

## Growth of brucite on portlandite crystal surfaces

Baumann, Christian<sup>1,2</sup>; Galan, Isabel<sup>2</sup>; Sakoparnig, Marlene<sup>3</sup>; Dietzel, Martin<sup>2</sup>

1 Chair of Resource Mineralogy, Montanuniversität Leoben, Peter-Tunner-Straße 5, A-8700 Leoben, Austria; 2 Institute of Applied Geosciences, Graz University of Technology, A-8010 Graz, Austria; 3 Institute of Technology and Testing of Construction Materials, Graz University of Technology, A-8010 Graz, Austria.

Brucite ( $\text{Mg}(\text{OH})_2$ ) and portlandite ( $\text{Ca}(\text{OH})_2$ ) are both hydroxide bearing minerals. But while portlandite is a main mineral phase in the cement matrix of concrete, brucite forms as a degradation product of concrete exposed to magnesium bearing solutions. Similar to other precipitates preferentially formed on the surface of concrete components, brucite may act as a protective barrier preventing or delaying the progress of concrete degradation. As portlandite has a significantly higher solubility compared to that of brucite, the effect of brucite formation as protective layer on portlandite is worth to be investigated. However, the corresponding reaction kinetics and mechanisms have not been fully explored. The present study gives insight into the potential protective effect that brucite may provide to prevent the mineral portlandite from dissolution. For this study, single crystals of portlandite were synthesized and exposed to  $\text{Mg}^{2+}$ -containing solutions for 72 h, where the impact of the following parameters was investigated: (i)  $\text{Mg}^{2+}$  ion sourced from chloride, sulfate and nitrate salt, (ii)  $\text{Mg}^{2+}$  concentrations of the initial reactive solution and (iii) mass ratio of exposed crystal surface to solution volume. Therefore, portlandite crystals were partly coated with nail polish forcing the brucite growth on a single hexagonal surface. The crystals and solutions were analyzed with FTIR, optical microscope, SEM, EPMA and IC, pH-sensor. Thermodynamic modelling was performed using PHREEQC. The results show brucite layers to be formed directly on or close to the portlandite crystal surface in all experiments. The factors influencing brucite formation were closely linked to the evolution of the calcium concentration of the reactive solution. Thus, aqueous  $\text{Ca}^{2+}$  content could be used as an indicator of the ongoing reaction process. The reactive solutions with chloride- and nitrate-based  $\text{Mg}^{2+}$  at high concentration levels provided optimum conditions for brucite formation to inhibit portlandite dissolution, where no further mineral was formed throughout the experimental runs. The presence of sulfate ions led to the formation of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) once a threshold concentration of sulfate and calcium in the reactive solution was reached. In those cases, a brucite layer is formed first and subsequently gypsum filled the space left open by the dissolution of portlandite. In a progressing stage gypsum created cracks in the brucite layer and accordingly lowered the protection against portlandite dissolution. Thus, the availability of the sulfate ions in reactive solution plays an important role for the concentration of aqueous  $\text{Ca}^{2+}$ . A crucial factor for brucite formation throughout all experimental runs was the initial  $\text{Mg}^{2+}$  concentration, which directly influenced the time-resolved evolution of the pH. The pH in turn determined the morphology of the brucite crystals, which was decisive for the effectiveness of protection against further dissolution of the portlandite crystal: higher  $\text{Mg}^{2+}$  concentrations are associated with lower pH and result in brucite layers with smaller, more densely packed crystals offering noticeably better protection against portlandite dissolution compared to the appeared thicker brucite layers consisting of larger crystals with a higher layer permeability. A conceptual model for the different interacting parameters was developed where the stages of distinct reaction kinetics and mechanisms are discussed and assessed.