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Research Article

Aqueous Mineral Carbonation of Red Mud for CO_2 Permanent Sequester

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Abstract: Red mud is a solid waste (slurry) produced during the extraction of alumina, containing minerals such as cancrinite, sodalite, tricalcium aluminate (TCA), and katoite. Due to the use of NaOH in alumina extraction, red mud has a high alkalinity (pH 12–13). Currently, the storage and management of red mud are suboptimal, as it is directly disposed of in landfills without treatment, leading to soil and water contamination and posing environmental risks. Indonesia produces a significant volume of red mud, amounting to 4.4 million tons per year, necessitating effective treatment methods to reduce its danger. One of the solution is mineral carbonation, which neutralizes red mud and serves as permanent CO_2 sequestration by injecting CO_2 into the red mud slurry. This process dissolves the minerals in red mud into the liquid phase, where they react with CO_2 to form mineral carbonates, especially calcium carbonate. The carbonation product of red mud can subsequently be used in cement, brick, tile, and fertilizer production.The red mud used in this research was sourced from Tayan mining in West Kalimantan, Indonesia. Initial characterization of the red mud using XRD and XRF revealed a CaO content 2.936%. The sequestration capacity of red mud, with various liquid/solid (L/S) ratios (1:1–5:1) at ambience temperature of 30°C, was analyzed using TIC (total inorganic carbon) over an observation period of 80 minutes. The optimal L/S ratio was determined to be 1:1, with a conversion rate of 23.886%, while the best CO_2 capture capacity is also at a 1:1 ratio with a capacity of 0.551 kg CO_2/kg red mud, with neutralization occurring at the 15-minutes. This method neutralizes red mud and provides sustainable CO_2 sequestration

Keywords: Carbon Capture, CO2 Sequestration, Mineral Carbonation, Red Mud,

1. Introduction

Carbon dioxide emissions increase every year due to the growth of various industrial sectors such as industry, agriculture, and energy. Globally, in 2023, CO_2 emissions rose by 2.8 ppm from 2022, reaching a total of 419.33 ppm. This is concerning, as CO_2 is one of the greenhouse gases that traps solar heat, causing an increase in Earth's surface temperature, leading to global warming and ultimately climate change.

On the other hand, one of the major issues related to industrial waste is red mud, an alkaline solid waste produced from the extraction of bauxite ore using NaOH in the Bayer process. Red mud is typically disposed of in landfills, leading to several environmental problems. The high alkalinity of red mud, with a pH range of 12-13, poses a risk to groundwater, which can be harmful to living organisms. Additionally, when red mud dries out, dust from its surface can be carried by the wind, affecting the surrounding plant rehabilitation and causing respiratory issues for humans [1].

For every ton of good-quality bauxite, 0.3 tons of red mud are produced, while low-quality bauxite can result in as much as 2.5 tons of red mud. With the increasing production of alumina from bauxite each year, the volume of red mud also rises, requiring additional storage facilities, which leads to higher maintenance costs [2].

Carbon Capture and Storage (CCS) is one of the most effective methods to prevent further CO_2 emissions. CCS involves capturing and storing CO_2 in natural reservoirs, preventing its release into the atmosphere. It is known that 60% of CO_2 emissions remain in the atmosphere, while the other 40% is absorbed naturally by magnesium silicates like olivine and serpentine, forming stable carbonates. However, this natural absorption process takes thousands of years [3].

Mineral carbonation is a technology designed to accelerate the reaction between CO_2 and minerals to form stable carbonates, thus permanently storing CO_2. The advantages of mineral carbonation include its exothermic reactions, which reduce energy consumption, the formation of thermodynamically stable carbonate products, and the potential use of these carbonates as construction materials. Moreover, mineral carbonation can neutralize red mud, making it less harmful to the environment [4].

The mineral carbonation process is complex, involving three phases: solid, liquid, and gas. The process follows three main mechanisms [5] :

1. CO_2 diffuses into the air, forming carbonic acid, which ionizes into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-})
   $CO_2 + H_2O \rightarrow H_2CO_3$
   $H_2CO_3 \rightarrow H^+ + HCO_3^-$
   $HCO_3^- \rightarrow 2H^+ + CO_3^{2-}$
2. OH- leaching increases the solution's pH, while calcium ions are released, with the calcium concentration peaking early in the carbonation process.
   $CaO + H_2O \rightarrow Ca(OH)_2$
   $Ca(OH)_2 \rightarrow Ca^{2+} + OH^-$
3. Ca^{2+} reacts with CO_3^{2-} to form calcium carbonate ($CaCO_3$), which permanently stores CO_2.
   $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$

The main objectives of this paper are the effect of temperature on neutralize red mud, determine the effective time required to neutralize red mud, assess the impact of the liquid-to-solid ratio on the red mud's ability to capture CO2, and conclude whether red mud from the Tayan West Kalimantan mine has the potential for carbon capture and storage.

2. Materials and Methods

2.1. Material

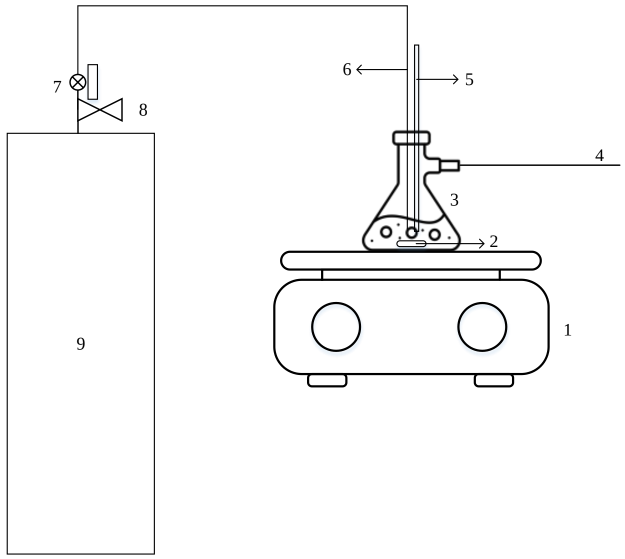
CO_2 with a concentration of 98.99% was supplied by CV Perkasa Gas Jogja (Sleman, Indonesia) and carried in CO_2 gas cylinders. Red mud was obtained from Tayan Bauxite Mining, operated by UBP Bauxite, West Kalimantan, Indonesia. The red mud sample was dried at 105°C for 8 hours to remove water content, then reduced to a particle size of 100 mesh and analyzed using XRF (X-ray fluorescence) to identify the oxide content.

Tabel 1. Composition of Red Mud determine by fluorescence X-ray

Compound	Conc. Unit
Al_2O_3	12,718%
SiO_2	17,99%
P_2O_5	0,482%
SO_3	0,359%
K_2O	0,232%
CaO	2,936%
TiO_2	3,738%
V_2O_5	0,257%
MnO	0,129%
Fe_2O_3	60,59%
Eu_2O_3	0,109%

2.2. Experimental Method

The experimental setup for red mud carbonation is shown in Fig. 1. CO2 was injected at a fixed flow rate of 4.7 LPM (liters per minute) into the red mud slurry, which was prepared by mixing 100 mesh dried red mud with distilled water at various L/S ratios (1:1 to 5:1), with a fixed volume of 200 mL. A stirring speed of 500 RPM was used to ensure the slurry was homogeneous. The experiment was conducted for 80 minutes under ambient temperature and pressure.



1. Hotplate and stirrer
2. Stirrer Bar
3. filter flask
4. Outlet CO_2
5. Termometer
6. Inlet CO_2
7. Regulator and flow meter
8. Valve
9. CO_2 Tank

Figure 1. Experimental Setup

After carbonation, the red mud slurry was filtered using a membrane filter (Whatman 42), dried at 105°C to remove moisture, and the particle size was further reduced to 200 mesh. The Total Inorganic Carbon (TIC) content after red mud carbonation was determined using an Elementar Soli TOC Cube, with a temperature ramping program between 600°C and 900°C at a heating rate of 70°C per minute to measure the carbon content in the red mud.

2.3. Carbonation Conversion and CO_2 capture capacity Determination

Carbonation conversion assumes that the calcium species (Ca) is the only component reacting, as shown in the equation [4] :

$$\delta Ca(\%) = \frac{\frac{CO_2(wt\%)}{100\text{-}CO_2} \times \frac{1}{MW_{CO_2}}}{\frac{CaO_{total}}{MW_{CaO}}}$$

Where MW_{CO_2} and MW_{CaO} are the molecular weights of CO_2 and CaO (44 and 56 g/mol, respectively), and CaO_{total} is the weight percentage of CaO in the red mud sample before the carbonation process, identified through XRF analysis.

CO_2 capture capacity (C_{cap}) is an index used to evaluate the amount of CO_2 absorbed into the carbonate product [4] :

$$C_{cap} = \frac{CaO_{total}}{MW_{CaO}} \times MW_{CO_2} \times \delta Ca$$

C_{cap} stan for CO_2 capture capacity (kg-CO_2/kg-Red Mud) and CaO_{total} is the weight fraction (g/g-Red Mud) of CaO in the red mud sample before carbonation.

3. Results and Discussion

3.1. Red mud Neutralization

The neutralization of red mud was carried out with a liquid/solid ratio of 1:1 for 90 minutes. It was observed that at both 25°C and 40°C, the red mud reached a neutral condition by the 15th minute, with a pH of around 7.7. The sequestration of CO_2 by red mud, which has high alkalinity, involves a reaction between OH- ions and CO2, resulting in the formation of bicarbonate ions (HCO_3^{-}), which neutralizes the red mud [6].

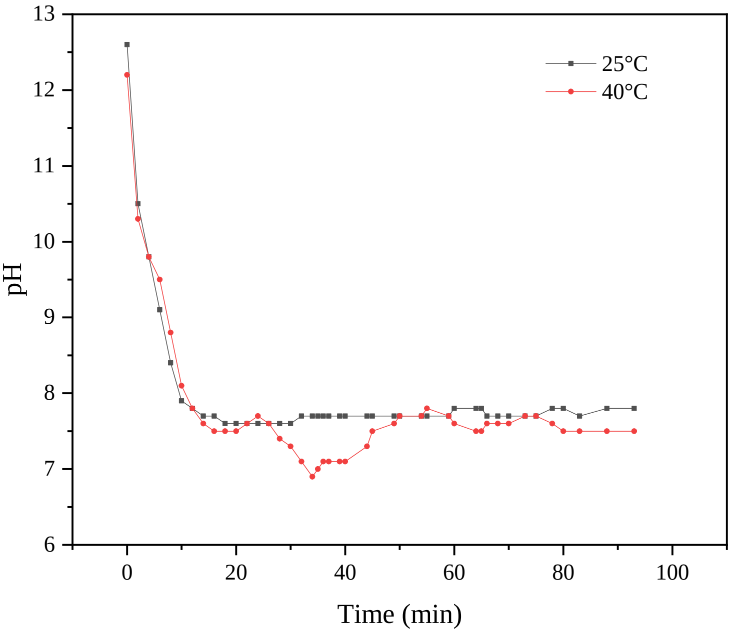


Figure 2. The effect of Reaction Temperature on Red Mud neutralization

The reaction mechanism can be described as follows [6]:

$OH^- + CO_2 \rightarrow HCO_3^-$

$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$

$H_2O + CO_2 \rightarrow HCO_3^- + H^+$

3.2. Effect of Liquid/Solid Ratio

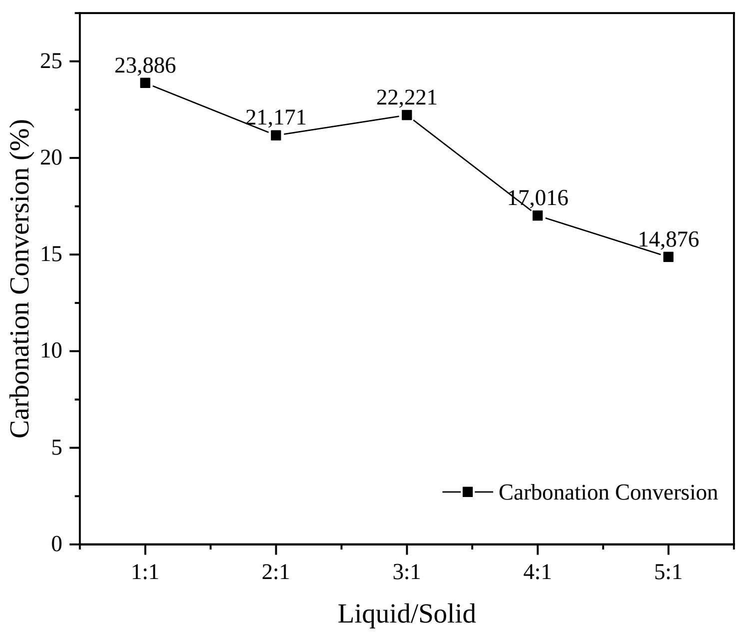


Figure 3. The effect of liquid/solid ratio on Red Mud Carbonation Conversion

Red mud carbonation was conducted with varying liquid/solid ratios (1:1, 2:1, 3:1, 4:1, 5:1) for 80 minutes. The results showed that a liquid/solid ratio of 1:1 provided the best carbonation efficiency of 23.886% and the highest capture capacity, with a sequestration rate of 5.5102 g CO_2/kg red mud (RM). In aqueous carbonation, the carbonation or carbonate formation reaction occurs in the water phase, meaning that the L/S (liquid/solid) ratio significantly impacts the diffusion of CO_2 into the water and the leaching of calcium ions. A low L/S ratio can inhibit the dissolution of calcium and CO_2 ions into the solution due to the thin water layer on the mineral surface. Conversely, a high L/S ratio can slow the migration of Ca^{2+} ions and hinder the rate of CO_2 diffusion. The reaction mechanism occurring in the water phase is as follows:

$CO_2 + H_2O \rightarrow H_2CO_3$
$H_2CO_3 \rightarrow H^+ + HCO_3^-$
$HCO_3^- \rightarrow 2H^+ + CO_3^{2-}$
$CaO + H_2O \rightarrow Ca(OH)_2$
$Ca(OH)_2 \rightarrow Ca^{2+} + OH^-$
$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$

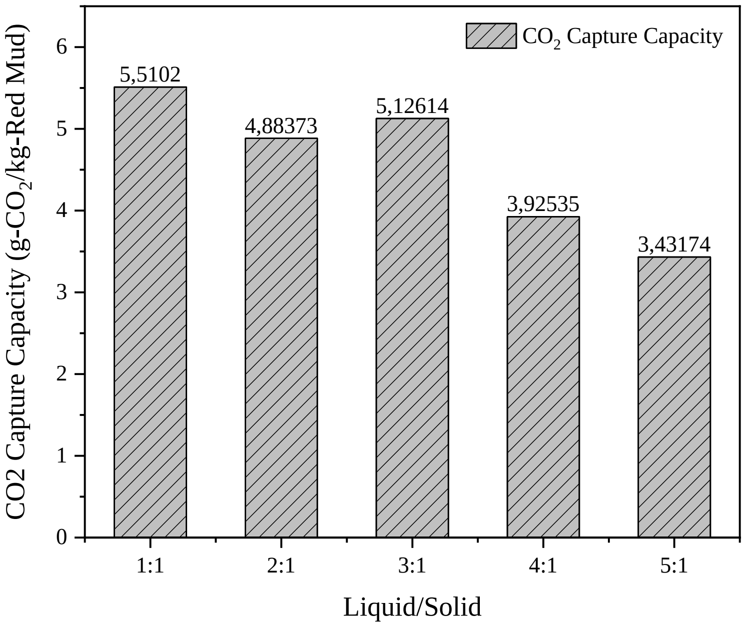


Figure 4. The effect of liquid/solid ratio on Red Mud CO_2 Capture Capacity

Based on Figures 3 and 4, as the L/S ratio increases, the ability of red mud to absorb CO_2 decreases. This is because water inhibits the diffusion of CO_2 gas molecules [7]

4. Conclusions

The pH decreased to near neutral, reaching 7.7 within 15 minutes after the carbonation process at both 25°C and 40°C. In the initial minutes, red mud reacts rapidly with CO2 gas when the dissolved CO2 is still free to react, neutralizing NaOH to form HCO3-, which causes a decrease in the pH of the red mud. The presence of water significantly affects the carbonation process; too much water inhibits the diffusion of CO2 gas molecules, while too little water hinders the dissolution of calcium and CO2 ions into the solution due to the thin water layer on the mineral surface. The optimal liquid-to-solid (L/S) ratio is 1:1, which results in a carbonation conversion and CO2 capture capacity of 23.886% and 5.5102 g CO2/kg-red mud, respectively. For every ton of alumina produced, 0.3–2.5 tons of red mud is generated. With the alumina production capacity from the Tayan mine's bauxite ore projected to reach 170,000 tons in 2024, red mud can absorb up to 1,032 tons of CO2 annually.

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References

1. Sahu, R. C., Patel, R. K., & Ray, B. C. (2010). Neutralization of red mud using CO2 sequestration cycle. *Journal of Hazardous Materials*, *179*(1–3), 28–34. https://doi.org/10.1016/j.jhazmat.2010.02.052
2. Silveira, N. C. G., Martins, M. L. F., Bezerra, A. C. S., & Araújo, F. G. S. (2021). Red mud from the aluminium industry: Production, characteristics, and alternative applications in construction materials—a review. In *Sustainability (Switzerland)* (Vol. 13, Issue 22). MDPI. https://doi.org/10.3390/su132212741
3. Rahmanihanzaki, M., & Hemmati, A. (2022). A review of mineral carbonation by alkaline solidwaste. In *International Journal of Greenhouse Gas Control* (Vol. 121). Elsevier Ltd. https://doi.org/10.1016/j.ijggc.2022.103798
4. Chen, T. L., Pei, S. L., & Chiang, P. C. (2020). Integrated leaching-carbonation kinetic model on CO2mineralization of alkaline solid wastes in a high-gravity rotating packed bed. *Reaction Chemistry and Engineering*, *5*(10), 1929–1938. https://doi.org/10.1039/d0re00239a
5. Zhang, Z., Zheng, K., Chen, L., & Yuan, Q. (2024). Review on accelerated carbonation of calcium-bearing minerals: Carbonation behaviors, reaction kinetics, and carbonation efficiency improvement. In *Journal of Building Engineering* (Vol. 86). Elsevier Ltd. https://doi.org/10.1016/j.jobe.2024.108826
6. Su, Z., Wang, D., Huang, X., Li, X., Yu, X., Huang, Y., & Feng, Q. (2020). Mechanism of CO 2 sequestration by high-alkaline red mud: conversion of katoite. In *Int. J. Global Warming* (Vol. 22, Issue 2). https://doi.org/10.1504/IJGW.2020.110293
7. Rushendra, T. D., Palanivelu, K., & Ramachandran, A. (2017). Sequestration of carbon dioxide by red mud through direct mineral carbonation at room temperature. In *Int. J. Global Warming* (Vol. 11, Issue 1). https://doi.org/10.1504/IJGW.2017.080988