Crystallization behavior of calcium carbonate polymorphs and the effect of magnesium ion

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The crystallization of calcium carbonate was carried out by mixing the $CaCl_2$ and Na_2CO_3 solutions , and the crystallization and transformation behavior of the polymorphs, and the effect of additives are investigated. It appeared that at 298 K both calcite and vaterite crystals tend to crystallize , however, the vaterite content is larger at 0.2mol/l than that at 0.05 mol/l. The transformation rate and the of calcium ion concentration at the stationary value changes with the feed concentration of $CaCl_2$. With magnesium chloride the transformation was retarded and the concentration of calcium ion was also influenced.

1. Introduction

Crystallization of calcium carbonate in sea water, i.e. biomineralization through seashells, is important problem in relation with the fixation of carbon dioxide in atmosphere. On the other hand, calcium carbonate is used as various materials in industries. However, calcium carbonate has three polymorphs of vaterite, aragonite and calcite[1]. As the physical properties as density, morphology of the calcium carbonate crystals depend on the polymorphs, the control of the polymorphism is required eagerly in industries. The crystallization behavior of the $CaCO_3$ polymorphs is influenced by the impurities and operational conditions. In this work the crystallization behavior of calcium carbonate polymorphs and the effect of additives was investigated.

2. Experimental

The crystallization of calcium carbonate was carried out by adding 0.05 or 0.2 mol/l concentrations of Na_2CO_3 solution to the same concentrations of $CaCl_2$ solution in the stirred tank crystallizer. The feed rate of Na_2CO_3 solution was changed As an additive, $MgCl_2 \cdot 6H_2O$ was dissolved in $CaCl_2$ solution previous to the crystallization. The concentration of calcium ion was measured by the ion selective electrode. The polymorphous composition was analyzed by X-ray diffraction measurement (XRD).

3.Result and Discussions

3. 1 . 0.05 mol/l solution

After the mixing of Na_2CO_3 and $CaCl_2$ solutions the concentration of calcium ion decreased and attained to the stationary values. Both calcite and vaterite crystallized, however, the addition rate of sodium carbonate solution affects on the composition and with slower addition rate (0.05ml/s) vaterite composition increased. With elapsed time the calcite content linearly increased (Fig.1). With microscopic observation it was confirmed that the transformation from vaterite to calcite proceeds via solution - mediated mechanism.

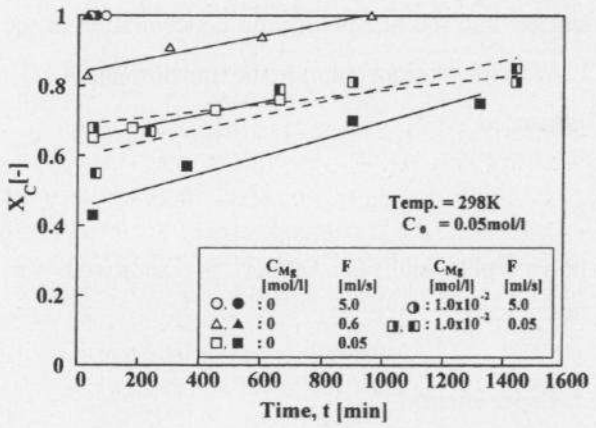

Fig. 1. Precipitation and transformation behavior of polymorphs.

3.2. 0.2 mol/l solution

When the solution concentrations are 0.2 mol/l, both calcite and vaterite also crystallizes. However, the content of vaterite seems to be larger than that in the case of 0.05 mol/l. (Fig.2). This means that the crystallization of vaterite is accelerated at the higher supersaturation. Furthermore, the stationary value of the calcium concentration at 0.2 mol/l was higher than that at 0.05 mol/l. When magnesium chloride was added in the solution, the transformation rate was retarded in comparison with that in the pure solution and the calcite content seems to increase slightly(Fig.2). Such effect of magnesium ion seems to be different from that in the case of 0.05 mol/l.

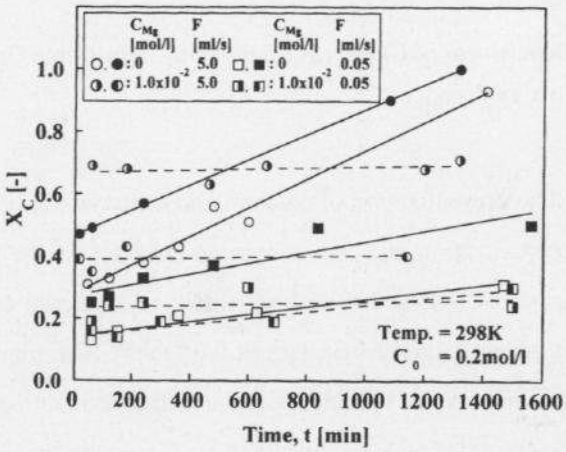

Fig. 2. Precipitation and transformation behavior of polymorphs

4 .Conclusion

The calcium concentration decreased rapidly after the mixing of Na_2CO_3 and $CaCl_2$ solutions and attained to the stationary values. Both calcite and vaterite crystallized and the transformation proceeds linearly. Mg ion retards the transformation rate.

5 . Acknowledgement

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