Effect of Calcination Temperature on the Powder of Freshwater Snail Shells (Sulcospira testudinaria) Properties

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Abstract

Gastropod shells, such as those from the freshwater snail (Sulcospira testudinaria), have garnered interest as potential sources of calcium precursors. These shells are rich in calcium carbonate (CaCO3), which can be thermally decomposed into calcium oxide (CaO) through calcination. However, more information is needed on optimizing calcium extraction from the Sulcospira testudinaria (SST) shells. This study aims to investigate the influence of calcination temperature on the characteristics of powder of these shells. The study involves two sample treatments, uncalcined shells and shells calcined at temperatures ranging from 500°C to 1100°C for 1 hour. Fourier transform infrared spectroscopy (FTIR) analysis of uncalcined shell powder revealed the presence of aragonite functional groups within the CaCO3 structure. X-ray diffraction (XRD) analysis provided insights into the transformation of crystalline phases of CaCO3, starting from aragonite to calcite and eventually to calcium oxide, explaining the material’s weight loss during calcination. The conversion of aragonite to calcite occurs between 500°C and 700°C, while optimal decomposition into CaO is achieved at 1000°C. X-ray fluorescence (XRF) analysis indicated reduced impurities in the samples post-calcination. Scanning electron microscopy (SEM) detailed the morphological characteristics of the shell powders, highlighting temperature-dependent surface features. In conclusion, the optimal calcination temperature for extracting calcium from SST shells is 1000°C. The resulting calcium oxide can be a valuable precursor for various material applications. This research contributes to the efficient utilization of biowaste resources, emphasizing the potential of freshwater snail shells in the sustainable production of calcium-derived materials.

Keywords: calcination temperature, calcium carbonate, calcium oxide, freshwater snail shell

1. Introduction

Gastropods, including freshwater snails, are mollusks characterized by their protective shells. After the meat (soft body part) has been consumed, the shell is disposed of as waste. Gastropod shells contain relatively high calcium carbonate (CaCO3). The content of calcium carbonate in the shell of the land snail (Achatina fulica) is 89-90% [1], in the sea snail (Gibbula umbilicalis) is about 94.8%, and in the sea whelk (Nucella lapillus) is around 98.5% [2].

CaCO3 can decompose into calcium oxide (CaO) and carbon dioxide (CO2) during the calcination process, transitioning from hydrates to oxides and leading to the formation of crystalline phases [3]. Calcination is the heating treatment of a material below its melting point with a restricted supply of ambient oxygen. The calcination temperature is a crucial factor in the decomposition of CaCO3 as it affects the microstructure, morphology, and crystal properties of the CaO powder [4,5].

Snail shells calcined at the temperature of 500°C still retain CaCO3 compounds. However, at 700°C, calcium carbonate has decomposed into CaO [6]. The increasing sintering temperature also influenced the decrease in the oxygen level and the increase in the calcium level. The smallest CaO crystal size was found in the sample with 850°C sintering temperature for 17.6 nm [7]. CaO serves the dual role of neutralizing lake water impacted by acid rain and contributing to pollution control through the use of scrubber machines. It also exhibits a propensity for facile solidification, rendering it conducive for utilization in the production of cement [8].

The calcination temperature can also affect the color of the CaO shell powder. The properties of the calcium produced from the calcination process can also be influenced by the duration of the calcination process [9]. Despite several studies investigating the properties of CaO powder from gastropod
shells, the impact of calcination temperature on the properties of SST powder still needs to be explored.

This study examines the powder extracted from SST shells as a source of CaO. Sample characterization was performed to observe the dependency of calcium properties on calcination temperature and to determine fabrication parameters with optimal Ca characteristics. As a result, a synthesis method was developed to yield Ca with optimal properties derived from SST shell material. The findings of this research hold the potential to contribute significantly to the development of calcium-based material applications from SST shell powder.

2. Methods

2.1 Preparation of The Shell

The SST shells (Fig. 1) must be prepared meticulously. The shells are cleaned of dirt and then boiled for 1 hour to remove the meat. Subsequently, the shells are brushed off the remaining meat, washed, and dried under sunlight for 1 hour. Next, the shells are oven-dried at 105°C for 1 hour. The dried shells are then immersed in a 5% H2SO4 solution.

After soaking, the shells are cleaned with distilled water while being brushed, ensuring a neutral pH. The shells are then placed in the oven at 100°C for another hour. Once dry, the shells are coarsely crushed with a hammer, ground using a grinder and further reduced in size using a mortar and pestle to obtain smaller shell particles. Subsequently, the materials are sieved to 20-50 mesh to obtain similar sample sizes. The snail shell powder is then kept in an airtight container.

The shell chemical composition was analyzed using X-ray fluorescence spectroscopy (XRF; PAN-Analytical Minipal 4) under vacuum conditions, while its spectra were recorded using Fourier transform infrared (FTIR) spectroscopy (Shimadzu). Its structural characteristics were determined by X-ray diffraction (XRD; PAN-Analytical) with Cu-Kα radiation (λ = 0.154 nm) generated at 40 kV and 30 mA, spanning a 2θ range from 10° to 90°. The microstructure of the shell was examined using a scanning electron microscope (SEM; Bruker).

2.2 The Calcination of Freshwater Snail

The SST shell powder, each weighing 30 grams, was calcined using a furnace (Carbolite) at temperatures of 500°C, 600°C, 700°C, 800°C, 900°C, 1000°C, and 1100°C for 1 hour. The percentage of shell shrinkage during the calcination process was determined using a precision balance with an accuracy of 0.01 grams. The shell structural characteristics and elemental content after calcination were determined by XRD (PAN-Analytical) and XRF (PAN-Analytical), respectively, with the same setting as those of uncalcined shell powder, while their microstructures were imaged using a SEM (Bruker).

3. Results and Discussion

CaCO3 represents a mineral form of Ca. The calcination process involves the extraction of Ca precursors by removing CO2, H2O, and other undesirable substances, leading to the formation of CaO.

a) Characterization of the calcium source

Fourier transform infrared (FTIR) analysis is a method employed to identify functional groups within a sample. It achieves this by quantifying the absorption or transmission of infrared radiation. Figure 2 illustrates the FTIR transmission spectra of a non-calcined SST shell powder, measured within the range of 400–4000 cm⁻¹. Vibration modes of the CO3²⁻ ion in the powder are marked by absorptions at wave numbers of 1082 cm⁻¹ (ν1), 864 cm⁻¹ (ν2), 1426 cm⁻¹ (ν3), 1780 cm⁻¹ (ν4), and 708 cm⁻¹ (ν4). Similar absorption peak observations have also been reported in reference [10] indicating the typical vibration modes of aragonite as a crystalline form of CaCO3. Additionally, the FTIR spectra display a combination of CO3²⁻ vibration bands observed at 2520 cm⁻¹ and 2918 cm⁻¹ [11]. Furthermore, the hydroxyl group from water is observed in a broad band with a peak at 3300 cm⁻¹ [12]. Subsequently, XRF analysis revealed the aragonite content in SST shells to be 99.6%, surpassing other snail shells such as Pila spp. (87.14%) [13], the Javanese apple snail (67.8%), and the golden snail (48.02%) [14]. These findings suggest the considerable potential of SST shells as a source of calcium precursor.

Figure 1. SST shells, (a) fresh and (b) dried.

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b) **Visual characteristic and weight loss due to calcination process**

Calcination temperature can also affect the color of SST shell powder. Before calcination, the SST shell exhibits a brown hue [Figure 3(a)]. This color changes to ash-brown after calcination at 800°C, whitish-gray at a calcination temperature of 900°C [Figure 3(c)], and white at a calcination temperature of 1100°C [Figure 3(d)]. The calcination process induces the thermal decomposition of the SST shell [15]. Changes in the filler elements within the SST shell due to the calcination process are evident from the color alterations [16]. Similar color changes are also observed in the calcination process of golden apple snail shells (*Pomacea canaliculate*) [17].

Apart from changes in the crystal structure, the calcination of the SST shell powder will influence the mass of the heat-treated sample. The mass loss percentage in Figure 4 is defined as the difference of mass before and after the calcination process. Analysis of mass loss in the SST shell indicates that within the temperature range of 500°C to 800°C, the mass loss remains consistently low at 2-3%. The initial decomposition process encompasses the release of water and the volatilization of readily evaporating organic impurities. The second mass loss occurs at 900°C due to a thermal endothermic process. This mass loss stage is associated with initiating CO$_2$ release from calcium carbonate until it reaches optimal decomposition at 1000°C, marked by a mass loss of 40%, which remains almost constant at 44% in subsequent temperatures. The reduction in mass of the SST shell due to calcination treatment observed in this study is slightly lower than the mass reduction in terrestrial snail shells at 47% [15] and marine shells at 45% [18].

**Figure 2.** FTIR test results of SST shell powder without calcination.
The changes in color and mass of the SST shell during the calcination process may also stem from modifications in the crystal phase [19] and morphology [15] of CaCO$_3$, the primary component of the turtle shell. These changes are confirmed through XRD and SEM analyses.

c) Changes in the crystalline phase of calcium and the composition of the SST shell

The CaCO$_3$ in the non-calcined SST shell powder exhibits a crystalline aragonite phase, verified by FTIR (section 3.a). The calcination process induces changes in the CaCO$_3$ of SST shell in two sequential stages: the transformation of the crystalline phase of CaCO$_3$ and the decomposition of CaCO$_3$ into CaO and CO$_2$ [20]. These changes are evident from the XRD analysis, marked by characteristic peaks in the XRD spectrum, as shown in Figure 5.

In the first stage, between 500°C and 800°C, the calcination of calcium carbonate transforms the aragonite polymorph into calcite. This process occurs gradually. Figure 5(a) shows the XRD spectrum at the initial stage, depicting the presence of predominantly aragonite phase CaCO$_3$ (marked by the blue box). The calcination process changes 69% of CaCO$_3$ into the calcite phase (marked by the green box) at 500°C [Figure 5(b)], increasing to 96.7% at 700°C [Figure 5(c)], and reaching an optimum of 97% at 800°C (XRD spectrum not displayed). These crystalline phases have sharp peaks at $2\theta$ corresponding to data reported for CaCO$_3$ [10].

The next stage involves the decomposition process of CaCO$_3$ into CaO. In various shells, this process occurs within calcination temperatures ranging from 650°C to 1000°C [15,21]. The decomposition depends on temperature, time, and the species of the snails. Thermal decomposition of CaCO$_3$ into CaO for blood cockle shells occurs at 700°C for 4 hours or 800°C for 1 hour, golden apple snail shells at 700°C for 3 or 4 hours [22], green mussel shells at 750°C for 2 hours [23], and river snails (Viviparidae) at 800°C for 4 hours [24]. Additionally, the sample purity of the shell can influence the decomposition temperature [25].

The XRD spectrum of the calcination-treated SST shell in Figure 5(d) indicates that the decomposition process of CaCO$_3$ into CaO begins at a calcination temperature of 900°C, evidenced by the reduction of CaCO$_3$ content to 55.7% and the emergence of CaO at 5.3%. The coexistence of CaO and CaCO$_3$ calcite at this temperature aligns with previous reports [13]. The predominant content of CaO, around 65%, occurs at the calcination temperature of 1000°C [Figure 5(e)], marked by a distinct peak at 39.4°. These findings confirm earlier explanations that the mass loss primarily results from the phase transition of CaCO$_3$ to CaO and the release of CO$_2$. At this stage, there still exists portlandite mineral, Ca(OH)$_2$, indicating an incomplete process of CaCO$_3$ decomposition into CaO. This might be due to the SST shell having a hard layer.

XRF determines the decomposition of chemically bound organic elements. It should be noted that in this study, the calcination process does not significantly alter the quantity of calcium elements but alters the compound phases formed from the calcium precursor, whether in aragonite, calcite, or calcium oxide. Apart from calcium, the SST shell contains organic impurity elements whose percentages progressively decrease after calcination compared to the initial state. Table 1 demonstrates the changes in some impurity elements contained in the SST from the initial state and at the final temperatures in each phase transition stage.

<table>
<thead>
<tr>
<th>Element</th>
<th>Uncalcined</th>
<th>800°C</th>
<th>1100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>0.18</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>0.30</td>
<td>0.20</td>
<td>0.16</td>
</tr>
<tr>
<td>Cu</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Sr</td>
<td>1.10</td>
<td>1.10</td>
<td>0.91</td>
</tr>
<tr>
<td>Mo</td>
<td>0.40</td>
<td>0.36</td>
<td>0.20</td>
</tr>
<tr>
<td>Lu</td>
<td>0.16</td>
<td>0.13</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Figure 5. XRD spectra showing the crystalline phase of SST shell powder (a) without calcination, and the phase transformation occurring at calcination temperatures (b) 500°C, (c) 700°C, (d) 900°C, and (e) 1100°C.
d) Surface morphology of SST shells

Scanning electron microscopy (SEM) characterization was conducted to observe the surface morphology evolution of uncalcined and calcined SST shells. SEM images at a magnification of 1000x of SST shell powder are presented in Figure 6. Morphology refers to the shape and size of crystals or particles within the sample that influence the physical characteristics of the material.

SEM image in Figure 6(a) shows aragonite CaCO$_3$ of uncalcined snail shell powder. In general, the surface of the material in this work consists of non-uniform multilayer crystals. We can also observe that some aragonite is in irregular small rod-shape. These structures have also been reported in previous studies [22,26,27]. The calcination process with 500°C shifts the morphology of the material due to water removal and organic impurities elimination. As we notice in Figure 6(b) the crystalline units are in stacked rod-like with size of 10–30 µm, which is a slightly bigger than that of reported for golden apple snail shells [22]. At this point, we cannot differentiate clearly which units are aragonite or calcite. As the temperature is raised, the morphology transforms the crystal structure of calcite into cleavage rhombohedral at 700°C (Figure 6(c)) and porous acute rhombohedral at 800°C (Figure 6(d)) with pore size of 2–10 µm. We can see that the crystals tend to brick and form large crystallites. However, it is clear from the SEM images that aragonite crystal size is smaller than that of the calcite as reported in reference [10].

The surface morphology of the shell powder calcined at 900°C presents a co-existence of calcite crystal and calcium oxide compounds. Figure 6(e) shows a smoother calcite crystal. This may have resulted from a transformation of the calcite into CaO while releasing CO$_2$ [10]. Nevertheless, we still observe that the calcite crystals are in chunks. It is interesting to note that at calcination of 1000°C (Figure 6(e)), the surface morphology of the SST shells displays a large agglomeration of small particles of various size. As we magnify the image point to 5000x (image is not presented in this work), we observe that the crystals are mostly in round shapes [22], which some of them exhibit small pores of 20–50 nm. The pores present in the sample as the CO$_2$ released [7].

![Figure 6](https://example.com/figure6.png)

**Figure 6.** SEM images of snail shell powder (a) without calcination, and after calcination at temperatures (b) 500°C, (c) 700°C, (d) 800°C, (e) 900°C, and (f) 1000°C.
4. Conclusions

This study has evidently showed that the transformation of the SST shells is significantly affected by the temperature treatment. The uncalcined shells contain 99.6% of aragonite CaCO₃. The calcination process at 700°C totally transforms aragonite into the calcite phase, indicated by the existence of both crystals. The optimum temperature parameter in calcination process for SST shells to obtain calcium precursor is 1000°C. The optimization is suggested by the maximum content of CaO of 65% in the sample.

References


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