



Barite formation in the presence of a commercial copolymer

Cristina Ruiz-Agudo (1), Christine Putnis (1), Encarnacion Ruiz-Agudo (2), Andrew Putnis (1,3)

(1) University of Münster, Institute für Mineralogie, Mineralogie, Münster, Germany (criss_ru@hotmail.com), (2) Department of Mineralogy and Petrology, University of Granada, Fuentenueva s/n 18071, Granada, Spain, (3) The Institute of Geoscience Research (TIGeR), Curtin University, Perth, Australia

Fluid composition can significantly modify the mechanisms of mineral formation. Particularly, the presence of organic additives in the aqueous media has been shown to alter the precipitation of minerals substantially (e.g. calcium carbonate, barium carbonate and barium sulfate). Despite the numerous studies dealing with barite precipitation and the influence of organic additives (e.g. Benton et al. 1993, Qi et al., 2000, Wang and Cölfen, 2006, Mavredaki et al., 2011), the details of the mechanism of barite formation in the presence of organic additives, particularly at the early stages of this process, are yet to be fully resolved.

Here, we present observations on the initial stages of barite formation from aqueous solutions, as well as the alterations induced by a commercial copolymer (maleic acid/allyl sulfonic acid copolymer with phosphonate groups), commonly used as a scale inhibitor in oil recovery. Most synthetic commercial additives contain the same functional groups (e.g. carboxylate, phosphonate and/or sulfonate groups). Thus our work may help to understand the mechanism by which copolymers modify crystallization processes and aid in the selection of the most appropriate inhibitors for hindering or controlling barite scale formation. Barite scaling is one of the main problems in many industrial processes (such as, paper-making, chemical manufacturing, cement operations, off-shore oil extraction, geothermal energy production).

Using Atomic Force Microscopy (AFM), we show that barite growth is significantly influenced by the presence of the copolymer. In its absence, barium sulfate growth occurs by 2D island nucleation and spreading. The addition of small amounts (0.1 ppm and 0.5 ppm) of the copolymer enhances 2D nucleation but blocks growth. Just 1 ppm of inhibitor is enough to block barite nucleation and growth by adsorption of a copolymer layer onto the barite surface. Transmission electron microscopy (TEM) was also used to gain better insights into the early stages of barite precipitation in the presence and absence of this copolymer. With this purpose, barite was precipitated by mixing of BaCl₂ and Na₂SO₄ solutions (with copolymer previously added to the sulphate solution). The process was quenched with ethanol at different times and the particles obtained were observed ex-situ using TEM. According to our observations, the organic molecule seems to be incorporated into barite nanoparticles, hindering or delaying their recrystallization into micron-sized crystals and stabilizing barite mesocrystals.

Benton, W.J.; Collins, I.R.; Grimsey, I.M.; Parkinson, G.M.; Rodger, S.A. *Faraday Discussions* 1993, 95, 281-297.

L. Qi; H. Cölfen; M. Antonietti. *Angew. Chem. Int. Ed.* 2000, 39 (3), 604-607.

Wang, T.; Coelfen, H. *Langmuir* 2006, 22, 8975-8985.

Mavredaki, E.; Neville, A.; Sorbie, K. S. *Cryst. Growth Des.* 2011, 11, 4751-4758.

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