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Neutralization of Acid Mine Drainage with Calcium Hydroxide in Sand Packed Bed Contactor

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Abstract. This study investigates the neutralization of acid mine drainage using calcium hydroxide in a sand packed bed contactor. The research aims to evaluate the effectiveness of this method by analyzing the relationship between the molar flow rate of $Ca(OH)_2$ and the resulting pH increase in the treated water. Nine experiments were conducted, utilizing sulfuric acid (pH 1) as the feed with molar flow rates ranging from 0,0015 to 0,0033 mole/s. The acid was neutralized with calcium hydroxide (pH 12-13) at flow rates between 0,002 and 0,004 mole/s. The pH of the output water product ranged from 4 to 7. Results indicate a direct correlation between the molar flow rate of $Ca(OH)_2$ and the pH increase in the treated water. However, variations in the acid-base molar ratio showed less significant effects on the pH increase. The findings suggest that utilizing $Ca(OH)_2$ in a sand packed bed contactor is a practical and effective approach for acid mine drainage neutralization. Further research could explore the application of CaO as a heap contactor to enhance treatment efficiency in mining environments.

Keywords: acid mine drainage, calcium hydroxide, sand packed bed contactor, neutralization

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1. Introduction

The increase in mining activities has exacerbated environmental issues, particularly concerning acid mine drainage (AMD) generated during the mining process. Acid mine drainage contains high acidity levels capable of dissolving,[1] which can detrimentally affect the environment and human health if not properly managed. Groundwater poses challenges to both underground and open-pit mining systems because the rock excavation process can lead to the formation of acid mine or Potential Acid Forming (PAF) water when groundwater interacts with rock alongside oxygen. This results in the oxidation of PAF minerals such as FeS_2, CuS, $CuFeS_2$, MoS_2, NiS, PbS, and ZnS .[2] This acidic water has a low pH and contains metal ions originating from sulfide minerals. Empirically, Equation 1 depicts the formation of acid mine drainage along with metal ions, particularly soluble iron, with pyrite minerals.[3] Identification of pyrite minerals is found in rocks that are a natural part of both overburden and inter-burden models.[4]

Iron (Fe^{3+}) cations along with hydroxide (OH^-) anions form a colloidal precipitate that ranges in color from yellow to reddish, constituting one of the wastes alongside the acidity resulting from the dissociation of H^+ and SO_4^{2-}, thereby contributing to the relative formation of sulfuric acid. The acidity levels of acid mine drainage vary, but field cases, such as those in the study,[5] indicate that the pH of acid mine drainage is typically <4. One commonly employed method to address this issue is by using quicklime as a neutralization agent. However, the effectiveness of quicklime (CaO) in reducing acidity levels and controlling metal pollution in acid mine drainage still requires further evaluation, particularly on a laboratory scale to understand the interaction processes between quicklime, water, and acid mine drainage. CaO, $Ca(OH)_2$, and $CaCO_3$ are commonly used materials in the process of neutralizing acid mine drainage.[6]. The reaction of an acid with CaO is more appropriately referred to as a neutralization reaction, the reaction of an acid with $Ca(OH)_2$ is better described as an acid-base titration reaction, while the reaction of an acid with $CaCO_3$ is called an acid-carbonate reaction.

$$FeS_2 + H_2O + O_2 \rightarrow Fe_3 + 3OH^- + H^+ + SO_4^{2-} \cdots (1)$$

This study aims to evaluate the effectiveness of neutralizing AMD using quicklime solution in a sand-packed column model on a laboratory scale. In this study, a packed-bed column filled with sand was chosen as the experimental model as it can simulate reactor conditions similar to field conditions. By conducting this research on a laboratory scale, we can better control experimental variables, thus allowing for a deeper understanding of the interaction between calcium hydroxide and AMD, as well as estimating its effectiveness in reducing acidity levels and controlling metal pollution. The results of this study are expected to provide valuable insights into the potential use of quicklime in addressing AMD issues and lay the groundwork for further development on a field scale. Calcium hydroxide is obtained from the reaction of CaO with water. CaO, known as quicklime, is derived from the calcination of calcium carbonate minerals or biogenic components[7] containing calcium. Quicklime is readily available and affordable. The AMD is neutralized until the pH meets the wastewater quality standards within the range of 6-9 according to SNI 6989.11:2019 2019.[8] The scope of the research is limited to neutralizing AMD and does not include handling of the formed metal cations.

2. Materials and Methods

2.1 Materials

In this study, the materials used include a model of acid mine drainage with a concentration of 65% H_2SO_4 for analysis, which was diluted to 0,818 mole/liter, representing the common acidic conditions found in mining environments with an acid pH of 1. As the neutralizing agent, quicklime (CaO) from the Merck brand was used and then dissolved in distilled water to form calcium hydroxide ($Ca(OH)_2$) according to reaction equation 2. The sand contact in the experiment was conducted using a fixed-bed column consisting of inert sand that had been cleaned, aiming to simulate representative reactor conditions by optimizing the contact between acid mine drainage and the neutralizing agent to maximize the effectiveness of the neutralization process. The fixed-bed column serves as an alternative mixing method to agitation methods, utilizing radial and axial dispersion mechanisms within the packed bed,[9,10] Radial dispersion entails mixing perpendicular to the flow direction, while axial dispersion involves mixing along the flow direction. Together, these dispersion mechanisms facilitate thorough interaction between the acid mine drainage and the neutralizing agent, promoting effective neutralization throughout the column.

$$CaO + H_2O \rightarrow Ca(OH)_2 \cdots (2)$$

2.2 Methods

The neutralization process of acid mine drainage using $Ca(OH)_2$ resembles an acid-base titration in chemistry. In this process, the acid mine drainage reacts with a base, resulting in the formation of salt and water as products. Through this interaction, the acidity level of the acid mine drainage can be significantly reduced, while the produced compounds tend to be chemically more stable, aiding in controlling adverse environmental impacts.

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + H_2O \cdots (3)$$

The neutralization method employed in this study is essentially an acid-base titration reaction, where the acid mine drainage (H_2SO_4 0,818 mole/l) acts as the acid and quicklime, dissolved in water to form calcium hydroxide ($Ca(OH)_2$), acts as the base. These two agents are then brought into contact within the sand-packed fixed-bed column as illustrated in Figure 1, with the molar flow rates varied to study their influence on the effectiveness of the neutralization process. The output from the fixed-bed column is a liquid whose pH is measured, providing an indication of the remaining acidity after the neutralization process. Thus, the pH measurement of the output liquid can be used as a parameter to evaluate the effectiveness of the neutralization method applied in reducing the acidity of the acid mine drainage.

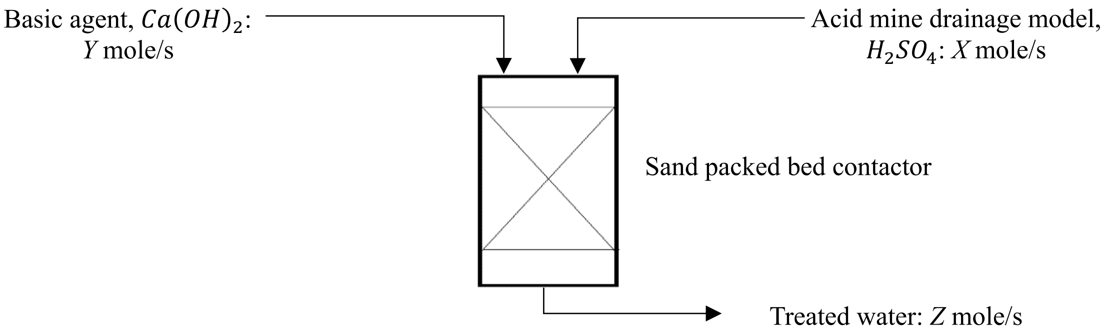

Figure 1. Schematic Model of Sand Packed Bed for Acid Mine Drainage Neutralization

The sand-packed fixed-bed column scheme depicted in Figure 1 operates continuously. The volumetric flow rate ($\dot{V}$) of the feed is calibrated beforehand. The molar flow rate (F) is obtained by multiplying the concentration (C) by the volumetric flow rate, as described in Equation 4. The molar flow rate of the acid is represented as X mol/s, and the molar flow rate of the base is represented as Y mol/s. The molar flow rate of the salt product, Z mol/s, is estimated using stoichiometric reaction calculations. This continuous operation allows for a steady flow of reactants and products within the system, ensuring efficient and consistent neutralization of the acid mine drainage.

$$F = C \times \dot{V} \cdots (4)$$

2.3 Estimating Acid-Base Ratio and Stoichiometric Conversion

Estimating the acid-base ratio and stoichiometric conversion is a crucial step in analyzing the neutralization process for pH 7 approach. The acid-base ratio can be calculated by considering the molar amounts of acid and base added to the system. For instance, if the molar amount of acid (X) and the molar amount of base (Y) are known, the acid-base ratio can be calculated as X/Y. Stoichiometric conversion is vital in estimating the amount of product generated from the reaction between acid and base. It involves calculating the number of moles of the product formed based on the chemical reaction that occurs. For example, if the reaction between acid and base produces salt as a product, stoichiometric conversion will compute the number of moles of salt produced according to that reaction.

$$Acid - basic\ Ratio = \frac{F_{H_2SO_4}}{F_{Ca(OH)_2}} \cdots (5)$$

Stoichiometric conversion of reactants is obtained from stoichiometric calculations when the molar flow rate of reactants is known. Here is an example of an acid-base neutralization stoichiometric reaction. The important reactant conversion to consider is the acid conversion. Determining the stoichiometric percentage acid conversion is as follows.

$$\%\ Acid\ Conversion = \left(1 - \frac{(X - Y)\ mole/s}{X\ mole/s}\right) \times 100\% \cdots (6)$$

	H_2SO_4 +	$Ca(OH)_2$	$\rightarrow CaSO_4 + H_2O \cdots (7)$
Beginning	*X* mole/s	*Y* mole/s	
Reacting	*Y* mole/s	*Y* mole/s	
Leftover	(*X*-*Y*) mole/s	(*Y*-*Y*) mole/s	*Y* mole/s

3. Results and Discussion

3.1 Conversion of CaO to $Ca(OH)_2$

The solubility of CaO in water, resulting in the formation of $Ca(OH)_2$, is reported to be minimal according to.[6] To overcome this limitation and accelerate the solubility process, interventions are necessary[11] suggest that increasing the reaction rate is essential. This can be achieved through strategic adjustments in contact duration and temperature. By optimizing these factors, the efficiency of the conversion process from CaO to $Ca(OH)_2$ can be enhanced, thereby facilitating the neutralization process more effectively. Such interventions are critical for ensuring that the neutralization reaction proceeds efficiently, enabling the mitigation of acidity in acid mine drainage.

3.2 The Result of The Acid Mine Drainage Neutralization Simulation in The Sand Packed Bed Contactor

The results of nine simulations, labeled A to I, conducted in the sand contactor reveal significant findings. These experiments involved feeding sulfuric acid with a pH of 1 at molar flow rates ranging from 0,0015 to 0,0033 mole/s. The acid was neutralized using calcium hydroxide with pH levels ranging from 12 to 13, at molar flow rates between 0,002 and 0,004 mole/s. The output products obtained had pH levels ranging from 4 to 7. These data illustrate the effective neutralization process, reducing the acidity of acid mine drainage to a more neutral level, as indicated by the pH range of the output products. Variations in the feed molar flow rates and pH of the neutralizing agent significantly impacted the pH of the output products.

When the acid-base molar ratio exceeds 1, it signifies a reduced need for the base. This circumstance is anticipated to arise as the water pH approaches 7, and the stoichiometric acid conversion estimate approaches 100%. Based on the data presented in Table 1, Experiment C seems plausible. However, Experiment G warrants attention as it exhibits an acid-base molar ratio of 3,29, despite the pH remaining at 4. This incongruity suggests inadequate interaction between the two reactants within the sand packed bed, emphasizing the need for further investigation or optimization of the contact process to achieve the desired neutralization outcome.

Table 1. Summary of Acid Mine Drainage Neutralization Simulation

Exp	$C_{H_2SO_4}$ (mole/L)	$F_{H_2SO_4}$ (mole/s)	pH Acid Mine Drainage	$C_{Ca(OH)_2}$ (mole/L)	$F_{Ca(OH)_2}$ (mole/L)	pH $Ca(OH)_2$	F_{CaSO_4} (mole/s)	pH Product	Acid/Basic Mole Ratio	Acid Stoichiometric Conversion (%)
A	0,188	0,003196	1	0,0424	0,000242	12,5	0,000242	4	13,2	7,57
B	0,188	0,003196	1	0,17	0,000969	13	0,000969	6	3,29	30,31
C	0,188	0,003196	1	0,51	0,002907	13	0,002907	7	1,09	90,95
D	0,188	0,003384	1	0,01780	0,000357	12	0,000357	6	9,47	10,54
E	0,188	0,003384	1	0,2314	0,004628	13	0,004628	7	0,73	100
F	0,188	0,003	1	0,04	0,00028	13	0,00028	6	10,71	9,33
G	0,188	0,003	1	0,13	0,00091	13	0,00091	4*	3,29	30,33
H	0,188	0,0035	1	0,0089	0,00008	12	0,00008	6	43,75	2,28
I	0,188	0,0015	1	0,1335	0,0004	13	0,0004	6	3,75	26,67

* poor feed dispersion in packed bed

3.3 Statistic Interpretation

The statistical interpretation indicates that, from the 9 experiments conducted, the average pH of the output products is 6. An independent paired T-test was performed to compare the pH of the acid mine drainage with the pH of the processed products. The calculated T-value is 5,55, exceeding the critical T-value of 1,85. Since the calculated T-value is greater than the critical T-value, the null hypothesis (H_0) stating no difference in values is rejected, and the alternative hypothesis (H_1)[12] suggesting a significant difference in pH values is accepted. Furthermore, it is observed that the acid-base molar ratio ranges from 0,7 to 13,2, with an average molar ratio of 9,92, while the average acid conversion is 34,22%.

The correlation between the molar flow rate of $Ca(OH)_2$ and the pH increase in the output water product is clearly depicted in Figure 2, where a discernible upward trend in the regression line is observed. This trend suggests that as the molar flow rate of $Ca(OH)_2$ rises, there is a proportional increase in the pH of the output water product, indicating a direct relationship between these variables. Conversely, Figure 3 presents a less pronounced decreasing trend, indicating that variations in the acid-base molar ratio may not exert a significant influence on the pH increase in the output water product. This observation suggests that other factors or mechanisms may be at play in determining the pH of the output water product in response to changes in the acid-base molar ratio. Further analysis is warranted to elucidate these relationships and their implications for the neutralization process.

3.4 Discussion

The results of acid mine drainage neutralization simulation modeling the reaction between H_2SO_4 and $Ca(OH)_2$ in sand-packed columns yield several significant findings. Firstly, there is a clear correlation between the molar flow rate of $Ca(OH)_2$ and the increase in pH of the output water product. This is evidenced by the ascending trend in the regression line depicted in Figure 2. Hence, the higher the molar flow rate of $Ca(OH)_2$.

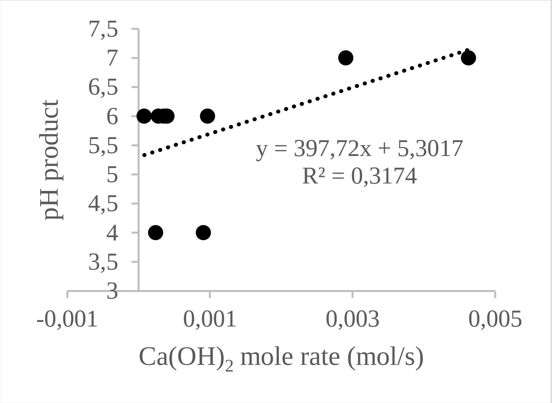

Figure 2. The Relationship Between Molar Flow Rate of $Ca(OH)_2$ and The pH of The Output Water Product

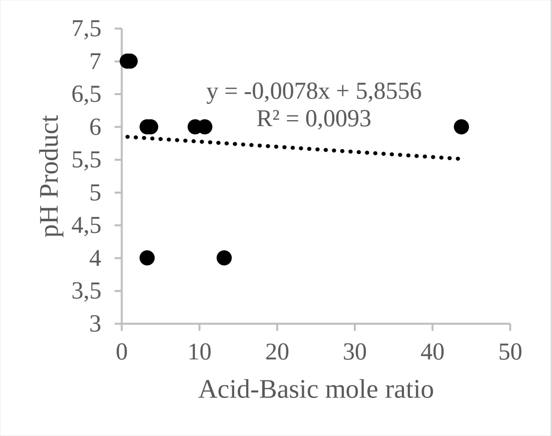

Figure 3. The Relationship Between The Acid-Base Molar Ratio and The pH of The Output Water Product

The higher the resulting pH of the output water product, indicating a direct relationship between these variables. However, upon examining Figure 3, a less significant decreasing trend is observed when the acid-base molar ratio is increased. This suggests that variations in the acid-base molar ratio may not significantly impact the increase in pH of the output water product. These findings suggest that there may be other factors or mechanisms influencing the pH of the output water product in response to changes in the acid-base molar ratio. Therefore, further analysis is required to elucidate these relationships and their implications for the overall neutralization process. The sand-packed column contact method is recommended for simple utility in treating acid mine drainage without the need for mechanical mixing units. This is because mass transfer phenomena occur in the packed bed column, where dispersion results in axial and radial dispersion between the acid and base.[9,10]

4. Conclusions

The research on acid mine drainage neutralization utilizing $Ca(OH)_2$ in sand-packed columns provides valuable insights into the effectiveness of this method in treating acidic mine water. Firstly, the study reveals a direct correlation between the molar flow rate of $Ca(OH)_2$ and the pH increase in the output water product, highlighting the importance of controlling this parameter for efficient neutralization. Additionally, while variations in the acid-base molar ratio may not significantly affect the pH increase in the output water product, further investigation is needed to understand the underlying mechanisms. Overall, the sand-packed column contact method emerges as a practical and effective approach for neutralizing acidic mine water, offering simplicity and feasibility in treatment processes without the need for mechanical mixing units. These findings contribute to the advancement of acid mine drainage treatment strategies, with potential implications for environmental remediation efforts in mining-affected areas.

A suggestion for further research is to explore the utilization of CaO as a contact heap with acid mine drainage. This approach could investigate the efficiency and effective ness of CaO in neutralizing acidic mine water when applied in heap contactor configurations. By utilizing CaO in this manner, researchers could assess its potential as a cost-effective and scalable solution for treating acid mine drainage in practical mining environments. Additionally, further studies could delve into optimizing the design and operation parameters of the CaO heap contactor to enhance its performance and applicability in real-world mining scenarios. This avenue of research has the potential to contribute valuable insights to the field of acid mine drainage treatment and environmental remediation

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