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Influence of ethylene glycol on $CaCO_3$ particles formation via carbonation in the gas–slurry system

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ABSTRACT

Calcium carbonate precipitation was investigated in the gas–slurry system in the reaction of calcium hydroxide and carbon dioxide. The precipitation process was occurred in the presence of ethylene glycol (EG). The used organic additive changed the viscosity of reactive mixture, the solubility of carbon dioxide and the solubility of calcium carbonate which influence $CaCO_3$ precipitation conditions. The course of reaction was monitored by conductivity probe. The increase concentration of ethylene glycol in the reactive mixture caused higher CO_2 usage to achieve the end point of reaction. Calcium carbonate was precipitated as calcite and produced $CaCO_3$ particles formed agglomerates in all experiments. The size of obtained $CaCO_3$ particles decreased when the EG concentration increased from 0% to 15% (by vol.). The further increase of EG concentration in solution up to 20% resulted in an increase of the size of $CaCO_3$ particles.

1. Introduction

Precipitated calcium carbonate is widely used in paints, paper, plastic adhesives, rubber as well as in pharmaceutical industries. This compound can be produced in the liquid–liquid system when solutions containing calcium ions and carbonates are mixed together. If the Ca^{2+} and CO_3^{2-} ions exceed the solubility product in the system, then the $CaCO_3$ precipitation proceeds, such as in the reaction of calcium chloride and sodium carbonate:

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$$

Another possibility to obtain calcium carbonate is a reaction realized in the gas–liquid system, where carbon dioxide is bubbled through calcium hydroxide solution or slurry. This reaction is written as:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

and it is the summary equation of steps such as the absorption of gaseous CO_2 in a liquid phase, formation of bicarbonate and carbonate ions in the solution and the reaction of carbonate ions with calcium ions.

The supersaturation of the solution is an important factor in the control of crystallization because it influences the nucleation and growth processes. The supersaturation S can be defined by equation:

$$S = \frac{\sqrt{[Ca^{2+}][CO_3^{2-}]}}{\sqrt{K_{sp}}} - 1 \quad (1)$$

where $[Ca^{2+}]$ and $[CO_3^{2-}]$ are concentrations of respective ions and K_{sp} is the solubility product of calcium carbonate. High suspersaturation favors the enhancement of the nucleation process [1] and it is required when small particles are synthesized. The suspersaturation decreases with the time of precipitation in liquid–liquid systems [2] or during the reaction of CO_2 and $Ca(OH)_2$ in the solution, meanwhile the precipitation of calcium carbonate in the carbonation process of $Ca(OH)_2$ slurry is a reaction at nearly constant supersaturation [3].

The size distribution and the shape of precipitated calcium carbonate mainly depend on both reagents concentrations but also on operating variables such as temperature, pH, reaction time [2,4,5] and the presence of inorganic and organic additives [2,6–10]. An important factor influencing the characteristics of calcium carbonate particles are the type of reactor, its geometry and mixing intensity [11–14].

Calcium carbonate can form three different crystalline polymorphs: calcite, aragonite, vaterite and amorphous structure. The $CaCO_3$ morphology can be controlled by different additives. Soluble additives can influence the crystallization or superstructure formation of nanoparticles. Other groups of additives are macroscopic templates or matrices which can act as a mold during precipitation of calcium carbonate particles [6]. The effect

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of additives on the size of precipitated particles is also reported [15–17].

The influence of inorganic ions as the soluble additives in the calcium carbonate precipitation process has been studied in details (e.g. [2, 18,19]). Some inorganic ions like Mg^{2+}, Ni^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+} or Cu^{2+} promote precipitation of $CaCO_3$ in the aragonite form, while the presence of Mn^{2+}, Cd^{2+}, Sr^{2+}, Pb^{2+} and Ba^{2+} ions in solutions results in calcium carbonate crystals in a calcite form. Detailed investigations of the effect of Mg^{2+} and Mn^{2+} ions on producing of different $CaCO_3$ polymorphs indicate that the creation of calcite or aragonite in precipitated calcium carbonate depends on the temperature, pH during the precipitation and the concentration of additives [18]. Nevertheless, calcite is formed as a precipitation product in the solutions containing Mg^{2+} ions if created crystals remain in the liquid for some time [19].

Experiments testing the influence of soluble organic compounds as additives during the $CaCO_3$ precipitation indicate that the presence of ethanol, isopropanol and diethylene glycol (10% v/v) in the reactive liquid–liquid system results in the acceleration of the crystals growth rate. The spontaneous precipitation of calcium carbonate in the vaterite form from aqueous solutions of mentioned compounds has been observed [20]. The preventing role of these additives is suggested as the stabilization of vaterite crystals. Other described processes occurring in the gas–liquid system indicate that calcite is formed when the ethanol concentration is 20% or 40% (vol.). The mixture of calcite, aragonite and vaterite is created in solutions of 60%, 80% and 100% ethanol [15]. Effect of the ethylene glycol concentration in the solution on the $CaCO_3$ form depends on the temperature [17]. At 25 °C, higher concentration of ethylene glycol in the solution causes an increase of the vaterite in the calcite–vaterite mixture. At 80 °C an increase of ethylene glycol concentration results in higher ratio of vaterite to aragonite in the obtained crystals.

Surfactants are important group of organic compounds that affect the characteristics of precipitated $CaCO_3$ particles. Different $CaCO_3$ crystal forms can be produced when the surfactant concentration is controlled [16,21]. Formation of interesting $CaCO_3$ crystal shapes depending on the surfactant concentration is reported as well [7–10,16].

The above discussion presents different ways of investigation on precipitated calcium carbonate controlled by the presence of additives. It should be stressed that the biggest part of described investigations have been conducted in the liquid–liquid system. Precipitation of calcium carbonate in a gas–liquid system in the presence of additional substances is a small part of described results [3,15,21]. Commercially $CaCO_3$ is produced through the carbonation process, i.e. the reaction of CO_2 and $Ca(OH)_2$, or as a by-product of some bulk chemical processes, e.g. caustic soda production [22–24]. The precipitation in liquid–liquid systems is usually applied in a laboratory study because it is easy to control the process variables [15]. On the other hand, there are important advantages of the carbonation process such as low cost and availability of substrates.

In this work precipitated calcium carbonate was obtained in the reaction of aqueous calcium hydroxide slurries with gaseous carbon dioxide. The presence of reagents in two phases causes that precipitation takes place in two regions: at the gas–liquid interface and in the bulk solution. The formation of calcium carbonate particles in this process depends mainly on the local substrate concentration, but it is also closely related to mass transfer and the chemical reaction. However, the gas and liquid flows depend on the reactor geometry and its hydrodynamic characteristics. The reaction of CO_2 with $Ca(OH)_2$ involves the dissolution of the reactant particles while the $CaCO_3$ particles are simultaneously formed [22]. It means that unreacted dissolved $Ca(OH)_2$, product carbonate particles, hydroxide particles coated with the precipitated $CaCO_3$ as well as complex agglomerates can be present in the reaction mixture. The rate of CO_2 absorption controls the rate of precipitation and depends on the solubility and the diffusivity of carbon dioxide in the liquid phase, the interface area, the liquid side mass transfer coefficient and pH of the solution [23]. The aim of this work was the investigation of the effect of ethylene glycol as an additive in the calcium carbonate precipitation process conducted in the gas–slurry system.

2. Experimental

2.1. Reagents

Calcium hydroxide (Reachim), carbon dioxide (Messer), ethylene glycol (Chempur) and ethanol (POCH) were of analytical reagent grade and were used without further purification. The water used in this work was distilled water.

2.2. Preparation

Calcium carbonate was precipitated in a tank-type reactor. The reactor of the diameter $D=110$ mm and the height $H=125$ mm was equipped with the propeller stirrer $d_s=30$ mm and the gas distributor made of fritted glass of diameter $d_d=35$ mm. A digital stirrer engine (IKA) was used to control the stirring rate. The volume of reactive mixture in the tank was 0.5 dm^3. The course of reaction was measured by the conductivity probe located in the reactor. Signals from the probe were collected by a computer with data acquisition software. The collected results of conductivity vs. time were used to determine the end point of precipitation as the time corresponding to the minimum of the conductivity. The reading of the volumetric gas flow rate was corrected to the atmospheric conditions at the top of the reactor by pressure and temperature measured below the gas distributor. The precipitation was carried out in a semi-batch manner at 20 °C. Concentration of $Ca(OH)_2$ was $10\ g\,dm^{-3}$, carbon dioxide flow $u_G=2.8\times 10^{-4}\ m\,s^{-1}$, and stirrer speed regulated at $15\ s^{-1}$ in all experiments. The reaction occurred in the presence of ethylene glycol at different concentration in the range from 0% to 20% (vol.).

2.3. Characterization of $CaCO_3$ particles

The size of calcium carbonate particles obtained at the end point of precipitation was determined by means of a laser diffraction method (Mastersizer E MALVERN). Precipitated $CaCO_3$ particles were characterized by scanning electron microscope (SEM) (Zeiss) with an accelerating voltage 20 kV and X-ray diffraction (XRD) (Philips) using Co-K_α radiation at a scan rate 0.2° and 2θ range 20–60°. The samples of $CaCO_3$ for SEM and XRD were filtered, washed with ethanol and dried at 100 °C for 6 h.

3. Results and discussion

An advancement of the precipitation was determined on the basis of conductivity measurements. Changes in the relative conductivity of the reactive mixture during precipitation are depicted in Fig. 1. At the beginning of the process a slight decrease of conductivity is observed. Similar "valleys" were recorded during experiments of the $CaCO_3$ formation from $Ca(OH)_2$ slurries in carbonation processes described by Garcia et al. [3] and Perić and co-workers [25]. The observed conductivity decrease at the initial course of the reaction could be caused by the precipitation