

# Experimental Study of Calcite Dissolution and Gypsum Precipitation in Acid Solutions

/ FRANCESCO G. OFFEDDU (1\*), JORDI CAMA (1), JOSEP M. SOLER (1), JIWCHAR GANOR (2), IGNASI CASANOVA (3), CHRISTINE V. PUTNIS (4), ANDREW PUTNIS (4)

(1) Institute of Environmental Assessment and Water Research (IDAEA). CSIC. C/ Jordi Girona 18-26. 08034 Barcelona (Spain)

(2) Dept. of Geological and Environmental Sciences Ben-Gurion University of the Negev. P.O. Box 653. 84105 Beer Sheva (Israel)

(3) School of Civil Engineering and Center for Research in Nanoengineering. UPC. Campus Nord B1-109C. 08034 Barcelona (Spain)

(4) Institut für Mineralogie. Corrensstrasse 24. D-48149 Münster (Germany)

## INTRODUCTION.

AMD waters usually contains elevated concentrations of sulfate, iron and other contaminant metals (Pérez-López et al., 2009). Essentially, treatment of AMD water consists of acid water neutralization and precipitation of metal contaminants. A common, used passive system is the Anoxic Limestone Drainage (ALD) that consists of ditches filled by limestone gravel. Acid water circulates through it, dissolving limestone (calcite) and increasing pH. Iron and aluminium are retained as hydroxides and sulfate as gypsum.

The precipitation of gypsum on the surface of the carbonate grains causes their passivation, preventing the treatment system to act as a barrier. (Offeddu et al., 2009, Soler et al., 2008).

To enhance our understanding of ALD systems, as well as our knowledge on the kinetics of the overall process, three types of experiments were performed: (1) column, (2) batch and (3) in-situ Atomic Force Microscope. Column experiments allowed quantification of the overall process as well as porosity variation. Batch experiments were used to assess the evolution of the overall process at the microscale, and in-situ AFM experiments shed light on the coupled mechanism at the nanoscale.

## EXPERIMENTAL METHODOLOGY.

### Column experiments.

Column experiments were filled with calcite fragments (1-2 mm diameter). Synthetic acid solutions ( $\text{H}_2\text{SO}_4$  at pH 2) with initial concentrations of Fe(III) that ranged from 100 to 1500 mg  $\text{L}^{-1}$  were injected into the column reactors at a constant flow rate ( $1 \times 10^{-3}$  L  $\text{m}^{-1}$  s $^{-1}$ ). Output solutions were collected every 48

h, pH was continuously measured, and output Al, Fe, S and Ca concentrations were measured by ICP-AES. Synchrotron X-Ray microtomography analyses and synchrotron X-Ray microdiffraction measurements were carried out (1) to quantify changes in initial porosity during the experiment due to changes in pore structure and secondary mineral precipitation and (2) to identify the phases precipitated.

### Batch experiments.

In batch experiments, a weighed amount of calcite or aragonite grains were placed into 250 mL Polyethylene bottles filled with a pH 2 solution equilibrated with respect to gypsum. The bottles were shaken in a thermostatic bath at 25 °C. Periodically, samples of approximately 0.5 mL of reacting solution were spiked with a syringe, filtered with a 0.22  $\mu\text{m}$  filter disk and diluted by a factor of  $\sim 1/100$  (by weight) for Ca,  $\text{SO}_4$ , alkalinity analysis and pH measurements. The experiments lasted up to 2 weeks and terminated when concentrations of Ca and  $\text{SO}_4$  were constant with time, i.e. reached equilibrium.

### In situ AFM experiments.

Examinations of calcite cleavage surface were performed by in-situ Atomic Force Microscopy using a fluid cell (flow-through experiment). Acid solutions (1 mmol/L  $\text{Na}_2\text{SO}_4$  and equilibrated with respect to gypsum at pH 3-4) reacted over the freshly calcite cleavage surface. Fragments of approximately 3x3x1 mm of Iceland spar (calcite) were used. The AFM observations were made on the basis of topographic variations of the cleavage surface with time and to observe the formation of any growth features.

## RESULTS AND DISCUSSION.

Columns were an efficient barrier as long as pH varied between pH 6 and 7. At this stage, metal removal occurred (Fe and Al drop was observed). Precipitation of gypsum and Me-hydroxides occurred. An important result was that time to passivate the carbonate system depended on the sulphate concentration of the input solution. X-ray microtomography showed a reaction front advancing along the columns as calcite dissolved and gypsum precipitated. A porosity decrease was caused by secondary mineral precipitation (e.g. gypsum, Fe-oxy-hydroxide). Formation of preferential flow paths in the porous medium was also observed (Fig.1).

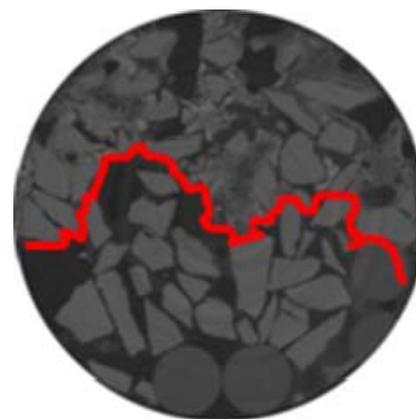


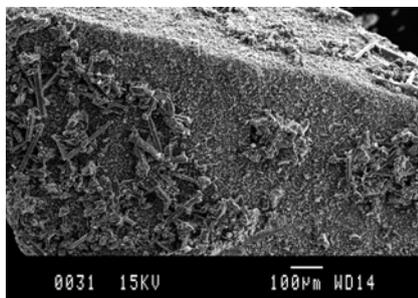
fig 1. The image shows a synchrotron X-Ray microtomography section of a passivated cylindrical column. The red line indicates the limit between a reacted and non-reacted area. Formation of these two areas was due to preferential flow path generation during the experiment.

In batch experiments no new solution was added to the system. Carbonates dissolved releasing Ca and the solution increased in pH and alkalinity. After an initial induction time  $\text{SO}_4$  was consumed because gypsum started to precipitate.

**palabras clave:** Calcita, Yeso, Disolución, Precipitación.

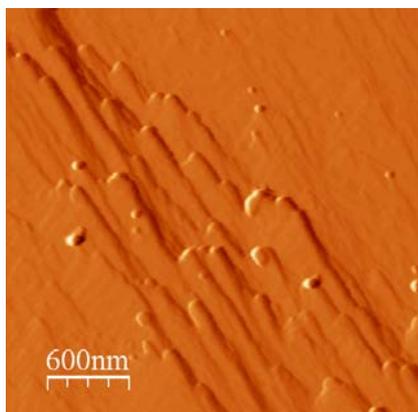
**key words:** Calcite, Gypsum, Dissolution, Precipitation.

Precipitation of gypsum occurred until equilibrium with respect to calcite was reached. No passivation of calcite was observed (Fig. 2).



**fig 2.** SEM image of a calcite grain partially coated by gypsum after reaching equilibrium with respect to calcite.

In situ sequential AFM images were taken to capture the nucleation of gypsum on a calcite cleavage surface and to observe subsequent growth. After an initial dissolution time, where the formation of rhombohedral etch pits on the calcite surface were visible, elongated epitaxial forms of gypsum started to grow (Fig. 3).



**fig 3.** In-situ AFM image that shows gypsum growth on the calcite cleavage surface. Precipitation seems to occur along a preferential direction.

The experimental results show that calcite passivation is only observed in the open systems (column and in situ AFM flow-through experiments). This fact suggests that a fully calcite passivation occurs when a continuous income of reactants ( $H^+$  and  $SO_4^{2-}$ ) is guaranteed, as it is the case of the ALD system.

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#### REFERENCES.

- Offeddu, F.G., Cama, J., Soler, J.M., Ayora, C. (2009): The passivation of calcite during the treatment of acid mine drainage. Laboratory experiments. Goldschmidt Conference Abstracts.
- Pérez-López, R., Cama, J., Nieto, J.M., Ayora C., Saaltink M. W. (2009): Attenuation of pyrite oxidation with fly-ash pre-barrier: Reactive transport modeling of column experiments. *App. Geochem.*, **24**, 1712-1723.
- Soler, J.M., Boi, M., Mogollon, J.L., Cama, J., Ayora, C., Nico, P. S., Tamura, N., Kunz, M. (2008): The passivation of calcite by acid mine water. Column experiments with ferric sulfate and ferric chloride solutions at pH 2. *App. Geochem.*, **23**, 3579-3588.