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1	Carboxylic acids: effective inhibitors for calcium sulfate precipitation?
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9	

10 Abstract

Here we report results from an investigation on the effects of three carboxylic acid additives 11 (tartaric, maleic and citric acids) on the precipitation of calcium sulfate phases. Precipitation 12 13 reactions were followed at pH 7 in the pure CaSO₄ system and in experiments with 0-20 ppm carboxylic acids added using in situ UV-VIS spectrophotometry (turbidity). The solid 14 15 products were characterized during and at the end of each reaction for their mineralogical 16 composition by X-ray diffraction (XRD) and for their morphological features by scanning electron microscopy. All additives increased the time needed for turbidity to develop 17 (induction time, start of precipitation) and the comparison between additive and additive-free 18 19 experiments showed that at equivalent concentrations citric acid performed far better than the other two carboxylic acids. In all cases first bassanite precipitated and with time it 20 transformed to gypsum. The addition of citrate stabilized bassanite and changed the final 21 22 gypsum habit from typical needle-like crystals in the pure CaSO₄ system to plates in the citrate additive experiments. 23

24



26 Introduction

Calcium sulfates are important rock forming minerals that occur in thick evaporitic deposits 27 throughout geologic history (Kinsman, 1969). In the calcium sulfate system three phases with 28 29 various degrees of hydration exist: the dihydrate gypsum (CaSO₄ 2H₂O), the hemihydrate bassanite (CaSO₄·0.5H₂O) and the anhydrous anhydrite (CaSO₄). The stability and formation 30 of these phases are highly temperature and concentration dependent (Freyer and Voigt, 2003). 31 Between ambient and ~ 40 $^{\circ}$ C the most stable phase is gypsum. With increasing ion 32 concentrations and / or temperature, the solubilities of bassanite and anhydrite decreases and 33 34 this leads to gypsum dehydrating and transforming to these less hydrous polymorphs (Freyer and Voigt, 2003). However, recently, the mechanisms controlling the nucleation and growth 35 of gypsum from aqueous solutions have gained renewed interest because gypsum likely does 36 37 not form directly from solution. One study (Wang et al., 2012) suggested that gypsum forms 38 through non-classical nucleation via an amorphous calcium sulfate intermediate, while another study (Van Driessche et al., 2012) suggested that gypsum forms not through 39 40 amorphous precursors but through the initial precipitation of nanocrystalline bassanite particles that self-assemble into larger gypsum crystals through oriented attachment. 41

The gypsum formation pathway is important because among calcium sulfates, gypsum is 42 mined extensively for use as the crucial component in plasters and cements (e.g., Camarini 43 44 and De Milito, 2011), yet to make plasters gypsum has to be dehydrated to bassanite through 45 the use of large amounts of energy. Equally important however, is the fact that in several industrial processes that rely on water handling systems (e.g., oil and gas production, water 46 desalination; Moghaddasi et al., 2006; Rahardianto et al., 2008), the precipitation of calcium 47 sulfate phases leads to the deposition of minerals on pipes, filters and heat exchangers 48 (forming mineral scales). Cleaning or removing such mineral scales is costly and undesirable 49

and is affecting efficiency and lifetime of processing technologies (e.g., Mi and Elimelech,2010).

In order to reduce or mitigate calcium sulfate scaling, various simple anti-scaling approaches 52 have been suggested, the most common being the use of inorganic (e.g., Mg²⁺; Guan et. al., 53 2010) or organic additives (e.g., sulfonic, phosphonic or carboxylic compounds; Shakkthivel 54 55 and Vasudevan, 2006; Prisciandaro et al., 2005; Akyol et. al., 2009). The main requirements for an effective additive are that (a) it is readily available, (b) it is effective at low 56 concentrations, (c) it is cheap and its addition will not significantly affect production costs, 57 58 (d) ideally it is biodegradable or non-toxic to the environment and (e) it reduces mineral formation or prevents nucleated phases from adhering to surfaces of crucial production 59 apparatus. Among additives fulfilling many of the above requirements are carboxylic acids 60 61 (Hasson et al., 2011; Cao et al., 2014). To date studies that tested the effects of carboxylic acids on calcium sulfate precipitation have primarily evaluated changes in precipitation onset 62 or the effect of high temperatures (Prisciandaro et al., 2005; Senthilmurugan et al., 2010; 63 64 Ling et al., 2012; Amjad and Koutsoukos, 2014). Still missing is a mechanistic understanding of the effects of variable concentrations of carboxylic acid and / or various carboxylic acid 65 moieties. 66

To address this gap we present results on the effects of three carboxylic acids (citric, maleic and tartaric) and variable additive concentrations (0-20 ppm) on the kinetics and phase morphologies that develop during homogeneous calcium sulfate formation reactions and derive a more mechanistic understanding of the processes.

- 72 Experimental methods
- 73

74 Inhibitor-free calcium sulfate precipitates (termed 'pure CaSO₄' hereafter) were produced by mixing equal volumes of a 100 mM CaCl₂·2H₂O solution and a 100 mM Na₂SO₄ solution (99 75 % purity, VWR) at room temperature (21 °C) and under constant and continuous stirring. The 76 mixed solutions were supersaturated with respect to gypsum (saturation index $SI_{Gyp} = 0.5$) but 77 undersaturated with respect to bassanite (SI_{Bas} = -0.37). The saturation indices (as the 78 logarithm of the ion activity product over the solubility product) and the related solubility 79 products (K_{sp,gypsum} = $10^{-3.66}$ and K_{sp,bassanite} = $10^{-4.53}$) were calculated with the 80 geochemical computer code PHREEQC using the LLNL database (Parkhurst and Appelo, 81 1999). 82

Carboxylic acids (citric, maleic or tartaric acid; 99-100 %, VWR) were added to the initial
sodium sulfate solution at concentrations between 5 and 20 ppm. In all experiments, prior to
mixing, the pH of the initial solutions was adjusted to 7, with 0.1 M NaOH.

86 The kinetics of the reactions in the absence and presence of carboxylic acids was monitored through the development of turbidity in the mixed solutions as measured with a UV-VIS 87 spectrophotometer (Uvikon XL) at 520 nm. Reactions were followed in triplicate at room 88 temperatures for up to 4 hours and the variations in the turbidity onset from the three repeats 89 are reported in minutes. At intermediate time steps and at the end of each experiment the 90 91 solutions were quench-filtered $(0.2 \ \mu m)$ under vacuum with isopropanol and the solids retrieved. These solids were characterized for their mineralogy using powder X-ray 92 diffraction (XRD; Bruker D8 diffractometer; CuKa1; 5-30 °20; 0.105 °20 / step), while the 93 morphology of the formed phases was imaged using a field emission gun scanning electron 94 95 microscope (FEG-SEM, FEI Quanta 650, 3 kV).

96

97 **Results**

99 Turbidity developed in all experiments but the onset of turbidity occurred after different 100 elapsed times (induction times) that were dependent on additive type and concentration. 101 Comparing the turbidity curve from the pure $CaSO_4$ experiment with equivalent curves from 102 experiments where 20 ppm of the 3 carboxylic acids were added (Fig. 1), revealed a 103 carboxylic acid dependent increase in induction time. In the pure $CaSO_4$ system the first 104 increase in turbidity was observed after 6 ± 1 min and the increase in absorbance took ~ 60 105 minutes to reach a steady value on a plateau. In the presence of 20 ppm carboxylic acids the

induction times increased to 9 ± 1 min, 16 ± 1 min and 25 ± 1 min for tartaric, maleic acid and citric acid, respectively, and specifically in the case of added citric acid the reaction curve took much longer to reach a plateau (~ 200 min; Fig. 1).

109

110 (Insert Fig. 1 here)

111

Testing variable concentrations of citric acid (5, 10, 20 ppm) showed a proportional increase in induction time with increasing additive concentration (Fig. 2). The 6±1 minute induction time observed in the pure CaSO₄ system almost doubled in the presence of 5 ppm citric acid (10±1 minutes), tripled with 10 ppm (17±1 minutes) and at 20 ppm citric acid added an induction time 4 times greater than that in the pure CaSO₄ system was observed (25±1 minutes).

118

^{119 (}Insert Fig. 2 here)

121 XRD analyses of the solids recovered at the end of each reaction (in both the pure and carboxylic acid amended experiments) revealed that the sole mineral end product was 122 gypsum. However, samples filter-quenched just after the onset of turbidity in the pure and 123 citric acid system (e.g., after 30 sec in the pure system and after 3 and 10 min in the presence 124 of 20 ppm citric acid; marked with * in Fig. 2 and corresponding to ~ 7, 26 and 35 minutes in 125 absolute time respectively) showed in the XRD patterns the presence of bassanite coexisting 126 127 with gypsum (Fig. 3a,c). In both cases with time, the proportion of bassanite decreased (bassanite peaks decreased in intensity or fully disappeared) showing that bassanite was an 128 129 intermediate phase (Fig. 3d) but that in both systems the final product was pure gypsum (Fig. 3b,e). As mentioned above, an increase in induction time prior to the onset of turbidity was 130 also observed in the presence of the other two carboxylic acids (maleic and tartaric; Fig. 1). 131 132 Although the shape and slope of the turbidity curves hint at a similar process, we do not have equivalent time resolved XRD evidence that these additives also stabilized bassanite (but see 133 below and Fig. 4 e,f). 134

135

136 (Insert Fig. 3 here)

137

Photomicrographs of the intermediate (~ 7 minutes, or 30 seconds after onset of turbidity) and end product (after 70 minutes of total reaction) materials in the pure CaSO₄ system revealed bassanite present at the beginning of the reaction only as elongated nanorods (up to ~ 200 nm long) while at the end of the experiment only gypsum was present as larger (~ up to μ m size), thin, needle-like crystals, in part twinned (Fig. 4a and b). These morphologies and sizes are equivalent with those reported by Van Driessche et al. (2012) and Wang et al. (2013) and the presence of bassanite in our samples had already been documented through 145 XRD (Fig. 3a,c). At the end of the pure system crystallization reaction (Fig. 4b) all bassanite had transformed and only large, elongated (between 5-50 µm) needle-like and twinned 146 gypsum crystals were present, again confirming the XRD data (Fig. 3b). In the presence of 20 147 ppm citric acid, after the onset of turbidity (3 minutes = 28 minutes after mixing of the initial 148 solutions) the bassanite identified by XRD (Fig. 3c) was present as very small but almost 149 isometric nanoparticles ($< \sim 90$ nm; Fig. 4c) that occurred together with larger gypsum 150 crystals. At the end of the reaction when the turbidity curve reached a plateau (after 200 151 minutes; Fig. 4d) only gypsum was present. It was striking that, compared to the pure $CaSO_4$ 152 153 system both the bassanite and gypsum in the citrate system did not exhibit the typical bassanite nanorod or gypsum needle-like habits, but rather far more isomeric (bassanite; Fig. 154 155 4c) and distinctly platy (gypsum; Fig. 4d) habits. Although we have no XRD evidence of 156 bassanite stabilization in the presence of maleic and tartaric acid, photomicrographs of samples removed a few minutes after the onset of turbidity in the 20 ppm experiments with 157 these carboxylic acids present revealed equivalent nanorod (particles < 200 nm) 158 morphologies that we infer to be bassanite. These occurred together with longer needle-like 159 crystals inferred to be gypsum (Fig. 4e and f). In contrary to the citric acid system however, 160 in the presence of 20 ppm tartaric or maleic acid the shape, size or habit of the intermediate 161 bassanite and end product gypsum were the same as in the pure CaSO₄ experiment, although 162 a slight 'thinning' of the gypsum needles was observed. 163

164

165 (Insert Fig. 4 here)

166

167 **Discussion**

Measuring turbidity and estimating induction times in the absence and presence of additives is one of the most common methods of evaluating the efficiency of additives as a mechanism to delay the nucleation and growth of sparingly soluble scale minerals.

Additives that are biodegradable, like the carboxylic acids used in the current study, and that also dramatically delay the nucleation and or growth of a phase at low concentrations, are considered effective and are often called 'inhibitors' although they do not inhibit nucleation and growth but most often just delay or change the reaction progress.

Our data revealed that at equal concentrations (20 ppm), among the three additives tested, 176 citric acid increased the induction time and decreased the slope of the turbidity curve more 177 than both the tartaric and maleic acid, inferring that citric acid is inherently a better inhibitor. 178 If we also consider the differences in molar concentrations of the used carboxylic acids 179 ($C_{cit} = 1.01 \ \mu\text{M}$, $C_{tart} = 1.33 \ \mu\text{M}$ vs. $C_{mal} = 1.72 \ \mu\text{M}$) further supports the fact that citric acid 180 is the most effective inhibitor despite it being present in the lowest molar concentration. 181 However, the exact reasons for its higher effectiveness are not yet clear but likely also stem 182 183 from the variations in molecular geometries and sorption capacities between these three 184 carboxylic acids.

It is well known that additives can affect the nucleation and growth of scale minerals, for example, by forming complexes or chelating agents with the active ions in the nucleating solutions (eq. 1; where x = 2 for maleic / tartaric acids or 3 for citric acid) or by sorbing to active crystal sites and inhibiting mineral growth (e.g., Crabtree et al., 1999; Badens et al., 1999; Ersen et al., 2006; Magallanes-Rivera et al., 2009).

190

191
$$R(COOH)_x + Ca^{2+} \rightarrow R(COOCa)_x + H^+$$
 (1)

193 In the case of the carboxylic acids tested, complexation with calcium is well known (Bazin et al., 1995) but sorption and growth inhibition also seems to play an important role. All 194 carboxylic acids delayed the onset of nucleation (increased induction time compared to pure 195 196 system, Fig.1 and 2). However, the citric acid additive also affected the growth of the scale mineral in that both bassanite and gypsum exhibited different habits compared to the additive 197 free phases (Fig. 4). Finally, of interest for mineral scale formation and inhibition is the fact 198 that compared to the pure system even low concentrations of citric acid stabilized the 199 200 bassanite phase for much longer periods.

In additive experiments one of the fundamental parameters that controls 'inhibition' either through complexation with the active ions (in this case Ca^{2+}) or sorption to active growth sites is the speciation and degree of protonation of the additive used. All our experiments with or without additives were carried out with the initial solutions adjusted to pH 7. At this pH value all carboxylic acids are to the largest extent deprotonated (Table 1).

206

207 (Insert Table 1 here)

208

The delay in precipitation, indicated by the increased induction time, is likely in part due to 209 Ca²⁺ complexation with these deprotonated species through the reduction of Ca²⁺ 210 supersaturation. Of the carboxylic acids tested, citric acid at pH 7 is the most deprotonated 211 and maybe therefore t acts as the most efficient inhibitor, as reflected in the longest induction 212 213 time. Nevertheless, the nucleation barrier in the presence of all additives is overcome and bassanite nucleates and eventually transforms to gypsum. The delay in precipitation in the 214 215 presence of the carboxylic acid may also be attributed to sorption onto bassanite and gypsum 216 growth sites. Badens et al. (1999) and Ersen et al. (2006) found that adsorption of citrate onto 217 active growth faces of both bassanite and gypsum inhibited growth in those directions more than other carboxylic acid (e.g., tartaric or malic). This suggests that with citric acid both 218 bassanite and gypsum grew with different habits from those in the pure CaSO₄ system, as our 219 220 imaging data also confirmed (Fig. 4a,b). Citric acid seems to have inhibited growth along the c axis and prevented the formation of typical long, needle-like habits. Instead, the growth of 221 gypsum was favoured in the a and b directions, leading to platy crystal habits (Fig. 4). 222 223 Similar morphological changes in gypsum habits in the presence of carboxylic acids have been reported by others (Li et al., 2007; Magallanes-Rivera et al., 2009), yet a molecular level 224 225 understanding of the process is still lacking.

For gypsum formed in the presence of citric acid Prisciandaro et al. (2005) showed that the 226 increase in induction time was due to a dramatic change in interfacial tension compared to an 227 228 additive free system. Although our work confirmed these findings, we also showed that bassanite is a metastable intermediate forming prior to gypsum not just in the pure CaSO₄ 229 system (Wang et al., 2012; Van Driessche et al., 2012) but also in the presence of carboxylic 230 acids. In the pure system, bassanite forms below its thermodynamic bulk solubility and its 231 transformation to gypsum is through hydration and self-assembly via a process controlled by 232 a particle size dependent surface energy (Van Driessche et al., 2012). This is different to the 233 non-classical nucleation, growth and dehydration pathways suggested for calcium carbonates 234 235 (Rodriguez Blanco et al., 2011; Bots et al., 2012) or calcium phosphates (Combes and Rey, 236 2010). However, the current study shows that in the presence of even low concentrations of carboxylic acid, (a) the onset of the precipitation reaction is delayed, (b) bassanite is 237 stabilized and its transformation to gypsum slowed down, and (c) citric acid changes the 238 239 shape and habit of the formed bassanite and gypsum.

Thus, if citric acid inhibitors are used in an industrial fluid handling system (where CaSO₄
scale minerals are a problem), they can substantially retard nucleation and growth even at low

concentrations. Importantly, citric acid may not just stabilize a nanoparticulate phase like bassanite and thus reduce clogging of filters, but the size effect may also prevent adherence to pipe surfaces. However, this latter process and further growth of $CaSO_4$ phases on surfaces is still under study.

246

247 Acknowledgements

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Akyol, E., Oner, M., Barouda, E., and Demadis, K.D. (2009) Systematic structural
determinants of the effects of tetraphosphonates on gypsum crystallization. Crystal
Growth & Design, 9, 5145-5154.

Amjad, Z. and Koutsoukos, P.G. (2014) Evaluation of maleic acid based polymers as scale
inhibitors and dispersants for industrial water applications. Desalination, 335, 55-63.

²⁵⁷ **References:**

- Badens, E., Veesler, S., and Boistelle, R. (1999) Crystallization of gypsum from hemihydrate
 in presence of additives. Journal of crystal growth, 198, 704-709.
- Bazin, H., Bouchu, A., Descotes, G. and Petit-Ramel, M. (1995) Comparison of calcium
 complexation of some carboxylic acids derived from D-glucose and D-fructose. Canadian
 Journal of Chemistry, 73, 1338-1347.
- 269 Bots, P., Rodriguez-Blanco, J.D., Roncal-Herrero, H., Shaw, S. and Benning, L. (2012)
- 270 Mechanistic insights into the crystallization of amorphous calcium carbonate (ACC).
 271 Crystal Growth & Design, 12, 3806-3814.
- Camarini, G. and De Milito, J.A. (2011) Gypsum hemihydrate–cement blends to improve
 renderings durability. Construction and Building Materials, 25, 4121-4125.
- 274 Cao, K., Zhou, Y., Liu, G., Wang, H. and Sun, W. (2014) Preparation and Properties of a
- Polyether-Based Polycarboxylate as an Antiscalant for Gypsum. Journal of applied
 polymer science, 131, 1-9.
- 277 Combes, C. and Rey, C. (2010) Amorphous calcium phosphates: synthesis, properties and
 278 uses in biomaterials. Acta Biomaterialia, 6, 3362–3378.
- Crabtree, M., Slinger, D., Fletcher, P., Miller, M., Johnson, A. and King, G. (1999) Fighting
 scale—removal and prevention. Oilfield Review, 11, 30-45.
- Ersen, A., Smith, A., and Chotard, T. (2006) Effect of malic and citric acid on the crystallisation of gypsum investigated by coupled acoustic emission and electrical conductivity techniques. Journal of materials science, **41**, 7210-7217.
- Freyer, D. and Voigt, W. (2003) Crystallization and phase stability of CaSO₄ and CaSO₄–
 based salts. Monatshefte für Chemic/Chemical Monthly, **134**, 693-719.
- Guan, B., Yang, L., and Wu, Z. (2010) Effect of Mg^{2+} ions on the nucleation kinetics of calcium sulfate in concentrated calcium chloride solutions. Industrial & Engineering
- 288 Chemistry Research, **49**, 5569-5574.

- Hasson, D., Shemer, H. and Sher, A. (2011) State of the Art of Friendly "Green" Scale
 Control Inhibitors: A Review Article. Industrial & Engineering Chemistry Research, 50,
 7601-7607.
- Kinsman, D.J. (1969) Modes of Formation, Sedimentary Associations, and Diagnostic
 Features of Shallow-Water and Supratidal Evaporites. The American Association of
 Petroleum Geologists Bulletin, 53, 830-840.
- Li, J., Li, G., and Yu, Y. (2007) The influences of gypsum water-proofing additive on
 gypsum crystal growth. Materials letters, 61, 872-876.
- Lide, D. R. (Ed.). (1988) CRC handbook of chemistry and physics. CRC press, 88, chapter 8
 page 49.
- Ling, L., Zhou, Y., Huang, J., Yao, Q., Liu, G., Zhang, P., Sun, W. and Wu, W. (2012)
 Carboxylate-terminated double-hydrophilic block copolymer as an effective and
 environmental inhibitor in cooling water systems. Desalination, **304**, 33-40.
- Magallanes-Rivera, R.X., Escalante-Garcia, J.I., and Gorokhovsky, A. (2009) Hydration
 reactions and microstructural characteristics of hemihydrate with citric and malic acid.
- Construction and Building Materials, **23**, 1298-1305.
- Mi, B. and Elimelech, M. (2010) Gypsum Scaling and Cleaning in Forward Osmosis:
 Measurements and Mechanisms. Environmental science and technology, 44, 2022-2028.
- Moghadasi, J., Sharif, A., Müller-Steinhagen, H. and Jamialahmadi, M. (2006) Prediction of
 scale formation problems in oil reservoirs and production equipment due to injection of
 incompatible waters. Developments in Chemical Engineering and Mineral Processing, 14,
 545-566.
- Parkhurst, D.L., and Appelo, C.A.J. (1999) User's guide to PHREEQC (Version 2): A
 computer program for speciation, batch-reaction, one-dimensional transport, and

- inverse geochemical calculations. US Geological Survey Water Resource Investigation.
 Report 99-4259, 312p.
- Prisciandaro, M., Santucci, A., Lancia, A. and Musmarra, D., (2005) Role of citric acid in
 delaying gypsum precipitation. The Canadian Journal of Chemical Engineering, 83, 586592.
- Rodriguez-Blanco, J.D., Shaw, S. and Benning, L.G. (2011) The kinetics and mechanisms of
 amorphous calcium carbonate (ACC) crystallization to calcite, via vaterite. Nanoscale, 3,
 265-271.
- Rahardianto, A., Mccool, C.B. and Cohen, Y. (2008) Reverse osmosis desalting of inland
 brackish water of high gypsum scaling propensity: kinetics and mitigation of membrane
 mineral scaling. Environmental science and technology, 42, 4292–4297.
- Senthilmurugan, B., Ghosh, B., Kundu, S.S., Haroun, M. and Kameshwari, B. (2010) Maleic
 acid based scale inhibitors for calcium sulfate scale inhibition in high temperature
 application. Journal of Petroleum Science and Engineering, 75, 189-195.
- Shakkthivel, P., and Vasudevan. T. (2006) Acrylic acid-diphenylamine sulphonic acid
 copolymer threshold inhibitor for sulphate and carbonate scales in cooling water systems.
- 329 Desalination, **197**, 179-189.
- Van Driessche, A.E.S., Benning, L.G., Rodriguez-Blanco, J.D., Ossorio, M., Bots, P. and
 Garcia-Ruiz, J.M. (2012) The role and implications of bassanite as a stable precursor
 phase to gypsum precipitation. Science, 336, 69-72.
- Wang, Y.W., Kim, Y.Y., Christensonb, H.K. and Meldrum, F.C. (2012) A new precipitation
 pathway for calcium sulfate dihydrate (gypsum) via amorphous and hemihydrate
 intermediates. Chemical Communications, 48, 504-506.
- Wang, Y.W., Christenson, H.K., and Meldrum, F.C. (2013) Confinement leads to control
- over calcium sulfate polymorph. Advanced Functional Materials, **23**, 5615-5623.

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Table 1. Dissociation constants of carboxylic acids used (from Lide, 1988)

Carboxylic acid moiety	pK _{a1}	pK _{a2}	pK _{a3}
Citric acid	3.13	4.76	6.40
Maleic acid	1.92	6.23	
Tartaric acid	3.03	4.34	

345 **Figures Rabidazeh et al:**

Fig. 1. The effect of adding 20 ppm tartaric, maleic or citric acid on the development of turbidity compared to the pure CaSO₄ system.

Fig. 2. The effect of variable concentrations of citric acid (5, 10, 20 ppm) on the development of turbidity; marked with * are the absolute times (~ 7 minutes in the pure system and 28 and 350 minutes respectively in the 20 ppm citric acid system) when solids were removed and analysed and data is shown in Fig. 3a, c and d and 4 a and c.

352 Fig. 3. XRD patterns of precipitated materials from (a) the pure CaSO₄ system removed from the reaction solution 30 seconds after turbidity onset (absolute time is ~ 7 minutes) with stars 353 marking bassanite peaks of low intensity that are better visible in the insets, where the low 354 intensity (101) and (400) bassanite peaks are highlighted; (b) same system but 63 minutes 355 after turbidity onset (absolute time 70 minutes) when the transformation to gypsum was 356 357 complete and no bassanite remained; (c-e) XRD patterns from the system with 20 ppm citric acid added; (c) 3 minutes after turbidity onset (absolute time 28 minutes) showing all four 358 359 distinct and very intense bassanite peaks ((101), (200), (301) and (400) all marked with a 360 star); (d) 10 minutes after turbidity onset (absolute time 35 minutes) showing smaller 361 bassanite peaks; and (e) 175 minutes after turbidity onset (absolute time 200 minutes) where only gypsum peaks remain and all bassanite has been transformed. 362

Fig. 4. SEM micrograph of precipitated materials from experiments in (a) the pure CaSO₄ system 30 seconds after turbidity onset showing bassanite nanorods and gypsum needles; (b) the pure CaSO₄ system 63 minutes after turbidity onset (= 70 minutes total time) showing only variably sized gypsum needles; (c) tiny bassanite nanoparticles formed in the presence of 20 ppm citric acid 3 minutes after turbidity onset together with some larger gypsum crystals; (d) plate like gypsum crystals formed in the presence of 20 ppm citric acid after 200 minutes of total reaction; (e) bassanite nanorods and single larger gypsum needle collected a

370	few minutes after the onset of turbidity in the 20 ppm maleic acid experiment; (f) bassanite
371	nanorods and single larger gypsum needle collected a few minutes after the onset of turbidity
372	in the 20 ppm tartaric acid experiment.
373 374	
375	
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409	(absolute time 200 minutes) where only gypsum peaks remain and all bassanite has been transformed.





414 415 416 417 418	after turbidity onset (= 70 minutes total time) showing only variably sized gypsum needles; (c) tiny bassanite nanoparticles formed in the presence of 20 ppm citric acid 3 minutes after turbidity onset together with some larger gypsum crystals; (d) plate like gypsum crystals formed in the presence of 20 ppm citric acid after 200 minutes of total reaction; (e) bassanite nanorods and single larger gypsum needle collected a few minutes after the onset of turbidity in the 20 ppm maleic acid experiment; (f) bassanite nanorods and single larger gypsum
419	needle collected a few minutes after the onset of turbidity in the 20 ppm tartaric acid experiment.
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