

Precipitation of CaCO₃ crystals from various solution conditions

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1. Introduction

The calcium carbonate minerals formed from various natural environments exhibit characteristic surface morphologies depending on their growth solution conditions and secondary alteration histories. The highly supersaturated solutions often growing minerals of more complicated surface morphology and the diluted solutions precipitate minerals of less complicated surface morphology (Mullin, 1991).

Surface-sensitive microscopic and spectroscopic techniques illustrate that the chemical reactivity of solid surface plays a crucial role in dissolution and sorption reactions (Liang and Baer, 1997). To understand metals interaction on calcium carbonate surface it is important to study the conditions of precipitating carbonate minerals as well as the surfaces of different polymorphs of calcium carbonate.

The aim of this work was to present the effect of solution supersaturation of calcium and carbonate on the developing nature/morphology of the calcium carbonate precipitates.

2. Experimental method

The calcium carbonate, CaCO₃, crystals were prepared by a spontaneous precipitation method from solutions of three different ratios of total calcium, [Ca]_T, over total carbonate, [CO₃]_T. The CaCO₃ precipitating solutions contain total calcium to total carbonate ratios as follows: [CO₃]_T/[Ca]_T >1, [CO₃]_T/[Ca]_T =1, and [CO₃]_T/[Ca]_T <1.

In this study, the calcite precipitation was started by mixing two concentrated solutions of CaCl₂·2H₂O and (NH₄)₂CO₃ in a 1000ml glass reaction vessel. The reaction vessel was immersed in a temperature controlled water bath at 25C and 1atm pressure, and continuously stirred by rotating the propeller at 250 - 300 rpm. The reaction vessel was covered by an acrylic plate but not sealed. When the two solutions were mixed, calcium carbonate crystals was started to precipitate almost instantaneously. The precipitation was usually lasted for a few minutes.

The mean size of the calcium carbonate precipitates was also measured by SEM observation and the surface areas of calcium carbonate precipitates were determined with the Brunauer-Emmett-Teller (BET) method. The phase identification and the purity analysis of the synthetic calcium carbonate precipitates crystals were done by a Philips X-ray diffractometer and the morphology and phase identification of CaCO₃ crystals were examined using a field emission scanning electron microscope (SEM).

3. Results and discussion

The CaCO₃ precipitated from $[\text{CO}_3]_{\text{T}}/[\text{Ca}]_{\text{T}} \geq 1$ supersaturation was mostly calcite with less than 1% of vaterite, while the CaCO₃ crystals precipitated from $[\text{CO}_3]_{\text{T}}/[\text{Ca}]_{\text{T}} < 1$ conditions were dominated by vaterite crystals with less than 1% of calcite crystals present. The CaCO₃ crystals showed a direct relationship among the observed surface morphologies, the size, and the surface areas of each precipitates. As the grain size increased, the surface area decreased. But the increased surface roughness increased the surface area. According to this study, it appears that the surface area of CaCO₃ precipitates was mainly affected not by the calcium concentration but by the carbonate concentration during the spontaneous precipitation. The surface roughness of vaterite increased with decreasing $[\text{CO}_3]_{\text{T}}$ from 0.8 and 0.5 of $[\text{CO}_3]_{\text{T}}/[\text{Ca}]_{\text{T}}$ ratios and the surface area of vaterite increased from 5.64 - 7.34 to 8.39 - 10.3.

4. Conclusions

Each CaCO₃ crystals exhibited characteristic surface morphologies depending on their solution compositions. The CaCO₃ precipitated from the solutions of different supersaturation conditions demonstrated a direct relationship among the observed surface morphologies, the surface areas, and the size of each CaCO₃ precipitates. The measured surface area of calcite showed a maximum value of 1.56 m²/g while the maximum surface area of vaterite was 10.3 m²/g although the mean size of both calcite and vaterite were similar. The fundamental differences in the nature of surfaces would lead to have different surface morphologies as well as different reactivity for each metal ion interested (Titiloye et al., 1998). The increased surface areas as well as the increased number of high energy surface site may play an important control on the metal ions surface reactions during removal or dissolution processes.

5. References

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