

The effect of the presence of zinc on the precipitation of CaCO₃ from supersaturated solutions

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Abstract

Precipitation and dissolution processes of calcium carbonate in natural aquatic systems, are responsible not only for the regulation of pH but also for the transport of pollutants to and from sediments. Of interest in these processes, is the role of the presence of heavy metals in the aquatic environment. In the present work the mechanism of calcium carbonate formation from supersaturated solutions in the absence and presence of zinc (II) was investigated at 25°C, pH 8.50, 0.1M NaCl, at conditions of constant supersaturation. Kinetics analysis suggested that the precipitation of calcium carbonate both in the absence and in the presence of zinc over a concentration range 10-30 μM, is controlled by surface diffusion. The presence of zinc in the supersaturated solutions reduced the rate of crystal growth of the calcite seed crystals and the rate reduction was smaller the higher the solution supersaturation. The inhibition was probably due to the adsorption of zinc species to the active sites of crystal growth of the seed crystals. Provided that the adsorption could be described according to the Langmuir model, the assumption was justified both by fitting kinetics data of calcium carbonate crystal growth and by independent equilibrium adsorption studies.

Keywords: calcium carbonate, precipitation of, inhibition of, zinc, adsorption

1. Introduction

CaCO₃ 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 [Mugwar et al. 2014; Schwartz et al. 1999]. Removal of heavy metal ions takes place through their adsorption and/or incorporation on the metal surface or through incorporation into the crystal lattice of the calcium carbonate precipitates. For the complete understanding of the interaction of heavy metal pollutants with minerals forming in aquatic systems it is necessary to understand their effect on the nucleation and crystal growth process of the pollutants. In the present work, the interaction between zinc and calcium carbonate in the corresponding supersaturated solutions was investigated through measurements of the rates of precipitation and crystal growth of calcium carbonate in the absence and in the presence of zinc at

concentration levels up to 50 mM, at 25°C, 0.1M NaCl. Moreover the equilibrium adsorption of zinc on calcite was investigated at the same conditions.

2. Experimental

Free drift experiments in the absence and in the presence of Zn in supersaturated solutions with respect to calcium carbonate were done for the determination of the stability domain of the calcium carbonate supersaturated solutions [Koutsoukos et al. 1984]. Seeded growth experiments were done in the domain of the stable supersaturated solutions, using the seeded growth method as sustained supersaturation [Koutsoukos et al. 1980].

3. Results and Discussion

The presence of zinc in the supersaturated solutions affected both the induction time preceding the onset of calcium carbonate precipitation and the concomitant rates of precipitation. The presence of 20 μM of Zn in the solution shifted the stability domain of the system to higher supersaturations, as may be seen in Figure 1.

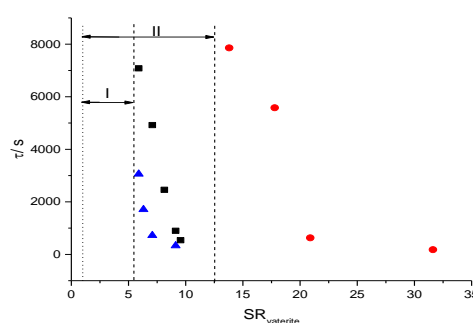


Figure 1. Stability diagram of calcium carbonate. (▲), (■) in the absence of Zn; (●) 20μM Zn; pH 8.50, 25°C, 0.10 M NaCl.

In the presence of Zn all three calcium carbonate polymorphs were identified in the precipitates (vaterite, aragonite and calcite). Zn retarded the transformation of the least stable vaterite polymorph, forming first. The effect of the presence of Zn on the crystal growth rates of calcite seed crystals was investigated in the stable domain of the supersaturated solutions over the

concentration range 12-20 μ M of Zinc. The rates of crystal growth were significantly reduced as may be seen in Figure 2.

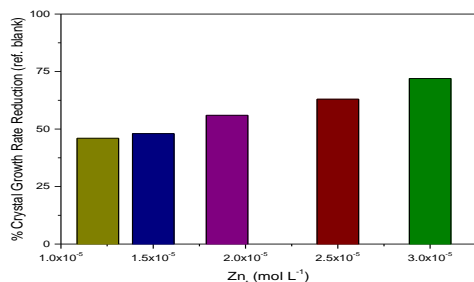


Figure 2. Reduction of the rate of crystal growth of calcite seed crystals in the presence of Zn

The crystal growth reduction was found to be due to the selective adsorption of zinc species on the calcitic surface. Assuming that adsorption is well described by the Langmuir model and that reduction of the rates of crystal growth are reduced proportionally to the unblocked sites available for crystal growth according to equation

$$\frac{R_0}{R_0 - R_i} = \frac{1}{1 - b} + \frac{1}{(1 - b)K_i C} \quad (1)$$

where R_0 , R_i are the rates of calcite seeds growth in the absence and in the presence of Zn, and b , K_i are constants. The latter is associated with the affinity of the test additive for the substrate (calcite). The data were fitted to the model of eq.1, as may be seen in Figure 3.

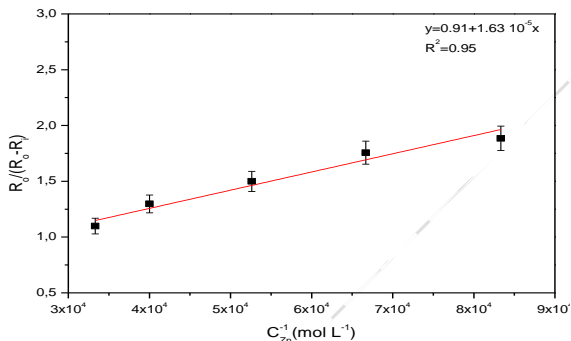


Figure 3. Fitting of the data from the measurements of the rates of crystal growth of calcite seed crystals in the presence of zinc according to equation (1).

The calculated value of $K_i = 5.4 \times 10^4$ suggested high affinity of the zinc (II) species in the aqueous medium for the calcite surface [Klepetsanis et al. 2002]. The limited reversibility of adsorption corroborated this finding. The strong interaction of zinc with calcite surfaces may be the reason of the inactivation of the effect of phosphonate inhibitors, often used as scale inhibitors [Wang et al. 2016].

4. Conclusions

The presence of Zinc in aquatic media supersaturated with respect to calcium carbonate resulted in the dramatic reduction of the kinetics of nucleation, of calcium carbonate polymorphs transformation and of the crystal growth of calcite crystals. The kinetics

effects were attributed to the high affinity of zinc aqueous species for calcite surfaces.

Acknowledgements

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