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Effect of comparison ratio of additives on changes in pH levels, TSS, Fe, and Mn metals in the acid mine water treatment process at KPL BB 13 PT. Bukit Asam, Tbk.

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Abstract

Open system mining activities at PT Bukit Asam Tbk. have the potential to produce acid mine water due to contamination by rocks with sulfur content. Acid mine water treatment is carried out by active methods in Sludge Deposition Ponds (KPL). The addition of alum ($Al2(SO4)_3$) and quicklime (CaO) to increase pH levels and reduce water turbidity. Management is carried out to meet environmental quality standards, namely with pH values of 6-9, maximum TSS values of 400, and for Mn and Fe a maximum of 4 and 7 mg/L, respectively. *Jar Test* was conducted on samples from KPL BB-13 with doses of a mixture of alum and quicklime used were 0.02 and 0.10 grams; 0.03 and 0.12 grams; 0.04 and 0.14 grams; 0.05 and 0.16; 0.06 and 0.18; and 0.7 and 0.20. The best test results at a mixture dose of 0.02 grams of alum and 0.10 grams of quicklime to obtain a pH value of 7 (neutral), besides that TSS and Fe metal levels decreased. Mn metal has also decreased, but has not met environmental quality standards. Increasing the dose for field scale under actual observation conditions required alum as much as 1.00 g/s and quicklime as much as 5.0052 g/s. The evaluation results show that acid mine water treatment carried out by the company is more effective and efficient than the dose of laboratory test results.

Keywords: acid mine water, alum, quicklime

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1. INTRODUCTION

PT Bukit Asam Tbk. is one of the largest coal mining companies in Indonesia. Mining activities carried out with an open-pit mining system have the potential to produce acid mine water due to contamination by rocks containing sulfur (Munawar, 2017). The rock interacts directly with free air, so sulfur can oxidize and come into contact with water. Acid mine water treatment can be done by active methods using chemicals or passive methods that use metal-absorbing plants. The use of active methods is considered more effective because the reaction process occurs faster. (Assyakiri et al, 2022).

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The process with the active method begins in the equalization pond then proceeds to the settling pond, pH and metal parameter processing pool, and organic parameter processing pool. The last process is in the indicator pond for compliance with wastewater quality standards. Based on Nurisman et al (2012), the liming process in acid mine water treatment aims to increase the pH value so that the water meets the standards. Alum administration plays a role in the coagulation and flocculation process in reducing TSS levels (Harahap, 2017). The government establishes Coal Mine Liquid Environmental Quality Standards through the Decree of the Minister of Environment Number 113 of 2003 concerning wastewater quality standards for coal mining businesses or activities in article 2 paragraph (1). The pH value of water based on environmental quality standards is 6-9, with a maximum TSS value of 400, and for Mn and Fe a maximum of 4 and 7 mg/L, respectively.

Operating conditions and the environment also affect the formation of acid mine water and the effectiveness of the treatment process. When high rainfall will affect the use of chemical doses, operating conditions technically affect the time of acid mine water treatment process including flow rate, type and concentration of metals in water, and type of chemicals used (Said, 2014). The use of chemicals will be less effective if you only rely on estimates. According to Hapsari (2015), excessive use of chemicals such as lime will have an impact on hardness and increase in water pH that exceeds standard limits, making it less safe for the environment. High hardness water can damage the equipment and machinery it flows, and can cause several health problems (Ulfah et al, 2010).

Related research conducted by Nurisman et al (2012) regarding the process of acid mine water treatment in the sludge settling pond (KPL) of PT Bukit Asam, Tbk Laya Water Mine using quicklime. The addition of quicklime will be able to raise the pH value and reduce metals in acid mine water, but the resulting water has a less clear color. Therefore, the use of alum and quicklime at the right dosage will be an effective combination. Research conducted at PT Bukit Asam, Tbk has the aim of analyzing the optimum dose of mixture between alum and quicklime for acid water treatment by determining the need for chemicals both on a laboratory scale and on a field scale. Operating conditions, environment and dosage of chemical use are the basis for the need for studies to evaluate the effectiveness of the acid mine water treatment process and see the results of the water produced have met environmental quality standards to flow into the environment.

2. MATERIALS AND METHODS

PT Bukit Asam, Tbk conducts acid mine water treatment using Sludge Deposition Ponds (KPL). The KPL location that is the focus for special tasks is located in KPL Banko Barat 13 which has an area of 0.8 Ha and a capacity of 21,000 m^3 for 5 compartments with a catchment area of 321.8 Ha. 7 acid mine water samples with 500 mL each were taken from the KPL 13 Banko Barat inlet of PT Bukit Asam Tbk then measured the pH value, Total Suspended Solid (TSS), and Fe and Mn metal content will be tested Jar Test based on the Standard Operating Procedure (SOP) of UPTD Coal Handling and Transportation Laboratory PT Bukit Asam, Tbk. Water discharge data, pH data, TSS, iron metal (Fe) and manganese (Mn) levels in the actual field scale obtained from company data are used as comparison data for evaluation of the results of research data analysis conducted in the laboratory.

The comparative data obtained from PT Bukit Asam, Tbk data contains Actual Data 1 and Actual Data 2. Actual Data 1 with the period 11-14 August while Actual Data 2 in the period 14-29 August. Both data showed differences in the pH value of the outlet after being treated with the addition of quicklime as much as 16 bags or 480 kg. Actual Data 1 shows an average pH of 6.45 while Actual Data 2 shows an average pH of 6.09.

2.1. Research Variables

2.1.1 Free Variable

In this study, a variation in the dosage of alum mixture was used from a range of 0.02 grams to 0.07 grams and quicklime with an amount of 0.1 to 0.2 grams. The details of these variables are shown in table 1

2.1.2. Bound Variables

The 4 parameters test below is carried out after the sample is given chemical treatment and the settling time is 1 day.

- pH value
- TSS value
- Fe metal content
- Mn metal content

Table 1. Dosage Ratio a Mixture of Alum and Quicklime Used

Alum Mass ($Al_2(SO_4)_3$) (gr)	Quicklime Mass (CaO) (gr)
0,02	0,10
0,03	0,12
0,04	0,14
0,05	0,16
0,06	0,18
0,07	0,20

2.2. *Jar Test* Determination of Alum &; Lime Dose

Acid mine water test samples were put into six *beaker glasses* of 500 mL each. Alum is weighed as many terms as needed and recorded, then inserted into each test sample. The sample is stirred on a mechanical stirrer (*Jar Test*) at a speed of 100 rpm for 2 minutes. Furthermore, the sample was added quicklime according to the provisions and the *Jar Test* was carried out again. The samples were analyzed for pH, TSS, Fe metal, and Mn metal after 1 day of deposition. The pH value is measured with the WTW Portable Meter ProfiLine pH 3310. The method for testing metal levels in acid mine water in the form of Atomic Absorption Spectrophotometry (SSA) is measured by the BK-AA453OF series BIOBASE tool, while the TSS level test is carried out by gravimetric methods.

2.3. Data Processing for Calculation of water volume in Compartment 1 KPL BB-13

Based on Aji et al (2018), the volume of KPL (Mud Deposition Pool) for compartment 1 can use the following trapezoidal volume equation:

2.3.1. Calculation of the volume of compartment 1

$$V = \frac{1}{3}\ x\ d\ x\ (LA + LB + (LA\ x\ LB)^{0,5}) \quad \ldots (1)$$

Information:

V = Compartment Volume (m$^{3)}$

LA = Upper Area (m^2)

LB = Bottom Area (m^2)

d = Depth (m)

The amount of water volume under actual conditions using the equation above by changing the depth of the pool according to field conditions at the time of sampling

$$d_{aktual} = d_{real} - Ds_{aktual} - d_{tidak\ terisi} \quad \ldots (2)$$

Information:

d_{aktual} = High Water on KPL (m)

d_{real} = Depth of KPL (m)

Ds_{aktual} = Depth of Mud (m)

$d_{tidak\ terisi}$ = High Estimation of Empty KPL (m)

Meanwhile, to determine the amount of sludge volume, according to Atawolo (2022) it can be calculated using the following equation:

2.3.2. Amount of sludge

$$Va = V\frac{(fl-fa)}{(ft-fa)} \quad \ldots (3)$$

Va = Mud Volume (m^3)

V = Water Volume (m^3)

ft = Mud Density (ton/ m^3)

fa = Water Density (ton/ m^3)

ft = Soil Density (ton/ m^3)

According to the Ministry of Public Works and Public Housing (2018), to find out the calculation of mud thickness, you can use the following equation:

2.3.3. Sludge Thickness

$$Ds = \frac{M}{LB} \qquad \dots (4)$$

Information:

Ds = Thick of Mud (m)

M = Total Mass of Mud (m^3)

V = Compartment Volume (m^3)

The calculation of the dose of alum and quicklime on a field scale can be determined by:

Chemical Requirement = Dose x Volume of Water ... (5)

2.4 Flow Chart

The acid mine water treatment process at KPL BB 13 Banko Barat PT Bukit Asam, Tbk begins with field orientation, followed by data collection, to data processing to determine the dose of chemicals used. The following is a flow diagram of the acid mine water treatment process at KPL BB 13 Banko Barat PT Bukit Asam, Tbk shown in Figure 1.

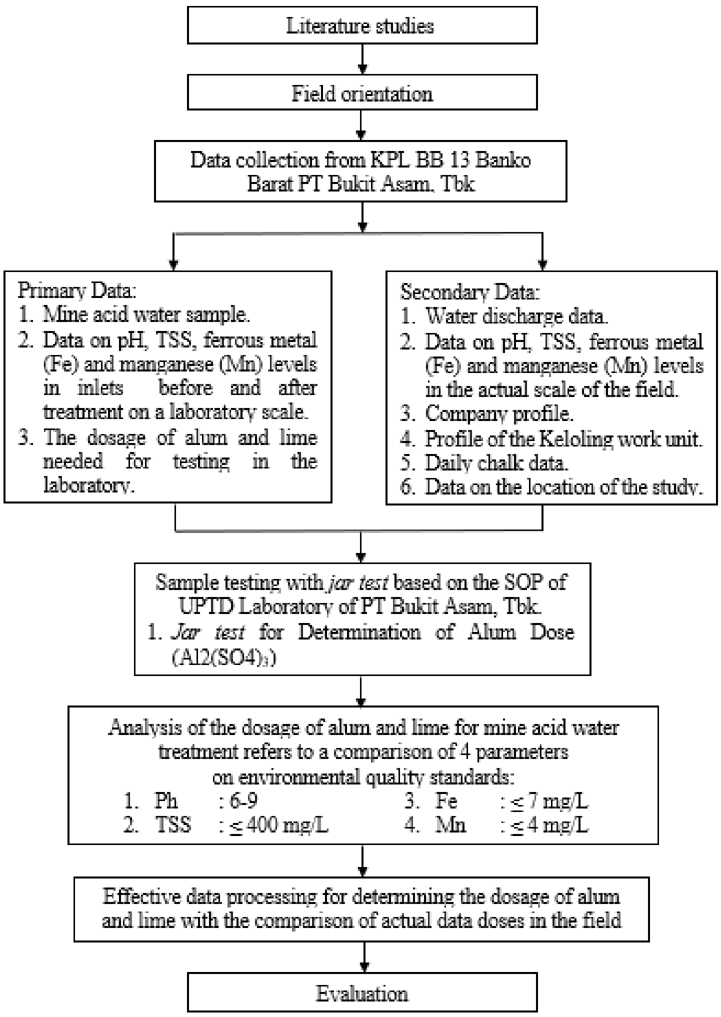

Figure 1. Flow Diagram of Acid Mine Water Treatment Process at KPL BB 13 Banko Barat PT Bukit Asam, Tbk.

3. RESULTS AND DISCUSSION

The results of the initial sample analysis taken have a pH of 6.12 which is stated to have met the environmental quality standards. The pH value produced is not only influenced by the dose of chemicals, but also influenced by the discharge of water in the pool. The greater the acid water discharge flowed, it affects the decrease in pH, increase in TSS, Fe metal, and Mn metal.

The use of quicklime is most often used in everyday life to raise the pH to meet environmental quality standards. Quicklime has advantages in terms of economy that is cheaper, its availability is plentiful, besides that the reaction to acidic water is also quite fast to raise the pH. In addition to the use of quicklime, the addition of alum is also carried out in mud settling ponds (KPL). The use of alum is carried out only under certain conditions when the flowing water has a high turbidity. Alum is used as a flocculator to agglomerate other solid materials.

The addition of quicklime to water will produce an exothermic reaction or release heat into the environment which turns into quenched lime ($Ca(OH)_2$), because acid mine water belongs to the sulfide group, quicklime will form calcium sulfide.

A mixed dose of alum and quicklime that has been tested on a laboratory scale using a pH meter has produced good results. For the initial sample, acid mine water was used which was muddy from the KPL BB-13 inlet as much as 500 mL and no chemical mixture was added, having a pH of 6.12. The sample is mixed with alum and then stirred using a *Jar Tester* at a speed of 120 rpm for 2 minutes, after which quicklime is added and stirred at the same speed and time. The process will proceed to the 4-parameter testing stage.

3.1. pH Value Parameters

Based on Figure 2, after adding alum and quicklime doses, there is an increase in pH as the chemical dose increases.

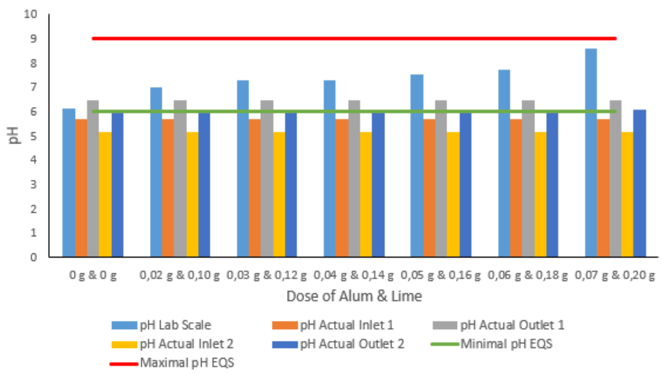

Figure 2. Comparison of Laboratory Scale pH Value after Alum and Quicklime Dosing with Actual Data in the Field

The optimum dose of the mixture to obtain a pH value of 7 (neutral) is indicated by the use of alum 0.02 grams and quicklime 0.10 grams. The resulting pH value was 6.12 respectively; 7,01; 7,29; 7,30; 7,53; 7,73; and 8.57. Comparison of laboratory-scale pH and actual data treated with chemicals has met environmental quality standards.

From the data that has been produced and looking at the graph in Figure 2, the mixing of chemicals between alum and quicklime is directly proportional to the pH value produced. In the analysis of the mixture dose sample 1 has shown a pH value of 7 which has met environmental quality standards. The reaction of water when given alum will be able to decrease the pH value, but it can be neutralized by giving quicklime.

According to Sisnayati et al (2021), alum when dissolved in water will produce H_2SO_4 compounds which have acidic properties so that they can reduce the pH level of water. The following is the mechanism of alum reaction in water in its ability to reduce pH levels by forming acidic compounds (Tandiarrang et al, 2016).

$$Al_2(SO4)_3 + H_2O \rightarrow 2Al(OH)_3 + 3H_2SO4$$

In Figure 2 it is shown that there is an increase in pH value as the dose of chemicals increases. This increase in pH value can be caused by quicklime which acts as a chemical that can neutralize acidity and is very reactive (Said, 2014). The presence of CaO in water reacts with H+, consequently increasing the pH value. The reaction of water with highly reactive CaO is seen as follows (Nurisman et al, 2012).

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_2O$$

$$CaO + 2H^+ \rightarrow Ca^{2+} + 2H_2O$$

Based on what is obtained on the chart, the pH value resulting from adding a mixture dose of alum and quicklime to the laboratory scale shows a better value compared to the actual data 1 and 2 done by the company. This is because, the pH value of laboratory test results can already obtain a pH of ≥ 7 while the average pH value of the actual data is still below the value of 7.

3.2. TSS Value Parameters

Based on the graph of TSS test results with the comparison of actual data of PT Bukit Asam, Tbk Test Results Certificate (SHU) results shown in Figure 3. The results of the TSS test after adding a mixture of alum and quicklime decreased with increasing doses of chemicals.

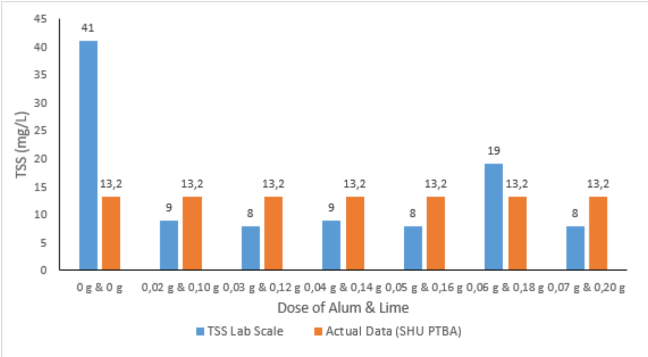

Figure 3. Comparison of Laboratory Scale TSS Value after Alum and Tohor Lime Dosing with Actual Data in the Field

The results of the TSS test after adding a mixture of alum and quicklime decreased with increasing doses of chemicals. The graph shows that the relationship between chemical dose and TSS is inversely proportional. Each sample experienced a significant decrease in TSS levels after adding a dose of the chemical mixture. All sample meet environmental quality standard, where the maximum TSS is 400 mg/L.

From the results of TSS testing, it can be seen from Figure 3 which experienced a significant decrease after adding a mixture dose of alum and quicklime. The amount of mud in the sample has a different ratio, the amount of mud certainly affects the level of turbidity in the water. Turbidity can affect water quality and can have an impact on the amount of suspended solids or *total suspended solids* (TSS) (Jewlaika et al, 2014). As happened in sample 5, where the TSS value rose to twice that of other test samples. According to Winnarsih et al (2016), this can be caused by the content of different sample suspended materials so that TSS has a high value even though treatment has been carried out by adding a mixture of alum and quicklime. The addition of alum dose is also one of the influential factors, where the H+ ions formed more and more make the pH drop and disrupt the stability of the floc that has been formed. The floc broke again and became a floc that passed the screening (Trimaily et al, 2017). In acid mine water treatment has a coagulation-flocculation method which is used to remove suspended material (colloids).

The process is carried out in stirring quickly using a *Jar Tester* tool, so that the coagulation process occurs or the formation of flocs. After the coagulation process, then a flocculation process is carried out where the flocculation process will occur clumping small particles deposited into larger particles. Coagulation is carried out to convert solid materials that are difficult to settle (float) into easy to settle, and a flocculation process is carried out for the removal of *Suspended Solids* (SS) (Rahma and Rahmiani, 2021).

3.3. Fe Metal Grade Parameters

The Spectrophotometry Atomic Absorption (SSA) method is used to analyze Fe and Mn metal levels in water due to SSA's high sensitivity to being able to analyze samples below 1 ppm (Adhitasari and Andrijanto, 2020). After analysis of each sample, it shows fluctuating graph results. Figure 4 shows the results of the analysis of Fe content levels with the comparison of actual data from the Test Results Certificate (SHU) of PT Bukit Asam, Tbk.

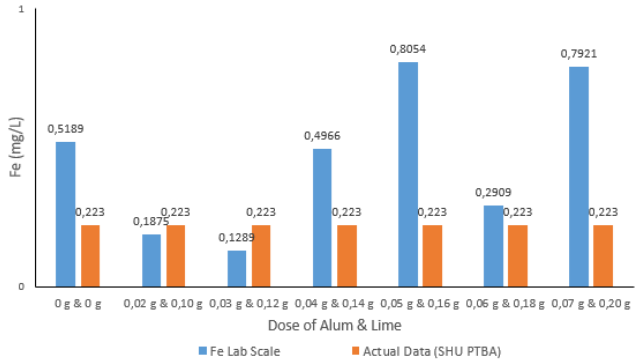

Figure 4. Comparison of Laboratory Scale Fe Levels after Alum and Quicklime Dosing with Actual Data in the Field

The initial sample tested had Fe content that met quality standards, but after adding the dose of chemicals, the most optimal condition was found in the sample with the addition of alum 0.03 grams and quicklime 0.12 grams because it showed the lowest Fe content. The addition of alum affects the concentration of Fe levels in acid mine water, where both have a relationship that the higher the alum concentration, the higher the decrease in Fe levels (Trimaily et al, 2017). This is because the affinity of $Al(OH)_3$ attracts Fe ions. Colloidal particles ($Al(OH)_3$) are formed as a result of hydrolysis of Al^{3+} ions, then $Al(OH)_3$ will remove negative charges from the sludge and coagulation occurs (Adhitasari and Andrijanto, 2020). Similarly, the addition of quicklime, where the more quicklime is added, the decrease in Fe levels should be greater (Saswita et al, 2018). Giving lime will bind ions that have a valence of +2, then Fe^{2+} will be eliminated by quicklime. The reaction of colloidal particle formation is seen as follows:

$$Al^{2+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$

Environmental quality standards show that the maximum tolerance level of Fe is 7 mg/L, where the initial samples taken from KPL BB-13 are in accordance with quality standards of 0.5189 mg/L. After adding doses of chemical mixtures, samples 1 and 2 decreased drastically to 0.1875 mg/L and 0.1289 mg/L, respectively. Samples 3 to 6 again increased with consecutive results of 0.4966 mg/L; 0.8054 mg/L; 0.2909 mg/L; and 0.7921 mg/L. The increase can be influenced by the factor of incomplete insoluble chemicals in acid mine water, it can be influenced by the large and agglomerated particle size of chemicals while the speed of stirring during the *Jar Test* process is unable to break down chemical solids.

3.4. Mn Metal Grade Parameters

The method used to analyze Mn metal is the same as Fe metal analysis, namely using the Atomic Absorption Spectrophotometry (SSA) method. The SSA method has the principle of absorbing light on atoms at certain wavelengths. The process of this method occurs absorption of energy by atoms that are at the basic energy level and causes electrons from excited free atoms unstable by emitting radiation energy, and certain waves (Torowati et al, 2008).

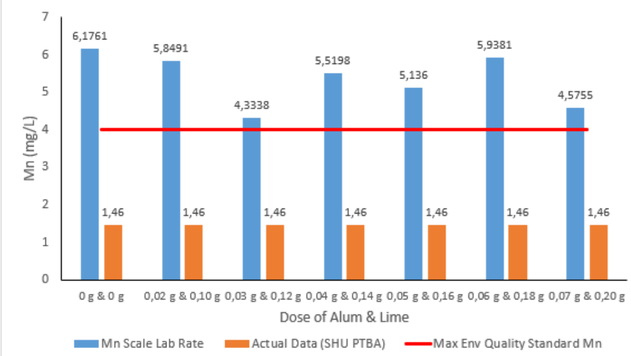

Figure 5. Comparison of Laboratory Scale Mn Levels after Dosing Alum and Quicklime with Actual Data

Figure 5 shows the results of the relationship between changes in Mn content in samples after adding doses of alum and quicklime mixture with a comparison of actual data from the Test Results Certificate (SHU) of PT Bukit Asam, Tbk. Based on the graph , there is a decrease in Mn levels as the dose of the chemical increases, but the resulting graph fluctuates. Samples that have the lowest Mn levels after adding doses of sample chemicals with the addition of alum 0.03 grams and quicklime 0.12 grams where the Mn content is 4.338 mg/L.

Added quicklime can affect the decrease in Mn metal levels in acid mine water. The results of Mn metal grade levels do not show a consistent decline. The addition of alum should reduce Mn due to the occurrence of chemical precipitation processes, this is characterized by metal elements being converted from ionic charges to particulates by coagulants (Busyairi et al, 2018).

The initial sample had an Mn content of 6.1761 mg/L, this value showed that it did not meet the quality standard where the maximum Mn content in water was 4 mg/L. After treatment, the Mn content in acid mine water from KPL BB-13 showed a decrease but one of the samples increased.

The results of Mn levels from samples 1 to 6 were 5.8491 mg/L; 4.3338 mg/L; 5.5198 mg/L; 5.1360 mg/L; 6.3821 mg/L; and 4.5755 mg/L. Elevated Mn levels in sample 5 can be considered a form of deviation influenced by precipitation before treatment is less effective, and quicklime coagulants that do not react perfectly (Saswita, 2018). The increase in Mn content is the same as the results of research conducted by Trimaily et al, (2017) which states that the higher the alum dose, the Mn metal content can increase. The results shown after the *Jar Test* still do not meet the environmental quality standards for acid mine water despite the decrease in manganese levels.

3.5. Comparison of Alum and Quicklime Dosage Effectiveness

Table 2. shows the results of a comparison of the use of daily alum and lime quantities in actual conditions and laboratory tests. Actual conditions using pH data after being treated with 16 bags of quicklime by PT Bukit Asam, Tbk.

In August 2022, KPL BB 13 gave quicklime 2 times with each treatment using 16 bags of quicklime with a total of 480 kg at the *inlet* in one day. The calculation results showed that the average use of quicklime for period 1 with a range of August 11-14 was 1.38 g/s. The average magnitude of the *inlet* pH value in that period was 5.7 and the average pH value at the *outlet* was 6.45. The average quicklime use for period 2 with a distance range of August 14-29 was 0.3472 g/s. The average pH value of the *inlet* in that period was 5.17 and the average pH value at the *outlet* was 6.09.

The determination of the right dose of chemicals for acid mine water treatment at KPL BB-13 can be compared with actual data on the use of quicklime, while the use of alum cannot be compared with actual data because the company has not used alum in recent times. TSS parameters, Fe metal content, and Mn metal content are not monitored every day but data are obtained from the Test Results Certificate (SHU) according to those in the table. The actual data on the condition when the observation was carried out with the dose of quicklime according to the treatment of PT Bukit Asam, Tbk was obtained at 5,555 g/s. The final results show that 4 parameters have met environmental quality standards with treatment using only quicklime.

Table 2. Compare Daily Dosage of Alum and Quicklime

Parameter	Quality Standards	PTBA Actual Data (Aug 29)	Test Data Laboratory (Aug 29)	
		Daily Lime Average	Daily Lime Average	Average Daily Alum
		5,555 (g/s)	5,0052 (g/s)	1,000 (g/s)
pH	6-9	7,30	7,01	
TSS (mg/L)	400	13,2	9	
Fe (mg/L)	7	0,223	0,1875	
Mn (mg/L)	4	1,46	5,8491	

The laboratory test results for samples observed on August 29, 2022 obtained the daily quicklime magnitude based on the calculation of water volume was 5.0052 g/s, while the average alum used for this condition was 1.00 g/s. The pH, TSS, and

Fe parameters have shown good results, where the three parameters have met environmental quality standards. However, the laboratory test results of Mn levels have not received good results because they are still above environmental quality standards.

This shows that the treatment by PT Bukit Asam, Tbk has more effective results for acid water treatment of KPL BB-13 mine. The use of quicklime alone can be considered efficient without the addition of alum. Processing of laboratory test results shows the use of quicklime is less than the company, this is more efficient in terms of economy but Mn levels have not been met. The advantages in terms of economy can be seen from the price of 1 kg of alum of Rp 10,000.00 while the price of 1 kg of quicklime is Rp 8,000.00. Therefore, the treatment of PT Bukit Asam, Tbk will be more profitable because the costs incurred are less.

4. CONCLUSION

The dose of a mixture of alum and quicklime based on a laboratory scale test of 1 liter of acid mine water KPL BB-13 in order to obtain pH 7 (neutral) requires alum as much as 0.04 grams and 0.20 grams of quicklime. The addition of alum and quicklime affects the parameters of pH, TSS, Fe levels, and Mn. The pH, TSS, and Fe parameters show better results where there is a decrease in the levels of each of the 3 parameters and has met quality standards. The use of quicklime in laboratory test results is also more economical, amounting to 5.0052 g / s, while the use of quicklime doses for the daily average in the actual data of PT Bukit Asam, Tbk is 5.555 g / s. Laboratory test results for Mn parameters also decreased after being treated with a mixture of alum and quicklime, but did not meet environmental quality standards. Therefore, the dosage for field scale carried out by PT Bukit Asam, Tbk can be declared effective because all parameters have met environmental quality standards and are more efficient because only the use of quicklime without the addition of alum.

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