Synthesis of amorphous calcium carbonate by gas-liquid reaction and its crystallization

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Abstract: We obtained amorphous calcium carbonate through the carbonation reaction of $Ca(OH)_2$, and through this reaction, observed changes in particle shape and phase by electric conductivity, XRD and TEM analysis. According to the result of the analysis, in the first declining stage of electric conductivity, amorphous calcium carbonate that has formed is coated on the surface of $Ca(OH)_2$ and obstructs its dissolution, and in the first recovery stage of electric conductivity, amorphous calcium carbonate is dissolved and re-precipitated and forms chains of fine calcite particles linearly joined. In the second decline of conductivity, viscosity increases due to the growth of chains of calcite particles, and finally the calcite particles are dissolved and separated into colloidal crystalline calcite, thereby increasing electric conductivity again.

1. Introduction

 With its excellent properties such as low cost, high whiteness and opacity, inertness and non-combustibility, calcium carbonate powder is used, as part of composite materials for inorganic filler, for the manufacture of rubber, plastics, paints, paper, adhesives, etc., in large quantities, and is one of the major raw materials used in the cement and glass industries. Generally, calcium carbonate added to polymers improves the modulus of elasticity and dimensional stability of the composite material, but deteriorates molding and forming capability resulting from degraded plasticity as well as mechanical properties such as tensile strength and impact strength. This is because insufficient cohesion between the polymer material and the surface of calcium carbonate reduces dispersion. To improve the situation, it is possible to conduct the surface treatment of calcium carbonate, which, however, has the adverse effect of lowering the surface energy of the powder. Therefore, studies on ultra fine powder, which maintains the state of fine particles without surface treatment, and amorphous calcium carbonate with different properties from existing crystalline calcium carbonate have been expected. Such ultra fine or amorphous calcium carbonate can be utilized as not only filler but also a functional material such as adsorbent, calcium agent, pharmaceutical and food additive. In calcium carbonate with a wide variety of applications as industrial raw material as mentioned above, the shape of crystallization and the size of the particles can be very important factors depending on usage. Consequently, it can be assumed that precipitated calcium carbonate chemically formed through the calcination, hydration and carbonation of limestone is more advantageous than ground calcium carbonate produced by crushing limestone physically, in the control of such characteristics of crystallization as purity, shape, size, and size distribution.
 In this study we intended to examine the mechanism of generating calcium carbonate from gas-liquid contact reaction during the carbonation reaction of calcium hydroxide and to find out the specific properties of precipitated calcium carbonate by measuring changes in electric conductivity and pH in conditions with varied reaction temperatures and solvent agents.

2. Experimental Procedures

 We prepared $Ca(OH)_2$ emulsion by obtaining CaO from the calcinations of $Ca(OH)_2$ at 650℃ for an hour, injecting 25 grams of prepared CaO and 500 ㎖ of distilled water at room temperature, and allowing the mixture to react for 30 minutes while agitating the reactor at 600 rpm. We allowed reaction to proceed by placing the prepared emulsion in a liquid-gas reactor and injecting CO_2 gas at the flow rate of 1ℓ/min. At this time, reaction temperature was kept at 15, 30 and 50℃, respectively, and agitation continued at 600 rpm. Changes in electric conductivity and pH were continuously measured during the reaction. According to changes in the electric conductivity curve, we collected emulsion with a Pipet-Aid, suctioned and filtered it rapidly, dried it for 24 hours at 60℃ in a vacuum drying oven, and subsequently analyzed the dried powder by use of XRD and TEM analysis.

3. Results and discussions

Fig 1 shows changes in electric conductivity and pH under different temperature conditions in the forming process of calcium carbonate in the $Ca(OH)_2$-H_2O-CO_2 system. Closely inspecting the overall pattern of Fig. 1, we can see that the electric conductivity curves can be divided into four stages: first decline (a), first recovery (b), second decline (c) and second recovery (d), and at higher temperature the first decline zone tends to disappear and the second recovery occurs more rapidly. With regard to pH, it was confirmed that, at the initial value of 12 to 13, pH fell along with electric conductivity in the second decline stage.
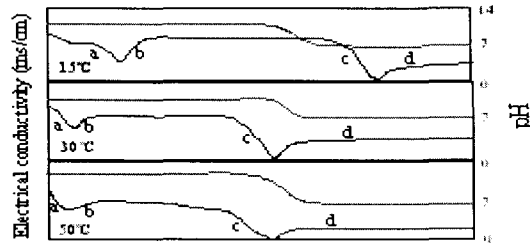

Fig. 1. Electrical conductivity curve and pH changes in $Ca(OH)_2$-H_2O-CO_2 system with variety temperature. (a:first decline stage, b:first recovery stage, c:second decline stage, d:second recover stage).

Fig. 2 and 3 show the results of XRD and TEM analysis on samples collected in each stage of (a) through (d) following changes in the electric conductivity curves. As shown in Fig. 2, at 15°C, the sample was amorphous in stage (a), and as the stage moved from (b) to (c), the peak of $Ca(OH)_2$ dropped and more crystalline calcium carbonate appeared. Also, according to Fig. 3, we noted that in stage (a) amorphous calcium carbonate formed, in (b) chain-shaped calcium carbonate formed, in (c) chain-shaped calcium carbonate grew, and in (d) chain-shaped particles fell apart individually, making colloidal precipitated calcium carbonate with sizes ranging from 0.02 to 0.04 μm. However at the reaction temperature of 30°C, it was observed that the peaks of $Ca(OH)_2$ and $CaCO_3$ coexisted from stage (a); as the stage moved from (b) to (c), the peak levels of $Ca(OH)_2$ disappeared and more chain-shaped calcium carbonate developed; finally colloidal precipitated calcium carbonate was created. At the reaction temperature of 50°C, the peak of calcium carbonate showed up in stage (a), and chain-shapes formed already in (a) and grew in (b) and (c) according to TEM analysis, finally creating colloidal precipitated calcium carbonate. Thus, as a result of XRD and TEM analysis according to the electric conductivity at different temperatures, the stages of formation of amorphous and chain-shaped material, the growth of chain shapes and the formation of colloidal precipitated calcium carbonate were most distinct at 15°C. In addition, the higher the temperature, the faster was the reaction with increased speed of forming chains and crystallization in general.
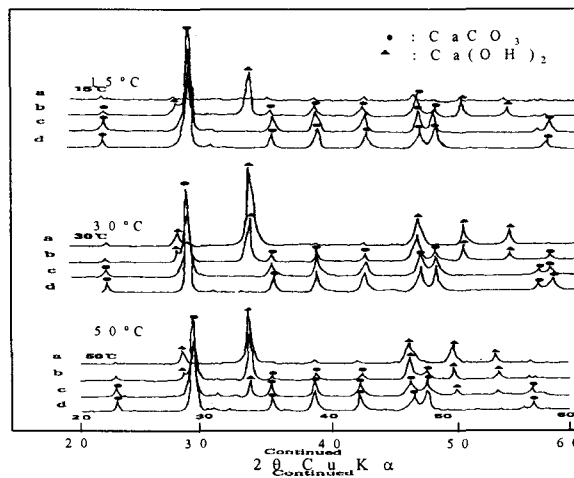

Fig. 2. X-ray dffraction patterns of $Ca(OH)_2$-H_2O-CO_2 system.

15 ℃

30 ℃

50 ℃
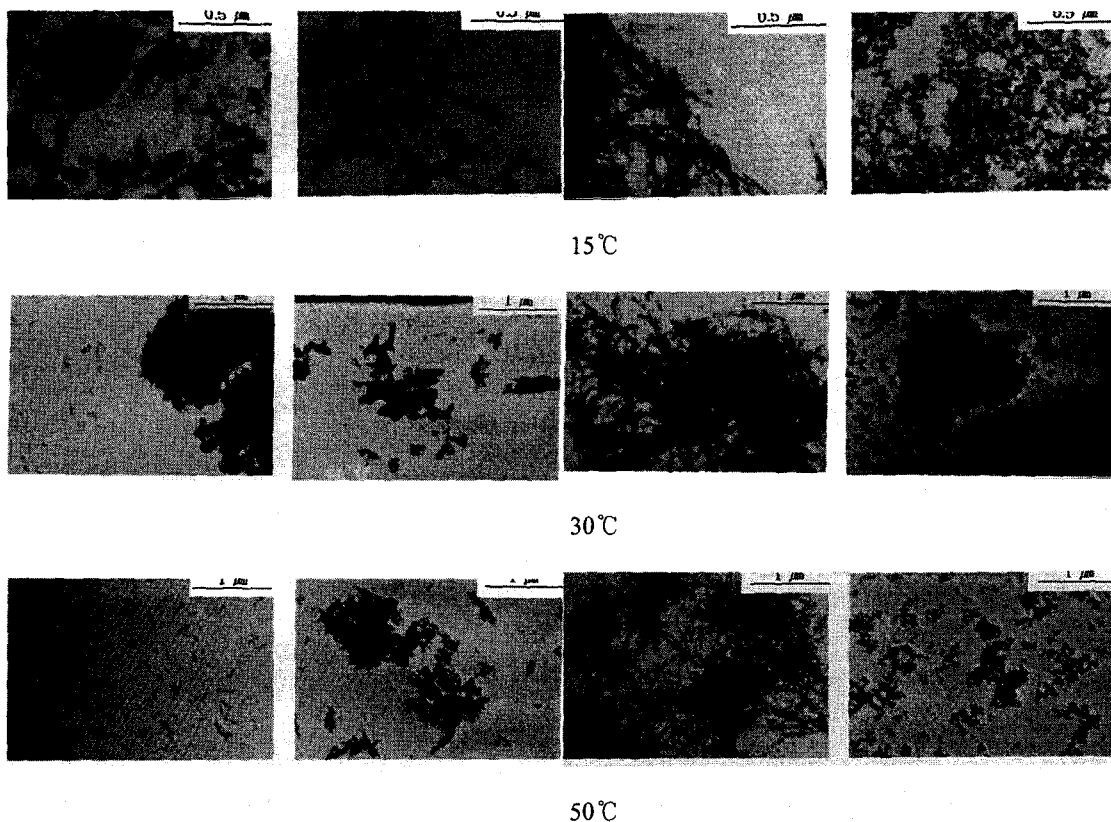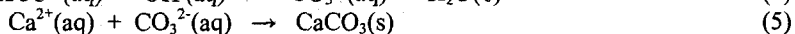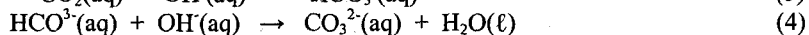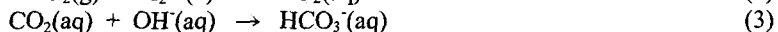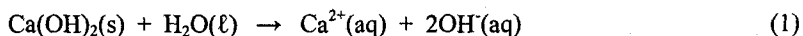
Fig. 3. TEM photographs for the specimens sampled at the point electrical conductivity.

Stage (a) (First decline stage)

Six types of ions: OH^-, HCO_3^-, CO_3^{2-}, Ca^{2+}, $CaHCO_3^-$ and $CaOH^+$ influence electric conductivity in $Ca(OH)_2$ emulsion, and therefore in the process of forming the precipitate, the dissolution of $Ca(OH)_2$ can be assumed as a major factor that influences changes in electric conductivity. In the electric conductivity curves in Fig. 1, Ca^{2+} ions and CO_3^{2-} ions that have been dissolved react momentarily and form amorphous calcium carbonate, and it is judged that the first decline stage results because amorphous calcium that has formed coats $Ca(OH)_2$ and obstructs its dissolution. According to Juvekar's film theory on mass transfer resistance in 5-step carbonation[9], there are three types of resistance, namely resistance through gas film, through liquid film on the side of gas-liquid boundary, and through liquid film on the side of liquid film on the side of solid-liquid boundary, of which one through gas film is the fastest, and because the third, fourth and fifth steps of the 5-step reaction are very rapid, rate limiting steps are the first step, the dissolution reaction of $Ca(OH)_2$ through liquid film, and the second one, the absorption reaction of CO_2 gas.

$$Ca(OH)_2(s) + H_2O(\ell) \rightarrow Ca^{2+}(aq) + 2OH^-(aq) \qquad (1)$$
$$CO_2(g) + H_2O(\ell) \rightarrow CO_2(aq) \qquad (2)$$
$$CO_2(aq) + OH^-(aq) \rightarrow HCO_3^-(aq) \qquad (3)$$
$$HCO^{3-}(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(\ell) \qquad (4)$$
$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) \qquad (5)$$

The location of reaction interface is determined by the difference between the dissolution speed of $Ca(OH)_2$ and the absorption speed of CO_2 gas or the difference between the concentration of $Ca(OH)_2$ and the supply quantity of CO_2 gas, such that the crystal precipitation takes place, at liquid film on the side of gas-liquid interface in case the

former is faster, and at liquid film on the side of solid-liquid interface if the latter is faster. It is judged that CO_2 gas absorption reaction in calcium carbonate occurs when reaction interface is at liquid film on the side of solid-liquid interface and the reaction product precipitates and adheres to the surface of the solid.

Under the conditions of this experiment, we can assume that the reason of decrease in electric conductivity at the initial stage of the reaction is that the supply speed of CO_3^{2-} ion is faster than that of Ca^{2+} ion. It is also believed that the location of the reaction interface moves from liquid film on the side of a gas-liquid interface to that on solid-liquid interface as the reaction moves on. In addition, at liquid film on the side of the solid-liquid interface, amorphous calcium carbonate covers the particle surface of $Ca(OH)_2$ and suppresses its dissolution, causing electric conductivity to decline.

Stage (b) (First recovery stage)

As can be seen in the result of TEM analysis (Fig. 3), the major change before and after the first recovery stage is the transfer of amorphous calcium carbonate into chain-shaped calcite. Accordingly, the first recovery in electric conductivity is assumed to be the process whereby $Ca(OH)_2$ particles whose dissolution was obstructed by amorphous calcium carbonate are transferred into chain-shaped calcite, losing the coating and resuming dissolution. That is, the first recovery of electric conductivity can be said to be essentially caused by re-dissolution of $Ca(OH)_2$, and the mode of transfer of calcium carbonate depends on the pH of the emulsion. If the concentration of $Ca(OH)_2$ is high during the first recovery stage, the apparent viscosity of the emulsion rises, which is assumed to be a result of entanglement between calcite chains. The recovery induction period of electric conductivity may be called the induction period of transfer from amorphous calcium carbonate to calcite chains.

Stage (b) through (d) (Second recovery stage after the first recovery stage)

The reaction in the first recovery stage can be seen as the growth reaction of chain-shape calcite. That is, because there are many calcite chains, due to the transfer of amorphous calcium carbonate, dissolved Ca^{2+} and CO_3^{2-} ions do not form new nuclei but are diffused and educed on the surface of calcite chains. After the first recovery, while un-reacted $Ca(OH)_2$ solids continue dissolving until consumed, the electric conductivity is assumed to gradually decline through changes in solid concentration following the reaction, finally causing the second decline accompanied by the removal of solid.

The second recovery takes place when calcium carbonate that has formed is re-dissolved into calcium hydrogen carbonate with higher solubility. In Fig. 3, it can be observed that calcite chains disassemble one after another into particles with sizes ranging 0.02 to 0.04 μm.

In conclusion, during the first stage of declining electric conductivity, amorphous calcium carbonate forms; in the first recovery, chain-shaped calcite forms by dissolution and precipitation of amorphous calcium carbonate; up to the second decline particles that constitute these chains continue to grow; and in the second recovery, colloidal calcium carbonate is created by the disassembly of calcite chains.

4. Conclusion

In accordance with the first decline and recovery and the second decline and recovery of electric conductivity following the carbonation reaction of $Ca(OH)_2$, we could clearly distinguish the stages of the formation of amorphous calcium carbonate, the formation and transfer of chain-shaped calcite, and the formation of crystalline calcium carbonate. We confirmed that the first decline stage of electric conductivity is a result of the process of forming amorphous calcium carbonate, and in the first recovery, unstable amorphous calcium carbonate dissolved and precipitated and formed chains of fine calcite particles joined side by side. In the second decline, viscosity increases by the growth and entanglement of calcite chains, and in the second recovery, the bonding parts of chains are dissolved and colloidal crystalline calcite particles form individually.

References

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