

# CACO<sub>3</sub> PRECIPITATION FROM ARTIFICIAL SEA WATER THE INFLUENCE OF ORGANIC AND INORGANIC ADDITIVES

Neda Vdovic\* and Damir Kralj

Rudjer Boskovic Institute, Zagreb, Croatia - vdovic@rudjer.irb.hr, kralj@rudjer.irb.hr

## Abstract

The influence of montmorillonite and fulvic acid on the precipitation of calcium carbonate from artificial sea water (ASW) is investigated. Precipitation from pure ASW results in formation of aragonite. Calcium montmorillonite, which was found to be a promotor of the precipitation of calcite from the system containing only constituent ions, does not cause the same effect on the precipitation from ASW. In this case aragonite is formed. Fulvic acid inhibits the precipitation, causing a delay in the precipitation process. When montmorillonite is added together with fulvic acid, no delay in the precipitation is observed.

**Keywords:** calcium carbonate, precipitation, montmorillonite, fulvic acid

## Introduction

Spontaneous precipitation of calcium carbonates may result in formation of one of the three polymorphs: vaterite, aragonite or calcite depending on the initial concentration of constituent ions, temperature and impurities. Vaterite usually precipitates from a solution containing only constituent ions (1), precipitation from artificial seawater (ASW) always results in formation of aragonite (2), calcium montmorillonite is found to be a suitable substrate for the precipitation of calcite (3), while organic impurities inhibit the process (4). The influence of montmorillonite and fulvic acid on CaCO<sub>3</sub> precipitation from ASW is investigated in this work. The main purpose was to find out if montmorillonite could promote the precipitation process and formation of calcite from ASW and in the presence of organic matter.

## Experimental

Artificial sea water was prepared as 5·10<sup>-1</sup> mol dm<sup>-3</sup> NaCl, 5·10<sup>-2</sup> mol dm<sup>-3</sup> MgSO<sub>4</sub>, 10<sup>-2</sup> mol dm<sup>-3</sup> CaCl<sub>2</sub>, 2·10<sup>-3</sup> mol dm<sup>-3</sup> NaHCO<sub>3</sub> and 2·10<sup>-4</sup> mol dm<sup>-3</sup> Na<sub>2</sub>CO<sub>3</sub>. Montmorillonite (g = 0.4 g l<sup>-1</sup>) and/or fulvic acid (c = 4 ppm) were added after the ASW was prepared. Finally, 10<sup>-1</sup> mol dm<sup>-3</sup> NaOH was used to increase the pH to initiate the precipitation. The propagation of reaction was followed by measuring the pH of the solution. Composition of the precipitate was determined by using a FT-IR spectroscopy.

## Results and discussion

The curves shown in Figure 1 represent the precipitation from the reference system (only ASW), from the ASW containing fulvic acid, and from the ASW with fulvic acid and montmorillonite. Precipitation of CaCO<sub>3</sub> from ASW started after approx. 40 minutes and resulted in formation of aragonite. Addition of fulvic acid significantly delayed the process – precipitation started after 150 minutes, and the resulting precipitate was again aragonite. This experiment confirmed the inhibiting effect of organic substances on the precipitation process.

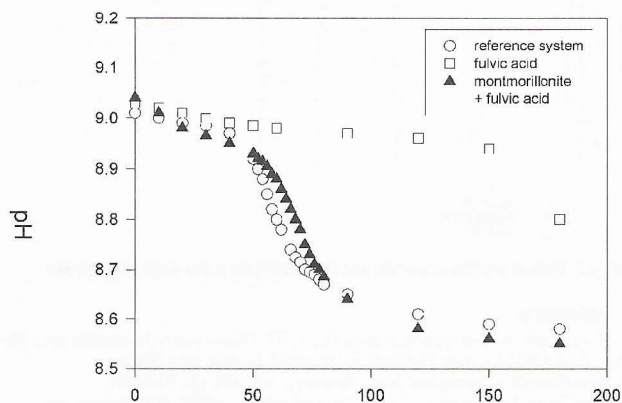


Figure 1. Variations of pH with time for the reference system (only ASW), system with fulvic acid added, and system with fulvic acid and montmorillonite.

The addition of montmorillonite did not have a significant effect on the CaCO<sub>3</sub> precipitation from ASW. As opposed to the precipitation from the system containing only constituent ions where the resulting precipitate was calcite (2), precipitation from ASW resulted in aragonite formation. Ionic species present in ASW (Mg<sup>2+</sup> especially) obviously have a much stronger influence on the formation of a certain polymorph than montmorillonite.

However, the role of solid substrate in the precipitation process is not so insignificant. When montmorillonite was added in the system together with fulvic acid, there was no delay in the process. The precipitation started after about 40 minutes – the same as with the reference system.

These experiments are the first in a series of investigations of the calcium carbonate precipitation from complex systems. Further experiments will be performed from the natural sea water with some other dissolved and undissolved additives included.

## References

1. Kralj D. Brecevic Lj. and Nielsen A.E., 1990. Vaterite Growth and Dissolution in Aqueous Solution I. Kinetics of Crystal Growth. *J. Crystal Growth* 104: 793-800.
2. Sabbides T.G. and Koutsoukos P.G., 1993. The crystallization of calcium carbonate in artificial seawater; role of the substrate. *J. Crystal Growth* 133: 13-22.
3. Kralj D. and Vdovic N., 2000. The influence of some naturally occurring minerals on the precipitation of calcium carbonate polymorphs. *Wat. Res.* 34/1: 179-184.
4. Vdovic N. and Kralj D., 2000. Electrokinetic properties of spontaneously precipitated calcium carbonate polymorphs: the influence of organic substances. *Colloids Surfaces* 161: 499-505.