BIS ENERGY AND ENGINEERING

Volume 2 2025 | DOI: 10.31603/biseeng.344
6th Borobudur International Symposium on Science and Technology (BIS-STE) 2024

UNIMMA PRESS
UNIVERSITAS MUHAMMADIYAH MAGELANG

Bauxite refinery residue neutralization using active wet carbonation technique

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Abstract

Bauxite refinery residue (red mud) is a solid by-product of the alumina refinery industry in which bauxite ore undergoes Bayer Process to produce alumina, which is then converted into aluminium. In fact, the amount of red mud (RM) is numerous, for each ton of alumina product yields 1 to 2 tons of RM. RM is a caustic material (pH 10-13) and carries valuable metals and minerals. Its disposal entangles intricate processes thus, conventional disposal practices comprise depositing it in open dams. The volume of RM continues to accumulate, and these acts possess the potential disaster to harm both environmental along with human health. Previous studies have show RM as environmental remedies, particularly for CO2 capture from flue gas. This study examines the RM originated from Indonesia to neutralize using active wet carbonation technique. The RM-cake-clay-form with 25.5% water content is transformed into a 40% solid content slurry then contacted using CO2 industrial grade at room temperature and atmospheric pressure at gas flowrate 5 L/min for 120 min. According to the study that has been conducted, CO2 showed its potential to neutralized the RM alkalinity from pH 11.25 to 7.44 and generate mineral-carbonate compounds with estimated sequestration capacity 1.424 g CO2/100 g RM from the obtained carbonated filtrate through bicarbonate and carbonate ion presence.

Keywords

Red mud, Carbonation, Indonesia, Carbon dioxide, Mineral carbonate Neutralization

Introduction

Aluminum is one of the most abundant elements in the Earth's crust and is primarily found in the form of bauxite. Obtained bauxite ore from mining will next transform into alumina during extraction process. Basically, there are several well-known extraction methods of alumina such as Bayer process, sintering process, and combined process, with 95% of plants use Bayer's process and the 5% use sintering or combination process [1]. Bayer's Process is involving addition of base solution at high temperature and pressure, the digestion process precipitates bauxite ore impurities in the form of slurry meanwhile the separated solution in form of sodium aluminate is further converted into alumina then transformed into aluminum through the Halt-Heroult process [2].

Published:
May 31, 2025

Selection and Peer-review under the responsibility of the 6th BIS-STE 2024 Committee

Separated slurry appearance is reddish-brown color due to the presence of iron oxide [3], well-known as red mud (RM). Red mud (RM) is commonly used as a synonym to represent bauxite refinery residue (BRR). RM is a solid by-product resulted from alumina production dominated by Fe_2O_3, SiO_2, Al_2O_3, and CaO [4]along with its heavy metal such as As, Cd, Cr, Pb and Hg [5]. RM presence in nature is abundant for a ton of alumina product resulted 1 to 2 tons of discharged RM [6]. RM categorized as alkaline material with pH range between 10-13, with 90% of its particle size under 0.75 μm and its specific surface area ranged between 10 to 25 m^2/g [7]. Both physical and chemical properties of RM possess serious environmental threat and potential impact to ecology especially living things in local or regional scale of its impact.

Rapid increasing of anthropogenic activity pushed current carbon dioxide concentration in earth's atmosphere into higher number. Based on Data NOAA, measured at the Mauna Loa Observatory by NASA 2024's carbon dioxide concentration in the atmosphere reached 425 ppm compared to 2019's concentration reported by IPCC year book 2023 concentration of carbon dioxide was 410 ppm. The International Aluminum Institute reported 5.6% annual growth in global power consumption from 301.7 TWh in 2000 to 611.9 TWh in 2013, accounting 3.5% of global electricity consumption [8], and aluminum production industry contribute to greenhouse gas emissions (Ho et al., 2019). There are several ways to prevent further carbon dioxide release one of them is capturing CO2 [9]. Carbon capture and storage techniques involve capturing CO_2, separating CO_2 from other impurities, transferring and isolating, some of technology uses geological formation, ocean storage, or mineral sequestration[10]. Among those technologies, mineral sequestration tends to be more stable and relatively easy to apply to form carbonate compound [11].

RM has been investigated from previous studies to its sequestration potential of CO_2 gas and CO_2 neutralization ability of RM high alkalinity in form of slurry with various liquid to solid ratio and various time. Aqueous red mud suspension at liquid-to-solid ratio of 10 kg/kg has a carbonation capacity of 4 g of CO_2/100 g red mud at ambient conditions with a 15% volume CO_2/N_2 mixture at flowrate 5 mL/min under agitation 200 rpm using concentrated RM from Canada [12]. Red mud from Renukoot India exposed by CO_2 atmosphere at pressure 3.5 barr for 3.5 hours with liquid-to-solid ratio 0.35 obtained carbonation capacity 5.3 g of CO_2/ 100 g RM [13]. Neutralization of RM originated from Ireland using various of reagent with solid concentration of red mud slurry 55% wt for dry basis RM [14]. Red mud originated from southwest of Korea investigated neutralization ability using carbon dioxide added with flue gas desulphurization gypsum and $CaCl_2$ solution at flowrate 1 L/min using 200 rpm agitation for 24 hours carbonation time [15]. Optimal ratio of liquid to solid 3:1 of Red mud originated from Shandong China with gas flowrate 5 L/min at 10 minutes reaction time carbonation capacity 14.11 to 16.72 g CO_2/100 g sintering RM using active wet grinding carbonation technique [16] and many more.

Based on previous studies have been conducted RM obtained from various places from all over the world, but till this study conducted no such studies show RM originated from Indonesia ability to sequestrate carbon dioxide without any laboratory oven dried to expel excess moisture in sample. Majority RM studies in Indonesia such as electro kinetic of RM using 30- and 45-volts direct current with highest removal efficiency of sodium ion 98.01% around anode with 45 volts current [17]. Naturally dried RM separated by magnetically and the magnetically sand composition consists of ferrosilite, hematite, and ilmenite [18]. And RM synthesis based SiO2 with various NaOH concentration and optimized at NaOH concentration 7.5 M for 4 hours extraction time [19].

In this study objective is to exercise carbon dioxide neutralization ability to neutralize high alkalinity of RM and its potential to form stable mineral carbonate as a carbon sequestration. The selection of the sample preparation method without laboratory drying using an oven aims to provide an overview if red mud is directly utilized in the field, and reduce emission releases due to RM drying in real practice, besides to see whether there is a significant difference in the ability to neutralize and mineral carbonate formation during the process in RM without a drying process. Typically, deposited RM as slurries contain solid 15 to 40% [20]. This attempt can carry on an actual picture and contribute to the development of research on the utilization of RM in Indonesia as a carbon sequestration through wet carbonation technique in facing the challenges of red mud abundance with various RM form in nature and mitigation further carbon release on transition to renewable energy.

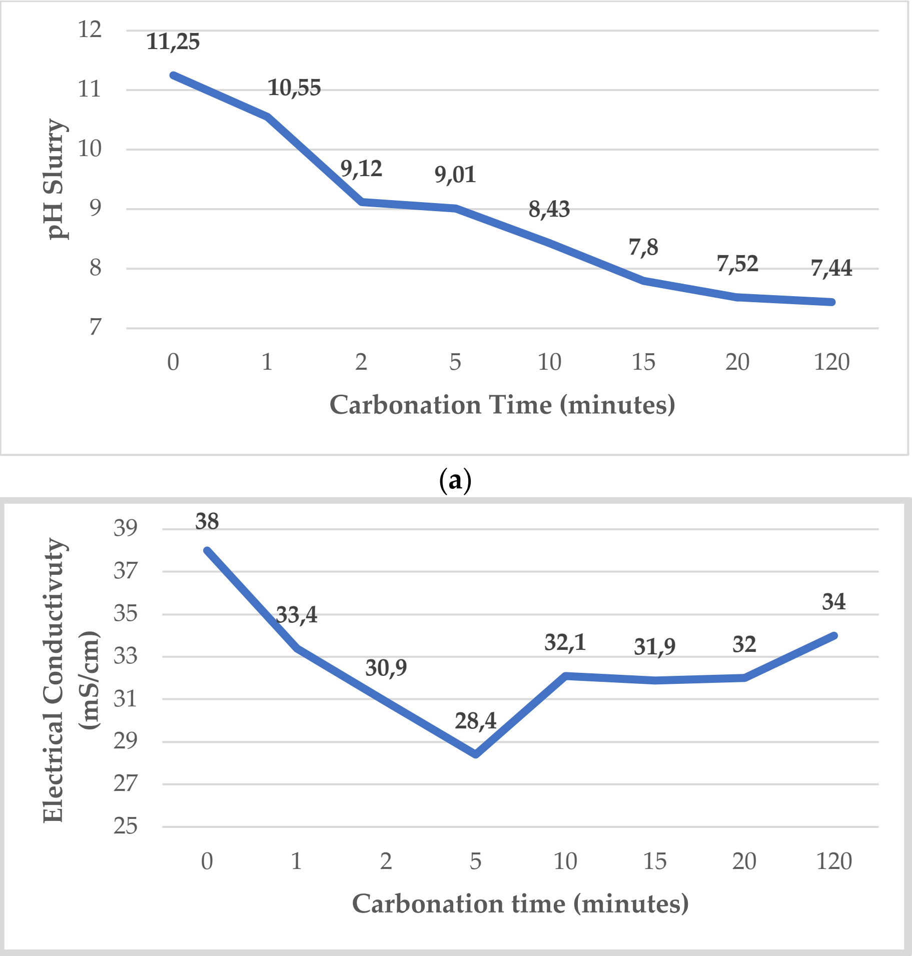
Method

Fresh red mud cake originated from Tambang Tayan, West Kalimantan, Indonesia. Its water content was 25.5%, initial pH value of RM 10.6 and initial electrical conductivity of RM slurry of 40% solid content was 34 mS/cm. Initial characterization chemical compositions of RM consist of Fe, Al, Si, Ca, Ti, and Zr from XRF analysis using dried RM sample. Carbon dioxide industrial grade with 99.9% concentration, laboratory distilled water with electrical conductivity value 2μS/cm and TDS under 2 ppm, vacuum conical flask 250 mL, flowmeter, titration Burette, Buchner funnel, and filter paper. Instrumentation used on this study were Smart sensor pH meter PH818T with measuring range pH 0.0 – 14.0 accuracy and resolution pH 0.1 and temperature range from 0-50°C to measure direct neutralization effect, Electrical Conductivity meter portable with resolution 1 μs/cm with accuracy 2% with calibration point 1413 μS/cm XRD for both fresh RM and carbonated RM using Bruker AXS GmbH operation mode 40 kV and 25 mA at angle 2θ at default angle reading 10°~80°, XRF for fresh RM oxide identification.

A slurry containing 40% solids was made from fresh RM with a water content of 25.5% (611 g/L). The initial pH for the slurry was 11.09 then the slurry was stirring for 20 hours using magnetic stirrer with 100-150 rpm this process aimed to make the metal ion enter aqueous phase before carbonation process. This experiment is designed to determine how CO_2 gas intensity affects the RM neutralization process at flowrate 5 L/min represent flowrate emission gas sampling at stack and also wants to assess the effectiveness of the neutralization process at 40% solid content slurry for 120 minutes neutralization process. The selection of 40% solid content is due to the discharged RM slurry in the industry ranging from 10-40% solid content. This study aims to see the effectiveness of red mud neutralization using carbon dioxide at the highest solid content range. To assess the neutralization capacity of CO_2 gas for caustic RM slurry, we selected durations of 0, 1, 2, 10, 15, 20, and 120 minutes for observing the decreasing of pH value. After neutralization process carbonated RM slurry was being filtrated using vacuum filtration to separate filtrate and residue, next the filtrate was being analysed using volumetric titration 0.1 N HCl with phenolphthalein indicator for carbonate ion investigation and methyl red for bicarbonate ion titration. On the other side residue obtained from the process was analysed with XRD.

Results and Discussion

Results



(a)

(b)

Figure 1. Effect of CO2 gas neutralization ability: (a) pH decreasing of caustic RM during carbonation process; (b) Electrical Conductivity of RM during carbonation process

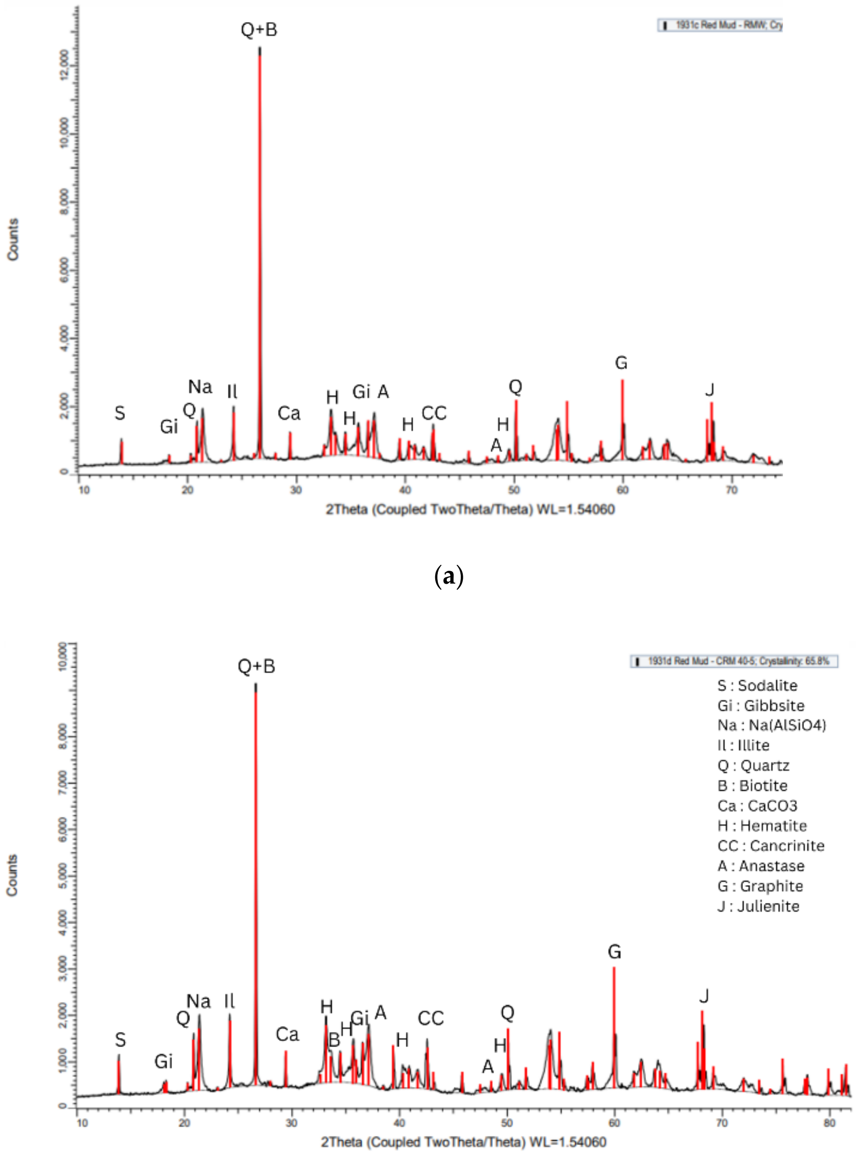
From the results of laboratory experimental that has been carried out at room temperature and also atmospheric pressure, resulted following data stated in result and also followed by discussion for explaining the obtained data. There were data graph of neutralization ability of carbon dioxide to neutralize high pH slurry of red mud and XRD pattern to identify mineral phase consists in red mud from initial fresh red mud before the process and neutralized red mud after the process. In result discussion also consist of obtained carbon sequestration capacity from bicarbonate and carbonate ions identification. The discussion was about the potential reaction mechanism happening during the process of neutralization.

Initial measured pH of the slurry was 11.09 and electrical conductivity (EC) was 34 mS/cm then the slurry was stirred using mild agitation at 100-150 rpm for 20 hours. Before the slurry was bubbled using carbon dioxide pH value and EC was being measured resulted increasing pH and EC value to 11.25 and 38 mS/cm (Figure 1). There was 0.16 point of pH and 4 mS/cm for EC. During neutralization process there was significant pH decreasing at first 20 minutes of neutralization process. From pH value 11.25 to 7.52 and from first 20 minutes to the end of the process pH decrease only 0.08 point quite less significant or tend to be stable for least 100 minutes. But from this significantly decreasing of pH for 120 minutes process showed that carbon dioxide has ability to neutralize high alkalinity of RM. Meanwhile at Fig 1b there was different behavior of electrical conductivity graph, EC value was showing sharp decrease of EC value from 38 to 28.4 mS/cm at first 5 minutes, after that EC value rebound to 32.1 mS/cm at 10 minutes and stable until 20 minutes of the process. At the end of the process EC value measured at 34 mS/cm, at this point showed that the value rebound to 34 mS/cm during the process but less than initial measured EC value of the slurry before neutralization process.

From carbonate and bicarbonate analysis using volumetric titration 0.1 N HCl with indicator PP for indicating carbonate ions and MO indicates bicarbonate ions obtain concentration of carbonate ion of the sample filtrate was 0.00965 M and bicarbonate ion concentration was 0.482521 M, from concentrations we could obtain mol of each carbonate ion and bicarbonate ion respectively 0.24 mmol and 12.05 mmol. Estimated CO2 sequestration capacity was 1.424 g CO_2/100 g RM.

XRD analysis angle 2θ 5°~80° both from fresh RM and Neutralized RM showed at Figure 2 , from the peaks identification using Profex.org software there are several mineral phase such as sodalite ($Na_8(Al_6Si_6O_{24})Cl_2$) 13.9° *d* value 6.35), Gibbsite ($Al(OH)_3$) (18,9° *d* value 4,84), sodium aluminum silicate ($Na(AlSiO_4)$) (21.4° *d* value 4.25), Illite ($K_{0.6}(H_3O)_{0.4}Al_{1.3}Mg_{0.3}Fe^{2+}{}_{0,1}Si_{3.5}O_{10}(OH)_2.(H_2O)$) (24,2° d value 3,66), Quartz (SiO_2) (20.8°,26.6°,50.1° *d* value 4.25, 3.34, 1.81 respectively) Biotite($KMg_{2.5}Fe^{2+}{}_{0.5}AlSi_3O_{10}(OH)_{1.75}F_{0.25}$), calcite ($CaCO_3$) (29.4° *d* value 3.03), Hematite (Fe_3O_3) (23.08°, 33.18°, 35.71°, 40.9°, 49.5°, 53.9°, 54.05°), Cancrinite ($Na_6Ca_2[(CO_3)_2.Al_6Si_6O_{24}].2H_2O$) (43.14° *d* value 2.09), Anatase (TiO_2) (37.66°, 48.5°, Graphite (C) (54.6° *d* value 1.67), and Julienite ($Na_2CO(SCN)_4.8H_2O$). There is no significant different of mineral phase between fresh RM and neutralized RM, but the intensity of some mineral phase at neutralized RM is higher than fresh RM. Sodalite relative intensity 5.40% to 8.50%, sodium aluminum silicate relative intensity 10.80%

before neutralization to 15.90% after the process, hematite relative intensity before neutralization was 9.30% to 14.50%, and the most significant increasing of relative intensity at graphite mineral phase from 19.80% in fresh RM to 30.80% in neutralized RM.



(**a**)

(**b**)

Figure 2. XRD Mineral phase analysis: (a) Fresh RM; (b) Neutralized RM

Create a Discussion

pH increased during stirring at mild agitation resulted from boost of alkaline concentration during water leaching. The most soluble alkali in this process was sodium contained in RM [21]. As it shown on Equation 1 and 2

$$Na_6[AlSiO_4]_6.2NaOH_{(s)} + H_2O_{(l)} \leftrightarrow Na_6[AlSiO_4]_{6(s)} + 2NaOH_{(aq)} + H_2O_{(l)} \quad (1)$$

$$2NaOH_{(aq)} + H_2O_{(l)} \rightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} + H_2O_{(aq)} \qquad (2)$$

The reaction mechanism from this study is similar to the reaction mechanism that occurs at CO_2 absorption in NaOH aqueous solution. Firstly, Na^+ and OH^- occurs ionization in water and performed as a powerful alkaline, as shown in (Eq 2). The gaseous CO_2 is injected into a slurry that contains the aqueous solution.

$$CO_{2(g)} \rightarrow CO_{2(aq)} \qquad (3)$$

$$CO_{2(aq)} + OH^-_{(aq)} \leftrightarrow HCO_3^-{}_{(aq)} \qquad (4)$$

$$HCO_3^-{}_{(aq)} + OH^-_{(aq)} \leftrightarrow H_2O_{(l)} + CO_3^{2-}{}_{(aq)} \qquad (5)$$

However, Eq 4 is a second-order reaction and it can be considered a pseudo-first-order reaction because the CO_2 concentration injected into aqueous phase is constant. Eq 4 and Eq 5 are reversible reactions with high-speed rates at the high pH range. Eq 5 occurs immediately after Eq 4. Aqueous CO_2 does not exist in the solution during the overall reaction because it immediately reacts with free ion OH^-. Once aqueous CO_2 is formed in the solution, it is instantaneously reacted, as represented in Eq 4 and Eq 5. Carbonate ion is dominant in early reactions because the solution has very high alkalinity, which further increases the carbonate ion concentration related to the formation of bicarbonate. Ion hydroxide is rapidly decreasing, in line with the decreased pH value of the slurry during the initial reaction period [22]. When carbonate ion concentration increased, this carbonate ion would interact with metal cations available in aqueous phase to form carbonate minerals [23].

$$CO_3^{2-}{}_{(aq)} + M^+/M^{2+}{}_{(aq)} \leftrightarrow MCO_{3(s)}/M_2CO_{3(aq)} \qquad (6)$$

In an experiment conducted by [22], to explain typical CO_2 absorption according to NaOH concentration, the initial pH was 10.91 after the carbonation pH decreased to 7.7. The carbonation process initiated, a significant amount of OH^- was utilized to produce CO_3^{2-} resulting pH decreasing and EC value was also significantly reduced. The decreasing EC value indicates the reaction was primarily conducted for highest CO_2 absorption with highest reaction rate.

$$2NaOH_{(aq)} + CO_{2(aq)} \leftrightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \qquad (7)$$

Conclusion

High alkalinity of RM slurry with solid content 40% can be neutralized by CO2 gas through wet carbonation technique using 5 L/min gas flowrate for 120 minutes. First 20 minutes neutralization process decrease significantly and quite stable until the process ended.

XRD peak pattern showed some increasing peak after neutralization process such as graphite, NaAlSiO4, hematite, cancrinite, showed there were precipitate carbonate mineral phase during the process. The biggest peak increasing was graphite mineral phase from 19.8% at fresh red mud to 30.8% at neutralized red mud. Through carbonate and bicarbonate ions from the filtrate obtained data carbon sequestration capacity was 1.424 g CO_2/100 g RM

Acknowledgement

The biggest appreciation would be given to INSPIRASI Funding and other financial support that employed for this study. The authors also much obliged to everyone that cannot be mentioned one by one for providing knowledge, support, and also raw material of this study.

References

[1] P. S. Reddy *et al.*, "Properties and Assessment of Applications of Red Mud (Bauxite Residue): Current Status and Research Needs," Mar. 01, 2021, *Springer Science and Business Media B.V.* doi: 10.1007/s12649-020-01089-z.
[2] S. Agrawal, V. Rayapudi, and N. Dhawan, "Extraction of Iron values from Red mud," 2018. [Online]. Available: www.sciencedirect.comwww.materialstoday.com/proceedings2214-7853
[3] M. A. Khairul, J. Zanganeh, and B. Moghtaderi, "The composition, recycling and utilisation of Bayer red mud," *Resour Conserv Recycl*, vol. 141, no. September 2018, pp. 483–498, 2019, doi: 10.1016/j.resconrec.2018.11.006.
[4] Z. X. Chen, N. T. Zhang, S. R. Yan, J. Fish, and S. H. Chu, "CO2 mineralization into waste-valorized lightweight artificial aggregate," *Constr Build Mater*, vol. 409, Dec. 2023, doi: 10.1016/j.conbuildmat.2023.133861.
[5] B. Ozden, C. Brennan, and S. Landsberger, "Investigation of bauxite residue (red mud) in terms of its environmental risk," *J Radioanal Nucl Chem*, vol. 319, no. 1, pp. 339–346, 2019, doi: 10.1007/s10967-018-6355-6.
[6] W. Cui *et al.*, "Current research status and emerging trends in utilization of red mud resources: A study based on bibliometric network analysis," *Constr Build Mater*, vol. 442, no. August 2023, p. 137605, 2024, doi: 10.1016/j.conbuildmat.2024.137605.
[7] M. Taneez and C. Hurel, "A review on the potential uses of red mud as amendment for pollution control in environmental media," Aug. 01, 2019, *Springer Verlag*. doi: 10.1007/s11356-019-05576-2.
[8] H. Hao, Y. Geng, and W. Hang, "GHG emissions from primary aluminum production in China: Regional disparity and policy implications," *Appl Energy*, vol. 166, no. 800, pp. 264–272, 2016, doi: 10.1016/j.apenergy.2015.05.056.
[9] G. Leonzio, P. U. Foscolo, E. Zondervan, and I. D. L. Bogle, "Scenario Analysis of Carbon Capture, Utilization (Particularly Producing Methane and Methanol), and Storage (CCUS) Systems," *Ind Eng Chem Res*, vol. 59, no. 15, pp. 6961–6976, Apr. 2020, doi: 10.1021/acs.iecr.9b05428.
[10] K. Kashefi, A. Pardakhti, M. Shafiepour, and A. Hemmati, "Process optimization for integrated mineralization of carbon dioxide and metal recovery of red mud," *J Environ Chem Eng*, vol. 8, no. 2, Apr. 2020, doi: 10.1016/j.jece.2019.103638.
[11] F. Abdul, A. Iizuka, H. J. Ho, K. Adachi, and E. Shibata, "Potential of major by-products from non-ferrous metal industries for CO2 emission reduction by mineral carbonation: a review," Jul. 01, 2023, *Springer Science and Business Media Deutschland GmbH*. doi: 10.1007/s11356-023-27898-y.
[12] D. Bonenfant *et al.*, "CO2 sequestration by aqueous red mud carbonation at ambient pressure and temperature," *Ind Eng Chem Res*, vol. 47, no. 20, pp. 7617–7622, Oct. 2008, doi: 10.1021/ie7017228.
[13] V. S. Yadav, M. Prasad, J. Khan, S. S. Amritphale, M. Singh, and C. B. Raju, "Sequestration of carbon dioxide (CO2) using red mud," *J Hazard Mater*, vol. 176, no. 1–3, pp. 1044–1050, Apr. 2010, doi: 10.1016/j.jhazmat.2009.11.146.
[14] L. J. Kirwan, A. Hartshorn, J. B. McMonagle, L. Fleming, and D. Funnell, "Chemistry of bauxite residue neutralisation and aspects to implementation," *Int J Miner Process*, vol. 119, pp. 40–50, 2013, doi: 10.1016/j.minpro.2013.01.001.
[15] Y. S. Han, S. Ji, P. K. Lee, and C. Oh, "Bauxite residue neutralization with simultaneous mineral carbonation using atmospheric CO2," *J Hazard Mater*, vol. 326, pp. 87–93, Mar. 2017, doi: 10.1016/j.jhazmat.2016.12.020.

[16] J. Yang *et al.*, "Rapid wet grinding carbonation of sintering red mud for highly efficient CO2 sequestration and Cr solidification," *Chemical Engineering Journal*, vol. 488, May 2024, doi: 10.1016/j.cej.2024.151134.
[17] A. J. Sipayung, D. T. Suryaningtyas, and B. Sumawinata, "Electrokinetic of red mud," *IOP Conf Ser Earth Environ Sci*, vol. 393, no. 1, 2019, doi: 10.1088/1755-1315/393/1/012090.
[18] Rossalina W, Zaharah T. A, and Silalahi I. H, "Komposisi Unsur dan Karakterisasi Mineral Magnetik dalam Red Mud, Residu Bauksit di PT Indonesia Chemical Alumina (ICA) Kalimantan Barat," *Indonesian Journal of Pure and Applied Chemistry*, vol. 4, no. 3, pp. 139–144, 2021, [Online]. Available: https://jurnal.untan.ac.id/index.php/IJoPAC/article/view/49660/pdf
[19] B. Dwi Meilani *et al.*, "Indonesian Journal of Chemical Science Synthesis of Red Mud-Based SiO 2 with Various NaOH Concentration and Extraction Times," *J. Chem. Sci*, vol. 12, no. 3, 2023, [Online]. Available: http://journal.unnes.ac.id/sju/index.php/ijcs
[20] S. K. Rout, T. Sahoo, and S. K. Das, "Design of tailing dam using red mud," *Central European Journal of Engineering*, vol. 3, no. 2, pp. 316–328, 2013, doi: 10.2478/s13531-012-0056-7.
[21] X. fei LI *et al.*, "Leaching optimization and dissolution behavior of alkaline anions in bauxite residue," *Transactions of Nonferrous Metals Society of China (English Edition)*, vol. 28, no. 6, pp. 1248–1255, Jun. 2018, doi: 10.1016/S1003-6326(18)64763-6.
[22] M. Yoo, S. J. Han, and J. H. Wee, "Carbon dioxide capture capacity of sodium hydroxide aqueous solution," *J Environ Manage*, vol. 114, pp. 512–519, 2013, doi: 10.1016/j.jenvman.2012.10.061.
[23] C. Si, Y. Ma, and C. Lin, "Red mud as a carbon sink: Variability, affecting factors and environmental significance," *J Hazard Mater*, vol. 244–245, pp. 54–59, 2013, doi: 10.1016/j.jhazmat.2012.11.024.