Supporting Information

Modified Wollastonite Sequestrating CO₂ and Exploratory Application of the Carbonation Products

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1. Detailed modification process and preparation of PP/carbonation product
composites

A typical surface modification was performed as following: 20 g of carbonation product powders was ultrasonically dispersed in 200 mL of absolute ethanol for 5 min, the mixture was then added into a three-mouth flask and stirred at 80 °C for 120 min. Titanate coupling agent was diluted in absolute ethanol and added into the above flask. Subsequent cool-down and drying resulted in the formation of final modified carbonation product powders. Different fractions (0~40 wt%) of carbonation product powders and PP resin were mixed using a high speed mixer (SHR-10A, Zhangjiaguang, China), and the mixtures were interfused using a twin-screw extruder (SJSH-30, Nanjing, China) with a length/diameter ratio of 25 at the speed of 50 rpm and the barrel temperature of 170~200 °C. The extruded materials were cooled in a water bath, and the as-cooled were then granulated into short rods with sizes of less than 3 mm before drying at 80 °C for 2 h. The dried granules were injection-molded into multipurpose test specimens using a screw-type injection molding machine (HTB-80, Ningbo, China) at a barrel temperature of 190~220 °C under the same injection pressure, respectively for physical property testing.

2. Calculation of carbonation ratio (η) and molar content (%) of CaCO₃ polymorphs

The carbonation ratio (η) was calculated according to the following equation:

\[
\eta = \frac{MW_{Ca} \times C_2 \times M}{MW_{CaCO_3} \times C_1 \times V} \times 100\%
\]  

where \( V \) is the volume of acid-leaching filtrate, \( C_1 \) is the percentage of calcium in acid-leaching filtrate, \( M \) is the mass of carbonation products and \( C_2 \) is the percentage of calcium in the carbonation products. \( M \) and \( V \) were obtained by direct weighing. The total Ca\(^{2+}\) contents of acid-leaching filtrate (\( C_1 \)) and carbonation products.
(C₂) could be determined using the EDTA titration method. The molar content (%) of CaCO₃ polymorphs can be calculated according to the intensity of the (104) plane of calcite and the (110) plane of vaterite.

\[
X_V = \frac{7.691I_{110}^V}{I_{104}^C + 7.691I_{110}^V} \quad (2)
\]

\[
X_C = 1 - X_V \quad (3)
\]

Where \(X_V\) and \(X_C\) are the molar content (%) of vaterite and calcite, respectively. \(I_{104}^C\) and \(I_{110}^V\) are the XRD intensity of (104) and (110) plane of calcite and vaterite, respectively.
**Fig. S1.** Effect of ammonia dosage on the wollastonite carbonation sample: (a) pH of solution, (b) carbonation ratio of product. Fig. S1a showed the change of the pH of the reaction solution with time. The initial pH value was approximately 9.5, but decreased over time as the ammonia reacted to form ammonium carbonate, while the carbonation ratio gradually increased (Fig. S1b). pH values eventually stabilized at approximately 7, which signified the end of the reaction. Except for 3 mL and 5 mL, the carbonation ratios were over 90% when the carbonation reactions were finished. In the cases of both 3 mL and 5 mL, however, the carbonation reaction was not completed due to a lack of ammonia. Because the carbonation ratio did not increase after 40 min (Fig. S1b), then it should correspond to the virtual termination of the reaction, which was confirmed from pH value of 6. The solution was weak acid, because the ammonia was consumed and carbon dioxide was continually bubbled to form carbonic acid. Thus, it could be determined that the termination time of carbonation was simply by monitoring the pH variation time as shown in Fig. S1a. For the high ammonia experiment, 10 mL, the terminal carbonation ratio did not increase significantly (Fig. S1b), indicating there was excess ammonia, thus 8 mL was chosen as the proper ammonia dosage.
Fig. S2. Effect of CO₂ flow rate on the wollastonite carbonation sample: (a) pH of solution, (b) carbonation ratio of product. The effect of the CO₂ flow rate on the wollastonite carbonation was evaluated by considering CO₂ flow rates of 50, 100 and 200 mL/min. The pH value of the solution was not significantly affected by changing the CO₂ flow rate. At 50 mL/min, the pH of the solution reached 6.8 after 50 min (Fig. S2a), indicating that the reaction had completed. When the flow rate was increased to 100 and 200 mL/min, the time required for the pH to reach 6.8 decreased to 35 and 25 min, respectively. This suggested that an increase in the CO₂ flow rate accelerated the carbonation reaction. In addition, over 90% of the Ca²⁺ in the solution was converted to calcium carbonate in approximately 25 min when the CO₂ flow rate was 200 mL/min (Fig. S2b). However, a comparable conversion was only achieved after 50 min when the flow rate was 50 mL/min. Despite this, it was not always advantageous to increase CO₂ flow rate to obtain a higher reaction rate. The CO₂ flow rate should be optimized by considering both the reaction time and the CO₂ sequestration efficiency. So, 100 mL/min was chosen as the optional CO₂ flow rate.
**Fig. S3.** Effect of volume of Ca\(^{2+}\) leaching solution on the wollastonite carbonation sample: (a) pH of solution, (b) carbonation ratio of product. The effect of the volume of Ca\(^{2+}\) leaching solution on the carbonation of wollastonite was evaluated by adjusting the volume from the range of 150~300 mL. A period of approximately 40 min was required to complete each reaction and the pH value of the solution was not significantly affected by changing the volume of Ca\(^{2+}\) leaching solution from 150 mL to 200 mL (Fig. S3a). However, the termination pH of the solution decreased to 6 when the volume of Ca\(^{2+}\) leaching solution was 300 mL. That was because the ammonia was consumed and carbon dioxide was continually bubbled to form carbonic acid. The volume of Ca\(^{2+}\) leaching solution affected the carbonation ratio, which fell from 92.5% for 150 mL and 200 mL to 86% when the volume of Ca\(^{2+}\) leaching solution was 300 mL (Fig. S3b), indicating that the carbonation reaction was incomplete due to the lack of ammonia. So, 150 mL of Ca\(^{2+}\) leaching solution was suitable for the carbonation reaction in the experiment.
Fig. S4. Effect of temperature on the wollastonite carbonation sample: (a) pH of solution, (b) carbonation ratio of product. Also we investigated the effect of the reaction temperature on the carbonation of wollastonite by considering the temperatures of 20, 30, 40 and 50 °C. The influence of reaction temperature on the wollastonite carbonation was not as strong as that of ammonia dosage and volume of Ca\(^{2+}\) leaching solution. Fig. S4a showed the pH variation of the reaction solution over time and showed that reaction time decreased with an increase in the reaction temperature. For all four experiments carbonation ratios of over 90% were observed (Fig. S4b). Considering the tradeoff between reaction time and energy consumption for heating, 30°C was chosen as the optional reaction temperature.
Fig. S5. Influence of technological conditions on modified effect of CaCO₃: (a) effect of surfactant dosage on activation grade and oil absorption value, (b) effect of time on activation grade and oil absorption value and (c) effect of temperature on activation grade and oil absorption value. The influence of surfactant dosage, modified temperature and modified time on the effect of modified carbonation product, which was characterized by activation grade and oil absorption value, were shown in Fig. S5, respectively. The surfactant dosage had a great influence on the effect of modified carbonation product (Fig. S5a). But, under the same surfactant dosage, the activation grade and oil absorption value have different effects. The initial activation grade and oil absorption value were 0 % and 78.3
mL/100g. When the surfactant dosage was 0.5 wt%, the activation grade and oil absorption value were 22.3 % and 69.2 mL/100g. With the increase of surfactant dosage to 2 wt%, the activation grade increased from 22.3 % to 67.6 %, and the oil absorption value decreased from 69.2 mL/100g to 47.5 mL/100g. Further increase the surfactant dosage to 4 wt%, the activation grade and oil absorption value were almost the same (68.2 % and 47.8 mL/100g, respectively). The modified time (Fig. S5b) and modified temperature (Fig. S5c) had the same effect on the activation grade and oil absorption value compared with the surfactant dosage. Under optimized conditions (2 wt%, 120 min, 80 °C), the activation grade was 98.4 % and almost all of the carbonation product particles were modified by titanate.

![Influence of technological conditions](image)

**Fig. S6.** Influence of technological conditions$^9$
on the FTIR spectra of carboination products: (a) different temperature: 20°C, 25°C, 30°C, 40°C and 50°C, (b) different ammonia dosage: 5 mL, 8 mL, 10 mL and 20 mL, respectively.