

The dependence of gypsum morphology on the over-saturation and $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio of the precipitating hyper-saline solutions

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The planned “Dead Sea-Red Sea Project”, which will convey seawater and reject brine after desalination to the Dead Sea, is expected to lead to massive gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) precipitation in the hypersaline Dead Sea. The size and form of the crystals will dictate the rate at which the gypsum will settle to the bottom, which in turn will determine if whitening of the surface water by suspended minute crystals will take place. Gypsum over-saturation is attained in all mixtures containing more than 40% wt of Dead Sea brine. The morphology of the precipitating gypsum is likely to be a function of the composition of the brine from which it will precipitate. Thus, a set of batch experiments was carried out to study the composition – morphology relationship in hyper-saline solutions. The solutions used were composed of Red Sea – Dead Sea mixtures enriched with Ca^{2+} and SO_4^{2-} . This enrichment allowed changing the degree of saturation of the mixtures with respect to gypsum without significantly changing the concentration of other major ions. The experimental solutions had ionic strength in the range of 5.5-10 m, oversaturations of 1.7-7.5, and $\text{Ca}^{2+}/\text{SO}_4^{2-}$ molar ratios of 13-45.

The morphology of the precipitated gypsum was found to be strongly influenced by both the distance from equilibrium and the $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio of the precipitating brine. Further from equilibrium (initial over saturations > 4) gypsum precipitated with a stellate morphology, whereas closer to equilibrium (initial over saturation < 2) gypsum precipitated as idiomorphic tabular or needle-like crystals. This change in morphology is attributed to a change in the mechanism of nucleation, i.e., homogenous vs. heterogenous nucleation respectively. Under the closer to equilibrium conditions, an increase in the $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio results in a decrease of the measured aspect ratio (length/width) of the precipitated crystals. The assumption is that this is due to a dependency of the relative growth rate of different crystal facies on the stoichiometry in the hyper-saline precipitating solution. This dependency is currently being studied by the use of atomic force microscopy (AFM).