



Synthesis of peanut-like calcium carbonate intermediates in silica system containing partially hydrolyzed polyacrylamide and heavy alkyl-benzene sulfonate

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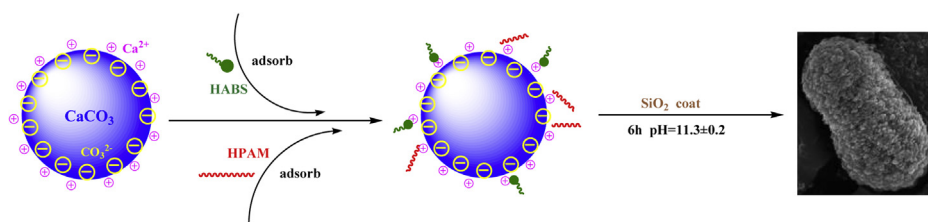
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HIGHLIGHTS

- HPAM and HABS roughen the surfaces of CaCO_3 particles.
- CaCO_3 underwent morphological transformation from spherical to cubic-like shape.
- Peanut-like CaCO_3 intermediates were obtained ascribe to package action of SiO_2 .

GRAPHICAL ABSTRACT



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ABSTRACT

Calcium carbonate (CaCO_3) crystals with various morphologies and polymorphs were synthesized from the aging calcium chloride (CaCl_2) and sodium carbonate (Na_2CO_3) solution using inorganic silica as well as organic partially hydrolyzed polyacrylamide (HPAM) and surfactant heavy alkyl-benzene sulfonate (HABS) as effective crystal growth modifiers by the rapidly mixing method at 45°C . The effect of different additives on controlling calcium carbonate morphology has been investigated by field emission scanning electron microscopy (FESEM), fourier transform infrared (FT-IR) spectrometer and X-ray diffraction (XRD). Peanut-like CaCO_3 particles were successfully obtained after the mixture system being aged for 6 h at pH of 11.3 ± 0.2 , and the transition from sphere through peanut-like shape to cubic shape for CaCO_3 particles occurred with increasing of aging time. All the CaCO_3 particles were pure calcite when pH was unadjusted ($\text{pH} = 11.2 \pm 0.1$), however, lower pH favored the formation of vaterite. The research results showed that the adsorption of HPAM and HABS on SiO_2 -coated CaCO_3 surfaces played a crucial role in modifying the crystals morphologies. A hypothetical mechanism for the formation process of the peanut-like CaCO_3 was presented.

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1. Introduction

As one of the most important and abundant minerals in nature, synthesis and shape-control of calcium carbonate (CaCO_3) crystal has been studied in great detail due to its wide industrial applica-

tion in paint, plastics, rubber and paper industries [1–6]. However, it is also responsible for serious problems caused by incrustation and scaling in flow devices and water pipelines ascribe to spontaneous precipitation at elevated temperatures [7]. CaCO_3 exists three polymorphic forms in nature: calcite, vaterite and aragonite, and thermodynamically their stability increases in the sequence of vaterite, aragonite and calcite [8].

Many studies showed that the presence of foreign ions or other substances not only could change the precipitation rate of CaCO_3 ,

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but also could define the nature of the precipitation phases and their morphology. Loste's [9] experiments demonstrated that Mg incorporation within amorphous calcium carbonate (ACC) significantly retarded transformation into crystalline phases, and that this effect increased with the quantity of Mg occluded within the ACC structure. Zinc, manganese and other elements inhibit the growth of CaCO_3 crystals through the formation of relevant carbonate precipitates on the active site of the crystal surface [10–12]. Besides, Kellermeier [13] reported that silica as a soluble additive during the crystallization process could strongly affect the precipitation of CaCO_3 . Zhao [14] proposed that polyvinylpyrrolidone, together with sodium dodecyl sulfonate, was employed as template for the controlled growth of hollow CaCO_3 microspheres. Moreover, the occurrence of a particular phase and morphology was found strongly depend on the chosen experimental parameters such as supersaturation, pH, aging time or the mixing procedure [15–17].

In recent years, the influence of uncharged polymers, surfactants, or the polymer-surfactant mixtures [18–24] on the crystallization process of inorganic crystals has been investigated. Nevertheless, the silica aqueous systems containing polymer-surfactant mixtures have never been used for the research of crystallization and aggregation behavior of calcium carbonate. Partially hydrolyzed polyacrylamide (HPAM) and heavy alkyl-benzene sulfonate (HABS), which are two main constituents of Oil-field ASP compound flooding to enhance oil recovery, leading to a series of serious problems that alkaline conditions result in the formation of large amounts of scales [25]. However, the mechanism of interaction between scale and each component is still unclear. In this work, peanut-like CaCO_3 crystals were successfully synthesized as intermediates using Na_2CO_3 and CaCl_2 through the precipitation reaction at 45°C . Silica together with HPAM and HABS was employed as modifier to control growth of peanut-like CaCO_3 intermediates.

2. Experiment

2.1. Chemicals

CaCl_2 , Na_2CO_3 and Na_2SiO_3 were analytical grade and used without further purification, which were purchased from Tianjin Chemical Reagent Factory (China). HPAM (weight-average molecular weight 1.900×10^7) was obtained from Daqing Refining and Chemical Company (China) and HABS was obtained from Daqing Donghao Investment Co., Ltd (China).

2.2. Preparation of the sample

All the reagent solutions were prepared with distilled water at 45°C and put in the electric thermostatic drying oven for 2 h. HPAM solution and HABS solution were added into the Na_2SiO_3 solution in turn and the mixture solution was allowed to stir for 5 min at 45°C . Crystallization of CaCO_3 was initiated by rapidly adding Na_2CO_3 solution and CaCl_2 solution in turn into the above mixture. The concentration of silicate solution was represented as SiO_2 , and the final concentration of Ca^{2+} , CO_3^{2-} , SiO_2 , HPAM and HABS were 640 mg/L, 960 mg/L, 150 mg/L, 100 mg/L and 100 mg/L, respectively. The reaction mixture was stirred for 10 min at 45°C . Then the resultant mixture was covered and kept in a 45°C oven for a certain time. Finally, precipitates were filtered and dried in the electric thermostatic drying oven at 45°C .

2.3. Characterization

Field emission scanning electron microscopy (FESEM, Zeiss Σ IGMA) images were used to observe the morphology of resulting CaCO_3 precipitates with an accelerating voltage of

20 kV. X-ray diffraction (XRD) data were recorded on an X-ray diffractometer (D/max-2200PC) using $\text{Cu-K}\alpha$ radiation to determine the identity of the crystalline phase. Patterns were acquired over a 2θ range of 20° – 60° at a scanning speed of $10^\circ/\text{min}$ under the accelerating voltage and applied current were 40 kV and 20 mA. Fourier transform infrared spectroscopy (FT-IR) was performed on FTIR-TENSOR27 using KBr pellets to assist in confirming polymorph.

3. Results and discussion

3.1. Influence of aging time on crystallization of CaCO_3 without additives

When CaCO_3 particles grew up in the absence of any additives, the aging time had an unobvious influence on the crystallization, where the pH value of system was unadjusted ($\text{pH} = 10.7 \pm 0.1$). Aging the solution for 1 h, cubic CaCO_3 particles with extremely smooth surfaces and angular edges were obtained (Fig. 1(a)), and the diameter of the cubes was $3 \mu\text{m}$ on average. As the aging time was prolonged to 6 h, 12 h and 24 h, the size and the morphology of CaCO_3 crystals remained unchanged (Fig. 1(b)–(e)) meaning that CaCO_3 particles had completely grown in 1 h when there were no additives in solution.

Fig. 2 showed the FT-IR spectra of pure CaCO_3 crystals obtained with different aging time. The appearance of peaks at 1384 cm^{-1} , 876 cm^{-1} and 713 cm^{-1} demonstrated the generation of calcite [26], which could be attributed to the characteristic calcite unsymmetric carbonate stretching (ν_3 mode), carbonate out-of-plane bending vibration (ν_2 mode), and in-plane bending vibration (ν_4 mode), respectively [27]. The peaks proved that calcite generated exclusively when CaCO_3 crystals in pure aquatic system were aged for more than 1 h.

3.2. Influence of aging time on crystallization of CaCO_3 with additives

The aging time had an obvious influence on the crystallization of CaCO_3 particles, which were obtained without adjusting the pH value of mixed system ($\text{pH} = 11.2 \pm 0.1$, in agreement with pH value of ASP flooding in the range of 10–13). When the solution was aged for 1 h, sphere-like CaCO_3 particles were obtained (Fig. 3(a)), and the diameter of the spheres ranged from 1 to $4 \mu\text{m}$. Increasing the aging time to 6 h, peanut-like crystals with the length of 6 – $10 \mu\text{m}$ were observed and the surfaces of peanut-like particles were rugged (Fig. 3(b) and (e)). For the reason that the concentration of Na_2SiO_3 was much lower than Ca^{2+} as well as the electron beam could reach a few microns under the surface of the sample to analyze the elemental distribution within the micron depth, the intensity of Si was relatively weaker than Ca in the EDX profile (Fig. 3(f)), which demonstrated the presence of Si. The above results proved that the core of the particles was rich in CaCO_3 while the outer layer consisted of silica. With the further prolongation of ripening time, such as 12 h and 24 h, peanut-like particles disappeared, and the main morphology of CaCO_3 crystals was cubic-shape with rough surfaces. Moreover, the longer the aging time was, the rougher the surface was (Fig. 3(c) and (d)). The average sizes (long side) of almost all the grains were approximately $4 \mu\text{m}$. The probable reason was that HPAM and HABS showed a strong influence on the crystal morphology. On the one hand, COO^- in HPAM and SO_3^{2-} in HABS would compete with CO_3^{2-} to attract Ca^{2+} , hindering the formation of calcium carbonate. While on the other hand, HPAM and HABS on crystals could provide the nucleation sites [28] for the crystallization of CaCO_3 owing to the electric attraction between anionic (COO^- or SO_3^{2-}) and cationic (Ca^{2+})

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