Effect of some organic solvent–water mixtures composition on precipitated calcium carbonate in carbonation process

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ABSTRACT

Precipitated calcium carbonate particles were obtained during carbonation of calcium hydroxide slurry with carbon dioxide. Aqueous solutions of isopropyl alcohol, n-butanol and glycerol were used as solvents. Concentration of organic additives in the reactive mixture was from 0% to 20% (vol). Precipitation process were performed in a stirred tank reactor equipped with gas distributor. Multimodal courses of particles size distribution were determined for produced $CaCO_3$ particles. Calcium carbonate as calcite was precipitated in all experiments. The mean Sauter diameter of $CaCO_3$ particles decreased when the concentration of all used organic additives increased. The amount of small particle fraction in the product increased with the increasing concentration of organic solvents. Similar physical properties of used liquid phase resulted in the similar characteristics of obtained particles.

1. Introduction

World consumption of calcium carbonate was 74 Mt in 2011 including 14 Mt of precipitated calcium carbonate [1]. The carbonation process is the most frequently used for the production of precipitated $CaCO_3$ [2] and a summary reaction of calcium carbonate formation can be written as:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{1}$$

Because calcium hydroxide is sparingly soluble in water (its solubility at 20 °C amounts to 0.165 g in 100 g of water [3]), the carbonation is usually conducted in the gas–slurry system, although the process using calcium hydroxide solution has been studied [4] and patented [5].

Following reactions are identified during the calcium carbonate formation in the gas–slurry system:
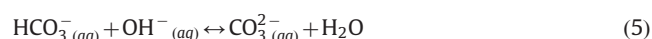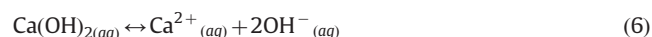
– CO_2 absorption

$$CO_{2(g)} \rightarrow CO_{2(aq)} \tag{2}$$

– hydration of dissolved CO_2

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_{3(aq)} \tag{3}$$
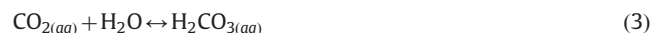
– reaction of hydroxyl ions with dissolved CO_2 in case of the high pH of the solution

$$CO_{2(aq)} + OH^-{}_{(aq)} \leftrightarrow HCO_{3(aq)}^- \tag{4}$$

$$HCO_3^-{}_{(aq)} + OH^-{}_{(aq)} \leftrightarrow CO_3^{2-}{}_{(aq)} + H_2O \tag{5}$$

– dissociation of calcium hydroxide

$$Ca(OH)_{2(aq)} \leftrightarrow Ca^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \tag{6}$$

– precipitation

$$Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CaCO_{3(s)} \tag{7}$$

The limiting step of the calcium carbonate precipitation is the absorption of carbon dioxide (Eq. 2). Bicarbonate ions can be formed rapidly in the solution of high pH value (Eq. 4) and then are quickly transformed to carbonate ions (Eq. 5) [6,7]. After the complete conversion of calcium hydroxide into the calcium carbonate, the pH is reduced because of the production of carbonic acid (Eq. 3) and then

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dissolution of $CaCO_3$ can be observed [7]:

$$CaCO_{3(s)} + H_2CO_{3(aq)} \leftrightarrow Ca(HCO_3)_{2(aq)} \tag{8}$$
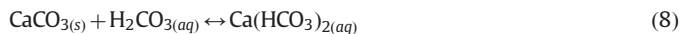
The first step of precipitation is the formation of nuclei in the solution. The nucleation mechanism can be homogenous, heterogeneous or secondary and depends mainly on the supersaturation [8]. High supersaturation of slightly soluble substances (e.g. $CaCO_3$) favors homogeneous nucleation. At the beginning of precipitation the nucleation dominates in the solution. Expected high nucleation rate is an argument for an occurrence of nanosized primary particles during $CaCO_3$ precipitation [8]. Typically, the supersaturation lowers with the precipitation time in batch processes, because substrates are consumed during nucleation and crystal growth. However, when the reaction is carried out with slaked lime as a substrate, the supersaturation is almost constant during the $CaCO_3$ formation [9]. Nucleation and crystal growth can be accompanied by secondary processes, i.e. agglomeration, breakage, and/or aging. Agglomeration is a result of interparticle collisions and the attachment of colliding particles [10]. The adhesion of the particles that form agglomerates, besides the kinetic energy of particles, depends on the contact angle of liquid–solid system, the surface tension of the liquid at the particle surface and the contact time. Breakage and/or attrition and size reduction of particles can be due to the turbulent shear force generated by the motion of the liquid in the reactor [11]. Ostwald ripening is due to the difference in solubility between small and large particles. This causes the dissolution of small particles and the growth of larger crystals [10].

Many parameters as supersaturation, pH, temperature, mixing intensity, type of reactor as well as additives can affect precipitation process of calcium carbonate. The effect of additives on calcium carbonate synthesis has been intensive investigated for last years. Substances added to the reactive mixture can be divided into three groups: low molecular soluble additives, soluble polymers and polymeric templates [12]. Complex effects of soluble additives on $CaCO_3$ precipitation can represent citric acid and ethylene glycol. The presence of citric acid during the $CaCO_3$ precipitation: (i) resulted in formation of $CaCO_3$ in vaterite form at low concentration of additive (the reaction was conducted in the liquid–liquid system) [13], (ii) promoted the formation of agglomerates of elongated particles of calcite (reaction in the slurry–gas system) [9], (iii) resulted in reduction of $CaCO_3$ crystal size synthesized by the citrate method [14]. Ethylene glycol added to the reaction mixture during synthesis of calcium carbonate: (i) resulted in the increasing share of vaterite in the product with the increase of additive concentration in the solution (reaction in the liquid–liquid system) [15–17], (ii) affect the particle size of precipitated $CaCO_3$ as calcite crystals in the gas–slurry system [18]. It was noticed that some soluble additives may prevent the transformation of less stable vaterite or aragonite to more stable calcite, have an influence on the size of precipitated particles and their shapes [13,19] as well as some organic additives contribute to the modification of the precipitation mechanism of $CaCO_3$ particles [9].

The additives, although not involved in the precipitation reaction, can affect the mass transfer during crystal formation. Their presence in the reactive mixture may modify the viscosity, the density, the surface tension and the dielectric constant of the liquid phase. Organic additives in the aqueous solutions affect the solubility of substrates and products as well as the particle–particle interactions.

The complexity of the precipitation in the gas–liquid systems causes that the intensive investigations are carried out to explain the effect of organic additives on the process. Our previous studies concerned the influence of ethylene glycol on the precipitation process of calcium carbonate and its characteristics [18]. It was observed that the composition of the solution affected the precipitation course and the particle size distribution of the product. The present study was conducted to compare the effect of selected aqueous solutions of organic solvents on the calcium carbonate characteristics. Organic components which do not react with the substrates were selected based on their physical properties. The tested solvents were aqueous solutions of isopropyl alcohol, n-butanol and glycerol.

2. Experimental

2.1. Reagents

Calcium carbonate was precipitated via reaction of calcium hydroxide and carbon dioxide using analar grade reagents. Calcium hydroxide purchased from Reachim, carbon dioxide from Messer, isopropyl alcohol, glycerol and ethanol from POCH and n-butanol supplied by Chempur were used without further purification. Distilled water was used for preparation of aqueous solutions. Selected properties of organic solvent–water mixtures are presented in Table 1.

2.2. Preparation

Calcium carbonate was precipitated in a tank-type reactor. The reactor of the diameter 110 mm and the height 125 mm was equipped with the propeller stirrer 30 mm in diameter and the gas distributor made of fritted glass of diameter 35 mm. The homogenization of the system was attained at a stirring rate of 900 RPM by a digital stirrer engine (IKA). The volume of reactive mixture in the tank was 0.5 dm^3. The conductivity probe was located in the reactor and its signals were collected by a computer with data acquisition software. On the basis of conductivity measurements the course of the reaction was controlled. The time corresponding to the lowest conductivity value can be ascribed to the end of precipitation process [4,9,20]. 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 at 20 °C. Calcium hydroxide concentration was 10 g/dm^3 and a carbon dioxide flow rate was 250 cm^3/min in all experiments. The reaction was investigated in the presence of a selected additive at different concentration in the range from 0% to 20% (vol).

2.3. Characterization of $CaCO_3$ particles

The samples of $CaCO_3$ were filtered, washed with ethanol and dried at 100 °C for 6 h. The size of calcium carbonate particles obtained at the

Table 1
Selected properties of organic solvent–water mixtures (20 °C).

Organic solvent	x_V [%]	ρ [kg/m^3]	η [mPa s]	γ [mN/m]	ε [dimensionless]	Refs
[a]	0	998	1.005	72.7	80.5	[3,20]
Isopropanol	5	992	1.09	48.6	77.4	[20–24]
	10	987	1.22	37.8	74.5	
	15	986	1.40	35.1	71.5	
	20	974	1.61	30.1	68.3	
n-butanol	5	992	1.23	34.6	78	[20,25–28]
	9	989[b]	1.31	26.7	75	
Glycerol	5	1015	1.174	71.7	78.6	[20,24,29–30]
	10	1031	1.343	70.9	76.9	
	15	1047	1.650	70.3	75.2	
	20	1062	1.998	69.8	73.5	

x_V – volume fraction; ρ – density; η – viscosity; and γ – surface tension.
[a] pure water.
[b] for $x_V = 0.08$.