Effects of Mg^{2+} on the nucleation and growth kinetics of calcium sulfate.

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Gypsum is the final crystalline product when precipitation starts from highly supersaturated aqueous $CaSO_4$ solutions. Despite a plethora of studies attempting to elucidate the various reaction stages, the actual pathways and mechanisms are still debated and gypsum formation may progress via precursor nano-bassanite [1] or amorphous $CaSO_4$ [2]. Furthermore, the kinetics and nature of the transformations of precursor phases is known to be highly altered by the presence of inorganic or organic additives [3] [4]. Since Mg^{2+} is a major cation in seawater used for desalination purposes where $CaSO_4$ scale formation is a big problem [5], we quantified the effects of Mg^{2+} on the nucleation and growth of phases in the $CaSO_4$ system and thus gained a better understanding of the gypsum formation reactions.

Our data reveal a clear Mg^{2+} concentration dependent delay in the development of turbidity in supersaturated $CaSO_4$ solutions. This data was cross-correlated with morphological images and quantitative mineralogical compositions of intermediate and end-stage solid products. Our results show that even low Mg^{2+} contents significantly affect the stability of the nanocrystalline precursor bassanite but Mg^{2+} also delays the start of calcium sulfate precipitation and slows the kinetics of crystal growth. For example, in solutions supersaturated with respect to gypsum (supersaturation index SI_{GPY} = 0.5) the addition 1 mmol/L Mg^{2+} delays the start of the precipitation reaction (increases induction time) by ~ 40% compared to the pure system. Furthermore, the intermediate bassanite is stabilized for much longer time periods with increasing Mg^{2+} contents and the transformation of bassanite to gypsum is delayed considerably. Interestingly, however this delay seems to be due the presence of Mg^{2+} in the supernatant solution, because ion chromatographic analyses revealed that Mg^{2+} was not incorporated into the $CaSO_4$ crystal structures.

[1] Van Driessche *et al*(2012) *Science*, **336**:69; [2] Saha *et al*(2012) *Langmuir*, **28**:11182; [3] Klepetsanis *et al*(1998) *J. Cryt. Gro.*, **193**:156; [4] Rabizadeh *et al*(2014) *Min. Mag.*, **78**:1465; [5] Guan *et al*(2010). *I&EC Research*, **49**:5569.