Growth inhibitors on calcite

Progress report

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The effect of organic molecules on calcite crystal growth is being investigated, testing sodium aspartate and glycine as precipitation inhibitors. Experiments were carried out using the constant composition method (Lakshtanov *et al.*, 2011) for calcite precipitation (Fig. 1).

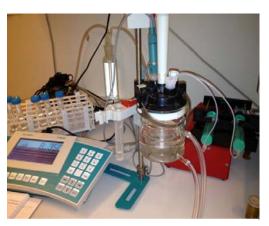


Fig. 1: Experimental setup for the constant composition method.

The reaction media consists of a supersaturated solution containing CaCl₂ and NaHCO₃ in NaCl with an ionic strength of 0.1 M. Calcite precipitation starts when a weighted amount of calcite seeds is introduced in the system and, as precipitation continues, a drop in pH will occur. This triggers the injection of CaCl₂ and NaCO₃ by a pH-dependent titration system, until the pH-threshold of 8.3 is reached. Then, when the precipitation rate becomes constant, the inhibitor-bearing solution is added to the reaction vessel, resulting in a change in the precipitation rate (slope in the pH/Volume of titrants added diagram). Samples of calcite were taken before and after the addition of the inhibitor for XPS (X-ray photoelectron spectroscopy) and SEM (scanning electron microscopy) to detect inhibitor adsorption and change in morphology. Figure 2a shows unreacted calcite seeds crystals. Calcite crystals grown in the pure system, without any inhibitor, present flat surfaces and welldefined edges (Figure 2b and 2c). Figure 2d shows calcite crystals after the addition of sodium aspartate. Visibly, there are serrated edges and smooth corners, indicating that the inhibitor has been adsorbed on calcite active sites. Similarly, glycine adsorption results in roughened shapes of the step edges (Figure 2e and 2f). Comparing growth rates, aspartate is a better inhibiting agent than glycine, which is active only for the highest concentrations investigated. The extra carboxylic group and the particular conformation of aspartate, which fits well on the calcite surface unit cell, can be the main factors promoting the interaction with surface sites. This finding can shed light on the parameters to take into account to predict and design a good scale inhibiting molecule.

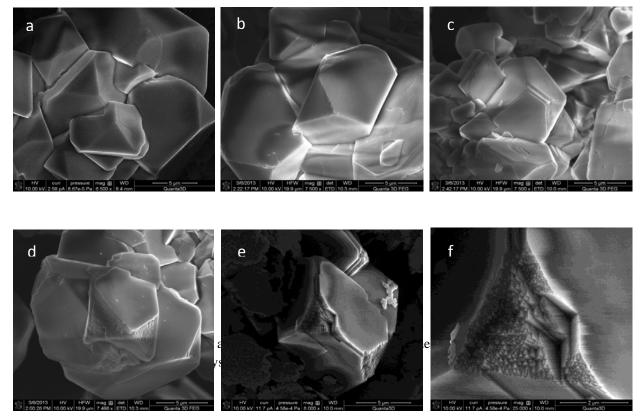


Fig. 2: SEM images of calcite crystals. Calcite seed crystals prior addition to the solution media (Fig. 2a). They present smooth and flat surfaces and sharp edges. Fig. 2b and 2c: calcite seed crystals after addition to the growing solution. Growth occurs with layer by layer accumulation and edges roughened slightly. Calcite surfaces after aspartate (Fig. 2d) and glycine (Fig. 2e) addition: step edges become visibly roughened. Fig. 2f shows in detail the morphology of the step edges.