Effects of calcium on sodium salt scaling with the presence of resin acids and fatty acids

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ABSTRACT: Reintroducing tall oil soap or its related products into high dry solids black liquor has been found to reduce sodium salt scaling in falling film evaporators. Aside from resin acids and fatty acids, which are the likely scale inhibitors, calcium is reintroduced into black liquor because of the relatively high calcium content of tall oil soap. One concern is that this increase in calcium content might lead to the formation of additional calcium and sodium scales in evaporators.

In this work, we investigated the relationship among trace amounts of calcium, sodium salts, resin acids, and fatty acids in a controlled system using a model salt solution and a benchtop setup. We studied the effects of the calcium carbonate addition and calcium carbonate scales on sodium salt scaling in the presence of resin acids and fatty acids. We found that some calcium carbonate is incorporated in the precipitated sodium crystals, and the suspended sodium crystals become larger and more compact with increasing calcium carbonate concentration. Experiments in the benchtop setup show that precipitating calcium carbonate scale on the heat exchanger does not lead to a higher rate of sodium salt scaling. The solubility of calcium carbonate is not affected by the addition of resin acids and fatty acids. These findings indicate that the reduction in sodium salt scaling through the addition of tall oil soap is primarily related to resin acids and fatty acids, rather than to calcium or to interactions between calcium and mixtures of resin and fatty acids.

Application: This work included resin acids and fatty acids when studying the interaction between calcium and sodium salts. It helps prepare mills for using tall oil soap as a scale inhibitor by clarifying the effects of calcium addition on sodium salt scaling.

Scaling caused by double salts of sodium, carbonate, and sulfate is the major scaling issue in black liquor evaporators from which many mills suffer [1,2]. This scaling usually occurs in concentrators or high dry solids evaporator bodies, where sodium double salts precipitate because their concentration exceeds their solubility limit. Since these sodium salts are highly soluble in water, sodium scale is referred to as "soluble" scale and is usually removed by washing with hot water or weak black liquor.

Recent industrial experiences and research [3] find that the sodium scale can be inhibited by the addition of a small stream of tall oil soap or its related products, such as tall oil and tall oil brine. The candidates of the active scale inhibitors are resin acid and fatty acid soap. Tall oil soap is a by-product of black liquor that is usually skimmed from black liquor at 26–30 wt% dry solids. Therefore, one major advantage of using soap as a scale inhibitor is that it saves the cost of purchasing scale inhibitors.

A common concern for re-introducing soap is that soap can promote calcium (Ca) scales due to its high calcium content (0.2–2 wt% [4]) compared to the calcium content in black liquor (0.01–0.11 wt% dry solids [1,2,3,5]. An increase in calcium scaling due to soap addition was reported in a rising film evaporator [6]. However, the dominant evaporator technique has transferred from the rising film evaporator to the falling film evaporator in the past few decades. One of the differences between falling film and rising film evaporators is that the former can increase dry solids to 65–75 wt%, where sodium salt crystallization occurs, whereas the latter typically concentrates black liquor below 50% to avoid sodium salt crystallization and scaling. The crystallization of sodium salts affects the scaling behavior of calcium carbonate. Ulmgren [5] reported that with the same calcium concentration, calcium scaling is less severe and is rather easy to remove in the mill that has calcium carbonate precipitation simultaneously with sodium salt crystallization, since sodium scale is water soluble. Another study using a pilot falling film evaporator found that sodium scale did not seem to be affected by the slow buildup of calcium scales [3].

Shi [7] concluded that sodium scale can form on top of calcium scale, on surfaces subjected to less flow turbulence. Nwaeri and DeMartini [8] saw a reduction in the fluctuation in the amount of sodium salt scale formed in the same bench top system used in this work when ethylenediaminetetraacetic acid (EDTA) was added to the solution. It was assumed that the EDTA was sequestering calcium and thus the fluctuations in scaling rate without EDTA were due to the impact of calcium ions on nucleation.

In the current study, scaling on the heat transfer surface

was measured in an aqueous solution containing sodium sulfate and sodium carbonate. Experiments were carried out with different levels of calcium carbonate, sodium oleate, and sodium abietate or tall oil soap. The aim of this work is to see if the reduction in sodium salt scaling might be due to a complex interaction among trace amounts of calcium, sodium salts, and resin and fatty acids.

MATERIALS AND METHODS

Sodium salt solution

For all scaling experiments in this paper, a model sodium salt solution containing 0.9 M sodium carbonate (Na_2CO_3, ACS grade, Fisher Scientific; Waltham, MA, USA) and 1.8 M sodium sulfate (Na_2SO_4, ACS grade, Fisher Scientific) was prepared to give a 28 wt% initial salt concentration, which is close to the solubility limit of burkeite at the conditions tested [9]. The pH of the solution was adjusted to higher than 12 by adding 0.064 M sodium hydroxide (NaOH, ACS grade, Sigma Aldrich; St. Louis, MO, USA). This solution will be referred to as the model salt solution in the remainder of the paper.

The model sodium salt solution inherently contains 4–8 mg/L of calcium, which was introduced as an impurity from the sodium carbonate powder during the preparation of the sodium solution. To have baseline runs in which calcium does not actively participate in sodium salt crystallization, 400 mg/L EDTA was added to chelate with calcium ions, preventing the interaction between calcium and sodium salt scaling. Thus, runs with EDTA addition are referred to as "no active calcium" runs. Calcium carbonate ($CaCO_3$) powder (ACS grade, Fisher Scientific) was added to the model sodium salt solution to adjust the calcium concentration between 90 and 640 mg/L, so that the sodium-to-calcium ratio in the model salt solution is the same as in black liquor.

Organic additives, either a mixture of resin acid and fatty acid (RFA) or tall oil soap, were introduced to the model salt solution with a concentration ranging from 0.02 to 0.3 mg/g solution. Most of the experiments were carried out with a 1:1 molar ratio of oleic acid (≥99%, MP Biomedicals, Fisher Scientific) and abietic acid (≥98%, Cayman Chemical; Ann Arbor, MI, USA). This ratio was chosen because the typical resin-to-fatty acid ratio in softwood black liquor is approximately 1:1. Using resin and fatty acids allowed us to isolate the effects of the RFA rather than any variability or influence of other organics in the raw tall oil soap. Oleic acid and abietic acid converted to their sodium salt forms, sodium oleate and sodium abietate, due to the high alkalinity of the solution. This simulates tall oil soap in black liquor since the major compositions of tall oil soap, resin acids and fatty acids, are in their sodium salt forms in black liquor.

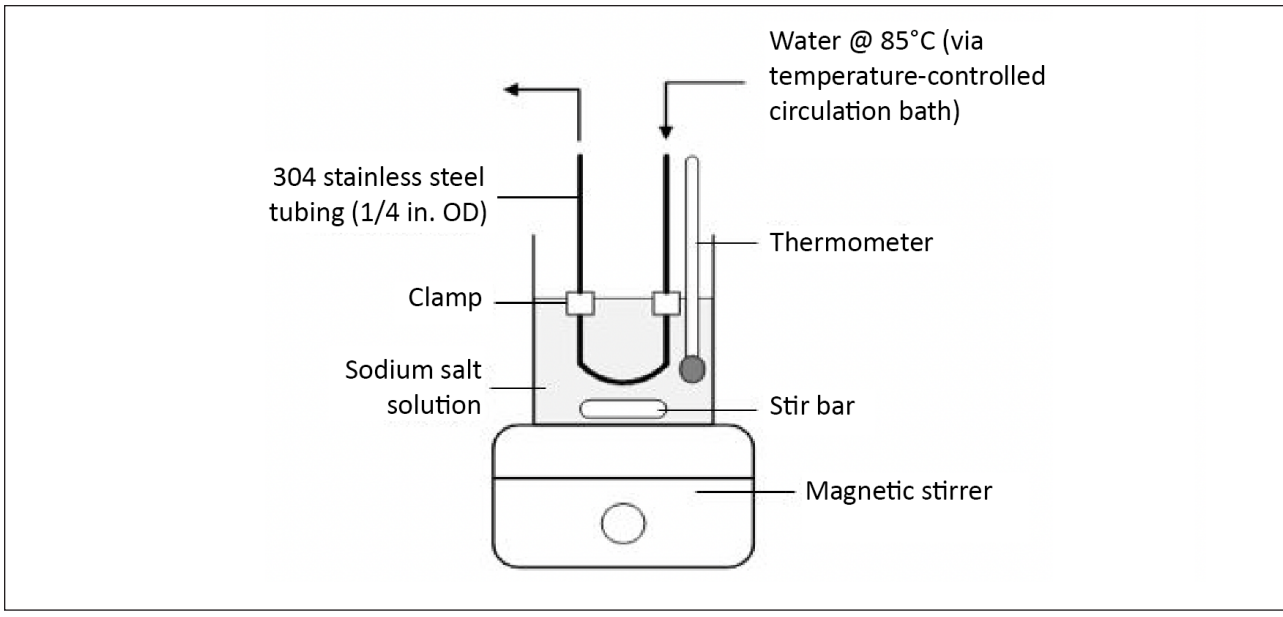
A raw tall oil soap sample was provided by a North American pulp mill that campaigned between softwood and hardwood. This sample contained 41 wt% fatty acids (24 wt% linoleic acid, 8 wt% palmitic acid, 7 wt% oleic acid, and 2 wt% stearic acid) and 2 wt% resin acid (abietic acid). This would indicate that the soap sample was likely taken at the end of a hardwood campaign. The 43% of resin plus fatty acids is the typical RFA content in raw soap, which contains a significant amount of residual black liquor [10,11]. While the RFA content of this soap is mostly fatty acids, we have seen in earlier work that both oleate and abietate have a similar effect on the reduction in scaling in this experimental system [8]. The soap composition was analyzed following the gas chromatography-mass spectroscopy (GC-MS) method described in Nwaeri [12], which was adapted from McGinnis [13].

In the soap addition runs, soap was added to an NaOH solution before dissolving sodium carbonate and sodium sulfate powder in the solution. This is because if sodium salts were added before soap, soap cannot be solubilized, as insoluble soap particles were observed floating on the surface. By first adding soap to the NaOH solution and mixing for about half an hour at room temperature, soap can be dispersed in the solution homogeneously. Subsequently, the addition of the sodium salts results in foaming on the solution surface, which is likely caused by the salting-out effect [14]. Based on the results from dry solids measurement, foaming does not affect the evaporation rate of water in this work.

Scaling setup

The scaling experiments were carried out in a bench-scale setup using a 1 L glass beaker, as shown in **Fig. 1** [8]. A removable piece of 304 stainless-steel tubing, with a 0.25-in. outer diameter and 22 cm^2 of exposed surface area, served as the heat exchanger in 600 g of the model sodium salt solution, which was constantly mixed by a stirring bar at 240 rpm. Heated water flowing through the tubing was maintained at 85°C by a temperature-controlled circulation bath (Polystat, Cole-Parmer; Vernon Hills, IL, USA). Through heat transfer, the temperature of the bulk solution was raised from room temperature to 73 ± 1°C within half an hour and remained constant. Once the heat exchange coupon was added to the salt solution, the solution was open to the atmosphere to allow water evaporation.

Total and dissolved salt concentrations were measured at regular intervals to monitor water evaporation and salt crystallization. Duplicate measurements of dry solids were conducted at each sampling point to ensure accuracy. The metastable limit was determined as the dissolved dry solids when the first crystal(s) were noticed in the supersaturated solution by direct observation. In some runs, 1–2 mL aliquots were withdrawn and examined under an optical microscope to ensure that no crystals formed in the solution before they were visible to the eyes. Nucleation during microscope analysis is unlikely because microscope images were all taken immediately after sampling, and no visible crystallization was observed in images captured at the same



1. Experimental apparatus used for evaporative scaling [8] (OD: outer diameter).

location 5 to 10 min after the samples were placed under the microscope.

After 4 h of water evaporation, the heat exchange coupon was disassembled from the scaling setup and dried in an oven overnight at 120°C. The buildup on the dried coupon comes from two sources. One is the deposition of crystals during the scaling experiment, and the other is the salt in the residue solution. To find the mass of the deposited crystals, salt in the residue solution is deducted from the mass of the total buildup (Eq. 1). The mass of salt from residue solution is calculated by the weight difference of the coupon before and after drying, as well as the final solids contents (Eq. 2).

$$m_{deposition} = m_{total\ buildup} - m_{salt\ in\ residue\ solution} \quad (1)$$

$$m_{salt\ in\ residue\ solution} = \frac{m_{coupon\ before\ drying} - m_{coupon\ after\ drying}}{1 - dry\ solids_{final}} * dry\ solids_{final} \quad (2)$$

The dried buildup was removed from the stainless-steel coupon by gently tapping the coupon to minimize the disruption of the surface characteristics of the stainless steel. For calcium analysis, the crystals removed from the stainless-steel coupon were dissolved in 70 wt% nitric acid, diluted with 5 wt% nitric acid, and analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent 5900, Agilent Technologies; Santa Clara, CA, USA).

Effect of calcium scales on sodium salt scales

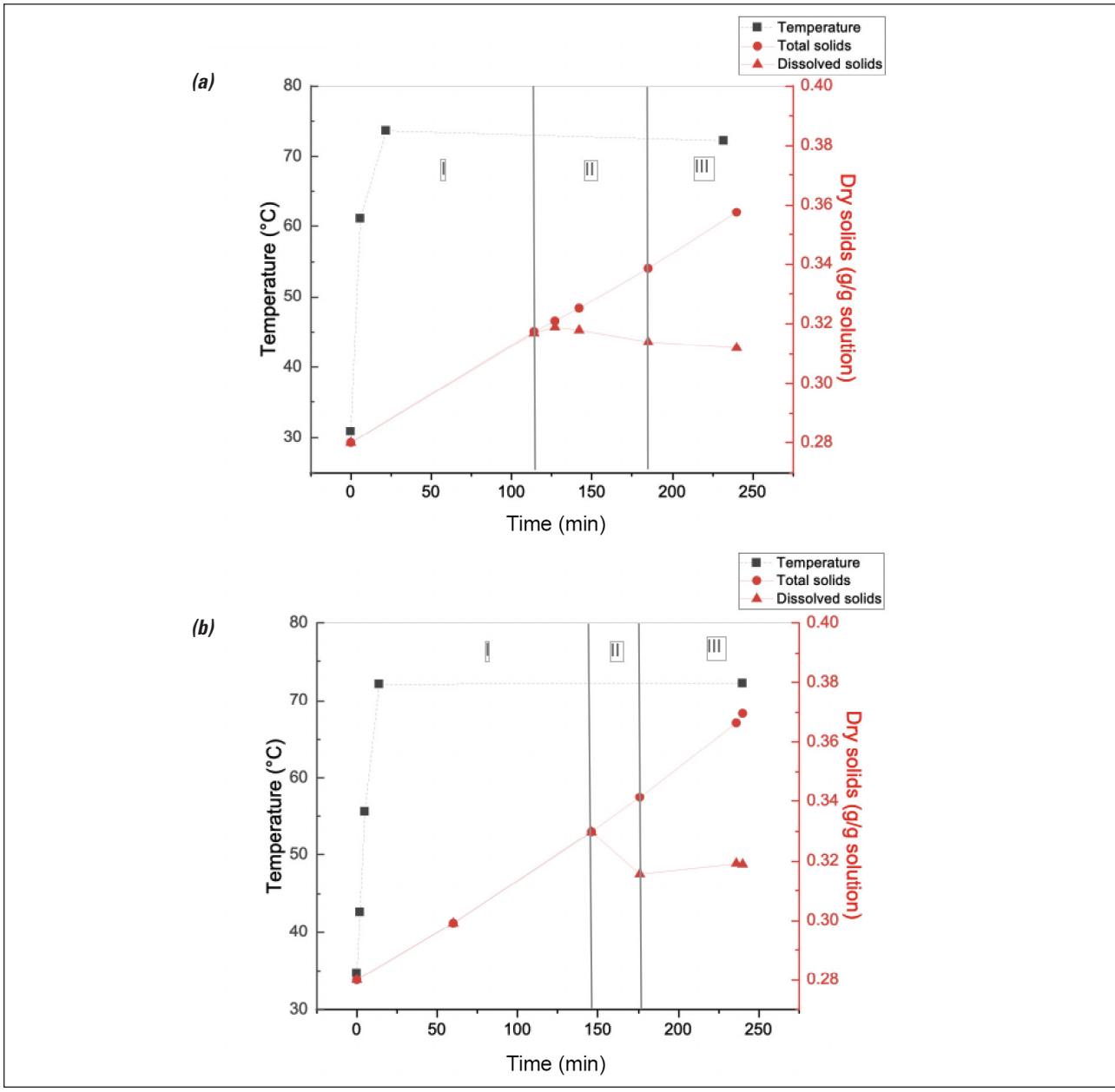
To build up calcium carbonate scales on a heat exchange surface, two salt solutions (Solution A and Solution B) were prepared. Solution A (500 g) contains 0.03 mol carbonate ion, supplied from equimolar Na_2CO_3 and potassium carbonate (K_2CO_3). Solution B (100 g) was prepared by adding 0.03 mol calcium acetate to water. Similar to the model salt solution, NaOH pellets were added to both Solution A and Solution B at 0.05 M to bring the solution pH to higher than 12. A coupon with hot water at 85°C circulating inside was placed in the room-temperature Solution A, which was constantly stirred at 240 rpm. Once the coupon was immersed in Solution A, Solution B was slowly poured into Solution A. Calcium ions from Solution B immediately reacted with carbonate ions in Solution A, becoming either calcium carbonate crystals suspended in the solution or calcium scale on the heat exchange surface. The crystals generated by mixing Solution A and Solution B were filtered from the solution, washed with water, and analyzed by ICP-OES. The calcium concentration in these crystals was 0.41–0.46 g Ca/g crystal, and no sodium was detected, confirming that the precipitated crystals were $CaCO_3$.

After being immersed for 25 min, the coupon was removed from the solution and air-dried for 30 min, while hot water continued to circulate in the coupon. The dried coupon with the calcium deposit on the surface was then placed in a model sodium salt solution for 4 h to build up sodium scales, as described in the "Scaling setup" section.

Effect of RFA and tall oil soap on calcium solubility

To understand whether RFA or tall oil soap solubilizes calcium as in calcium carbonate, the solubility of calcium was measured in a model sodium salt solution without any organic additives, and model sodium salt solutions containing either RFA or tall oil soap. Calcium carbonate was added to adjust the calcium concentration to 100 mg/L, which is significantly beyond the measured calcium solubility.

Prepared at room temperature, the solution was placed



2. Sample profiles of total dry solids, dissolved dry solids, and temperature during scaling experiments: (a) without active calcium and organic additives, and (b) with 4–8 mg/L calcium and 0.3 mg/g solution of resin acid and fatty acid mixture. The evaporative crystallization process is separated into three regimes based on the trends of the dissolved and total dry solids curves.

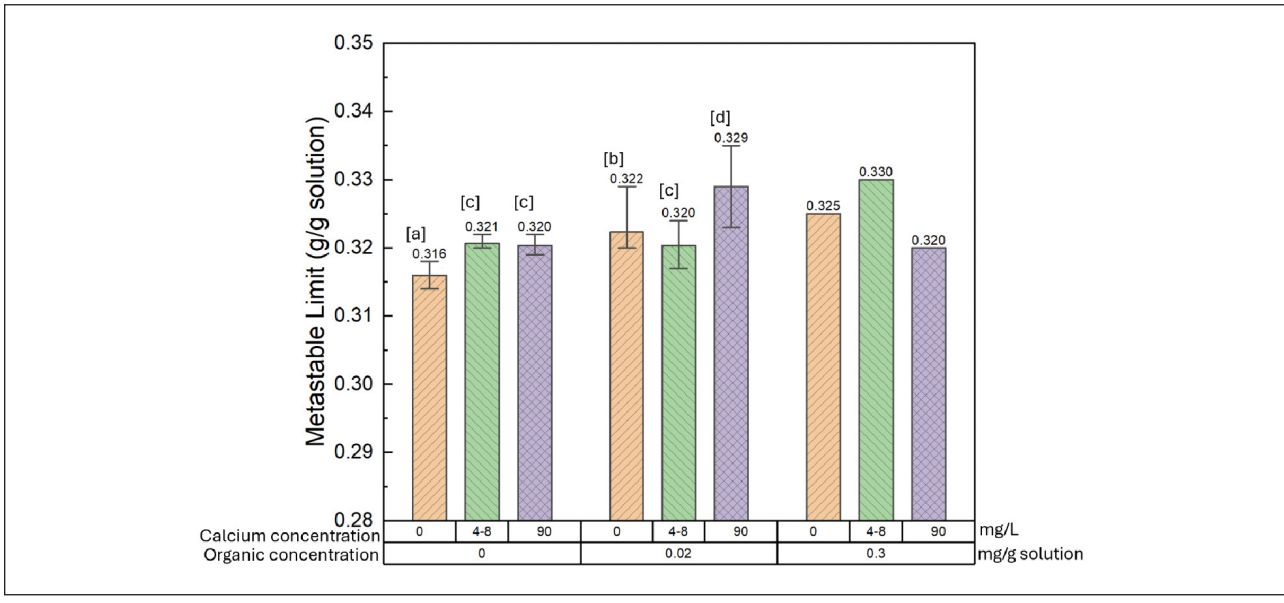
in an 80°C water bath at time "0", and the temperature was raised to 73 ± 1°C within half an hour. The solution was constantly stirred by a stirring bar at 240 rpm. Two aliquots of samples were withdrawn from the solution after 0.5 h, 1 h, 2 h, 4 h, and every 24 h. The run without organic additives and the RFA additive run continued for 72 h, while the soap run lasted 168 h to ensure that equilibrium was reached. The sample solution was immediately filtered through a syringe filter with a pore size of 0.2 µm. The filtrate was acidified by 70 wt% nitric acid and diluted by 5 wt% nitric acid. The calcium concentrations in the acid-diluted samples were analyzed by ICP-OES.

RESULTS AND DISCUSSION

Crystallization process during the scaling experiments

The crystallization process of sodium double salts was monitored by measuring total dry solids, dissolved dry solids, and bulk temperature intermittently during the scaling experiments. Sample profiles are divided into three regimes based on the trends in dissolved and total dry solid curves, as shown in **Fig. 2**.

At time "0", a heat exchange coupon is placed in a sodium salt solution, and the evaporation starts. As measured by inserting a thermometer in the solution intermittently,



3. Metastable limit of sodium salt crystallization in solutions containing various concentrations of calcium and organics. Error bars represent the maximum and minimum values of repeated runs: [a] n=8; [b] n=6; [c] n=3; and [d] n=2. For runs without error bars, the results are based on one individual run for each column. The label at the outside end of each column represents the average of repeated runs or the value of an individual run if there is no error bar. Raw data for all scaling experiments are provided in Table B1 of Appendix B.

the solution temperature rises from room temperature to 73 ± 1°C in half an hour and remains the same. The steady increase in the total dry solids indicates constant water evaporation. In Regime I, no difference in the total and dissolved dry solids was detected, and no crystal was observed by direct observation or under an optical microscope.

Regime II initiates when concentrations of sodium carbonate and sodium sulfate exceed their metastable limit and crystals start to precipitate. For example, crystals are first observed after 114 min of water evaporation in the solution with EDTA and no organic additives (Fig. 2a), and the metastable limit is the dissolved solids at this moment, 0.317 mg/g solution. With 4–8 mg/L Ca and 0.3 mg/g solution of RFA, the metastable limit rises to 0.330 mg/g solution, and crystal nucleation is postponed to 146 min (Fig. 2b). Longer evaporation time before the presence of the first crystal(s) indicates higher dissolved dry solids when crystals start to precipitate, and consequently, an increase in the metastable limit. The effect of calcium and RFA on the metastable limit of sodium salts is discussed in the "Metastable limit" section. After reaching the metastable limit, the supersaturation was quickly released as indicated by the steep drop in dissolved dry solids over the next 40–80 min. The gap between the total and dissolved dry solids represents the percentage of crystals precipitated in the basis of the solution mass.

In Regime III, the dissolved solids remain constant while total solids continue to increase steadily due to water evaporation. The growing gap between the total and dissolved solids indicates the continuing crystallization. All scaling runs were conducted for 4 h to ensure that all experiments had passed Regime II, since the onset of nucleation can vary depending on the presence of calcium and RFA. The idea is to end the scaling experiments at the same crystallization stage, Regime III, and have similar amounts of crystals precipitated. The mass of crystals generated at the end of runs is discussed in "Mass of crystals" section.

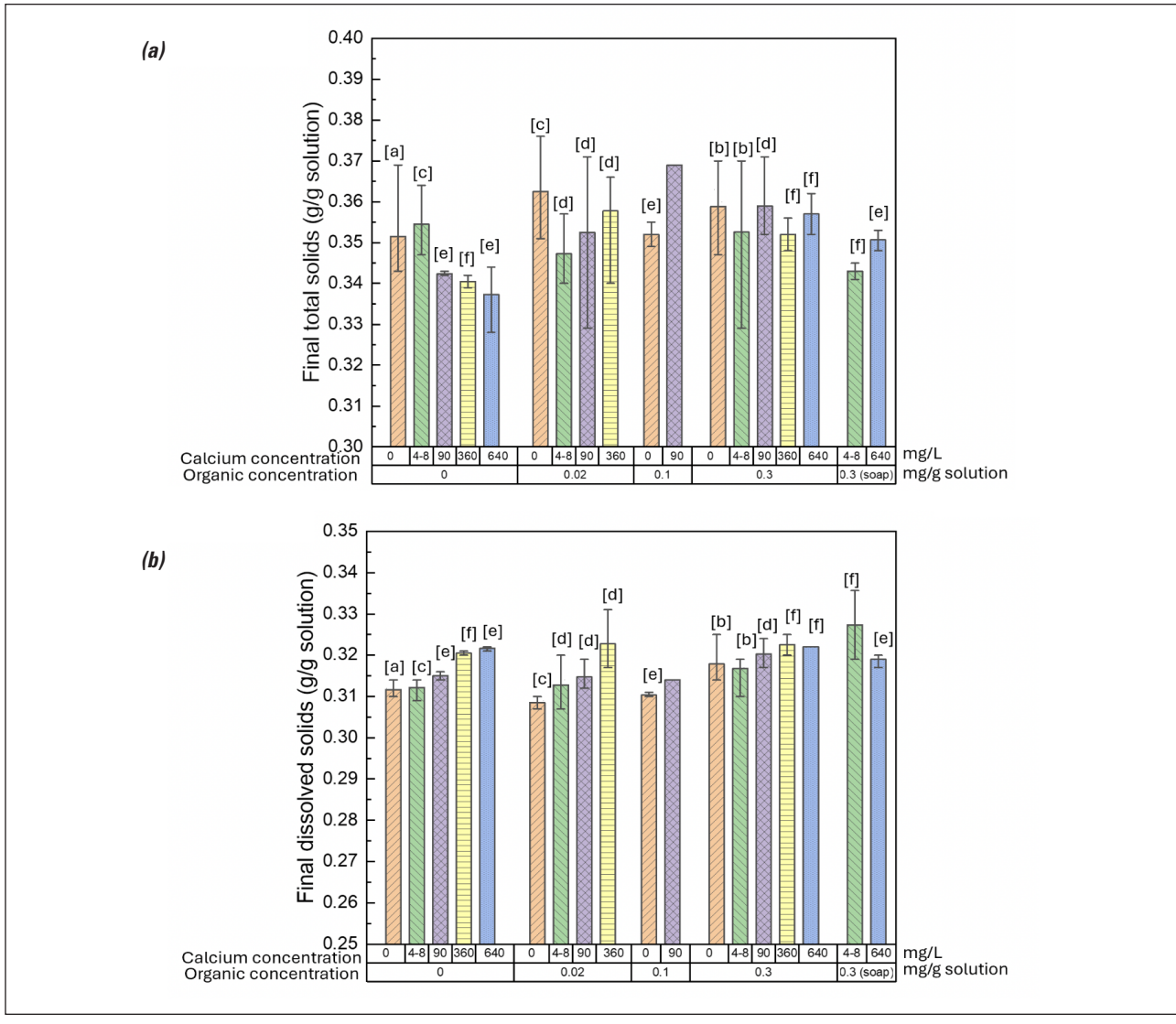
Photomicrographs of the Regimes I, II, and III for the various runs in this study are shown in Appendix A.

Metastable limit

Figure 3 presents metastable limits of sodium salt crystallization in the bench-top evaporation setup. The metastable limits are determined as the dissolved dry solids when the first crystal(s) were detected, either by direct observation or an optical microscope.

It is noteworthy that the metastable limit is difficult to measure precisely because nucleation is inherently stochastic, despite efforts to improve accuracy by repeating experiments. The metastable limit is highly sensitive to impurities, surface conditions, hydrodynamics, and detection method [15]. Meanwhile, technical difficulties arise at high calcium and RFA concentrations. When calcium concentrations are equal to or higher than 360 mg/L, it is not possible to confirm when crystals start to precipitate due to large amounts of insoluble calcium carbonate particles. Thus, the metastable limit is only determined in runs with calcium concentrations lower than 360 mg/L. Solutions containing 0.3 mg/g initial solution of RFA also look opaque, and it is hard to determine the onset of crystallization even with an optical microscope. Only one result per calcium level is available for the runs with 0.3 mg/g initial solution of RFA.

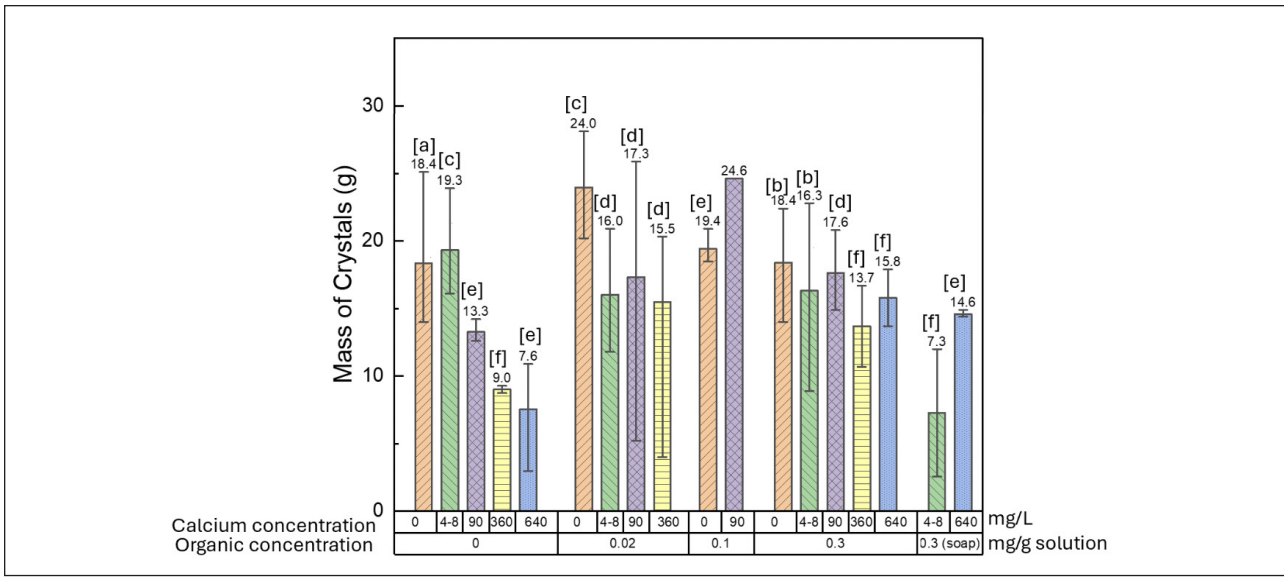
The presence of calcium results in a slight increase in the



4. (a) Total dry solids and (b) dissolved dry solids of the solution at the end of evaporative crystallization under various concentrations of calcium and organic additives. Error bars represent the maximum and minimum values of repeated runs: [a] n=10; [b] n=7; [c] n=6; [d] n=4; [e] n=3; and [f] n=2. For columns without error bars, the results are based on only one run for each column. Raw data for all scaling experiments are provided in Table B-II of Appendix B.

metastable limit in runs without RFA, as Fig. 3 demonsrates, because the average of the metastable limit increases from 0.316 in runs with EDTA addition to 0.321 in 4–8 mg/L Ca runs and to 0.320 in 90 mg/L Ca runs. The *p*-values between 4–8 or 90 mg/L Ca runs and EDTA runs are 0.45% and 2.24%, respectively. Both *p*-values are below the 5% significance level, indicating significant differences in metastable limits between the 4–8 mg/L Ca and the EDTA runs, as well as between the 90 mg/L Ca and the EDTA runs. Shi et al. [16] also reported an increase of 0.01–0.03 in metastable limits in runs without EDTA addition at 115°C. Similar metastable limit values are reported in Nwaeri and DeMartini [8] in which the metastable limit was determined in the same experimental setup by the same method as the current study. However, no difference in metastable limits was observed in runs with and without EDTA addition. One difference between the current study and Nwaeri and DeMartini's work is that the initial solution is 600 g in the current study, whereas it is 500 g in Nwaeri and DeMartini's work, leading to a 2°C lower bulk temperature and a 0.1 g/min lower evaporation rate in the current study. It is noteworthy that the limitation of comparing metastable limits from different studies, or different systems, is that the metastable limit is strongly system-dependent, as it is affected by many factors such as bulk temperature, evaporation rate, and mixing intensity [15].

The addition of 0.02 mg/g solution of RFA increases the metastable limits in EDTA runs, but this level of RFA addition does not clearly affect metastable limits in calcium runs. The *p*-value for the comparison between no RFA and a 0.02 mg/g solution of RFA is 0.5% in EDTA runs, confirming a statistical difference between the two groups. How-



5. Mass of precipitated crystals analyzed at the end of evaporative crystallization under various concentrations of calcium and organics. The mass of precipitated crystals is calculated by multiplying the mass of solution by the difference between the total solids (Fig. 4a) and dissolved solids (Fig. 4b). Error bars represent the maximum and minimum values of repeated runs: [a] n=10; [b] n=7; [c] n=6; [d] n=4; [e] n=3; and [f] n=2. The label at the outside end of each column represents the average of repeated runs or the value of an individual run if there is no error bar. Raw data for all scaling experiments are provided in Table B-I of Appendix B.

ever, the *p*-values are above 5% when comparing no RFA and 0.02 RFA runs at the same calcium level (89.0% for 4–8 Ca; 38.9% for 90 Ca), indicating that a 0.02 mg/g solution of RFA does not result in statistical significance in calcium runs. Furthermore, it is difficult to draw a conclusion from a 0.3 mg/g solution of RFA, given the technical difficulty of determining the metastable limit in an opaque solution and the potential measurement error. A previous study found the metastable limit rises when equimolar oleic acid and abietic acid were added with a total concentration of 0.15 mg/g solution of RFA [8]. It is reasonable to assume that a low concentration of calcium exists in the solution since EDTA was not added in the RFA runs. Conversely, Shi and Rousseau [17] found that the addition of 1 wt% of black liquor results in a decrease in the metastable limit in the aqueous solution containing Na_2CO_3 and Na_2SO_4 with a molar ratio of 1 to 2, and it was suggested that this decrease was attributed to the presence of RFA in black liquor. Results from the current work suggest another possible explanation for this decrease, which is that calcium is bound to lignin, and this removal of calcium reduces the metastable limit.

Total solids and dissolved solids

Figure 4 shows total solids and dissolved solids measured at the end of the scaling experiments. They are the endpoints in the two dry solids curves corresponding to the crystallization profiles (Fig. 2). Final total solids and final dissolved solids are important factors for calculating the mass of precipitated crystals, which is presented in **Fig. 5**. To test whether adding calcium or RFA results in a statistical difference in total solids, *p*-values for the comparison between runs with additives and base case runs (with EDTA and no RFA) are presented in **Table I**.

RFA Concentration, mg/g solution \ Ca Concentration, mg/L	0	4–8	90	360	640
0	–	42.0%	0.4%	0.6%	7.8%
0.02	2.7%	36.2%	91.9%	39.2%	–
0.1	87.0%	–	–	–	–
0.3	9.9%	86.9%	19.4%	92.5%	42.6%
0.3 (soap)	–	4.2%	–	–	77.3%

I. The p-values for final total solids for the comparison between runs with additives and base case runs, with EDTA and no mixture of resin acid and fatty acid (RFA).

Generally, the final total solids in Fig. 4a are similar under various concentrations of calcium and RFA, as the majority of *p*-values in Table I are larger than 5%. The fact that all the solutions start at the same initial dry solids and the water evaporation was conducted for the same time length in all scaling runs is likely the reason that similar total solids were measured at the end of the scaling runs. The determining factors of the water evaporation rate are the stirring speed and the temperature of the bulk solution. Since the stirring speed was set as constant at 240 rpm and the solution temperature was maintained at 73 ± 1°C, the water evaporation rate was consistent in runs with various concentrations of calcium and RFA, resulting in the constancy of total dry solids at the end of the experiments. Ambient temperature and humidity were recorded, and they showed no correlation with water evaporation rate.

In runs without organic additives but containing calcium at 90 mg/L or 360 mg/L, the total dry solids are unusually low and are significantly different from the baseline runs, as the *p*-values are lower than 5% (Table I). The reason is likely because sodium crystals precipitated in these runs are compact and large, as confirmed by both the photomicrographs shown in Appendix A and the SEM pictures that are discussed and depicted later in the "Calcium in sodium crystals without organic additives" section. As a result, the large cluster of crystals quickly blocked the tip of the transfer pipette when aliquots of the solution samples were withdrawn for total solids measurements. Consequently, the final total solids measured in these runs are not representative of the actual total solids in the solution. This is clarified further in the following "Mass of crystals" section.

Under various solution compositions, the dissolved solids are found between 0.31 and 0.32 g/g solution at the end of each run (Fig. 4b). The dissolved solids analyzed in this work match the findings in previous literature. Nwaeri and DeMartini [8] found that the solubility limit of burkeite at 75°C is 0.300 + 0.005 g/g solution, as burkeite is generated from the sodium solution containing carbonate to sulfate with the molar ratio of 1 to 2. The solubility limit of burkeite analyzed by Caspari [18] is 0.318 g/ g solution as the carbonate-to-sulfate ratio in the aqueous solution is 1 to 2.3. The other finding in the dissolved solids is that a slight increase is observed with the increasing total calcium concentrations, especially when there is no organic additive in the solution.

Mass of crystals

The mass of crystals precipitated under various solution compositions, presented in Fig. 5, was calculated from the difference between total solids and dissolved solids multiplied by the mass of total solution. To test whether adding calcium or RFA results in a statistical difference in mass of crystals, *p*-values for the comparison between runs with additives and base case runs (with EDTA and no RFA) are presented in **Table II**.

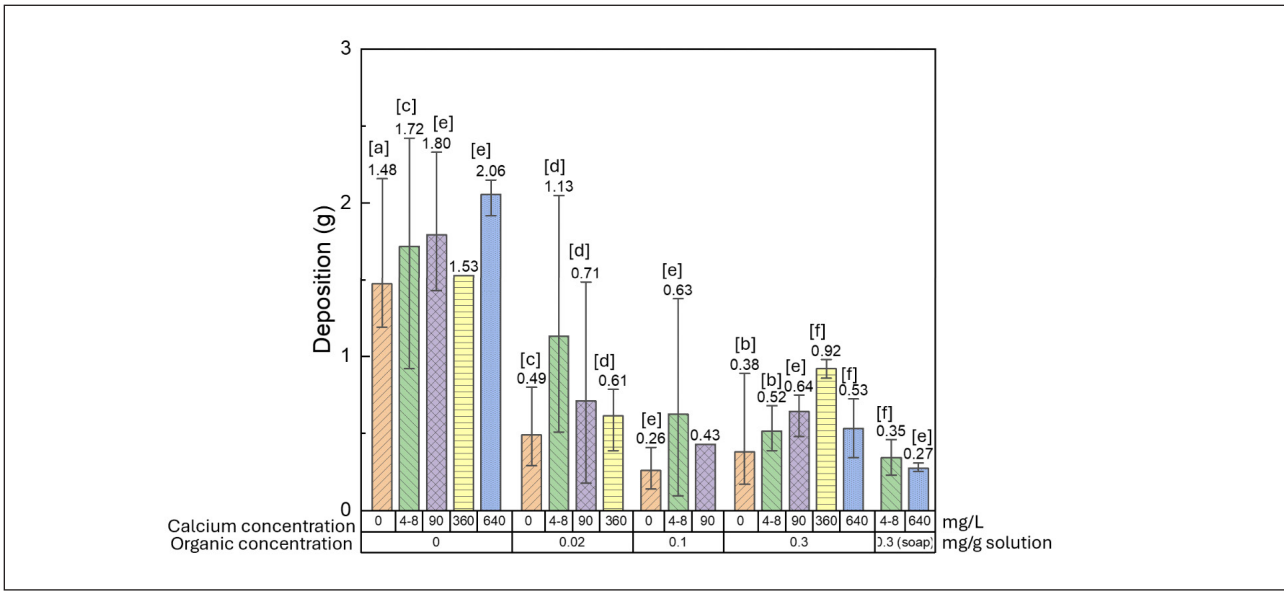
In general, calcium and RFA do not result in a statistically significant difference in crystal mass, as the majority of *p*-values in Table II are greater than 5%. Consistent with the low total solids measured in no organic runs with 90 mg/L and 360 mg/L calcium, the masses of crystals are significantly lower than base case runs, as their *p*-values are lower than 5%, as shown in Table II. As previously discussed in "Total solids and dissovlved solids" section, the measured total solids is lower than the actual total solids for runs containing calcium with concentrations equal to or higher than 90 mg/L and no organic additives, since large crystals block the transfer pipets during sampling. This explains the unusually low mass of crystals calculated in these runs. To prove this idea, crystals were filtered from the solution at the end of one run that contained 360 mg/L calcium and had no organic additives. Then, the crystals were washed with a sequence of solvents (a mixture of 1:1 ethylene glycol: water; ethylene glycol; a mixture of 1:1 ethanol:ethylene glycol; and ethanol [7]) to remove the residual solution. After drying in an oven, it was found that there were 16.6 g of crystals precipitated in this run, instead of 9.3 g as calculated.

Sodium salt scaling under various calcium and RFA concentrations

Without organic additives in the sodium solution, the average amount of crystal deposition shows an increasing trend

RFA Concentration, mg/g solution \ Ca Concentration, mg/L	0	4–8	90	360	640
0	–	55.0%	0.1%	0.0%	2.4%
0.02	0.3%	31.7%	83.2%	52.3%	–
0.1	62.1%	–	–	–	–
0.3	98.0%	31.7%	66.4%	37.8%	46.7%
0.3 (soap)	–	26.1%	–	–	0.4%

II. The p-values for mass of crystals precipitated at the end of experiments for the comparison between runs with additives and base case runs, with EDTA and no mixture of resin acid and fatty acid (RFA).



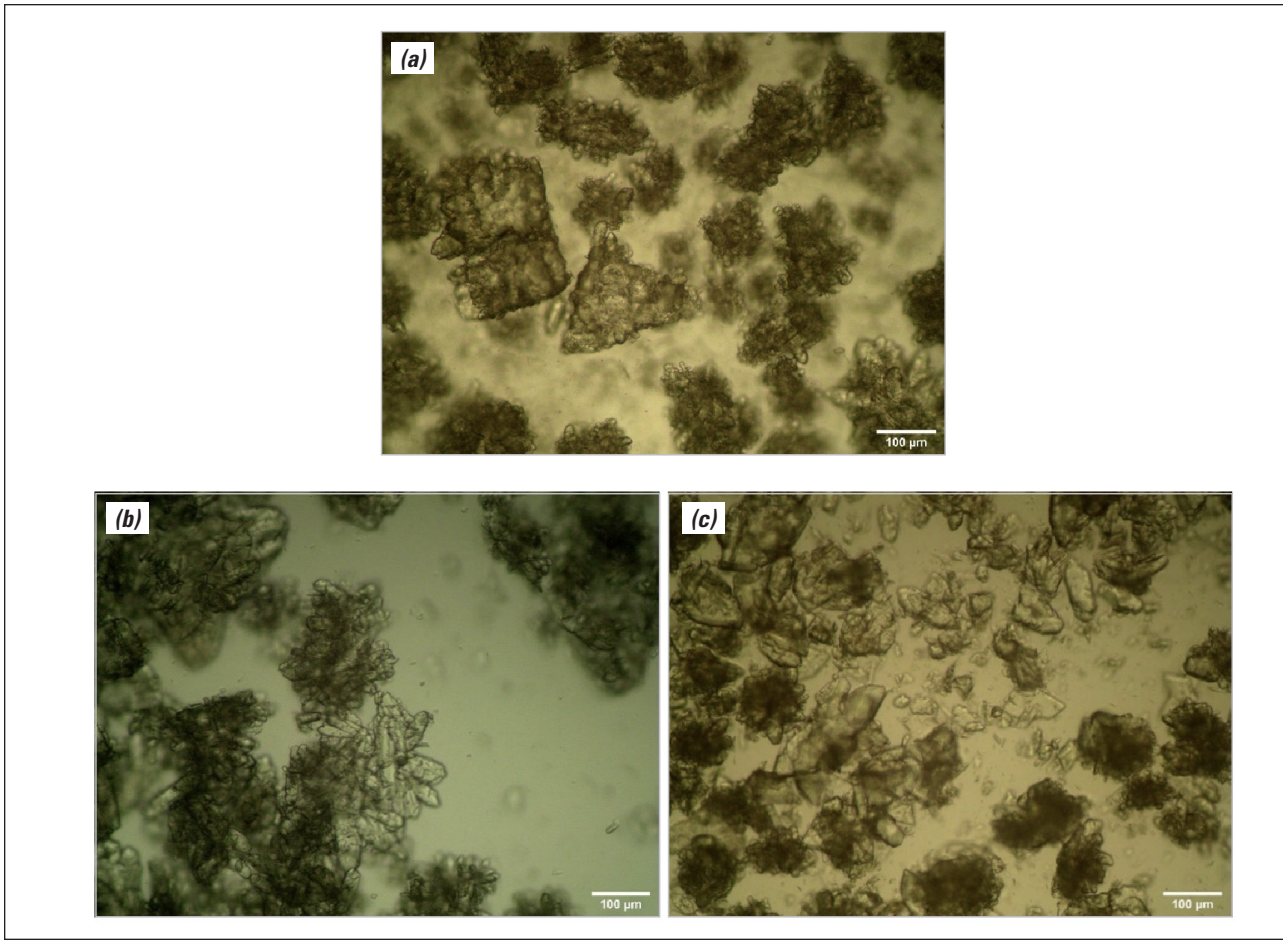
6. The amount of sodium salt scale on the heat exchange surface under various concentrations of organic additives and calcium. The organic additives are either RFA mixtures or tall oil soap. Tall oil soap is added in runs that are labelled as "(soap)". Bars show the average value of the measured deposition. Error bars represent the maximum and minimum values of repeated runs: [a] n=10; [b] n=7; [c] n=6; [d] n=4; [e] n=3; and [f] n=2. The column without an error bar represents the result of only one run.

in general as the calcium concentration rises from 0 to 640 mg/L. However, no statistical difference is observed at calcium concentrations below 90 mg/L, as the *p*-values for comparisons between the 4–8 or 90 mg/L Ca runs and the EDTA runs are both above 5% at 30.6% and 37.6%, respectively. Akin to the current work, a similar large variability in scaling is observed by Nwaeri and DeMartini [8] in the solutions without EDTA addition, and the variability is reduced by adding 400 mg/L EDTA. The improvement of the repeatability with EDTA addition suggests that the low concentration of calcium that was introduced to the sodium solution as an impurity is the source of the variation in scaling. It is worth noting that though the variabilities in the amount of scaling are different in the solutions with and without EDTA, the amounts of crystals precipitated are similar in these runs, as shown in the first two columns in Fig. 5. This suggests that the fluctuation in scaling is not attributed to experimental variations, which were monitored as solution temperature, dissolved and total solids, and mass of crystals generated, but caused by the chemistry variation, which is the presence of calcium.

When the RFA concentration increased to 0.3 mg/g initial solution, sodium salt scales were inhibited with high repeatability in the entire spectrum of calcium concentrations that was chosen in this study. Increasing calcium concentration from 0 mg/L to 360 mg/L results in a gradual rise in sodium scales. Still, even the highest amount of scales, which is 0.92 g at 360 mg/L calcium, is 40% less than the buildup generated under the same total calcium concentration but without RFA addition. A decrease is observed at 640 mg/L calcium, and the reason for this decrease is unclear. The reason for high repeatability in scale inhibition, even at low calcium concentration, is likely because the scale-inhibiting effect of RFA suppresses the scale-fluctuating effect caused by low concentrations of calcium.

When RFA concentrations are at or lower than 0.1 mg/g initial solution, a decreasing trend in the average deposition is observed in comparison with the runs without organic additives, indicating that RFAs limit sodium scaling. In these runs, high repeatability in scale inhibition is observed in runs with EDTA addition, while there are large variations with the presence of 4–8 mg/L calcium and 90 mg/L calcium, showing that low concentrations of calcium result in variability in scaling. This is consistent with runs that do not contain organic additives. The variation in sodium scaling means that there is a possibility of building up large amounts of scales under low calcium and low RFA concentrations from the perspective of each individual run. Industrially, it is preferable to minimize the possibility of severe fouling, achieve repeatable scale inhibition, and maintain high heat transfer efficiency.

In the runs without the interference of calcium on sodium scaling, increasing RFA concentrations from 0 to 0.02 mg/g initial solution helps inhibit 67% of sodium scales, and increasing RFA concentrations to 0.1 mg/g initial solution helps inhibit 81% of sodium scales. **Figure 6** shows that the average scale goes down from 1.48 g to 0.49 g for 0.02 mg/g initial solution of RFAs and to 0.28 g for 0.1 mg/g initial solution of RFA. The average scale remains the same when the RFA concentration continues to raise to 0.3 mg/g initial solution. Nwaeri and DeMartini [8] also reported an inhibiting effect of RFAs on burkeite scaling. In that work, the scaling experiments were divided into two types, nucleation and continuous crystallization,



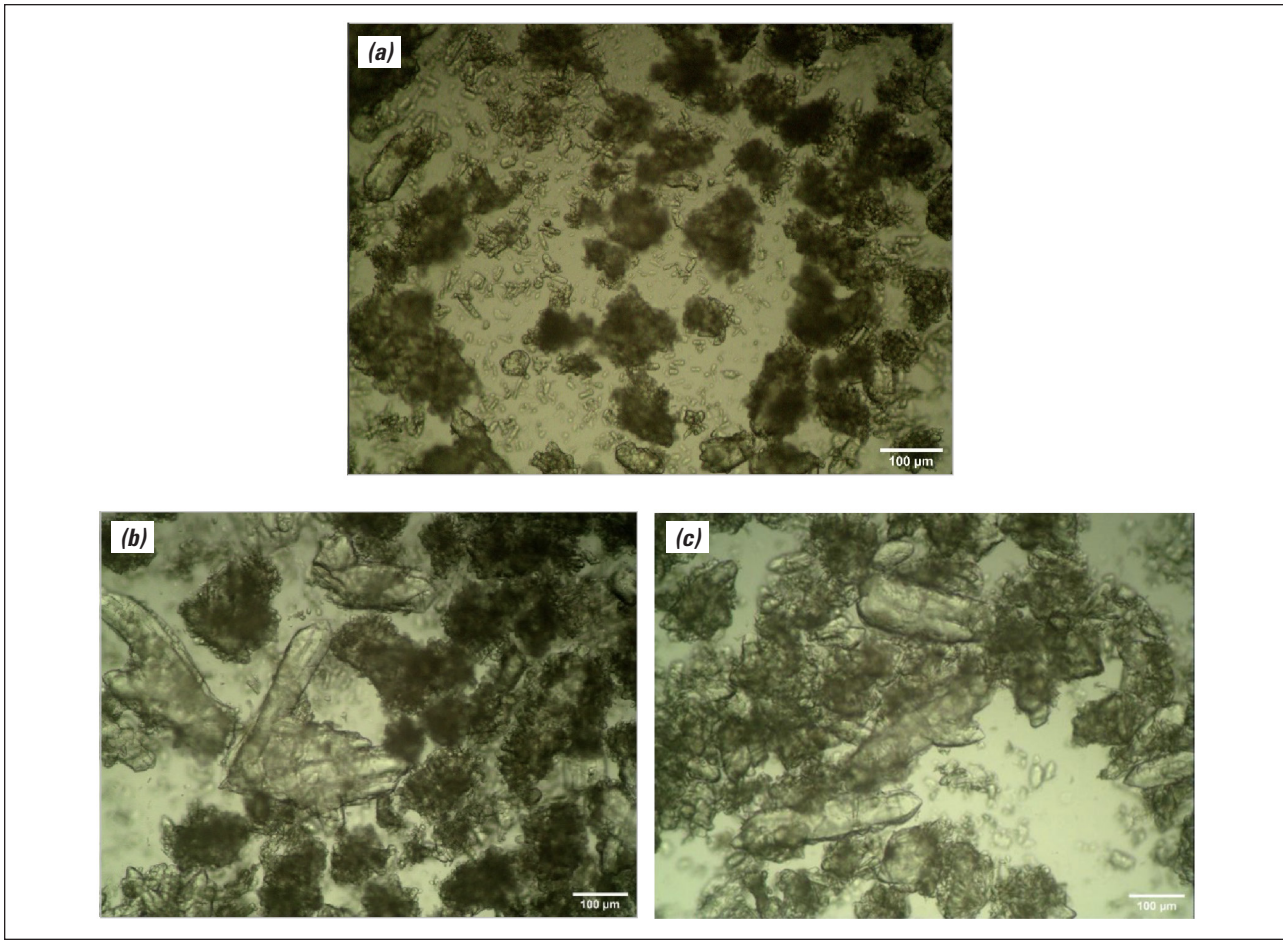
7. Photomicrographs of the suspended crystals collected at the end of scaling experiments from: (a) the run without resin acid and fatty acid (RFA); (b) the run with the addition of 0.02 mg/g initial solution RFA; and (c) the run with the addition of 0.3 mg/g initial solution of RFA. EDTA was added at 400 mg/L as a calcium scavenger to bind with calcium, the impurity introduced from sodium carbonate powder, in all three runs.

based on the burkeite crystallization behavior in the bulk solution, and it was found that burkeite scaling was inhibited by RFA during both nucleation and continuous crystallization processes.

By adding soap with a concentration of 0.3 mg/g solution, sodium scales are reduced by more than 70% compared with runs without organic additives. The soap sample used in the current study consists of 41 wt% fatty acids and 2 wt% resin acids, as determined by GC-MS. Thus, RFA concentrations are approximately 0.1 mg/g solution in soap runs. In the 0.1 mg/g solution RFA runs, a similar reduction in scaling is observed, indicating that the scale reduction is attributed to RFA in soap runs. The difference between the 0.3 mg/g solution soap runs and the 0.1 mg/g solution RFA runs at 4–8 mg/L Ca is that large variability is observed in RFA runs, while high repeatability is observed in soap runs. To achieve similar repeatability in RFA runs, EDTA needs to be added, which acts as a chelating agent for calcium and prevents calcium from participating in sodium scaling. This indicates that the fluctuation in sodium scales caused by calcium can be reduced by certain chemicals in soap. The possible candidate is lignin or lignin fragments that are degraded from lignin at high temperatures. Though it only makes up a small portion of tall oil soap [10,11], lignin has been reported to have a strong complexing ability to calcium due to the presence of a structural feature, two adjacent hydroxyl groups on the aromatic ring [6]. Likely because of the formation of the soluble complex between lignin and calcium, an increase in calcium solubility is observed and discussed later in the "Effect of RFA and soap on calcium solubility" section.

Crystal morphology

When the RFA concentration increases to 0.3 mg/g initial solution, individual crystals can be observed, showing a lower level of crystal agglomeration, as **Fig. 7** demonstrates. The presence of these individual crystals suggests that RFA helps reduce crystal agglomeration by dispersing sodium salt crystals. However, RFA does not completely prevent crystal agglomeration, as dark spots, which are agglomerates of numerous small crystals, are present in these solution samples whether RFA is present or not. Nwaeri and



8. Photomicrographs of the solution withdrawn at the end of scaling experiments containing 4–8 mg/L calcium and: (a) no organic additives; (b) 0.02 mg/g solution of RFA; and (c) 0.3 mg/g solution of RFA.

DeMartini also found that oleic acid results in more dispersed crystal agglomeration and longer rod-shaped crystals while studying the effect of oleic acid and abietic acid individually on sodium salt crystals under optical microscopy [8]. In black liquor, large and flat crystals were observed with tall oil brine added, while blocky crystals were reported in runs without additives [19,20]. This change in crystal morphology was also attributed to the fatty acids in tall oil brine.

At 4–8 mg/L of calcium, crystals with sizes larger than 200 µm are noticed, as shown in **Fig. 8**. This observation suggests that calcium results in the formation of large crystals. In runs without RFA, the agglomeration of crystals makes it hard to distinguish whether large crystals form in the presence of calcium, as shown by comparing Fig. 7a and Fig. 8a. With RFA helping disperse crystals and reducing the tendency for crystal agglomeration, large individual crystals are observed in the scaling runs when both calcium and RFA exist, as shown in Fig. 8b and Fig. 8c. A precipitation of large burkeite crystals was also reported by Shi et al. [9] and was attributed to the introduction of a calcium impurity during preparation of the sodium solution.

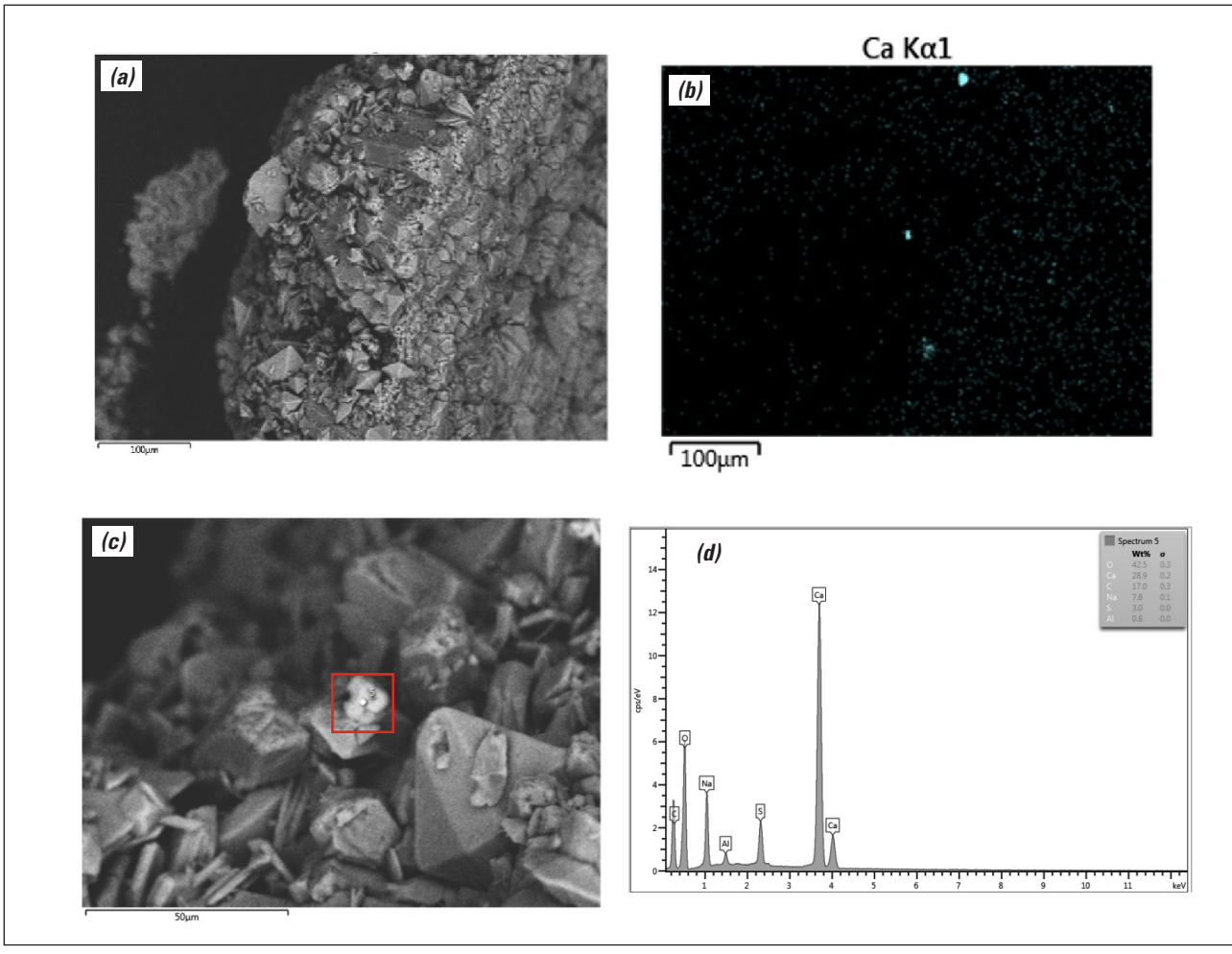
Calcium in sodium crystals without organic additives

Table III shows that calcium concentrations in the suspended crystals and in scales increase with the total calcium concentration in the solution. Among different portions, calcium concentration in scales is the highest, followed by calcium concentration in suspended crystals and the concentration in the solution. The high concentration of calcium in crystals indicates the incorporation of calcium in burkeite crystals. Shi et al. [9] also reported the accumulation of calcium in sodium crystals in the evaporative crystallization of burkeite. In that work, the sodium solution inherently contains 3–5 mg/L calcium, and 150–300 mg/kg of calcium, which is higher than the results in this work, is detected in the sodium crystals precipitated. By adding calcium carbonate powder and increasing calcium concentration to 20 or 40 mg/L, calcium concentration in sodium crystals became in the range of 300 to 500 ppm, which matches the result in Table III.

To understand the incorporation of calcium in sodium crystals, the distribution of calcium was analyzed in the sodium crystal generated from the solution containing 360 mg/L calcium (**Fig. 9**). Calcium is unevenly distributed in sodium crys-

Ca Concentration in Solution		Ca Concentration in Suspended Crystals	Ca Concentration in Scales
mg/L	mg/kg dry solids	mg/kg	mg/kg
8	22	38	45
40	112	409	664
360	1005	1939	8259

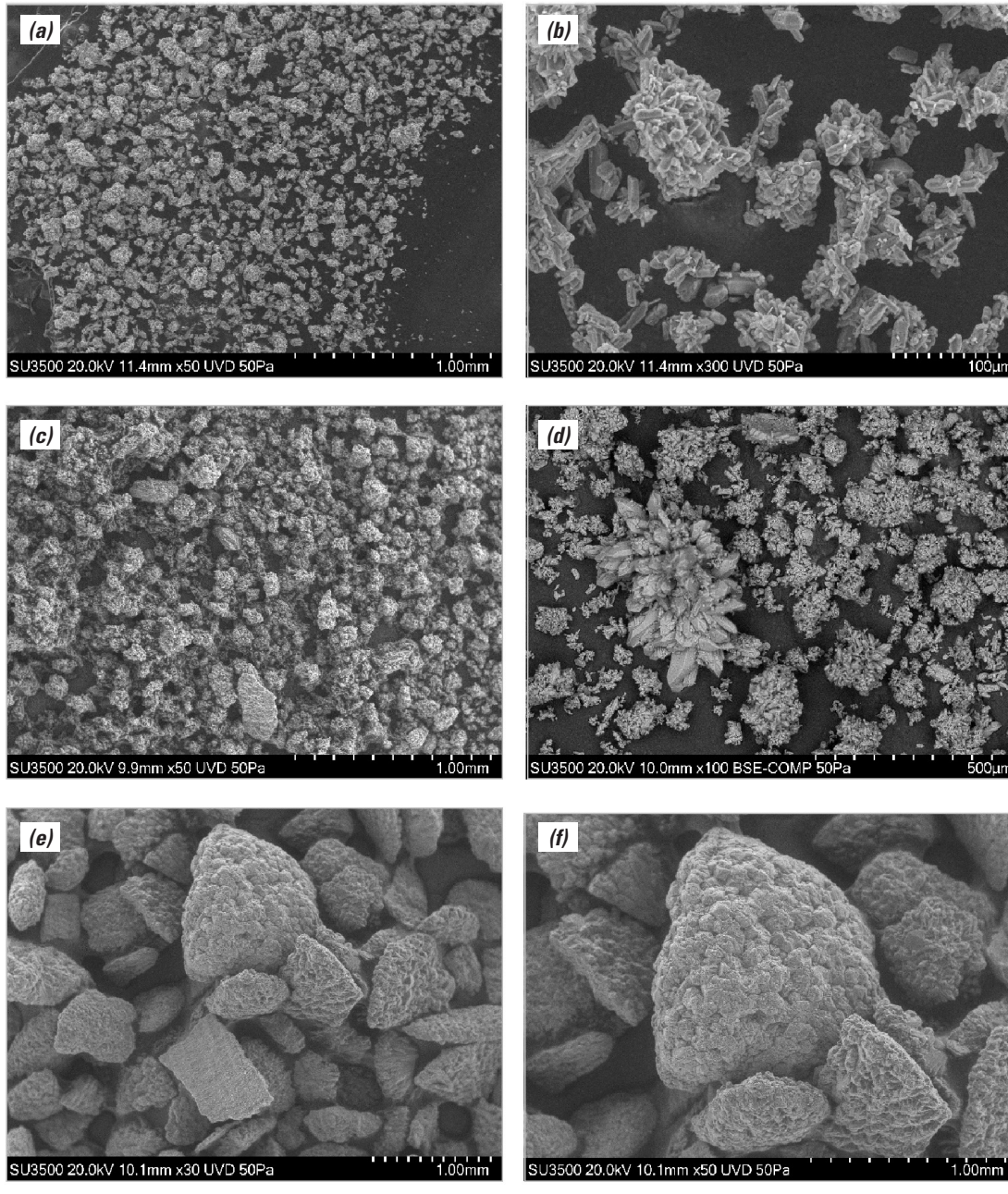
III. Calcium (Ca) concentrations in suspended crystals and in crystals deposited on the heat exchange surface under various total concentrations of calcium in the solution. No organic additives were in these runs. Calcium carbonate powder was added to the sodium solution to adjust the calcium concentration to 40 or 360 mg/L. The inherent calcium concentration in the sodium solution is 8 mg/L.



9. (a) Scanning electron microscope (SEM) image of a crystal precipitated from the sodium solution containing 360 mg/L calcium; (b) the distribution of calcium on the same location analyzed by energy-dispersive x-ray spectroscopy (EDX); (c) the zoom-in version of Fig. 9a, with the location having a high concentration of calcium pinned at the center; and (d) the spot analysis by EDX showing chemical compositions at the location highlighted in Fig. 9c.

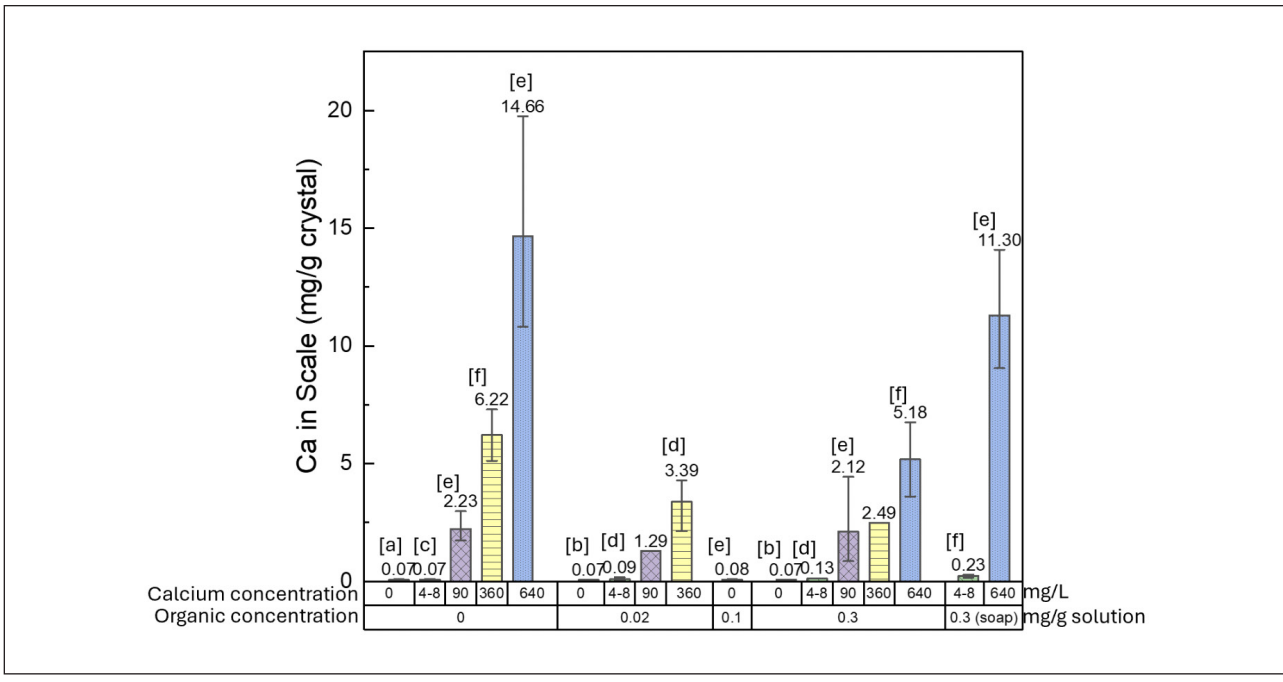
tals and gathers at some spots with high concentration as analyzed by energy-dispersive x-ray spectroscopy (EDXS), as shown in Fig. 9b and Fig. 9d. The uneven distribution of calcium in sodium crystals is also noted as an assumption in Shi et al. [9] when they discussed the formation of large burkeite crystals with calcium in the solution. They proposed that since the incorporation of calcium disrupts crystal nuclei, those sodium nuclei that contain less calcium are less inhibited by calcium and can rapidly grow into large crystals under high supersaturation. Though the current finding confirms the non-uniform distribution of calcium, it is yet uncertain whether calcium incorporates into sodium crystals as calcium ions or calcium carbonate.

As examined by scanning electron microscope (SEM)



10. The SEM images of suspended crystals obtained from the solutions containing: (a),(b) 4–8 mg/L calcium; (c),(d) 40 mg/L calcium; and (e),(f) 360 mg/L calcium. The scale bar for photos in Figs. 10a, 10c, and 10e is 1 mm, while photos in Figs 10b, 10d, and 10f are their zoomed-in views, respectively.

in **Fig. 10**, the increase in calcium concentrations in the suspended burkeite changes the crystal morphology. Figures 10a, 10c, and 10e are SEM images of bulk crystals generated from model sodium solutions containing 8 mg/L, 40 mg/L, and 360 mg/L of calcium, respectively, with a scale bar of 1 mm. The reason that the lengths of the calibration bars are used in Fig. 10e compared to Fig. 10a and 10c is that different magnifications were used (the magnification of Fig. 10e is 30, while the magnifications of Fig. 10a and Fig. 10c are 50, as seen at the bottom left of the figures) to accommodate the significantly larger size of crystals in Fig. 10e. Similarly, different magnifications are used in their zoomed-in versions, Figs. 10b, 10d, and 10f, to obtain a close yet comprehensive view of the morphology of these bulk crystals. With a total calcium concentration of 8 mg/L in the solution, crystals agglomerate loosely with a size of approximately 100 µm, as shown in Figs. 10a–10b. When the total calcium concentration increases to 360 mg/L, significantly larger and more compact crystals are produced, Figs. 10e and 10f. These large crys-



11. The concentration of calcium in sodium scales that are generated from solutions containing various concentrations of organic additives and calcium. Error bars represent the maximum and minimum values of repeated runs: [a] n=9; [b] n=6; [c] n=5; [d] n=4; [e] n=3; and [f] n=2. The column without an error bar represents the result of only one run.

tals observed under SEM confirm the visual observation mentioned earlier in the section on "Total solids and dissolved solids," that large crystals quickly blocked the transfer pipette when solution samples were withdrawn at the end of runs with calcium concentrations higher than 90 mg/L for total solid measurements. The size of crystals that are generated from a 40 mg/L calcium solution is a mixture of approximately 100 µm and half a millimeter. The zoomed-in photos of crystals from all three runs with different calcium concentrations show that crystals are not homogeneous and could be the result of the agglomeration of many small crystals.

Meanwhile, the compositions of crystals are heterogeneous and vary greatly from spot to spot. The molar ratios of carbonate-to-sulfate were sampled at different areas by EDXS, a semi-quantitative analysis since no standard was used for this measurement. The results were 1:2.9 and 1:3.3 for crystals from the solution containing 8 mg/L calcium; 1:4.5 and 1:2 for crystals from the solution with 40 mg/L calcium; and 1:2.4 and 1:2.2 for crystals from the solution with 360 mg/L calcium.

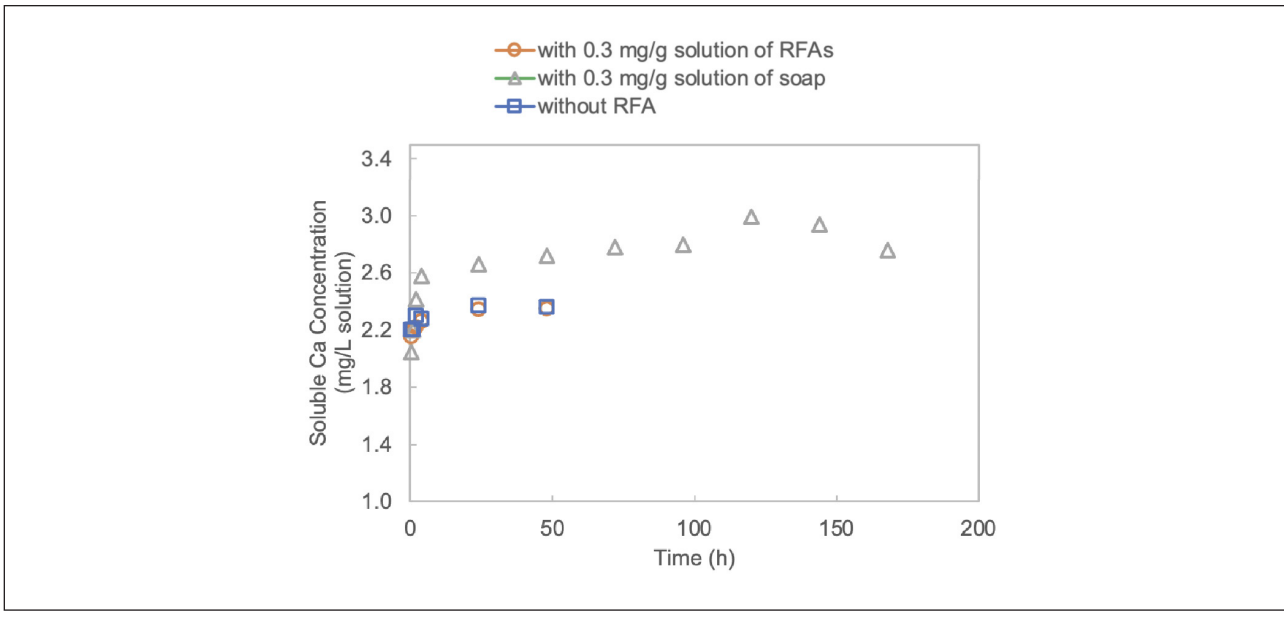
Calcium in sodium scales

A steady rise is noticed in the calcium concentrations in scales along with the increase of total calcium concentrations in the solution, regardless of whether RFA is present in the solution or not, as **Fig. 11** demonstrates. This suggests that the calcium aggregation in scales is primarily controlled by calcium concentrations in the solution. The RFA may help disperse either calcium carbonate or calcium ions, thereby preventing calcium from incorporating into sodium scales. The supporting evidence is that lower concentrations of calcium in scales are detected in RFA additive runs than in runs without RFA, especially in runs with 640 mg/L of calcium in solution and 0.3 mg/g initial solution of RFA.

For soap addition runs, calcium is introduced to the sodium solution with a concentration of 2.5 mg/g soap, as analyzed by ICP-OES. Since soap was added to the sodium solution with a concentration of 0.3 mg/g solution, only 0.00075 mg/g solution of calcium, which equals 0.96 mg/L, was introduced. With this amount of calcium added to the sodium solution, the concentration of calcium in solution increases approximately 20% in comparison with runs without soap but containing 4–8 mg/L of calcium. However, the calcium concentration in scales becomes twice as high. The possible explanation is that the calcium that is introduced with soap is bound with organic molecules [5] such as lignin fragments, and this calcium is transported in sodium scales along with soap. For runs containing 640 mg/L of calcium, the calcium concentration in solution is not considerably affected. As expected, the calcium concentration in the soap runs at 640 mg/L of calcium is similar to that in the no organic additive runs at the same calcium concentration.

Effect of RFA and soap on calcium solubility

To test whether RFA or soap helps solubilize calcium in the experimental conditions in this study, calcium solubility was measured in sodium salt solutions without organic



12. Soluble calcium concentrations in a solution with 28 wt% sodium salt and the molar ratio between Na_2CO_3: Na_2SO_4 is 1:2. The solution is heated from room temperature to 75°C in less than half an hour. The total calcium concentration is 100 mg/L, which is significantly higher than the soluble calcium concentrations. Three aliquots of samples were withdrawn at each sampling point, and each data point is an average result of these three samples.

additives, with RFA and with soap (**Fig. 12**). For reference, the solubility product of calcium carbonate at 25°C in water (pH=7) is $4.55 * 10^{-9}$ [21]. If calcium ions and carbonate ions dissolve in an equimolar manner in water, 2.7 mg/L of calcium ions is soluble, which is in the same order of magnitude as the calcium solubility analyzed in this experiment.

Both in the run without organic additives and the run with RFA, an equilibration is reached after 24 h, and the calcium solubility is the same, indicating that RFA does not solubilize calcium. Palonen et al. [22] found that a 5% soap mixture containing equimolar sodium oleate and sodium abietate (pH around 9) can solubilize 160 mg/L calcium ions at 60°C. One possible reason that RFA does not influence calcium solubility in the current study is that RFA content is only 0.03%, which is significantly lower compared to the dosage in Palonen et al. [22].

For the soap additive run, the soluble calcium concentration increased by 26% in the first 4 h and continued to rise until the solution was mixed for 120 h. The solubility of calcium with the addition of soap is 15% higher than that without organic additives. Similarly, Ulmgren [5] reported that during cooking, the product of total dissolved calcium and carbonate ion concentrations is one logarithmic unit larger with organic substance present. This solubility increase was attributed to the formation of a soluble complex between calcium ions and organic anions generated from lignin. Frederick and Grace [6] found that the strong complexing ability of calcium ions comes from the structural feature, an aromatic ring with two adjacent hydroxyls, in lignin compounds, or fragments degraded from lignin.

Effect of calcium scales on sodium scales

Because calcium concentration in scale is higher than its concentration in solution, which is discussed in the previous section on "Calcium in sodium crystals without organic additives," one explanation for the effect of calcium on sodium scales is that calcium scale deposits on the heat exchange surface before sodium scale, providing spots for the deposit of burkeite nuclei and inducing burkeite scales. To test this proposed mechanism, calcium scales were built on the heat exchange surface prior to sodium scaling.

No matter whether there is calcium scale on the heat exchange surface or not, similar amounts of sodium scales deposit on the heat exchange surface, with an average of 1.52 g of sodium scales formed on the heat exchange surface pre-deposited by calcium scale (**Table IV**), while 1.72 g of sodium scales built up on the clean heat exchange surface (Fig. 6). This implies that the presence of calcium scales on the heating surface does not necessarily result in more sodium scales in the bench-top evaporative scaling setup.

At first glance, this finding is contrary to Shi's conclusion that calcium carbonate scale induces sodium scales [7]. This is likely because the prerequisite for Shi's finding is that the surface where sodium scale was induced by calcium scale is subjected to less sweeping force exerted by the fluid, while the scaling surface in the current experimental setup, which is the heat exchanger, is subjected to a high sweeping force as the heat exchanger works as a baffle in the solution. Because of the high sweeping force, the calcium scale, which was deposited before the heat exchanger was inserted in the model sodium salt solution, disperses in the

Number of Runs	Na Scales, g	Ca Concentration in Scales, mg/g crystal	Ca Concentration in Scales near Heating Surface, mg/g crystal	Ca Concentration in Solution, mg/L
1	1.3970	0.56	2.81	43.3
2	2.3387	0.41	–	48.5
3	1.2698	0.39	0.72	26.8
4	1.0734	0.25	0.49	18.7
Average	**1.5197**			

IV. Features of sodium (Na) scales that have built up on the heat exchange surface, with calcium (Ca) scales covered.

solution during the sodium scaling experiment. As shown in Table IV, the calcium concentrations in the runs with the pre-built calcium scales are all at least three times higher than the inherent calcium concentration in the model salt solution, which is 4–8 mg/L. For clarification, not all calcium scale is dispersed in the bulk solution, because the calcium concentration near the heat exchange surface is higher than its concentration in the bulk scale samples.

CONCLUSIONS

The addition of calcium carbonate did not result in a more severe sodium salt scale, but the crystal agglomerates did look more compact, and crystals appeared larger. Calcium scale on the heat exchange surface did not result in higher sodium salt scaling. Interestingly, increasing the calcium concentration to 360 mg/L generally resulted in a smaller variation in sodium salt scaling observed when compared to lower concentrations. The mechanism is not clear, but could in part be due to the apparent formation of larger crystals. Resin acids and fatty acids, which are scale inhibitors of sodium scales, also help suppress variation in sodium scales. The oleate and abietate did not affect the calcium solubility, but the tall oil soap did result in slightly higher calcium solubility, likely due to lignin fragments in the tall oil soap. These results tend to indicate that there is some interaction of calcium with sodium salt scales, but it does not clearly increase the rate of scaling. Combined with earlier studies, these results seem to indicate that the reduced scaling seen in the presence of tall oil soap or similar is not due to an interaction with calcium, but rather to the interactions between the resin and fatty acids and the sodium salt crystals.

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ABOUT THIS PAPER

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About this journal

ABOUT THE AUTHORS

Though recent industrial experience and research show that reintroducing tall oil soap to high dry solids black liquor reduces sodium salt scaling, one common concern with reintroducing soap is that its high calcium content can induce sodium scaling. Thus, we chose to study the effects of calcium on sodium salt scaling in the presence of the major soap compositions, laying the foundation for understanding whether we need to worry about calcium in soap addition.

This work focuses on the effects of calcium on sodium salt scaling rather than solely on crystallization as in the previous study by Shi et al. Meanwhile, resin acids and fatty acids, major components of tall oil soap, were included in the current investigation.

Because sodium salt crystallization is a dynamic process, it is difficult to capture the interaction between sodium crystals and calcium. Thus, we chose features such as crystal morphology and the metastable limit to monitor the crystallization process and interpret interactions from changes in these features.

Though resin acids and fatty acids improve the repeatability of scaling results like EDTA, surprisingly, resin acids and fatty acids do not form a soluble complex with calcium like EDTA. It was particularly interesting to discover that higher calcium levels do not necessarily result in more severe sodium salt scaling with the presence of resin acids and fatty acids.

When sorting the root causes of scaling issues during black liquor evaporation, mills can use the information in this study to better understand the role of calcium in sodium scaling with the presence of high or low tall oil soap. This helps mills make appropriate decisions regarding scale removal and prevention.

The next step in this research is to add lignin to the consideration and conduct experiments at high temperatures. More work needs to be carried out to determine whether calcium originally bound to lignin can be released at high temperatures and whether this reaction affects sodium salt scaling.

Huang

DeMartini

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APPENDIX A

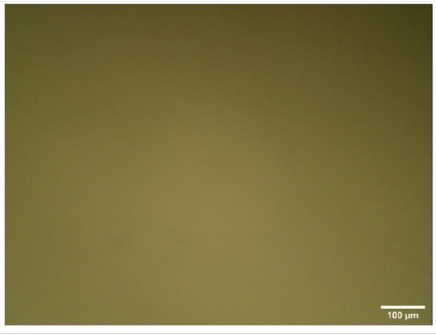
Photomicrographs of scaling experiments

Run Number	Calcium or EDTA Concentration	RFA Concentration
	mg/L	mg/g solution
1	400 mg/L EDTA	0
2	400 mg/L EDTA	0.02
3	400 mg/L EDTA	0.3
4	4-8 mg/L Calcium	0
5	40 mg/L Calcium	0
6	360 mg/L Calcium	0
7	4-8 mg/L Calcium	0.02
8	4-8 mg/L Calcium	0.3
9	360 mg/L Calcium	0.02

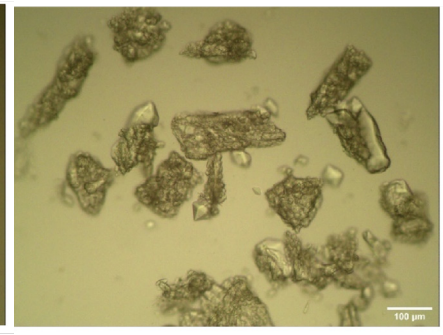
EDTA: ethylenediaminetetraacetic acid; RFA: mixture of resin acid and fatty acid.

A-I. Composition of runs used in the study as analyzed by micrographs in this Appendix.

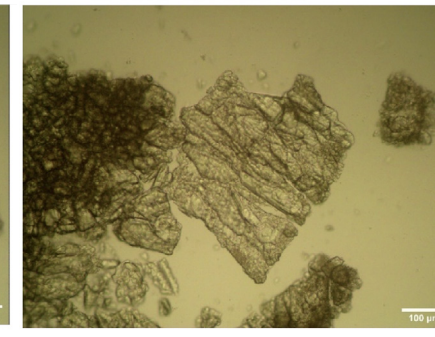
Run 1: 400 mg/L EDTA; no organic additive



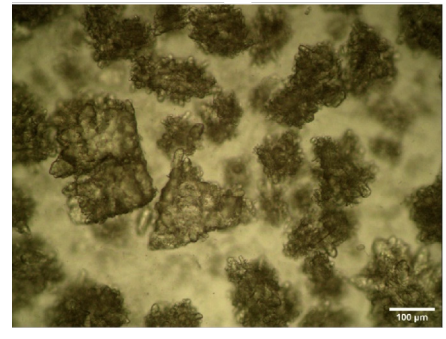
Before the onset of crystallization (Regime I)



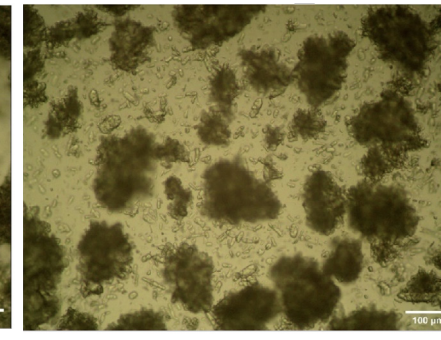
Crystallization initiates



Regime II

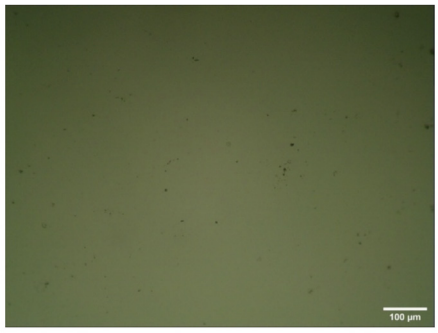


At the end of the experiment



At the end of the experiment

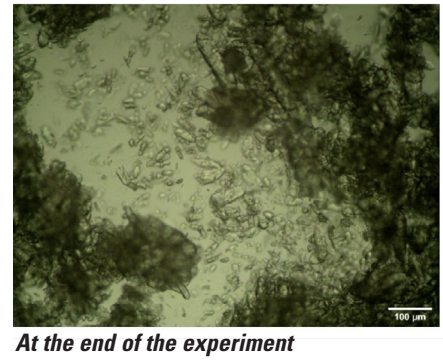
Run 2: 400 mg/L EDTA; 0.02 mg/g solution of RFA



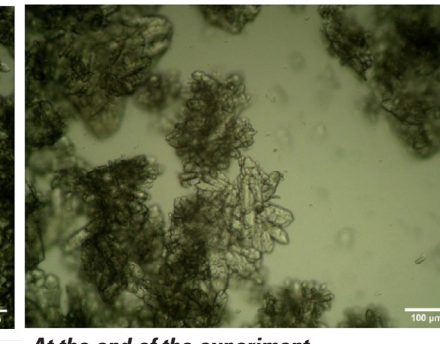
Before the onset of crystallization (Regime I)

Crystallization initiates

Regime II

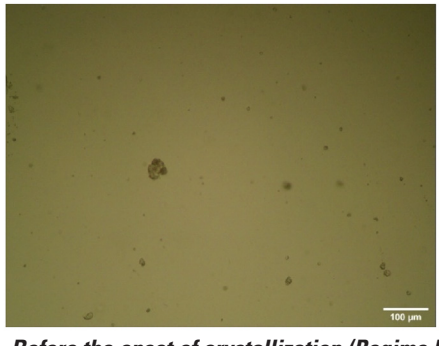


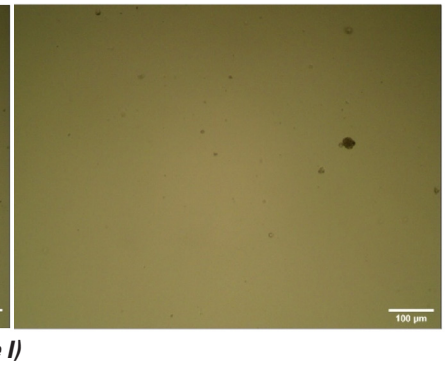
At the end of the experiment



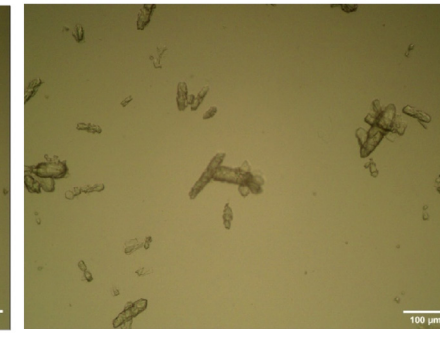
At the end of the experiment

Run 3: 400 mg/L EDTA; 0.3 mg/g solution of RFA

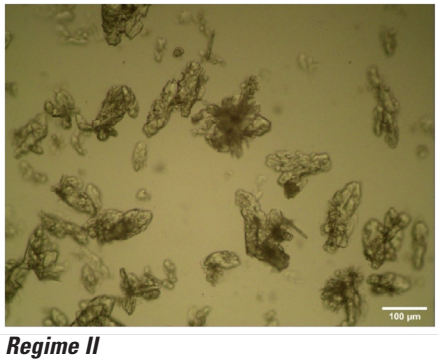




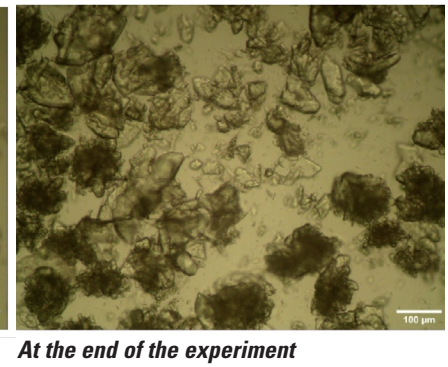
Before the onset of crystallization (Regime I)
The spots are RFA that are dispersed in the solution.



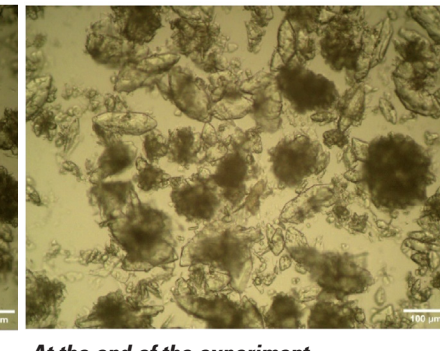
Crystallization initiates



Regime II

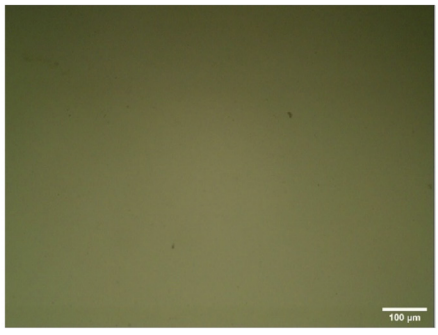


At the end of the experiment

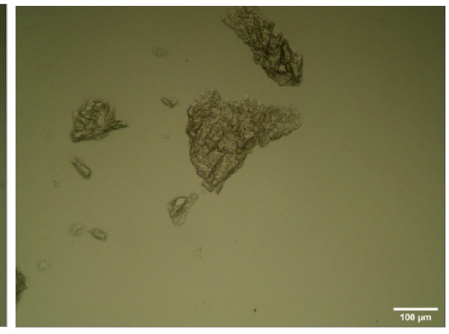


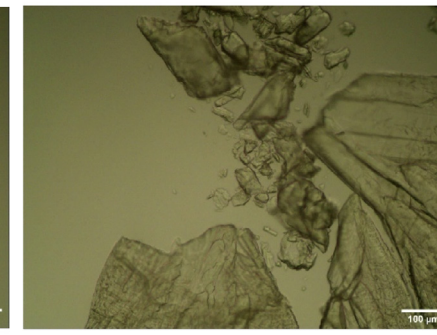
At the end of the experiment

Run 4: 4-8 mg/L Ca; no organic additive

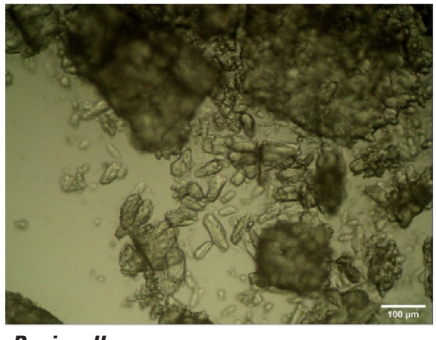


Before the onset of crystallization (Regime I)

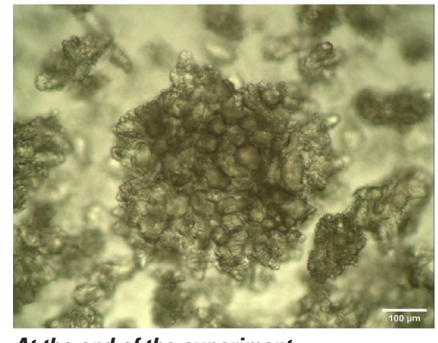




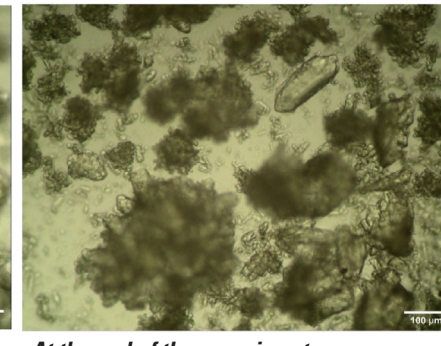
Crystallization initiates



Regime II

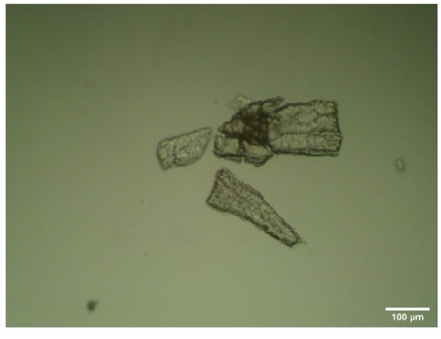


At the end of the experiment

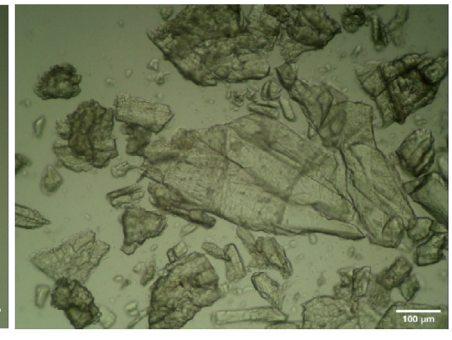


At the end of the experiment

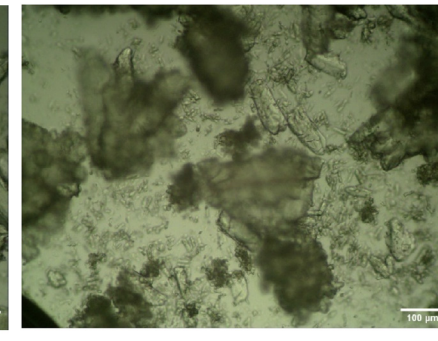
Run 5: 40 mg/L Ca; no organic additives



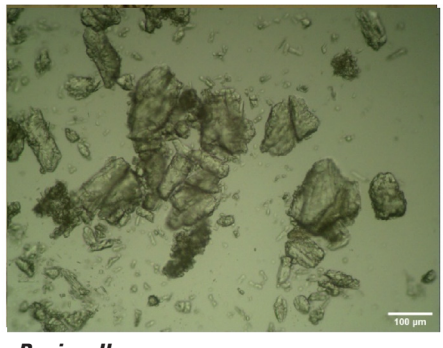
Crystallization initiates



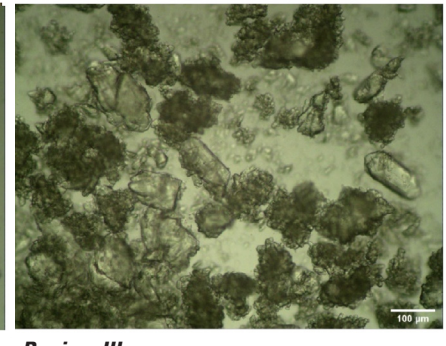
Crystallization initiates



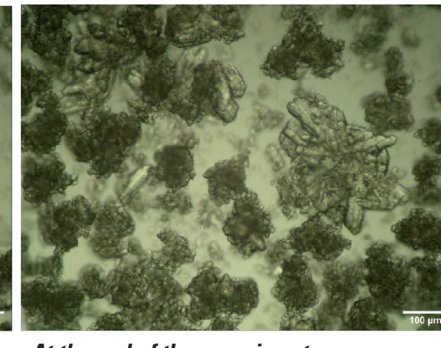
Regime II



Regime II



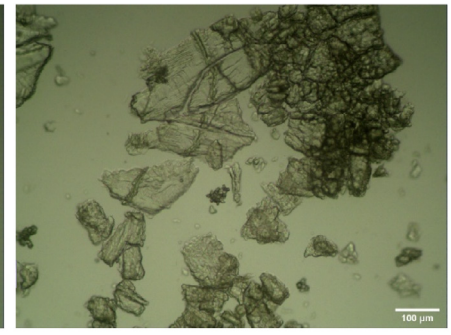
Regime III



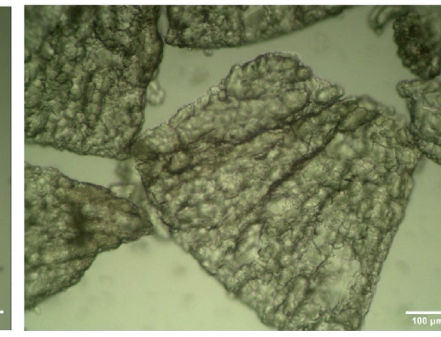
At the end of the experiment

Run 6: 360 mg/L Ca; no organic additives

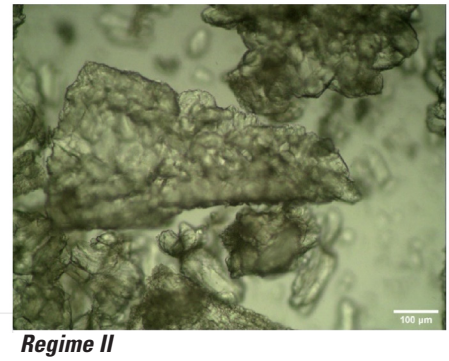
Before the onset of crystallization (Regime I). The dark spots are insoluble calcium carbonate powder



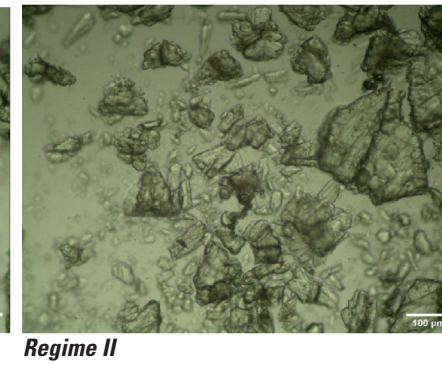
Crystallization initiates



Regime II



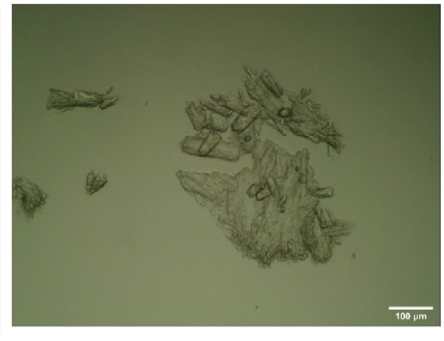
Regime II



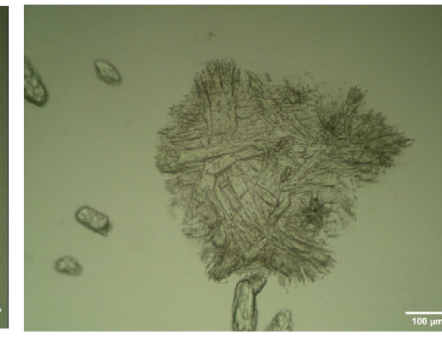
Regime II

Run 7: 4-8 mg/L Ca; 0.02 mg/g solution of RFA

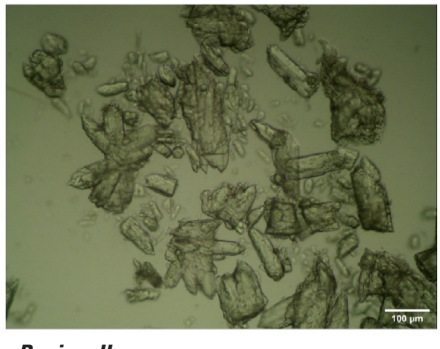
Before the onset of crystallization (Regime I)



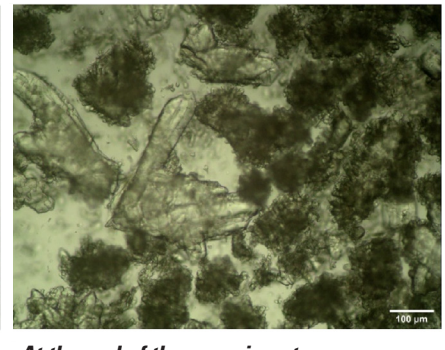
Crystallization initiates



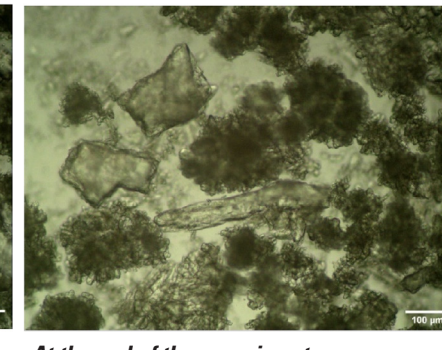
Regime II



Regime II

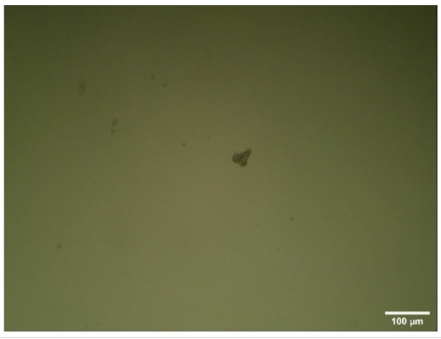


At the end of the experiment



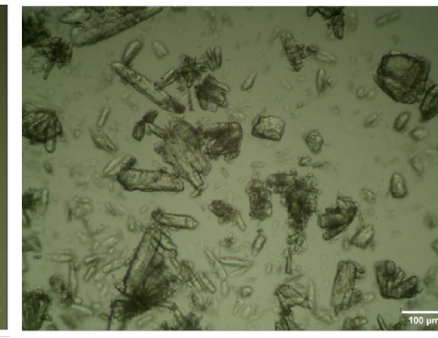
At the end of the experiment

Run 8: 4-8 mg/L Ca; 0.3 mg/g solution of RFA

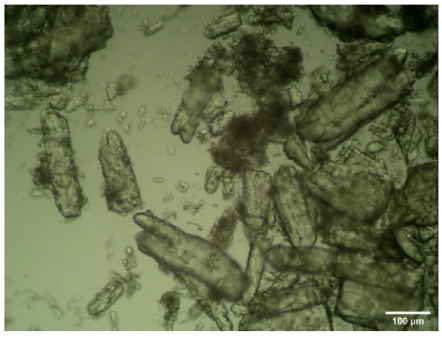


Before the onset of crystallization (Regime I)

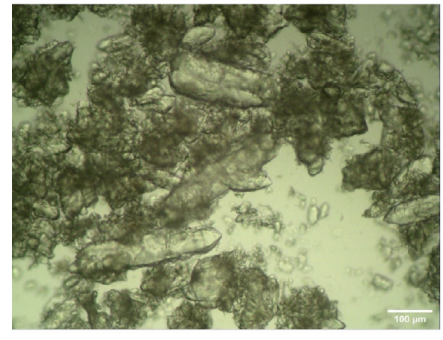
Crystallization initiates



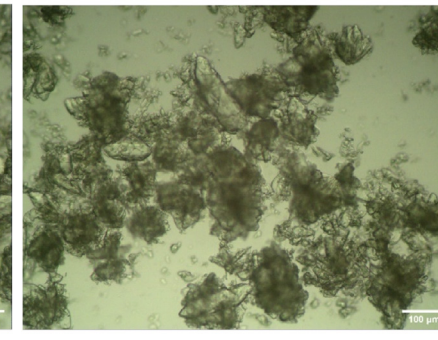
Regime II



Regime III

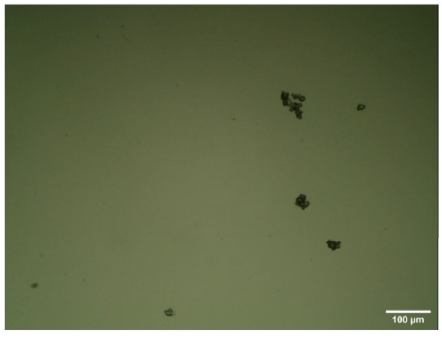


At the end of the experiment



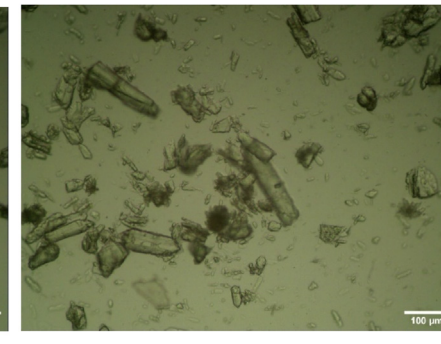
At the end of the experiment

Run 9: 360 mg/L Ca; 0.02 mg/g solution of RFA

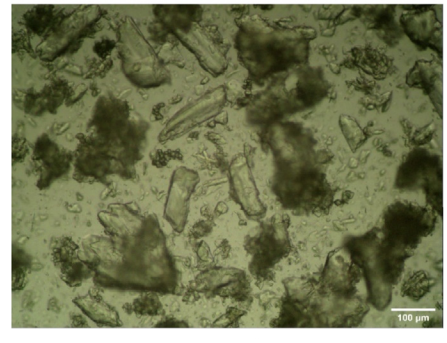


Before the onset of crystallization (Regime I)

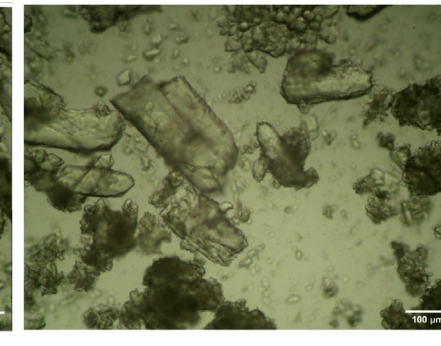
Crystallization initiates



Regime II



At the end of the experiment



At the end of the experiment

APPENDIX B

Summary table of scaling experiments under various calcium and RFA concentrations

B-I. Summary table of metastable limit and mass of crystals in sodium salt scaling experiments under various calcium and RFA (mixture of resin acid and fatty acid) concentrations.

Run No.	Calcium Concentration	RFA Concentration	Metastable Limit	Mean (metastable limit)	Standard Deviation (metastable limit)	Maximum (metastable limit)	Minimum (metastable limit)	Mass of Crystals	Mean (crystal mass)	Standard Deviation (crystal mass)	Maximum (crystal mass)	Minimum (crystal mass)
	mg/L	mg/g solution	g/g solution					g				
1	0	0	0.316	0.316	0.00131	0.318	0.314	14.0	18.4	3.03	25.1	14.0
2	0	0	–					18.5				
3	0	0	0.315					15.2				
4	0	0	0.316					16.7				
5	0	0	0.314					18.6				
6	0	0	0.318					17.3				
7	0	0	–					19.1				
8	0	0	0.317					25.1				
9	0	0	0.315					18.8				
10	0	0	0.317					20.3				
11	4-8	0	–	0.321	0.00115	0.322	0.320	21.3	19.3	2.99	23.9	16.1
12	4-8	0	–					16.3				
13	4-8	0	0.32					16.1				
14	4-8	0	–					18.8				
15	4-8	0	0.322					19.5				
16	4-8	0	0.32					23.9				
17	90	0	0.319	0.321	0.00212	0.322	0.319	12.6	13.3	0.83	14.2	12.6
18	90	0	0.322					13.0				
19	90	0	–					14.2				
20	360	0	–					8.7	9.0	0.38	9.3	8.7
21	360	0	–					9.3				
22	640	0	–					3.0	7.6	4.11	10.9	3.0
23	640	0	–					8.8				
24	640	0	–					10.9				
25	0	0.02	0.32	0.322	0.00339	0.329	0.320	20.2	24.0	2.79	28.1	20.2
26	0	0.02	0.32					24.3				
27	0	0.02	0.321					23.4				
28	0	0.02	0.322					25.8				
29	0	0.02	0.329					22.0				
30	0	0.02	0.322					28.1				

RECOVERY CYCLE

Run No.	Calcium Concentration	RFA Concentration	Metastable Limit	Mean (metastable limit)	Standard Deviation (metastable limit)	Maximum (metastable limit)	Minimum (metastable limit)	Mass of Crystals	Mean (crystal mass)	Standard Deviation (crystal mass)	Maximum (crystal mass)	Minimum (crystal mass)
	mg/L	mg/g solution	g/g solution					g				
31	4-8	0.02	0.317	0.320	0.00351	0.324	0.317	15.8	16.0	3.73	20.9	11.8
32	4-8	0.02	–					15.6				
33	4-8	0.02	0.32					11.8				
34	4-8	0.02	0.324					20.9				
35	90	0.02	–	0.329	0.00849	0.335	0.323	17.6	17.3	8.77	25.9	5.2
36	90	0.02	0.323					5.2				
37	90	0.02	–					25.9				
38	90	0.02	0.335					20.6				
39	360	0.02	–					4.0	15.5	7.70	20.3	4.0
40	360	0.02	–					18.5				
41	360	0.02	–					19.2				
42	360	0.02	–					20.3				
43	0	0.1	–					18.5	19.4	1.29	20.9	18.5
44	0	0.1	–					18.9				
45	0	0.1	–					20.9				
46	90	0.1	0.326					24.6				
47	0	0.3	–					14.0	18.4	3.21	22.4	14.0
48	0	0.3	–					19.8				
49	0	0.3	–					15.8				
50	0	0.3	–					19.2				
51	0	0.3	–					21.7				
52	0	0.3	–					15.9				
53	0	0.3	0.325					22.4				
54	4-8	0.3	–					13.3	16.3	5.71	22.8	8.9
55	4-8	0.3	–					9.6				
56	4-8	0.3	–					8.9				
57	4-8	0.3	–					19.5				
58	4-8	0.3	–					22.8				
59	4-8	0.3	–					18.2				
60	4-8	0.3	0.33					21.9				
61	4-8	0.3 (soap)	0.315					2.6	7.3	6.67	12.0	2.6
62	4-8	0.3 (soap)	–					12.0				

Run No.	Calcium Concentration	RFA Concentration	Metastable Limit	Mean (metastable limit)	Standard Deviation (metastable limit)	Maximum (metastable limit)	Minimum (metastable limit)	Mass of Crystals	Mean (crystal mass)	Standard Deviation (crystal mass)	Maximum (crystal mass)	Minimum (crystal mass)
	mg/L	mg/g solution	g/g solution					g				
63	90	0.3	–					20.8	17.6	2.58	20.8	14.9
64	90	0.3	–					14.9				
65	90	0.3	0.32					16.3				
66	90	0.3	–					18.5				
67	360	0.3	–					10.7	13.7	4.24	16.7	10.7
68	360	0.3	–					16.7				
69	640	0.3	–					17.9	15.8	2.97	17.9	13.7
70	640	0.3	–					13.7				
71	640	0.3 (soap)	–					14.4	14.6	0.26	14.9	14.4
72	640	0.3 (soap)	–					14.5				
73	640	0.3 (soap)	–					14.9				

B-II. Summary table of final total solids and final dissolved solids in sodium salt scaling experiments under various calcium and RFA (mixture of resin acid and fatty acid) concentrations.

Run No.	Calcium Concentration	RFA Concentration	Final Total Solids	Mean (final total solids)	Standard Deviation (final total solids)	Maximum (final total solids)	Minimum (final total solids)	Final Dissolved Solids	Mean (final dissolved solids)	Standard Deviation (final dissolved solids)	Maximum (final dissolved solids)	Minimum (final dissolved solids)
	mg/L	mg/g solution	g/g solution					g/g solution				
1	0	0	0.343	0.352	0.00762	0.369	0.343	0.314	0.312	0.00157	0.314	0.310
2	0	0	0.349					0.310				
3	0	0	0.343					0.311				
4	0	0	0.348					0.312				
5	0	0	0.350					0.310				
6	0	0	0.351					0.314				
7	0	0	0.354					0.313				
8	0	0	0.369					0.311				
9	0	0	0.350					0.310				
10	0	0	0.358					0.312				
11	4-8	0	0.359	0.355	0.00653	0.364	0.347	0.313	0.312	0.00172	0.314	0.309
12	4-8	0	0.348					0.314				
13	4-8	0	0.347					0.312				
14	4-8	0	0.353					0.312				
15	4-8	0	0.356					0.313				
16	4-8	0	0.364					0.309				
17	90	0	0.342	0.342	0.00058	0.343	0.342	0.316	0.315	0.00100	0.316	0.314
18	90	0	0.342					0.315				
19	90	0	0.343					0.314				
20	360	0	0.339	0.341	0.00212	0.342	0.339	0.320	0.321	0.00071	0.321	0.320
21	360	0	0.342					0.321				
22	640	0	0.328	0.337	0.00833	0.344	0.328	0.322	0.322	0.00058	0.322	0.321
23	640	0	0.340					0.322				
24	640	0	0.344					0.321				
25	0	0.02	0.351	0.363	0.00853	0.376	0.351	0.308	0.309	0.00105	0.310	0.307
26	0	0.02	0.360					0.307				
27	0	0.02	0.360					0.309				
28	0	0.02	0.368					0.308				
29	0	0.02	0.360					0.310				
30	0	0.02	0.376					0.309				
31	4-8	0.02	0.340	0.347	0.00714	0.357	0.340	0.307	0.313	0.00562	0.320	0.307
32	4-8	0.02	0.347					0.314				
33	4-8	0.02	0.345					0.320				
34	4-8	0.02	0.357					0.310				
35	90	0.02	0.353	0.353	0.01746	0.371	0.329	0.315	0.315	0.00310	0.319	0.312
36	90	0.02	0.329					0.319				
37	90	0.02	0.371					0.313				
38	90	0.02	0.357					0.312				

Run No.	Calcium Concentration	RFA Concentration	Final Total Solids	Mean (final total solids)	Standard Deviation (final total solids)	Maximum (final total solids)	Minimum (final total solids)	Final Dissolved Solids	Mean (final dissolved solids)	Standard Deviation (final dissolved solids)	Maximum (final dissolved solids)	Minimum (final dissolved solids)
	mg/L	mg/g solution	g/g solution					g/g solution				
39	90	0.02	0.340					0.331				
40	360	0.02	0.366	0.358	0.01212	0.366	0.340	0.324	0.323	0.00624	0.331	0.317
41	360	0.02	0.360					0.317				
42	360	0.02	0.365					0.319				
43	360	0.1	0.349					0.310				
44	0	0.1	0.352	0.352	0.00300	0.355	0.349	0.311	0.310	0.00058	0.311	0.310
45	0	0.1	0.355					0.310				
46	0	0.1	0.369					0.314				
47	90	0.3	0.347					0.317				
48	0	0.3	0.370					0.325				
49	0	0.3	0.354					0.320				
50	0	0.3	0.360	0.359	0.00884	0.370	0.347	0.318	0.318	0.00372	0.325	0.314
51	0	0.3	0.363					0.314				
52	0	0.3	0.350					0.315				
53	0	0.3	0.368					0.316				
54	0	0.3	0.346					0.318				
55	4-8	0.3	0.329					0.310				
56	4-8	0.3	0.338					0.319				
57	4-8	0.3	0.360	0.353	0.01532	0.370	0.329	0.317	0.317	0.00317	0.319	0.310
58	4-8	0.3	0.367					0.316				
59	4-8	0.3	0.358					0.318				
60	4-8	0.3	0.370					0.319				
61	4-8	0.3 (soap)	0.341	0.343	0.00283	0.345	0.341	0.336	0.327	0.01181	0.336	0.319
62	4-8	0.3 (soap)	0.345					0.319				
63	4-8	0.3	0.371					0.324				
64	90	0.3	0.353	0.359	0.00876	0.371	0.352	0.320	0.320	0.00287	0.324	0.317
65	90	0.3	0.352					0.317				
66	90	0.3	0.360					0.320				
67	90	0.3	0.348	0.352	0.00566	0.356	0.348	0.325	0.323	0.00354	0.325	0.320
68	360	0.3	0.356					0.320				
69	360	0.3	0.362	0.357	0.00707	0.362	0.352	0.322	0.322	0.00000	0.322	0.322
70	640	0.3	0.352					0.322				
71	640	0.3	0.348					0.317				
72	640	0.3 (soap)	0.351	0.351	0.00252	0.353	0.348	0.320	0.319	0.00173	0.320	0.317
73	640	0.3 (soap)	0.353					0.320				