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Acid Mine Water Neutralisation Analysis Using CaO and Fly Ash at PT. Alamjaya Bara Pratama Kutai Kartanegara District, East Kalimantan Province

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Abstract
The handling of Acid Mine Water done at PT. Alamjaya Bara Pratama utilizes CaO and from prior research, fly ash is used as an adsorbent in neutralising Acid Mine Water. Hence the researcher conducted the research to compare the effectiveness of CaO and fly ash in neutralising Acid Mine Water. The usage of CaO and fly ash uses a laboratory scale with 1000ml of Acid Mine Water, a CaO mass variation of 0.4, 0.5 and 0.6 gram whereas with a fly ash mass variation of 50, 55 and 60 gram and a stirring speed of 50 and 100 rpm. Results shows that the addition of CaO and fly ash and stirring speed increases the pH and reduces the content of Fe and Mn. The adsorption of the metals Fe and Mn by CaO and coal fly ash can occur as most CaO contains the mineral compound Epistilbite (CaAl2Si6O16.5H2O), before conducting the experiment it shows that most of the fly ash contains the mineral compound Quartz (SiO2) and mullite (Al6Si2O13). Silica and Alumina has a polar side with an active hydroxyl group (-OH) which acts in the adsorption process between heavy metals and adsorbents in a solution containing water.

Keywords:
CaO, fly ash, acid mine water, adsorbent

1. Introduction
In general, every industrial activity creates environmental problems if not managed well. One of these problems faced by the coal mining industry is Acid Mine Water (AMW). As the development of coal
mining businesses particularly in the Kutai Kartanegara District region rises, some of the residents worry for the condition of the environment. Coal mining companies are feared to lack environmental management. The mining conducted by PT. Alamjaya Bara Pratama is an open pit mining, mining with this system can result in the degradation of environmental quality due to the extent of land cleared vegetation, rock overburden containing heavy metals and the formation of acid mine water which has pH of <6, and total suspended solids level and metal content contained therein. This research is conducted because the quality of water at PT. Alamjaya Bara Pratama is not in accordance with quality standards hence processing is needed to improve water quality. One of the process to improve water quality is by active processing, which uses chemicals. The chemicals that can be used to process Acid Mine Water namely CaO and fly ash. Based on this background, the authors conducted a study by analysing the characteristics of the adsorbents so that the utilization of CaO and fly ash as an adsorbent in neutralising acid mine water can be considered effective.

The formulation of the several problems in this research are:
1) Whether CaO and fly ash can be used as an adsorbent for the metals Fe and Mn?
2) How effective the fly ash is in increasing pH levels and decreasing the metal content of Fe and Mn?

The aims of this study are:
1) Analyse the adsorbent characteristics by testing for X-Ray Diffraction (XRD) and Scanning Microscopy (SEM) before and after laboratory tests;
2) Analyse the ratio of CaO and fly ash effectivity based on dosage, time, and stirring speed in neutralising the contents of acid mine water.

2. Method
Data collection methods carried in this study includes literature study and field research. Literature studies are carried out by obtaining information related to the research so that secondary data can be obtained as a reference when compiling the writing. Field research is conducted by sampling which uses Acid Mine Water which originated from the inlet of the settling pond Pit 7 in which an initial pH measurement is done using a pH meter, whereas the CaO sample came from the company PT. Alamjaya Bara Pratama and the fly ash samples are from PT. SLJ Global Tbk Loa Jananllir. Further research in laboratory scale is done by utilizing CaO and fly ash as an adsorbent for the metals Fe and Mn in neutralising Acid Mine Water through batch adsorption. Tests are conducted to describe each parameter variation, so that optimal conditions can be obtained in neutralising Acid Mine Water. The treatment done on a laboratory scale using a jar test kit with the stirring speed of 50 and 100 rpm. During testing, stirring is done so that the adsorbent is spread more evenly, and the entire adsorbent surface is in contact with Acid Mine Water. The results show that CaO and fly ash can increase the pH level of Acid Mine Water and reduce the Fe and Mn content. The acid mine water volume used is 1000 ml with 9.94 mg/l of Fe Content while the content of Mn in the test is 7.31 mg/l. The dosage of adsorbent used varied, for CaO 0.4, 0.5 and 0.6 grams whereas 50, 55 and 60 grams for fly ash. Control of changes in
each parameter after treatment is carried out with the following scheme:

A) pH: control is done at 0, 15, 30, 45 and 60 minutes.

B) Fe and Mn: control is done at 60 minutes.

3. Result

The parameters used in laboratory testing, namely Acid Mine Water content test which consists of pH, the metals Fe and Mn, whereas testing for CaO and fly ash content consists of XRD and SEM. Hereinafter, the data analysis methods used is the descriptive quantitative method which consists of:

A) Analysis of the changes in morphology and content of CaO and fly ash before and after testing so that changes in Acid Mine Water content occurs.

B) Analysis of the effect of CaO and fly ash mass and stirring speed on changes in Acid Mine Water content.

Discussion of the results of the research is carried out by testing in the laboratory so that the results obtained refers to Minister of Environment Decree No. LH 113 Year 2003 concerning Standard Acid Mine Water Quality. On test results using CaO and fly ash, changes in pH of Acid Mine Water based on experimental variations shows a change in proportion to the addition of CaO and fly ash or increase in stirring speed.

3.1 pH Test Results

| Material | Dosage | Time | pH 50 rpm | pH 100 rpm |
|----------|--------|------|-----------|-----------|
| CaO      | 0,4    | 0    | 3,11      | 3,11      |
|          |        | 15   | 5,93      | 6,59      |
|          |        | 30   | 6,02      | 6,78      |
|          |        | 45   | 6,17      | 6,82      |
|          |        | 60   | 6,29      | 6,95      |
|          | 0,5    | 0    | 3,11      | 3,11      |
|          |        | 15   | 6,62      | 7,70      |
|          |        | 30   | 6,81      | 7,74      |
|          |        | 45   | 6,93      | 7,88      |
|          |        | 60   | 7,04      | 7,92      |
|          | 0,6    | 0    | 3,11      | 3,11      |
|          |        | 15   | 7,69      | 8,63      |
|          |        | 30   | 7,81      | 8,70      |
Based on the test results, it showed that the addition of CaO greatly affects the change in Acid Mine Water pH. The results obtained for 0.4 gram with a stirring speed of 50 rpm showed the effectiveness of pH increment of 47.58% at t = 15 minutes, 48.31% at t = 30 minutes, 49.59 at t = 45 minutes, 50.56% at t = 60 minutes. Achieving the average effectiveness of pH increment of 49.01%, namely with a range from the initial pH of 3.11 to 6.29. Then, for a mass of 0.4 gram with a stirring speed of 100 rpm, the effectiveness of pH increments when t = 15 minutes is 52.83%, t = 30 minutes is 54.15%, t = 45 minutes is 54.42%, t = 60 minutes is 55.80%. Achieving the average effectiveness of pH increment of 54.17%. With a range from the initial pH of 3.11 to 7.92. For a mass of 0.6 gram with a stirring speed of 50 rpm, the effectiveness of pH increments when t = 15 minutes is 59.94%, t = 30 minutes is 60.20%, t = 45 minutes is 60.91, t = 60 minutes is 61.33%. Achieving the average effectiveness of pH increment of 60.50%. With a range from the initial pH of 3.11 to 8.04. Then, for a mass of 0.6 gram with a stirring speed of 100 rpm, the effectiveness of pH increments when t = 15 minutes is 63.98%, t = 30 minutes is 64.24%, t = 45 minutes is 64.68%, t = 60 minutes is 65.48%. Achieving the average effectiveness of pH increment of 64.59%. With a range from the initial pH of 3.11 to 9.01.

Table 2. Data on Changes in pH Level Based on the Addition Fly Ash Dosage and Stirring Speed

| Material  | Dosage | Time | pH | Total  |
|-----------|--------|------|-----|--------|
| Fly Ash   | 0      | 3,11 | 3,11|        |
|           | 15     | 5,77 | 6,20|        |
|           | 50     | 5,94 | 6,31|        |
|           | 45     | 6,00 | 6,42|        |
| Fly Ash   | 60     | 6,16 | 6,57|        |
|           | 0      | 3,11 | 3,11|        |
|           | 15     | 6,09 | 6,97|        |
|           | 55     | 6,24 | 7,10|        |
|           | 45     | 6,35 | 7,21|        |
|           | 60     | 6,52 | 7,40|        |
|           | 60     | 3,11 | 3,11|        |
Based on the test result, it indicates that the addition of fly ash mass greatly affects the change in Acid Mine Water pH. The results obtained for a mass of 50 gram with a stirring speed of 50 rpm showed the effectiveness of pH increment of 46.10% at t = 15 minutes, 47.61% at t = 30 minutes, 48.20 at t = 45 minutes, 49.54% at t = 60 minutes. Achieving the average effectiveness of pH increment of 47.86%, namely with a range from the initial pH of 3.11 to 6.16. Then, for a mass of 50 gram with a stirring speed of 100 rpm, the effectiveness of pH increments when t = 15 minutes is 49.84%, t = 30 minutes is 50.74%, t = 45 minutes is 51.56%, t = 60 minutes is 52.64%. Achieving the average effectiveness of pH increment of 51.19%. With a range from the initial pH of 3.11 to 6.57. For a mass of 55 gram with a stirring speed of 50 rpm, the effectiveness of pH increments when t = 15 minutes is 48.96%, t = 30 minutes is 50.16%, t = 45 minutes is 51.05, t = 60 minutes is 52.30%. Achieving the average effectiveness of pH increment of 50.62%. With a range from the initial pH of 3.11 to 6.52. Then, for a mass of 55 gram with a stirring speed of 100 rpm, the effectiveness of pH increments when t = 15 minutes is 55.40%, t = 30 minutes is 56.22%, t = 45 minutes is 56.89%, t = 60 minutes is 57.95%. Achieving the average effectiveness of pH increment of 56.61%. With a range from the initial pH of 3.11 to 7.40. For a mass of 60 gram with a stirring speed of 50 rpm, the effectiveness of pH increments when t = 15 minutes is 55.95%, t = 30 minutes is 57.38%, t = 45 minutes is 58.01, t = 60 minutes is 58.92%. Achieving the average effectiveness of pH increment of 57.56%. With a range from the initial pH of 3.11 to 7.57. Then, for a mass of 60 gram with a stirring speed of 100 rpm, the effectiveness of pH increments when t = 15 minutes is 60.26%, t = 30 minutes 60.57%, t = 45 minutes is 60.80%, t = 60 minutes is 61.24%. Achieving the average effectiveness of pH increment of 60.72%. With a range from the initial pH of 3.11 to 8.02.

3.2 Fe an Mn Test Results

The results of the metal iron (Fe) and Manganese (Mn) adsorption test showed a significant reduction in content.

| Material | Dosage | Fe Result |
|----------|--------|-----------|
| Initial  | 9,94   | 9,94      |
| CaO      | 0,4    | 3,19      | 2,53      |

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Based on the Table 3 above, the effectiveness of decrement of Fe content using CaO is as follows:

a. The effectiveness of 0.4 gram of CaO with a stirring speed of 50rpm is 67.92% namely from the initial content of 9.94 mg/l to 3.19 mg/l, while the effectiveness of 0.4 grams of CaO with a stirring speed of 100 rpm is 75.52% from the initial content of 9.94 mg/l to 2.53 mg/l.

b. The effectiveness of 0.5 gram of CaO with a stirring speed of 50rpm is 73.32% namely from the initial content of 9.94 mg/l to 2.65 mg/l, while the effectiveness of 0.5 grams of CaO with a stirring speed of 100 rpm is 82.60% from the initial content of 9.94 mg/l to 1.73 mg/l.

c. The effectiveness of 0.6 gram of CaO with a stirring speed of 50rpm is 67.27% namely from the initial content of 9.94 mg/l to 2.36 mg/l, while the effectiveness of 0.6 grams of CaO with a stirring speed of 100 rpm is 83.44% from the initial content of 9.94 mg/l to 1.65 mg/l.

For the fly ash the effectiveness of decrement of Fe content is as follows:

a. The effectiveness of 50 gram of Fly Ash with a stirring speed of 50 rpm is 65.81% namely from the initial content of 9.94 mg/l to 3.40 mg/l, while the effectiveness of 50 grams of Fly Ash with a stirring speed of 100 rpm is 73.38% from the initial content of 9.94 mg/l to 2.65 mg/l.

b. The effectiveness of 55 gram of Fly Ash with a stirring speed of 50 rpm is 64.33% namely from the initial content of 9.94 mg/l to 3.55 mg/l, while the effectiveness of 55 grams of Fly Ash with a stirring speed of 100 rpm is 72.54% from the initial content of 9.94 mg/l to 2.73 mg/l.

c. The effectiveness of 60 gram of Fly Ash with a stirring speed of 50 rpm is 58.23% namely from the initial content of 9.94 mg/l to 4.15 mg/l, while the effectiveness of 60 grams of Fly Ash with a stirring speed of 100 rpm is 72.34% from the initial content of 9.94 mg/l to 2.75 mg/l.

Table 4. Results of CaO and Fly Ash Adsorption Test of Mn

| Material | Dosage | Mn Result |
|----------|--------|-----------|
|          | 0.5    | 2.65      |
|          | 0.6    | 2.36      |
|          | 50     | 3.40      |
| Fly Ash  | 55     | 3.55      |
|          | 60     | 4.15      |
|          |        | 2.75      |
|                | 50 rpm | 100 rpm |
|----------------|--------|---------|
| Initial        | 7.31   | 7.31    |
| 0.4            | 3.68   | 3.36    |
| CaO 0.5        | 2.81   | 2.46    |
| 0.6            | 2.04   | 1.72    |
| 50             | 4.37   | 3.78    |
| Fly Ash 55     | 3.85   | 3.26    |
| 60             | 3.05   | 2.65    |

Based on Table 4 above, the effectiveness of decrement of Mn content is as follows:

a. The effectiveness of 0.4 gram of CaO with a stirring speed of 50 rpm is 49.70% namely from the initial content of 7.31 mg/l to 3.68 mg/l, while the effectiveness of 0.4 grams of CaO with a stirring speed of 100 rpm is 54.08% from the initial content of 7.31 mg/l to 3.36 mg/l.

b. The effectiveness of 0.5 gram of CaO with a stirring speed of 50 rpm is 61.61% namely from the initial content of 7.31 mg/l to 2.81 mg/l, while the effectiveness of 0.5 grams of CaO with a stirring speed of 100 rpm is 66.35% from the initial content of 7.31 mg/l to 2.46 mg/l.

c. The effectiveness of 0.6 gram of CaO with a stirring speed of 50 rpm is 72.05% namely from the initial content of 7.31 mg/l to 2.04 mg/l, while the effectiveness of 0.6 grams of CaO with a stirring speed of 100 rpm is 76.50% from the initial content of 7.31 mg/l to 1.72 mg/l.

For the fly ash the effectiveness of decrement of Mn content is as follows:

a. The effectiveness of 50 gram of Fly Ash with a stirring speed of 50 rpm is 40.71% namely from the initial content of 7.31 mg/l to 4.37 mg/l, while the effectiveness of 50 grams of Fly Ash with a stirring speed of 100 rpm is 48.34% from the initial content of 7.31 mg/l to 3.78 mg/l.

b. The effectiveness of 55 gram of Fly Ash with a stirring speed of 50 rpm is 47.33% namely from the initial content of 7.31 mg/l to 3.85 mg/l, while the effectiveness of 55 grams of Fly Ash with a stirring speed of 100 rpm is 55.45% from the initial content of 7.31 mg/l to 3.26 mg/l.

c. The effectiveness of 60 gram of Fly Ash with a stirring speed of 50 rpm is 58.32% namely from the initial content of 7.31 mg/l to 3.05 mg/l, while the effectiveness of 60 grams of Fly Ash with a stirring speed of 100 rpm is 63.70% from the initial content of 7.31 mg/l to 2.65 mg/l.
3.3 Characterization of the Adsorbents CaO and Coal Fly Ash
The results of XRD testing on CaO and fly ash aims to determine the characteristics of constituent minerals.

Table 5. CaO XRD Test Results Prior to Experiment

| No | 2theta (deg) | Intensity (cps) | theta/2 | d     | Mineral       | Mineral Percentage | Chemical Formula         |
|----|--------------|----------------|---------|-------|---------------|-------------------|-------------------------|
| 1  | 18,08        | 57,728467      | 9,04    | 4,871 | Epistilbite   | 15,7%             | CaAl$_2$Si$_6$O$_{16}$·5H$_2$O |
| 2  | 29,45        | 119,01441      | 14,73   | 3,011 | Calcite       | 32,4%             | CaCO$_3$               |
| 3  | 34,13        | 72,23142       | 17,07   | 2,608 | Sepiolite     | 19,7%             | Mg$_2$Si$_6$O$_{13}$(OH)$_2$·6H$_2$O |
| 4  | 39,45        | 19,254594      | 19,73   | 2,268 | Sepiolite     | 5,2%              | Mg$_3$Si$_6$O$_{13}$(OH)$_2$·6H$_2$O |
| 5  | 43,22        | 19,104866      | 21,61   | 2,078 | Diaspore      | 5,2%              | (AlO(OH))             |
| 6  | 47,56        | 33,829291      | 23,78   | 1,898 | Anatase       | 9,2%              | TiO$_2$                |
| 7  | 48,56        | 19,094354      | 24,28   | 1,861 | Calcite       | 5,2%              | CaCO$_3$               |
| 8  | 50,88        | 26,602791      | 25,44   | 1,782 | Dolomite      | 7,3%              | CaMg(CO$_3$)$_2$        |

Table 6. Fly Ash XRD Test Results Prior to Experiment

| No | 2theta (deg) | Intensity (cps) | theta/2 | d     | Mineral       | Mineral Percentage | Chemical Formula         |
|----|--------------|----------------|---------|-------|---------------|-------------------|-------------------------|
| 1  | 12,01        | 5,564537       | 7,315   | 7,315 | Serpentine    | 3,1%              | Mg$_6$(Si$_2$O$_9$)(OH)$_8$ |
| 2  | 20,90        | 10,237461      | 10,45   | 4,219 | Quartz-Low   | 5,7%              | Alpha-SiO$_2$           |
| 3  | 26,61        | 20,204461      | 13,31   | 3,325 | Augite       | 11,2%             | (Ca, Na)(Mg, Fe, Al)(Al, Si)O$_6$ |
| 4  | 33,37        | 22,754713      | 16,69   | 2,666 | Dolomite     | 12,6%             | CaMg(CO$_3$)$_2$        |
| 5  | 39,67        | 50,41417       | 19,84   | 2,255 | Mullite      | 27,9%             | Al$_2$Si$_2$O$_5$       |
| 6  | 40,48        | 18,140841      | 20,24   | 2,212 | Mullite      | 10,0%             | Al$_2$Si$_2$O$_5$       |
| 7  | 42,68        | 20,7842        | 21,34   | 2,103 | Periclase    | 11,5%             | MgO                     |
| 8  | 42,92        | 18,140841      | 21,46   | 2,092 | Calcite      | 10,0%             | CaCO$_3$               |
| 9  | 54,07        | 6,632376       | 27,04   | 1,684 | Rutile       | 3,7%              | TiO$_2$                |
| 10 | 60,68        | 7,76397        | 30,34   | 1,515 | Hematite     | 4,3%              | Alpha-Fe$_2$O$_3$       |
3.4 SEM Test Results

Figure 1. (a) CaO SEM Analysis Results Prior to Experiment. 1(b) CaO SEM Results Following Experiment

Figure 2(a). Fly Ash SEM Analysis Prior to Experiment. 2(b) Fly Ash SEM Results Following Experiment

Based on SEM test results on CaO and fly ash prior to experiment, it shows that there are few pores with a small size. In contrast with the results of the SEM test on CaO and fly ash following the experiment, the pores appear to be many and are enlarged, and the surface looks denser. In Figure 2.1 b and 2.2 b shows that more pores are formed and are larger, this indicates an increase in surface area. The presence of small pores that are larger following the experiment shows that Acid Mine water is acidic and can damage the surface of CaO and fly ash. The availability of silica and alumina is shown in white. Silica and alumina are porous media and as a functional group has the potential to adsorb metal ions. As functional groups, silica and alumina will surface when there is damage to the surface layer so that they can adsorb Fe and Mn. In addition to the presence of porin with a significant difference which illustrates that the adsorbent has adsorbed Fe and Mn on the pore surface, which is on the surface of CaO and can illustrate that the adsorbent has adsorbed Fe and Mn which is on the pore surface of CaO and fly ash before experiments looks very hollow whereas after the experiment it appears to have its cavities filled with a lot of solid material. This shows that the materials enter and...
adhere to the surface of the adsorbent.

4. Discussion

1) Based on the characteristics of CaO and fly ash with XRD and SEM testing the following results is as followed

2) The results of the XRD diffractogram on CaO before the experiments showed that most CaO contained Epistilbite (CaAl2Si6O16.5H2O). For the results of XRD diffractogram on fly ash before the experiment showed that most of the fly ash contained Quartz (SiO2) and mullite (Al6Si2O13). Silica and alumina have a polar side with anfunctional hydroxyl group (-OH) which plays a role in the adsorption of heavy metals and as an adsorbent in a solution containing water. In addition, it also contains carbonate minerals which functions as an alkali compound such as Calcite (CaCO3) which forms an alkaline atmosphere in a solution so that it can increase the pH of Acid Mine Water

3) The results of the SEM test on CaO prior to the experiment shows that it has few pores with a small size, whereas in the SEM test results after the experiment shows that there are more pores and of a larger size. Likewise, the results of the SEM test on fly ash before the experiment had few small pores, whereas the SEM test results after the experiment shows that there are more pores formed and the surface becomes denser

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