Characterization Study of Coal-Combustion Ash For Acid Mine Drainage Prevention

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***Abstract*— Prevention of the acid mine drainage generation is the best effort to reduce one of the environmental issues in mining activities. This effort can be done by covering sulphide-bearing rocks by suitable and available rocks or materials to prevent the oxidation reaction of sulphide minerals with water and air. One of the materials that might be utilized is coal-combustion ash from the power plants, in the form of fly ash and bottom ash. It is necessary to conduct material characteristization of the ash so that the plan to form a cover layer can be carried out optimally. The test is carried out for mineralogical analysis using XRD and XRF; static geochemical tests with Paste pH, Net Acid Generation (NAG), Acid Neutralizing Capacity (ANC), Maximum Potential Acidity (MPA); and kinetic test with the free drainage column test. The test results show that FA and BA have non acid forming (NAF) characteristics so that they have the potential to be used as cover layer for potentially acid forming (PAF) material. In addition to geochemistry, geophysically FA has the ability to reduce water infiltration because it contains a lot of clay minerals, while BA has the ability to maintain moisture in the cover layer due to sandy properties of the material.**

Keywords—coal-combustion ash, geochemical, acid mine drainage

I. Introduction

Acid mine drainage (AMD) or acid rock drainage (ARD) has been recognized as an important issue in environmental management in the coal and mineral mining industry, which are characterized by high levels of acidity and dissolved metals content. High acidity occurs as a result of the natural oxidation of sulfide minerals in the rocks by the presence of air and water, through the following chemical reactions [1]:

$$FeS_2 + {}^{15}/_2\, H_2O_2 \rightarrow Fe^{3+} + 2SO_4^{2-} + H^+ + 7H_2O$$

The general management to deal with this issue is to prevent the formation of AMD and / or treatment of the AMD that has been formed. The principle of preventing is to remove one of the main components of the oxidation reaction, namely rock that contains sulfide minerals (as a source of acid), water (H_2O) or air (O_2). The principle of prevention is then applied with sulphide-bearing rock (known as Potentially Acid Forming – PAF) covering techniques to prevent them from reacting with water and air. There are two known covering methods, namely dry cover and wet cover.

In dry cover method, solid materials that are commonly used are rocks that do not contain sulphide minerals and do not have the potential to produce AMD (known as Non-Acid Forming - NAF rock), clay, or other materials commonly found in mining operations.

Currently, fly ash (FA) and bottom ash (BA), which are produced from the coal-fired steam power plant (PLTU), are alternative materials to use as a cover material of PAF. To determine its reliability, it is necessary to understand the geochemical characteristic of FA and BA. This paper describes the results of FA and BA characterization and their potential as a cover material for PAF.

II. Methodology

The characterization method is carried out through geochemical testing in the laboratory. Mineral or elemental contents in FA and BA samples can be determined through mineralogy analysis, where total alkaline could be also determined using equation as follow:

$$Total\ alkaline\ (\%\ weight\ CaO) = \left(\frac{\%\ weight\ CaO}{56.1\ g/mol} + \frac{\%\ weight\ N2O}{61.8\ g/mol} + \frac{\%\ weight\ MgO}{40.31 g/mol} + \frac{\%\ weight\ K2O}{94.2\ g/mol}\ \mathrm{X}\ 56.1\ \mathrm{g/mol}\right.$$

Mineralogy analysis was carried out using X-Ray Diffraction (XRD) with the Rigaku SmartLab and Xray Flourescence (XRF) with the Rigaku Supermini 200 machines. Both tests were carried out at Hydrogeology and Hydrogeochemical Laboratory ITB. Meanwhile, prediction of the acid mine drainage generation is conducted through geochemical static test and kinetic tests, which were carried out at Environmental Laboratory Itenas Bandung. The tests are intended to predict whether a rock sample has acid-producing and/or acidneutralising capacities [2] using most widely accepted methods.

A. Paste pH/EC

This test is carried out to determine the pH of the mixed-sample with distilled water in a ratio of 1: 2 which is left for 16 hours [3].

B. Maximum Potential Acidity (MPA)

MPA shows the maximum potential acidity value based on the assumption that all sulfur elements contained in the sample can produce acid. MPA can be calculated based on the percent value of Total Sulfur (TS), where MPA (kg H_2SO_4 / ton) is TS (%) x 30.6.

C. Acid Neutralizing Capacity (ANC)

ANC states the capacity of a sample to neutralize acid based on its carbonate mineral content. The ANC value was obtained through experiments, namely by reacting a sample with a standard acid HCl solution, then back titrating with NaOH solution. The amount of acid equivalent to NaOH consumed. ANC value testing is carried out based on SNI 13-7170-2006 testing standard.

D. Net Acid Production Potential (NAPP)

NAPP is the difference between MPA and ANC, which represents the balance between the capacity of the sample to produce acid and the capacity of the sample to neutralize the acid. The NAPP value is expressed in units of kg H_2SO_4 per tonne of rock. Samples that have the potential to be acidic are indicated by a positive NAPP value (NAPP> 0), while samples that do not have the potential to produce acidity are indicated by a negative NAPP value (NAPP <0).

E. Net Acid Generation (NAG) test

NAG test is proposed to evaluate the generation of sulfuric acid. This test is based on the principle that a strong oxidizing agent (hydrogen peroxide) will accelerate the sulfide oxidation reaction. During the NAG test, the acid formation and acid neutralizing reactions occur simultaneously so that the final result obtained shows the residual acid value that is still present in the sample after all acid formation and neutralization has occurred. Samples with a final NAG pH greater than or equal to 4.5 are categorized as NAF, while a NAG pH below 4.5 is categorized as PAF. The NAG test is carried out based on the SNI 13-6599-2001 testing standards.

F. Kinetic Column Test

In addition to the static testing, kinetic geochemical testing is also carried out in the laboratory using the free draining column test principle. This test aims to determine the long-term trend of the leachate quality discharged from the column, including the physical condition of the material in the column. The schematic of the test column is as shown in Figure 1, where tests are carried out for FA and BA individually, and mixing FA and BA with ratio of 1: 1. 20 cm height of material is filled on the column for the test. Already known material as PAF is also tested as comparison.

A total of 300 mL of water / kg sample was poured into the column on days 1, 2, 3, and 4, and leachate was collected for 15 hours period. Furthermore, heating using a 60-Watt spot light was carried out for 9 hours. For days 5, 6, and 7, heating is carried out for 24 hours, hoping can drying, and it is ready for the next round of testing. The leachate samples formed were then analyzed for pH, Electric Conductivity (EC) and Total Dissolve Solid (TDS) parameters.

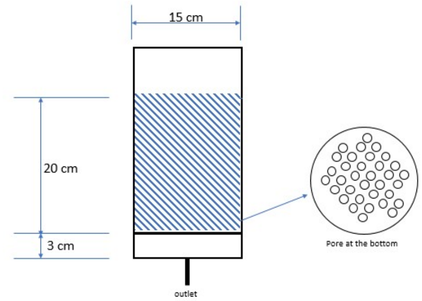

Fig 1. Colum test design

III. Result And Discussion

A. Mineralogical Analysis with XRD and XRF

The X-Ray Diffraction (XRD) test was carried out to determine the composition of minerals contained in the sample, with perticular reference to the source of the acid-carrying minerals and acid-neutralizing minerals contained in the sample. XRD test results are shown in Figure 2 and Figure 3.

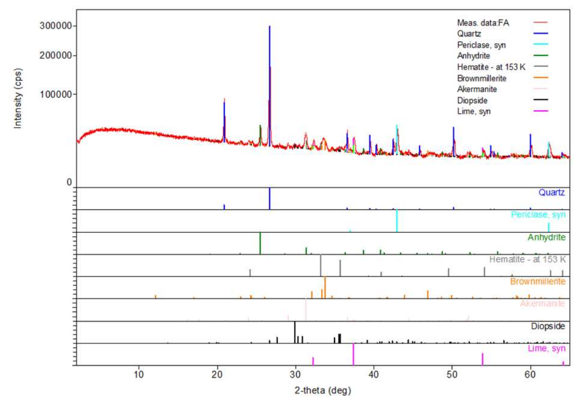

Fig 2. XRD result for FA sample

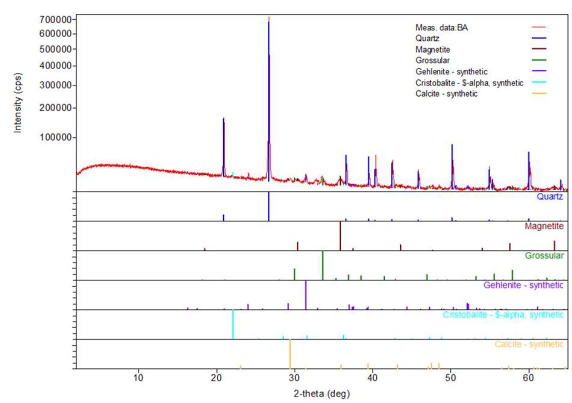

Fig 3. XRD result for BA sample

The results of XRF analysis for FA both in terms of oxides and elements are as shown in Table 1.

TABLE 1. XRF result as oxides for FA

No.	Component	Result	Unit
1	Na2O	0.339	mass%
2	MgO	13.9	mass%
3	Al2O3	8.97	mass%
4	SiO2	37.6	mass%
5	P2O5	0.282	mass%
6	SO3	6.43	mass%
7	Cl	0.0990	mass%
8	K2O	0.723	mass%
9	CaO	24.2	mass%
10	TiO2	0.391	mass%
11	MnO	0.190	mass%
12	Fe2O3	6.39	mass%
13	SrO	0.216	mass%
14	ZrO2	0.0075	mass%
15	Rh2O3	0.262	mass%

TABLE 2. XRF result as elements for FA

No.	Component	Result	Unit
1	Na	0.334	mass%
2	Mg	11.5	mass%
3	Al	7.09	mass%
4	Si	27.9	mass%
5	P	0.219	mass%
6	S	4.64	mass%
7	Cl	0.183	mass%
8	K	1.13	mass%
9	Ca	34.5	mass%
10	Ti	0.536	mass%
11	Mn	0.345	mass%
12	Fe	10.6	mass%
13	Sr	0.464	mass%
14	Zr	Trace	mass%
15	Rh	0.540	mass%

From the XRD and XRF results for FA samples, it can be seen that for oxide, the content of Quartz (SiO_2) was detected as much as 37.6%, Periclase (MgO) as much as 13.9%, and Aluminum Oxide (Al_2O_3) as much as 8.97%. Lime (CaO) was detected as much as 24.2%, which can be derived from lime which is included in the coal combustion process which is intended to reduce sulfur levels in air emissions. From the calculation, total alkaline of FA is 43.9% as CaO. Sulfur trioxide (SO_3) was detected as much as 6.43%, which is also formed when sulfur dioxide (SO_2) reacts with water in low concentrations in the air. This may occur during the process of controlling emission pollution in the chimney which then results in the reaction.

While in terms of elements, the Ca content was detected as much as 34.5%, Si as much as 27.9%, and Mg as much as 11.5%. The total S of 4.64% indicates the presence of sulfur content from the coal combustion process contained in the FA.

TABLE 3. XRF result as oxide for BA

No.	Component	Result	Unit
1	Na2O	0.245	mass%
2	MgO	8.11	mass%
3	Al2O3	5.97	mass%
4	SiO2	58.9	mass%
5	P2O5	0.122	mass%
6	SO3	0.904	mass%
7	K2O	0.703	mass%
8	CaO	19.4	mass%
9	MnO	0.0760	mass%
10	Fe2O3	5.55	mass%
11	ZnO	0.0231	mass%
12	SrO	0.0652	mass%

TABLE 4. XRF result as elements for BA

No.	Component	Result	Unit
1	Na	0.229	mass%
2	Mg	6.92	mass%
3	Al	4.84	mass%
4	Si	45.5	mass%
5	P	0.106	mass%
6	S	0.726	mass%
7	K	1.20	mass%
8	Ca	30.0	mass%
9	Mn	0.151	mass%
10	Fe	10.1	mass%
11	Zn	0.0517	mass%
12	Sr	0.156	mass%

For BA samples, the oxide was dominated by Quartz (SiO_2) minerals which were detected as much as 58.9%, Periclase (MgO) as much as 8.11%, Aluminum Oxide (Al_2O_3) as much as 5.97%. High silicate content will give some advantages for neutralization, because nearly all silicate weathering reactions also consume acid and increase the pH [4]. Lime (CaO) was detected as much as 19.4% which came from lime which was included in the coal combustion process, lower than the content in the FA sample. The presence of lime was also detected from the mineral Calcite ($CaCO_3$). From the calculation, total alkaline of BA is 31%. SO_3 was detected at 0.904%, lower than the content in the FA sample.

While in elemental terms, the Ca content was detected as much as 30%, 45.5% Si, and 6.92% Mg. Total S was 0.726%, lower than FA.

Based on the results above, some important notes are as follows:

1. The Ca content, which is also shown by the CaO content, in FA and BA materials is quite high, which is the residue that comes from adding $CaCO_3$ in the coal combustion process. The presence of this mineral is very important in the process of neutralizing the potential acid in the PAF material.

2. The high S content in FA material correlates with SO_3, which comes from SO_2 which reacts with water in the air. This is not found in BA because it is the bottom ash which

does not float due to weight, it can be seen from the high SiO_2 value.

B. Geochemical static tests

The results of the static geochemical test performed are as shown in Table 5. The results of the static test show that the BA sample indicates alkaline characteristics, which means that it has the potential to neutralize the acid formed from PAF. The result that needs to be further investigated is the FA sample, where the NAG pH value is 8.68, which means it has alkaline properties. However, from the parameter Total Sulfur, it is known that the content is 4.64%, and does not show a positive ANC value. Therefore, for FA samples, it is necessary to do another test to determine the classification of the sample.

TABLE 5. XRF result as elements for BA

Test	Unit	***Fly Ash* (FA)**	***Bottom Ash* (BA)**
Paste pH	pH unit	11.77	11.60
Paste Electical Conductivity (EC)	µS/cm	6.47	4.64
Total Sulfur (as S)	%	4.64	0.73
Maximum Potential Acidity (MPA)	kg H_2SO_4/t	141.98	22.34
Acid Neutralising Capacity (ANC)	kg H_2SO_4/t	933.13	947.16
Net Acid Producing Potential (NAPP)	kg H_2SO_4/t	-791.15	-924.82
Net Acid Generation (NAG) pH 4,5	kg H_2SO_4/t	-	-
Net Acid Generation (NAG) pH 7,0	kg H_2SO_4/t	-	-
NAG pH	pH unit	8.68	11.2
Sampel classification		Non-Acid Forming (NAF)	Non-Acid Forming (NAF)

*Classification is based on NAPP and NAG pH. If NAPP > 0 and NAG pH < 4.5 = PAF. And if NAPP < 0 and NAG pH > 4.5 = NAF. Apart from that it is considered UC (uncertain) and needs further analysis.

C. Kinetic column tests

The results of measurement and calculation of the initial infiltration rate on the layers of FA, BA, FABA, and PAF are as shown in Figure 4. These results indicate that BA has a higher permeability than other materials, where this is strongly influenced by the physical composition of the material. BA is influenced by high sand content, as has been shown by the XRD / XRF results.

Infitration rate plays an important role in passing the water which then affects the moisture condition of the material layer. The water content in the layer will then affect the oxidation reaction, where decreasing the rate of such reactions will then minimise the occurrence of AMD [5], the quality of the water produced, and the quantity or volume of leached-water. Also, a slight increase in fines on the surface will decrease the permeability and this leads to a difference in the infiltration rate [5].

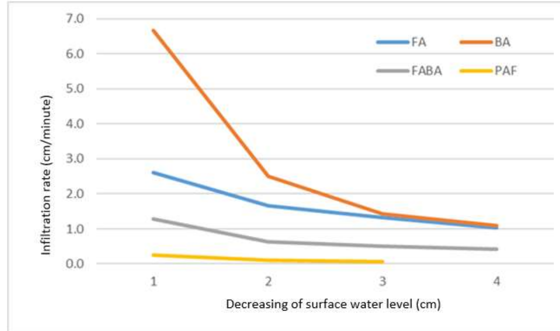

Fig 4. Infiltration rate

The average weekly pH values (up to 6 weeks) of the leached-water for the various wet-dry cycles are as shown in Figure 5. FA, BA, and FABA mixtures (with a composition of 1: 1) show a value greater than 7 consistently, which means they have potential as neutralizers.

The results of water quality analysis for the parameters of Electrical Conductivity (EC) and Total Dissolved Solids (TDS) are as shown in Figure 6 and Figure 7. FA has relatively high weekly mean EC and TDS values compared to FABA, meanwhile BA has the lowest value. This shows that the leachate from BA has a low dissolved ion content, which means that the mineral content in BA is relatively unreactive or unavailable.

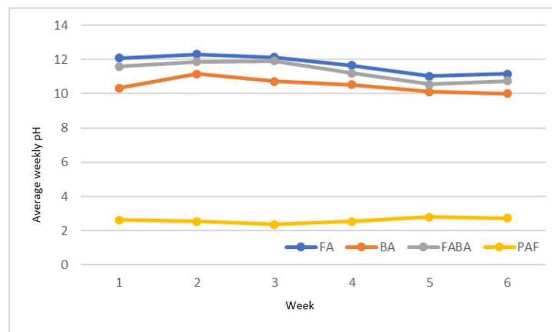

Fig 5. Average weekly pH

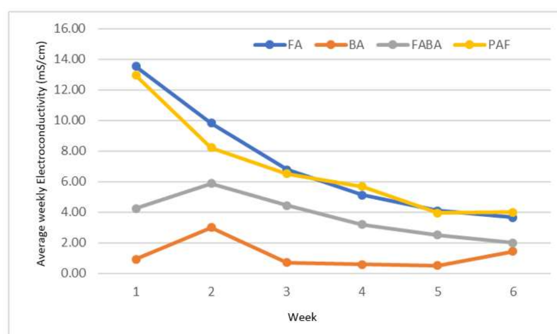

Fig 6. Average weekly electroconductivity (mS/cm)

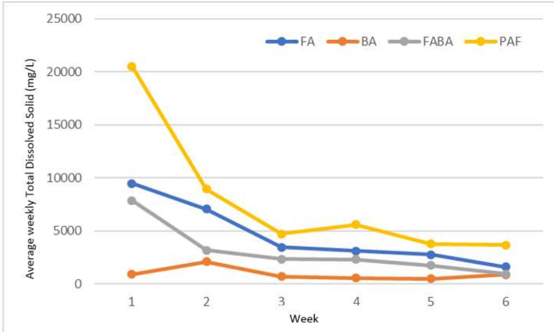

Fig 7. Average weekly Total Dissolved Solid (mg/L)

D. *Optimum FA:BA ratio*

Based on the foregoing, then additional paste pH testing is carried out to determine the effective FABA ratio to neutralize the acid potential of PAF. The FABA used has a composition of FA and BA with different ratios, as shown in Table 6. The paste pH test shows the results as in Figure 8.

TABLE 6. Composition FA and BA in mixture

Code	Composition	
	FA	BA
A	25%	75%
B	50%	50%
C	75%	25%
D	90%	10%

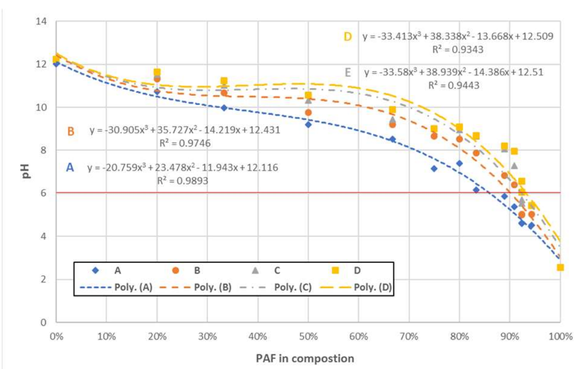

Fig 8. Effects of FABA and PAF to the paste pH value

The pH value graph shows that the FABA sample with FA ratio greater than BA gives a greater pH value compared to samples with a lower FA ratio, at the same amount of PAF. For example, sample D with a ratio of FA: BA = 9:1 can give a pH value of 6 at a higher percentage of PAF compared to other FA: BA ratios. Or in other words, at the same percentage of PAF, sample D can provide a higher pH value than other samples. This result suggests that increasing the portion of FA in FABA has a better neutralizing potential.

This finding is also supported by the results of the analysis which shows the effect of the proportions of FA and BA in the samples tested on the paste pH value, as shown in Figure 9. The increase in pH appears to be more significant and has a correlation with an increase in the proportion of FA compared to the proportion of BA in the mixture. This correlates with previous results, where FA played an important role in determining a better pH value.

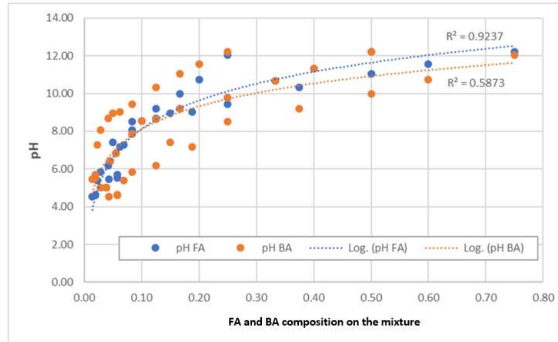

Fig 9. Effect of FA and BA proportion in the samples to the paste pH value

IV. Conclusion and Recommendation

Based on the results of the material characterization test, the following conclusions were obtained:

1. The mineral content of Ca in FA and BA materials is quite high and is very important in the process of neutralizing the acid potential of PAF.
2. The results of the static test show that the FA and BA samples shows alkaline characteristics, which means that it has the potential to neutralize the acid formed from PAF.
3. Further static using paste pH analysis also shows that increasing the portion of FA in FABA has a better neutralizing potential than that of BA
4. The results of the kinetic test show that FA produces a pH value which is greater than BA.

Further research related to the metal parameters of the leachate water quality produced from the column is needed, to better understand the effect of rock characteristics on the water quality of oxidation products.

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