TEM analysis of the initial stages of $BaSO_4$ crystallization

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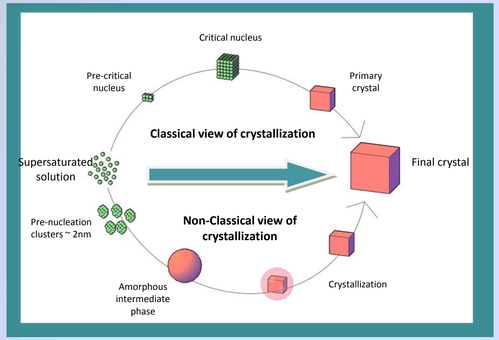
Introduction

Barite ($BaSO_4$) scale formation is a problem in many industrial processes, especially in oilfields where mixing sea water with reservoir water can result in solid layers of barite scale that can completely block pipes.

Additives that act as inhibitors of barite precipitation are widely used. Different additives can affect different stages involved in crystal nucleation and growth, including the formation of prenucleation clusters, the aggregation of nanoparticles and the precipitation of precursor phases. Thus, the lack of knowledge of the early stages of barite formation limits the selection and use of additives to prevent scale formation.

The aim of this work is to gain a better understanding of $BaSO_4$ precipitation process before the performance of additives can be assessed.

Classical Vs non-classical nucleation theory



Experimental procedure

Transmission electron microscopy (TEM) analysis of barite nanoparticles were carried out using a Philips CM20, operated at 200 kV and a FEI Titan, operated at 300 kV. Prior to TEM observations, 1 ml droplet of 1 mM $BaCl_2$ solution and 1 ml droplet of 1 mM Na_2SO_4 solution were mixed in a 10 ml beaker. At different times (0 min, 5 min, 15 min, 60 min) barite precipitation was quenched by addition of 8 ml ethanol to replace water molecules absorbed to barium sulfate surfaces and to prevent the solid from dissolving (*Ihli et al., 2013*). $BaSO_4$ particles in the water/ethanol dispersions were collected in carbon/Formvar grids for TEM observations and analysis.

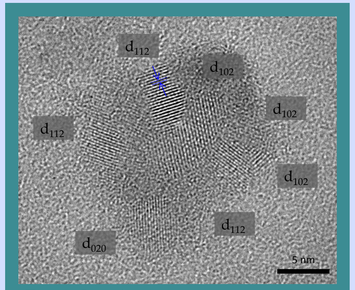


Fig. 1. Set of primary nanoparticles with the characteristic 2.83 Å (d_{112}), 3.32 Å (d_{102}) and 2.72 Å (d_{020}) for barite (t = 0 min).

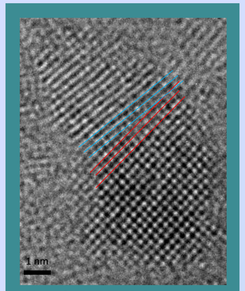


Fig. 2. HRTEM image of two attached $BaSO_4$ nanoparticles. The edge dislocation at the interface is highlighted.

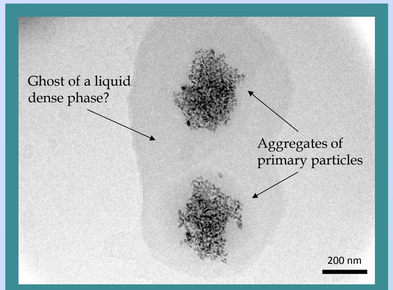


Fig. 3. Ghost shadow surrounding two aggregates of nanorods particles. (t = 15 min).

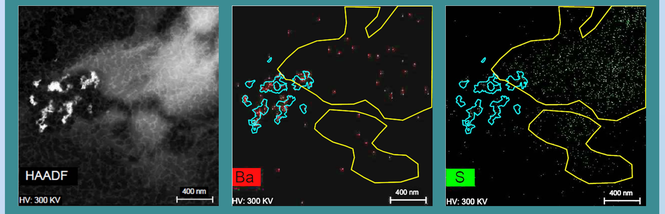


Fig. 4. The first image is high angle annular dark field image (HAADF) taken in STEM mode using FEI-TITAN. The line in blue delimited the aggregates of barium sulphate nanorod particles and the yellow line is around the "ghost" area. EDX mapping carried out in this area. Ba and S are mainly concentrated in the "ghost" area (t = 15 min).

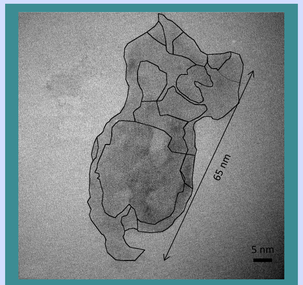


Fig. 5. Nanorod particle formed from the assembly of primary nanoparticles. Different nanocrystalline domains have been delimited in the image (t = 5 min).

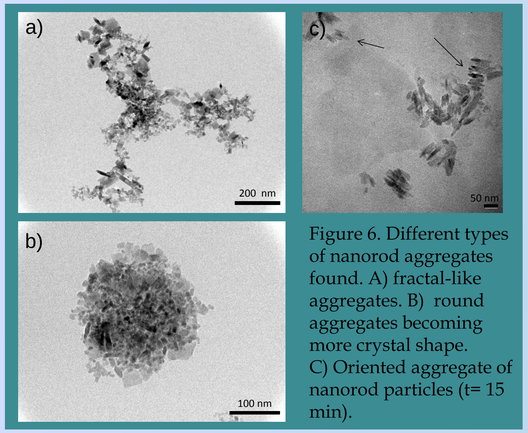


Figure 6. Different types of nanorod aggregates found. A) fractal-like aggregates. B) round aggregates becoming more crystal shape. C) Oriented aggregate of nanorod particles (t= 15 min).

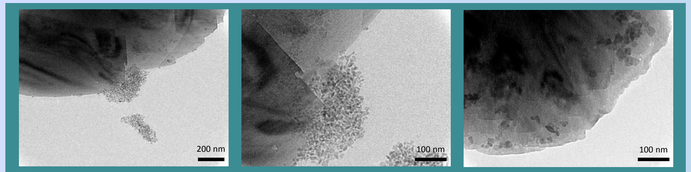


Figure 7. When nanorods are in the vicinity of a crystal it grows at the expense of the small particles (t = 60min).

Conclusions

- Barite precipitation at high supersaturation follows **a non-classical** crystallization **route**.
- Evidence of **liquid-liquid spinodal decomposition** previous to barite nucleation is observed.
- **Two hierarchical** levels of **aggregation** are detected:
  1. Aggregation of 5-10 nm particles to form larger, but still nanometer-sized (20-60 nm) particles (fig. 5).
  2. Aggregation of these particles to produce bigger crystals (200-500 nm) that can be observed in fig. 6.
- **Ripening processes** in which large crystals seem to grow at the expense of aggregates of nanoparticles are observed.
- There is **no** evidence of an amorphous or crystalline **precursor phase** previous to crystalline barite. The 5-10 nm particles found at t=0 were already crystalline.

Mineral Scale Formation
From the nano ... ... to the field scale
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