

Influence of some polysaccharides on the production of calcium carbonate filler particles

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ABSTRACT

The influence of different water-soluble polysaccharides, dextrans (cationic, anionic and non-ionic) and soluble starch, on the precipitation of calcium carbonate, has been investigated in the model system in which calcium hydroxide and carbonic acid were reactants. In the absence of additives, the formation of metastable phases, vaterite and amorphous calcium carbonate is observed at the early stage of the process, and as a consequence of the solution-mediated transformation process calcite appears in the system as the only solid phase in equilibrium. In the presence of starch, vaterite is found in the final precipitate, with the content increasing with the increase of starch concentration, probably as a consequence of calcite nucleation and crystal growth inhibition. Non-ionic dextran causes the inhibition of vaterite nucleation, which results in the formation of calcite as a predominant solid phase throughout the precipitation process. The crystal size of the so-formed calcite reduces by increasing the relative molecular mass (M_r) of neutral dextran. The presence of charged dextrans, either cationic or anionic, causes inhibition of the overall precipitation process: in the case of anionic dextran the inhibition seems to be the consequence of its reaction with Ca^{2+} ions (supersaturation decrease), while cationic dextran most probably adsorbs electrostatically onto the negatively charged surfaces of calcite and vaterite.

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1. Introduction

Calcium carbonate is the most widely used mineral filler, primarily in the paper, plastics, paints and coatings industries. Industrial applications of calcium carbonate are determined by the control of chemical purity, polymorphism, particle size and morphology. Various controllable syntheses of calcium carbonate have received much research interest [1–7]. The product of a controlled synthesis of calcium carbonate, with the characteristics required, is called precipitated calcium carbonate (PCC). The conventional method of PCC production, due to its low cost and the availability of raw materials, is the carbonation process [8]. This method consists of bubbling carbon dioxide gas through the aqueous slurry of $\text{Ca}(\text{OH})_2$ or slaked lime. PCC has higher purity than ground calcium carbonate (GCC), obtained by the mechanical treatment of minerals directly from the stone pit. There are several types of PCC grades; however, the purity of PCC is usually over 99% in all cases. Among the three polymorph modifications (calcite, aragonite and vaterite), calcite is the most important PCC polymorph in industrial applications. It appears in various

crystalline forms (scalenohedral, rhombohedral, spheroidal, etc.), but the scalenohedral form is favoured in most of the applications.

In papermaking, calcium carbonate is valued worldwide as an inexpensive filler and, due to its special white colour, as a coating pigment. Besides, due to its good ink absorption, it ensures opacity, brightness, smoothness and improved printability. These characteristics are related to the particle size distribution and to the shape of calcium carbonate particles. Thus, for example, narrow particle size distribution and high refractive index of PCC promote paper sheet light scattering. The desirable properties of paper can be achieved by using the appropriate combinations of pigment, binder and thickener, as well as the additives for the control of pigment dispersion. The aggregation of calcium carbonate particles can be controlled by the addition of different surfactants, wetting agents and dispersants.

Depending on the application, a wide variety of soluble organic additives have been examined for their effects on the crystallization of calcium carbonate [9–22]. It is a well-known fact that the affinity of macromolecules to adsorb at the solid–liquid interface is great, even when they are present at a low concentration in the aqueous media. The crystal growth rate, as well as the particle size, morphology and stability of solid particles, may be greatly influenced by the presence of macromolecules. Two classes of macromolecules should be distinguished: ionic (charged) and non-ionic (neutral charge) [23].

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The commonly used charged type macromolecules for calcium carbonate applications are polyorganic acids, such as polymerising acrylic and maleic acids, and their mixtures [24]. Used as opacifiers in paints and paper coatings, polyacrylates disperse calcite particles. Cationic additives based on polyacrylamide cause the anionic colloidal filler particles to flocculate and to deposit onto wood pulp fibers before the paper sheet is formed.

A large group of organic macromolecular additives important for optimizing the calcium carbonate properties are water-soluble polysaccharides, such as soluble starch and dextrans [9,17,19,25]. Starch is a mixture of the soluble straight-chain amylose and the insoluble branched-chain amylopectin molecules. Usually, these are found in the ratio of 30:70 or 20:80, respectively, and both consist of the polymers of α -D-glucose units. To obtain water-soluble ionic or non-ionic polymers from corn or potato starch, starch should be modified through the reactions with organic or non-organic acids or their salts. Thus, by partial acid hydrolysis of starch followed by neutralisation with an alkali, a water-soluble product of high relative molecular mass, M_r ("molecular weight"), known as dextrin, is produced. Dextran, such as amylose and cellulose, is a polymer composed of repeating glucose molecules joined into chains of varying lengths, differing in their linkages. Dextran consists of 1,>6 α glycosidic linkages between glucose molecules, the branches being composed of 1,>3 α linkages (in some cases of 1,>2 and 1,>4 α linkages as well). This polysaccharide can be modified by introducing some charged or hydrophobic groups.

In our previous work [26,27] we studied the effect of inorganic ions, possible impurities in the precipitation system, on the physical and chemical properties of calcium carbonate precipitated from a homogeneous system in which calcium hydroxide and carbonic acid were reactants. The preparation of calcium carbonate in the present study was performed in a way that any possible effects of ions other than the calcium carbonate constituent ions were avoided. The study focused on the preparation of calcium carbonate particles in the presence of various organic macromolecules, soluble starch and dextrans, which find a widespread use in the paper and non-paper industries. The role of ionic charge, molecular masses and concentration of the selected polysaccharide, in the process of spontaneous precipitation of calcium carbonate, its phase composition, crystal size and morphology, was systematically investigated. Because of the model system chosen, CaCO_3 precipitation proceeds through the formation of precursor phases, vaterite and amorphous calcium carbonate (ACC). Therefore, some general conclusions on the mode of substrate/polysaccharide interactions are possible by considering the formation dynamics and/or disappearance of specific solid modifications. In addition, because of the chosen range of initial reactant concentrations, the results could be relevant to the industrial PCC production and used for the prediction of the physical–chemical properties of the precipitate thus produced.

2. Experimental procedure

The precipitation of calcium carbonate was initiated by pouring 500 cm^3 of carbonic acid solution ($c = 0.022\text{ mol dm}^{-3}$) into the same volume (500 cm^3) of calcium hydroxide solution ($c = 0.020\text{ mol dm}^{-3}$). The additive was added to the carbonate solution prior to mixing the reactants. All reactants used were prepared from analytically pure chemicals and deionised water of high quality ($\kappa < 0.1\text{ }\mu\text{S cm}^{-1}$). The stock solution of carbonic acid was prepared by bubbling CO_2 gas into water until the saturation was achieved, which occurred when the solution conductivity became constant. The concentration of thus freshly prepared

carbonic acid solution was determined by potentiometric titration using a standard NaOH solution. The calcium hydroxide solution was prepared by adding an excess solid Ca(OH)_2 into water. The suspension was then filtered through a membrane filter with nominal pore size of $0.22\text{ }\mu\text{m}$, and the saturated solution was kept under a nitrogen atmosphere. The concentration of calcium hydroxide solution was determined by ion chromatography, IC (Dionex, ICS-1000 fitted with a CS16 Analytical Column).

A thermostated glass reactor of 1.6 dm^3 total volume capacity was used throughout the experiments. The reactor was closed by a Teflon cover through which a thermometer and a combined glass–calomel electrode (Radiometer, PHC 2002-8) were immersed into solution. The solution was continuously stirred during reaction at a constant rate (150 min^{-1}) by means of a flat-bladed stirrer. The electrode was connected to a pH meter (Radiometer, PHM 240). The experiments were carried out at 25°C .

The progress of the precipitation process was continuously monitored by measuring the pH of the liquid phase and by periodical determination of the total dissolved calcium concentration. Changes in the physical–chemical properties of the respective samples of the solid phase were determined by combining Fourier transform infrared, FT-IR, spectroscopy (Mattson, FT-IR spectrophotometer, Genesis Series), thermogravimetry, TG (Mettler, TG 50 thermobalance with TC 11 TA processor) and X-ray powder diffraction, XRD (Philips 1710 with a $\text{CuK}\alpha$ radiation). The samples for analysis were also taken at the end of each experiment, and the final suspension was filtered through a $0.22\text{ }\mu\text{m}$ membrane filter. The precipitates were washed with small portions of water and dried at 105°C . The content of calcium ions was determined by means of the IC system mentioned above.

The quantitative composition of the vaterite–calcite mixture was determined by using a relatively precise and simple procedure based on infrared spectroscopy, as described elsewhere [28]. For that purpose, an aliquot of suspension was taken, filtered through a $0.22\text{ }\mu\text{m}$ membrane filter and the precipitate was dried at 105°C for 1 h. The pellets were prepared by weighing about 2–2.5 mg of the precipitate and 300 mg of KBr. The IR spectra of the pellets were recorded and from the ratio of the absorbencies of the vaterite and calcite bands at 746 and 713 cm^{-1} , respectively, $R = A_c/A_v$, the content of each polymorph was calculated by using the expression

$$\% \text{ calcite} = 100R/(R + K)$$

In this expression, $K = k_c/k_v$, where k is the slope of the respective calibration line, based on the Lambert–Beer law. The subscripts c and v refer to calcite and vaterite, respectively. Calibration lines were obtained by plotting the respective values of the absorbencies as a function of calcite and vaterite masses used for the preparation of KBr standard pellets. Vaterite and calcite for the preparation of standard pellets were obtained by a method described by Kralj et al. [29].

The morphology and the size of the precipitated crystals were determined by using scanning electron microscopy, SEM (Tescan TS 5136), and an electronic counting device (Coulter Electronics, Multisizer II) fitted with a $50\text{-}\mu\text{m}$ -orifice tube. The aperture diameter of this tube enabled the crystals in the size range between about 1 and $30\text{ }\mu\text{m}$ to be measured and distributed into up to 256 size classes. Since the crystals were agglomerated, the agglomerates were agitated before characterisation by using ultrasound for 3 min. The specific surface area was determined by the multiple BET method (Micromeritics, Gemini) using nitrogen gas as adsorbate.

The chemicals used as additives were soluble starch (Riedel-de-Haën) and dextrans (Polydex Chemicals Ltd.). These commercial additives were used without further purification.

Table 1List of polysaccharides, relative molecular masses, M_r , types and mass concentrations, γ , used in experiments

Polysaccharide (chain fragment)	M_r	Type	$\gamma/\text{mg dm}^{-3}$
Starch	Not defined	Non-ionic	0.5 2 5 50 500
Dextran	6000 20,000 40,000 500,000	Non-ionic	60
DEAE dextran	500,000	Cationic	60
Dextran sulphate	500,000	Anionic	60

The mass concentrations of soluble starch in the precipitation system varied in the range $0.5\text{--}500\text{ mg dm}^{-3}$. Dextran of $M_r \approx 500,000$ was used in the cationic (diethylaminoethyl dextran, DEAE-Dextran), anionic (Dextran sulphate) and non-ionic forms. The non-ionic form of lower relative molecular masses was also used, the lowest being $M_r \approx 6000$. The mass concentration of all types of dextran used in the experiments was 60 mg dm^{-3} . Table 1 shows relative molecular masses, types and mass concentrations of polysaccharides used in the experiments.

3. Results and discussion

3.1. Effect of different dextrans

Fig. 1 shows the changes in pH as a function of time during the precipitation process in the model system (with no additives) and in the systems to which one of the diverse dextran types (non-ionic, cationic or anionic, all of $M_r \approx 500,000$) was added. The step-like shape of the experimental curves is typical for the solution-mediated transformation process, which, when compared to the model system, seems to be accelerated in the presence of the non-ionic dextran and slowed down in the presence of cationic and anionic dextrans. In all experiments, the solid phase appeared in the system immediately after mixing the reactants, and an abrupt pH decrease from $\text{pH} \approx 10.3$ to the values of about $\text{pH} = 9.3\text{--}9.5$ was obtained. The samples isolated from the precipitation systems 1800 s after mixing the reactants were mixtures of calcite and vaterite, except for the system with the addition of the non-ionic dextran, when the samples consisted predominantly of calcite. Thus, for instance, the content of a typical sample isolated from the model system was found to be composed of 81% of calcite and 19% of vaterite, whereas in the

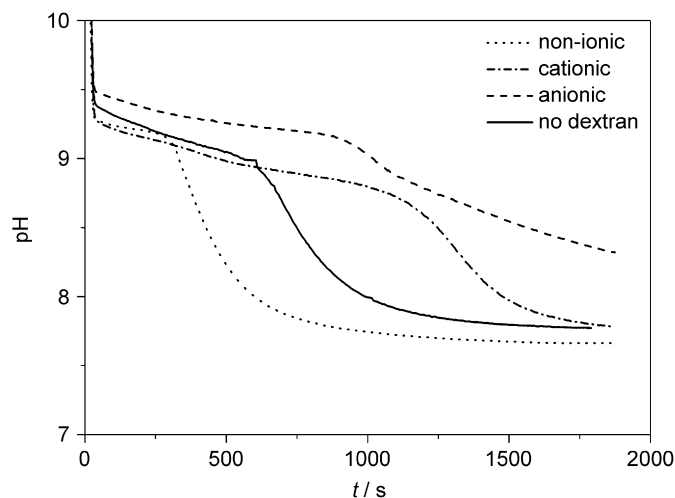


Fig. 1. pH as a function of time obtained at 25°C in the model system $c(\text{H}_2\text{CO}_3) = 0.011\text{ mol dm}^{-3}$, $c(\text{Ca}(\text{OH})_2) = 0.010\text{ mol dm}^{-3}$ and in the systems in which anionic, cationic and non-ionic dextran (all $M_r \approx 500,000$) were present.

samples isolated from the systems with cationic and anionic dextrans, the contents of vaterite were 35% and 25%, respectively. This was estimated on the basis of the FT-IR spectra analyses (Fig. 2). However, the spectra of the samples separated 24 h after mixing the reactants (not shown here) exhibit the characteristics of calcite only, since vaterite had already been transformed into calcite, which is consistent with our previous findings [26,30,31]. Fig. 2A shows the FT-IR spectra of pure calcite and vaterite, recorded in the region from 800 to 650 cm^{-1} , in which absorbencies of vaterite, $\nu_4 = 746\text{ cm}^{-1}$ (spectrum a), and calcite,

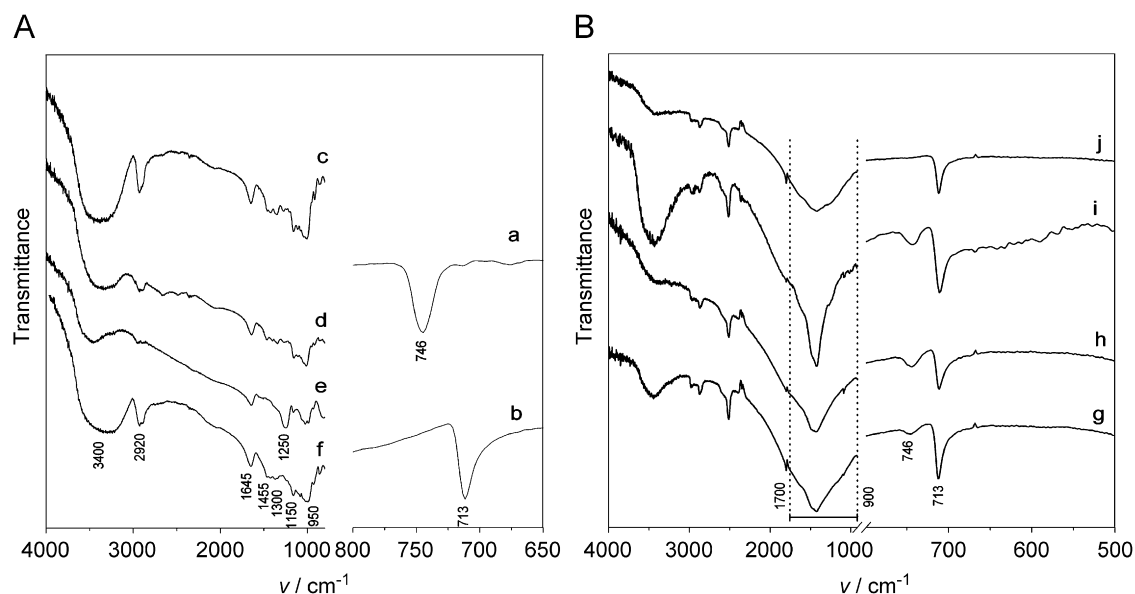


Fig. 2. (A) FT-IR spectra of vaterite (a), calcite (b), non-ionic (c), cationic (d) and anionic (e) dextran and soluble starch (f). (B) FT-IR spectra of the samples taken at 1800 s after the onset of the process from the systems given in Fig. 1: model system (g), system with cationic (h), anionic (i) and non-ionic (j) dextrans.

$\nu_4 = 713 \text{ cm}^{-1}$ (spectrum b), bands appear [28,32]. A compilation of the FT-IR spectra of the non-ionic (spectrum c), cationic (spectrum d) and anionic (spectrum e) dextrans, as well as that of soluble starch (spectrum f) is also shown in the region from 4000 to 800 cm^{-1} , in which the vibrations of different groups characteristic of the additives [33–37] exhibit their bands. Fig. 2B demonstrates the spectra of the samples taken from the systems given in Fig. 1. The FT-IR spectrum of the sample with cationic dextran (spectrum h) shows no significant changes compared to the model system (spectrum g). However, considerable changes are observed in the spectra of the samples precipitated in the presence of anionic (spectrum i) and of non-ionic (spectrum j) dextrans. The major differences appeared in the region of $1700\text{--}900 \text{ cm}^{-1}$, which is characteristic of the vibration frequencies of O–H bending ($\approx 1645 \text{ cm}^{-1}$), C–O/C–C ($1150\text{--}950 \text{ cm}^{-1}$) and S=O ($1250\text{--}1240 \text{ cm}^{-1}$) stretching modes [34,37]. In the case of the non-ionic dextran (spectrum j), the absorption bands, characteristic both of carbonate ion normal vibrations ($1500\text{--}1400 \text{ cm}^{-1}$) [32] and of the dextran C–H bending mode ($1455\text{--}1300 \text{ cm}^{-1}$) [34], overlap and lead to a broad band formation. As distinguished from this sample, the sample of calcium carbonate precipitated in the presence of anionic dextran shows clearly the bands at about 1084, 1014, 980 and 1246 cm^{-1} , which are characteristic of C–O, C–C and S=O stretching modes [34,37].

In order to comprehend the events taking place during the precipitation process, an additional consideration was given to the model system. To that purpose, samples were taken from the precipitation system during the process, and mineralogical composition of the solid phase as well as the concentration of the total dissolved calcium from the liquid phase were determined. Fig. 3 shows the progress curve pH vs. time (Fig. 3A), the corresponding changes in the total dissolved calcium concentration (Fig. 3B) and the FT-IR spectra of the solid-phase samples (Fig. 3C) isolated from the precipitation system at time intervals a–d indicated in Fig. 3A. Spectrum a in Fig. 3C undoubtedly shows the absorption bands characteristic of both amorphous calcium carbonate, ACC (at about 1075 , 1030 and 1640 cm^{-1}) [32,38] and

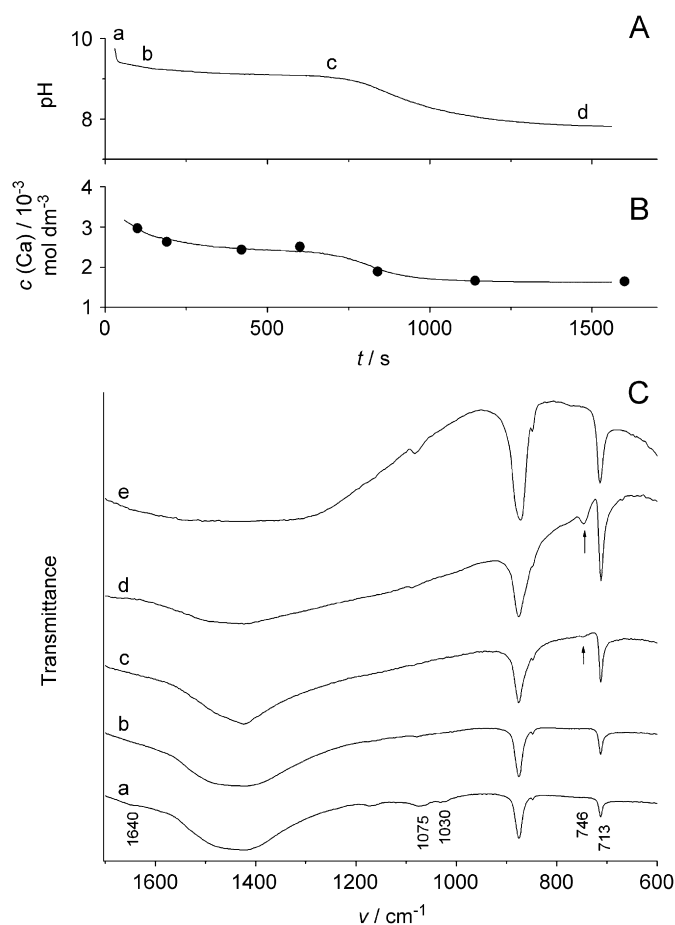


Fig. 3. Changes in pH (A) and total dissolved calcium concentration (B) as functions of time during the precipitation of calcium carbonate in the model system, $c_i(\text{H}_2\text{CO}_3) = 0.011 \text{ mol dm}^{-3}$, $c_i(\text{Ca}(\text{OH})_2) = 0.010 \text{ mol dm}^{-3}$, at 25°C . (C) The corresponding FT-IR spectra of the precipitates isolated at time intervals a–d, as indicated in (A), and 24 h after the onset of the process (e).

of calcite (713 cm^{-1}) [32]. Spectrum b, corresponding to the sample isolated 100 s after the onset of the process, shows that, apart from calcite, only traces of ACC were yet present in the system. Spectra c and d exhibit the absorption bands characteristic of calcite (713 cm^{-1}) and of vaterite (746 cm^{-1}) without any traces of the amorphous phase, the content of vaterite in the sample taken at time d (spectrum d) being higher than that in the sample taken at time c (spectrum c). Spectrum e of the sample taken 24 h after the onset of the process shows the bands characteristic of calcite only.

On the basis of the presented results and those of some previous investigations on the precipitation systems in which several solid phases can be formed [31,39–42], it can be concluded that the precipitation of calcium carbonate in these particular systems occurs through the formation of precursor phases, ACC and vaterite, and the subsequent solution-mediated transformation of these phases into calcite. Thus, during the first stage of the process, a–b in Fig. 3A, observed as a pH drop from about $\text{pH} \approx 10.3$ to 9.5, a simultaneous formation of three calcium carbonate phases takes place: the most unstable ACC, the metastable vaterite and a thermodynamically stable calcite. During the period of slow pH decrease, b–c, from $\text{pH} \approx 9.5$ to 8.8, the processes of simultaneous ACC dissolution and of calcite and vaterite crystal growth takes place. Calcite and vaterite crystal growth become predominant processes during the periods c–d. Simultaneous dissolution of vaterite and crystal growth of calcite (d–e, not shown in Fig. 3A) are the processes that take place during the last stage of transformation of the unstable phases into calcite.

It is to be believed that the described sequence of events found in the model system is followed as well in the systems with the addition of polysaccharides. An exception seems to be the system to which the non-ionic dextran was added (Fig. 4). Since practically no vaterite was found to precipitate in that system, it can be concluded that the non-ionic dextran affects the nucleation of vaterite (Fig. 4c,d). Apart from its influence on the vaterite nucleation, the non-ionic dextran also affects the size of the calcite crystals by adsorbing at their surfaces and, when compared to the model system (Fig. 4a,b), slows down the crystal growth. This is in agreement with the findings [9,43] that such molecules can affect the formation of calcium carbonate particles in the solution by interacting with the solutes and/or solids already formed. The support for this conclusion is provided by the FT-IR spectrum of the sample taken from the system precipitated in the presence of the non-ionic dextran (see Fig. 2B), which shows the bands characteristic both of carbonate and of dextran. The calcite crystals thus obtained were rather monodisperse (Fig. 4c,d), having a specific surface area of $1.25\text{ m}^2\text{ g}^{-1}$ and an average size of about $8\text{ }\mu\text{m}$. A comparable behaviour was demonstrated by a series of non-ionic dextrans with different molecular masses. Fig. 5 shows the size distributions of calcite crystals, obtained in the presence of some of those dextrans, isolated from the systems at the same time (1800 s) as the sample containing $M_r = 500,000$. The average size of crystals decreases by increasing the relative molecular mass of the non-ionic dextran.

The anionic dextran affects both the morphology and the size of calcite and of vaterite crystals (Fig. 4e,f). The typical calcite rhombohedra became imperfect, with rounded edges and smooth steps on their surfaces (Fig. 4e), whereas vaterite took a shape of more or less spherical compact aggregates (Fig. 4f) of originally spherical vaterite particles, the aggregates of which are characterized as poorly developed crystalline material. The average size of those crystals was about $22\text{ }\mu\text{m}$, as compared to the model system aged for the same time (1800 s), with an average particle size of about $16\text{ }\mu\text{m}$. Apart from the well-developed calcite

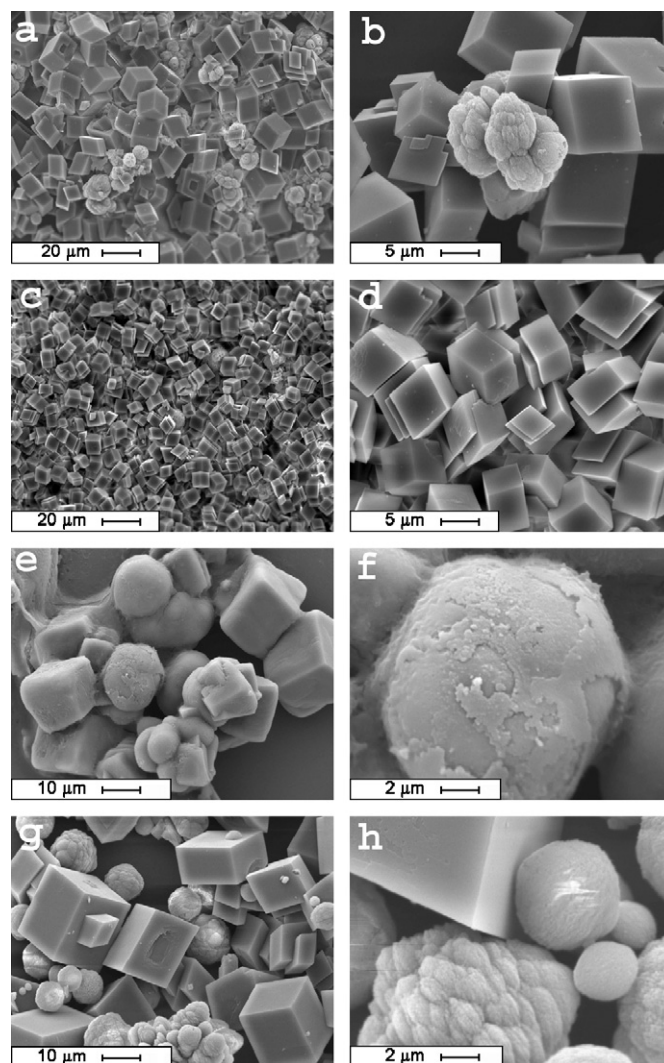


Fig. 4. SEM images of PCC samples taken 1800 s after the onset of the process in the model system (a,b), and in the systems with the addition of different types of dextran (all $M_r = 500,000$): non-ionic (c,d), anionic (e,f) and cationic (g,h) dextrans.

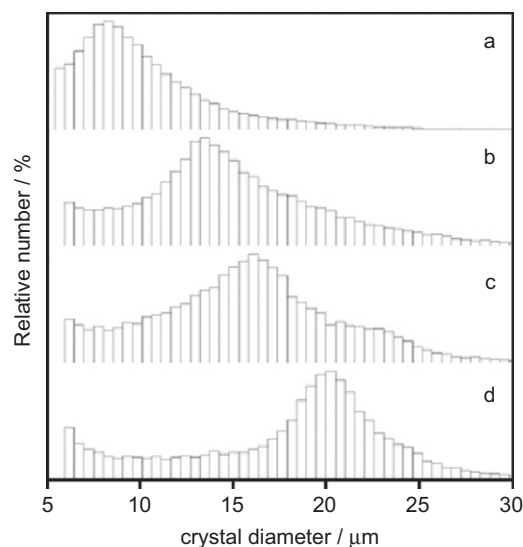


Fig. 5. Crystal size distribution of the samples taken 1800 s after the onset of the process from the systems to which non-ionic dextrans of different M_r were added: 500,000 (a), 40,000 (b), 20,000 (c) and 6000 (d).

rhombohedra, the precipitate in the model system also contained cauliflower-shaped agglomerates of spherical vaterite particles and the agglomerates of mixed vaterite and calcite particles (see Fig. 4a,b). All these lead to the conclusion that the anionic dextran most likely reacts with Ca^{2+} ions at the early stage of the precipitation process, thus decreasing the ion concentration/supersaturation in the solution and consequently the number of nuclei, i.e. the crystals of the resulting precipitate. It seems as well that it slows down the crystal growth of vaterite and its transformation to calcite (see Figs. 1 and 2b), which is consistent with the findings by some other authors [22]. The anionic dextran affects the shape of the crystals although it is not completely clear and can only be speculated about the way of its interaction with the surface of calcium carbonate crystals [9,22]. Yet, it is certain that the FT-IR spectrum shows the presence of the anionic dextran at the surface of the solid phase isolated from the system (see Fig. 2b).

The cationic dextran, similar to the anionic one, affects the kinetics of calcium carbonate precipitation and, when compared to the model system, slows down the growth and transformation processes (see Fig. 1). The shape of the crystals is not significantly affected but a number of non-aggregated vaterite spherical particles of varying dimensions are produced (Fig. 4g,h), many of them smaller than $10\mu\text{m}$. The mechanism of the cationic dextran interaction with the calcite and the vaterite particles can be characterized as an electrostatic adsorption, since both calcite and vaterite particles were found to be negatively charged at $\text{pH} \geq 7.5$ (unpublished results).

3.2. Effect of soluble starch

In order to obtain more information on the effect of polysaccharides on the properties of PCC, a set of experiments with the addition of soluble starch to the precipitation system was performed.

Fig. 6A shows the FT-IR spectra of the precipitates obtained in the presence of different concentrations of soluble starch 1800 s after mixing the reactants. The spectra contain the absorption bands characteristic of both calcite (713 cm^{-1}) and of vaterite (746 cm^{-1}) as well as those characteristic of starch (see Fig. 2A). The intensity of the bands characteristic of starch increases with increase in its concentration in the system, and the mode of interaction between this polysaccharide and the precipitated solid phase can be most probably ascribed to the physical forces, van der Waals forces or hydrogen bonding [19,35]. As obtained with TG analysis (not shown here), about 2.5% of starch was bound to the calcium carbonate particles separated from the system containing 500 mg dm^{-3} of starch. Such was the weight loss of the organic matter that was decomposed between 150 and 350°C during the process of heating the sample, the peak temperature being about 250°C at a heating rate of $20^\circ\text{C min}^{-1}$. The contents of calcite and of vaterite in the systems with different starch concentrations were estimated according to the FT-IR spectra. As shown in Fig. 6B, low starch concentrations (0.5 , 2 and 5 mg dm^{-3}) do not affect the formation of either vaterite or calcite to a considerable extent, but the concentrations of 50 and 500 mg dm^{-3} promote the formation of vaterite. Such an effect can be attributed to the adsorption of starch on the calcite crystals to the extent that the growth rate is slowed down and possibly even prevented when the starch concentration is high enough. In this way, more supersaturation of the system can be spent on vaterite formation and growth. The vaterite particles grow, forming the cauliflower-shaped agglomerates ranging up to about $25\mu\text{m}$, while calcite crystals appear in an average dimension of about $16\mu\text{m}$. This is illustrated in Fig. 7, in which SEM images of the systems containing 0.5 and 500 mg dm^{-3} of starch are represented. Starch had no significant effect on the morphology of either calcite or vaterite at the concentrations used in this work. Typical rhombohedra remained the most abundant shape of the calcite crystals, forming sometimes rhombohedra twins, and vaterite appeared mostly in the cauliflower-shaped agglomerates.

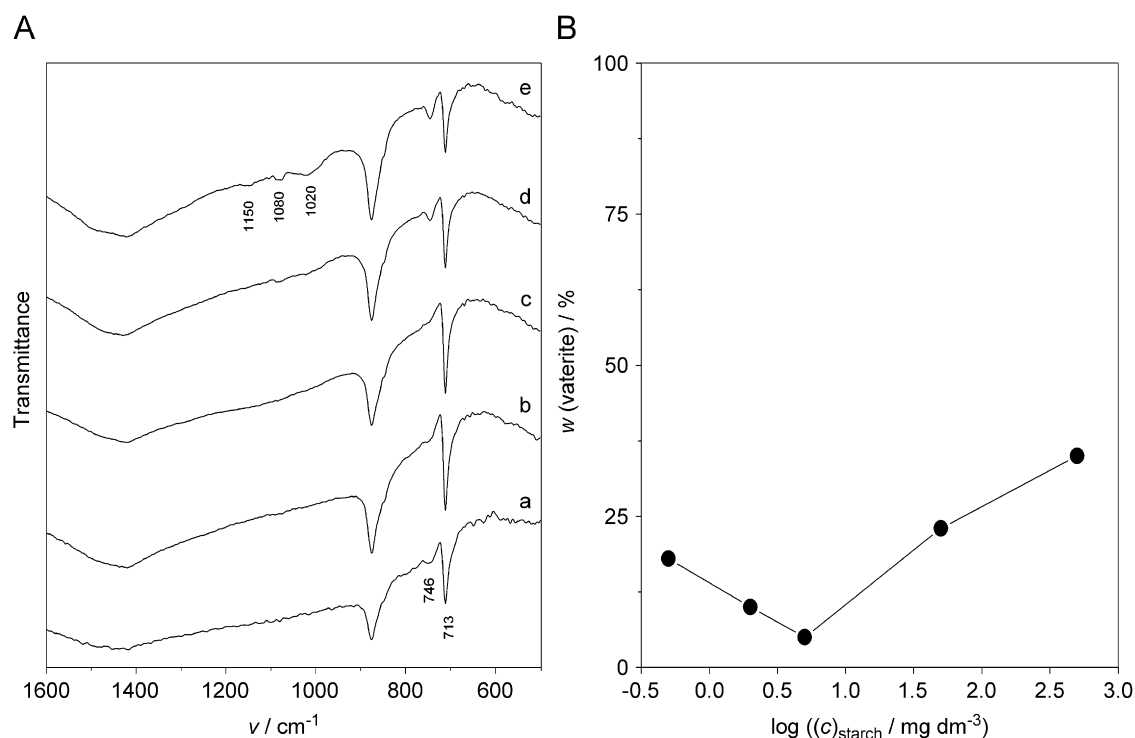


Fig. 6. (A) FT-IR spectra of the samples, taken 1800 s after the onset of the process from the systems to which different mass concentrations of soluble starch were added: (a) 0.5, (b) 2, (c) 5, (d) 50 and (e) 500 mg dm^{-3} . (B) Mass fraction of vaterite as a function of mass concentrations in the samples shown in Fig. 6A.

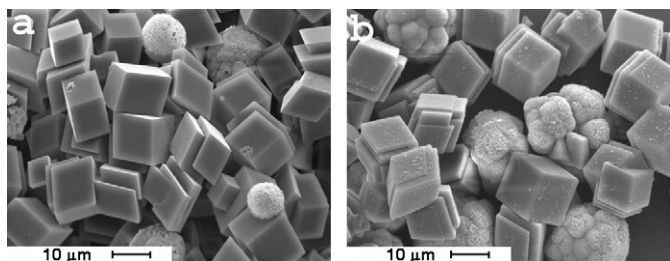


Fig. 7. SEM images of PCC obtained in the systems with the addition of different mass concentrations of soluble starch: (a) 0.5 mg dm^{-3} , (b) 500 mg dm^{-3} .

4. Conclusions

The influence of polysaccharides, dextrans (cationic, anionic and non-ionic) and soluble starch, on the precipitation of calcium carbonate from a homogeneous system in which calcium hydroxide and carbonic acid were reactants, has been investigated. These additives modify the morphology and the size of the precipitated particles, as well as the composition of the precipitate. Precipitation of calcium carbonate in the model system (with no additives) results in the formation of calcite and vaterite, and an amorphous precursor phase at the early stage of the precipitation process. During the solution-mediated processes, this amorphous phase transforms into vaterite and/or calcite and vaterite transforms into calcite, which becomes the final solid phase of precipitation. The average particle size of the thus-formed calcite is about $16 \mu\text{m}$. Calcite is found to be the predominant solid phase formed in the system with the addition of the non-ionic dextran. In this system, by ranging M_r of dextran from 6000 to 500,000, the particle size of calcite decreases to about $8 \mu\text{m}$. In the presence of the anionic dextran the kinetics of the precipitation process is greatly affected. The results show that the adsorption of anionic dextran inhibits crystal growth of the PCC. Among all additives used, the anionic dextran alters the most the morphology of calcite and of vaterite. Cationic dextran slows down the growth and the transformation processes, but its influence on the crystal shape is not pronounced. Similarly, the addition of soluble starch has no effect on the morphology of either calcite or vaterite at the concentrations used in this work. At higher concentrations it promotes the formation and the growth of vaterite, most probably due to the adsorption on the calcite crystal surfaces.

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References

- [1] M. Kitamura, J. Crystal Growth 237–239 (2002) 2205.
- [2] P.C. Chen, C.Y. Tai, K.C. Lee, Chem. Eng. Sci. 52 (1997) 4171.
- [3] W.M. Jung, S.H. Kang, W.S. Kim, C.K. Choi, Chem. Eng. Sci. 55 (2000) 733.
- [4] J. García-Carmon, J. Gómez-Morales, R. Rodríguez-Clemente, J. Colloid Interface Sci. 216 (2003) 434.
- [5] J. García-Carmon, J. Gómez-Morales, R. Rodríguez-Clemente, J. Crystal Growth 249 (2003) 561.
- [6] M. Ukrainczyk, J. Kontrec, V. Babić-Ivančić, Lj. Brečević, D. Kralj, Powder Technol. 171 (2007) 192.
- [7] Y.S. Han, G. Hadiko, M. Fuji, M. Takahashi, J. Eur. Ceram. Soc. 26 (2006) 843.
- [8] K. Uebo, R. Yamazaki, K. Yoshida, Adv. Powder Technol. 3 (1992) 71.
- [9] V.V. Hardikar, E. Matijević, Colloids Surf. A 186 (2001) 23.
- [10] C. Wang, Y. Liu, H. Bala, Y. Pan, J. Zhao, X. Zhao, Z. Wang, Colloids Surf. A 297 (2007) 179.
- [11] N. Vdović, D. Kralj, Colloids Surf. A 161 (2000) 499.
- [12] Y. Sheng, B. Zhou, J. Zhao, N. Tao, K. Yu, Y. Tian, Z. Wang, J. Colloid Interface Sci. 272 (2004) 326.
- [13] Y. Sheng, B. Zhou, X. Zhao, C. Wang, Y. Liu, Z. Wang, Mater. Lett. 60 (2006) 1366.
- [14] Y. Pan, X. Zhao, Y. Sheng, C. Wang, Y. Deng, X. Ma, Y. Liu, Z. Wang, Colloids Surf. A 297 (2007) 198.
- [15] Y. Huang, Q. Shen, W. Sui, M. Guo, Y. Zhao, D. Wang, D. Xu, Colloid Polym. Sci. 285 (2007) 641.
- [16] N. Wada, K. Kanamura, T. Umegaki, J. Colloid Interface Sci. 233 (2001) 65.
- [17] L. Pach, S. Duncan, R. Roy, S. Komarneni, J. Mater. Sci. 31 (1996) 6565.
- [18] Q. Yu, H.D. Ou, R.Q. Song, A.W. Xu, J. Crystal Growth 286 (2006) 178.
- [19] L. Yang, X. Zhang, Z. Liao, Y. Guo, Z. Hu, Y. Cao, J. Inorg. Biochem. 97 (2003) 377.
- [20] J. Yu, M. Lei, B. Cheng, X. Zhao, J. Solid State Chem. 177 (2004) 681.
- [21] C. Wang, J. Zhao, X. Zhao, H. Bala, Z. Wang, Powder Technol. 163 (2006) 134.
- [22] A. Szczes, E. Chibowski, L. Holysz, Colloids Surf. A 297 (2007) 14.
- [23] H.N. Stein, The Preparation of Dispersions in Liquids, Marcel Dekker, New York, 1995.
- [24] J. Yu, M. Lei, B. Cheng, Mater. Chem. Phys. 88 (2004) 1.
- [25] R. Nyström, G. Hedström, J. Gustafsson, B. Rosenholm, Colloids Surf. A 234 (2004) 85.
- [26] D. Kralj, J. Kontrec, Lj. Brečević, G. Falini, V. Noethig-Laslo, Chem. Eur. J. 10 (2004) 1647.
- [27] J. Kontrec, D. Kralj, Lj. Brečević, G. Falini, S. Fermani, V. Noethig-Laslo, K. Miroslavljević, Eur. J. Inorg. Chem. (2004) 4579.
- [28] F.A. Andersen, D. Kralj, Appl. Spectrosc. 45 (1991) 1748.
- [29] D. Kralj, Lj. Brečević, A.E. Nielsen, J. Crystal Growth 104 (1990) 793.
- [30] D. Kralj, J. Kontrec, Lj. Brečević, Chem. Eng. Trans. 1 (2002) 287.
- [31] D. Kralj, Lj. Brečević, J. Kontrec, J. Crystal Growth 177 (1997) 248.
- [32] F.A. Andersen, Lj. Brečević, Acta Chem. Scand. 45 (1991) 1018.
- [33] L. Yang, X. Zhang, Z. Liao, Y. Guo, Z. Hu, Y. Cao, J. Inorg. Biochem. 97 (2003) 377.
- [34] F. Delval, G. Crini, S. Bertini, N. Morin-Crini, P.M. Badot, J. Vebrel, G. Torri, J. Appl. Polym. Sci. 93 (2004) 2650.
- [35] J. Wang, P. Somasundaran, J. Colloid Interface Sci. 309 (2007) 373.
- [36] B. Zümreoglu-Karan, H. Mazi, A. Güner, J. Appl. Polym. Sci. 83 (2002) 2168.
- [37] A.S. Amarasekara, G. Opoku, X. Qiu, V. Doctor, Carbohydr. Polym. 68 (2007) 116.
- [38] T. Dupuis, J. Ducloux, P. Butel, D. Nahon, Clay Miner. 19 (1984) 605.
- [39] Lj. Brečević, D. Kralj, J. Crystal Growth 79 (1986) 178.
- [40] R.J. Davey, P.T. Cardew, D. McEwan, D.E. Sadler, J. Crystal Growth 79 (1986) 648.
- [41] J. Kontrec, D. Kralj, Lj. Brečević, J. Crystal Growth 240 (2002) 203.
- [42] V. Babić-Ivančić, J. Kontrec, Lj. Brečević, D. Kralj, Water Res. 40 (2006) 3447.
- [43] M. Onofusa, E. Matijević, J. Colloid Interface Sci. 71 (1979) 167.