- Technical Paper -

A MECHANOCHEMICAL APPROACH TO CALCIUM BICARBONATE SYNTHESIS FROM MARINE SHELL WASTE USING SATURATED CARBONIC ACID SOLUTIONS

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ABSTRACT

This study investigates the effects of shell powder particle size and stirring methods on the dissolution of calcium carbonate ($CaCO_3$) into calcium bicarbonate ($Ca(HCO_3)_2$), focusing on mechanochemical principles. Smaller particle sizes increased dissolution efficiency by providing more reactive sites. Among stirring methods, impact stirring was most effective, followed by rolling and hand shaking. In contrast, the control group with saturated carbonated water alone showed no significant dissolution. These findings underscore the importance of optimizing particle size and stirring methods for efficient mechanochemical processes.

Keywords: Mechanochemical process, Calcium bicarbonate synthesis, Marine shell waste, Stirring methods, Dissolution efficiency

1. INTRODUCTION

The effective utilization of waste materials is crucial for addressing global environmental challenges, especially in the context of marine shell waste, which is primarily composed of calcium carbonate ($CaCO_3$) [1)]. This abundant waste material, generated worldwide, has been identified as a valuable raw material for diverse industrial applications [2)]. However, improper disposal of shell waste presents significant environmental risks, including habitat destruction, contamination, and the release of stored carbon into the environment [3)]. Previous studies highlight the need for sustainable recycling solutions to mitigate environmental pollution and reduce landfill costs [4)].

Marine ecosystems, including calcifying organisms, play a key role in the global carbon cycle by sequestering CO_2 in the form of calcium carbonate structures [5)]. Uncontrolled disposal of shell waste exacerbates environmental issues, contributing to organic pollution and eutrophication in marine sediments [6)]. Converting this waste into value-added products, such as calcium bicarbonate ($Ca(HCO_3)_2$), offers a promising solution to these challenges while supporting circular economy practices [7)]. Calcium bicarbonate, characterized by its higher solubility compared to calcium carbonate, holds potential applications in environmental remediation, construction, and water treatment [8)].

Ocean acidification, driven by elevated CO_2 levels, adversely affects calcifying organisms, leading to the dissolution of their calcium carbonate shells [9)]. This underscores the importance of innovative recycling approaches, such as mechanochemical methods, to mitigate the ecological and economic impacts of ocean acidification [10)]. Previous studies have demonstrated that controlled processing methods, including calcination and hydration, can convert marine shell waste into high-purity calcium carbonate and other commercially valuable compounds [11)]. Biogenic calcium carbonate derived from seashell waste has been successfully utilized in producing advanced materials for water treatment and polymer reinforcement, showcasing its versatile applicability [12)].

In this study, a mechanochemical approach is employed to optimize the conversion of marine shell waste into calcium bicarbonate. The conversion process is facilitated using saturated carbonic acid water, generated through a home carbonation device that dissolves CO_2 into water, creating a saturated solution necessary for transforming $CaCO_3$ into $Ca(HCO_3)_2$. The reaction follows the equation:

$$CaCO_3\ (\text{solid}) + H_2O + CO_2 \rightarrow Ca(HCO_3)_2\ (\text{aqueous})$$

By leveraging this method, the study focuses on enhancing the solubility and utilization of calcium bicarbonate, addressing both environmental challenges and industrial demands.

To evaluate the dissolution efficiency, changes in pH were monitored, and solubility was quantified based on

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Table 1 Materials and Characteristics

Material	Abbreviation	Characteristics
Shell powder	SC	Mainly composed of $CaCO_3$
Saturated carbonic acid water	CW	Prepared using compressed CO_2 with a carbonation device

Table 2 Grouping and Experimental Conditions

Group	Stirring Method	Particle Size (mm)	Reaction Temperature	Reaction Time
CW-S	None	None	5°C	12, 24, 48 hours
H1	Hand shaking	(1) >2.5 (2) 0.6–1.2 (3) 0.25–0.6 (4) <0.25		
H2				
H3				
H4				
R1	Rolling			
R2				
R3				
R4				
I1	Impact stirring			
I2				
I3				
I4				

the weight loss of residual solids after the reaction. This approach emphasizes the importance of optimizing particle size and stirring conditions to improve the dissolution efficiency of marine shell waste into calcium bicarbonate.

2. EXPERIMENTAL AND DETAILS

2.1 Materials

The main materials used in this study include shell powder (SC) and saturated carbonic acid water (CW). The shell powder, derived from marine waste, primarily consists of $CaCO_3$ and was ground and sieved into four particle size groups: >2.5 mm, 0.6–1.2 mm, 0.25–0.6 mm, and <0.25 mm. Saturated carbonic acid water was prepared using a home carbonation device by dissolving compressed CO_2 into water. The characteristics of the materials are summarized in Table 1.

2.2 Experimental Conditions and Methods

The experiment was designed with four particle size groups of shell powder, three stirring methods, and two control groups, as detailed in Table 2. The particle size groups were: >2.5 mm (1), 0.6–1.2 mm (2), 0.25–0.6 mm (3), and <0.25 mm (4). The stirring methods included hand shaking (H group), rolling (R group), and impact stirring (I group). In the hand shaking method (H group), the shell powder was manually mixed with the saturated carbonic acid water. The rolling method (R group) used a roller mixer for continuous rotation, while the impact stirring method (I group) involved the addition of four iron balls to enhance mechanical force. All experiments were conducted under identical temperature and semi-closed container conditions to minimize external variability.

To evaluate the dissolution efficiency, both pH changes and solubility were monitored during the reaction. pH measurements were recorded at various stages of the process to track the progress of the dissolution. In addition, solubility was assessed by collecting, drying, and weighing the solid residues after the reaction to calculate the amount of dissolved calcium carbonate. The weight loss of the residues served as a direct measure of solubility. This combined approach of monitoring pH and quantifying solubility provides a comprehensive understanding of the dissolution process, highlighting the effects of particle size and stirring methods on dissolution efficiency.

In the control groups, CW-S (static condition with no stirring) was employed to observe the natural dissolution behavior of the shell powder without mechanical agitation. For each reaction, 1.00 g of shell powder (SC) was accurately weighed and placed in a 50 mL beaker containing saturated carbonic acid water (CW). After the reaction, unreacted residues were separated by vacuum filtration. The pH of the solution was recorded at regular intervals during the reaction. The dried residual solid was then weighed to determine the extent of calcium carbonate dissolution. These measurements provided quantitative solubility data, which were compared across different particle size groups and stirring methods.

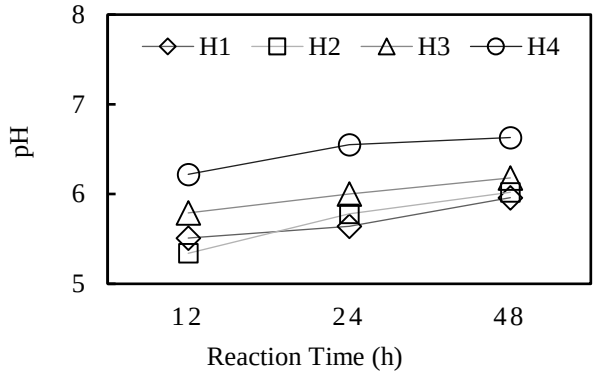

Figure 1(a) pH Change of H group

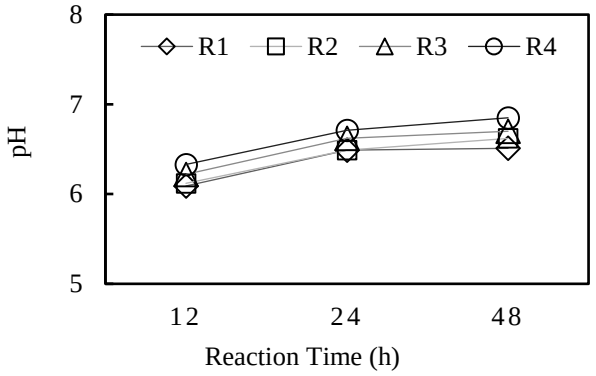

Figure 1(b) pH Change of R group

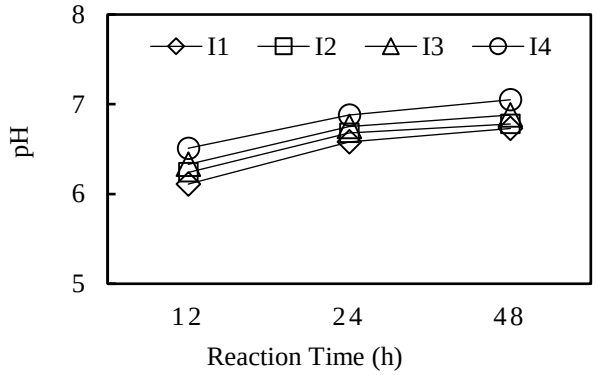

Figure 1(c) pH Change of I group

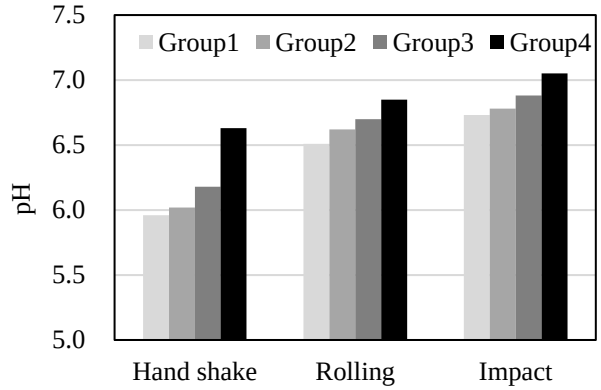

Figure 2 Comparison of pH Changes in Each group

The dissolution of $CaCO_3$ into $Ca(HCO_3)_2$consumes H^+ ions, reducing the solution's acidity and causing a rise in pH. Monitoring this pH increase is essential as it directly indicates the efficiency of the reaction. Higher pH values correspond to a more effective conversion of $CaCO_3$, which is the goal of optimizing the dissolution process. Additionally, solubility analysis quantifies the mass of calcium carbonate dissolved, providing further confirmation of the reaction's extent. Together, these methods offer a comprehensive assessment of the mechanochemical transformation process.

3. RESULTS AND DISCUSSION

3.1 Effect of Particle Size on Dissolution Efficiency

The dissolution efficiency of shell powder was significantly affected by particle size, confirming that increased surface area facilitates more efficient dissolution [13]. Smaller particle sizes present more reactive sites, accelerating the conversion of calcium carbonate ($CaCO_3$) to calcium bicarbonate ($Ca(HCO_3)_2$) through enhanced interaction with the saturated carbonic acid solution. This observation is consistent with mechanochemical studies, which indicate that finer particles enhance the reaction rate due to greater surface contact [14,15].

Figure 1(a) presents the pH changes over 48 hours for the various particle size groups under hand-shaking conditions. The <0.25 mm group (H4) exhibited the highest pH increase, reaching 6.63, which indicates the most efficient dissolution. In contrast, the >2.5 mm group (H1) showed the lowest pH of 5.96, reflecting slower dissolution due to reduced surface area available for reaction with the carbonic acid solution.

Figure 1(b) shows the results for rolling stirring. The <0.25 mm group (R4) showed the highest pH increase, reaching 6.85 after 48 hours. This suggests that rolling stirring, which provides continuous motion, enhances the dissolution process compared to hand shaking, likely by promoting more consistent interaction between shell powder and carbonic acid water.

Figure 1(c) illustrates the effect of impact stirring, where the introduction of mechanical force through iron balls significantly improved the dissolution process. The <0.25 mm group (I4) reached a pH of 7.05, indicating that impact stirring significantly enhances the mechanochemical conversion. The added mechanical energy accelerates the breakdown of $CaCO_3$, thereby promoting faster dissociation in the saturated carbonic acid solution.

3.2 Effect of Stirring Methods on Dissolution Efficiency

The stirring method significantly impacts the dissolution efficiency of shell powder, highlighting the role of mechanochemical activation in this process. Impact stirring (I group), which introduces additional mechanical energy, demonstrated the highest dissolution efficiency.

While the specific surface areas of rolling and impact stirring groups were comparable, the significantly higher dissolution efficiency observed in impact stirring can be attributed to the additional mechanical force. The repeated impact force induces microcracks and structural defects in the calcium carbonate particles, increasing their reactive surface area beyond what is measured by conventional surface area analysis. This enhanced solid-liquid interaction accelerates calcium ion dissolution, leading to a greater pH increase[16].

This enhanced efficiency is likely due to the increased mechanical force that facilitates better contact between the shell powder and the saturated carbonic acid solution, promoting the conversion of calcium carbonate ($CaCO_3$) into calcium bicarbonate ($Ca(HCO_3)_2$).

Rolling stirring (R group) also improved dissolution efficiency, though not to the same extent as impact stirring. The continuous rotation likely enhances the mixing and contact between reactants but to a lesser degree than the additional mechanical energy provided by impact stirring. Hand shaking (H group) exhibited the lowest efficiency, likely due to insufficient mechanical energy to facilitate a faster reaction.

This trend of increasing dissolution efficiency with greater mechanical force is consistent with mechanochemical principles [14,15]. In particular, previous studies have shown that mechanical agitation, such as that provided by milling or stirring, increases the surface area available for chemical reactions and can accelerate the dissolution of substances like calcium carbonate, especially when interacting with acidic solutions [17].

Figure 2 presents a comparison of final pH values for different particle size groups (Group 1: >2.5 mm, Group 2: 0.6–1.2 mm, Group 3: 0.25–0.6 mm, Group 4: <0.25 mm) under the three stirring methods. For each group, the final pH progressively increased from hand shaking to rolling stirring to impact stirring. The <0.25 mm group (Group 4) under impact stirring achieved the highest pH of 7.05, emphasizing the synergistic effect of both particle size reduction and mechanical energy input on dissolution efficiency.

3.3 Observations from the Control Group (CW-S)

The control group (CW-S), which only contained saturated carbonated water without shell powder, showed a stable pH of approximately 3.8 throughout the 48-hour experiment. This suggests that the saturated carbonic acid alone does not significantly contribute to calcium bicarbonate formation.

Figure 3 illustrates that while the pH in the CW-S group remained stable, the H4 group (particle size <0.25 mm, hand shaking) increased to 6.63 after 48 hours. This highlights the critical role of shell powder in enhancing dissolution efficiency, emphasizing the importance of its surface area in promoting the mechanochemical reaction and accelerating dissolution.

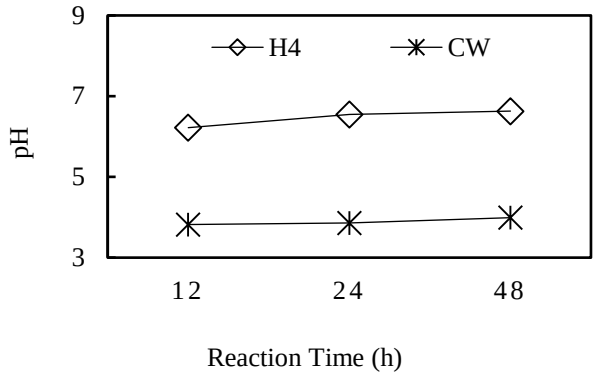

Figure 3 Comparison of pH Changes Between H4 and CW-S

3.4 Solubility Analysis: Quantitative Assessment of Dissolution Efficiency

This section evaluates the dissolution efficiency of calcium carbonate ($CaCO_3$) using solubility analysis, quantified as the percentage of the dissolved mass relative to the initial mass of calcium carbonate. The dissolved mass was calculated as the difference between the initial mass of solid and the mass of residual solid after drying. This calculation ensures an accurate measure of solubility trends, reflecting the effects of different stirring methods and reaction times. The solubility percentage was then plotted to compare dissolution efficiencies across experimental conditions.

Figure 4 illustrates the solubility percentages over time for the three stirring methods (hand shaking, rolling,and impact stirring) under the <0.25 mm particle

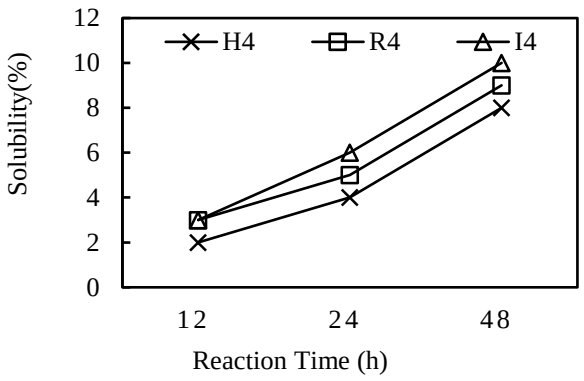

Figure 4 Solubility of Calcium Carbonate by Stirring Methods and Reaction Time

size group. The solubility values increased progressively with reaction time, confirming that extended exposure to mechanical agitation enhances dissolution efficiency. Among the stirring methods, impact stirring (I4) achieved the highest solubility percentages, reaching nearly 10% after 48 hours, followed by rolling stirring (R4) and hand shaking (H4), which showed the lowest solubility.

The results emphasize that impact stirring, with its additional mechanical energy, facilitates better mixing and more effective reactant contact, thereby maximizing dissolution efficiency. Rolling stirring provided moderate improvement, likely due to continuous rotation promoting steady reactant interaction, while hand shaking, with limited mechanical force, resulted in comparatively lower dissolution.

As shown in Figure 4, the solubility percentages for all stirring methods increased consistently at 12, 24, and 48 hours, with the fastest increase observed during the early stages of the reaction. This indicates that reaction kinetics are more pronounced initially and tend to stabilize over time.

The data trends in Figure 4 align closely with pH monitoring results discussed in earlier sections, reinforcing the complementary relationship between solubility analysis and pH data. Together, these findings underscore the synergistic effects of reduced particle size and mechanical energy in optimizing calcium carbonate dissolution.

3.5 Comprehensive Discussion

This study demonstrates that the dissolution of $CaCO_3$ into $Ca(HCO_3)_2$ is significantly influenced by particle size and stirring method. Smaller particle sizes provide a greater surface area, which accelerates the dissolution rate. Furthermore, impact stirring, which introduces mechanical energy, enhances dissolution efficiency by improving mixing and reactant contact. These results align with mechanochemical principles, where both reduced particle size and mechanical force contribute to faster reaction rates. Among the stirring methods, impact stirring was found to be the most effective, followed by rolling, with hand shaking showing the least effect. This emphasizes the critical role of both particle size reduction and mechanical energy in promoting efficient dissolution and mechanochemical transformations [18].

As demonstrated by pH monitoring, the highest pH increase was observed for smaller particle sizes, particularly under impact stirring. This suggests that particle size reduction and mechanical energy significantly enhance the conversion of $CaCO_3$. To further confirm these findings, solubility analysis was conducted, showing that smaller particle sizes, particularly under impact stirring, achieved the highest dissolution rates. This quantitative measure of dissolution efficiency supports the conclusion drawn from pH data, providing a comprehensive understanding of the mechanochemical process.

These findings suggest that impact stirring provides not only continuous mixing but also repeated mechanical collisions that enhance the mechanochemical activation of calcium carbonate. This activation process likely increases the number of reactive sites and facilitates faster dissolution, even when the specific surface area is similar to that of rolling stirring. Such an effect aligns with previous studies on the role of impact energy in solid-state reactions, reinforcing the mechanochemical contribution to dissolution efficiency[19].

Together, the pH changes and solubility analysis highlight the importance of particle size reduction and mechanical energy in optimizing dissolution efficiency. These findings suggest that mechanochemical methods can be effectively applied to improve dissolution processes in various industrial applications, particularly those involving mineral dissolution and carbonation.

4. SUMMARY

This study investigated the effects of shell powder particle size and stirring methods on the mechanochemical transformation of calcium carbonate ($CaCO_3$) into calcium bicarbonate ($Ca(HCO_3)_2$). The main findings are summarized as follows:

(1) Particle Size Effect: Reducing the particle size significantly enhanced the dissolution efficiency of shell powder. The <0.25 mm group demonstrated the highest pH increase and solubility, indicating that smaller particle sizes provide more reactive sites, accelerating the dissolution process. This observation aligns with mechanochemical principles that smaller particles lead to faster reactions by increasing the surface area for interaction[14,15].

(2) Stirring Method Effect: Impact stirring was found to be the most effective method for enhancing dissolution efficiency, followed by rolling and hand shaking. The mechanical energy introduced by impact stirring improved the contact between the shell powder and carbonic acid solution, leading to a higher dissolution rate. Rolling stirring also improved dissolution efficiency, but to a lesser extent, while hand shaking exhibited the least effect. These findings emphasize the importance of both particle size and mechanical force in optimizing dissolution [20].

(3) Control Group Observation: In the control group (CW-S), which contained only saturated carbonic acid water without shell powder, the pH remained stable at around 3.8, and solubility was negligible. This highlights that saturated carbonic acid water alone is insufficient for efficient calcium bicarbonate

formation, confirming the necessity of shell powder and optimized stirring methods for effective dissolution[14,15] .

Overall, the results demonstrate the synergistic effects of reduced particle size and mechanical force in enhancing mechanochemical transformations. The combination of pH monitoring and solubility analysis provided a comprehensive evaluation of the dissolution process. These findings offer a framework for optimizing calcium bicarbonate production, with potential applications in environmental remediation, water treatment, and efficient mineral dissolution processes.

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