

# Factors influencing the porosity development during replacement reactions: a modeling approach

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## INTRODUCTION

A critical aspect to consider during mineral replacement processes occurring by a dissolution-precipitation mechanism is the porosity evolution. The generation of porosity enables the progress of the replacement reaction, providing paths for the fluid to be in permanent contact with the reacting solid. On the contrast, if porosity does not form during the reaction, its advancement is hampered. This has enormous implications as it will determine, for example, the maximum capability of CO<sub>2</sub> storage in a geological formation, the durability of cements in contact with aqueous solutions during long periods of time (in dams or radioactive waste disposal facilities), the long term performance of passive treatment systems for acid mine drainage remediation or the effectiveness of protective treatments for building stones based on replacing the original material by a secondary phase less soluble and thus more durable than the substrate.

The porosity created depends on the difference between the molar volumes of reagent and product as well as the relative solubility of the two phases in the reaction fluid (Putnis, 2009). This latter parameter will be determined by physicochemical properties of the reacting solutions, such as pH, temperature and concentration of reactants. In addition, an aspect that may influence the existence of paths for the fluid to reach the unreacted mineral surface is the type of growth mechanism (i.e. 3D island growth -Volmer-Weber mechanism- or layer-by-layer growth - Frank van der Merwe mechanism-).

In the present work, geochemical calculations performed using PHREEQC (Parkhurst and Appelo, 1999) and the phreeqc.dat database will be used to illustrate the effect of such parameters on the porosity development during two

replacement reactions: the replacement of calcite (CaCO<sub>3</sub>) by calcium sulfates and the replacement of portlandite (Ca(OH)<sub>2</sub>) by calcite.

## ESTIMATION OF VOLUME CHANGES DURING REPLACEMENT REACTIONS

The relative volume change  $\Delta V_{\text{reaction}}$  during a replacement reaction is given by Pollock et al. (2011):

$$\Delta V_{\text{reaction}} = 100 \cdot \left( \frac{n_d}{n_p} \cdot \frac{V_{M,\text{Prod}}}{V_{M,\text{Reac}}} - 1 \right)$$

where  $n_d$  is the amount of moles dissolved,  $n_p$  is the amount of moles precipitated,  $V_{M,\text{Reac}}$  is the molar volume of the reacting mineral and  $V_{M,\text{Prod}}$  is the molar volume of the reaction product.

As pointed out in Pollock et al. (2011), the replacement process can be modelled considering different approaches. First, it can be considered that the initial mineral reacts (partially or completely) and both the parent phase and the product are in equilibrium with the bulk solution. This approach assumes that the total amount of dissolved mineral mixes with the entire solution and a solid in equilibrium with this solution precipitates.

In a second scenario, incremental layers of product are successively formed in local equilibrium with the bulk solution at the reacting front. Finally, a third case can be considered. During replacement reactions the dissolution and precipitation processes are confined to a fluid layer at the reaction interface with a different composition to the bulk (Putnis et al., 2005). Thus, calculations assuming equilibration of the parent crystal with the bulk fluid phase are an oversimplification. Our simulations consider that the replacement process takes place in a series of small reaction steps. In each of these steps, a monolayer of the reacting mineral dissolves in a thin layer of solution and

local equilibrium is reached with respect to the product. The resulting solution at the interface then mixes with the bulk and a new reaction step begins, with a slightly modified composition of the solution at the interface. Since we are considering a system whose composition evolves continuously with time and thus the solubility of the replacement product, the porosity will also change with the course of the reaction. However, the initial steps of the replacement are critical, as if  $\Delta V_{\text{reaction}}$  is positive, the reaction may eventually stop.

The  $\Delta V_{\text{reaction}}$  can be calculated following the different approaches described above, for different initial compositions, T and/or boundary layer thickness.

## ANALYSIS OF FACTORS INFLUENCING THE POROSITY DEVELOPMENT DURING REPLACEMENT REACTIONS

### Effect of pH and temperature: the replacement of calcite by calcium sulfates

Passive treatment systems based on the dissolution of coarse calcite grains are widely used to remediate acid mine drainage. However, these substrates tend to lose their reactivity due to coating by the formation of secondary phases, mainly gypsum (Soler et al., 2008). To evaluate the effect of solution pH and temperature on the passivation of calcite grains, the reaction of an acid solution (H<sub>2</sub>SO<sub>4</sub>) with an initial concentration of Fe(III) of 1000 ppm and calcite was simulated for a range of pH (1.5-3.1) and two temperatures (25 and 60 °C).

At T = 25 °C, gypsum (Ca<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O) is the less soluble and thus the most stable Ca-sulfate phase. If one assumes that both the parent phase (CaCO<sub>3</sub>) and the replacement product (CaSO<sub>4</sub>·2H<sub>2</sub>O) are in equilibrium with the bulk solution, an increase in pH results in a decrease in the volume change occurring during

**palabras clave:** reacciones de reemplazamiento, porosidad, PHREEQC, modelización geoquímica.

**keywords:** replacement reactions, porosity, PHREEQC, geochemical modeling.

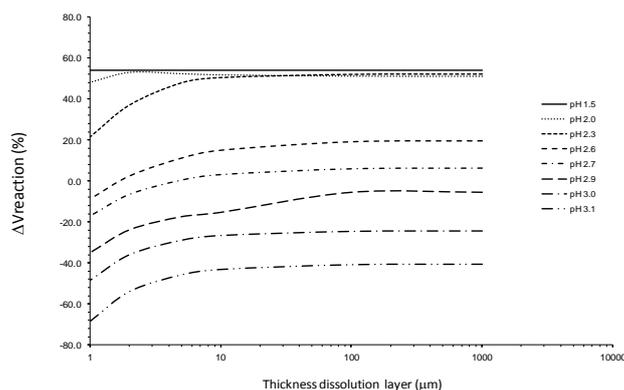


fig 1. Relative volume change ( $\Delta V_{\text{reaction}}$ ) during the replacement of calcite by anhydrite (60 °C) as a function of pH and thickness of the dissolution layer.

the replacement reaction. As a result, the porosity of the replacement product changes from 40.0 % (pH 1.5) to -55.9 % (pH 3.1).

However, calculations performed assuming a more realistic scenario in which a calcite monolayer dissolves in a thin layer of solution show that, at 25 °C, porosity is not developed in any case for the pHs tested. On the contrary, if calculations are performed at 60 °C assuming that anhydrite ( $\text{Ca}_2\text{SO}_4$ ) is the most stable (and thus the precipitating) Ca-sulfate phase, the initial steps of the reaction result in the generation of porosity for pH between 2.7-3.1 (fig 1). All in all, these preliminary results suggest that increasing the temperature and adjustment of the pH of the treated effluent could avoid passivation of the calcite substrate and thus increase the performance of these treatments for acid mine drainage remediation. Experiments will be carried out to confirm these simulations.

#### **Influence of epitaxial growth mechanism: the replacement of portlandite by calcite**

During the reaction of Portland cement with water, the cement paste becomes supersaturated with respect to portlandite, which then precipitates in the bulk of the hardened cement paste. Carbonation of portlandite is a critical process that conditions the long-term behavior of cements. As well, it is the key process in the setting of traditional lime mortars, as the textural and structural characteristics of the newly precipitated  $\text{CaCO}_3$  determine the physical and mechanical properties of such mineral assemblages, which are currently the choice as compatible materials for interventions in the built heritage.

Montes-Hernandez et al. (2010) found that non-zero water activity is required for portlandite carbonation to proceed.

However, the presence of water is not a requirement when the solution takes place in the solid-state. In contrast, water is critical during interface-coupled dissolution-precipitation processes. This suggests that the most likely mechanism for portlandite carbonation is a dissolution-precipitation reaction.

At T 20 °C and relative humidity (RH) = 93 %, optimal conditions for portlandite carbonation, there are 7 monolayers of water molecules adsorbed on portlandite surfaces (Beruto and Botter, 2000). This adsorbed water behaves like a liquid-like nanometric phase, and thus carbonation in air under this high relative humidity could occur in fact via a dissolution-precipitation reaction. PHREEQC calculations show that the amount of portlandite that has to dissolve in this liquid phase to become saturated with respect to calcite is  $1.72 \cdot 10^{-14}$  moles, which represents an amount significantly smaller than that corresponding to a portlandite monolayer (thickness 0.3 nm), considering a prismatic hexagonal crystal of size ca. 4 mm length and 2 mm width. If a complete portlandite monolayer dissolves into such a layer of adsorbed water in equilibrium with air (i.e.  $\text{PCO}_2 = 10^{-3.5}$  atm) and calcite precipitates,  $\Delta V_{\text{reaction}}$  will be positive (12.5 %) and porosity will not be generated during the reaction. The coverage of the portlandite surface would result in the blockage of the carbonation reaction, assuming that calcite precipitates as a continuous layer over the whole portlandite surface. However, nanoscale AFM observations show that calcite precipitates as discrete, thick 3D islands (a few hundred nm high, fig. 2). Passivation of the surface may eventually occur as a result of the merging of these islands as they grow, but the amount of portlandite dissolved at this point cannot be simply estimated considering differences in molar volumes or relative solubility of the two phases involved.

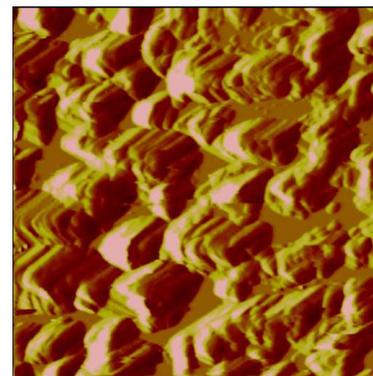


fig 2. Atomic Force Microscopy (AFM) image of calcite precipitates on portlandite surfaces upon contact with carbonate-bearing solutions.

#### **ACKNOWLEDGEMENTS**

This research project was funded by the EC (grant MRTN-CT-2006-035488), the Spanish Government (grant MAT2012-37584) and the Junta de Andalucía (research group RNM-179 and project P11-RNM-7550). E. Ruiz-Agudo also acknowledges the receipt of a Ramón y Cajal grant from Spanish Ministry of Economy and Competitiveness.

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