Early stages of $BaSO_4$ precipitation

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Barium sulphate is known for being a problematic scale in oilfields due to its low solubility and its hardness. Barite scales are formed as a consequence of the mixing of seawater with high SO_4^{2-} content and formation water (high Ba^{2+} content) in the reservoir. The improvement in preventive methods designed to reduce the damage associated with scale formation needs a better understanding of the mechanisms of barite nucleation and growth at the early stages. The effectiveness of scale inhibitors depends on numerous parameters, such as pH, temperature and concentration, and they can act modifying one or several stages of the precipitation process (e.g. blocking active growth sites at the surface, sequestering the scale-forming metal ion, affecting the type of amorphous phase or crystalline polymorph formed, as well as promoting solid-cluster formation).

The precipitation of several minerals, e.g. calcite, gypsum, magnetite and iron oxyhydroxide has been shown to follow a non-classical crystallization process. With the aim of studying barite crystallization process at early stages, $BaCl_2$ and Na_2SO_4 solutions were mixed and the precipitation was quenched at different times. The particles obtained were observed ex-situ using a FEI TITAN G2 Transmission Electron Microscope. Our results show that barite precipitation involves the initial formation of nanometer-size (5-10 nm) particles that fuse 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). Neither amorphous or crystalline precursor phases previous to crystalline barite was found. These findings have implications in the development of scale prevention methods, especially in the selection of the most suitable scale inhibitor.