ASEAN Engineering Journal

Full Paper

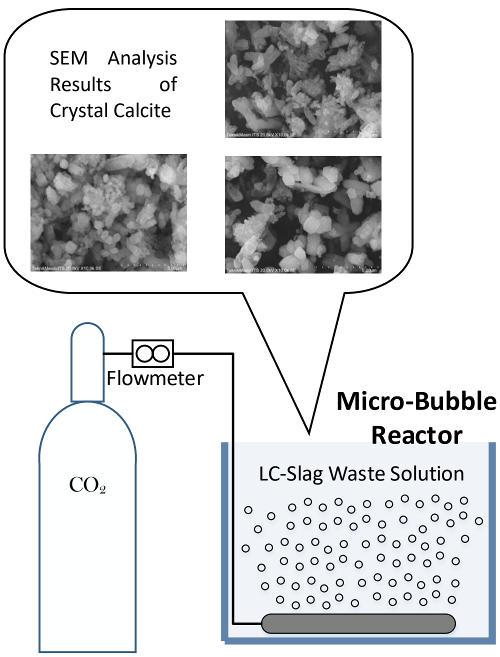
SYNTHESIS OF PRECIPITATED CALCIUM CARBONATE IN THE FORM OF CALCITE CRYSTALS AS A VALORIZATION OF LIME CARBIDE SLAG WASTE

Article history
Received
05 October 2023
Received in revised form
04 December 2023
Accepted
01 January 2024
Published online
31 August 2024

Wahyu Tri Amliah Provito, Fadlilatul Taufany*, Ali Altway

Chemical Engineering Department, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, 60117, Surabaya, East Java, Indonesia

*Corresponding author
f_taufany@chem-eng.its.ac.id



Abstract

The presence of high level of calcium oxide (CaO) has been detected in lime carbide (LC) slag waste generated form the acetylene gas industry. There is untapped potential for the valorization of LC-slag waste, where the calcium oxide content can be converted into Precipitated Calcium Carbonate (PCC/$CaCO_3$) which is valuable and can contribute to carbon dioxide sequestration. Calcium carbonate has unique advantages as a carrier, but some critical problems need to be addressed, such as low productivity, disordered structure, and weak adsorption ability. In this study, the desired type of crystal is calcite which has the most stable characteristics from the other types of crystals. Micro-bubble reactor is used as a method of dispersing CO_2 in converting CaO to PCC/$CaCO_3$. This method has the advantage of being able to maintain CO2 gas bubbles longer in solution so that the reaction time that occurs can also be optimize. The LC-Slag valorization process was carried out by varying the LC-slag concentration between 3-7% w/w and the reaction time between 15 - 35 minutes. The dispersion of CO_2 gas is fixed at a flow rate of 2.5 L/m. From the yield, it can be seen that the longer the reaction time, the yield of PCC/$CaCO_3$ produced is also greater. At 35 minute reaction time and concentration LC-Slag Waste varied 3, 5, and 7% w/w, the produced yields were 89.44, 95.00, and 93.76%, respectively. This is evidenced by the results of SEM and XRD analysis. In the future, this treatment method is expected to provide more insight and guidance for the valorization of LC-slag waste and CO_2 mineralization in the acetylene gas industry.

Keywords: Precipitated Calcium Carbonate, Micro-bubble Reactor, Acetylene Waste, Calcite Crystal, CO_2 gas.

1.0 INTRODUCTION

Acetylene is an important hydrocarbon compound and has a very broad function in today's industrial world. Acetylene is widely used in the world of welding (oxy-acetylene welding) and as lamp fuel for underground work [1]. Apart from that, the latest is the use of acetylene as a raw material for ethylene which will later be used in making various kinds of polyethylene plastic [2]. There are several known methods for producing acetylene gas, including the dry process, arc process and partial oxide process from natural gas. Of the several processes for making acetylene, the dry process is made from calcium carbide as a raw material, which has high effectiveness and efficiency, namely with a yield of 93-95%, cheap manufacturing costs and a simple process [3].

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

However, in this carbide process the problem that arises is the presence of waste or by-products in the form of calcium hydroxide or $Ca(OH)_2$ or also commonly called carbide lime [4]. Carbide lime, which is a by-product of making acetylene gas, is a blackish-white or grayish solid. Initially, carbide waste was produced in the form of colloids (semi-liquid) because this gas contains gas and water. After 3-7 days, the gas slowly evaporates and the lime water from the carbide waste begins to dry, becoming brittle lumps that are easily crushed and can become powder [5]. The largest compound contained in carbide waste or acetylene gas industrial waste is CaO, namely 59.7%. With this high Ca or lime content, it will cause the soil to become barren or arid if it is simply thrown into the environment [6]. What can be done to process carbide lime waste is to use it as raw material to produce products that have added value. In this case it can be used for the production of precipitated calcium carbonate (PCC) [7].

PCC is synthetic calcium carbonate ($CaCO_3$) produced from a chemical reaction. In nature, calcium carbonate comes from limestone rock. PCC is more popular for industrial processes because it contains less impurities compared to calcium carbonate from processed limestone [8]. In addition, PCC has added value because its morphology, particle size, particle size distribution and brightness can be adjusted to suit industrial needs. PCC is be widely used in industry as a filler in paper, rubber and polymers and as an additive in paint, toothpaste, cosmetics, detergents, pharmaceutical and food products, as well as other uses [9]. Figure 1 shows the application of PCC in industry.

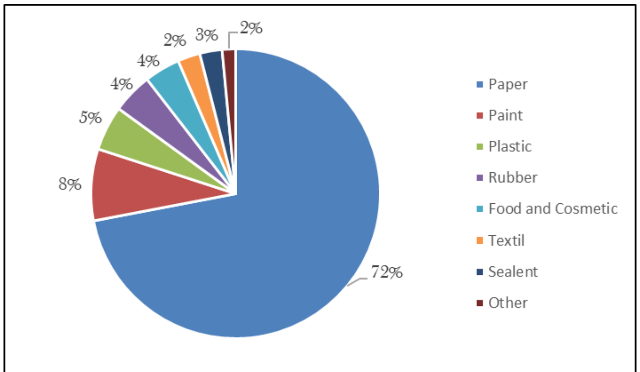


Figure 1 Application of PCC in industry

Calcium carbonate is polymorphic, meaning it can crystallize into different but chemically identical crystal forms. This can form calcite (triagonal-rhombohedral), aragonite (orthorhombic) and vaterite (hexagonal). Calcite is the most thermodynamically stable phase. Aragonite is metastable, as vaterite is the least stable of the three polymorphs. Of the three polymorphs of calcium carbonate, only calcite and aragonite are used commercially. Typical calcite crystal shapes sought are rhombohedral, prismatic and scalenohedral, while aragonite in a needle-like shape is usually desired. The formation behaviour of each polymorph is influenced by several synthesis factors such as pH, temperature, concentration, ratio of carbonate and calcium ions, additives, stirring, reaction time, etc [10].

PCC can be synthesized via two methods, namely by precipitation from aqueous solution (liquid-liquid and solid-liquid) and also by carbonation from the lime process (liquid-gas and solid-liquid-gas) [11]. Commercially, the carbonation of limestone process focuses on the use of slaked lime which consists of calcination to obtain lime (CaO), hydration of CaO to obtain $Ca(OH)_2$, and CO_2 gas bubbling to obtain precipitated $CaCO_3$ [12]. This carbonation process is profitable due to the low cost of the raw materials used and the ease of handling procedures. However, the mass transfer between $Ca(OH)_2$ and CO_2 gas to produce calcium carbonate takes a long time and hence this is the focus of current research to produce effective and efficient PCC. Seeing the importance of PCC in the industrial world and to reduce industrial waste, this research aims to utilize waste from the acetylene gas industry to produce PCC using the microbubble CO_2 gas bubbling method [13]. The type of PCC that will be produced is PCC with the polymorph calcite type.

2.0 METHODOLOGY

2.1 Material

The LC-slag waste sample used in this study was collected from PT. Dwigasindo Abadi in Bekasi, West Java, Indonesia. The chemical composition of LC-Slag Waste is descripted Table 1. Carbon dioxide gas with a high purity (99.9%) was purchased from PT. Sumber Gas in Sidoarjo, East Java, Indonesia. Aquadest (pH: 6.7) was used in each experiment.

Table 1 Composition of LC-Slag Waste from PT. Dwigasindo Abadi

Parameter	Unit	Result
Iron Trioxide (Fe_2O_3)	%	0.61
Aluminium Trioxide (Al_2O_3)	%	1.25
Calcium Oxide (CaO)	%	56.65
Calcium Carbonate ($CaCO_3$)	%	26.77
Magnesium Oxide (MgO)	%	0.1
Silicon Dioxide (SiO_2)	%	6.29
Moisture Content (MS)	%, AR	8.33

2.2 Synthesis of PCC from LC-Slag Waste

Precipitated Calcium Carbonate (PCC) was synthesized using the carbonation method by reacting LC slag waste ($Ca(OH)_2$) with CO_2 gas (99.9%). Milk of Lime (MOL) solution was made by dissolving LC slag waste with concentrated distilled water (3, 5, and 7%w/w) in a beaker and measuring the pH with a pH meter. Then the MOL solution is heated using a heater to a temperature of 45 ^oC [11]. The solution that has reached the desired temperature is then put into a micro-bubble type carbonation reactor (Figure 2) and flowing with CO_2 gas. The carbonation process was carried out for the specified time (15, 25, and 35 minutes). Next, filtration was carried out using Whatmann No.5. Then the filtrate obtained is dried in an oven and cooled in a desiccator. The resulting filtrate is PCC with a physical condition in the form of white powder [14]. The particles were dried by air to remove the remaining moisture content. The calcium carbonate nanoparticles were weighed to calculate the yield of the product based on Eqn 1 below.

$$\text{Yield of the product} = \frac{\text{mass of product}}{\text{mass of feed}} \times 100\% \quad \text{(Eqn. 1)}$$

2.3 Characteristic Test

X-Ray Diffraction (XRD), is a technique used to identify the molecular structure of a crystal, where the atoms contained in the crystal will be shot by X rays so that they are diffracted in certain directions. X-ray diffraction techniques can be used for qualitative analysis because each element or compound has a certain diffraction pattern. Thus, if the diffraction pattern of an element or compound is known, the element or compound can be identified. The wavelength to be used is 2θ and is from 2° to 14° with an interval of 0.02° [15].

.

Scanning Electron Microscopy (SEM) testing is used to determine the surface morphology of materials. Material characterization using SEM is used to see the surface topographic structure, grain size, structural defects, and pollution composition of a material [16]. SEM results in the form of morphological images present the surface shape of the material with various indentations and protrusions. SEM analysis was carried out at the ITS Department of Mechanical Engineering using the SEM INSPECT S50 tool.

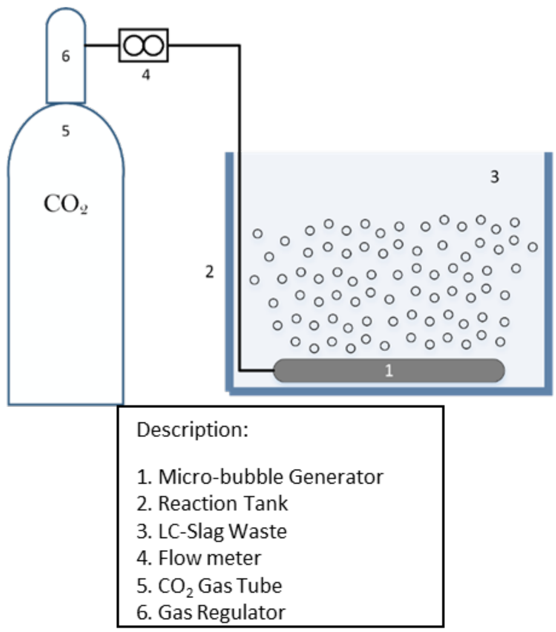


Figure 2 Micro-Bubble Reactor Schematic

3.0 RESULTS AND DISCUSSION

3.1 PCC Yield

Yield analysis is carried out by comparing the amount of product with the amount of raw materials used. The results of the PCC yield analysis can be seen in the Figure 3.

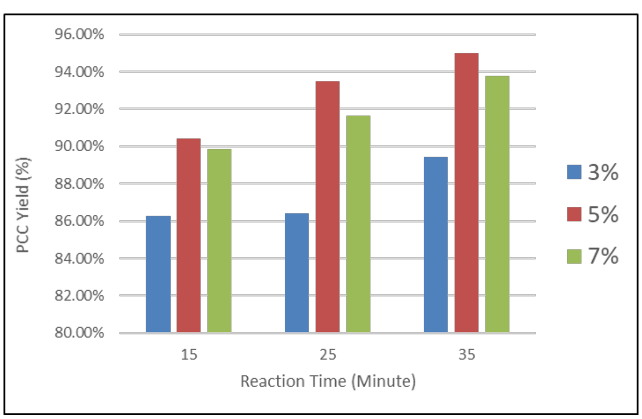


Figure 3 Analysis of PCC Yield at 3%, 5%, and 7% LC-Slag Waste Concentration

It can be seen from Figure 3 that the PCC synthesis with a CO_2 gas flow rate of 2.5 L/m has the most effective condition at 5% LC-Slag Waste concentration and 35-minute reaction time. This can be concluded because at each reaction time the largest yield is always at a concentration of 5%, which is equal to 90.40; 93.47; and 95.00% at reaction times of 15, 25 and 35 minutes, respectively. Apart from that, it can also be seen that the longer the carbonation reaction time, the PCC yield will also increase. This happens because the longer the reaction time, the greater the conversion from $Ca(OH)_2$ to PCC/$CaCO_3$. However, the selection of the best reaction time in industrial set-up must also consider cost factors [17].

3.2 XRD Analysis

The phase structure of the prepared product calcium carbonate particles was investigated by XRD pattern. Figure 4 shows the XRD diagram of calcium carbonate under the conditions of 99.9% CO_2 gas concentration, and 2.5 L.min−1 flow gas CO_2.

In this XRD analysis, it can be seen that the peaks of the PCC product overlap with the peaks of PCC in the form of calcite crystals. It can be seen that the most dominant peak of the product is at an angle of 29.89 [18]. This peak is a typical peak of calcite crystals. In this PCC synthesis, not only the calcite type of PCC polymorph is produced but also a small amount of aragonite is produced. Overall, in this research using a simple synthesis method from LC slag waste, 85-90% PCC can be produced with calcite [19].

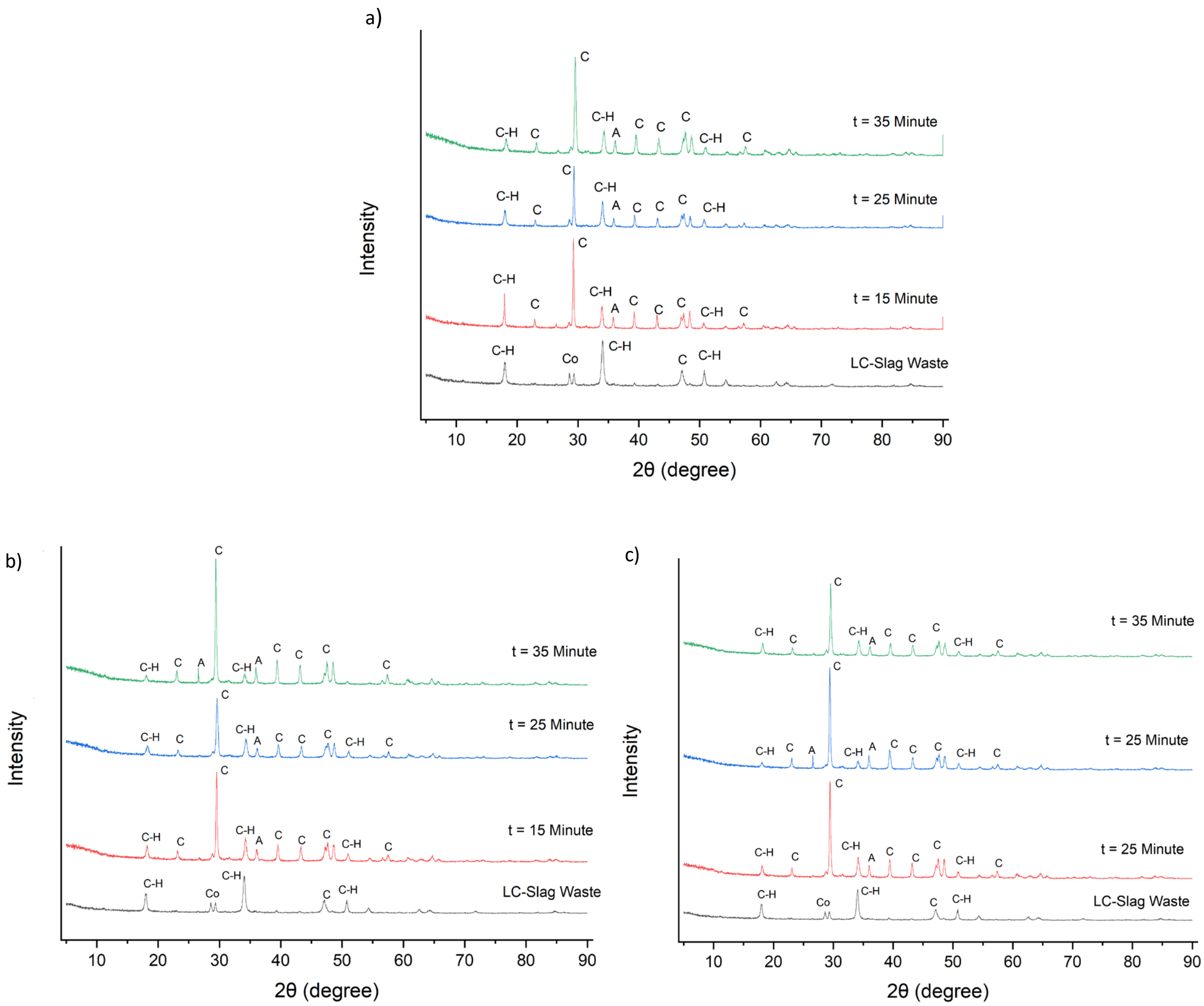


Figure 4 XRD Analysis Results of PCC at Concentration of LC-Slag Waste (a) 3%; (b) 5%; and (c) 7% (C=Calcite; A=Aragonite; C-H=Calcium Hydroxide; Co=Coesite)

SEM Analysis

From the results it can be seen that the crystal form of LC-Slag Waste experiences significant changes due to the carbonation reaction by CO_2 gas which is distributed using micro-bubble.[20]. Figure 5 presents SEM results for LC-slag waste, and the crystal form results can be categorized as calcite crystals, as showed in Figure 6. It can be seen that the longer the carbonation reaction takes, the smaller the particle size will be [21]

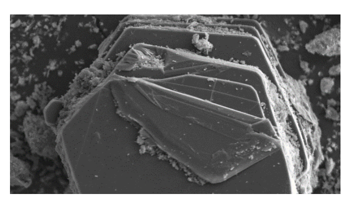


Figure 5 SEM Analysis from LC-Slag Waste

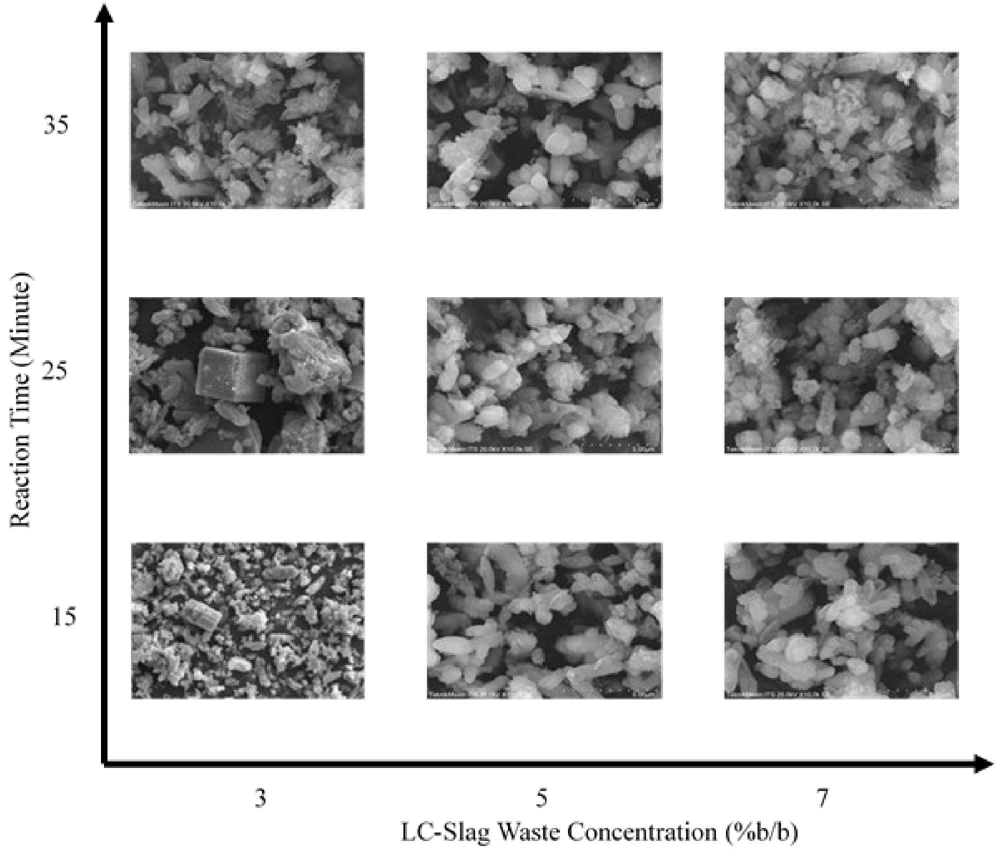


Figure 6 SEM analysis results from PCC on all experimental variables

4.0 CONCLUSION

According to the findings of this study, the optimum concentration of LC-Slag Waste to synthesis precipitated calcium carbonate (PCC/$CaCO_3$) is 5% w/w and a reaction time of 35 minutes with a yield of 95%. Aside from that, the longer the reaction time, the more PCC/$CaCO_3$ is generated. This simple micro-bubble reactor synthesis method can also be used to produce PCC/$CaCO_3$ with the dominating form of calcite. The potential for processing LC-Slag waste into PCC is highly intriguing. This is undoubtedly a possibility and opportunity for the acetylene gas sector. Aside from that, the PCC market, which is still expanding, expands the prospects for this utilization.

Acknowledgement

This research is fully supported by Direktorat Jendral Pendidikan Tinggi - Ministry of Education and Culture Republik Indonesia, 0563/E5/PG.02.00/2023 with schema Penelitian Thesis Magister. The authors fully acknowledged Ministry of Higher Education (DIKTI) and Institut Teknologi Sepuluh Nopember, Surabaya for the approved fund which makes this important research viable and effective.

References

[1] S. Mao, Y. Liu, T. A. Zhang, and X. Li. 2020. Nano-CaCO3synthesis by jet-reactor from calcium carbide slag. *Materials Research Express*. 7(11): 11503. https://doi.org/10.1088/2053-1591/abc654

[2] O. A. Jimoh, N. Mahmed, P. U. Okoye, and K. S. Ariffin. 2016. Utilization of milk of lime (MOL) originated from carbide lime waste and operating parameters optimization study for potential precipitated calcium carbonate (PCC) production. *Environmental Earth Sciences*. 75(18): 1251. https://doi.org/10.1007/s12665-016-6053-z

[3] O. Rahmani, A. Kadkhodaie, and J. Highfield. 2016. Kinetics analysis of CO2 mineral carbonation using byproduct red gypsum. *Energy and Fuels*. 30(9): 7460–7464. https://doi.org/10.1021/acs.energyfuels.6b00246

[4] S. N. M. Sabri, R. Othman, and A. Othman. 2017. Morphology and phase identification of synthesized precipitated calcium carbonate from acetylene gas industry waste. *AIP Conference Proceedings*. 1901(1): 070006. doi: 10.1063/1.5010515

[5] S. M. Lee *et al.* 2017. Calcium extraction from steelmaking slag and production of precipitated calcium carbonate from calcium oxide for carbon dioxide fixation. *Journal of Industrial and Engineering Chemistry.* 53: 233–240. http://dx.doi.org/doi:10.1016/j.jiec.2017.04.030

[6] R. S. Fakhri and E. T. Dawood. 2023. Properties Evaluation of Green Mortar Containing Waste Materials. *ASEAN Engineering Journal.* 13(2): 115–123. https://doi.org/10.11113/aej.V13.18986

[7] N. M. Farrag, R. A. Bayoumi, and T. A. Mohamed. 2022. Factorial analysis of nano-precipitated calcium carbonate via a carbonation route using Solvay wastewater. *Case Studies in Chemistry and Enviromental Engineering.* 6: 100236. https://doi.org/10.1016/j.cscee.2022.100236

[8] M. Altiner, S. Top, B. Kaymakoğlu, I. Y. Seçkin, and H. Vapur. 2019. Production of precipitated calcium carbonate particles from gypsum waste using venturi tubes as a carbonation zone. *Journal of CO_2 Utilization.* 29: 117–125. https://doi.org/10.1016/j.jcou.2018.12.004

[9] M. M. H. Al Omari, I. S. Rashid, N. A. Qinna, A. M. Jaber, and A. A. Badwan. 2016. *Calcium Carbonate*, 1st ed. 41. Elsevier Inc.

[10] M. Singh, S. Vinodh Kumar, S. A. Waghmare, and P. D. Sabale, 2016. Aragonite-vaterite-calcite: Polymorphs of CaCO3 in 7th century CE lime plasters of Alampur group of temples, India. *Construction and Building Materials.* 112: 386–397. https://doi.org/10.1016/j.conbuildmat.2016.02.191

[11] C. J. Grimes, T. Hardcastle, M. S. Manga, T. Mahmud, and D. W. York. 2020. Calcium Carbonate Particle Formation through Precipitation in a Stagnant Bubble and a Bubble Column Reactor. *Crystal Growth & Des*ign. 20(8): 5572–5582. https://doi.org/10.1021/acs.cgd.0c00741

[12] O. A. Jimoh, K. S. Ariffin, H. Bin Hussin, and A. E. Temitope. 2018. Synthesis of precipitated calcium carbonate: a review. *Carbonates and Evaporites.* 33(2): 331–346. https://doi.org/10.1007/s13146-017-0341-x

[13] J. H. Bang *et al.* 2011. Precipitation of calcium carbonate by carbon dioxide microbubbles. *Chemical Engineering Journal.* 174(1): 413–420. https://doi.org/10.1016/j.cej.2011.09.021

[14] N. X. T. Tram. 2020. Synthesis and characterization of calcite nano-particle derived from cockle shell for clinical application. *ASEAN Engineering Journal.* 10(1): 49–54. https://doi.org/10.11113/aej.v10.15538

[15] A. U. Badnore and A. B. Pandit. 2015. Synthesis of nanosized calcium carbonate using reverse miniemulsion technique: Comparison between sonochemical and conventional method. *Chemical Engineering Processing: Process Intensification.* 98: 13–21. https://doi.org/10.1016/j.cep.2015.10.003

[16] S. Van der Zee and F. Zeman. 2016. Production of carbon negative precipitated calcium carbonate from waste concrete. *The Canadian Journal of Chemical Engineering.* 94(11): 2153–2159. https://doi.org/10.1002/cjce.22619

[17] J. H. Bang, K. Song, S. Park, C. W. Jeon, S. W. Lee, and W. Kim. 2015. Effects of CO2 bubble size, CO2 flow rate and calcium source on the size and specific surface area of CaCO3 particles. *Energies*. 8(10): 12304–12313. https://doi.org/10.3390/en81012304

[18] E. Sari *et al.* 2023. Synthesis of precipitated calcium carbonate with the addition of aloe vera extract under different reaction temperatures. *International Journal of Applied Science and Engineering.* 20(1): 1–7. doi: 10.6703/IJASE.202303_20(1).007

[19] X. Y. Lye. 2019. Synthesis of precipitated calcium carbonate using calcium carbide waste for acid mine drainage remediation. Accessed: August 24, 2023 [Online]. http://eprints.utar.edu.my/3939/

[20] S. Tanaka, K. Takahashi, M. Abe, M. Noguchi, and A. Yamasaki. 2022. Preparation of High-Purity Calcium Carbonate by Mineral Carbonation Using Concrete Sludge. *ACS Omega*. 7(23): 19600–19605. https://doi.org/10.1021/acsomega.2c01297

[21] R. Chang, S. Kim, S. Lee, S. Choi, M. Kim, and Y. Park. 2017. Calcium carbonate precipitation for CO 2 storage and utilization: A review of the carbonate crystallization and polymorphism. *Frontiers in Energy Ressearch.* 5: 1–12. https://doi.org/10.3389/fenrg.2017.00017