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https://doi.org/10.1180/minmag.2014.078.6.13

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Carboxylic acids: effective inhibitors for calcium sulfate precipitation?

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Abstract

Here we report results from an investigation on the effects of three carboxylic acid additives (tartaric, maleic and citric acids) on the precipitation of calcium sulfate phases. Precipitation 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 products were characterized during and at the end of each reaction for their mineralogical 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 (induction time, start of precipitation) and the comparison between additive and additive-free 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 transformed to gypsum. The addition of citrate stabilized bassanite and changed the final gypsum habit from typical needle-like crystals in the pure CaSO₄ system to plates in the citrate additive experiments.

Keywords: gypsum, bassanite, carboxylic acids, inhibition, crystallization;
Introduction

Calcium sulfates are important rock forming minerals that occur in thick evaporitic deposits throughout geologic history (Kinsman, 1969). In the calcium sulfate system three phases with various degrees of hydration exist: the dihydrate gypsum (CaSO$_4$·2H$_2$O), the hemihydrate bassanite (CaSO$_4$·0.5H$_2$O) and the anhydrous anhydrite (CaSO$_4$). The stability and formation of these phases are highly temperature and concentration dependent (Freyer and Voigt, 2003). Between ambient and ~ 40 °C the most stable phase is gypsum. With increasing ion concentrations and/or temperature, the solubilities of bassanite and anhydrite decreases and 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 of gypsum from aqueous solutions have gained renewed interest because gypsum likely does not form directly from solution. One study (Wang et al., 2012) suggested that gypsum forms through non-classical nucleation via an amorphous calcium sulfate intermediate, while another study (Van Driessche et al., 2012) suggested that gypsum forms not through amorphous precursors but through the initial precipitation of nanocrystalline bassanite particles that self-assemble into larger gypsum crystals through oriented attachment.

The gypsum formation pathway is important because among calcium sulfates, gypsum is mined extensively for use as the crucial component in plasters and cements (e.g., Camarini and De Milito, 2011), yet to make plasters gypsum has to be dehydrated to bassanite through 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 desalination; Moghaddasi et al., 2006; Rahardianto et al., 2008), the precipitation of calcium sulfate phases leads to the deposition of minerals on pipes, filters and heat exchangers (forming mineral scales). Cleaning or removing such mineral scales is costly and undesirable.
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 have been suggested, the most common being the use of inorganic (e.g., Mg$^{2+}$; Guan et. al., 2010) or organic additives (e.g., sulfonic, phosphonic or carboxylic compounds; Shakkthivel 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 concentrations, (c) it is cheap and its addition will not significantly affect production costs, (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 apparatus. Among additives fulfilling many of the above requirements are carboxylic acids (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 or the effect of high temperatures (Prisciandaro et al., 2005; Senthilmurugan et al., 2010; 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 moieties.

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.

**Experimental methods**
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 % purity, VWR) at room temperature (21 °C) and under constant and continuous stirring. The mixed solutions were supersaturated with respect to gypsum (saturation index SI_{Gyp} = 0.5) but undersaturated with respect to bassanite (SI_{Bas} = -0.37). The saturation indices (as the logarithm of the ion activity product over the solubility product) and the related solubility products (\(K_{sp,gypsum} = 10^{-3.66}\) and \(K_{sp,bassanite} = 10^{-4.53}\)) were calculated with the geochemical computer code PHREEQC using the LLNL database (Parkhurst and Appelo, 1999).

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.

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 spectrophotometer (Uvikon XL) at 520 nm. Reactions were followed in triplicate at room temperatures for up to 4 hours and the variations in the turbidity onset from the three repeats are reported in minutes. At intermediate time steps and at the end of each experiment the solutions were quench-filtered (0.2 µm) under vacuum with isopropanol and the solids retrieved. These solids were characterized for their mineralogy using powder X-ray diffraction (XRD; Bruker D8 diffractometer; CuKα1; 5-30 °2θ; 0.105 °2θ / step), while the morphology of the formed phases was imaged using a field emission gun scanning electron microscope (FEG-SEM, FEI Quanta 650, 3 kV).

**Results**
Turbidity developed in all experiments but the onset of turbidity occurred after different elapsed times (induction times) that were dependent on additive type and concentration. Comparing the turbidity curve from the pure CaSO$_4$ experiment with equivalent curves from experiments where 20 ppm of the 3 carboxylic acids were added (Fig. 1), revealed a carboxylic acid dependent increase in induction time. In the pure CaSO$_4$ system the first increase in turbidity was observed after 6±1 min and the increase in absorbance took ~ 60 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).

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 CaSO$_4$ 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 CaSO$_4$ system was observed (25±1 minutes).
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 gypsum. However, samples filter-quenched just after the onset of turbidity in the pure and citric acid system (e.g., after 30 sec in the pure system and after 3 and 10 min in the presence of 20 ppm citric acid; marked with * in Fig. 2 and corresponding to ~ 7, 26 and 35 minutes in absolute time respectively) showed in the XRD patterns the presence of bassanite coexisting 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 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 also observed in the presence of the other two carboxylic acids (maleic and tartaric; Fig. 1). 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 below and Fig. 4 e,f).

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 µm 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
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 gypsum crystals were present, again confirming the XRD data (Fig. 3b). In the presence of 20 ppm citric acid, after the onset of turbidity (3 minutes = 28 minutes after mixing of the initial solutions) the bassanite identified by XRD (Fig. 3c) was present as very small but almost isometric nanoparticles (< ~ 90 nm; Fig. 4c) that occurred together with larger gypsum crystals. At the end of the reaction when the turbidity curve reached a plateau (after 200 minutes; Fig. 4d) only gypsum was present. It was striking that, compared to the pure CaSO₄ 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. 4c) and distinctly platy (gypsum; Fig. 4d) habits. Although we have no XRD evidence of 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 these carboxylic acids present revealed equivalent nanorod (particles < 200 nm) morphologies that we infer to be bassanite. These occurred together with longer needle-like crystals inferred to be gypsum (Fig. 4e and f). In contrary to the citric acid system however, in the presence of 20 ppm tartaric or maleic acid the shape, size or habit of the intermediate bassanite and end product gypsum were the same as in the pure CaSO₄ experiment, although a slight ‘thinning’ of the gypsum needles was observed.

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, citric acid increased the induction time and decreased the slope of the turbidity curve more than both the tartaric and maleic acid, inferring that citric acid is inherently a better inhibitor.

If we also consider the differences in molar concentrations of the used carboxylic acids ($C_{cit} = 1.01 \mu M, C_{tart} = 1.33 \mu M$ vs. $C_{mal} = 1.72 \mu M$) further supports the fact that citric acid is the most effective inhibitor despite it being present in the lowest molar concentration. However, the exact reasons for its higher effectiveness are not yet clear but likely also stem from the variations in molecular geometries and sorption capacities between these three 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).

$$R(COOH)_x + Ca^{2+} \rightarrow R(COOCa)_x + xH^+$$
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 carboxylic acids delayed the onset of nucleation (increased induction time compared to pure 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 free phases (Fig. 4). Finally, of interest for mineral scale formation and inhibition is the fact that compared to the pure system even low concentrations of citric acid stabilized the 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).

The delay in precipitation, indicated by the increased induction time, is likely in part due to Ca\(^{2+}\) complexation with these deprotonated species through the reduction of Ca\(^{2+}\) supersaturation. Of the carboxylic acids tested, citric acid at pH 7 is the most deprotonated and maybe therefore t acts as the most efficient inhibitor, as reflected in the longest induction 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 presence of the carboxylic acid may also be attributed to sorption onto bassanite and gypsum growth sites. Badens et al. (1999) and Ersen et al. (2006) found that adsorption of citrate onto
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 bassanite and gypsum grew with different habits from those in the pure CaSO$_4$ system, as our 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 gypsum was favoured in the a and b directions, leading to platy crystal habits (Fig. 4). 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 understanding of the process is still lacking.

For gypsum formed in the presence of citric acid Prisciandaro et al. (2005) showed that the increase in induction time was due to a dramatic change in interfacial tension compared to an 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 CaSO$_4$ system (Wang et al., 2012; Van Driessche et al., 2012) but also in the presence of carboxylic acids. In the pure system, bassanite forms below its thermodynamic bulk solubility and its transformation to gypsum is through hydration and self-assembly via a process controlled by a particle size dependent surface energy (Van Driessche et al., 2012). This is different to the non-classical nucleation, growth and dehydration pathways suggested for calcium carbonates (Rodriguez Blanco et al., 2011; Bots et al., 2012) or calcium phosphates (Combes and Rey, 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 stabilized and its transformation to gypsum slowed down, and (c) citric acid changes the shape and habit of the formed bassanite and gypsum.

Thus, if citric acid inhibitors are used in an industrial fluid handling system (where CaSO$_4$ 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 CaSO₄ phases on surfaces is still under study.

Acknowledgements

This study was supported by the Marie Curie grant from the European Commission in the framework of the MINSC ITN (Initial Training Research network), Project number 290040. The authors would like to thank the Cohen Laboratories in the School of Earth and Environment, and the Leeds Electron Microscopy and Spectroscopy Centre (LEMAS) for help and access to instruments during the course of this study. We would like to also thank three reviewers and the associate editor for their constructive comments, which helped improve our paper.

References:


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

<table>
<thead>
<tr>
<th>Carboxylic acid moiety</th>
<th>pK&lt;sub&gt;a1&lt;/sub&gt;</th>
<th>pK&lt;sub&gt;a2&lt;/sub&gt;</th>
<th>pK&lt;sub&gt;a3&lt;/sub&gt;</th>
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<td>Citric acid</td>
<td>3.13</td>
<td>4.76</td>
<td>6.40</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>1.92</td>
<td>6.23</td>
<td></td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>3.03</td>
<td>4.34</td>
<td></td>
</tr>
</tbody>
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**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 CaSO$_4$ 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 35 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.

Fig. 3. XRD patterns of precipitated materials from (a) the pure CaSO$_4$ system removed from the reaction solution 30 seconds after turbidity onset (absolute time is ~ 7 minutes) with stars marking bassanite peaks of low intensity that are better visible in the insets, where the low intensity (101) and (400) bassanite peaks are highlighted; (b) same system but 63 minutes after turbidity onset (absolute time 70 minutes) when the transformation to gypsum was 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 distinct and very intense bassanite peaks ((101), (200), (301) and (400) all marked with a star); (d) 10 minutes after turbidity onset (absolute time 35 minutes) showing smaller bassanite peaks; and (e) 175 minutes after turbidity onset (absolute time 200 minutes) where only gypsum peaks remain and all bassanite has been transformed.

Fig. 4. SEM micrograph of precipitated materials from experiments in (a) the pure CaSO$_4$ system 30 seconds after turbidity onset showing bassanite nanorods and gypsum needles; (b) the pure CaSO$_4$ 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
few minutes after the onset of turbidity in the 20 ppm maleic acid experiment; (f) bassanite nanorods and single larger gypsum needle collected a few minutes after the onset of turbidity in the 20 ppm tartaric acid experiment.
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