The Crystal Growth of Calcite Crystals in the Presence of a Cyclic Polycarboxylic Acid

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Introduction

The crystal growth of calcium carbonate is a very important process for a number of biological, biogeochemical, and industrial processes. The polymorphism of calcium carbonate is an important aspect, since it is possible to form more than one crystal phases in supersaturated solutions: vaterite, aragonite or calcite (in the order of increasing stability- decreasing solubility) [1]. The rapid transformation of the less stable polymorphs to the thermodynamically most stable calcite is a process that depends on the solution supersaturation, pH and/or the presence of additives in solution [2, 3]. Since the various calcium carbonate polymorphs have quite different solubility and formation properties, it is important to understand the interaction of additives that inhibit crystal growth with the crystallizing substances. Accurate measurements of the crystal growth process are therefore needed, and these may be achieved through the best possible control of the solution parameters, of which supersaturation is of key importance. The evaluation of the role of additives, often used as crystal growth inhibitors, is relying very much on the precision of kinetics measurements of crystal growth in their presence. The methodology of constant solution composition is an excellent tool for the evaluation of the effect of additives on the crystal growth of salts from supersaturated solutions as it allows for maximum reproducibility and precision of the measurements [4]. Inhibitors interact with growing calcite crystal faces by adsorption or surface complexation, etc. [5]. Among other compounds found to inhibit efficiently the crystal growth of calcium carbonate are compounds containing multiple carboxylic groups. Carboxylate-rich molecules influence calcification by binding to calcite mineral surfaces, modifying calcite crystal growth rates [6]. In the present work we present the results of the effect of cyclopentane tetracarboxylic acid (CPETCA) on the crystal growth rates of calcite crystals. The investigation was carried out at sustained solution supersaturation which allowed accurate and reproducible measurement of calcite crystal growth rates in the presence of CPETCA.

Experimental

All experiments were done in a double walled water jacketed Pyrex® glass reactor thermostatted with circulating water from a thermostat at $25.0\pm0.2°C$. The supersaturated solutions were prepared directly in the reactor mixing equal volumes of equimolar solutions of calcium chloride and sodium bicarbonate, prepared from the respective stock solutions. In all experiments the ionic strength was adjusted to 0.1M with KNO_3. All stock solutions were

prepared from the respective crystalline solids using triply distilled water and they were filtered through polycarbonate membrane filters 0.2 μm (Sartorius). For the experiments done in the presence of CPETCA, the additive was introduced in the supersaturated solution as well. The pH was adjusted to 8.5 and the solutions were homogenized by magnetic stirring. Stability of the solution for more than two hours suggested that the solutions were stable. Following the verification of the solution stability, accurately weighted quantity of calcite seed crystals, prepared, aged and characterized at the laboratory, was transferred into the reactor with the supersaturated solution and was dispersed in the fluid. The introduction of the seed crystals in the supersaturated solution triggered the onset of crystal growth without the lapse of measurable induction time. Drop of the solution pH as little as 0.005 pH units triggered the addition of titrant solutions from two coupled burettes of a computer driven system. The titrant solutions consisted of calcium chloride and sodium carbonate with the stoichiometry of the precipitating salt, $CaCO_3$, i.e. 1:1. The titrant solutions contained the appropriate concentrations to avoid dilution or changes of the ionic strength. Random sampling, filtration of the suspensions and chemical analysis of the filtrates for calcium by atomic absorption spectrometry (AAS) confirmed that crystal growth proceeded at conditions of constant supersaturation. From the plots of the titrant solutions added as a function of time the rates were measured. The reproducibility was in all cases better than 5% (mean of five experiments). The solids forming during and at the end of the experiments were characterized by x-ray diffraction (XRD, Siemens D-5000), scanning electron microscopy (SEM, Zeiss Leo Supra V-35) and thermo gravimetric analysis (TGA, TA Q50). Zeta potential measurements of dilute calcite suspensions were done in a Nanosize instrument (Malvern).

Results and Discussion

The supersaturation with respect to the calcium carbonate polymorphs were calculated taking into consideration all equilibria possible, using the PHREEQC software [6]. The supersaturation ratio, $\Omega_{CaCO3\ polymorph}$, is defined as:

$$\Omega_{CaCO3\ polymorph} = \frac{\alpha_{Ca^{2+}}\alpha_{CO_3^{2-}}}{K^0_{s,CaCO_3\ polymorph}} = \frac{IAP}{K^0_{s,CaCO_3\ polymorph}} \quad (1)$$

In eq. 1, the numerator is the product of the activities of the subscripted ions and the denominator the thermodynamic solubility product of the calcium carbonate polymorphs. The solutions used in the present work were supersaturated with respect to calcite, aragonite and vaterite in the order of increasing solubility. Calcite is known to crystallize on seed crystals with surface diffusion controlled mechanism with an apparent order of 2 [8]. As a consequence, substances interacting with the surface of the calcite crystals by either adsorption of surface complexation or even hydrogen bonding, are expected to modify the availability of the crystal growth sites resulting in reduced calcium carbonate crystal growth rates. In the present work, the water soluble tetracarboxylic acid was tested at conditions in which all four carboxyl groups were ionized. The molecular structure and the geometry of the molecule is shown in Figure 1:
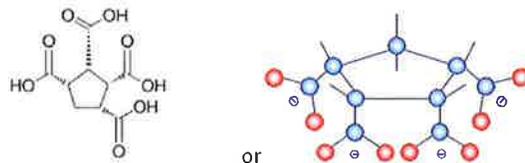

Figure 1. Molecular formula and structure of CPETCA

Despite the fact three of the four carboxyl groups of CPETCA were dissociated at the experimental conditions of the present work (pK values at ionic strength 0.5M for CPETCA are: pK_1=2.54, pK_2=3.97, pK_3=5.05, and pK_4=9.25 [9]) the extent of calcium sequestration was negligible and it did not affect the calculated supersaturation over the range of concentrations it was used. Calcite growth-rates were markedly reduced in the presence of microgram per liter (ppb) concentrations of CPETCA, C_{CPETCA}. The relative reduction of the rate of calcite growth, $R_{calcite}$, with respect to the rate in the presence of CPETCA, R_{CPETCA} may be seen in Figure 2.
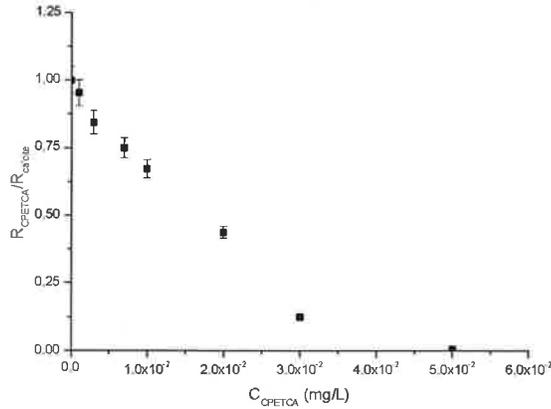

Figure 2: Ratio of the rates in the presence over the respective value in the absence of CPETCA in the supersaturated solutions as a function of the concentration of CPETCA; pH 8.50, 25°C.

Assuming that the rate of crystal growth in the presence of CPETCA was reduced to an extent depending on the fraction of surface coverage, θ of the seed crystals by CPETCA which may adsorb reversibly, the respective rate, R_{CPETCA}, is related with the rate in the absence of the additive, $R_{calcite}$ with equation (2):

$$R_{CPETCA} = R_{calcite}(1 - \theta b) \qquad (2)$$

In equation (2), b is a constant such that 0<b≤1). Calculating θ from the Langmuir adsorption isotherm [10], equation 2 may be modified:

$$\frac{R_{calcite}}{R_{calcite} - R_{CPETCA}} = \frac{1}{b} + \frac{1}{bK_{aff}} \cdot \frac{1}{C_{CPETCA}} \qquad (3)$$

In eq.(3) K_{aff} is a constant equal to the ratio of the specific rates of adsorption over the respective of desorption. Provided that the model assumptions are valid, the plots of the right hand side of eq. 3 as a function of $1/C_{CPETCA}$, are expected to be linear. From the slope and the intercept of the linear plots the values of b and K_{aff} may be calculated. The rate of calcite crystal growth was measured over a range of CPETCA concentrations between 1 to 50 ppb. Significant rate reduction was found at these low concentrations and the plot according to eq, 3, is shown in Figure 3.
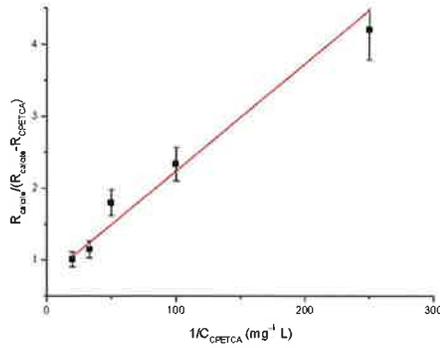
Figure 3: Kinetics plot of the seeded crystal growth of $CaCO_3$ in the presence of CPETCA; pH 8.50, 25°C.

As may be seen from Figure 3, the linear fit is quite satisfactory, thus suggesting that CPETCA adsorbs onto calcite over the concentration range of 0 to 50 ppb blocking the active growth sites. It should be noted that although CPETCA adsorption is fast, some time (ca. 10-20 min) is needed for the equilibration of the adsorbate with the seed crystals. A slow CPETCA adsorption step or CPETCA reorientation may cause the observed brief, initially accelerated calcite-growth rate before the steady-state reduced calcite growth rate at low CPETCA concentrations is established. From the slope and the intercept of the linear fit of the kinetics data a value of 7.1×10^6 was calculated for K_{aff}, which has been in the literature for comparison of the inhibitory activity of various additives [10]. This value compares well with other ions which are strong inhibitors of calcite crystal growth, like orthophosphate ions which at concentrations of 1 µM, stopped completely the crystallization of calcite. The assumption of adsorption was further supported by the curves obtained by thermogravimetric analysis shown in Figure 4. Similar conclusions were drawn from the zeta potential measurements of calcite suspensions without and with adsorption (Figure 5).
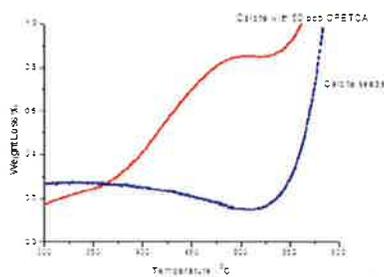

Figure 4: Thermogravimetric analysis of calcite: (Blue line) seed crystals (red line) calcite crystals crystallized in the presence of 50 ppb CPETCA.
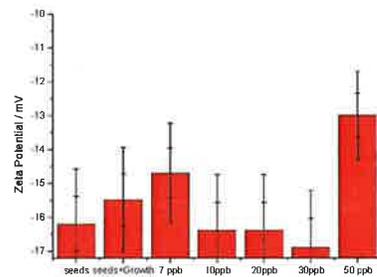
Figure 5: Zeta potential measurements of calcite seed crystals grown in the absence and in the presence of CPETCA

The presence of the organic material adsorbed on calcite is shown by the significant weight loss in the temperature range between 400-500°C, corresponding to CPETCA uptaken by calcite.

The morphological examination of the crystals showed that uninhibited, growth occurs in smooth planes on the crystal faces. (25% mass increase). Scanning Electron Microscopy (SEM) demonstrates calcite seed crystal growth morphology differences in the absence and presence of alicyclic five-atom PCAs (Figure 6). Unreacted calcite seed crystals are well-formed, sharp edged rhombs with a mean crystal edge length of 3 μm. Calcite seed crystals size grown for 100 minutes in the absence inhibitors increased mass by about 25% and exhibited uniform growth planes with step features on the growing-face perimeter (Figure 6a). Surface and edge irregularities are almost absent on growth surfaces in the absence of CPETCA. In the presence of CPETCA adsorption of this solutes reduced the growth rate by blocking the propagation of the uniform growth steps causing a more irregular, discontinuous growth surface (Figure c and d) than that observed for growth in the absence of the inhibitors (Figures 6a and b).
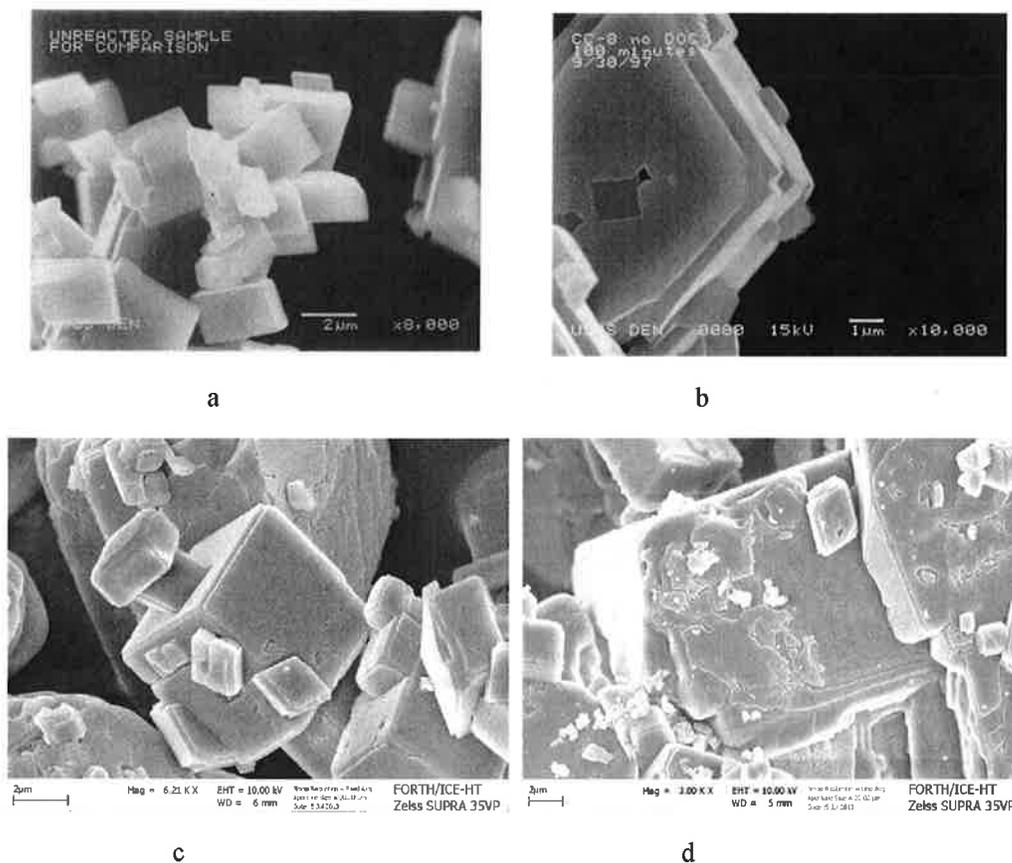

a

b

c

d

Figure 6: Calcite crystals: a: seed crystals b: seed crystals grown at constant supersaturation ca. 60% crystal growth w.r.t seed crystals c: calcite grown in the presence of 10 ppb CPETCA; d: calcite grown in the presence of 20 ppb CPETCA

Conclusions
CPETCA, a tetraacarboxylic compound, at pH 8.50, 25°C, proved to be a strong inhibitor of calcite seeded crystal growth. The inhibition of the rate of crystal growth was due to adsorption of the compound onto the calcite active crystal growth sites, as shown by TGA and zeta potential measurements. Finally the presence of CPETCA in the supersaturated solutions

resulted in morphological changes which led to surface irregularities, possibly through the interference with the advancement of steps on the surface of the crystals.

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