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Qualitative discussion of prenucleation cluster role in crystallization of calcium carbonate under high concentration of magnesium based on experimental phenomena

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Crystallization of calcium carbonate under high concentration of magnesium was studied. Interesting phenomena were observed. Approximately 80% of calcium ions stably existed in the solution up to 60 min after amorphous calcium carbonate was separated by centrifugation, and induction time was significantly affected by concentration and feeding rate of sodium carbonate when other operating conditions remained unchanged. Experiments and computer simulation have proved that prenucleation cluster exists during crystallization of calcium carbonate in solutions. This paper tried to figure out specific crystallization process of calcium carbonate under high concentration of magnesium, and to interpret unforeseen phenomena combining with the idea of prenucleation cluster. With regarding prenucleation cluster which can incorporate magnesium into its structure as amorphous calcium carbonate, most of the phenomena including significant influence of local mixing could be better understood. Prenucleation cluster played an important role in crystallization of calcium carbonate, which was related to the induction time, morphology and final product, thus more fundamental studies of prenucleation cluster structure and magnesium role in it should be done.

1. Introduction

Calcium carbonate possesses many types of polymorphs, such as calcite, aragonite, vaterite and ACC (Amorphous Calcium Carbonate). Many bio-mineralizing organisms utilize the ACC to precisely control the particle shape and crystalline of their sells or spines precisely [1]. Abiotic and biogenic formation of calcium carbonate minerals (e.g. calcite) occurs in a wide range of natural environments (e.g. soils and calcifying marine plankton), and is a key component of the global carbon cycle [2]. Calcium carbonate precipitation is also one of main problems of desalination and some other industrial processes. Great interest in studying crystallization of $CaCO_3$ has been generated to understand its crystallization mechanism, due to its non-classical crystallization phenomena.

Studies indicate that multiple nucleation pathways of $CaCO_3$ may simultaneously occur, including crystallizing directly from solution and indirectly through transformation of amorphous precursors [3]. After mixing of high concentration of Na_2CO_3 solution and $CaCl_2$ solution, ACC comes into being firstly. Usually ACC will transform into more stable polymorphs rapidly (seconds to minutes) [2]. Vaterite, aragonite or calcite crystallizes out of solution via ACC (dissolution-reprecipitation) or directly [2–5]. Vaterite also will transform into more stable polymorphs such as aragonite or calcite, due to its unstable characteristic [6]. The evolution of $CaCO_3$ polymorphs has been detailedly studied via latest technologies such as small- and wide-angle X-ray scattering (SAXS/WAXS) or in situ transmission electron microscopy (in situ TEM) [3,6,7]. Although some processes such as direct formation of calcite and aragonite and transformation of ACC to aragonite or calcite, have been observed directly, the detailed microscopic processes remain unclear and controversial, because crystallization of calcium carbonate is rapid (within minutes) and often via multi-pathways which are difficult to be distinguished from each other. Nucleation is one of the key step in the crystallization, which is difficult to study in detail due to its short time and micro- scale space [6,8].

The nucleation of $CaCO_3$ is believed to present non-classical and multistep mechanism. Other than abiding by classical nucleation theory, which was first developed by Gibbs, multistep nucleation pathways of calcium carbonate minerals have been discovered and debated. Several considerable studies have promoted understanding about multistep nucleation pathways of calcium carbonate minerals. cryo-TEM analysis revealed that pre-nucleation

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clusters with dimensions of 0.6–1.1 nm which were smaller than ACC (several ten nanometers). Pre-nucleation cluster is quite stable rather unstable as predicted by classical theory and could be the primary material of ACC and nucleation [5]. Computer simulation also indicates the existence of pre-nucleation clusters (liquid cluster), and verifies its fast nature of reaction [9–11]. The prenucleation cluster is disordered, flexible and strongly hydrated which could be as small as several ions [9].

ACC can incorporate lots of Mg^{2+} ions in its structure, due to its hydrated and disordered nature and similar properties of calcium ion and magnesium ion [12,13]. Therefore, Mg^{2+} can be incorporated into their structure as calcium. Prenucleation cluster is more disordered and hydrated than ACC, it is also believed that ACC is formed by agglomeration of pre-nucleation clusters [11,14,15]. The hindrance effect of Mg^{2+} on the crystallization of calcium carbonate has been discovered and reported, and it is believed that stable crystalline polymorphs (calcite and aragonite) come into being later (several minutes to hours) due to stabilization of ACC-Mg (Amorphous Calcium Carbonate with magnesium) and vaterite by Mg^{2+} [7,8]. This phenomenon allows the possibility to study evolution of ACC-Mg and the process of crystallization of calcium carbonate in detail. The important influence of Mg^{2+} on crystallization of calcium carbonate manifests that pre-nucleation cluster and ACC may play an important role in the crystallization of calcium carbonate.

Demichelis et al. pointed out that it is improper to name cluster form of calcium carbonate as 'pre-nucleation cluster', because clusters of calcium and carbonate ions also existed after nucleation. Therefore they referred this stable cluster form as calcium carbonate dynamically ordered liquid-like oxyanion polymer (DOLLOP) [9]. However, this study still refers it as pre-nucleation cluster (Prc) as it has been widely accepted.

This research aims to explain non-classical phenomena of calcium carbonate crystallization in the experiments under high concentration of Mg^{2+} by assuming that pre-nucleation cluster with magnesium (Prc-Mg) plays an important role in crystallization of calcium carbonate, which cannot be well interpreted by classical crystallization ideas. Calcium carbonate crystallization under high concentration of magnesium is slower than under general condition. Thus, processes are easy to be observed, and we try to reveal the role of Prc-Mg in nucleation according to the phenomena observed in experiments. Maybe, this mechanism can be generalized to nucleation in other circumstances and crystallization of other materials.

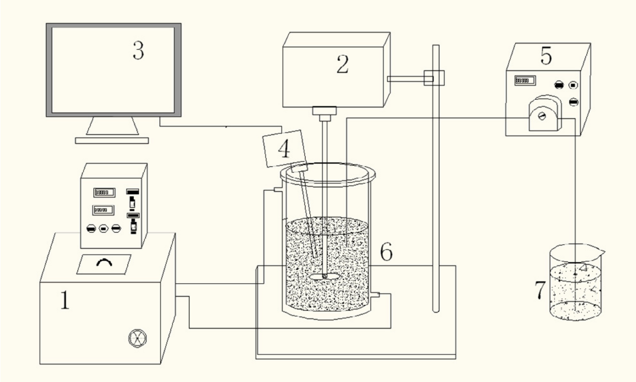

Fig. 1. Schematic diagram of experiment set-up: 1-Water bath; 2-Stirrer; 3-Computer; 4-FBRM; 5-Peristaltic pump; 6-$CaCl_2$ and $MgCl_2$ solution; 7- Na_2CO_3 solution.

2. Materials and methods

Schematic diagram of experiment set-up is shown as Fig. 1. The reactor is a 500 mL glass vessel with rapid agitation by a stirrer (EUROSTAR 20 digital, IKA, Germany). Solution of sodium carbonate (Na_2CO_3, AR, Shanghai Lingfeng) was injected into mixing solution of calcium chloride ($CaCl_2$, AR, Sinopharm) and magnesium chloride ($MgCl_2 \cdot 6H_2O$, AR, Sinopharm) by a peristaltic pump. The solution temperature was controlled by a thermostatic water bath (DC2006, SHP, China). The particle number in the solution was monitored by Focused Beam Reflectance Measurement (FBRM, Lasentec S400A, Mettler Toledo, USA) which recorded 30 times per minute.

Experiments were carried out by injecting Na_2CO_3 solution (20 ml, 0.2 mol/L) into mixing solution of 0.01 mol/L $CaCl_2$ and other salts (400 ml) in a stirred glass reactor (300 r/min). The concentration of NaCl, Na_2SO_4 and $MgCl_2$ set as 0.47 mol/L, 0.03 mol/L and 0.06 mol/L separately when we studied the influence of individual salt in the seawater on crystallization of calcium carbonate. And brine was sampled directly from the sea near Tangshan, China. In experiments studying ACC-Mg and concentration of calcium and magnesium in the solution varied with time, solution of sodium carbonate was injected into mixing solution of calcium chloride and magnesium chloride. The mixing ratio of Ca^{2+}/CO_3^{2-} was 1:1 and the volume ratio V ($CaCl_2$ 0.01 mol/L, $MgCl_2$ 0.06 mol/L) to V (Na_2CO_3) was 400 ml/20 ml. This was also the experimental condition of study the influence of feeding speed. When studying in the influence of sodium carbonate volume, sodium carbonate solutions were prepared by dissolving 0.004 mol sodium carbonate into 5 ml, 10 ml, 20 mL and 40 mL separately. All the experiments were performed at 30 °C, 300 r/min, and pH was not strictly controlled.

The size and distribution of particles in solution were measured by FBRM. The probe was rinsed thoroughly by distilled water before it was immersed in solution， and then Na_2CO_3 solution was added. Solid phase in the solution at different times after mixing was centrifuged at 5000 rpm and filtered out by micro-filtrate membrane, and solution separated was analyzed by Inductive Coupled Plasma Emission Spectrometer (ICP-OES, ARCOS, SPECTRO, Germany). Some of the solids were analyzed by Raman, before they were washed and dried off for maintaining their existential state in the solution to avoid interference of drying. The residual solid phase was washed by isopropanol and dried off at 50 °C under vacuum to prevent solid phase from transforming into crystalline forms, then the solid phase became stable [13]. All solid powders were prepared by this method in this study. Subsequently, the dried solid phase was analyzed by X-ray Powder Diffraction (XRD, D8 Advance, Bruker) and Field Emission Scanning Electron Microscope (FESEM, Nova NanoSEM 450, EU). After solid phase was dissolved in diluted hydrochloric acid, contents of calcium and magnesium were measured by ICP-OES.

Possible paths of formation of stable crystal under condition of high concentration of Mg^{2+} are illustrated in Fig. 2, ion direct transformation into crystal and ACC following route 1 is well known as classical nucleation theory. Route 3 is believed to be dissolution-precipitation process based on observed results of in situ TEM and scattering XRD [3,6]. ACC-Mg can be formed by attachment of Prc-Mg as route 6 and simulation， and experiment have given evidence of route 4 [5,9,10,16]. This study focused on discussing possible route via Prc-Mg, which can be the main raw material of ACC and crystal, and this route is shown as route 5 and route 6.

3. Results

Magnesium exhibits significant influence on the induction time of crystallization of calcium carbonate. Induction time means the