Settling Characteristics and Physic-Geochemical Stability of Fly Ash for Acid Mine Drainage Neutralization in Pit Lakes: A Laboratory-Scale Study

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Abstract

This study examines the use of Fly Ash (FA), a byproduct of coal combustion, as an in-situ neutralizing agent for AMD in pit lake. Due to its alkaline composition, FA is well-suited for AMD treatment. Although FA is no longer classified as hazardous waste under Indonesian regulations, proper management is crucial to avoid potential environmental impacts. This research focuses on the sedimentation characteristics and physic-geochemical stability of FA in AMD under controlled laboratory conditions.

The experimental setup consisted of acrylic tubes with a diameter of 11.2 cm, each containing varying volumes of AMD (5, 10, and 15 L) resulting in different water heights, while maintaining a consistent solid-to-water ratio of 1:5. FA was allowed to settle for 24 hours, during which its settlement velocity and stratification of FA in AMD were monitored. The pH of AMD was recorded hourly for 12 hours, with a final measurement at 24 hours. After stabilization, the grain size distribution, mineralogical composition, and chemical properties of the FA were analysed. Post-treatment water samples were analysed using Ion Chromatography (IC) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The results demonstrated significant improvements in water quality, with pH levels rising from 2.77 to 6.24, 6.81, and 7.65 in the three different acrylic tubes, and the concentrations of Fe and Al decreasing by over 100%. Manganese concentrations were reduced by 19.88% to 40.06%, highlighting the effectiveness of FA as a neutralizing agent for AMD. Remarkably, the pH improvement to near-neutral levels occurred within the first hour, with a stable pH recorded over the next 24 hours. The contact time between FA and AMD is directly proportional to the improvement in water quality. Smaller FA particles have a larger surface area in contact with AMD, resulting in longer settling times. The settling velocity of FA particles ranged from 15.38 to 21.88 cm/s. After neutralization, iron precipitated as goethite (FeOOH), hematite (Fe_2O_3), and hydrohematite, while aluminum precipitated as gibbsite ($Al(OH)_3$), and manganese as pyrolusite ($Mn(OH)_2$) and manganite (MnOOH). These results confirmed the formation of secondary minerals through the precipitation of Fe, Al, and Mn.

Keywords: Pit Lake, Fly Ash, Neutralization, Acid Mine Drainage, In-situ Treatment

Introduction

Open-pit mining often results in the formation of pit lakes, which, if not properly managed, can accumulate acid mine drainage (AMD). Once AMD develops, treatment is required to neutralize acidity and remove dissolved metals to comply with environmental standards. Various AMD treatment methods are available and are generally classified as active, passive, or in situ. The selection of an appropriate method depends on site-specific conditions and treatment objectives.

One in situ approach for AMD neutralization in pit lakes involves the dispersion of an alkaline neutralizing agent across the water surface. This method has been implemented in a former coal pit lake in South Kalimantan (Gautama, 2014). Among potential neutralizing agents, fly ash (FA), a by-product of coal combustion, has demonstrated effectiveness due to its alkaline mineral content. Calcium oxide (CaO), a primary component of FA, reacts with sulfuric acid (H_2SO_4) to reduce acidity, making FA a promising material for AMD treatment.

Despite significant production, the utilization of fly ash and bottom ash (FABA) in Indonesia remains low, accounting for only 0.47% in 2012. Although FABA applications have expanded in construction materials, such as lightweight concrete, paving blocks, and bricks, as well as in soil improvement, its use remains below production levels (Aisyana, 2022). Given the prevalence of open-pit mines and the widespread formation of pit lakes, enhancing FABA utilization for AMD neutralization presents a strategic opportunity for sustainable environmental management.

This study aims to investigate the in-situ treatment mechanism of FA surface-spreading in pit lakes. Furthermore, the research will examine the physical and chemical properties of FA before and after exposure to AMD, determine the settling velocity of FA particles, and analyse the chemical reactions involved. The findings are expected to contribute to the development of more effective AMD treatment strategies, promoting the utilization of FA in pit lake management.

Methods

Samples Characterization

Fly ash (FA) samples were sourced from a coal-fired power plant in Tanjung Enim, South Sumatra, Indonesia, and oven-dried prior to characterization. XRD analysis identified quartz as the dominant mineral phase (90%), with minor amounts of nepheline (4.8%), goethite (4.4%), and hematite (0.8%). XRF results showed Si (46.6 wt%) as the major element, followed by Al (23.1 wt%) and Fe (12.1 wt%), with trace levels of Na, Mg, K, Ca (4.06%), and Sr. The main oxides were SiO_2 (52.9 wt%), Al_2O_3 (27.9 wt%), and Fe_2O_3 (6.23 wt%).

Static testing revealed a paste pH of 8.07. Net Acid Generation (NAG) testing indicated low acid-forming potential, with NAG pH values of 4.5 and 7 producing 0 and 3.67 kg H_2SO_4/ton, respectively. The Net Acid Producing Potential (NAPP) was −92.4 kg H_2SO_4/ton. The Acid Buffering Characteristic Curve (ABCC) showed rapid initial pH decline with acid addition, suggesting high initial reactivity.

The FA had a specific gravity of 2.48 and was predominantly silt-sized (57%), with sand (33.17%) and clay (8.08%) fractions, classifying it as poorly graded. AMD was generated via column leaching of potentially acid-forming (PAF) overburden using distilled water. The resulting leachate was analyzed using multiparameter probes, ion chromatography (IC), ICP-MS, and strong acid-base titration. Summary of AMD characteristics is presented in Table 1.

***Table 1** AMD sample for neutralization test.*

Parameter	Value	Parameter	Value
pH	2,77	K^+	3,39 mg/L
TDS	1,46 ppt	SO_4^{2-}	1.258,41 mg/L
ORP	254,4 mV	Cl^-	6,32 mg/L
EC	2,93 mS/cm	HCO_3^-	-
Temperatur	27,9 oC	F^-	4,8 mg/L
Acidity	1.939,33 mg CaCO3/L	Al	90,47 mg/L
Na^+	27,57 mg/L	Fe	80,94 mg/L
Ca^{2+}	75,63 mg/L	Mn	15,5 mg/L
Mg^{2+}	224,65 mg/L		

Settling of FA and AMD Neutralization Test Set-up

For the settling test, a custom-designed acrylic tube was used with three variations of AMD and FA volumes, each maintaining a constant solid-to-water ratio of 1:5 (Fig. 1). The tubes had a uniform diameter of 11.2 cm, while the height varied based on the volume requirements for each variation. The first acrylic tube (Tab1) was filled with 5 L of AMD, and 1 kg of FA was introduced at the start of the test (0 hours). The second tube (Tab2) contained 10 L of AMD, with 2 kg of FA added in two stages: 1 kg at 0 hours and another 1 kg at 4 hours. The third tube (Tab3) held 15 L of AMD, with 3 kg of FA added incrementally in three stages: 1 kg at 0, 4, and 8 hours.

After the FA was introduced into the AMD-filled test tubes, it was left to settle for 24 hours. During this period, observations were made on the settling rate and precipitate stratigraphy. To ensure accuracy and minimize errors, the testing process was documented. Additionally, the physical parameters of the AMD were measured hourly from the 1st to the 12th hour using a multiparameter device.

Post-Neutralization Testing

Following the 24-hour settling period, the sediment precipitates and treated water were analysed. The sediment was divided into two portions for physical and chemical assessments. The post-neutralization FA samples were examined for physical characterization, static test, and mineralogical composition. The treated AMD samples were analysed for pH and oxidation-reduction potential (ORP) using a multiparameter device, while IC and ICP-MS were employed for further chemical characterization.

Results and Discussions

The results of pH and ORP measurements for Tab1, Tab2, and Tab3 are presented in Fig. 3. In general, all test variations showed an increase in pH and a decrease in ORP, indicating a progressing neutralization process. In Tab1, the pH increased sharply from 2.77 at hour 0 to 6.03 at hour 1 and then stabilized around this value until hour 24, demonstrating rapid and effective neutralization. Meanwhile, ORP decreased significantly from 254.4 mV at hour 0 to 58.2 mV at hour 1 and stabilized between 42.3 and 61.6 mV, reflecting a shift in oxidation-reduction conditions.

In Tab2, the pH increased more gradually from 2.77 at hour 0 to 4.36 at hour 1, then increased sharply to 6.15 at hour 5 and remained stable until hour 24. The ORP decreased from 254.4 mV at hour 0 to approximately 159 mV at hour 1, followed by a steady decline to near zero at hour 24. Meanwhile, in Tab3, the pH increase was slower than in the other tubes but ultimately achieved more optimal results. The trends in pH and ORP across all tubes followed a similar pattern, with pH increasing and ORP decreasing as neutralization progressed.

The differences in pH progression were influenced by the solid-to-water (S/W) ratio applied over time. In Tab1, a constant S/W ratio of 1:5 was maintained throughout the experiment. In Tab2, the ratio shifted from 1:10 at hour 0–4 to 1:5 from hour 4–24. In Tab3, the S/W ratio varied from 1:15 at hour 0–4, 1:7.5 at hour 4–8, and 1:5 from hour 8–24. These variations in FA addition influenced

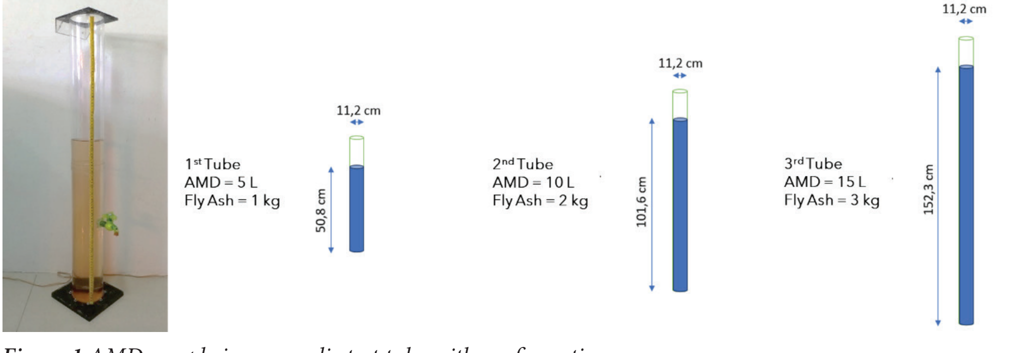

Figure 1 *AMD sample in an acrylic test tube with configuration.*

the rate and efficiency of pH increase. The percentage error for all three neutralized water samples was minimal, ranging between 0.5% and 0.7%. The ion balance error of the final samples is presented in Fig. 4.

The height of FA sediment was monitored over time, as shown in Fig. 5. Sedimentation began approximately one hour after FA addition, aligning with the peak period of AMD neutralization. Sediment height initially increased as particles settled, followed by a gradual decrease due to compaction.

In each of the precipitates, quartz was identified as the dominant mineral. The respective percentages were 97.9% in the upper sediment and 90.1% in the lower sediment of Tab1, 88.6% in the upper sediment and 87.4% in the lower sediment of Tab2, and 81% in the upper sediment and 77.8% in the lower sediment of Tab3. In addition to quartz, other minerals not previously detected in the FA were formed, including gypsum, goethite, hematite, and gibbsite.

XRF analysis showed that the fly ash sample contained 4.06% CaO. When CaO react with water, they form hydroxides such as $Ca(OH)_2$, which generate hydroxyl ions (OH^-) that contribute to pollutant degradation and acid neutralization (Shirin, 2021). XRD analysis also detected 4.8% aluminosilicate, primarily nepheline ($KNa_3Al_4Si_4O_{16}$). Nepheline dissolution can raise pH without CO_2 release (Noort *et al.*, 2018), though its reactivity is relatively low. Compared to lime, aluminosilicates dissolve more slowly, are kinetically controlled, and provide long-term buffering capacity (Petronijevic *et al.*, 2022).

According to Stokes' Law, the settling velocity of a particle in a fluid is directly proportional to its diameter. However, in addition to particle size, the density of the material also plays a significant role in determining settling velocity. The average settling velocities of FA particles observed in this study are presented in Fig. 6. The results indicate that the frequency of FA addition influences the uniformity of particle size distribution within the sediment, subsequently affecting the overall settling behaviour. This finding aligns with previous research by Koch *et al.* (2008), which highlights the importance of reaction time in the effective neutralization of acid mine drainage using fly ash.

The concentrations of alkali and alkaline earth metals in AMD increased after neutralization with fly ash, with the highest levels observed at elevated pH. The most notable increase occurred in Tab3, where the final pH reached 7.65, indicating the active role of these metals in the neutralization process. Their oxide forms promoted

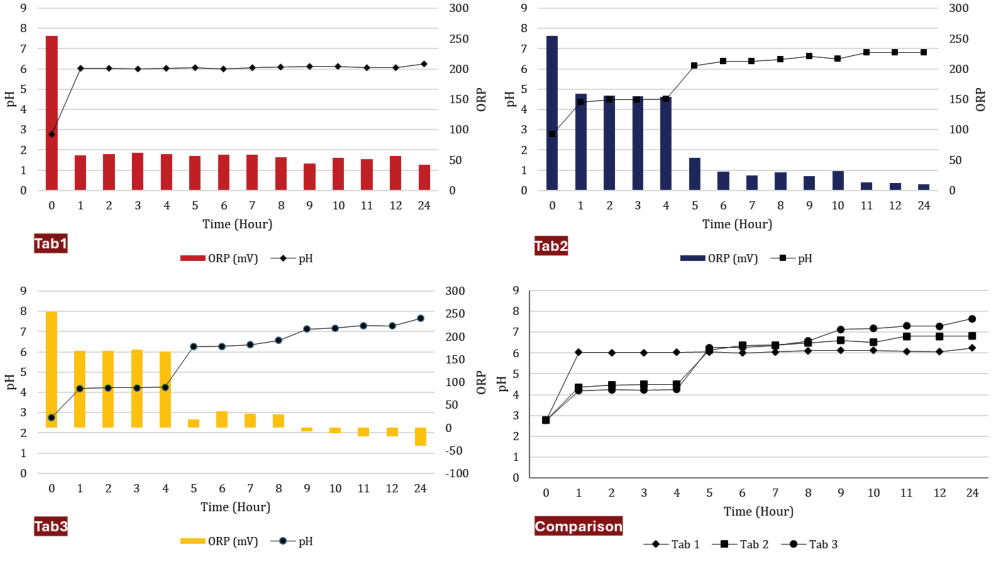

Figure 2 *pH and ORP measurement results of three tubes and the comparison.*

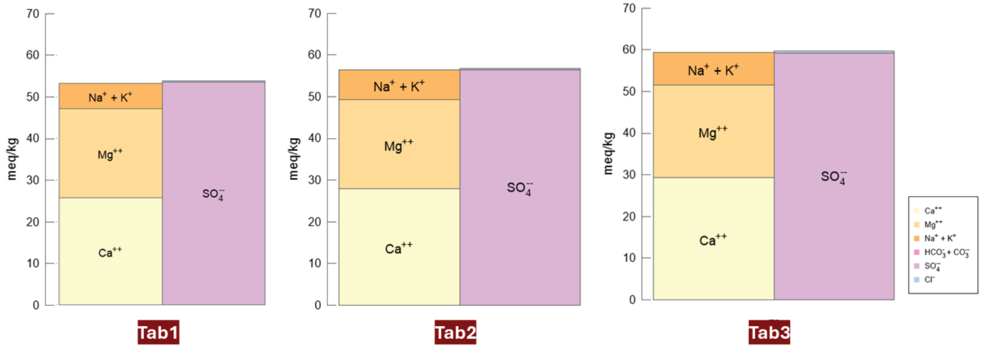

Figure 3 *The ion balance after neutralization.*

hydroxyl generation, contributing to pH elevation. Variations in metal concentrations are shown in Fig. 7.

Additionally, the NAPP values of sediment from Tab1, Tab 2 and Tab3 increased compared to the original FA, suggesting the dissolution of sulfur species during AMD interaction. This is supported by elevated sulfate concentrations in the treated water.

Based on acidity measurements, the AMD sample showed an acidity value of 1,030.33 mg $CaCO_3$/L. In contrast, the acid neutralization capacity (ANC) of the FA sample was determined to be 104.7 kg H_2SO_4/ton, equivalent to 106.84 kg $CaCO_3$/ton. This indicates that a minimum of 10 g of FA is required to neutralize 1 L of AMD. However, only 10 kg H_2SO_4/ton of the total neutralization capacity of FA demonstrated high reactivity. This limited reactivity can be attributed to the composition of reactive neutralizing components, such as Ca and Mg, which constitute only 9.14% of the total FA mass.

Conclusions

This study demonstrated the potential of fly ash (FA) to neutralize acid mine drainage (AMD) in a pit lake. Post-treatment pH increased to 6.24 in Tab1, 6.81 in Tab2, and 7.65 in Tab3. Static test showed a decrease in acid-neutralizing capacity in the sediment, though it remained classified as Non-Acid Forming (NAF) with retained neutralization potential. A reduction in alkali and alkaline earth metal content was also observed in the sediments.

The proposed protocol for studying the leachates provides useful information for designing mitigation strategies and environmental monitoring in mining areas.

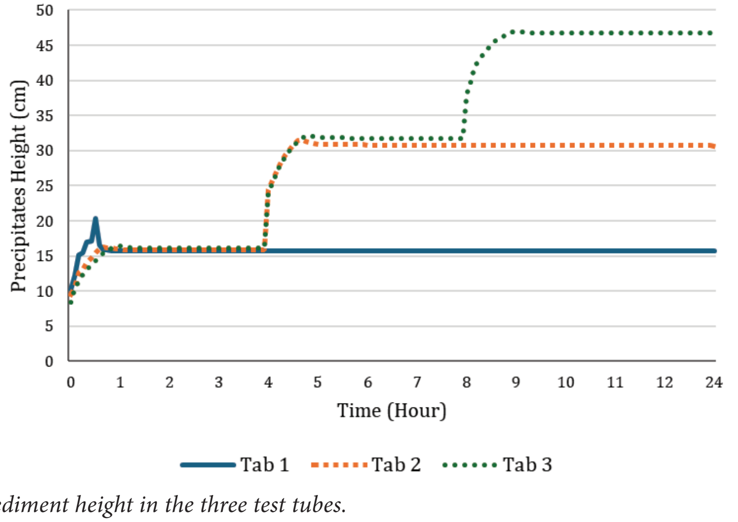

Figure 4 *FA sediment height in the three test tubes.*

Table 2 XRD result of sediments

Mineral	Weight Percentage (%)					
	Upper Tab1	Lower Tab1	Upper Tab2	Lower Tab2	Upper Tab3	Lower Tab3
Quartz (SiO_2)	97,9	90,1	88,6	87,4	81,0	77,8
Gypsum ($CaSO_4$)	0,4	1,4	3,7	3,7	1,5	3,7
Goethite (FeOOH)	0,4	2,0	3,6	3,6	1,9	2,5
Hematite (Fe_2O_3)	0,5	1,4	0,7	0,7	11,6	1,9
Gibbsite ($AlOH_3$)	0,8	5,1	4,5	4,5	4,0	14,1

Table 3 Effectiveness of Fly Ash in AMD Neutralization.

Criteria	Tab1	Tab2	Tab3
Acidity (mg $CaCO_3$/L)	40,8	37,51	33,45
Neutralization Efficiency (%)	96,04	96,36	96,75
FA needed in 1 L of AMD (kg)	0,5	1	1,5
FA Utilization Efficiency (%)	50,48	50,48	50,48

The highest settling velocity (21.88 cm/s) occurred in the lower sediment layer of Tab3, associated with coarser particles. In contrast, the upper layers of Tab1 and Tab2 showed slower settling (15.52 cm/s and 15.38 cm/s) due to finer particle sizes. Longer contact time between FA and AMD improved water quality, with finer particles enhancing neutralization efficiency through increased surface area and extended settling time.

References

Aisyana, M. (2022). Politik Kebijakan Limbah Energi: Analisis Kebijakan Penghapusan Limbah FABA dari Daftar Limbah Berbahaya di Indonesia. Jurnal Ilmu Sosial Indonesia (JISI), Vol. 3, No 90–98.

Gautama, R. S. (2014). Pembentukan, Pengendalian, dan Pengeloaan Air Asam Tambang. Penerbit ITB.

Koch, C., Graupner, B., Werner, F. (2008). Pit Lake Treatment Using Fly Ash Deposits and Carbon Dioxide. 10th International Mine Water Association Congress.

Shirin, S., Jamal, A., Emmanouil, C., & Yadav, A. K. (2021). Assessment of Characteristics of Acid Mine Drainage Treated. Applied Sciences.

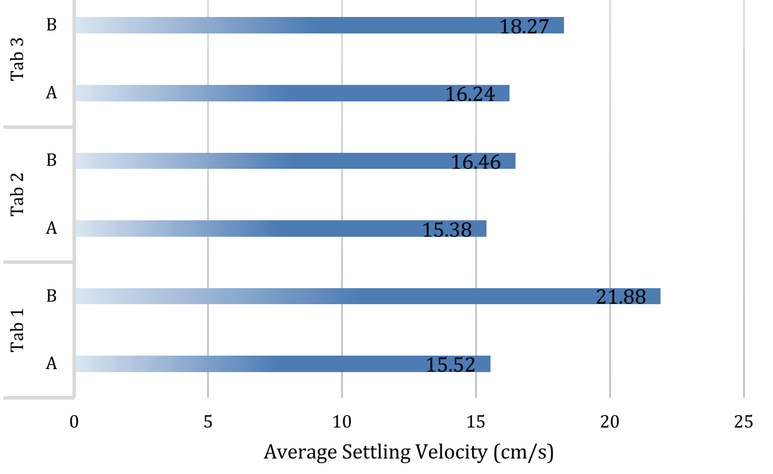

Figure 5 Average settling velocity of FA.

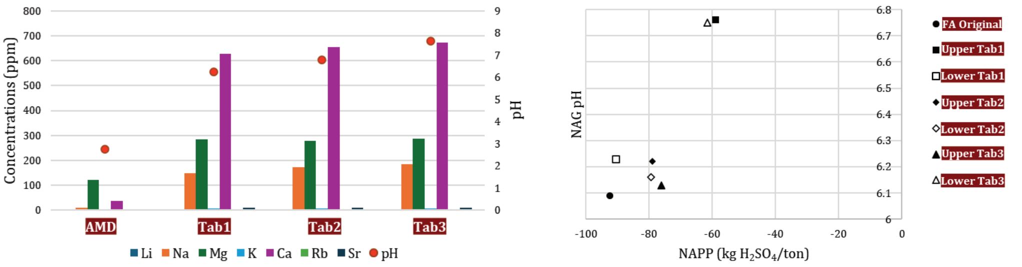

Figure 6 *(a) Left – Post-Neutralization Concentrations of Alkali and Alkaline Earth Metals in AMD (b) Right – Initial Fly Ash and Post-Neutralization Sediment Samples.*

Noort, R. V., Morkved, P. T., and Dundas, S. H. (2018). Acid Neutralization by Mining Waste Dissolution under Conditions Relevant for Agricultural Applications. Geosciences 8, 308.

Petronijevic, N., Radovanovic, D., Stulovic, M., Sokic, M., Jovanovic, G., Kamberovic, Z., Stankovic, S., Stopic, S., & Onjia, A. (2022). Analysis of the Mechanism of Acid Mine Drainage Neutralization Using Fly Ash as an Alternative Material: A Case Study of the Extremely Acidic Lake Robule in Eastern Serbia. Water 14, 3244.