

Calcium sulfate precipitation with and without inhibitors

Progress report

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1. Introduction:

Mineral scaling and the formation of mineral scales like calcium sulfate is one of the most common and critical problems for different industries like oil, gas and water treatment because it often results in considerable losses in production and a dramatic decline in efficiency.

To retard or decrease scale formation, a number of methods such as the use of chemical additives or inhibitors have been suggested as possible solution to decrease the problem.

2. Experimental procedure:

Calcium sulfate phases were precipitated in additive-free systems with total concentrations between 25 and 100mM. To investigate the effects of additives as inhibitors, magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) were used at concentrations between 1-100mM. The reactions were followed in situ and for ex situ analyses. At the end of the experiments the solutions were filtered under vacuum through 0.2 μm pore size filter papers, quenched with isopropanol and the solids analysed.

2.1. Characterization methods

2.1.1. *In situ* techniques

Calcium sulfate precipitation kinetics and the influence of inhibitors on the crystallisation and growth rates in the pure and additive experiments were followed by UV-VIS spectrophotometry through monitoring of the development of turbidity with time. In addition, Ca^{2+} -ion selective electrode and conductivity measurements were used to follow the changes in these parameters with time.

2.1.2. *Ex-situ* techniques

The morphology of the particles was characterized by scanning electron microscopy (SEM) with the mineralogical characterization was carried out using powder X-ray

diffraction (PXRD)

3. Results and discussion:

The data show that by increasing the supersaturation level of the mixed solutions, the induction time of calcium sulfate precipitation decreases. Both Mg^{2+} and citrate increase the induction time of $CaSO_4$ formation. Mg^{2+} is more effective than citrate in delaying the precipitation as confirmed by the turbidity plots (Fig. 1 and 2) and Ca^{2+} -ISE curves (Fig. 3).

For example, adding 50mM magnesium retarded the crystallization by ~ 400% (from 6 min to 32 min), while citrate, regardless of concentration, produced a ~3 fold decrease in induction time. Citrate and Mg^{2+} both stabilized bassanite with respect to the final product gypsum (Fig. 4-6); citrate also acts as a shape modifier in that it changes the bassanite morphology from nanorods to platelets

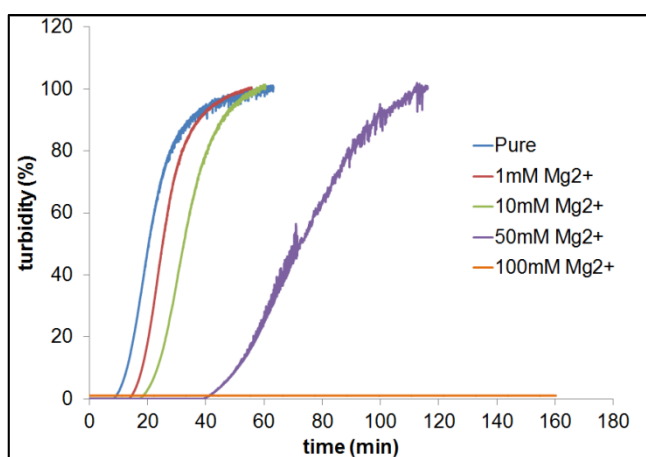


Fig. 1. Increase in induction time as a function of Mg^{2+} concentration

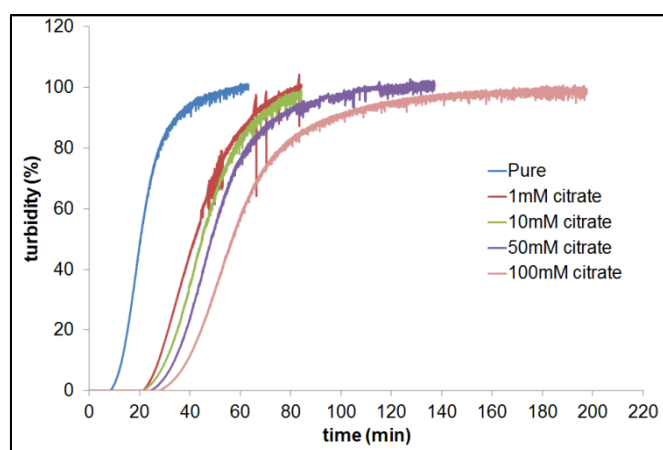


Fig. 2. Increase in induction time as a function of citrate concentration

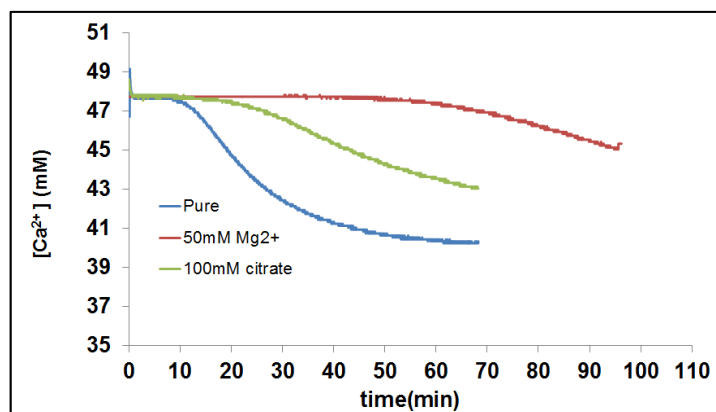


Fig. 3. The influence of additives on the behaviour of the Ca^{2+} -ion selective electrode response

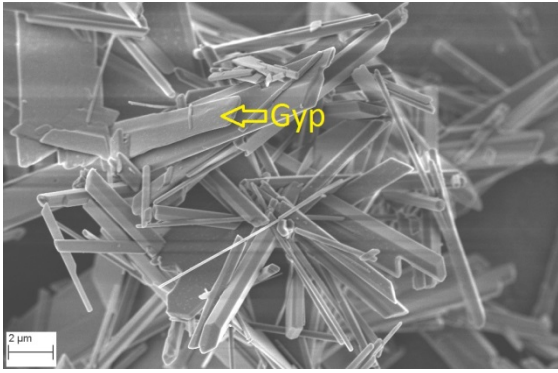


Fig. 4. Photomicrograph of gypsum (Gyp) crystals in the pure CaSO_4 system

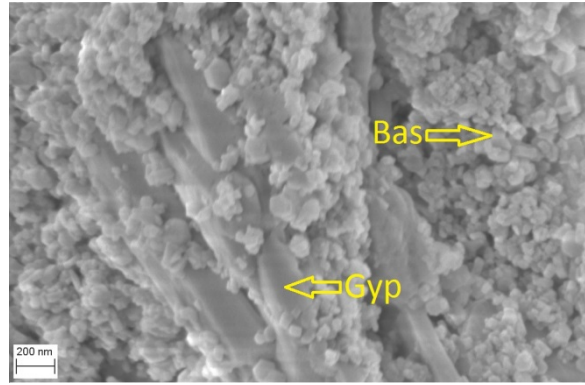


Fig. 5. Photomicrograph of bassanite (Bas) platelets and gypsum needles (Gyp) from an experiment with 100mM citrate

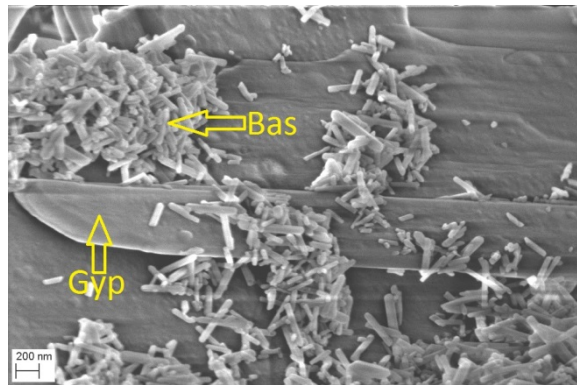


Fig. 6. Photomicrograph of bassanite (Bas) nanorods and gypsum needles (Gyp) in a system containing 10mM Mg^{2+}