



Precipitation of calcium carbonate in aqueous solutions in presence of ethylene glycol and dodecane.

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The formation of calcium carbonate (CaCO_3) in aqueous supersaturated solutions has been intensively studied over the past decades, because of its significance for a number of processes of industrial and environmental interest. In the oil and gas production industry the deposition of calcium carbonate affects adversely the productivity of the wells. Calcium carbonate scale deposits formation causes serious problems in water desalination, CO_2 sequestration in subsoil wells, in geothermal systems and in heat exchangers because of the low thermal coefficient of the salt. Amelioration of the operational conditions is possible only when the mechanisms underlying nucleation and crystal growth of calcium carbonate in the aqueous fluids is clarified. Given the fact that in oil production processes water miscible and immiscible hydrocarbons are present the changes of the dielectric constant of the fluid phase has serious impact in the kinetics of calcium carbonate precipitation, which remains largely unknown. The problem becomes even more complicated if polymorphism exhibited by calcium carbonate is also taken into consideration.

In the present work, the stability of aqueous solutions supersaturated with respect to all calcium carbonate polymorphs and the subsequent kinetics of calcium carbonate precipitation were measured. The measurements included aqueous solutions and solutions in the presence of water miscible (ethylene glycol, MEG) and water immiscible organics (n-dodecane). All measurements were done at conditions of sustained supersaturation using the glass/Ag/AgCl combination electrode as a probe of the precipitation and pH as the master variable for the addition of titrant solutions with appropriate concentration needed to maintenance the solution supersaturation. Initially, the metastable zone width was determined from measurements of the effect of the solution supersaturation on the induction time preceding the onset of precipitation at free-drift conditions. The rates of crystal growth were measured as a function of the solution supersaturation using the highly accurate and reproducible methodology of constant supersaturation. The dependence of the rates of crystal growth on supersaturation suggested surface diffusion controlled mechanism. At constant supersaturation it was possible to extend the time period for the growth of the initially forming polymorph, in a way that sufficient amount is precipitated for characterization with X-ray diffraction (XRD). Moreover, scanning electron microscopy (SEM) was used for the characterization of the morphology of the precipitated solid. In all cases and depending on the solution supersaturation vaterite formed first from solutions of high supersaturation while at low supersaturations calcite formed exclusively. The presence of dodecane reduced the stability of the supersaturated solutions with the crystals forming at the oil-water interface. The presence of ethylene glycol (concentrations between 10-80%) also affected the stability and the kinetics of calcium carbonate precipitation. The morphology of the formed crystals showed habit modifications: Spherical formations consisting of aggregated nanocrystals and calcite crystals with profound pits on the faces were the characteristic feature in the presence of dodecane.

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