INFLUENCE OF SODIUM STEARATE ON THE PRECIPITATION OF CALCIUM CARBONATE IN A SEMICONTINUOUS PROCESS

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The influence of sodium stearate (NaS) on the precipitation of calcium carbonate during the semicontinuous carbonation process of slaked lime was studied in the systems in which process parameters, like temperature, CO_2 flow rate and addition rate of slaked lime, have been controlled. It was found that calcite was the only calcium carbonate polymorph that appeared under the investigated experimental conditions, while FT-IR spectroscopy and thermogravimetric analysis of samples confirmed the presence of stearate on the surface of precipitated calcium carbonate (PCC). Specific surface area of PCC increased with increasing stearate content: the highest value, $s = 52.8 \text{ m}^2 \text{ g}^{-1}$, was obtained at $t = 20$ °C, $\kappa_{25} = 7.0 \text{ mS cm}^{-1}$ and the stearate content of $w_{\text{NaS}} = 2$ %. It was also found that hydrophobic PCC could be prepared at $w_{\text{NaS}} > 1$ %.

1. Introduction

The most widely used method of the production of precipitated calcium carbonate (PCC) in industrial scale is the so called carbonation route, comprising a batch process of CO_2 bubbling through an aqueous $Ca(OH)_2$ suspension. However, bench scale investigations have shown that an additional control of the morphology and size of precipitated particles is possible [GAR93, UKR07] by running carbonation as a semicontinuous process.

Introduction of new technologies, caused by the market demands for the high quality products, requires the PCC of different physical and chemical properties. Thus for example, final properties of the polymer/PCC composites depend strongly on the morphology, size distribution, surface characteristics and degree of dispersion of the PCC filler. Since the incompatibility of the PCC hydrophilic surface with the hydrophobic polymers is of particular problem, PCC is often modified by a variety of surfactants, among which fatty acids are most commonly used [PAP84, FEK90, SON03, REZ06]. On the other hand, many studies have shown that the presence of additives or impurities during the precipitation process can affect nucleation and/or crystal growth of PCC [MAN89, CAR03, KRA04] and, consequently, the morphology and crystal size distribution.

In this work, we have studied the influence of sodium stearate on the precipitation of calcium carbonate during the semicontinuous carbonation process. In order to find out the possible impact of existing impurities on the PCC properties, the analytical grade quicklime, as well as the technical grade one has been used.

2. Experimental Section

CaO was obtained from calcium carbonate raw material, provided by the Kamen Sirač Inc., Croatia. According to chemical analysis, major components of lime were found to be: CaO (94.66 % w/w), MgO (3.14 % w/w), SiO_2 (0.40 % w/w) and CO_2 (1.80 % w/w). Analytical grade $Ca(OH)_2$ (Merck) contained at least 96 % $Ca(OH)_2$, while the content of magnesium was below 0.5 %. The semicontinuous carbonation process was carried out in a thermostated bench-scale glass reactor of 6.0 dm^3 total volume. The electrical conductivity was controlled and kept constant at the predetermined values of κ_{25} = 1.0 mS cm^{-1} or κ_{25} = 7.0 mS cm^{-1} by the addition of $Ca(OH)_2$ suspension. Peristaltic pump was used as actuator which dosed the previously prepared $Ca(OH)_2$ suspension, ($\gamma(Ca(OH)_2)$ = 132 g dm^{-3}) into the reactor. Gas mixture containing approximately 20 % CO_2/80 % N_2 (Messer) was used, simulating the flue gases that are commonly used in large scale PCC production. The gas mixture was introduced at a constant flow rate, Q = 1.0 dm^3 min^{-1} through the nozzles on the bottom of baffles. Stirring was performed at n = 1400 min^{-1} and the temperature was kept constant during each experiment, 20 °C < t < 50 °C. The flow of the $Ca(OH)_2$ suspension was stopped 15 min after starting the experiment, while the gas flow was kept constant until the endpoint of carbonation reaction, indicated as a drop of conductivity. Sodium stearate (Kemika, puriss.), NaS, was added during the slaking stage of quicklime. The NaS content, m_{NaS}/m_{CaO}, was varied from 0.0 to 0.02. The composition of the solid phase was determined by FT-IR spectroscopy (Mattson, Genesis Series) and X-ray powder diffraction (Phillips PW1830 with a CuKα radiation), while the size and morphology of particles were observed by transmission electron microscopy, TEM (FEI, Morgagni 268 D). The specific surface area, s, was determined by the multiple BET method (Micromeritics, Gemini) using nitrogen gas as adsorbate. Thermogravimetric analysis (TGA) was performed using thermogravimetric analyzer TG–50 (Mettler Toledo), the heating rate of 10 °C min^{-1} and the air atmosphere. The content of Mg^{2+} and Ca^{2+} was determined by ion chromatography using an ion chromatography system ICS-1000 (Dionex) fitted with a CS16 analytical column. The contact angle was measured on a horizontal surface of a PCC pellet sample (400 mg) by using contact angle analyzer OCA 20 (Dataphysics).

3. Results and Discussion

The X-ray diffraction and FT-IR spectroscopy revealed that at all investigated conditions calcite was the only crystalline phase obtained at the end of carbonation process. In spite the fact that the PCC samples, prepared from technical quicklime contained 0.83 % w/w Mg^{2+}, the X-ray diffraction pattern did not reveal any shift of the calcite peaks coming as a consequence of possible magnesium ion incorporation into the calcite structure [FAL97]. Figure 1 shows the X-ray diffractograms of PCC samples obtained from both, analytical and technical grade quicklime, and the addition of sodium stearate (NaS), m_{NaS}/m_{CaO} = 0.01. However, the FT-IR spectra of the same PCC samples exhibited not only the absorption bands specific of calcite, but also absorbencies at 2930 cm^{-1} and 2850 cm^{-1} assigned as asymmetrical and symmetrical C-H stretching vibrations of the stearate alkyl group adsorbed on the PCC surface. Furthermore, the intensities of the peaks ascribed to the stearate alkyl group increased with the increase of m_{NaS}/m_{CaO}. TGA analysis also confirmed the presence of stearate molecules at the PCC surfaces. The weight loss at about 300 °C, corresponding to the elimination of adsorbed stearate [REZ03], and the loss at about 800 °C, attributed to the decomposition of mineral phase, $CaCO_3$, were obtained.

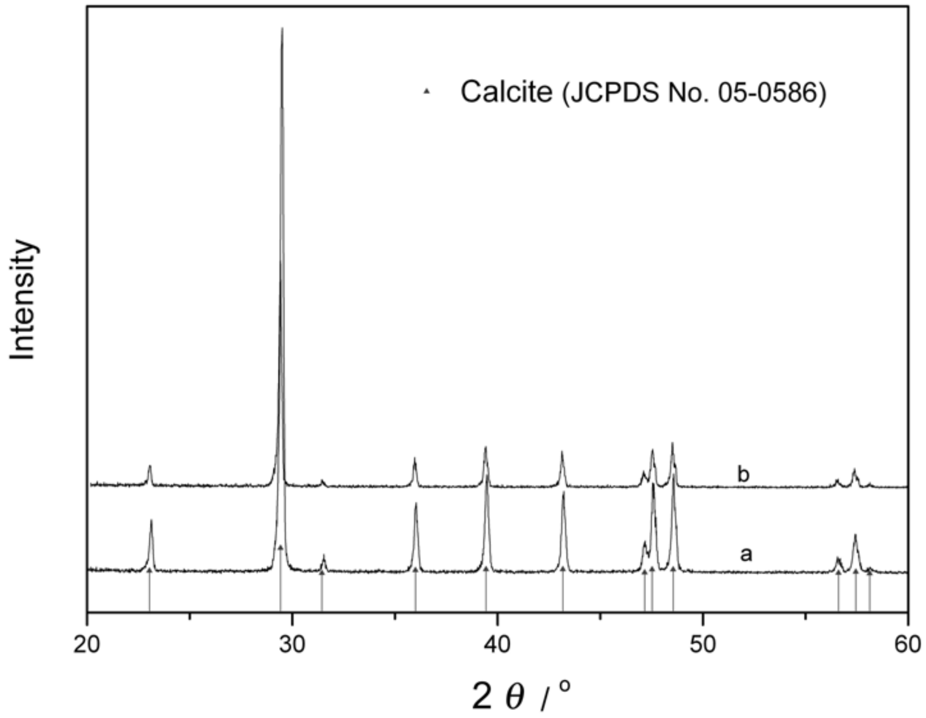

Fig. 1. Powder X-ray diffraction pattern of PCC obtained a t = 20 °C, κ_{25} = 1.0 mS cm^{-1} and m_{NaS}/m_{CaO} = 0.01, from (a) analytical grade $Ca(OH)_2$ and (b) technical grade quicklime.

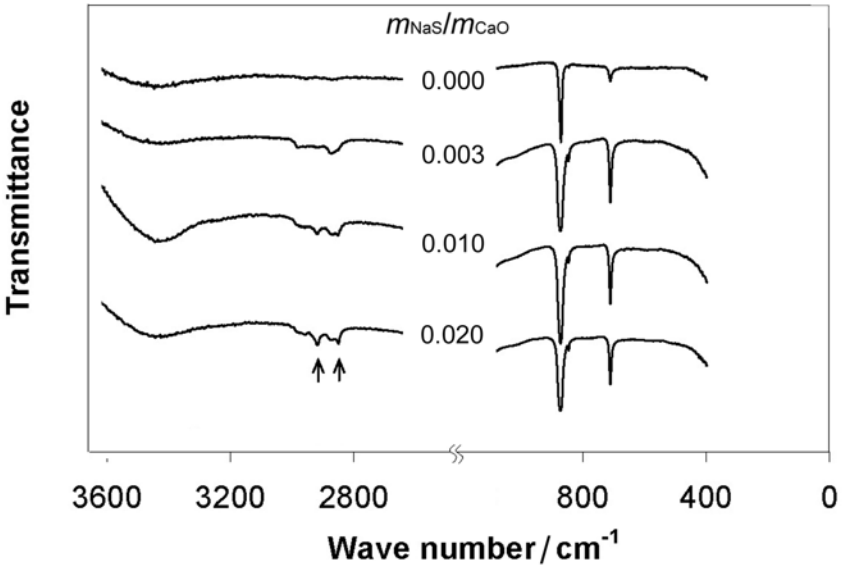

Fig. 2. FT-IR spectra of PCC obtained at t = 20 °C, κ_{25} = 1.0 mS cm^{-1} and different mass ratios m_{NaS}/m_{CaO}.

Figure 3 shows the specific surface area, s, of PCC measured in experiments at 20 °C in which the conductivity (supersaturation) and the addition of NaS, varied. It is evident that s is much higher when the process is conducted at κ_{25} = 7.0 mS cm^{-1} than at κ_{25} = 1.0 mS cm^{-1}, the highest specific surface area, s = 52.8 m*2* g^{-1}, obtaining at t = 20 ° C, κ_{25} = 7.0 mS cm^{-1} and $m_\mathrm{NaS}/m_\mathrm{CaO}$ = 0.02. However, the increase of stearate addition caused the increase of s in any case. TEM microphotographs (Fig. 4) show that PCC samples prepared at t = 20 °C and κ_{25} = 7.0 mS cm^{-1} appeared in a form of nanosized calcite particles of a mean particle diameter of $d_\mathrm{m} \approx$ 30 nm (without NaS addition). The size of particles produced in the presence of 2 % NaS were even smaller, $d_\mathrm{m} \approx$ 5 nm.

At κ_{25} = 1.0 mS cm^{-1} and t = 20 °C, micrometric rhombohedral crystals of calcite were produced, while at κ_{25} = 7.0 mS cm^{-1} and t = 50 °C calcite precipitated in the form of micrometric scalenohedral particles. Figure 5 shows typical rhombohedral calcite crystals and the crystals produced in the presence of stearate: the edges of calcite crystals produced without NaS are relatively smooth, while some protuberances and the rounded edges are found in samples of PCC treated by stearate.

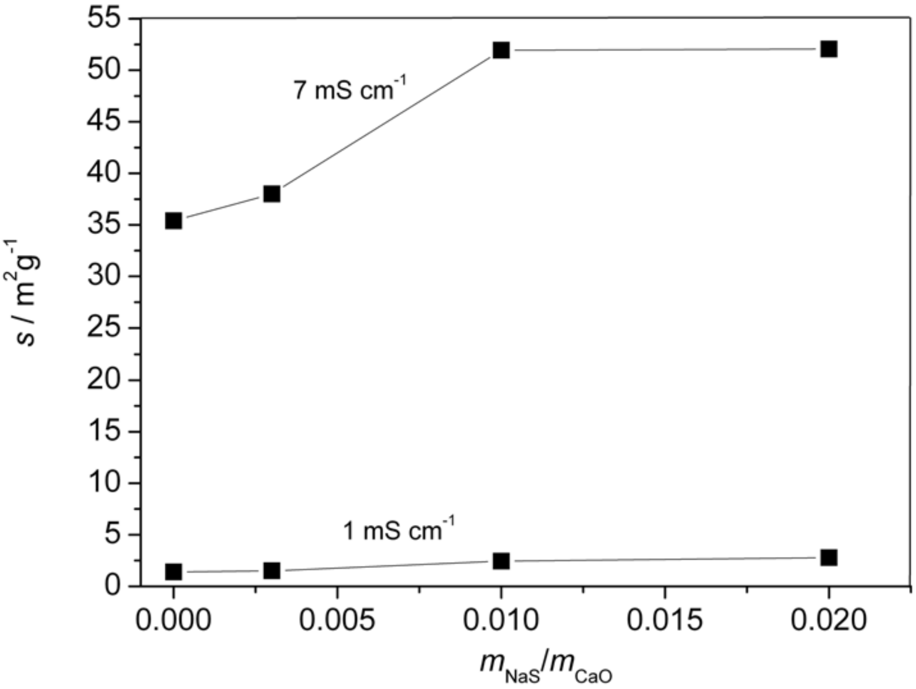

Fig. 3. Plots of specific surface area, s, as a function of mass ratio, $m_\mathrm{NaS}/m_\mathrm{CaO}$, at t = 20 °C and different conductivities.

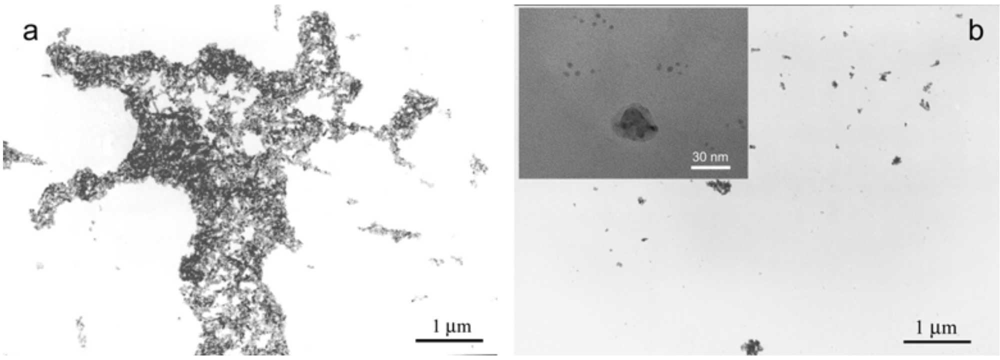

Fig. 4. TEM images of PCC nanoparticles obtained at t = 20 °C and κ_{25} = 7.0 mS cm^{-1}: (a) in the absence of NaS and (b) in the presence of NaS at $m_{\mathrm{NaS}}/m_{\mathrm{CaO}}$ = 0.02.

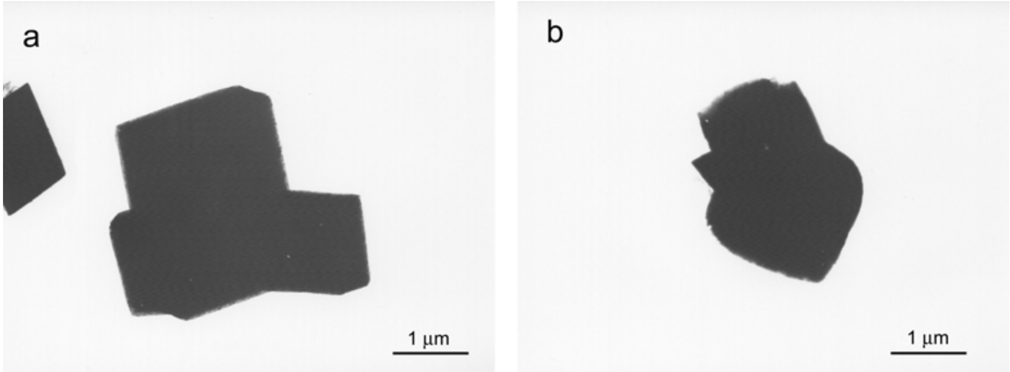

Fig. 5. TEM images of PCC particles obtained at t= 20 °C and κ_{25} = 1.0 mS cm^{-1}: (a) without NaS and (b) with NaS at $m_{\mathrm{NaS}}/m_{\mathrm{CaO}}$ = 0.02.

The extent of hydrophobicity of PCC surface was estimated by measuring the contact angle. The results, shown in Fig. 6, are represented as a relationship between the contact angle and the mass ratio $m_{\mathrm{NaS}}/m_{\mathrm{CaO}}$ for the samples prepared at different conductivities and temperatures. Hydrophobic properties (contact angles, α > 90°) were obtained in the systems in which the mass ratios $m_{\mathrm{NaS}}/m_{\mathrm{CaO}}$ were above 0.01. The only different behaviour exhibited the system carried out at t = 20 °C and κ_{25} = 7.0 mS cm^{-1} in which the hydrophobic property was not obtained even at $m_{\mathrm{NaS}}/m_{\mathrm{CaO}}$ = 0.02, probably because the PCC nanoparticles have an extremely high specific surface area (s = 52.8 m^2 g^{-1}). Therefore, in order to obtain the hydrophobic PCC nanoparticles an additional experiment was performed in which the addition of NaS was significantly increased ($m_{\mathrm{NaS}}/m_{\mathrm{CaO}}$ = 0.225). At such concentration of NaS a complete coverage of the PCC surface with a monolayer of the stearate molecules, s = 52.8 m^2 g^{-1}, is possible; calculation takes into account the surface area of one vertically oriented stearate molecule of 0.21 nm^2 [PAP84, REZ06, FEN99]. Indeed, the contact angle of the PCC sample obtained in this way was found to be, α= 128.0°. This indicates that PCC nanoparticles with good hydrophobic property can be obtained by applying higher NaS concentrations, $m_{\mathrm{NaS}}/m_{\mathrm{CaO}}$ > 0.22.

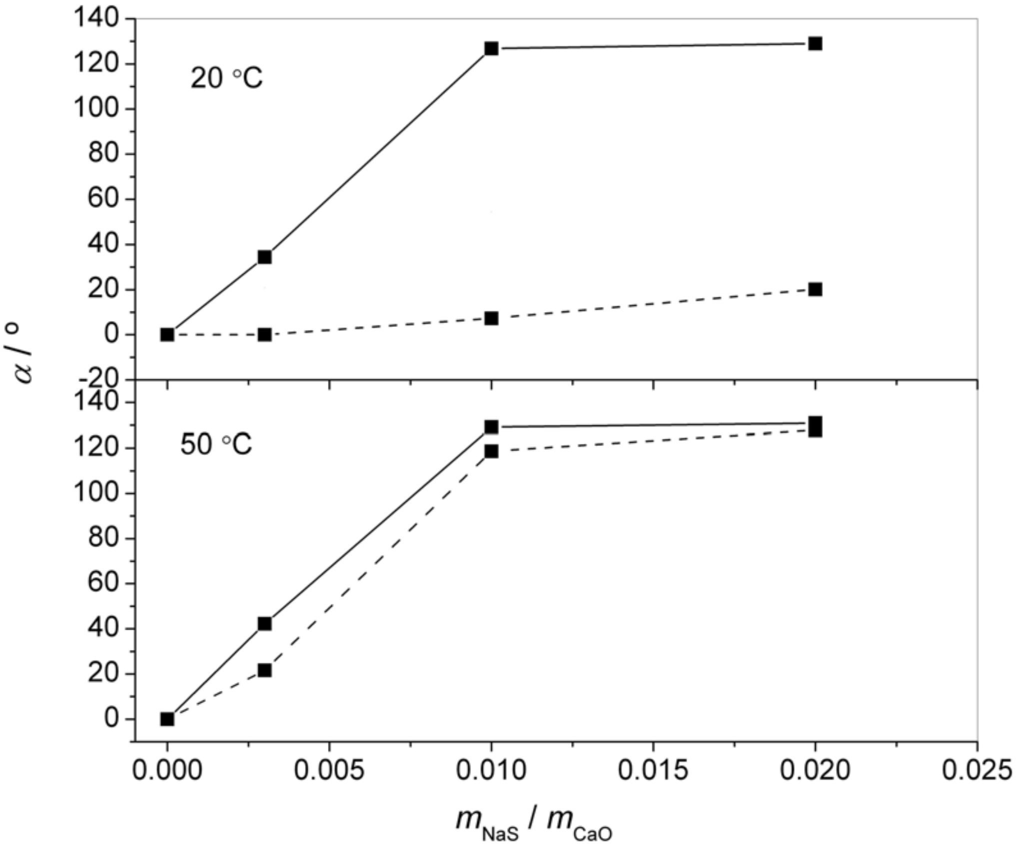

Fig. 6. Plots of the contact angle, α, of PCC particles as a function of mass ratio, $m_{\mathrm{NaS}}/m_{\mathrm{CaO}}$, obtained at different temperatures and conductivities: (–) κ_{25} = 1.0 mS cm^{-1} and (---) κ_{25} = 7.0 mS cm^{-1}.

4. Conclusions

The influence of sodium stearate on the precipitation of calcium carbonate, performed in a semicontinuous bench scale reactor, has been investigated. At that, in order to find the optimal conditions for preparation of PCC of desired physical-chemical properties (particle size distribution, morphology and hydrophobicity), a range of process parameters, like temperature, rate of addition of $Ca(OH)_2$ suspension and concentration of NaS was systematically varied. The results obtained show that nanosized PCC of the highest surface area, s = 52.8 m^2 g^{-1}, is produced at t = 20 °C, κ_{25} = 7 mS cm^{-1} and w_{NaS} = 2%, while the micrometric rhombohedral crystals of calcite are formed at κ_{25} = 1.0 mS cm^{-1} and t = 20 and 50 °C. Moreover, at κ_{25} = 7.0 mS cm^{-1} and t = 50 °C calcite precipitates in the form of micrometric scalenohedral particles. Hydrophobic calcite crystals can be produced at the addition of more than 1 % of NaS. The exception is the case of nanosized PCC production, when much higher concentrations of NaS are needed.

5. References

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