Effect of the pH and Basic Additives on the Precipitation of Calcium Carbonate during Carbonation Reaction

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Abstract

CaCO₃ was synthesized under various basic conditions through carbonation reaction. CO₂ gas was blown into calcium hydroxide solution and the reaction pH was controlled constantly with NH₄OH and KOH aqueous solution at specific levels which are 12.5, 11.5, 10.5, 9.5 and 8.5. Each sample prepared was analyzed with X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM) and BET surface area. And concentration of Ca²⁺ ion of filtered solution was measured with inductively coupled plasma-atomic emission spectrometer (ICP-AES). It was found that the pH affect on the crystallization when the NH₄OH was used as pH control additives. In the case of the NH₄OH addition, the particle size grew larger with decreasing of pH and increasing of reaction time. Ammonia induced the calcium carbonate dissolution, so that the small nuclei were dissolved and re-precipitated on the surface of larger nuclei. Because of the effect of ammonia, calcite particle prepared grew gradually as the reduction of pH. On the contrary, there are not influences of pH for precipitation of calcium carbonate when the KOH solution was added. It was suggested that the additives to control pH affect on the precipitation of calcium carbonate rather than reaction pH.

Key words: Precipitated calcium carbonate (PCC), Basic condition, Additives

Introduction

High functional products such as paper, plastics, rubber and paint are developed and properties required of these are having been increasing. These improvements of properties are affected by shape, size, dispersion state and surface treatment of the filler.

The precipitated calcium carbonate is one of the most available fillers and has been attended by many researchers because the phase, shape and size of CaCO₃ can be controlled by the synthesis conditions like pH, temperature, ion concentration, ionic strength, CO₂ gas flow rate and additives. So that, many researchers had investigated roles of these factors.

However, it is not clear whether the reaction pH affects on the precipitation of CaCO₃. There are some reports about the pH influence; even so the results seem contradictory. J.G. Morales et al. were reported that the initial pH of the reaction determines the induction time which related with the onset of the precipitation. As the initial pH was low, induction time increased and meta-stable vaterite was synthesized rather than stable calcite. Likewise, P. C. Chen represented that the induction time decreased with pH increasing. Another result about the pH effect was published by N. Spanos. He presented that pH does not affect the phase transformation but the solution supersaturation affects on this. It was used KOH aqueous solution as pH control additives in above researches. Recently, Y. S. Han reported the pH effect on the crystallization of CaCO₃ in which ammonia was added to control the reaction pH. In this paper, solution pH influenced the CO₂ gas ionization and the supersaturation changed with form of carbonate ion.

The research about the reaction pH of CaCO₃ synthesis is worth investigating because of these
confused results. In this study, CaCO₃ was precipitated with carbonation reaction which the CO₂ gas was blown into the Ca(OH)₂ aqueous solution under specific pH level of 8.5~12.5. The pH was controlled constantly during carbonation reaction with the addition of ammonia.

Experiments

1) Carbonation reaction
5 g of calcium hydroxide (99% up, Kojundo chemical, Japan) was diluted with 500 ml of secondary distilled water in cylindrical glass reactor of 1 l. When pH of solution achieved above pH 12.6 and was kept constantly, CO₂ gas (99% up) was blown into the solution at a flow rate of 200 ml/min. From this moment, carbonation reaction occurred and the pH level decreased. In order to control reaction pH, 95 ml of 28% ammonia and 4% KOH aqueous solution which were pH 13.64 were dropped into the reaction solution. In this experiment, reaction pH was controlled form 12.5 to 8.5 and each reaction was finished at pH 12, 11, 10, 9 and 8. The slurry prepared was filtered and washed with absolute alcohol. The filtered solution was collected and diluted 100 times with water to analyze Ca²⁺ ion concentration using ICP-AES. The washed particle was filtered again and dried at room temperature in desiccators.

2) Characterization
During carbonation reaction, the pH and conductivity of the solution were measured with Corning pH meter 450 and conductivity meter 440. Phase of the precipitate was analyzed with XRD (M18XHF-XRA, MacScience Co.) measurement using CuKα radiation. The scanning step was 5°/min and 2θ range was from 10~60°. The shape and size of the particle were measured with FE-SEM (JEOL 6330F, Japan). Specific surface area was calculated with BET method (ASAP 2010, Micrometrics). Ca²⁺ ion concentration of the filtered solution was analyzed with ICP-AES (Shimadzu ICPS-1000IV).

Results and discussion

General process of carbonation occurs through below reactions.

\[
\text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^- \quad (1)
\]
\[
\text{CO}_2(g) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \quad (2)
\]
\[
\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-} \quad (3)
\]
\[
\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3 \quad (4)
\]

Because the carbonation reaction is involved Ca²⁺ and CO₃^{2-} ions, the nucleation moment is not decided with pH change. So, we would present the conductivity profile which changes with total amount of ions dissolved in solution such as Ca²⁺, OH⁻, HCO₃⁻, CO₃^{2-}, CaOH⁻ and CaHCO₃⁻. The controlling step in the carbonation is the dissolution of CO₂ gas [eq.(2)]. After the dissolution of CO₂, the generated CO₃^{2-} ion through equation (2) and (3) reacts with Ca²⁺ ion and formed CaCO₃ precipitate immediately. Consequently, the conductivity of the solution decreases steeply at the moment of the nucleation of calcium carbonate.

1) Control of the reaction pH with NH₄OH solution
When the Ca(OH)₂ is dissolved in water, it is known that the conductivity and pH of the solution are about 7 mS/cm and 12.6. Fig. 1 shows profiles of pH and conductivity of the reaction solution which is added ammonium hydroxide. Before the CO₂ gas is injected in reactor, Ca(OH)₂ ionizes
and then the conductivity and pH reach the values of above explanation. The conductivity achieves at about 7 mS/cm with equation (1). When CO₂ gas is injected into the reactor, the amount of ions in water decreases with reaction (5) and the conductivity reduces remarkably. This means that dissolved ions are nucleated into CaCO₃ within 10 minutes. All of the particles prepared in this research are stable calcite which is not dissolved almost in water and then the XRD graphs are not presented in paper.

The induction time which is same as nucleation time is within 10 minutes as shown in Fig. 1. After nucleation of calcite is finished, NH₄OH solution is added to control pH and CO₂ gas is blown continuously into the reactor. The conductivity of the solution increases again for the ions of NH₄OH and CO₂ gas dissolved. The reaction is ended when the reaction pH decreases below value kept.

The reaction time increases as the reaction pH is low. Though NH₄OH solution is weak base, it makes the solution pH keep basic for longer time during carbonation reaction. NH₄OH is weak base which is almost dissociated into the NH₃ and H₂O in aqueous solution. A small amount of it ionizes into NH₄⁺ and OH⁻ ions and then it indicates weak base [6].

In this research, H⁺ ions exist excessively in reaction solution because CO₂ gas is injected at constant flow rate and it is dissociated like equations (2) and (3). Excess H⁺ ions react with NH₃ in solution.

\[
\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+ \tag{5}
\]

pH decreasing of the reaction solution moderates because of the limitation of H⁺ ion increasing like equation (2) and (3).

Fig. 2 shows SEM images of the shape and size of particles which are precipitated at constant pH level. The CaCO₃ synthesized at pH 12 is almost 100 nm size and well dispersed. The BET surface area is 25.43 m²/g ± 0.05 and specific surface area is 23.44 m²/g which is calculated with mean particle size of 10 and equation (6). S means

\[
S = \frac{6}{d \rho} \tag{6}
\]

<table>
<thead>
<tr>
<th>Reaction pH</th>
<th>BET surface area</th>
<th>Mean particle size</th>
<th>Measured particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄OH</td>
<td>pH 12</td>
<td>25.32 m²/g ± 0.05</td>
<td>0.081 µm</td>
</tr>
<tr>
<td></td>
<td>pH 10</td>
<td>3.67 m²/g ± 0.01</td>
<td>0.56 µm</td>
</tr>
<tr>
<td></td>
<td>pH 8</td>
<td>5.42 m²/g ± 0.02</td>
<td>0.48 µm</td>
</tr>
</tbody>
</table>

**Table 1** BET surface area and particle size in the case of NH₄OH added.

Ammonia is oxidized in reverse way of equation (5) in water and make H⁺ ion spring up which
is know to dissolve the calcium carbonate precipitated. In the same manner of this, NH$_4$OH dropped in carbonate solution induces dissolution of the nuclei of calcium carbonate. The solubility increases as specific surface area of the particle increases, so that relatively small nuclei are more soluble than large those. Small particles are in the high solubility and relatively large particles are below in the low solubility condition in a heterogeneous system. In this case, small particles are favor to dissolve and re-precipitate on the surface of large particles through Oswald ripening. And crystals take the form of the most stable crystal shape. It can be verified that the Ca$^{2+}$ ion concentration in filtered solution is higher than the case of KOH addition with ICP-AES in Fig. 5. The concentration of calcium ion is kept high and continuous though pH level changes which says that the dissolution and re-precipitation of calcium carbonate occurs in this solution. This means that NH$_4$OH induces the CaCO$_3$ precipitated to dissolve. That is to say that the phenomena of dissolution and re-precipitation of small particles is accelerated with reaction time. The growth of particle occurs with increasing of reaction time as the pH decreases. And the growth of the particle progresses toward the most stable shape of calcite which is rhombohedral, so that the particle is an ellipsoid but the surface of the particle reveals step-like shape. Consequently, oxidation of ammonia induces H$^+$ ion generation and H$^+$ ion dissolves CaCO$_3$. Concentration of Ca$^{2+}$ ion is high, re-precipitation occurs on the surface of the large particles and calcite grows up to 2 µm.

2) Control of the reaction pH with KOH solution

KOH is strong base and then it ionizes quickly when it is added in water. OH$^-$ ions react with directly H$^+$ ions which are generated with ionization of H$_2$CO$_3$ in equation (2) and (3) and then pH decreases (Fig. 3). K$^+$ ion is known that co-precipitates with aragonite which is meta-stable phase and has larger lattice parameter than calcite. So that KOH addition does not affect on the processing time and crystallization of calcite. Ca$^{2+}$ con-
centration in Fig. 5 is lower than the case of NH$_4$OH addition. Fig. 4 shows SEM images of particle prepared with KOH addition. Likewise samples without additives, the particles just aggregate according to decreasing of reaction pH.

Conclusion

The most stable phase of calcium carbonate which is calcite was synthesized under various basic conditions and the effect of the reaction pH and additives were investigated with results of SEM and ICP-AES.

The reaction pH affects on the synthesis of calcium carbonate in carbonation when the NH$_4$OH adds to control the pH of the solution. The size of calcium carbonate increases and the surface of the particles take the clear form of step-like shape as the reaction pH decreases. Unlike NH$_4$OH, KOH does not vary the processing condition and the result of the product.

Consequently, the effect of additives added to control pH of the solution is larger than the reaction pH.

References