수성 에탄올과 이소프로판올 용액에서의 탄산칼슘 특성에 관한 연구

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A Study on the Characteristics of Calcium Carbonate in Aqueous Ethanol and Isopropanol Solutions

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Introduction

Calcium carbonate, as one of most widely existed biominerals produced by organisms, has three crystal phases calcite, aragonite, and vaterite[1,2]. The calcium carbonate used in industries could be classified into limestone powder, ground calcium carbonate, and PCC by their shape, particle size and preparation method. PCC is synthesized by modifying the morphology of calcium ore and by using the compound that has a calcium and carbonate radical. Due to its properties such as uniform shape and size, which are more effective than any other type CaCO₃, applications of PCC are as diverse as rubber, plastics, paper, paints, food, adhesives, and so on.

From an aqueous slurry of Ca(OH)2 suspension, CaCO₃ can be synthesized via a couple of processes such as coprecipitation or the carbonation route [3–5]. The coprecipitation method is often adapted in a laboratory study because of its simplicity of operation or its ease in the control of process variables. The most widely used method to synthesize CaCO₃ on an industrial scale is the carbonation route [6,7] which consists of bubbling CO₂ gas through the aqueous slurry of Ca(OH)₂ in a batch process, due to its low cost and the availability of the raw materials[8]. This paper intends to investigate the effect of aqueous ethanol and isopropanol solutions as a solvent on the morphology of precipitation of calcium carbonate in the carbonation process. We focus on the synthesis of PCC in ethanol and isopropanol as a solvent and how PCC was synthesized at constant experimental conditions.

Results and discussion

To investigate the effect of ethanol and isopropanol solution as a solvent on the morphology of PCC at constant experimental conditions in the carbonation process, the calcium carbonate was precipitated in pure ethanol, in pure water and in the five kinds of ethanol(20~80mol%)water mixing solutions. Also calcium carbonate was precipitated in the four kinds of isopropanol(2~10 mol%)-water mixing solutions. Each solution, a suspension of 30g of Ca(OH)₂ (Junsei, EP.) in 500ml of each solvent, was prepared in the Pyrex reactor(Φ =120mm; *h*=150mm) as shown in Fig. 1.

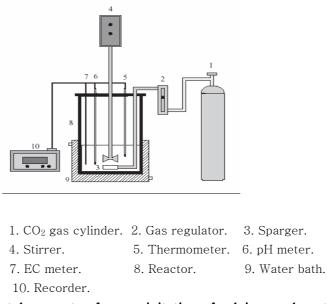
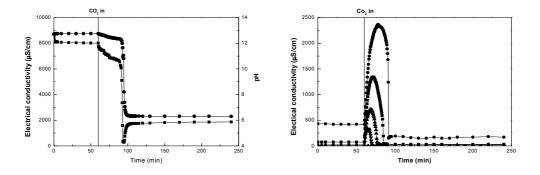
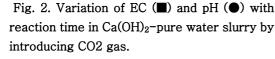
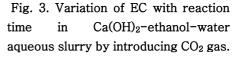


Fig. 1. Experimental apparatus for precipitation of calcium carbonate.

1. Precipitation of CaCO₃ in pure water and in ethanol water mixing solution as the solvent



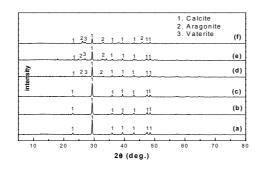




The traditional carbonation experiment in pure water was carried out at 25 °C. It's EC and pH variations are shown in Fig. 2 and the traditional carbonation trend clearly appears. After 36min of carbonation reaction, the dissolving rate of CO₂ is larger than its consumption rate, owing to the limited amount of Ca²⁺, resulting in the accumulation of HCO₃⁻, CO₃²⁻, and H⁺

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ions and the increase of the EC. However, very different EC variations of more than 20mol% ethanol added to the pure water as the solvent were as shown in Fig. 3. The five kinds of solvent including pure ethanol have protruding peaks. The height and width of the peaks become even bigger with the increase in water composition. These mean that the introduced CO_2 gas in water could make more than 100times the HCO_3^- and $CO_3^{2^-}$ than those in ethanol, and the formation of HCO_3^- and $CO_3^{2^-}$ in ethanol is so unstable that this reaction would be more reversible. The XRD peaks of $CaCO_3$ synthesized under these conditions including pure water are shown in Fig. 4. In the solution of less than 40mol% ethanol, the PCC is all calcite; therefore, water has a dominant effect as the solvent.



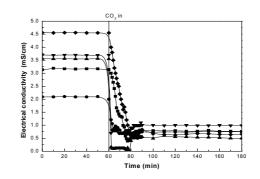


Fig. 4. X-ray diffraction patterns of the calcium carbonate precipitated: from (a) pure water; (b) 20 mol% EtOH; (c) 40mol% EtOH; (d) 60 mol% EtOH; (d) 80 mol% EtOH; and (e) pure EtOH.

Fig. 5. Variation of EC with reaction time in Ca(OH)₂-isopropanol-water aqueous slurry by introducing CO₂ gas: (a) 2mol% isopropanol
(●); (b) 4mol% isopropanol (■); (c) 6mol% isopropanol (▲); (d) 8mol% isopropanol (▼); and (e) 10mol% isopropanol (♦).

2. Precipitation of $CaCO_3$ in isopropanol water mixing solution as the solvent

To make the precipitation steps clear for PCC in isopropanolwater mixing solution, the variations of EC in the suspension of $Ca(OH)_2$ isopropanolwater mixing solution were shown in Fig. 5. Increase of isopropanol composition increased the initial EC. By introducing the CO₂, each EC dwindled to 0.5~1.0mS/cm. This time, five kinds of typical PCC were obtained as shown in Fig. 6.

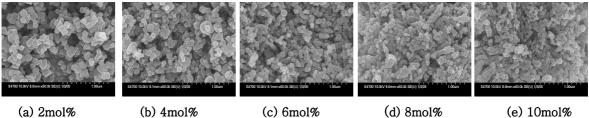


Fig. 6. Scanning electron micrographs of CaCO₃ inpresence of isoprpanol and water.

When calcium carbonate was formed in the low concentration of isopropanol (less than 2mol %), it appeared as the cubic type. However, the high concentration of isopropanol (more than

4mol %) brought colloidal calcium carbonate. Also, in case of isopropanol additive system, calcite, which was the most stable form of PCC, was dominant. This mean that particle size of PCC and PCC type can be controlledin the isopropanol-water system. However, effect of reaction temperature, Ca(OH)₂ concentration, CO₂ flow rate etc.. may have to be considered to create equal particle.

Conclusion

Particle size and types of PCC could be controlled in ethanol-water and isopropanol-water solution systems. In the aqueous solution of less than 40 mol% ethanol, PCC is all calcite; therefore, water has dominant effect as the solvent. On the other hand, in the solution of more than 60 mol% ethanol, the solvent acts as the pure ethanol and calcite, aragonite and vaterite can be precipitated.

PCC from homogeneously dispersed 0.1µm to heterogeneous 0.2µm could be obtained in isopropanol-water system. When calcium carbonate was formed in the low concentration of isopropanol (less than 2mol %), it appeared as the cubic type. However, the high concentration of isopropanol (more than 4mol %) brought colloidal calcium carbonate.

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