

Nucleation and Crystal growth of Calcium Carbonate in the Presence of Zn

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ABSTRACT

The effect of the presence of Zn in solutions supersaturated with respect to calcium carbonate was investigated at 25°C, pH 8.50. The stability domain of the calcium carbonate solutions was measured in the supersaturation ratio (SR_{calcite}) values between 20.89–32.36. Below the least SR_{calcite} value the solutions were stable. Above it, precipitation was spontaneous past induction time, inversely proportional to SR_{calcite} according to the classical nucleation theory (CNT). In the presence of 1.3 ppm of Zn in the supersaturated solutions, the stability domain was shifted to higher SR_{calcite} values ($47.86 < SR_{\text{calcite}} < 112.2$). The presence of Zn stabilized all three calcium carbonate polymorphs. In the absence of Zn only vaterite and calcite were identified in the precipitated. In all cases no Zn oxides were formed. The rate of spontaneous precipitation of calcium carbonate in the presence of Zn, was reduced by as much as 98% at the least SR_{calcite} values tested. Adsorption of Zn at the active sites of the supercritical nuclei of vaterite is responsible for the reduction of the rates of CaCO_3 precipitation and for the delay of conversion of unstable polymorphs. Finally, induction times in the presence of Zn were significantly longer for the same SR_{calcite} values without Zn, suggesting that Zn is a nucleation inhibitor as well.

INTRODUCTION

Calcium carbonate precipitation in the presence of pollutants is a carrier of importance for their transport to the sediments and for their subsequent release

depending on the local microenvironment conditions^{1,2}. Zinc is often present in industrial waters (heat exchangers and boilers) mainly for corrosion protection. Depending on the alkalinity and calcium concentration of waters used in water intensive processes, calcium carbonate fouling is common. Moreover, among other metals, is present in natural waters together with iron and copper, where the concentration of Zn(II) may reach at levels of several ppm. Zinc has been reported to retard precipitation of calcium carbonate scale in heat exchangers and in oil production wells even at concentration of 2 ppm^{3,4}. Similar calcium carbonate precipitation inhibition was attributed to the presence of zinc species released from the surface of the equipment involved with physical water treatment^{5,6}. It is interesting to note that the presence of just 50 ppb of zinc in solutions of rather high supersaturation with respect to all calcium carbonate polymorphs, resulted to dramatic reduction of both nucleation and subsequent crystal growth⁶. The presence of zinc in the solutions in which calcium carbonate precipitated, favored the stabilization of the metastable aragonite polymorph⁶. Interestingly, it has also been reported that zinc acted as an accelerator of heterogeneous nucleation in the bulk solution and the effect was more pronounced at higher concentrations⁷. In general, the addition of chemical inhibitors to control scale formation by crystallization is the practice used most often. Commonly used antiscalants include condensed polyphosphates, organophosphates, and polyelectrolytes containing carboxylic and sulfonate functional groups. The mechanism of inhibition is quite diverse and includes chelation, dispersion and retardation of the growth of inorganic minerals due to poisoning of the active growth sites^{8,9}. Metallic cations such as iron, copper and zinc are very important, because of their natural origin in water and the investigation of their role in the kinetics and the mechanism of inorganic fouling deserves further and deeper exploration. Despite research interest for the role of the presence of zinc in calcium carbonate supersaturated solutions, the related literature is short of investigations of the spontaneous precipitation of calcium carbonate polymorphs and their subsequent growth in aqueous solutions, supersaturated with respect to the calcium carbonate polymorphs containing zinc at concentration levels precluding the formation of sparingly soluble salts of zinc carbonate ($\text{Zn}(\text{OH})_2$, ZnCO_3 or $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$).

In this study the role of the presence of zinc on the nucleation and crystal growth of calcium carbonate, was investigated. For the complete understanding of the interaction of zinc with CaCO_3 , the rates of precipitation and crystal growth of calcium carbonate in the absence and in the presence of zinc at concentration levels up to 1.3 ppm, at 25°C, 0.1M NaCl were measured. The highest concentration tested was defined by the highest possible zinc concentration in solution, value in which the precipitation of any zinc hydroxide and carbonate solid was ruled out thermodynamically.

MATERIALS AND METHODS

Calcium carbonate precipitation experiments were done at constant supersaturation in the experimental setup shown in Figure 1. Specifically, a double walled, Pyrex® glass water jacketed reactor (200mL) was used for all experiments and the supersaturated solutions were prepared in the reactor by direct mixing of solutions of the component ions of calcium carbonate. The reactor temperature was maintained at 25±0.2°C. All solutions were made from stock solutions, prepared from the corresponding crystalline reagents:

Calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), sodium bicarbonate (NaHCO_3), sodium carbonate (Na_2CO_3) and zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) (Merck) were dissolved in deionized, triply distilled water and filtered through $0.22\mu\text{m}$ cellulose membrane filters. The calcium and zinc stock solutions were standardized by atomic absorption spectrometry (AAS). Sodium bicarbonate and sodium carbonate stock solutions were freshly prepared before each experiment. The solutions were adjusted to a pH value of 8.5 with standard 0.1M NaOH solution.

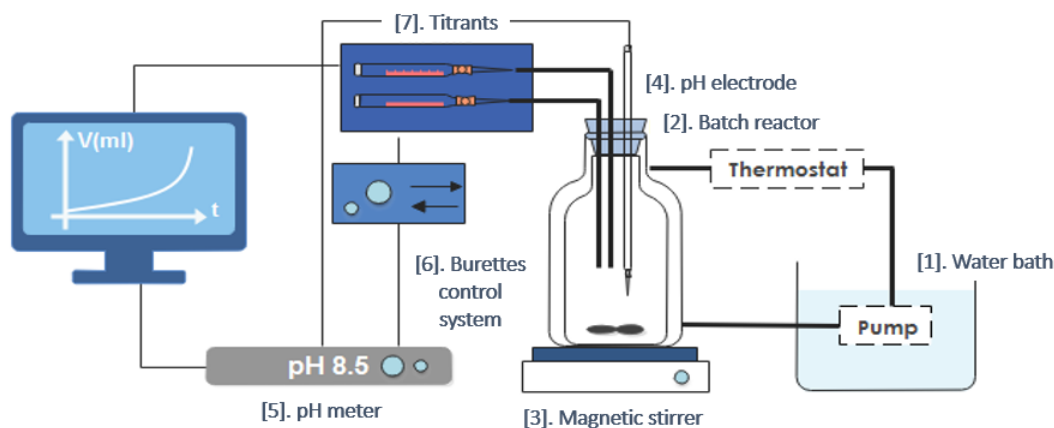


Figure 1: Schematic outline of the experimental device. [1] Thermostatted water bath (25°C), [2] Pyrex® double wall batch reactor, [3] Magnetic stirrer, [4] pH measuring electrode, [5] pH-meter, [6] Control system of mechanically coupled burettes, [7] Burettes containing titrant solutions to keep supersaturation constant.

pH decrease, related with the initiation of precipitation of calcium carbonate, triggered the addition of titrant solutions consisting of CaCl_2 , Na_2CO_3 and NaOH of concentrations appropriate to replace the ions from the supersaturated solutions migrating to the solid phase. The added volume of the titrant solutions during the precipitation process was recorded as a function of time and was used for the calculation of the precipitation rates of CaCO_3 . Samples were withdrawn during the experiments and filtered through membrane filters. The filtrates were analyzed for total calcium concentration, using atomic absorption spectrometry, to check the constancy of the solution composition throughout the course of precipitation. The solids on the filters were examined for morphological features by electron microscopy (SEM), optical microscopy and by X-ray diffraction (XRD).

RESULTS AND DISCUSSION

First, the stability diagram of the calcium carbonate supersaturated solutions was constructed measuring the time lapse from the preparation of the supersaturated solutions till the verification of the start of the precipitation process. The starting point was recorded at the time moment in which the first change of the solutions characteristics (pH or concentration) was detected. The stability diagrams were constructed from plots of the time lapse recorded (start of experiments till first addition of titrants -induction time, τ) as a function of the initial supersaturation of the solutions. The supersaturation, i.e. the departure

of the solution from equilibrium was expressed using the saturation ratio, SR_x , with respect to calcium carbonate polymorphs (x):

$$SR_x = \frac{(Ca^{2+})(CO_3^{2-})}{K_s^0} \quad (1)$$

In Equation (1), (..) denote activities of the enclosed ions and K_s^0 is the thermodynamic solubility product of the precipitating calcium carbonate polymorph. The relative supersaturation with respect to polymorph x is defined by Equation (2):

$$\sigma_x = (SR_x)^{\frac{1}{2}} - 1 \quad (2)$$

The stability diagram of the calcium carbonate system, in the absence and in the presence of 1.3 ppm of zinc, is shown in Figure 2.

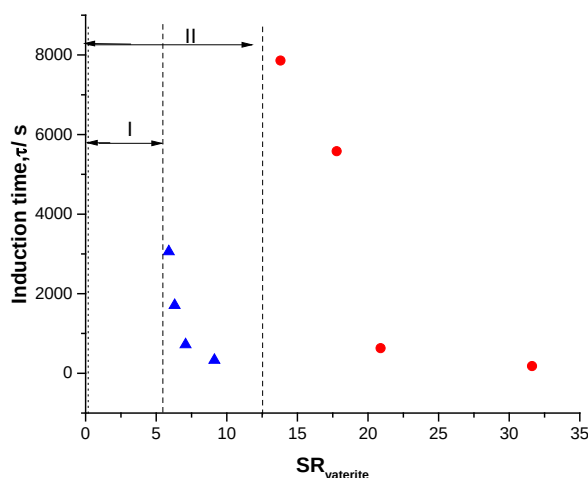
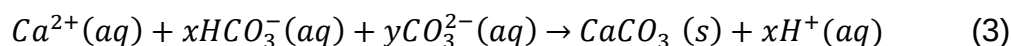


Figure 2: Stability diagram of supersaturated calcium carbonate solutions. Induction time as a function of the supersaturation ratio, SR , with respect to vaterite; pH 8.50, 25°C, NaCl 0.1M; (▲) In the absence of Zn; (●) in the presence of 1.3 ppm zinc, in the supersaturated solution.

As may be seen, the presence of zinc in the supersaturated calcium carbonate solutions, at concentrations as low as 1.3 ppm, shifted their destabilization limit at significantly higher SR values, suggesting that Zn is a nucleation inhibitor. Apparently, Zn is an effective threshold inhibitor, as its presence in the supersaturated solutions, shifted dramatically the threshold for the spontaneous precipitation of calcium carbonate.

Past the lapse of induction time, the precipitation onset was accompanied with proton release in the supersaturated solutions, according to Equation (3):



In Figure 3 the volume of titrant solutions added to the supersaturated solution, to maintain supersaturation, as a function of time is shown. As may be seen, in the supersaturated solutions with SR (with respect to calcite) = 112.2, precipitation started immediately upon the establishment of the solution

supersaturation and was accompanied by the addition of titrant solutions to compensate not only for the released H^+ in solutions, but also for the reduction of the concentrations of the consumed calcium and carbonate ions. For the lower supersaturation ratio values tested, precipitation started past the lapse of induction times, which were inversely proportional to the solution saturation ratio. As may be seen from Figure 3, the plots of titrants addition as a function of time, allowed for the accurate and reproducible measurement of the induction times preceding the onset of precipitation. The results of the induction time measurements, and the rate of precipitation, calculated in the early stages of precipitation (initial stages of precipitation corresponded to the time where 5% of the mass of calcium carbonate that could have precipitated in the specific experimental conditions based on the corresponding solubility), are summarized in Table 1. The calculation of the rates of precipitation at any point of the curves V-t (Figure 2) was calculated from Equation (4):

$$R = \left(\frac{dV}{dt} \right)_t C_{\text{Titrant}} V_{\text{Total}} \quad (4)$$

In Equation (4) the slope of the V-t curves at time t, C_{Titrant} the concentration of the titrant solutions needed to maintain supersaturation and V_{Total} the volume of the solution and the respective of the titrant added at time t.

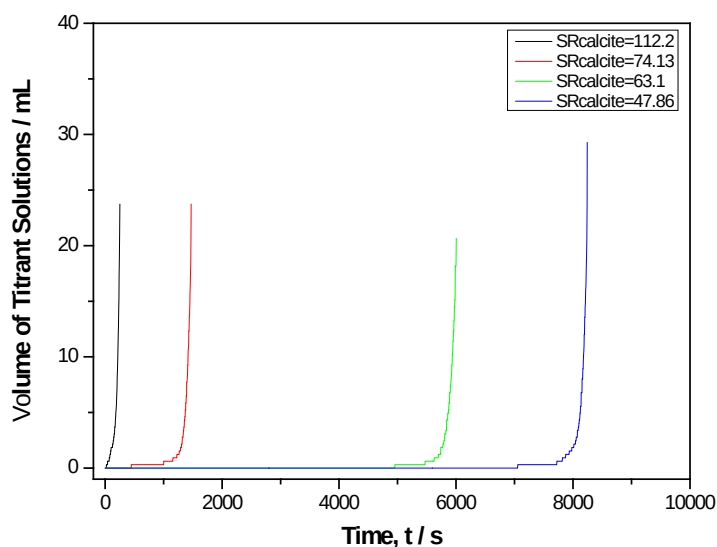


Figure 3: Spontaneous precipitation of calcium carbonate in the presence of 1.3 ppm Zn, at constant supersaturation. Added volume of titrant solutions as a function of time, to maintain supersaturation; pH 8.50, 25°C, NaCl 0.1M.