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The Challenge of the Use of Potentially Acid Forming for the Cover Layer to Prevent Acid Mine Drainage

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Abstract

The coal production has been increasing every year in Indonesia, leading to the increase of Acid Mine Drainage (AMD) problem which is environmental problem in mining operation. The backfill of rocks by the types is performed to prevent AMD in mining operation: they are classified into Potentially Acid Forming (PAF) or Non-Acid Forming (NAF) by Net Acid Generation (NAG) test. However, more than eighty percent of waste rocks consist of PAF in some open pit coal mines in Indonesia, and the water pollution is a major problem there. It is difficult to perform the prevention in the case due to the lack of NAF. In this research, geochemical and physical analysis of rocks was conducted to understand the properties of PAF. The results suggested that some rocks were classified into PAF in which the net acid producing potential (NAPP) was different, and some of them might not be the main source of AMD on the site. Moreover, sulfur and iron existed in a different form in each sample, and they were dissolved in a different condition. These facts indicate that some of PAF possibly can be used as cover layer to prevent AMD instead of NAF in such a region.

1. Introduction

1.1. Coal Production in Indonesia

More than 90 percent of the development of coal in Indonesia is open pit mining. The removal of forest and topsoil for an excavation of coal has a negative impact on the environment. Rehabilitation activities for the reclamation of land are required in mining operation to decrease the impact. Acid Mine Drainage (AMD) is one of the environmental problems caused by such activities, and it has been considered as a serious problem in many mines. The acidic water is harmful for human body for the low pH and the content of heavy metals. This problem is expected to increase with the expansion of coal production in Indonesia; therefore, they have to be dealt with immediately.

1.2. Acid Mine Drainage

The exposure of sulfide minerals to water and oxygen leads to AMD. The exposure of them is inevitably caused during the excavation of waste rock in mining operation. The main chemical reaction is described as below;

$$FeS_2+7/2O_2+H_2O \rightarrow Fe^{2+}+2SO_4^{2-}+2H^+ \quad 1)$$

$$Fe^{2+}+1/4O_2+H^+ \rightarrow Fe^{3+}+1/2H_2O \quad 2)$$

$$FeS_2+14Fe^{3+}+8H_2O \rightarrow 15Fe^{2+}+2SO_4^{2-}+16H^+ \quad 3)$$

The ferrous iron produced in Equation 1 becomes ferric iron through the oxidation caused by oxygen as shown in Equation 2. The ferric iron is a strong acid and oxidizes a sulfide mineral as shown in equation 3. The ferrous iron is oxidized by oxygen again as shown in Equation 2. Thus, the reaction of the generation of AMD is continued to proceed once the first reaction proceeds. For the reason, it is important to prevent the exposure of sulfide minerals to water and oxygen at the first stage of the reaction.

The cover system is one of the

countermeasures to prevent AMD by separating sulfide minerals and water and oxygen. In this method, waste rock is classified into Potentially Acid Forming (PAF) and Non-Acid Forming (NAF) based on the geochemical characteristics of them.[1] PAF are covered with NAF after the classification to prevent the exposure of PAF to water and oxygen. This system has been widely introduced in coal mines in Indonesia since the fundamental mechanism is simple and the cost is low compared to other methods. However, it is difficult to perform the system in some area due to the lack of NAF: more than 80 percent of waste rocks consist of PAF in some pit in coal mines in Indonesia. Acidic water is generated from the large amount of untreated PAF in the area. The treatment of PAF is important to prevent AMD in the situation.

The classification of waste rock is performed by Net Acid Generation (NAG) test.[2] In NAG test, the potential of acid in rocks is evaluated by oxidation of rocks with hydrogen peroxide. It is suggested in some studies that this procedure leads to problems for the evaluation of AMD. The problem is caused by the effect of physical and chemical factors: weathering of rocks by climate, components in rocks, particle size, and chemical reaction and so on. These effects and the dissolution time of elements are not considered in the evaluation method. AMIRA which is the Australian Mineral Industries Research Association Limited indicates that an improved method is to be more reliable for the prediction of AMD.[2] Some researchers have tried to evaluate correctly the potential to cause acidic water from several points of view such as mineralogy and geochemical property by improving the method; however, a reliable way to evaluate it by considering these effects has not been established so far.[3] The classification of rocks in detail by the reliable evaluation of acidity in rocks might lead to the use of PAF as a cover layer or the guideline of the management of PAF: the potential of AMD could be reduced through a special treatment or some rocks which are classified into PAF in the current method could be treated as NAF.

For the reasons, sample analysis was performed as a first step of trying to use PAF as a cover layer to prevent AMD, and the effects of geochemical and geophysical properties of rocks to AMD were discussed in this study.

2. Methods and Samples

Waste rocks were sampled in the open pit coal mine in Indonesia. They were obtained from the inside of wall in which they had not been exposed to rainfall and oxygen for long terms. 4 types of rock samples were used in each analysis. They were named as sample A, B, C, and D respectively in this study.

2.1. Geochemical Analysis

The X-ray Diffraction analysis (XRD) and the X-ray Fluorescence analysis (XRF) were performed to understand the geochemical properties of rock samples. Major elements in the waste rocks were analyzed by using wide angle goniometer RINT 2100 XRD under the following condition: radiation CuKα, operating voltage 40 kV, current 26 mA, divergence slid 1 deg, anti-scatter 1deg, receiving slit 0.3 mm, step scanning 0.050 °, scan speed 2.000 °/minute, scan range was from 2.000 ° to 65.000 °. Additionally, NAG test was conducted in accordance with the procedure in mining operation in order to classify these samples into PAF or NAF based on the geochemical properties. In NAG test, rock samples can be classified into PAF or NAF by oxidizing 2.5 g of less than 250 μm sample with 7.5 % of hydrogen peroxide. Samples are classified based on the change of pH which is affected by the dissolved substances in the analysis. A hydrogen peroxide can acidize all of the sulfide minerals in rocks since the oxidation-reduction potential of hydrogen peroxide is higher than that of sulfide minerals. Waste rocks are classified into 5 types by

NAG test in coal mines in Indonesia and they are backfilled based on the classification: Type 1, 2, 3a, 3b, 4. Type 3a, 3b, and 4 are classified into PAF, and the others are classified into NAF which are used in cover layer.

Acid Base Accounting (ABA) test was, furthermore, conducted to quantify the potential of AMD. ABA test was proposed in 1974 and it has been widely used for the evaluation of the potential to cause acidic water.[4] In ABA test, the potential in rocks to cause AMD is expressed as NAPP which is calculated with Acid Potential (AP) and Acid Neutralizing Capacity (ANC) as shown below;

$$NAPP = AP - ANC$$

NAPP value indicates the balance of AP and ANC, and it is related to the potential in rocks to cause AMD. Rocks with the high value of NAPP can cause strong acidic water, and that with negative value of NAPP have a potential to neutralize acid.

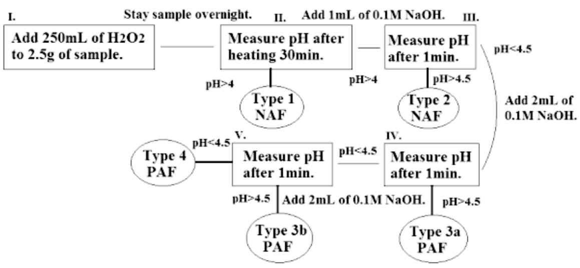

Figure 1. Flowchart of NAG test which is used in the mining operation in Indonesia.

Paste pH and EC test were conducted by following the standard of AMIRA to discuss the water quality with the rock samples.[2] The mixture ratio of sample to deionized water was 1 to 2, and the solution was left more than 8 hours to promote the dissolution. The water quality was measured by pH and EC meter after the process.

The sequential extraction with acid was conducted with the 2.5 g of sample before and after wetting and drying cycles in order to elucidate a change of minerals in the samples. This analysis was conducted in accordance with the method performed in 2002.[5] Each sample was extracted with 1 M of hydrochloric acid for 16 hours, with 10 M of hydrogen fluoride for 25 hours in total, and with concentrated nitric acid for 2 hours at each step. Soluble substances such as precipitate and oxidation products can be extracted at the stage of extraction with hydrochloric acid step, and silicate minerals can be obtained at that with hydrogen fluoride. Refractory materials like sulfide minerals can be extracted at that with nitric acid. In this study, the time for the extraction with nitric acid was set as 6 hours to dissolve all of the sulfide minerals.

2.2. Geophysical Analysis

Slaking Index test was performed to discuss the effects of wetting and drying cycles to formation of rocks along with AMD. Rocks disintegrate with wetting and drying cycles owing to slaking. This test was conducted in accordance with the method proposed in 2003.[6] The process of wetting and drying cycles of sample for 24 hours was repeated until 5 times, and less than 2 mm of samples were removed by sieving at each cycle. The change of weight at each step was reported as Slaking Index (SI) which was calculated by dividing the changed weight with the initial weight. Slaking is caused by the swelling and shrinkage pressure due to a swell and shrink of clay minerals in rocks. The increase of surface area of rocks with the disintegration can promote the chemical reaction. Therefore, the slaking has to be considered for the discussion of AMD.

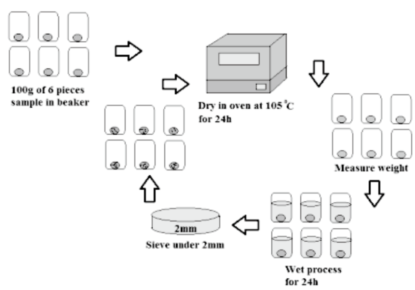

Figure 2. Procedure of Slaking Index test: the wetting and drying cycles is repeated until 5 times in the test.

3. Results and Discussion

3.1. Potential of Rock Samples to cause AMD

The result of the XRD patterns of each sample showed the patterns of sulfide minerals such as pyrite and sphalerite were found in each sample, indicating that these samples can cause AMD. The patterns of clay minerals, additionally, could lead to the slaking of rocks. Moreover, the result of XRF indicated that the elements related to AMD such as iron, sulfur, and arsenic were obtained and the content varied in each sample. These facts indicate that the water quality of AMD could be different in each sample. It is expected that the amount of sulfide minerals and clay minerals in rocks affects the water quality for the results in these samples.

Table 1 shows the potential to cause AMD which is expressed as NAPP value and the classification. Table 2 is the summary of the results in Paste pH and EC test. All of the samples were classified into PAF, and it supported the result of XRD. Acidic water was generated in Paste pH and EC test in each sample. The difference of NAPP values in sample B and D reflected the change of pH: the higher NAPP value was, the lower pH was. However, the results of Paste pH and EC disagreed with the NAPP value like in sample A and B. These values also disagreed with NAG pH in sample A and B: the potential to cause AMD is currently evaluated by NAG pH in mining operation in some coal mines in Indonesia. This was due to the procedure of ABA test and NAG test. In ABA test, the total sulfur content in rocks is directly calculated as Acid Potential (AP), and then NAPP value is calculated by the equation: NAPP = AP – ANC. Rocks consist of different types of sulfur such as sulfide minerals, precipitate, and oxidation materials and so on, and the dissolution rate is different. The differences between in Paste pH test and in ABA test were observed for the reasons. Moreover, the total sulfur content disagrees with the result of Paste pH and EC for the effects of the form of sulfur as noted above. This suggests that the effects of the form of elements in rocks and the dissolution time are not considered in the current method. The consideration of these effects in the test procedure is important to predict AMD.

The sample C was classified into Type 3a in Table 1. However, the pH is not low and the EC is not high compared to that in other samples in Table 2 even if it can be classified into PAF. The low value of EC indicates that the concentration of dissolved metals in sample C is lower than that in others. It suggests that sample C which is treated as PAF in mining operation could possibly be classified into NAF. The increase of the volume of NAF materials in mining operation could lead to the solution of the current problem caused by the lack of NAF in mining operation.

Table 1. Summary of the results of ABA and NAG test.

Sample	A	B	C	D
Sulfur content (%)	0.83	5.52	0.03	12.54
NAPP (kgH_2SO_4/ton)	25.5	169.0	0.9	384.0
NAG pH	2.3	2.2	3.1	1.0
Type	Type 4	Type 4	Type 3a	Type 4

Table 2. Results of Paste pH and EC.

Sample	A	B	C	D
Paste pH	2.79	2.83	3.42	1.21
Paste EC (mS/cm)	4.00	6.00	0.79	136

3.2. The Change of Forms of Substances in Rocks before and after wetting and drying cycles

Figure 3 shows the extract concentration of each sample at each step. The amount of Fe is compared at each step of the extraction with hydrochloric acid, hydrogen fluoride, and nitric acid before and after wetting and drying cycles in Figure 3. “Non-Weather” indicates the sample before the cycle, and “Weather” indicates that after the cycle. For the results, Fe which generally constituted sulfide minerals in the samples was contained in rocks in 3 different types: soluble materials, silicate minerals, and sulfide minerals. Soluble materials were extracted at hydrochloric acid step, silicate minerals were extracted at hydrogen fluoride step, and sulfide minerals were extracted at nitric acid step in this experiment. The substances extracted at hydrochloric acid step are related to AMD since it is soluble in water. In Figure 3, the extract concentration at hydrogen fluoride step was random in each sample. The rock samples mainly consisted of silicate minerals and the uneven distribution of them in rocks caused it. The substances contained in silicate minerals could be dissolved with hydrogen peroxide in NAG test, and they are calculated as sulfur content in ABA test. Silicate minerals are rarely dissolved in water; therefore, the current method is not reliable to predict the dissolution of them and AMD for the reasons.

The extract concentration of Fe which were extracted at nitric acid step was higher before wetting and drying cycles, whereas that which were extracted at hydrochloric acid step was higher after the cycles in sample A and D. Sulfide minerals are extracted at nitric acid step and soluble substances are extracted at hydrochloric acid step. Thus, sulfide minerals in rocks changed into precipitates or oxidation products after wetting and drying cycles with AMD generation. AMD is accelerated through wetting and drying cycles by the dissolution of the precipitates or oxidation products which are derived from sulfide minerals. These facts suggest that sulfur which forms sulfide minerals in rocks leads to AMD for a long term. Additionally, few Fe were obtained in sample C after wetting and drying cycles. This indicates that AMD could be stopped after several times of the cycles like in sample C. The waste rock with low potential to cause AMD might be treated as NAF rocks after exposing to rainfall to decrease the potential in mining operation. This idea will be useful to implement the cover system to the site where the problem is the lack of NAF and a large amount of PAF. The time for the removal of the potential should be studied in future research.

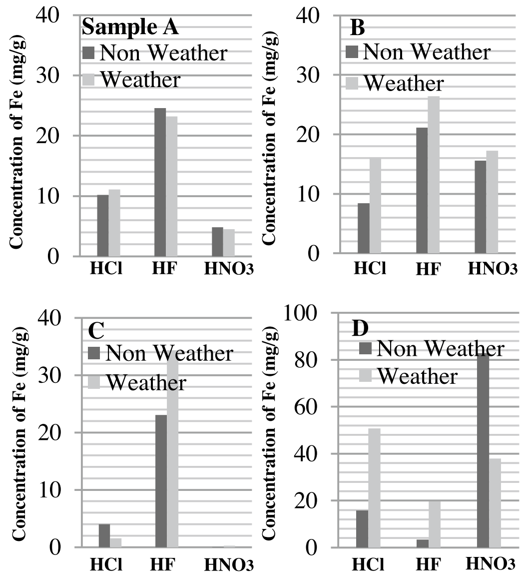

Figure 3. Comparison of the extract concentration of Fe in each sample: the concentration is shown at each step of the extraction with acids before and after wetting and drying cycles.

3.3. Effects of wetting and drying cycles on the Disintegration of Rocks

Figure 4 shows the summary of the change of Slaking Index (SI) at each step of 5 times of wetting and drying cycles. The change of SI was different in sample A, B, and D which were classified into Type 4. NAPP value was high and Paste pH was low in sample D, and the disintegration of rocks was promoted at each stage of wetting and drying cycles as shown in Figure 4. The water quality has deteriorated with the progress of the disintegration by slaking since the increase of surface area accelerates the chemical reaction. The increase of surface area with slaking in each stage causes AMD for a long term. For the reason, the waste rock like sample D should not be left on site for a long period. On the other hand, the others were rapidly broken down after the first step of wetting and drying cycles. The disintegration of rocks at first step leads to the dissolution of large quantity of the metals. These rocks like sample A, B, and C should be carefully treated in mining operation since the dissolution of them could cause acidic water and contaminate ground water especially in stock pile in the site. Sample C with low potential to cause AMD could be used as NAF by exposing them to water in order to promote the slaking and chemical reaction for the reduction of the potential.

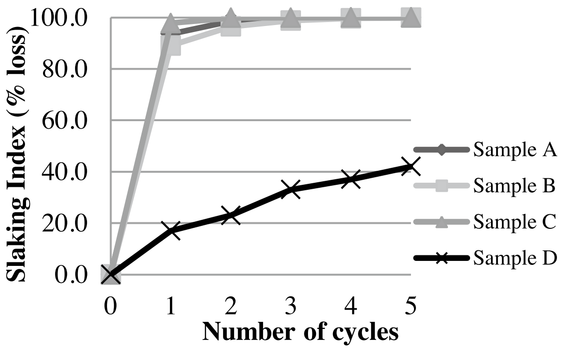

Figure 4. Change of Slaking Index (SI) in each sample.

4. Conclusions

The obtained results in this study are summarized below:

-It is difficult to predict AMD by performing only NAG test and ABA test since the total sulfur content is directly calculated in the values and evaluated in the method.

-Rocks which contain few substances such as sulfide minerals and iron could be used as NAF by exposing them to rainfall even if they are classified into PAF; however, the study about the terms to decrease the potential to cause AMD is required.

-The slaking caused by clay minerals affects AMD and it should be considered to evaluate the potential of AMD in rocks.

These results suggest that the volume of PAF on the site could be decreased by classifying some of them into NAF with the revised classification. The revised classification of waste rocks should consider not only geochemical properties but also weathering rate of rocks like slaking with wetting and drying cycles. The promotion of chemical reaction by slaking is useful to decrease the potential to cause acidic water. The decrease of PAF and the increase of NAF lead to the solution of the problem in which it is difficult to construct cover system due to the lack of NAF. However, the time for the removal of the potential should be studied in future research. The method which can be performed on the site and with low cost should additionally be established.

Acknowledgment

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