



## TEM analysis of the initial stages of BaSO<sub>4</sub> crystallization

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Barite scales in oilfields are formed by mixing of seawater with high SO<sub>4</sub><sup>2-</sup> content and formation water (high Ba<sup>2+</sup> content) in the reservoir. Although barite precipitation has been widely studied, a lack of a complete understanding of the mechanisms of barite nucleation and growth at the early stages poses a problem in the development of preventive methods designed to reduce the damaging consequences associated with scale formation.

A general strategy to reduce scale formation is the use of additives that act as inhibitors of barite precipitation. These scale inhibitors act by hampering and delaying nucleation and growth of barite and in most cases they modify the habit of the crystal. The performance of these inhibitors depends on numerous parameters, such as pH, temperature and concentration, and they can affect different stages of the precipitation process (e.g. blocking active growth sites at the surface, sequestering the scale-forming metal ion, influencing the type of amorphous phase or crystalline polymorph formed, as well as promoting solid-cluster formation (Gebauer et al., 2009)). In recent studies, the precipitation of several minerals, e.g. calcite (Gebauer et al., 2008), gypsum (Van Driessche et al., 2012), magnetite (Baumgartner et al., 2013) and iron oxyhydroxide (Li et al. 2012) has been shown to follow a non-classical crystallization process. Primary crystalline nanoparticles that coalesce after previous co-alignment, and amorphous and crystalline precursor phases have been observed in the crystallization processes of these minerals.

The purpose of the present work was to gain a better understanding of the early stages of barium sulfate precipitation with the objective of obtaining fundamental knowledge that allows us to select the appropriate inhibitors for barite scale formation. With this aim, barite was precipitated by mixing BaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> solutions. The process was quenched with ethanol at different times and the particles obtained were observed ex-situ in a Transmission Electron Microscope.

We found that barite precipitation involves the initial formation of nanometer-size (5-10 nm) particles that fuse in an oriented way to form larger particles. Two hierarchical levels of aggregation are observed: first, the aggregation of 5-10 nm particles to form larger, but still nanometer-sized (20-60 nm) particles. In a second stage, these latter particles aggregate to produce larger single crystals (200-500 nm). No evidence of an amorphous or crystalline precursor phase previous to crystalline barite was found. These results are of importance for the design of scale prevention methods, particularly in the choice of the most suitable scale inhibitor.

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