# SUSTAINABLE PROCESS ENGINEERING: CARBON DIOXIDE CAPTURE FOR CRYSTALLIZATION OF CALCIUM CARBONATE FOR BIOMEDICAL APPLICATION

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**TÓM TẮT**

## KỸ THUẬT QUY TRÌNH BỀN VỮNG: THU GIỮ KHÍ CARBON DIOXIDE ĐỂ KẾT TINH CALCIUM CARBONATE ỨNG DỤNG TRONG Y SINH HỌC

*Nghiên cứu phát triển hệ thống kết tinh kết hợp với hệ thống hấp thụ khí $CO_2$ là một quy trình kỹ thuật bền vững thân thiện với môi trường, tuần hoàn, tiết kiệm năng lượng và vật liệu khi sử dụng khí thải $CO_2$ làm nguyên liệu. Chúng tôi đã thành công khi sản xuất được các cấu trúc tinh thể khác nhau của $CaCO_3$ bao gồm vaterite và calcite. Các cấu trúc tinh thể này có các hoạt tính khác nhau đối với tế bào trong các ứng dụng y sinh học. Chúng tôi nhận thấy quá trình kết tinh phụ thuộc nhiều vào các thông số công nghệ như nồng độ và nhiệt độ. Đối với calcite, quá trình kết tinh được thực hiện ở nhiệt độ thấp với nồng độ tác chất ban đầu cao nhằm kết tinh chọn lọc và tiết kiệm thời gian. Cấu trúc vaterite kém bền hơn cấu trúc calcite nên sẽ có sự chuyển pha từ dạng cấu trúc kém bền này sang dạng cấu trúc bền calcite trong quá trình kết tinh. Do vậy, quá trình kết tinh cần thời gian để hoàn tất quá trình chuyển pha nhằm thu hồi 100% sản phẩm calcite; ở đây, thời gian chuyển pha hoàn toàn là 30-240 phút tùy thuộc vào từng điều kiện vận hành. Đối với vaterite, chúng tôi đã sử dụng các chất phụ gia như gelatin/collagen để ngăn chặn quá trình chuyển pha từ dạng vaterite sang dạng calcite nhằm thu hồi thành công sản phẩm vaterite.*

**Từ khoá***: vaterite, calcite, kết tinh calcium carbonate, hấp thụ carbon dioxide, mầm tinh thể, đa cấu trúc tinh thể.*

## 1. INTRODUCTION

Green growth is a global trend and an inevitable development path for Vietnam. Reducing greenhouse gas emissions to 0 (Net Zero) by 2050 is the target of the Vietnamese economy. Net zero emissions is an environmental goal to reduce greenhouse gas emissions such as carbon dioxide ($CO_2$) to a level equal to the Earth's ability to absorb or remove emissions [1].

Sustainable development represents a technological approach that can meet the needs of today's generation without compromising the ability of future generations to meet their own needs. Sustainable process engineering offers new opportunities for sustainable development through the invention, research, and development of more efficient, environmentally friendly, circular processes using renewable raw materials and renewable energy. It provides designs, operates, controls, and optimizes industrial processes and products to save energy and materials, minimize waste, and limit negative environmental impacts [2].

To calcium carbonate crystal, seven polymorphs of calcium carbonate ($CaCO_3$) are known to date; six are crystalline, and one is amorphous. Three polymorphs of calcite, aragonite, and vaterite are pure can. Meanwhile, three polymorphs of hemihydrate (CCHH) ($CaCO_3$•½$H_2O$), monohydrocalcite (MHC) ($CaCO_3$•1$H_2O$), and ikaite ($CaCO_3$•6$H_2O$) are hydrated crystalline phases [3].

Since $CaCO_3$ crystals have remarkable potential in bone tissue engineering applications, the metabolic activity of hFOB cells upon interaction with these crystals was investigated using an MTT assay. The results showed that cells were viable and increased for up to 5 days when interacting with calcium carbonate crystals. Aragonite exhibited the least cellular proliferation, while a decrease in cellular proliferation was less for calcite and vaterite at the same concentration. The properties of calcium carbonate polymorphism, solubility, and morphology are essential because they directly affect the cellular. In the case of solubility, it determines the ionic concentration in the medium, which affects cellular densities [4]. For morphology, the frequency of particle internalization, which was inversely correlated with cell viability, increased with an increase in aspect ratio for ellipsoidal, cuboidal, and spherical shape [5-6]. Since the aragonite has a needle-like shape, which is more likely to damage cellular membranes than smaller and lower aspect ratio particles, the coupled effect of these parameters could lead to a sharp decrease in cellular density concentration. Thus, the ellipsoidal vaterite and rhombohedral calcite, rather than needle-like aragonite particles, are promising for orthopedic applications.

Calcium carbonate crystallization has been investigated by numerous previous studies [7-13]. For example, a single crystal of vaterite can contain three orientation variants, and studying the structure of vaterite can offer advanced perspectives on the biomineralization process of calcium carbonate [7]. The nucleation rate of calcite is measured on the sulfated chitosan derivatives with varied positions and degrees of sulfation to understand the effect of these anionic macromolecules on the $CaCO_3$ biomineralization in diverse organisms [8]. The rhombohedron-like calcite was predominantly produced under stoichiometric reaction conditions. Moreover, increasing the excess concentration promoted crystal agglomeration by enhancing the crystals' collision efficiency [9].

In this study, we aim to use $CO_2$ emissions as input materials for the $CaCO_3$ crystallization to obtain the vaterite and calcite products since they have many applications in biomedicine. The combination of $CO_2$ absorbent and crystallization process is a sustainable process engineering that is environmentally friendly and circular, reducing $CO_2$ emissions that cause greenhouse effects and saving energy and raw material inputs to create high-value products. Moreover, the mechanism of nucleation, crystal growth, and phase transformation of vaterite and calcite will be explored in this study, leading to a partial understanding of the biomineralization process in species and the human body.

## 2. EXPERIMENT

The materials, including calcium chloride $CaCl_2$ (purity≥96%), sodium hydroxide NaOH (purity≥99%), gelatin, and collagen, were bought from Sigma-Aldrich Company without further purification. In atmospheric pressure

(1atm) and ambient temperature (20-30 °C), the $CO_2$ is scarcely soluble in water. However, the $CO_2$ absorption is enhanced by increasing the alkalinity of the solution by adding the NaOH. The pH significantly modifies the ionic species in the aqueous solution. Thus, specific carbonate concentrations could be achieved by controlling the pH of water for $CO_2$ dissolution. To increase the absorption amount of $CO_2$ in water and to achieve a particular concentration of carbonate, the pH value of 9-12 was fixed. The $CO_2$ gas from the aluminum cylinder device (ISTA, Taiwan) is fed to the water at a specific pH, demonstrating the carbon dioxide capture process.

The stirred tank crystallizer was designed based on the standard Rushton tank made of Pyrex glass and had four baffles for adequate mixing [14]. The working volume of the crystallizer was 400 mL. In the crystallizer, 200 mL of $CaCl_2$ solution at the concentrations of 0.005-0.05 M was prepared and agitated at 300 rpm. The temperature of solution in the crystallizer was controlled via the circulating coolant from the chiller through the outer jacket of crystallizer. The crystallization process was carried out at a range temperature of 10-30 $^oC$. The gelatin or collagen additive with a concentration of 1.0 g/L was added to the $CaCl_2$ solution. For the crystallization of $CaCO_3$, the carbonate solution of 200 mL from the carbon dioxide capture process was pumped to the crystallizer via a Masterflex pump with a flow rate of 10mL/min, as shown in Figure 1.

The suspension from the crystallization system was withdrawn to harvest the $CaCO_3$ crystalline product. The $CaCO_3$ crystalline products were separated by vacuum filtration, washed with distilled water, and dried in a desiccator over silica gel. The crystals were observed and analyzed using an optical microscope (AmScope 40X-2500X) and SEM (JEOL-Japan-Model: IT 500). X-ray diffraction determined the $CaCO_3$ crystalline products' structure (MAC Science, M18XHF-SRA). Moreover, the crystal structures were simulated by the software programs Mercury and Material Studio; here, the morphology module BFDH of the Material Studio software was applied.

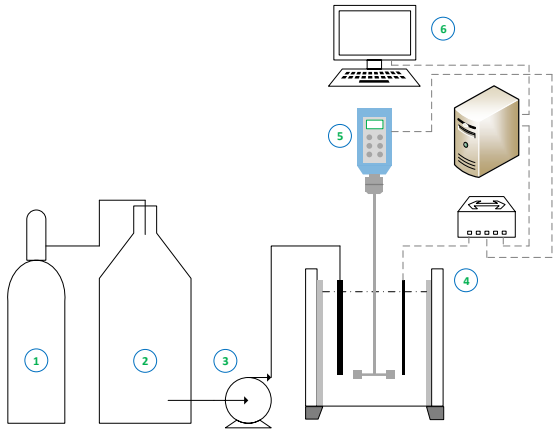


Figure 1. $CO_2$ absorption system for the crystallization of $CaCO_3$: (1)-$CO_2$ tank; (2)-Absorbent solution-water; (3)-Pump; (4)-Stirred tank; (5)-DC motor; (6)-Computer system

## 3. RESULTS AND DISCUSSION

The vaterite and calcite crystals have a spherical and rhombohedral shape, as shown in Figure 2a.

The unique shape of these crystals is based on their distinct structure. The structure of vaterite belongs to the hexagonal system. The number of molecules in a unit cell is Z=12, and the parameters of a unit cell are a=b=7.29 Å, and c=25.302 Å with angles $\alpha=\beta=90^o$ and $\gamma=120^o$, as shown in Figure 2b(I). Meanwhile, the structure of calcite belongs to the rhombohedral system. The number of molecules in a unit cell is Z=12, and the parameters of a unit cell are a=b=c=6.36 Å with angles $\alpha=\beta=\gamma=46.1^o$, as shown in Figure 2c(I).

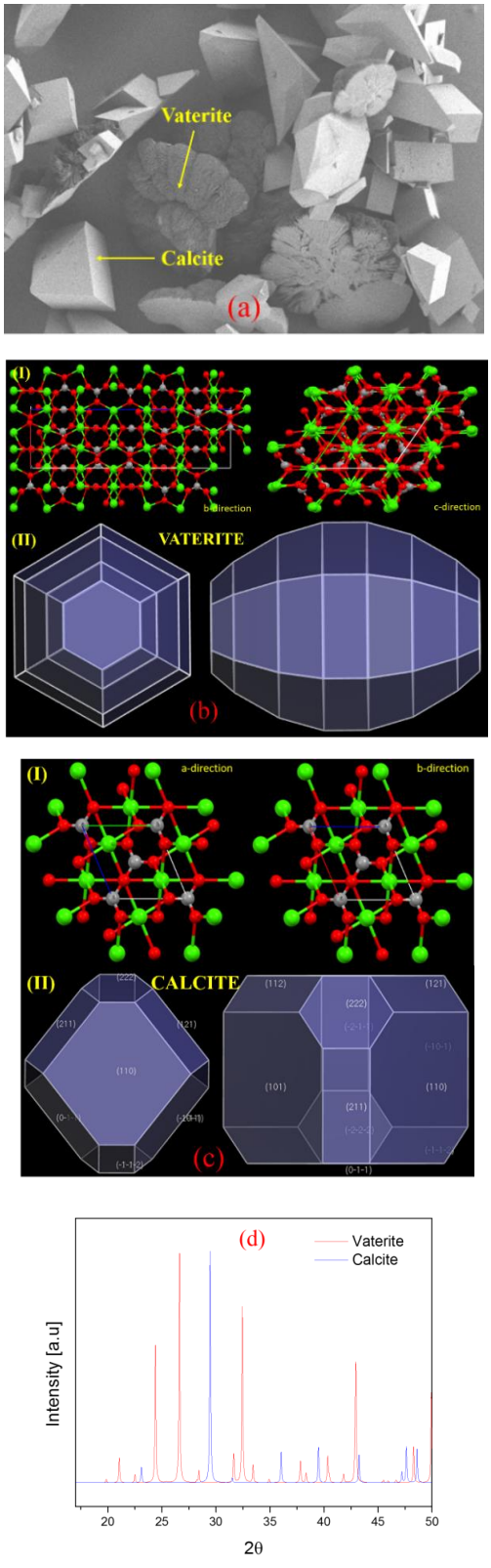


Figure 2. (a) SEM images of vaterite and calcite, (b) predicted shape of vaterite, (c) predicted shape of calcite, and (d) XRD pattern of vaterite and calcite

The shape of vaterite and calcite were also simulated by the BFDH module in Material Studio software, as shown in Figure 2b(II)-c(II). The results showed that the distinct predicted shapes of these crystals matched well with those obtained in the experimental results (see Figure 2a). The structures of vaterite and calcite were confirmed through X-ray spectroscopy, as displayed in Figure 2d. The spectrum indicated that the characteristic peaks of vaterite were $2\theta$~21.04$^o$, 24.4$^o$, 26.6$^o$, and 32.4$^o$. Meanwhile, the distinguished peaks of calcite were $2\theta$~23.06$^o$, 29.52$^o$, 36.08$^o$, and 39.61$^o$. Thus, the XRD analysis could define the crystalline product of $CaCO_3$.

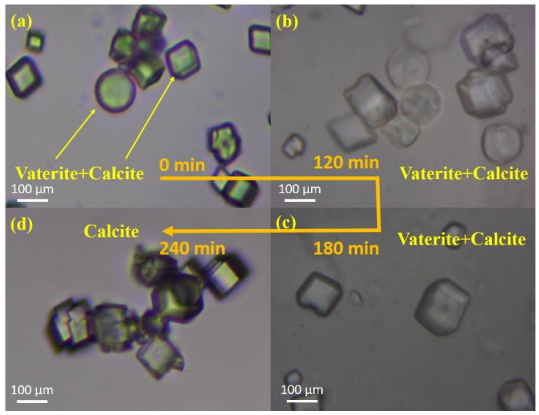


Figure 3. Phase transformation of vaterite to calcite: (a) at t=0 min, (b) t=120 min, (c) t=180 min, and (d) t=240 min

The polymorphism and phase transformation of $CaCO_3$ were continuously monitored with the crystallization time via the optical microscope, as shown in Figure 3. It revealed the transformation of the crystal structures of $CaCO_3$ from the beginning of crystal appearance to the end of the crystallization process. Here, the mixture of vaterite and calcite was concomitantly precipitated at the beginning of crystallization (see Figure 3a). Although the phase transformation occurred continuously, the mixture of vaterite and calcite was still observed until 240 min

(see Figure 3b-c). At the end of crystallization of t=240 min, only calcite crystals were observed (see Figure 3d); that means the phase transformation of vaterite to calcite was completed. Thus, pure calcite can be obtained after a 240 minutes crystallization process. The phase transformation of vaterite to calcite proceeded due to the solubility of two polymorphs. Here, the vaterite has a higher solubility than calcite. Thus, the vaterite was unstable, while the calcite was stable, and the vaterite would be transformed to calcite via the Oswald ripening mechanism [15].

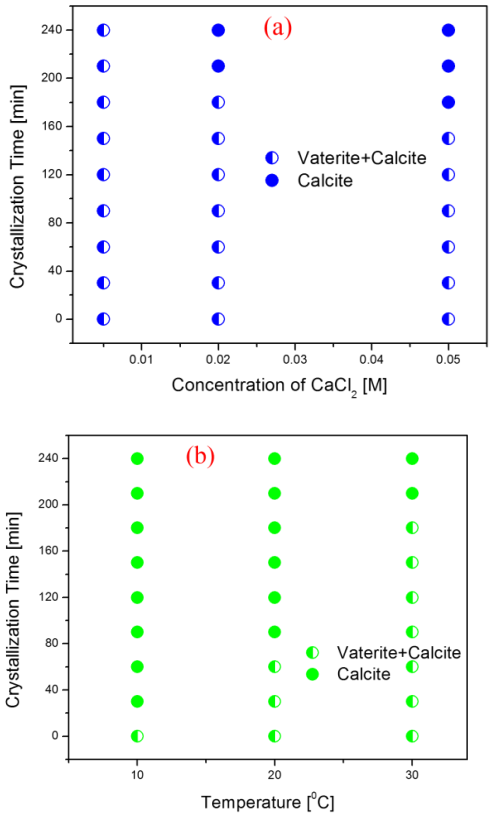


Figure 4. Polymorphism mapping of vaterite and calcite: effect of (a) $CaCl_2$ concentration and (b) temperature according to crystallization time

The effect of $CaCl_2$ concentration on $CaCO_3$ crystallization is illustrated in Figure 4a. At a low concentration of 0.005 M, the crystalline product is a mixture of vaterite and calcite regardless of the crystallization time. However, when the concentration was increased to 0.02 M, we found that the crystal product was 100% calcite just after the crystallization time of 210 minutes; below this period, a mixture of vaterite and calcite was still obtained. When the concentration increased to 0.05 M, the pure calcite would be obtained after only 180 minutes. Thus, it concluded that when the concentration of $CaCl_2$ is increased, the crystallization time required to get 100% calcite will be decreased. Accordingly, it was expected that the nucleation and crystal growth of calcite and the phase transformation from vaterite to calcite would be promoted when the concentration of $CaCl_2$ is increased. Therefore, to selectively crystallize the pure calcite in the shortest time to save production expense and energy, we need to use a high concentration of $CaCl_2$.

The influence of temperature on $CaCO_3$ crystallization is also demonstrated in Figure 4b. At a temperature of 30 $^oC$, the crystalline product was also a mixture of vaterite and calcite until the crystallization time was 180 minutes. After this period time, pure calcite was obtained. When the temperature was reduced to 20 $^oC$, it was revealed that the crystal product was 100% calcite after the crystallization time of 90 minutes; yet, below this period time, a mixture of vaterite and calcite was observed. Further decreasing the temperature to 10 $^oC$, the pure calcite was harvested at the crystallization time of only 30 minutes. Thus, we believed that reducing the crystallization temperature would decrease the crystallization time to achieve pure calcite. Consequently, it implied that the nucleation and crystal growth of calcite and the phase transformation from vaterite to calcite would be accelerated by decreasing the

temperature. Thus, we should operate the $CaCO_3$ crystallization at low temperatures to obtain pure calcite for sustainable process engineering in the shortest time possible.

When the $CaCO_3$ crystallization process was carried out with gelatin/collagen additives, we found that the mixture of vaterite and calcite was maintained until the crystallization time was prolonged by up to 240 minutes, as shown in Figure 5.

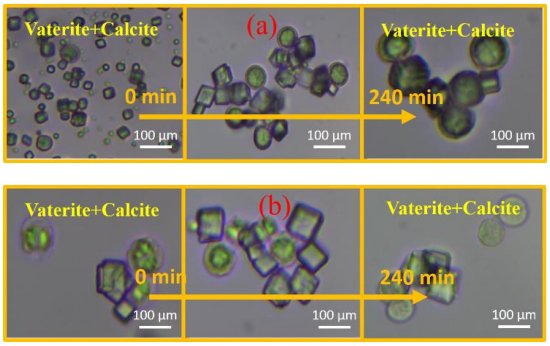


Figure 5. Effect of additive on crystallization process: (a) gelatin, and (b) collagen

This result showed that the gelatin/collagen additives inhibited the nucleation, crystal growth of calcite, and the phase transition from vaterite to calcite. Thus, it could not recover 100% calcite if there was a specific concentration of gelatin/collagen in the crystallization solution. From the above phenomenon, we believed that gelatin/collagen were the long-chain polymers that covered the vaterite crystal grains, making it impossible to undergo the phase transition to calcite. Accordingly, the significance of using gelatin/collagen additives is maintaining the unstable vaterite during crystallization, preventing the phase transition to the stable calcite to produce the vaterite.

## 4. CONCLUSION

The study shows a high potential for success in using $CO_2$ emissions as raw material for $CaCO_3$ production for biomedical applications. We have accurately produced $CaCO_3$ crystal structures, including vaterite and calcite, as these crystal structures have different activities toward cells. The crystallization process depends on technological parameters such as concentration and temperature. Calcite's crystallization process should be carried out at a low temperature and with a high initial concentration of reactants to prioritize its selective crystallization. Since the vaterite is less stable than the calcite, it would transform into calcite. Thus, it required a period to recover 100% calcite product; here, the completed crystallization time was 30-240 minutes, depending on each operating condition. For vaterite, additives such as gelatin/collagen could prevent the phase transformation from vaterite to calcite to recover the vaterite product. Accordingly, the $CO_2$ absorbent system combined with the crystallization process is a sustainable process engineering that is environmentally friendly and circular, saving energy and materials when using $CO_2$ emissions as raw material.

## REFERENCES

[1] Helm D. (2020). *Net Zero: How We Stop Causing Climate Change*. New York: HarperCollins Publishers.

[2] Szekely G. (2021). *Sustainable Process Engineering*. Berlin: De Gruyter.

[3] Dove P.M., Yoreo J.J.De, Weiner S. (2018). *Biomineralization*. Berlin: De Gruyter.

[4] Trushina D.B., Bukreeva T.V., Borodina T.N., Belova D.D., Belyakov S., Antipina M.N. (2018). Heat-driven size reduction of biodegradable polyelectrolyte multilayer hollow capsules assembled on CaCO3 template. *Colloids Surfaces B Biointerfaces*, **170**, 312-321.

[5] Parakhonskiy B., Zyuzin M.V, Yashchenok A., Carregal-Romero S., Rejman J., Möhwald H., Parak W.J., Skirtach A.G. (2015). The influence of the size and aspect ratio of anisotropic, porous CaCO3 particles on their uptake by cells. *J. Nanobiotechnology*, **13**, 1-13.

[6] Sun X.Y., Gan Q.Z., Ouyang J.M. (2017). Size-dependent cellular uptake mechanism and cytotoxicity toward calcium oxalate on Vero cells. *Scientific Reports*, **7**, 1-12.

[7] Xingyuan S., Junwei H., Mingyi C., Haiyang N., Paul J.M.S., Christos D.M., Jie D., Kunmo K., Roberto dos R., Vinayak P.D., Xiaobing H. (2023). Unlocking the mysterious polytypic features within vaterite CaCO3. *Nature Communications*, **14**, 1-11.

[8] Brenna M.K., Ronnie M., Nizhou H., Nicholas F.P., Brady A.H., Kevin J.E., Valerie V.W., Louis A.M., James J.D.Y., Patricia M.D. (2024). Kinetics of Calcite Nucleation onto Sulfated Chitosan Derivatives and Implications for Water-Polysaccharide Interactions during Crystallization of Sparingly Soluble Salts. *Crystal Growth & Design*, **x**, x-x.

[9] Jung T., Kim W.S., Choi C.K. (2004). Effect of Nonstoichiometry on Reaction Crystallization of Calcium Carbonate in a Couette-Taylor Reactor. *Crystal Growth & Design*, **4**, 491-495.

[10] Denis G., Stephan E.W. (2019). Designing Solid Materials from Their Solute State: A Shift in Paradigms toward a Holistic Approach in Functional Materials Chemistry. *J. Am. Chem. Soc.*, **141**, 4490-4504.

[11] Patrick D., Philipp I.S., Simon L., Thi Q.N.D., Shifi K., Maria R.C., Dominique de L., Vitaliy P., David E., Asher S., Dirk Z., Stephan E.W. (2022). Small-Molecular-Weight Additives Modulate Calcification by Interacting with Prenucleation Clusters on the Molecular Level. *Angew. Chem. Int. Ed.*, **61**, e202208475.

[12] Luca T., Remi R., Adrienn M.S., Melanie M., Juan D.R.B. (2024). Impact of Rare Earth Elements on $CaCO_3$ Crystallization: Insights into Kinetics, Mechanisms, and Crystal Morphology. *Crystal Growth & Design*, **24**, 632-645.

[13] Pupa U.P.A.G., Kristin D.B., Nicholas B., Sylvie T., Tali M., Frederic M., Jess F.A., Jonathan E., Benjamin G., Vanessa K., Marjorie C., Javier O.H., Andrew H.K. (2022). Biomineralization: Integrating mechanism and evolutionary history. *Science Advances*, **8**, 1-16.

[14] Trinh Thi Thanh Huyen, Nguyen Thi Kim Phuong, Khuu Chau Quang, Wolf S.E., Nguyen Anh Tuan. (2022). Influence of Taylor Vortex Flow on the Crystallization of L‑Glutamic Acid as an Organic Model Compound. *Ind. Eng. Chem. Res.*, **61**, 10205-10223.

[15] Mullin J.W. (2001). *Crystallization*, Oxford: Butterworth-Heinemann.