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Towards More Sustainable Hydraulic Binders: Controlling Calcium Sulfate Phase Selection via Specific Additives

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Abstract: Bassanite (calcium sulfate hemihydrate) is one of the most extensively used inorganic binders in construction applications. Current industrial processes for the large-scale production of the mineral rely almost exclusively on the thermal dehydration of gypsum (calcium sulfate dihydrate), which consumes considerable amounts of energy. Here we show that phase-pure bassanite can be obtained in high quantities by spontaneous precipitation from supersaturated solutions at moderate temperatures, where gypsum usually forms as predominant solid phase. Key to control over phase selection is the presence of specific additives during crystallization, which carry functional groups for binding onto calcium sulfate surfaces as well as additional moieties that withdraw water in the local microenvironment. Some of the investigated additives allowed bassanite to be recovered in large amounts at temperatures as low as 40 °C and added concentrations of only 0.1 M or even less. The concepts described in this work pave the way towards alternative approaches enabling a less energy-intensive and thus more sustainable production of bassanite for use in construction and other applied systems.

Keywords: Calcium sulfate; bassanite; hydraulic binders; additive-controlled crystallization; specific ion effects.

Introduction

Calcium sulfate minerals are widespread in geochemical settings and play a central role in various industrial processes.^[1] For example, precipitation and dissolution of CaSO₄-based deposits have important implications for the global sulfur cycle,^[2] while the presence of different calcium sulfate phases on Mars is thought to serve as proof for past environmental conditions on the red planet.^[3,4] A major problem related to the crystallization of calcium sulfate is scale formation, as observed in many industrial fields of application like water purification by desalination, oil recovery or mining activities.^[5-7] Here, unwanted incrustation of pipe and heat exchanger surfaces with CaSO₄-containing deposits results in a loss of efficiency and considerable costs due to cleaning and downtimes of facilities. On the other hand, calcium sulfate-based minerals have been used since ancient times as raw materials for construction.^[8,9] In this context, the most relevant phase is bassanite, i.e. calcium sulfate hemihydrate (HH), due to its ability to react with water to form gypsum (calcium sulfate dihydrate, DH).^[10-12] Today, bassanite – also referred to as Plaster of Paris – represents one of the most extensively produced hydraulic binders (annual worldwide consumption: ca. 150 million metric tons) and serves as a key component in stucco, wallboards, cements and mortars.^[13,14] However, established processes to recover bassanite on large scales rely on thermal dehydration of naturally mined or industrially recycled gypsum.^[15,16] As temperatures of up to 160 °C are required for effective dehydration, currently available technologies for bassanite production are expensive (with ca. 95 % of the total costs caused by heating) and consume considerable amounts of energy,^[17] thus leaving a significant carbon footprint. In this regard, alternative approaches to synthesize bassanite in scalable processes with more sustainable energy balance appear highly desirable,^[18] all the more in times when global energy supply and climate change become increasingly critical.

Very recent work has shown that organic solvent-assisted milling of gypsum raw materials may be one such alternative technology.^[19] Another way to bassanite with potentially improved carbon footprint and no need for organic solvents could be precipitation from supersaturated aqueous solutions, a process that has been extensively studied over the past ten years.^[1,20-28] So far, however, this strategy was prevented by the fact that crystallization at moderate temperatures predominantly yields gypsum, the thermodynamically stable phase under these conditions.^[1,20,29] While anhydrite (i.e. the anhydrous crystalline form of calcium sulfate) replaces gypsum as stable phase at temperatures above 60 °C,^[18,29-31] bassanite remains metastable across all relevant conditions as indicated by solubility data.^[1,20,32] Nevertheless, it is known that bassanite forms spontaneously as primary mineral phase upon

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3 precipitation from water at ≥ 90 °C, likely due to kinetic inhibition of thermodynamically favored
4 anhydrite.^[33-35] Previous studies have also shown that the temperature required for preferential
5 bassanite formation is reduced in media of high ionic strength, as achieved for example by addition of a
6 non-specific salt like sodium chloride.^[34,35] Nevertheless, the conditions needed to recover pure
7 bassanite (70 °C, 4.3 M NaCl)^[35] hardly appear attractive for large-scale production. Inspired by these
8 findings, the goal of the present work was to investigate the effects of additives with specific interaction
9 patterns on calcium sulfate precipitation from aqueous solutions, in order to search for conditions where
10 moderate amounts of added crystallization modifiers shift phase selection towards bassanite at as low
11 temperatures as possible. By screening a comprehensive set of candidates in standardized direct
12 precipitation experiments, we have identified several types of additives that allow bassanite to be formed
13 spontaneously at 40 °C at added concentrations of generally less than 1 M and in some cases only
14 0.02 M. Their mode of action seems to rely on chemical moieties that serve two key functions: sufficiently
15 strong binding to calcium sulfate surfaces (while avoiding direct precipitation of the additive with calcium
16 ions) and modulation of the water household in the local microenvironment. The results obtained in this
17 study may devise a novel route to a more sustainable production of CaSO₄-based hydraulic binders in
18 the future.

33 Results

34 *Initial Screening of Additives*

35
36 The main goal of this work was to find specific additives that promote bassanite formation from
37 supersaturated aqueous CaSO₄ solutions at low temperatures and moderate additive concentrations.
38 For the most promising candidates, further studies were performed to shed light on the mechanism(s)
39 underlying the observed effects. To this end, we systematically investigated the influence of various
40 organic and inorganic additives on phase selection during calcium sulfate crystallization in direct
41 precipitation assays. Solid phase(s) formed under the different chosen conditions were characterized
42 routinely by optical microscopy and quantified with respect to the contents of bassanite and gypsum
43 using an infrared (IR) spectroscopy-based method as in previous work^[35] (see Section S1 in the
44 Supporting Information (SI) for detailed experimental procedures). In a first round of preselection,
45 precipitation was carried out at 90 °C and a final CaSO₄ concentration of 0.1 M. The behavior observed
46 in the presence of the selected additives was compared to results obtained under the same conditions
47 for sodium chloride, which was chosen as a reference system because NaCl can be classified as a
48 neutral (or borderline) salt without pronounced chaotropic or kosmotropic effects (see Fig. S1 in the SI
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for an overview of the Hofmeister series).^[36,37] Based on this rationale, the studied additives were classified into four groups with respect to their ability to promote HH formation: (A) unsuitable due to unwanted side reactions and/or issues during workup, (B) less efficient than NaCl, (C) yielding bassanite as main solid phase at similar added concentrations as for NaCl (i.e. 2.8 M at the given conditions),^[23] and (D) more efficient than NaCl, i.e. favoring HH precipitation at significantly lower (molar) concentrations. A list of all additives studied in the present work and their observed behavior according to the above classification is given in Table 1, while the molecular structures are shown in Fig. S2 of the SI. In the following, only additives from groups (C) and (D) will be discussed explicitly; more information on the behavior of type (A) and (B) additives can be found in the SI (Table S1).

Table 1. Additives investigated in this work and their classification with respect to the ability to promote bassanite formation upon precipitation at 90 °C and 0.1 M CaSO₄. For explanations see text.

Group	Additives
(A)	Citrate, cyclohexane hexacarboxylate (CHC), polyacrylate (PAA), poly(ethylene glycol) (PEG), sodium trimetaphosphate (STMP).
(B)	Ammonium chloride, ammonium thiocyanate, benzoate, D-(+)-glucose, magnesium chloride, tetramethylammonium chloride (TMACl), urea.
(C)	Methyl sulfate, myo-inositol, sodium thiocyanate, D-(+)-trehalose, trimethyl amine oxide (TMAO).
(D)	Acetate, betaine, butanoate, dextran sulfate, guanidinium chloride, hexanoate, lithium chloride, 1-pentane sulfonate, polyoxyethylene(8) octyl ether carboxylate (AEC), L-proline, propionate, taurine.

As a first family of additives, the influence of simple (inorganic) salts was tested to probe potential specific ion effects according to the Hofmeister series.^[37] Of the considered candidates (LiCl, NaSCN, MgCl₂, NH₄Cl and NH₄SCN), only LiCl showed an improvement with respect to NaCl and produced bassanite as main phase at 90 °C and 0.8 M added salt. Interestingly, HH formation was also observed at 4.3 M LiCl, but not at 2.8 M (where DH was obtained). This seemingly inconsistent behavior can be explained by solubility calculations using PHREEQC,^[32] which indicate that the solution with 2.8 M LiCl is indeed undersaturated with respect to HH (in contrast to 0.8 and 4.3 M LiCl), and the reported fact that the supersaturation ratio of HH and DH determines phase selection in these systems.^[35] While NaSCN gave similar results as NaCl, the observed lower efficacy of both NH₄Cl and NH₄SCN (which failed to give HH even at 4.3 M) suggests that chaotropic ammonium cations favor DH formation, likely due to their weak hydration and soft character (i.e. low charge density; cf. Fig. S1 in the SI). In turn, the likewise strongly chaotropic guanidinium cation (applied as chloride salt) gave bassanite as major precipitating phase at all studied concentrations (0.8, 2.8 and 4.3 M) at 90 °C, indicating that a plain

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3 categorization along the lines of the Hofmeister series cannot account for all observations made in this
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5 study and that further subtle effects may also play an important role.

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7 The second class of additives investigated included various types of carboxylates. By using simple alkyl
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9 carboxylates (i.e. acetate, propionate, butanoate and hexanoate), the additive concentration required
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11 for preferential HH formation at 90 °C and 0.1 M CaSO₄ could be considerably reduced as compared to
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13 NaCl, from 2.8 M to 0.2 M (acetate and butanoate) or even 0.075 M (propionate and hexanoate), with
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15 no clear trend of efficiency as a function of alkyl chain length. Due to these promising results, additives
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17 with higher density of carboxylate groups, i.e. citrate, cyclohexane hexacarboxylate (CHC) and
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19 polyacrylate (PAA), were also tested but proved to be unsuitable, mainly due to precipitation of
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21 corresponding calcium salts (cf. Table S1 in the SI). Another interesting additive evaluated in this context
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23 was a surfactant with a carboxylate headgroup and ethylene oxide (EO) units, more specifically
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25 polyoxyethylene(8) octyl ether carboxylate (hereinafter referred to as alkyl ether carboxylate, AEC),
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27 which forms micelles in water at concentrations higher than ca. 0.01 M.^[38] Precipitation experiments
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29 showed that added amounts of only 0.02 M AEC (ca. 1 wt%) are sufficient to obtain HH at 90 °C, which
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31 is much lower (factor of >100) than in the case of NaCl. A general observation made for all studied
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33 carboxylate-containing additives was their retarding effect on (macroscopic) CaSO₄ precipitation,
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35 especially at higher concentrations (>0.8 M for alkyl carboxylates and >0.5 wt% for AEC), where the
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37 induction time increased from <1 min up to several hours.

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39 In analogy to (hard) carboxylates, we also investigated selected salts carrying (softer)^[39] sulfate and
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41 sulfonate groups. While methyl sulfate did not provide any advantage over NaCl, 1-pentane sulfonate
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43 induced HH formation already at 0.8 M, i.e. with lower efficiency compared to its (harder) homologue
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45 hexanoate. Dextran sulfate, a strongly kosmotropic polysaccharide with high functional group density,
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47 in turn performed much better than NaCl, as added concentrations of only 0.01 M (0.2 M when referred
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49 to monomer units concentration) were sufficient to produce HH at 90 °C. By contrast, the other tested
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51 sugar-type additives (including glucose, myo-inositol and trehalose), which can all be regarded as
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53 moderately strong nonionic kosmotropes, did not promote HH formation, indicating a key role of charged
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55 functional groups and confirming the notion that the Hofmeister series cannot explain all experimental
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57 observations.

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59 Finally, osmoprotectants were considered as a promising class of additives, due to their ability to
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withdraw hydration water in local microenvironments,^[40,41] which may be leveraged to favor HH formation
over DH. Here we chose betaine, L-proline, taurine and trimethyl amine oxide (TMAO) as candidates,

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3 which all exist in a zwitterionic state under the investigated conditions. While TMAO showed comparable
4 efficiency to NaCl, the other three osmoprotectants performed considerably better. For example, typical
5 concentrations of 0.05, 0.1 and 0.2 M were sufficient for betaine, taurine and proline, respectively, to
6 produce HH as main solid phase at 90 °C and 0.1 M CaSO₄. Noteworthy, precipitation experiments
7 with tetramethyl ammonium chloride (TMACl) – used to imitate the ammonium part of betaine – resulted
8 in less HH than corresponding references with NaCl, highlighting the superior performance of the
9 zwitterionic structures. As another advantage (e.g. over carboxylates), the studied osmoprotectants did
10 not cause any noticeable delay of CaSO₄ precipitation.

11
12 Taken together, our prescreening approach has identified several promising candidates for efficient
13 control over phase selection in the calcium sulfate system. The observed trends suggest that multiple
14 factors may contribute to the ability of an additive to promote HH formation. In particular, the following
15 structural features appear to be beneficial: functional groups to bind onto CaSO₄ surfaces (e.g.
16 carboxylates), predominantly kosmotropic character (e.g. dextran sulfate), moieties with strong
17 hydration to locally withdraw water (e.g. osmoprotectants) and/or amphiphilicity to induce additive self-
18 assembly and cooperative effects (e.g. AEC).

31 32 *Variation of Temperature and Supersaturation*

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34 In order to further explore the potential of the identified candidates and find optimum (i.e. most
35 sustainable) conditions for spontaneous bassanite formation, precipitation experiments were performed
36 at varying temperature and supersaturation (as given by the used concentrations of CaCl₂ and Na₂SO₄).
37 Results obtained for betaine and propionate are visualized in Fig. 1. Generally, the amount of bassanite
38 recovered from these (and many other) experiments decreases at lower temperatures, for reasons
39 described above and in earlier work.^[34,35] However, the presence of both betaine (Fig. 1a-c) and
40 propionate (Fig. 1d-f) allows HH to be formed as main solid phase (i.e. ≥50 wt% HH in the precipitated
41 material, green symbols in Fig. 1) at lower temperatures and, most notably, also at much lower additive
42 concentrations than in the case of NaCl (of which 4.3 M was needed to yield 68 wt% HH at 50 °C and
43 0.2 M CaSO₄).^[35] For betaine, the ability to promote HH formation was found to increase with decreasing
44 levels of supersaturation (i.e. better efficiency at 0.1 M CaSO₄ compared to 0.2 and 0.4 M), whereas an
45 opposite trend was observed for propionate as well as its shorter-chain homologue acetate (see Fig. S3
46 in the SI), indicating certain differences in the mode of action of simple carboxylate and betainic
47 additives. Under the same conditions, sodium chloride showed the best results in terms of HH formation
48 at intermediate levels of supersaturation (i.e. 0.2 M CaSO₄), while hexanoate proved to be more efficient
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than acetate and propionate at 0.1 M CaSO_4 but could not be applied at higher supersaturation due to precipitation of calcium hexanoate (see Fig. S3 in the SI). These experiments demonstrate that alkyl carboxylates and betaine can induce preferential HH formation upon precipitation from solutions at a temperature of 50 °C and additive concentrations lower than 1 M.

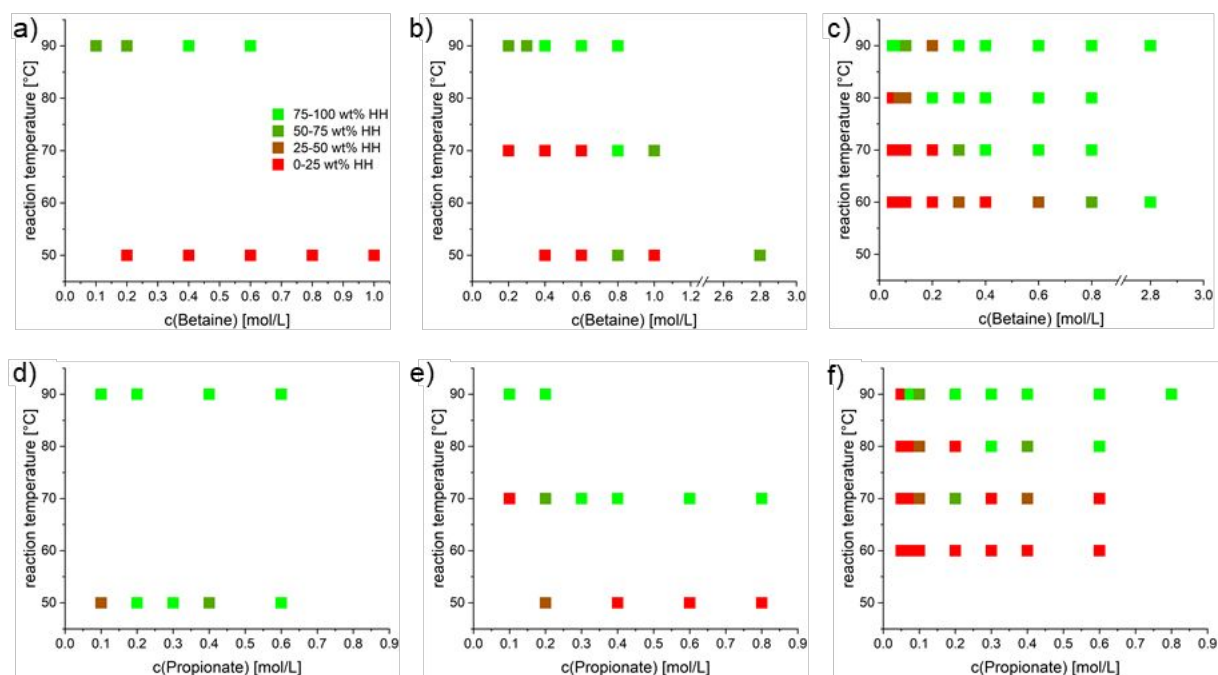


Fig. 1. Results of calcium sulfate precipitation experiments in the presence of varying amounts of added (a-c) betaine and (d-f) propionate at different temperatures and final CaSO_4 concentrations of 0.4 (a,d), 0.2 (b,e) or 0.1 M (c,f). Symbol colors indicate the weight fraction of HH in the isolated precipitate as deduced from ATR-IR measurements.

Fig. 2 provides an overview on selected results obtained for the carboxylate-based surfactant AEC as another lead candidate from the prescreening tests. Here, the fraction of HH formed under the influence of 1 wt% (= 0.02 M) surfactant is given as a function of the reaction temperature at different levels of supersaturation. The data clearly shows that the efficacy of the additive decreases with temperature, yet to quite different degrees as depending on the CaSO_4 content. Indeed, added amounts of only 0.02 M were sufficient to yield 60 wt% HH at 0.4 M CaSO_4 and 40 °C. To our knowledge, this is the lowest temperature reported so far for spontaneous bassanite formation from aqueous solutions. Compared to NaCl, AEC thus provides a substantial improvement in terms of both the required temperature and additive concentration. Moreover, the higher efficiency observed at higher CaSO_4 content appears attractive as it would allow syntheses to be conducted with less water.

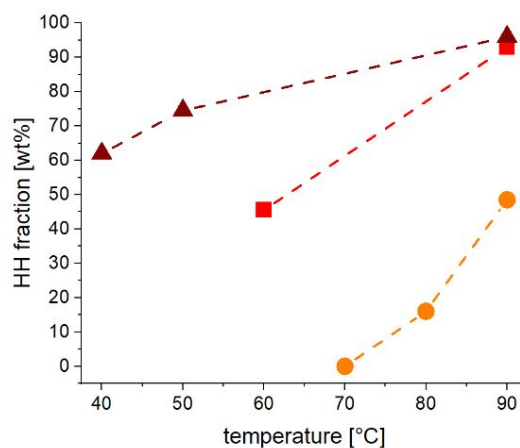


Fig. 2. Effects of the anionic surfactant polyoxyethylene(8) octyl ether carboxylate (AEC) on phase selection during calcium sulfate precipitation at different temperatures and varying levels of supersaturation: plot of the weight fraction of HH recovered in experiments performed at 1 wt% (= 0.02 M) AEC and final CaSO₄ concentrations of at 0.1 (orange), 0.2 (light red) and 0.4 M (dark red).

Analyses like those depicted in Fig. 1 and Fig. 2 were performed in the same way for other additives, which were identified as promising in the prescreening tests according to Table 1. Based on the collected data, we chose to define an optimum set of conditions in terms of HH formation for each of the additives along the following criteria: lowest possible temperature (first priority), lowest possible additive concentration (second priority) and highest possible CaSO₄ content (third priority) to obtain precipitates with a HH fraction of at least 50 wt%. This rationale allows the additives to be ranked with respect to their potential in a graphical overview as provided in Fig. 3.

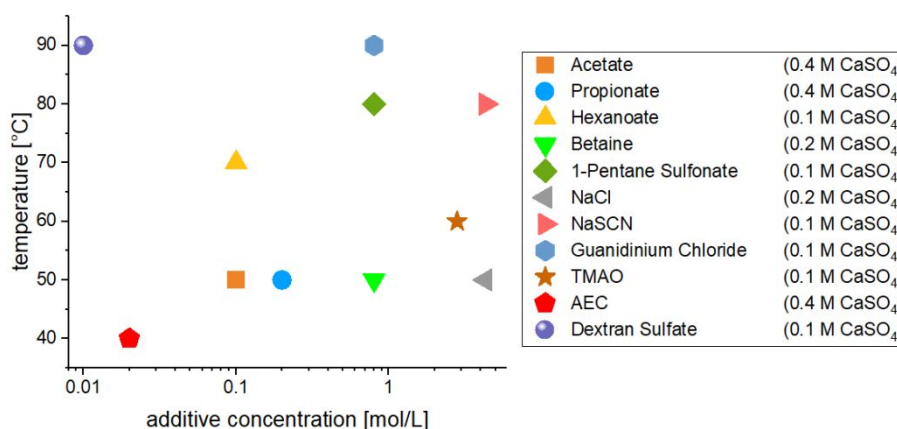


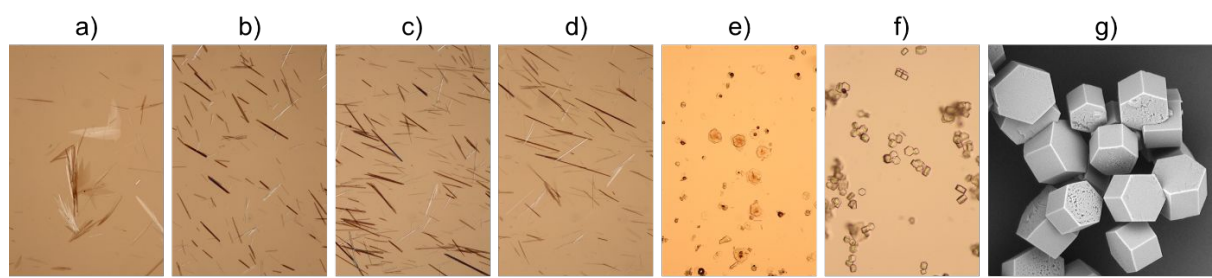
Fig. 3. Graphical summary of the best conditions for preferential HH formation identified for selected additives based on the precipitation experiments performed in this work. The shown values give the lowest possible temperature (y-axis, first priority), the corresponding lowest possible additive concentration (x-axis, second priority) and the corresponding highest possible CaSO₄ content (in brackets in the legend, third priority) required to obtain at least 50 wt% HH upon precipitation from aqueous solutions.

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3 Regarding additive concentration, highest efficiency was observed for the different alkyl carboxylates
4 (≤ 0.2 M), the surfactant AEC (0.02 M) and dextran sulfate (0.01 M), all of which can be considered as
5 more or less strongly kosmotropic species. While the temperature required for HH formation could not
6 be sufficiently reduced with dextran sulfate (90 °C) and hexanoate (70 °C), both the shorter-chain alkyl
7 carboxylates (acetate and propionate) and the surfactant allowed a substantial decrease to 50 or even
8 40 °C. Furthermore, these latter additives appear to be most efficient at high CaSO_4 contents as desired
9 in view of synthesis yields. On the other hand, acetate tends to delay calcium sulfate precipitation quite
10 considerably, a clear disadvantage with respect to any possible production process, which was less
11 pronounced for propionate, AEC and especially betaine (where moderately higher concentrations of
12 0.8 M were required to obtain HH at 50 °C and 0.2 M CaSO_4). Altogether, we therefore conclude that
13 AEC, betaine and propionate appear to be the most promising additives with specific effects during
14 calcium sulfate precipitation that promote HH formation at low temperatures.
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27 *Mechanisms of Additive-Controlled Phase Selection*

28 Based on the results presented above, further studies were undertaken to investigate the mechanisms
29 underlying the beneficial influence of the three lead candidates on phase selection in the CaSO_4 system.
30 One of the most frequently discussed modes of action in additive-controlled crystallization is (selective)
31 adsorption on (one or more faces) of the growing solid phase.^[42] Such effects were probed for the
32 present systems in two ways. First, the concentration of dissolved additive was determined before and
33 after CaSO_4 precipitation, in order to quantify the amount removed from solution through adsorption on
34 and/or incorporation into the forming bassanite and/or gypsum crystals under reactive conditions at
35 90 °C. Second, additive adsorption on mature (i.e. preformed) gypsum crystals was measured under
36 “static” conditions at room temperature. In both cases, no significant ad- or absorption could be detected
37 (see Tables S2 and S3 in the SI), irrespectively of the initial additive concentration used. This suggests
38 that (specific) adsorption is not a key driver for the observed effects in terms of phase selection –
39 although temporary interactions of the additives with (nanoscale) CaSO_4 precursors and/or growing
40 crystals cannot be excluded at this point. The former notion is supported by optical micrographs of
41 particles obtained from precipitation experiments at 90 °C, as shown in Fig. 4. While regular (and
42 partially twinned) gypsum crystals with plate- or needle-like morphologies were obtained in the absence
43 of additives (Fig. 4a), precipitation in the presence of 4.3 M NaCl, 0.2 M propionate and 0.8 M betaine
44 (Fig. 4b-d) gave uniform bassanite rods with typical lengths of 50-150 μm and widths in the range of 1-
45 10 μm (see Fig. S4 in the SI for corresponding IR spectra, which confirm phase selection as well as the
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3 absence of significant amounts of any of the used additives on or in the particles isolated at the end of
4 the precipitation experiments).

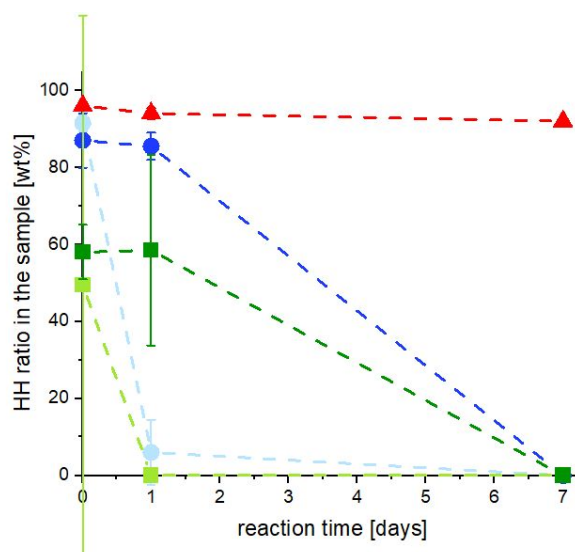


17 **Fig. 4.** Morphologies of calcium sulfate particles obtained from precipitation experiments under the following
18 conditions: (a) 0.1 M CaSO_4 at 90 °C without additives, (b) 0.1 M CaSO_4 at 90 °C with added 4.3 M NaCl, (c) 0.1 M
19 CaSO_4 at 90 °C with added 0.2 M propionate, (d) 0.1 M CaSO_4 at 90 °C with added 0.8 M betaine, (e) 0.4 M CaSO_4
20 at 90 °C with added 0.02 M AEC, (f) and (g) 0.4 M CaSO_4 at 50 °C with added 0.02 M AEC. Images were acquired
21 by optical (a-f) and scanning electron (g) microscopy. Scale bars are 200 μm (a-f) and 10 μm (g).

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25 Similar morphologies were observed with most of the other additives found to promote HH formation
26 under these conditions, indicating that (face-specific) adsorption does indeed not occur during growth.
27 The only exception in this context was the surfactant AEC, which modified the morphology of bassanite
28 substantially and induced the formation of hexagonal crystals with much lower aspect ratios (at both
29 90 °C and lower temperatures, see Fig. 4e-f). SEM imaging further reveals that the basal planes of these
30 crystals occasionally appear somewhat corroded (Fig. 4g), which suggests that the additive has
31 interacted with these faces during growth. Indeed, similar effects have been reported in a previous study
32 about the influence of malic acid on the crystallization of α -HH from glycerol solutions at 90 °C,^[43] where
33 the formation of particles with low aspect ratios was ascribed to preferential adsorption of the additive
34 on the tip faces of bassanite, inhibiting their growth along the long axis. We assume that this mechanism
35 also accounts for the observations made for AEC in the present work (as evidenced by the pits seen on
36 some crystals in Fig. 4g). However, the fact that adsorption measurements do not show significant
37 binding of the additive on the formed HH particles (cf. Table S2 in the SI) suggests that the interactions
38 of AEC with the tip faces of bassanite are dynamic and do not rely on permanent adsorption.

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52 In another approach to elucidate the role of the additives, the stability (i.e. persistence) of initially formed
53 bassanite was monitored over extended periods of time in contact with the original mother liquor. From
54 the resulting time-dependent behavior, it could be deduced whether the additives directly induce and
55 favor initial HH formation over DH, or if they “just” increase the persistence of a bassanite phase that
56 generally nucleates first in the course of a multi-step crystallization pathway.^[1,20,23-25] Fig. 5 shows typical
57 plots of the fraction of HH determined for precipitates isolated after different times of ageing (5 min, 1 d
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3 and 7 d) in mixtures containing either 0.4 or 0.1 M CaSO_4 and 0.2 M (betaine and propionate) or 0.02 M
4 (AEC) additive at a reaction temperature of 90 °C. In reference experiments performed under the same
5 conditions without any additive, phase-pure gypsum was obtained already after five minutes. By
6
7 conditions without any additive, phase-pure gypsum was obtained already after five minutes. By
8
9 contrast, HH is found to be the main phase (i.e. ≥ 50 wt%) with all three additives at both levels of
10 supersaturation. Further important differences are observed upon ageing: while the initially formed
11 fraction of HH remained more or less stable for one day with all additives at 0.4 M CaSO_4 (dark-colored
12 symbols in Fig. 5), only the surfactant AEC proved to be able to preserve bassanite for longer periods
13 of time under these conditions, whereas complete transformation into gypsum occurred within one week
14 for both propionate and betaine. This indicates that AEC stabilizes HH particles by temporary adsorption
15 on their surfaces, while a different mode of action appears to underlie the control over phase selection
16 achieved by propionate and betaine. Interestingly, time-dependent stabilities of initially formed HH show
17 a different trend for the latter two additives when a lower CaSO_4 content of 0.1 M is used (light-colored
18 symbols in Fig. 5). Here, more or less complete transformation into gypsum occurred already after one
19 day of ageing. This means that the stabilizing influence of propionate and betaine is linked to the total
20 ion strength in the system (given as the sum of salinity contributed by the additive as well as calcium,
21 sulfate, sodium and chloride ions), hinting towards (local) water availability as key factor – rather than
22 the amount of additive per mineralizing species, as expected for a mechanism based on (specific)
23 adsorption. Indeed, similar observations were made for the surfactant AEC in terms of the trends
24 regarding phase selection after 5 min (cf. Fig. 2).



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Fig. 5. Stability of bassanite formed upon precipitation from solutions containing 0.4 M CaSO_4 and 0.2 M propionate (dark blue), 0.1 M CaSO_4 and 0.2 M propionate (light blue), 0.4 M CaSO_4 and 0.2 M betaine (dark green), 0.1 M CaSO_4 and 0.2 M betaine (light green), or 0.4 M CaSO_4 and 0.02 M AEC (red) at 90 °C as a function of time upon prolonged ageing in contact with the mother liquor.

Further insights into the occurring processes could be gained by monitoring the precipitation reaction by means of *in-situ* Raman spectroscopy^[44] at 0.1 M CaSO₄ and 90 °C. In a reference experiment without additives (see Fig. S5 in the SI), a mixture of HH and DH was detected at the onset of the precipitation reaction. Transformation of the initially formed bassanite occurred over a period of 40 min, after which gypsum was the only phase observed in the spectra. This implies that bassanite and gypsum nucleate concomitantly in the pure system (i.e. even in the absence of larger amounts of NaCl) at 90 °C, but the metastable bassanite is not preserved upon isolation (cf. Fig. S3 in the SI).

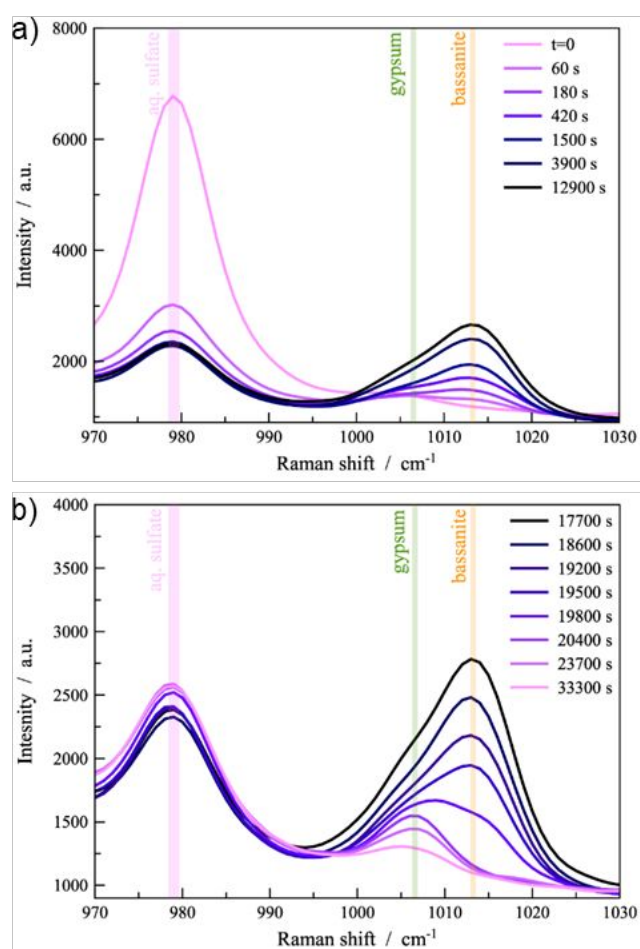


Fig. 6. Time-dependent development of crystalline phases in the course of calcium sulfate precipitation from supersaturated solutions (0.1 M CaSO₄) at 90 °C in the presence of 0.4 M betaine, as monitored by *in-situ* Raman spectroscopy during (a) the first 4 hours and (b) the subsequent 5 hours of the reaction. Bands characteristic for dissolved sulfate ions (978 cm⁻¹), gypsum (1007 cm⁻¹) and bassanite (1013 cm⁻¹) are highlighted.

Corresponding results obtained in the presence of 0.4 M betaine are summarized in Fig. 6. Again, a mixture of bassanite and gypsum was observed at the beginning of the reaction (Fig. 6a), which however developed in an entirely different way in the following hours, where HH became increasingly dominant (evident from the main band at 1013 cm⁻¹), although DH remained present in certain amounts (shoulder

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3 at ca. 1007 cm^{-1}). After about 5 h (Fig. 6b), relatively fast transformation of bassanite took place, until
4 finally (i.e. after ca. 6 h) only gypsum was detected. Overall, these *in-situ* observations are fully
5 consistent with the *ex-situ* data presented in Fig. 4. Moreover, the Raman data suggests that betaine
6 inhibits the growth of more stable gypsum, as evident from a comparison of the observed transformation
7 rates to the reference experiment (cf. Fig. S5 in the SI) as well as an increase in the intensity of dissolved
8 sulfate ions (peak at 978 cm^{-1}) upon and after transformation.

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10 To further substantiate the above hypotheses, additional experiments were performed to probe the
11 effects of betaine and AEC on the nucleation of gypsum and the transformation of HH into DH at ambient
12 conditions (Fig. 7). Turbidimetric monitoring of gypsum precipitation from supersaturated solutions
13 (0.075 M CaSO_4) shows a clear delay of nucleation in the presence of 0.4 M betaine and especially
14 0.02 M AEC, with induction times increasing from ca. 2-3 min in the control experiment to about 25 min
15 and almost 3 h, respectively, under the influence of the additives (Fig. 7a). This strongly supports the
16 notion that additives, which were found to be efficient in promoting HH formation, inhibit the
17 crystallization of gypsum and thereby offer metastable bassanite the chance to grow and develop into
18 the dominating phase over significant periods of time, before transformation into more stable gypsum
19 occurs (in line with the *in-situ* Raman data reported for betaine in Fig. 6). Monitoring the hydration of HH
20 into DH with and without added betaine or AEC by means of conductometry reveals that both additives
21 also hinder the transformation process to some extent (Fig. 7b), although these effects are less
22 pronounced compared to the inhibition of gypsum formation. Both additives do not affect the initial
23 dissolution of HH and the early steps of hydration (first 5 min in Fig. 7b), but rather interfere with the
24 later stages where, again, nucleation and growth of DH take place. It is worth noting at this point that
25 the delaying influence of betaine and AEC discussed here is much weaker under the conditions of the
26 experiments depicted in Figs. 1-3 (due to the higher CaSO_4 content, i.e. larger supersaturation, used for
27 bassanite synthesis) and thus considered uncritical for the targeted application.

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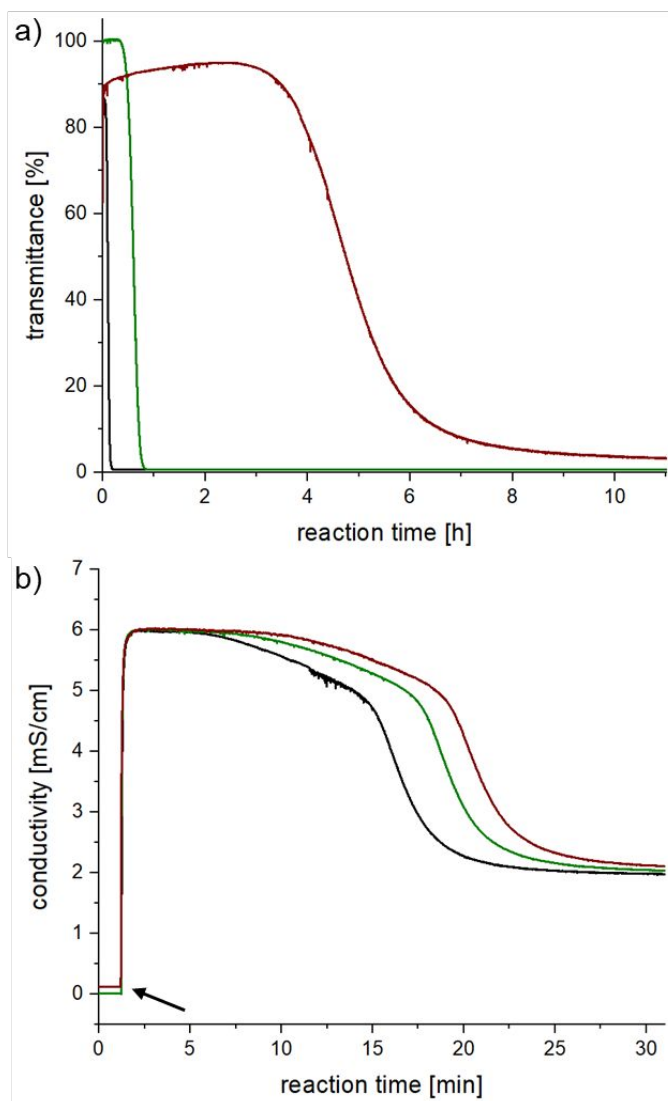


Fig. 7. Effects of additives on the nucleation and transformation of calcium sulfate phases at ambient temperature. (a) Turbidimetric monitoring of CaSO_4 precipitation at 0.075 M CaSO_4 and no additive (black), 0.4 M betaine (green) or 0.02 M AEC (red). (b) Hydration of bassanite into gypsum at a solid content of 5 wt% HH, as probed by an immersed conductometric sensor (same color code as in (a)). The arrow indicates the time at which solid HH was added to the respective solution. Conductivities around 6 mS/cm correspond to a saturated solution in contact with HH, while ca. 2 mS/cm signifies completed transformation in equilibrium with solid DH.

Finally, we have investigated the effect of the osmoprotectant betaine on the activity of water of the aqueous media under study. For this purpose, the vapor pressure of betaine solutions was measured at various concentrations and the results were compared to corresponding solutions of sodium chloride. The rationale behind these analyses was as follows: if water activity was the main driver for phase selection in the CaSO_4 system – as proposed in previous studies^[1,20,34] but questioned in a recent work^[35] – then a HH-promoting osmolyte like betaine should reduce water activity much more strongly than sodium chloride at equal concentration, given that considerably higher amounts of NaCl are required to form bassanite under otherwise identical conditions. However, the experimental data collected by vapor

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3 pressure osmometry (see Table S4 in the SI) do not support this notion and rather show lower water
4 activities in NaCl-containing solutions. This suggests that, under the conditions investigated in the
5 present work, changes in bulk water activity are not key to HH formation at moderate temperatures and
6 additive concentrations. On the other hand, these experiments do not exclude, and perhaps even
7 support, a mechanism based on additive-induced modulations of the local water household in the direct
8 vicinity of CaSO₄ precursors during the early stages of crystallization. This may especially be true for
9 additives with functional groups allowing them to bind to the precursor species and other moieties that
10 locally withdraw water – both features that apply to the lead candidates propionate, betaine and AEC.
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19 **Discussion**

20 The precipitation experiments performed in this work have shown that phase selection during calcium
21 sulfate precipitation from aqueous solutions can be controlled by means of properly selected additives.
22 Based on specific interactions provided by some of the tested additives, it was possible to obtain
23 metastable bassanite at conditions where gypsum otherwise represents the major solid phase formed,
24 and at added amounts much lower than observed previously with an unspecific salt like sodium
25 chloride.^[34,35] In particular, certain specific additives were able to induce HH formation at concentrations
26 smaller than 1 M or even 0.1 M and temperatures as low as 40 °C. To our knowledge, spontaneous
27 crystallization of bassanite from aqueous solutions at such moderate conditions has not been reported
28 so far.
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38 While sugars and other uncharged species did not have any significant effect on the precipitation
39 behavior, additives containing sulfate or sulfonate group already proved to be more efficient than NaCl
40 in terms of HH formation. Particularly pronounced control over phase selection could be achieved with
41 most of the investigated carboxylates which, except for benzoate, gave bassanite as main solid phase
42 upon precipitation at relatively low added concentrations (<1 M). Among the carboxylate-bearing
43 additives, propionate and the surfactant AEC showed most promising behavior and allowed HH to be
44 formed preferentially at 50 °C, or even 40 °C, without critical side effects such as strong delay of
45 crystallization or precipitation of calcium carboxylates salts. Zwitterionic additives like betaine were also
46 identified as powerful phase selection modifiers, enabling HH formation at 50 °C without any noticeable
47 inhibiting influence.
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57 The observed trends in the precipitation experiments and the results of complementary studies on the
58 mode of action of selected additives suggest that the following mechanisms, either alone or in
59 combination, underlie the desired shift in phase selection towards the less hydrated bassanite: (i)
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3 changes in the solubilities and thus (relative) levels of supersaturation of calcium sulfate phases; (ii)
4 modulations of the activity and/or structure of water in the microenvironment where mineralization takes
5 place; (iii) adsorption of additives on CaSO₄ precursors and/or growing particles; and/or (iv) selective
6 inhibition of the crystallization of distinct phases. For any of these possible mechanisms, it is important
7 to consider that the additives can interact with the different species occurring in the course of a
8 multistage crystallization process,^[1,20-28,45] i.e. dissolved ions or ion pairs, disordered nanoparticulate
9 precursors and (more or less) mature crystals.

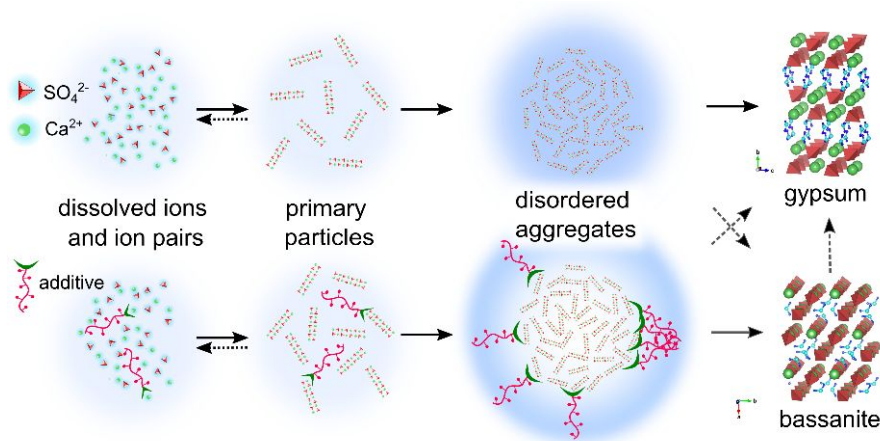
10 Direct influence on the relative solubilities of the different calcium sulfate phases according to
11 mechanism (i) has indeed been verified for certain additives, especially simple salts for which solution
12 speciation calculations with PHREEQC^[32] can readily be performed. One example was lithium chloride,
13 which shows different concentration-dependent effects on the solubility of gypsum and bassanite, thus
14 inducing critical relative levels of supersaturation^[35] for HH to form under some of the tested conditions.
15 However, such calculations are not trivial for many of the more complex additives investigated in this
16 work and will be subject of future studies.

17 The most intriguing and powerful mode of action observed for some of the studied additives relies on
18 modulations of the water household in the vicinity of the developing mineral particles (mechanism (ii)).
19 Restricted availability of water during crystallization is known to drive CaSO₄ phase selection towards
20 less hydrated products, as reported for precipitation from aqueous solutions containing high amounts of
21 salt^[33-35,46] and organic solvents with low enough water content,^[47,48] which can be considered as a direct
22 manifestation of the often neglected but inherently important role of water in crystallization
23 processes.^[49,50] The initial hypothesis in the present work was that additives may locally withdraw water
24 from the CaSO₄ precursors and thus promote HH formation over DH at much lower dosages compared
25 to the bulk approaches with excess electrolytes and organic solvents mentioned above. In principle, this
26 requires suitable additives to show certain affinity for interacting with the relevant precursor species and
27 the ability to sequester water or at least modify the local water structure. With regard to the latter
28 criterion, an obvious first approach was to explore the effects of kosmotropic and chaotropic ions in the
29 sense of the classical Hofmeister series (see Fig. S1 in the SI).^[36,37] Following this logic, additives with
30 kosmotropic character (i.e. high degrees of hydration) should withdraw water more strongly than their
31 (less hydrated) chaotropic counterparts and thus favor precipitation of bassanite. The experimental
32 evidence collected in this work (cf. Table 1 and Fig. S2 in the SI) indeed confirms that the majority of
33 tested ions behave as expected based on the Hofmeister series. For example, chaotropic cations (e.g.

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3 NH_4Cl) and anions (e.g. NaSCN at lower temperatures) were less efficient in terms of HH formation than
4 more kosmotropic references (NaCl in both cases). This rationale also explains the results obtained at
5 $90\text{ }^\circ\text{C}$ for various other studied additives (e.g. alkyl carboxylates, NH_4SCN , dextran sulfate, TMACl and,
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7 in part, alkyl sulfates and sulfonates). The main exceptions from this general trend are magnesium
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9 (strongly kosmotropic) and guanidinium (strongly chaotropic) chloride, which proved to be less and more
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11 efficient, respectively, than NaCl . Again, solution speciation calculations^[32] provide a clue to explain
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13 these exceptions, as the mixtures containing 0.8 and 2.8 M MgCl_2 are predicted to be undersaturated
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15 with respect to HH. This may imply that, while withdrawing water in the mineralizing microenvironment
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17 via mechanism (ii), strongly kosmotropic ions counteract bassanite formation by destabilizing the solid
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19 phase relative to gypsum according to mechanism (i). Conversely, chaotropes may enhance HH stability
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21 while not being able to modulate local water households in a favorable manner, although the different
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23 behavior of guanidinium and ammonium and the lack of speciation data allowing for corresponding
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25 calculations^[32] do not allow us to draw general conclusions yet.

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28 Further differentiation of the promising kosmotropic species was observed when decreasing the additive
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30 concentration and reaction temperature (cf. Fig. 1-3 and Fig. S3 in the SI). Here, the second criterion
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32 related to mechanism (ii) – i.e. the affinity to bind to the relevant mineral structures – becomes important.
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34 Indeed, highest efficiencies in terms of HH formation were found for additives containing carboxylate
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36 moieties, which are known to interact preferably with calcium sulfate surfaces.^[50] However, too strong
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38 interactions (as in the case of molecules carrying multiple carboxylate groups) result in the precipitation
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40 of other phases and disqualify corresponding additives (e.g. citrate, CHC or PAA) for the present
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42 purpose (cf. Table 1 and Table S1 in the SI). Another potential disadvantage of carboxylate-containing
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44 additives is their inhibiting effect on CaSO_4 crystallization, which may render any related industrial
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46 process economically unattractive. Considering all these factors, the most balanced property profiles
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48 are displayed by short- to medium-chain alkyl carboxylates (especially propionate), zwitterionic species
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50 (e.g. betaine, proline or the sulfonate analogue taurine) and amphiphilic structures like AEC. A
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52 conceptual drawing illustrating the envisaged mode of action of these highly efficient additives is shown
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54 in Scheme 1. In the case of simple alkyl carboxylates, local dehydration of mineral precursors is likely
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56 to be governed by the aforementioned kosmotropic effects of the charged headgroup, possibly along
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58 with a certain degree of hydrophobization towards the surrounding aqueous bulk. Zwitterions like betaine
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60 bear an additional charged moiety in close proximity to the “anchoring” carboxylate group. This will likely
withdraw water even more effectively from the mineral precursors, as reflected in the osmoprotectant

properties of such molecules.^[40,41] The same structural principle is also found in AEC, the most efficient additive identified in this work (cf. Fig. 3). Here, the eight EO units next to the carboxylate headgroup bind considerable amounts of water^[38] and thus dehydrate CaSO_4 species in a most extensive manner, while avoiding precipitation of the carboxylate with calcium ions due to the high entropy of the EO segments. The amphiphilicity of the molecule caused by the relatively long alkyl chain adds further benefits in terms of additive efficiency: on the one hand, self-assembly of the amphiphilic molecules into micellar structures will likely lead to cooperative phenomena at the interfaces of mineral precursors, where multiple adjacent carboxylate headgroups and EO segments in the corona of the micelles reinforce the described effects and sequester water in the local microenvironment most efficiently. On the other hand, (temporary) binding of AEC micelles to the mineral interfaces will establish a (hydrophobic) barrier, which hinders rehydration of the precursor species by bulk water.



Scheme 1. Sketch of the early stages of calcium sulfate crystallization in the absence (top) and presence (bottom) of additives, which modulate the availability and/or structure of water in the vicinity of mineral precursors and thus may favor the formation of bassanite over gypsum. Efficient additives contain an anchoring group with balanced affinity to bind to CaSO_4 surfaces and kosmotropic character (indicated in green, e.g. carboxylate) as well as specific water-withdrawing and/or hydrophobizing moieties in close proximity (indicated in red). For further explanations see text.

Thus, the combination of specific anchoring groups with kosmotropic character and additional water-withdrawing and/or hydrophobizing moieties appears to yield most promising additive structures for the targeted precipitation of bassanite at moderate conditions. This notion is further supported by two important experimental observations: on the one hand, stability tests showed that both propionate and betaine could preserve initially formed HH for longer periods of time at higher total amounts of CaSO_4 species present in the system (cf. Fig. 5). Such behavior is *per se* unexpected, as additive effects usually become stronger as their amount related to the mineral phase is increased.^[28] An opposite trend as

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3 observed here suggests that bulk medium properties, especially the total salinity established by reagents
4 (CaCl₂/Na₂SO₄) and additives (betaine or propionate), contribute to control over phase selection. On the
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6 other hand, actual measurements by vapor pressure osmometry (cf. Table S4 in the SI) indicate that
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8 even strong osmolytes like betaine do not reduce (or rather increase) bulk water activity compared to
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10 an unspecific electrolyte like NaCl – confirming the key role of specific anchoring groups and local effects
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12 in terms of water household.

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14 Although we consider interactions according to mechanism (ii) to mainly account for the observed
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16 additive efficiencies in promoting HH formation, there is compelling evidence that mechanisms (iii) and
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18 (iv) – i.e. additive adsorption on solid calcium sulfate surfaces and selective inhibition of gypsum
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20 crystallization – also contribute to control over phase selection and time-dependent stabilities in the
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22 present systems. In particular, studies by means of *in-situ* Raman spectroscopy (cf. Fig. 6) as well as
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24 turbidimetric and conductometric monitoring (cf. Fig. 7) have clearly shown that promising additives such
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26 as betaine or AEC indeed preferentially inhibit the formation of gypsum according to mechanism (iv) and
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28 thereby increase the resistance of bassanite against transformation in contact with aqueous solutions
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30 (cf. Fig. 5). These effects may be caused to some extent also by reduced availability of water for
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32 hydration in the local microenvironment, but evidence provided by optical and electron microscopy (cf.
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34 Fig. 4) suggests that specific adsorption on calcium sulfate surfaces according to mechanism (iii) plays
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36 an important role as well, at least for the most efficient additive AEC. The dramatic shift in bassanite
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38 morphology induced by the surfactant (cf. Fig. 4g) may be considered as another benefit, since the lower
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40 aspect ratios (and corresponding higher specific surface areas) could lead to different (ideally faster)
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42 hydration kinetics compared to the otherwise obtained rods (cf. Fig. 4b-d). On the other hand, actual
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44 measurements of additive adsorption during CaSO₄ precipitation (cf. Table S2 in the SI) as well as on
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46 mature gypsum crystals (cf. Table S3 in the SI) have revealed that only minor amounts of all promising
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48 additives remain bound on the particles. These seemingly contradictory results may be reconciled by a
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50 scenario where additive molecules interact dynamically with CaSO₄ precursor phases and crystals
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52 during progressive ripening, for example by interfering at actively growing faces without actually
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54 adsorbing to these interfaces permanently (and/or only in trace amounts sufficient for growth poisoning
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56 but too low to be detected by bulk analyses). This notion is supported by a recent study,^[28] in which
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58 strong inhibitors of gypsum crystallization were found to not always show strong adsorption on calcium
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60 sulfate surfaces. Taken together, our data indicate that potent additives for the desired control over
phase selection operate on two levels, as they enhance the primary formation of HH and inhibit its

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3 transformation to DH in contact with water through a combination of multiple types of interaction.
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5 Moreover, the fact that these additives do not remain permanently adsorbed on the obtained bassanite
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7 particles has potential relevance for (i) future upscaling, as (expensive) additives may thus be recovered
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9 after precipitation and used multiple times, and (ii) their application as more sustainable hydraulic
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11 binders, which are essentially free of organic species that may cause undesired retarding effects –
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13 although both of these features clearly require further investigation.

14 15 **Conclusion**

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17 In this work, we have studied the crystallization of calcium sulfate from aqueous solutions of various
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19 chemical additives at different temperatures and degrees of supersaturation. The goal was to identify
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21 conditions at which bassanite forms preferentially with as little energy input as possible, in order to
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23 devise an alternative strategy for a more sustainable production of this utterly important hydraulic binder.
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25 Of the many additives investigated in this respect, several candidates indeed allowed the lower limit of
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27 temperature required for the desired shift of phase selection to be reduced to 50 or even 40 °C at
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29 moderate additive concentrations, when compared to previous studies on the influence of simple
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31 electrolytes on CaSO₄ crystallization. While bassanite (and even anhydrite) were successfully obtained
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33 at even lower (i.e. ambient) temperatures in previous studies by grinding in^[19] or precipitation from^[47,48]
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35 organic solvents, the concept described in the present work relies on purely aqueous systems and can
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37 thus be considered as more sustainable – although a more detailed evaluation of all relevant factors
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39 (e.g. energy consumption, safety, recyclability etc.) is required for a profound comparison of the different
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41 proposed methods for bassanite production. Systematic studies of the mechanisms underlying the
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43 observed effects showed that the most suitable additives operate through specific interactions at the
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45 interfaces of mineral precursors and growing crystals, which seem to modulate the availability of water
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47 in local microenvironments, thus favoring the initial formation of less hydrated metastable bassanite and
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49 inhibiting its subsequent transformation into the stable dihydrate phase gypsum. These features appear
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51 to be most readily realized in surface-active alkyl ether carboxylates. Structural variations within this
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53 class of additives and combinations with other bassanite-promoting species such as osmolytes will be
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55 subject of future studies to further improve the overall energy balance and reduce the carbon footprint
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57 of our approach.

58 59 **Supporting Information**

60 Detailed description of experimental procedures used for sample preparation and characterization
(Section S1); supplementary figures providing a graphical representation of the classical Hofmeister

series, the molecular structures of all tested additives, and additional data on additive-controlled phase selection, product characterization and in-situ Raman spectroscopy (Section S2, including Figs. S1-S5); supplementary tables summarizing the outcome of precipitation trials with less efficient additives and the results of adsorption studies on bassanite and gypsum (Section S3, including Tables S1-S3); supplementary references (Section S4).

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11 Data Availability Statement

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13 Additional results supporting the conclusions of this work are available as online supplementary material.
14 The raw data required to reproduce these findings can be made available upon reasonable request.
15

16 Author Contributions

17
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