Increases in pH of acid mine drainage with coal fly-ash application

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Abstract. Coal fly-ash (CFA), waste materials resulted from coal processing in power plants, contains oxides that have capability to neutralize hydrogen ions of acid mine drainage (AMD). A batch reactor experiment was conducted by adding different amounts of CFA (0, 50, 100, 150, 200, and 250 Mg ha\(^{-1}\)) to reclaimed mining soils (RMS) to quantify the effect of CFA addition on changes in the pH of AMD. AMD was then flowed into the reactors following the incubation of the mixtures of RMS and CFA for 7 days, and the changes in pH of AMD in the reactors were monitored over 35 days. Results of the study showed pH and specific surface areas (SSA) of soils increased significantly with the addition of CFA. pH of AMD over 35 days also improved with CFA application, in which the degree of pH improvement was controlled by the amounts of added CFA. The addition of CFA <200 Mg ha\(^{-1}\) was not able to result in pH of AMD >6.0, and AMD pH of 6.0 was obtained when the amount of applied CFA reached to 200 Mg ha\(^{-1}\). Increasing pH of AMD is attributed to the CaO and MgO contained in the CFA neutralizing the H\(^+\) ions of AMD. Results of the study demonstrate the potential of CFA in remediation of AMD, in particular in increasing pH of AMD.

Keywords: neutralization, coal-mining, acid capacity, pyrite oxidation, passive treatment

1. Introduction

One of the crucial problems in mining activities around the world is the formation of acid mine drainage (AMD). AMD is formed when tailings containing sulfide compounds are lifted to the surface and then exposed to oxygen [1, 2]. This AMD generally has a very low pH [3,4] and high heavy metal concentrations [5,6], so it will be a serious environmental problem when AMD flows into public waters. The presence of AMD in open water systems lead to serious problem to benthic invertebrates [7] and fish community [8, 9]. Rice production has decreased by 62% through disruption of the physiological process of rice plants when AMD flows into agricultural land [10], and it takes a long time for the restoration of agricultural land contaminated with the AMD [11]. Thus, AMD management is required to meet environmental quality standards before the AMD is distributed to open water systems.

AMD management is generally carried out by the application of alkaline compounds such as limestone to neutralize acidity and raise the pH of AMD [2,12]. This AMD management is easy to
implement, does not require complex technology and has a high success rate [12, 13]. Research conducted by Elghali, Benzaazoua, Bouzahzah and Bussière [14] showed that the application of limestone increased pH of AMD from acidic (pH < 2.5) to circumneutral (pH 7.5). The disadvantage of AMD remediation using this approach is that the cost is very high, and limestone is not considered as a renewable natural resource, so that the use of limestone for long term may lead to a new environmental problem. Thus, other lime materials than limestone are required for AMD remediation.

Coal fly ash (CFA), produced from the process of using coal in power plants, contains high amounts of CaO and MgO [15,16]. Thus, CFA has the potential to be used as a substitute for limestone in AMD remediation. Utilization of industrial waste materials as a substitute for limestone in AMD remediation is expected to reduce the operational costs of mining activities and at the same time reduce waste management costs. The aim of this study was to quantify the effect of application of different amounts of CFA on the increase in pH of treated-AMD.

2. Materials and Methods

2.1. Sampling and characterization of soil and coal fly-ash

The soil used for this study was sampled from reclaimed-mining soil at Desa Palam, Cempaka Sub-district, Banjarbaru Regency, South Kalimantan, Indonesia. Soils were sampled at a depth of 0-30 cm using a soil drill at several different points. After being cleaned for plant debris, the sampled soils were then homogenized, placed in a plastic bag and stored at 4°C before being used for research. A portion of the sample was then air-dried for the determination of soil physical and chemical characteristics. Selected physico-chemical characteristics of soil were presented in Table 1.

Coal fly-ash (CFA) was collected from the power plant at Desa Kasiyau Raya, Murung Pudak Sub-district, Tabalong Regency, South Kalimantan, Indonesia. The concentrations of Ca and Mg in CFA were determined using an atomic absorption spectrophotometry (Shimadzu AA6300G) after digestion of CFA using the mixture of HNO₃ and HClO₄ (Table 1). Meanwhile, acid mine drainage was obtained from a wastewater treatment pond in Desa Palam, Cempaka Sub-district, Banjarbaru Regency, South Kalimantan, Indonesia.

2.2. Batch reactor experiment

A batch reactor experiment was carried out to quantify the effect of coal fly-ash application on changes in pH of treated-AMD. Different amounts of coal fly-ash: 0, 50, 100, 150, 200 and 250 Mg ha⁻¹ were applied to 2000 g of reclaimed-mining soils (RMS) in a reactor with dimension of 35 cm (length), 15 cm (width), and 9 cm (height), then the RMS-CFA was mixed homogenously. An amount of aquadest was then applied to mixtures of RMS-CFA to obtain soil water content of 60% water holding capacity, then the mixtures were incubated at dark for 7 days. For each treatment, three replicates were prepared and incubated. Following the completion of incubation period, AMD was gradually added into the reactor until the level of AMD in the reactor reached to 3 cm from the soil surface. The pH of treated-AMD in each reactor was measured at 0, 1, 2, 3, 4, 7, 12, 21, 28, and 35 days using a Hanna HI-2211 pH meter.

2.3. Data analysis

The effect of CFA application on changes in pH of treated-AMD was quantified by analysis of variance. Normality and homogeneity of experimental data were checked using Shapiro–Wilk and Bartlett tests, respectively, prior to the analysis of variance. Mean comparison using least significant difference (LSD) at P <0.05 was performed in the case of the treatments significantly affected the pH of treated-AMD. All statistical tests were performed using GenStat 12nd Edition.
3. Results and Discussion

3.1. Characteristics of soil and coal fly-ash

The soil used for the study had a clay texture with a relatively high bulk density. This soil had an acidic reaction (pH 3.34) with relatively low organic C and total N contents. Exchangeable Ca and Mg contents were also relatively low with medium cation exchangeable capacity (CEC). Coal fly-ash had an alkaline pH with a relatively high bulk density (Table 1). Most notable was the high Ca and Mg contents of coal fly-ash which reached to 1533 mg kg\(^{-1}\) and 1499 kg\(^{-1}\), respectively.

| Characteristics          | Soil         | Coal Fly-ash |          |
|--------------------------|--------------|--------------|----------|
| Texture                  |              |              |          |
| - Sand (%)               | 30.57 (3.61) | -            |          |
| - Silt (%)               | 26.87 (3.41) | -            |          |
| - Clay (%)               | 42.56 (6.34) | -            |          |
| Bulk density (g cm\(^{-3}\)) | 1.42 (0.16)   | 1.87 (0.18)    |          |
| pH (H\(_2\)O)            | 3.34 (0.07)  | 7.67 (0.12)   |          |
| Organic C (g kg\(^{-1}\)) | 16.16 (1.92) | 0.95 (0.06)  |          |
| Total N (g kg\(^{-1}\)) | 2.65 (0.07)  | 0.14 (0.04)   |          |
| P (g kg\(^{-1}\))       | 7.53 (0.09)  | 0.21 (0.06)   |          |
| Ca (mg kg\(^{-1}\))     | 3.53 (0.49)  | 1532.54 (9.67)|          |
| Mg (mg kg\(^{-1}\))     | 5.54 (0.43)  | 1498.98 (9.66)|          |
| CEC (cmol kg\(^{-1}\))  | 19.94 (1.54) | -            |          |

3.2. Effect of coal fly-ash application on increasing pH of acid mine drainage

The results showed that the addition of CFA up to 50–100 Mg ha\(^{-1}\) was only able to increase the pH of AMD from 3.17 to pH 3.57–5.86 for 35 days of observation. However, when the amount of CFA added reached to 200–250 Mg ha\(^{-1}\), the pH of AMD increased from 3.17 to pH 6.97–7.56 (Figure 1). The results of this study indicate that the application of CFA with different amounts affect the pH of AMD. Based on the observation time, the increase in AMD pH occurred after 7 days of CFA application, in which the AMD pH increased from pH 3.17 to pH 4.21–7.85 (Figure 1).

![Figure 1](image_url)  
*Figure 1*. Changes in pH of acid mine drainage due to different amounts of coal fly-ash application observed during 35 days.
The increase in pH of AMD with the application of CFA with different amounts after 35 days of observation is presented in Figure 2. Application of CFA with an amount of 50 Mg ha$^{-1}$ increased the pH of AMD compared to AMD without the application of CFA (control). Increasing the amount of CFA applied up to 250 Mg ha$^{-1}$ was always followed by increasing the pH of treated-AMD. The results of this study indicate the high efficiency of CFA in neutralizing acidity in AMD, which in turn increases the pH of treated-AMD.

![Figure 2](image-url)

**Figure 2.** Changes in pH of acid mine drainage with various amounts of coal fly-ash observed 35 days after application. The line above the bar is the standard deviation of the mean (n=3). The same letter above the line indicates the similar effect of treatment based on the least significant difference (LSD) test at $P <0.05$.

The increase in AMD pH with the addition of CFA is attributed to the presence of Ca- and Mg-oxides in the soil reacting to produce OH ions which neutralized AMD acidity [17, 18]. In another study, Gitari, Petrik [16] reported a buffering capacity at pH 6.20–6.80 in a mixture of AMD–CFA due to the dissolution of MgO and CaO oxides from CFA. The effect of the addition of CFA on changes in AMD is controlled by the sulfur content of the coal [19]. Anthracite coal with high sulfur content produces acidic coal ash (pH < 7.0) [20], while lignite coal with low sulfur content and high Ca content produces alkaline coal ash [20], while lignite coal with low sulfur content and high Ca content produces alkaline coal ash [21]. The potential for neutralization of acidity by CFA varies from 20 kg CaCO$_3$ Mg$^{-1}$ in CFA from lignite coal to 25 kg CaCO$_3$ Mg$^{-1}$ in CFA from bituminous coal [22].

The increase in AMD pH with the addition of CFA with different amounts in this study was in accordance with several previous studies. Mungazi and Gwenzi [23] measured the change in pH in the excavated rock mixed with CFA through column experiments and reported an increase in pH from very acidic (2.9) to alkaline (8.0). Research conducted by Nasir, Ibrahim and Arief [24] also showed an increase in the pH of AMD which was passed on an experimental column containing CFA. With its potential to contain high amounts of CaO and MgO, coal ash generated from power generation activities is used as an ameliorant in waste-based AMD remediation [25,26]. By using industrial waste as a substitute for limestone, the operational costs of mining activities may be reduced so that it can benefit the company. Research conducted by Potgieter-Vermaak, Potgieter Potgieter-Vermaak, Potgieter, Monama and Van Grieken [27] showed a 23–48% chemical cost savings when CFA was applied instead of limestone in AMD remediation.
4. Conclusion
The results showed that the application of coal fly-ash in the amount of 50 Mg ha$^{-1}$ increased the pH of acid mine drainage compared to acid mine drainage without coal fly-ash application (control). An increase in the amount of coal fly-ash applied up to an amount of 250 Mg ha$^{-1}$ is always followed by an increase in the pH of acid mine drainage. Increasing the pH of treated-acid mine drainage may attribute to dissolution of CaO and MgO contained in coal fly-ash released OH$^{-}$ which then neutralizes acidic acid mine drainage. The results showed the potential of coal fly-ash as a substitute for limestone in the remediation of acid mine drainage.

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References
[1] Tabelin C B, Corpuz R D, Igarashi T, Villacorte-Tabelin M, Alorro R D, Yoo K, Raval S, Ito M, and Hiroyoshi N 2020 *J Hazard Mater* 399 122844
[2] Acharya B and Kharel G. 2020. *J Hydrol* 588 125061
[3] Petronijević N, Stanković S, Radovanović D, Sokić M, Marković B, Stopić S R, and Kamberović Ž. 2020 *Metals* 10
[4] Dean A P, Hartley A, McIntosh O A, Smith A, Feord H K, Holmberg N H, King T, Yardley E, White K N, and Pittman J K. 2019 *Sci Total Environ* 647 75-87
[5] Luo C, Routh J, Dario M, Sarkar S, Wei L, Luo D, and Liu Y. 2020 *Sci Total Environ* 724 138122
[6] Núñez-Gómez D, Rodrigues C, Lapolli F R, and Lobo-Recio M Á. 2019. *J Environ Chem Eng* 7 102787
[7] Mocq J, and Hare L. 2018. *Water Air Soil Pollut* 229 28
[8] Lebepe J, Oberholster P J, Ncube I, Smit W, and Luus-Powell W J. 2020 *J Environ Sci Health, Part A* 55 421-32
[9] Carneiro Brandão Pereira T, Batista dos Santos K, Lautert-Dutra W, de Souza Teodoro L, de Almeida V O, Weiler J, Homrich Schneider I A and Reis Bogo M. 2020 *Chemosphere* 253 126665
[10] Choudhury B U, Malang A, Webster R, Mohapatra K P, Verma B C, Kumar M, Das A, Islam M, and Hazarika S. 2017 *Sci Total Environ* 583 344-51
[11] Wang H, Zeng Y, Guo C, Bao Y, Lu G, Reinfelder J R, and Dang Z. 2018 *Sci Total Environ* 616-617 107-16
[12] Othman A, Sulaiman A, and Sulaiman S K. 2017 *J Water Process Eng* 15 31-6
[13] Wang X, Jiang H, Fang D, Liang J, and Zhou L. 2019 *Water Res* 151 515-22
[14] Elghali A, Benzaazoua M, Bouzahzah H, and Bussière B. 2021. *Minerals* 11
[15] Saidy A R, Hayati A, and Septiana M. 2020 *J Soil Sci Plant Nutr* 10 1001-12
[16] Gitari W M, Petrik L F, and Akinyemi S A. 2018 Coal Fly Ash Beneficiation: Treatment of Acid Mine Drainage with Coal Fly Ash. ed S A Akinyemi and W M Gitari: IntechOpen) pp 79-99
[17] Jones S N and Çetin B. 2017 *Fuel* 188 294-309
[18] Gitari W M, Petrik L F, Etchebers O, Key D L, Iwuoha E, dan Okuji Ken C 2008 *Fuel* 87 1637-50
[19] Plank C O and Martens D C. 1974 *Soil Sci Soc Am J* 38 974-7
[20] Furr A K, Parkinson T F, Hinrichs R A, Van Campen D R, Bache C A, Gutenmann W H, St. John L E, Pakkala I S, and Lisk D J. 1977 *Environ Sci Technol.* 11 1194-201
[21] Page A L, Elseewi A A, and Straughan I R. 1979 Residue Reviews, ed G F A and G J D. (New York: Springer)
[22] Qureshi A, Jia Y, Maurice C, and Öhlander B 2016 *Environ Sci Pollut Res* 23 17083-94
[23] Mungazi A A and Gwenzi W 2019 *Mine Water Environ* 38 602-16
[24] Nasir S, Ibrahim E, and Arief A 2016 *J Mater Environ Sci* 8 2912-8
[25] Keller V, Stopić S, Xakalashe B, Ma Y, Ndlovu S, Mwewa B, Simate G S, and Friedrich B 2020 Minerals 10
[26] Yang Z, Dong Y, Li Z 2020 Acid mine drainage remediation with simulated permeable reactive barrier filled with fly ash and its composite materials as reactive media Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 1-14
[27] Potgieter-Vermaak S S, Potgieter J H, Monama P, and Van Grieken R 2006 Min Eng 19 454-62