BaSO$_4$ crystallization in the presence of polymers: evidence of barite crystallization via non-classical pathways

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Barium sulphate is widely known for being a problematic and costly scale-forming mineral in industrial processes. In oil recovery, barite forms when injection water which is sulfate rich and barium-containing formation water interact downhole. Scale minerals can clog formation pores near the wellbore reducing porosity and permeability of the reservoir and they also can form a thick deposit in production pipes. A common strategy aimed at reducing scale formation is the addition of organic of additives (usually phosphonates or carboxylates) to the water injected into the reservoir (threshold treatment, Shakkthivel et al., 2006).

Thus a better understanding of the mechanism of barite formation from aqueous solutions and the role of organic macromolecules on such a process may be relevant for the design and optimization of treatments to prevent scale formation. Here, we investigate the initial stages of barium sulphate precipitation from pure and polymer-containing aqueous solutions. Barium sulphate was precipitated at room temperature by combining equimolar Ba$^{2+}$-bearing and SO$_4^{2-}$-bearing solutions. The precipitation process was quenched at different times by the addition of ethanol or quick immersion in liquid nitrogen and subsequent freeze-drying, and the precipitates were studied by various analytical methods, XRD, TG/DSC, FESEM, ESEM and TEM. As well, precipitation experiments (with and without polymers) were performed by the slow addition of 10 mM BaCl$_2$ solution to a 1 mM Na$_2$SO$_4$ solution. During these experiments, the Ba$^{2+}$ potential, pH, conductivity and turbidimetry were continuously monitored and allowed to get better insights into interactions between copolymers and prenucleation species before nucleation occurs (Gebauer et al. 2009).

AFM growth experiments were additionally carried out. Observations of the nanostructure evolution indicate that barite forms by two-levels of oriented aggregation of nanosized particles. In pure solutions, most of the porosity in the micron-sized aggregates formed in the second step is annealed, resulting in perfect single crystals. However, in the presence of polymers, this step is retarded and BaSO$_4$ mesocrystals are commonly observed. Furthermore, evidence supporting the existence of liquid and solid amorphous precursors that precedes the formation of the first solid (primary) particles is given.

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References