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Abstract

Carbonates: classical and nonclassical nucleation and transformation pathways

Due to many simultaneous and fast nucleation pathways, carbonate precipitation is a complex and difficult-to-follow process. Kinetic and thermodynamic aspects control the nucleation, growth, and transformation of minerals. The main goal of this doctoral thesis was to understand, at the molecular level, the classical and non-classical calcium carbonate nucleation and transformation pathways and develop an innovative experimental approach to follow these processes.

This thesis shows the new approach to calcium carbonate nucleation and transformation pathways investigation by using time-resolved potentiometric and electrokinetic methods. The experimental results of zeta potential, Ca^{2+} ion concentration, crystal structure, and morphology are presented. Monitoring *in situ* early stages of the process showed that after initially fast changes of electrokinetic potential (ζ) and Ca^{2+} ions concentration, the data kinetics of the process is changed. A slow stabilization to the equilibrium state occurred. The changes in monitored parameters coincide with the spontaneous formation of unstable (metastable) polymorphic forms, and their subsequent transformation indicates existence of the multiple steps in the precipitation process.

The magnesium ion's effect on the growth rate, morphology, transformation, and composition of the precipitated carbonates was also studied. The presence of Mg^{2+} ions shifts the zeta potential changes to lower absolute values compared to the precipitation of pure calcium carbonate. Mg^{2+} ions addition also delays stabilization of Ca^{2+} ions concentration. The results show that stable crystal forms are formed later, the precipitation process is prolonged and not stable amorphous forms stay longer in the solution.

In addition to experimental studies, thesis includes theoretical model of calcium carbonate formation. The combinations of Surface Complexation and kinetic modelling with electrokinetic and potentiometric experiments make it possible to monitor and predict the

course of the precipitation process of carbonate minerals. The approach used in the presented work allows for a more detailed insight into the processes of nucleation, growth and transformation of carbonates *in situ*.