# Additives Stabilize Calcium Sulfate Hemihydrate (Bassanite) in Solution Yun-Wei Wang and Fiona C. Meldrum

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**Figure S1**: Raman spectra of reference samples (a) calcium sulfate hemihydrate produced after 1 minute and (b) calcium sulfate dihydrate (gypsum) precipitated from a 100 mM solution and isolated after 1 hour.



**Figure S2**: IR spectra of calcium sulfate precipitated in the absence of additives and isolated after (a) 1 min, corresponding to hemihydrate and (b) 1 hour, corresponding to gypsum.



**Figure S3**: XRD patterns of (a) a natural gypsum sample [1] and (b) Hemihydrate as reported in reference [2] (c) gypsum precipitated from a 100 mM solution after 1 hour, (d) calcium sulfate hemihydrate, produced by annealing gypsum at 120 °C for 10 hours, (e) hemihydrate precipited from a supersaturated solution after 1 min in the absence of additives, and analysed after 1 hour, (f) hemihydrate precipitated in the presence of 100  $\mu$ g/ml PAA, isolated after 1 hour, and analysed after 1 hour.



**Figure S4:** XRD patterns of calcium sulfate precipitated in the absence of additives, isolated from solution after 1 minute and then left in air for (a) 1 hour, showing that the sample is primarily hemihydrate, (b) 3 hours, showing peaks at  $2\theta = 11.575$  and 47.88, demonstrating the presence of gypsum, (c) after 10 hours, where only traces of hemihydrate remain (as shown by the principal hemihydrate peak at  $2\theta = 14.746$ ) and (d) 24 hours, showing that all hemihydrate has transformed to gypsum.



**Figure S5**: TEM images of calcium sulfate crystals precipitated in the presence of 50  $\mu$ g/ml PAA after 1 hour. The precipitates were a combination of (a) gypsum and (b) hemihydrate.



**Figure S6**: TEM images of calcium sulphate hemihydrate isolated after 1 hour and precipitated in the presence of (a) 100  $\mu$ g/ml PSS and (b) 200 mM Mg<sup>2+</sup>. These are the corresponding TEM images of the samples shown in Figures 6a and 6b.



**Figure S7:** XRD spectra of calcium sulfate precipitated with (a)  $100\mu$ g/ml PSS, showing a mixture of hemihydrate and gypsum (b)  $100\mu$ g/ml sodium triphosphate, (c)  $100\mu$ g/ml PAA, and (d) 200 mM MgCl<sub>2</sub> 6H<sub>2</sub>O. (b, c and d) all correspond to hemihydrate, while the starred peaks in (a) correspond to gypsum.



**Figure S8**. X-ray diffraction spectra of calcium sulfate hemihydrate precipitates (a) from additivefree solution, (b) with 100  $\mu$ g/ml of sodium triphosphate (STP), (c) 100  $\mu$ g/ml PAA and (d) 200 mM Mg<sup>2+</sup>.



**Figure S9**: (a) Amorphous calcium sulfate and (b) calcium sulfate hemihydrate precipitated in the presence of 100  $\mu$ g/ml phosphate, and isolated after 1 hour. These are the larger images of Figure 6c and its inset.



**Figure S10:** CaSO<sub>4</sub> particles precipitated in the presence of 100  $\mu$ g/ml sodium triphosphonate, and isolated after 1 hour (a) TEM image of amorphous particles, where the inset shows the corresponding EDX spectrum with Ca and S peaks. (b) A selected area electron diffraction pattern of this sample, showing that it is amorphous. (c) After heating the sample to 200 °C for 4 hour, the sample crystallises to CaSO<sub>4</sub> hemihydrate.

