

# Synthesis of Needle-like Aragonite from Limestone without Calcinations in the Presence of Magnesium Sulfate

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## Abstract

Much attention has been paid to the processing of inorganic whisker, especially calcium carbonate whisker, which can be used as reinforcement materials of polymer composite due to its low price. Unfortunately, the present synthesis technique of calcium carbonate whisker starts from calcinations of limestone, which involves high energy consumption and furthermore is a highly environment polluting reaction. In this report, needle-like aragonite was synthesized with a reversible solution reaction from limestone without calcination. Optical microscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques were used to characterize the morphology and crystal structure of intermediates as well as that of the product, aragonite. GCC (grinding calcium carbonate) powder was dissolved in an aqueous solution of magnesium sulfate with reflux and air flush. EDTA titration was used to evaluate reaction rate of the dissolution. A kinetics equation of the dissolution reaction was constructed, which displayed second-order kinetics with respect to the concentration of magnesium sulfate. A rate constant of  $0.0015 \text{ l}^{-3} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$  was obtained. The dissolution reaction gave fiber-like magnesium hydroxide sulfate and gypsum crystal. Then needle-like aragonite with a length of  $9.13 \pm 1.02 \mu\text{m}$  and an aspect ratio of  $5.64 \pm 1.37$  was synthesized from the dissolution product with  $\text{CO}_2$  bubbling at  $70^\circ\text{C}$ .

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## Keywords

Aragonite, synthesis, needle-like, whisker, calcium carbonate

## 1. Introduction

It is well known that calcium carbonate is a readily available and important inorganic material. Calcium carbonate has been widely applied as filler in paper,

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plastics, and rubber products due to its low price. It is estimated that \$2.50/ton is saved for each 1% increase of filler in paper [1]. Calcium carbonate shows three crystal structures, i.e., calcite, aragonite and vaterite. Calcite is the thermodynamically stable phase. Aragonite is less thermodynamically stable and is liable to give needle-like morphology [2]. It was thought that needle-like calcium carbonate filler might give excellent properties of paper for bulk, brightness, opacity and strength, as well as improved retention [3–7]. Shang *et al.* [8] found that whisker aragonite was much better than calcite as PVC and PP composite filler. The improvements included higher tensile strength and impact strength of the composite.

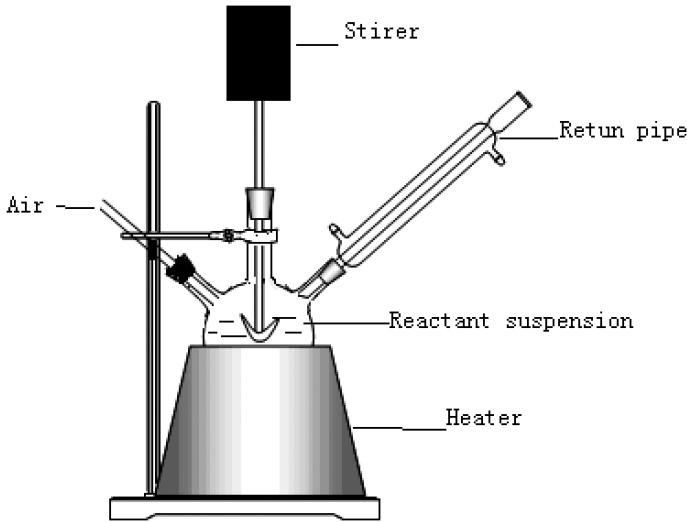
It is well known that the most economic route of calcium carbonate synthesis is a reaction between  $\text{Ca(OH)}_2$  and  $\text{CO}_2$  in water. Many factors influence polymorphism and morphology of the product, such as temperature [9, 10], solution pH [9, 11] and additives [12, 13]. Supersaturation degree of the solution was found to play an important role in the synthesis of metastable aragonite [6, 7, 9, 14]. Low supersaturation favors the formation of aragonite. To decrease supersaturation of the synthesis,  $\text{MgCl}_2$  was used as additive [15–17] while  $\text{Ca(OH)}_2$  and  $\text{CO}_2$  were used as the reactants. In previous work we synthesized needle-like aragonite using sparingly dissoluble salt as reactant [18, 19]. We also synthesized aragonite whisker using the method of Ota *et al.* [15, 16] and investigated paper properties with aragonite whisker filler [20]. We found that too high a reaction temperature such as  $90^\circ\text{C}$  resulted in a decrease of  $\text{Ca(OH)}_2$  conversion in the presence of high  $\text{Mg}^{2+}$  concentration. It seems that the reaction is reversible in this case. In other words, it is possible that natural limestone powder or GCC can be dissolved in aqueous solution of high concentration  $\text{MgCl}_2$  at high temperature. Then at lower temperature a reverse reaction can happen and result in the formation of aragonite whisker. In other words, that aragonite whisker can be synthesized from limestone through a solution reaction without calcination.

Traditionally, synthesis of calcium carbonate begins from calcination of limestone at a temperature higher than  $1000^\circ\text{C}$ . Then  $\text{CaO}$  hydrolysis of the calcination product gives  $\text{Ca(OH)}_2$ , which finally is carbonated with  $\text{CO}_2$  in water. The calcination is a process of high energy consumption. This investigation aims at synthesizing needle-like aragonite using a reversible reaction of aqueous solution between GCC and magnesium sulfate. The main advantages of this research are that calcination can be avoided in the synthesis of needle-like aragonite.

## 2. Experimental

### 2.1. Dissolution of GCC and Synthesis of Needle-Like Aragonite

In a typical procedure, 1.000 g of 200 mesh GCC (calcium carbonate content > 99%) was added to 200 ml of 1.045 mol/l magnesium sulfate (reactant agent) aqueous solution, which then was refluxed with agitation in a device illustrated in Fig. 1. The product  $\text{CO}_2$  was removed by flushing with air. After complete conversion of GCC, the reaction temperature was decreased to a synthesis temperature of arago-



**Figure 1.** Diagram of GCC dissolution device.

nite, such as 70°C. The product suspension was bubbled with CO<sub>2</sub> (reactant agent) at a rate of 60 ml/min.

## 2.2. Measurement of Reaction Rate and Conversion

In the dissolution reaction of GCC, the concentration of Mg<sup>2+</sup> will decrease due to the formation of magnesium hydroxide sulfate. Therefore, reaction rate and conversion can be measured in terms of the change of Mg<sup>2+</sup> concentration, which was analyzed using EDTA titration. In a given interval of reaction time, 2.000 ml of reaction suspension was withdrawn and filtrated. After cooling to room temperature 1.000 ml of the filtration solution was withdrawn and was diluted with 9 ml of DI water. Twenty millilitres of 0.1000 mol/l EDTA (reactant agent) and 10 ml of NH<sub>4</sub>OH (reactant agent) solution were added to the diluted solution. After aging for 30 min under seal, the solution finally was titrated with 0.1000 mol/l magnesium sulfate where chrome black T was used as indicator. All the analysis data came from an average of three measurements.

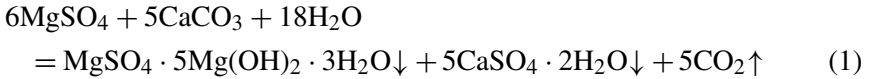
## 2.3. Characterization of Intermediate Product and Needle-Like Aragonite

The dissolution of GCC in magnesium sulfate solution will give magnesium hydroxide sulfate and calcium sulfate whisker. A 4XB optical microscope (Shanghai, China) was used to visualize the morphology of the intermediate product. A KYKY1000B scanning electron microscope (SEM) was used to characterize morphology of the needle-like aragonite. Statistical measurements of the needle-like aragonite length and aspect ratio have been carried out. A DX-2500 X-ray diffractometer (XRD, Dandong, China) was used to measure the XRD pattern of both the intermediate product and needle-like aragonite.

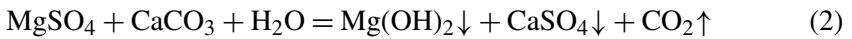
### 3. Results and Discussion

#### 3.1. Dissolution of GCC in Magnesium Sulfate Solution

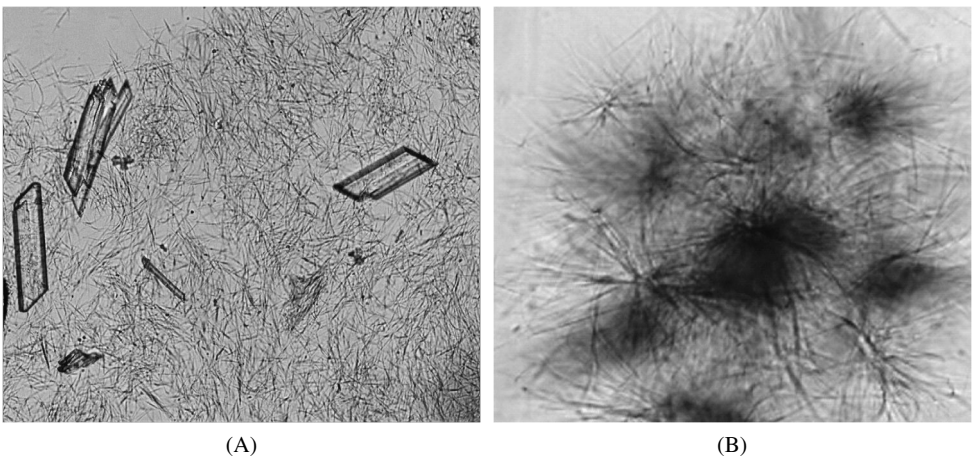
In aqueous solution of magnesium sulfate, a hydrolysis reaction of GCC will take place at reflux temperature:



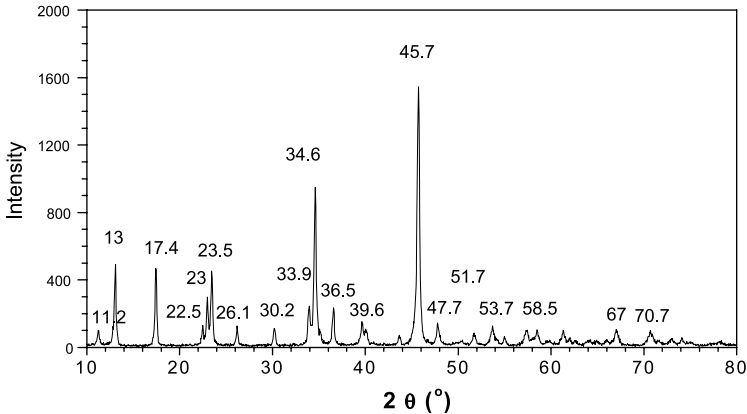
The equilibrium constant of reaction (1) cannot be calculated due to the absence of thermodynamic data of magnesium hydroxide sulfate. The thermodynamics of reaction (1) is close to that of reaction (2) below:



A calculation indicates that the equilibrium constant  $K_p$  of reaction (2) at 25°C is  $1.9 \times 10^{-7}$ . In other words, reaction (2) is not thermodynamically spontaneous. Similarly, reaction (1) cannot happen at room temperature. Reaction (2) as well as reaction (1) are both endothermic. High reaction temperature will favor the reaction. As a reversible reaction, high reactant concentration and removal of product will be advantageous. Therefore, high temperature, high concentration of magnesium sulfate and air flushing were used to promote GCC dissolution in magnesium sulfate solution. The morphology of the intermediate product is given in Fig. 2. Image A is an optical microscope image of the mixture. Those big crystals are typical gypsum whiskers, which is liable to precipitate in water. After agitation and aging for about 2 min, almost pure magnesium hydroxide sulfate can be obtained from the top suspension. Image B of Fig. 2 shows the morphology of magnesium hydroxide sulfate fiber. The X-ray diffraction pattern of the fiber-like magnesium hydroxide



**Figure 2.** Morphology of intermediate product: (A) Mixture of magnesium hydroxide sulfate and gypsum whisker; (B) Fiber-like magnesium hydroxide sulfate.



**Figure 3.** X-ray diffraction pattern of fiber-like magnesium hydroxide sulfate.

sulfate is given in Fig. 3. All of the diffraction peaks can be ascribed to magnesium hydroxide sulfate with a JCPDS card number of 13-0340. Detailed structure characterization of the fiber-like magnesium hydroxide sulfate was given in our previous report [21].

### 3.2. Dissolution Kinetics of GCC

Synthesis of needle-like aragonite from GCC shows two advantages over the traditional technique of PCC (precipitation calcium carbonate) preparation. First of all, calcination can be avoided so that energy cost can be decreased. Then needle-like morphology of product can be obtained. It is obvious that a short reflux time will be beneficial to decrease the energy cost further. Therefore, it is necessary to investigate dissolution kinetics of GCC. Concentration of magnesium sulfate and conversion of calcium carbonate at different reaction time are given in Table 1. There are three kinds of products as discussed above. Two of them are precipitates of magnesium hydroxide sulfate and gypsum. The other is gaseous  $\text{CO}_2$ , which was flushed out. Therefore, the content of  $\text{CO}_2$  in air, which is a constant, can be taken as its fraction pressure in the dissolution reaction.

As a result, only magnesium sulfate concentration should be considered in the construction of the kinetics equation. The relation between reaction time and inverse of magnesium sulfate concentration are given in Fig. 4. A linear regression analysis gave a related coefficient of 0.9966. The regression equation is given below:

$$\frac{1}{c} = 0.0015t + 0.9686. \quad (3)$$

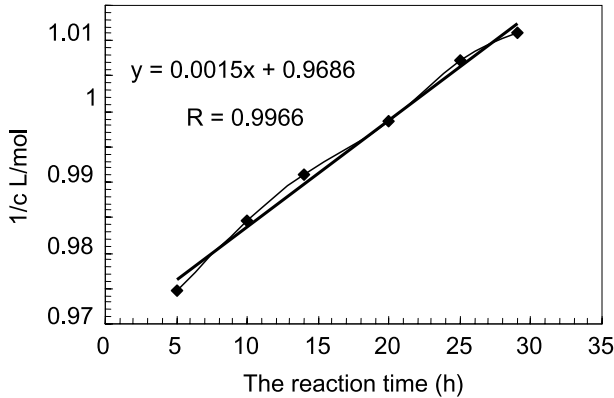
This result suggests that considering experimental error, the dissolution of GCC in magnesium sulfate solution should obey the kinetic of a second-order reaction. The

**Table 1.**

Conversion of calcium carbonate and concentration of magnesium sulfate

Reaction time (h)	5	10	14	20	25	29
GCC conversion (%)	31.73	48.8	59.8	72.89	86.84	93.4
1/C* l/mol	0.975	0.985	0.991	0.999	1.007	1.011

\* Concentration of magnesium sulfate.

**Figure 4.** Dependence of inverse of magnesium sulfate concentration on reaction time.

corresponding kinetics equation can be written as:

$$\frac{1}{c_A} - \frac{1}{c_{A_0}} = kt. \quad (4)$$

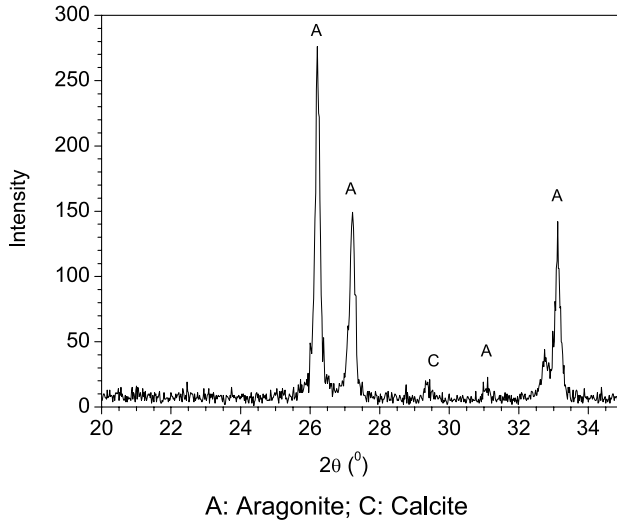
The differential form of the kinetics equation is:

$$-\frac{dc}{dt} = kc_A^2, \quad (5)$$

where  $c_A$  is the concentration of magnesium sulfate at reaction time  $t$  and  $c_{A_0}$  is its original concentration. The rate constant of the dissolution reaction is  $k = 0.0015 \text{ l}^{-3} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ . In terms of regression equation (3), a  $c_{A_0} = 1.033 \text{ mol/l}$  can be obtained, which is slightly different from the real  $c_{A_0} = 1.045 \text{ mol/l}$ . A  $-1.2\%$  relative error should be in the experimental error region. In the dissolution of GCC, both  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  participated in the reaction. Therefore, the kinetics equation should be written as

$$-\frac{dc}{dt} = kc_{\text{Mg}^{2+}}c_{\text{SO}_4^{2-}} = kc_A^2 = 0.0015t. \quad (6)$$

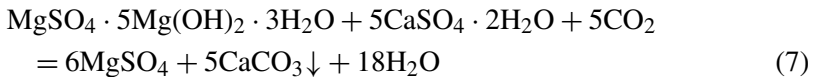
In other words, the dissolution reaction is a first-order reaction with respect to both  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$ . This is the reason that second-order reaction kinetics with respect to the concentration of magnesium sulfate was observed.



**Figure 5.** X-ray diffraction pattern of product aragonite.

### 3.3. Synthesis of Needle-Like Aragonite

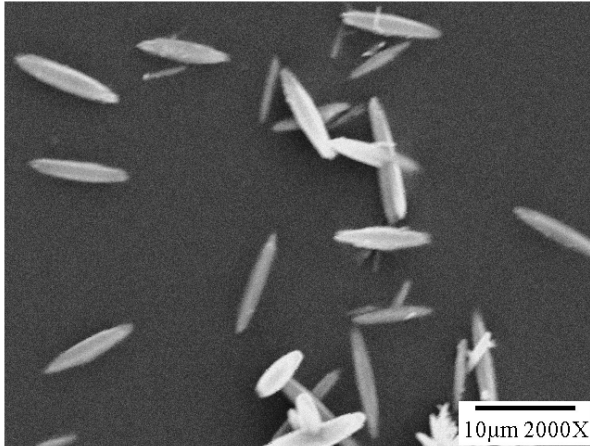
After complete dissolution of GCC, the reaction product suspension was bubbled with  $\text{CO}_2$  at lower temperature  $70^\circ\text{C}$ . At this temperature and under pure  $\text{CO}_2$  atmosphere an inverse reaction of (1) will happen:



Magnesium sulfate will be released. Therefore, magnesium sulfate only acts as additive in the synthesis of needle-like aragonite. Both magnesium hydroxide sulfate and gypsum are sparingly dissoluble salts. Dissolution equilibrium of magnesium hydroxide sulfate and gypsum will give low concentration of  $\text{Ca}^{2+}$ ,  $\text{OH}^-$  and  $\text{CO}_3^{2-}$ . Low concentration of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  means low supersaturation of calcium carbonate formation. It is well known that low supersaturation favors the formation of aragonite. The XRD pattern of calcium carbonate prepared in this way is given in Fig. 5. This indicates that almost pure aragonite was obtained. The SEM morphology of needle-like aragonite prepared in this way is given in Fig. 6. Some needle-like product can be seen. The length of the needle is  $9.13 \pm 1.02 \mu\text{m}$  and the aspect ratio is  $5.64 \pm 1.37$ .

## 4. Conclusion

GCC can be dissolved in aqueous solution of magnesium sulfate by reflux and air flushing. The dissolution reaction showed a second-order kinetics with respect to the concentration of magnesium sulfate. A reaction constant of  $0.0015 \text{ l}^{-3} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$  was obtained. The dissolution reaction gave fiber-like magnesium hydroxide



**Figure 6.** SEM image of needle-like aragonite.

sulfate and gypsum crystal. Needle-like aragonite can be synthesized from the dissolution product. CO<sub>2</sub> bubbling of the suspension at 70°C gave aragonite needles of  $9.13 \pm 1.02 \mu\text{m}$  in length with an aspect ratio of  $5.64 \pm 1.37$ . These results mean that needle-like aragonite can be synthesized with a reversible solution reaction from limestone without calcination.

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