolution process. The alumina extraction efficiency obtained was 93%. In addition, the sodium aluminate solution produced from the second stage of alkaline dissolution was utilized in the synthesis of ultrafine aluminum hydroxide. [6] Researched the extraction of alumina from fly ash using the alkaline method. In this process, of potassium hydroxide then produces efficient results of up to more than 90%.

The present study is founded upon the premise that the extraction of aluminum from fly ash using NaOH solvent is a viable proposition, as evidenced by extant research that supports the use of alumina extraction with NaOH solvent. The procedure employed in this study to obtain sodium aluminate draws upon the research procedure outlined by [7] who utilized 8 M and 20 M NaOH concentrations for the extraction of alumina from fly ash. Furthermore, the precipitation process utilizes 4 M HCl to obtain $Al(OH)_3$ precipitates with pH variations of 6 and 6.5, as within this pH range $Al(OH)_3$ will begin to form. As [8] asserts, the form of aluminum species at pH below 4.5 is $Al3^+$. As demonstrated in the research by [9] $Al(OH)_3$ is formed at a pH of 6.3, with a minimum solubility limit of 0.03 mg/L. As posited by [10] the association process of aluminum and hydroxide is characterized as a mononuclear process, which occurs in a series of steps. The initial step in this process is the formation of $Al(OH)_2^+$. As the pH level rises, $Al(OH)_3$ solids begin to precipitate. It has been established that increasing the pH above 7 will result in the dissolution of the $Al(OH)_3$ precipitate back into the $Al(OH)_4^-$ anion. The reduction process of $Al(OH)_3$ to Al metal involves the utilization of Mg reductant, with temperature variations ranging from 600 to 700°C, with an interval of 50°C. The reduction results were subjected to qualitative testing using alizarin-specific reagents and quantitative testing using an AAS spectrometer. This was done to confirm the presence or absence of Al metal in the samples that had been treated until the end of the procedure.

EXPERIMENTAL

Sample Preparation

In the study conducted by [11] a quantity of up to 150 grams of fly ash samples from PLTU Paiton-Probolinggo were immersed in hot water for a duration of two hours.

Acidification

Acidification was achieved by the addition of 90 mL of a H_2SO_4 solution to the sample (fly ash) at ambient temperature, followed by stirring for 30 minutes. Furthermore, the material was dried at 115°C for 5 hours [12].

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Extraction to get The Desilication Product

The extraction process employed is solid-liquid extraction, also known as leaching. The sample (Fly Ash) utilizes a sodium hydroxide solution with a concentration of 8 M, with a volume of up to 250 mL. Subsequently, the mixture was subjected to an elevated temperature, and agitation was initiated using a stirrer. This process was continued for 150 minutes at a temperature of 95°C. The subsequent step involved the separation of the filtration and residue by filtration. After this treatment, desilicated fly ash products were obtained [13].

Aluminum Hydroxide Preparation

The desilicated fly ash product (16.67 grams) and calcium hydroxide (7.17 grams) were mixed with 50 mL of a 20 M sodium hydroxide solution in a nickel cup. The mixture was then heated at 250°C for 60 minutes. In addition, a $NaAlO_2$ solution is to be obtained, which is then to be added to $NaHCO_3$ at 95°C for two hours. This is to be followed by stirring, which will result in the production of sodium tetrahydroxyaluminate (Shuang et al., 2011). Subsequently, a 4 M HCl solution was added, with the pH being controlled to form $Al(OH)_3$ precipitates. The pH variations employed in this study ranged from 6 to 6.5, as reported by [14]. After this, the precipitation obtained was filtered and washed with cold distilled water. Moreover, the precipitation was subjected to an oven temperature of 110°C for one hour [15].

Reduction

The reduction process was initiated by subjecting the dried $Al(OH)_3$ precipitate to a reduction reaction with a molar ratio of Mg:Al of 2:3. This reaction was carried out at a temperature ranging from 600 to 700°C, with an increment of 50°C, for 2.5 hours. Furthermore, the experimenter washed the subject with hot water on three separate occasions. The results obtained from the reduction process will then be analyzed both qualitatively and quantitatively.

Qualitative Analysis

The qualitative analysis of the reduced sample was conducted through the dissolution of 0.5 grams of the sample into a 50 mL HCl solution. The solution was then heated until dissolution occurred, at which point 2 drops of 0.2% alizarin solution were added. Subsequently, NH_4OH is added to the solution in a drop-by-drop manner until the color of the solution transitions to a purplish blue. Thereafter, 0.1 M CH_3COOH is introduced until the color of the solution becomes clear. The positive reaction of this qualitative test produces a red precipitate in the clear sample solution. Furthermore, the results of the analysis were measured using a UV-VIS spectrophotometer in the wavelength range of 440-600 nm with an interval of 5 nm [11].

Quantitative Analysis

Aluminum Hydroxide Extraction Results

Quantitative analysis of initial fly ash samples and extraction results was carried out by measuring the absorbance of the samples using an Atomic Absorption Spectrometer (AAS). Before undergoing testing using AAS, a preliminary treatment was conducted on the sample (0.1 g). This involved the addition of 50 mL of HCl to a 100 mL Erlenmeyer flask containing the sample, followed by heating. Subsequently, 10 mL of the sample was transferred into a 25 mL volumetric flask, followed by the addition of distilled water until the limit mark was reached. Subsequently, the sample was measured for its degree of absorption at a wavelength of 309.3 nm. The measured value of the extinction coefficient is then substituted into the standard solution's linear regression equation, which has been previously measured.

Reduced Aluminum

A quantitative analysis of the reduced sample was conducted by measuring the sample's extinction coefficient with an AAS. Before undergoing testing using AAS, a preliminary treatment was conducted on the sample (0.625 grams) in a 100-mL Erlenmeyer flask. This involved the addition of 50 mL of HCl and subsequent heating. Subsequently, 10 mL of the sample was transferred into a 25 mL volumetric flask, followed by the addition of distilled water until the limit mark was reached. Subsequently, the sample was measured for its degree of absorption at a wavelength of 309.3 nm. The measured value of the extinction coefficient is then substituted into the standard solution's linear regression equation, which has been previously measured.

RESULT AND DISCUSSION

Effect of pH variation to obtain $Al(OH)_3$ precipitate

The process of obtaining aluminum hydroxide entails the precipitation of the sodium tetrahydroxy aluminate solution, which is derived from the extraction process. This solution is characterized by its alkaline nature, attributable to the presence of substantial quantities of sodium, a strong base that readily binds with aluminum metal. To facilitate the formation of the desired aluminum hydroxide precipitate, it is necessary to neutralize the solution to ensure the desired chemical equilibrium is achieved. Calcium aluminate will react with sodium bicarbonate ($NaHCO_3$) to form sodium aluminate, with calcium carbonate being produced as a residue. The $Al(OH)_3$ precipitation process utilizes pH variations of 6 and 6.5 by employing HCl. The utilization of HCl in this process is to reduce the pH of the filtrate, thereby inducing alumina precipitation and resulting in the formation of a NaCl salt. The data presented in Table 1 below provides a quantitative overview of the weight and yield outcomes.

Table 1. Extraction Result of $Al(OH)_3$

pH	Weight $Al(OH)_3$ (g)	Average weight(g)	Yield (%)
	1.604		
6	1.528	1.581	61.830
	1.612		
	1.672		
6.5	1.704	1.688	66.015
	1.688		

It is evident from the calculation that, based on the use of 16.67 grams of fly ash for extraction, complete extraction of aluminum hydroxide will result in the production of 2.557 grams of $Al(OH)_3$. The mean mass of aluminum hydroxide obtained from this study was 1.581 grams and 1.688 grams, respectively, with a yield of 61.830-66.015%. The presence of aluminum oxide, which has not dissolved in NaOH solvent during the initial extraction stage, is likely to be the reason for the reduced formation of sodium tetrahydroxy aluminate. This, in turn, reacts with HCl to form aluminum hydroxide. The findings of the study are consistent with the solubility diagram of aluminum species, which demonstrates that the formation of $Al(OH)_3$ predominantly occurs within the pH range of 6-6.5. The diagram elucidates the pH of the formation of Al species predicated on the solubility of each Al species, which is influenced by the concentration of the constituent ions of the Al species. Precipitation is formed when the solution is exactly saturated, i.e., when Qc > Ksp. The present study has obtained the initial aluminum concentration present in fly ash, with a view to its subsequent use in determining the occurrence of $Al(OH)_3$ precipitation. The Qc value of the results of this study is greater than the Ksp value of $Al(OH)_3$, which is 5.942×10^{-8} for pH 6 and $5.942\times10^{-7.5}$ for pH 6.5. The Ksp value of $Al(OH)_3$ is very small at 4.6×10^{-33}, indicating that the compound is easy to precipitate. The following equation is provided for reference:

$$Al(OH)_3 \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$$
$$Ksp = [Al^{3+}]\,[3OH^-]^3$$

It is evident from the equation presented that the Qc value in this study exceeds the Ksp of $Al(OH)_3$. This indicates that the solution is saturated, resulting in the formation of $Al(OH)_3$ precipitates. The results of the calculation demonstrate that the most efficient precipitation of $Al(OH)_3$ is achieved at a pH level of 6.5. The log S value of Al from this study is very small because the S value is directly proportional to the Ksp value.

Effect of Reduction Temperature Variation on the Al Metal Obtained

The effect of the reduction of aluminum hydroxide to aluminum was investigated by subjecting the sample to temperatures of 600°C, 650°C, and 700°C, at which temperatures the desired effect was observed. The subsequent reaction is as follows:

$$3Mg(s) + 2Al(OH)_3(s) \xrightarrow{T^oC} 3Mg(OH)_2(s) + 2Al(s)$$

Magnesium is an effective reducing agent for metals that are positioned on the right in the voltaic series, or metals that possess a more positive reduction potential value. The presence of magnesium results in a reduction of aluminum hydroxide, with the subsequent formation of magnesium hydroxide dihydrate ($Mg(OH)_2$). This process involves the binding of magnesium to hydroxide ions (OH^-), thereby leading to the formation of $Mg(OH)_2$. Magnesium will release two electrons when it is employed to reduce aluminum hydroxide, thereby undergoing oxidation. Magnesium possesses an oxidation number of 0 when present in either a solid or liquid state, with an oxidation number of +2 being attributed to its respective phases. The optimum temperature for the results of this study is 650°C, as this is the melting point of magnesium. This finding suggests a high degree of reactivity between magnesium and aluminum hydroxide. The reduction process gives rise to a mixture of solids comprising $Mg(OH)_2$ and Al, which exhibit divergent coloration at varying temperatures. The reduction product is a mixture of aluminum (Al) and $Mg(OH)_2$; therefore, it is necessary to wash the mixture to separate the two. The utilization of hot water during the washing process has been demonstrated to result in the dissolution of $Mg(OH)_2$, as evidenced by the cloudiness observed in the water during the process. The 650°C product exhibits a white coloration, indicative of a favorable reaction between magnesium and aluminum hydroxide. As stated in the relevant literature, aluminum is typically white. However, the reduction product exhibits a white hue, albeit not a pure white shade. This observation suggests the presence of residual impurities during the extraction process.

A Qualitative Analysis of the Reduction Results

A qualitative analysis was conducted using a specific reagent for aluminum, namely alizarin red S. The qualitative identification results of the fly ash reduction samples with the specific reagent alizarin red S showed positive aluminum if the sample was red. The following are the sample identification results:

Table 2. Identification Results of Reduced Samples with Alizarin Red S

pH	T (°C)		
	600	650	700
6	+	+	+
6.5	+	+	+

The measurement of alizarin *red s* extinction coefficient, as a function of wavelength, was conducted within the 440-600 nm range, with a step size of 5 nm. The maximum wavelength recorded was 495 nm, with an extinction coefficient of 0.021. The observed value of the extinction coefficient indicates that the atoms of alizarin undergo an electronic transition to a higher level. As asserted by [16] the red color produced by the aluminum complex in conjunction with alizarin constitutes a complementary color to the color absorbed by the complex, which exhibits a bluish green hue with a wavelength of 500 nm.

As demonstrated in Table 3, it can be concluded that the sample contains aluminum, given its capacity to absorb wavelengths within the range of 475-510 nm. In the samples with pH 6 and pH 6.5, and temperature variations of 600 °C- 700 °C, the maximum wavelength is almost equal to the maximum wavelength of alizarin. This indicates a wavelength shift between alizarin and the sample. Wavelength shift may be observed in this instance due to the conjugation of free electron pairs on the O atom of the -OH group in the alizarin structure, which coordinates with the central atom (Al^{3+} ion). This results in a longer wavelength shift in the sample. The -OH group, a constituent of the chromophore, has been observed to induce a wavelength shift of greater magnitude (i.e., a bathochromic shift), which is more commonly designated as a red shift. This phenomenon is attributable to an electronic transition in the d orbital of the complex compound. At a temperature of 600°C, both pH levels exhibited maximum wavelengths exceeding 500 nm. This phenomenon is likely attributable to the presence of -OH groups that remain bound to Al, thereby preventing complete reduction of $Al(OH)_3$ to Al. At a temperature of 600°C, magnesium (Mg) is unable to reduce aluminum hydroxide trihydrate ($Al(OH)_3$) completely. This allows the remaining hydroxyl groups (–OH) that have not been reduced to bind to the aluminum-alizarin complex. At a temperature of 650°C, both pH values exhibited a wavelength that closely approximated the wavelength of alizarin, which is 495 nm. As the temperature increased to 700°C, a decrease in wavelength of 5 nm was observed at both pH values when compared to the wavelength at 650°C. This finding indicates the presence of impurities that persist during the reduction process.

Table 3. Absorbance Data of Sample Qualitative Test Results

pH	T (ºC)	Absorbance	Wavelength (nm)
6	600	0,017	510
	650	0,019	480
	700	0,018	475
6.5	600	0,018	505
	650	0,020	485
	700	0,019	480

Quantitative Analysis of Reduction Results

The quantitative analysis in this study employed the AAS (Atomic Absorption Spectrophotometric) method to ascertain the aluminum content at a wavelength of 309.3 nm.

Table 4. Aluminum hydroxide ($Al(OH)_3$) yields extraction results

pH	yields (%)
6	37.024
6.5	41.723

As demonstrated in Table 4, the aluminum hydroxide content is greater at a pH of 6.5 than at a pH of 6. This is because the optimum pH for the precipitation of aluminum hydroxide is 6.5. The prevailing theory posits that pH 6.5 represents the optimal pH for $Al(OH)_3$ precipitation. At this pH, a state of equilibrium is achieved between $Al(OH)_3$ and its constituent OH^- ions, with Al^{3+} ions. The -log Ksp value of $Al(OH)_3$ at pH 6.5 is negative, indicating that the Ksp value of $Al(OH)_3$ precipitation at this pH is minimal, thereby facilitating the precipitation of the compound. It has been established that increasing the pH above 7 will result in the dissolution of the $Al(OH)_3$ precipitate back into the $Al(OH)^{4-}$ anion.

Table 5. Aluminum yields of the reduction

pH	T (oC)	Yields (%)
	600	7.476
6	650	8.667
	700	8.186
	600	8.862
6.5	650	9.013
	700	8.888

As demonstrated in Table 5, an increase in Al levels was observed at each pH value. This phenomenon occurred due to the favorable reaction of magnesium (Mg) with $Al(OH)_3$ at 650°C, resulting in the formation of Al. It has been demonstrated that aluminum hydroxide, when subjected to temperatures of 600°C and 700°C, is not fully reduced by magnesium. Consequently, the percentage of the desired substance obtained is reduced.

The alumina content in fly ash has been determined to be 14.52%. In this research, only 8.109% was achieved for pH 6 and 8.921% for pH 6.5. These results suggest the presence of residual impurities during the reduction process. The most probable explanation for this phenomenon is that the residual magnesium is not fully dissolved during the washing process with hot water.

CONCLUSION

At a pH of 6, the mass and content of $Al(OH)_3$ produced were found to be lower, with a value of 1.581 grams and a percentage content of 37.024%. Conversely, at a pH of 6.5, the mass and content of Al(OH)3 increased, with a value of 1.688 grams and a percentage content of 41.723%. It was established that at reduction temperatures of 600°C and 700°C, the aluminum metal content obtained was lower than at a reduction temperature of 650°C.

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