Crystallization and control of sodium salt scales in black liquor concentrators

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ABSTRACT: In this report on a four-year study, the researchers identify a double salt of Na_2CO_3 and Na_2SO_4 that crystallizes in most kraft black liquors. This double salt causes soluble-scale fouling in high-solids black liquor concentrators. Calcium ion inhibits the primary nucleation of the newly identified double salt, which could be used to help control soluble scaling through the development of nucleation or crystal growth inhibitors. Careful control of the Na_2CO_3 and Na_2SO_4 content of black liquor can also reduce sodium salt fouling in black liquor concentrators.

Application: It may be possible to develop crystal nucleation inhibitors or crystal growth inhibitors to prevent dicarbonate scaling.

Many black liquor evaporators and high-solids concentrators suffer from the fouling of their heat transfer surfaces, which reduces their capacity. The fouling problem in about a third of these evaporators and concentrators results from the deposition of Na_2CO_3 and Na_2SO_4. The scale formed is often referred to as "soluble" scale because these sodium salts are moderately soluble in water and can be readily removed by washing with hot water.

In the 1970s, Grace [1, 2] identified the problem of soluble scales in LTV evaporators as rapid crystallization of burkeite when the product liquor concentration exceeded the solubility limit for burkeite. Based on Grace's results, burkeite scale in LTVs was largely eliminated and was not problematic when the more modern, falling-film evaporators came into use.

With the introduction of high-solids black liquor concentrators, however, soluble-scale problems appeared again, but their characteristics were different from the earlier burkeite scale problems. The onset of scale deposition was erratic, not predictable, and it seemed to be associated with high ratios of Na_2CO_3 to Na_2SO_4 in the black liquor. Fouling was rapid, and evaporator bodies often had to be shut down and boiled out every few days.

In reality, black liquor evaporators and high-solids concentrators become crystallizing evaporators as soon as the total solids concentration in the black liquor exceeds the solubility limit of the Na_2CO_3 and Na_2SO_4 that it contains. Soluble-scale deposition in these evaporators and concentrators is a crystallization problem, controlled by crystallization phenomena and the influence of fluid flow and heat transfer on those phenomena. Although this knowledge has been no secret, there has been relatively little information reported about the crystallization behavior of Na_2CO_3 and Na_2SO_4 during the evaporation of black liquor.

In 1998, we began an investigation of the crystallization behavior of Na_2CO_3 and Na_2SO_4 during black liquor evaporation. Here, we summarize the results of a four-year effort. The results reported here are entirely new. In brief, a new double salt of Na_2CO_3 and Na_2SO_4 that is rich in Na_2CO_3 has been identified; the primary nucleation of the crystals of this double salt causes soluble-scale fouling in high-solids black liquor concentrators, and calcium ions control the onset of nucleation of both burkeite and this newly identified double salt.

Here, we review the basic concepts of crystallization as related to evaporative crystallization and fouling. We then summarize the results obtained in our study of the crystallization of Na_2CO_3 and Na_2SO_4 from black liquor and aqueous solutions of these salts. Finally, we explore the implications of the new findings with regard to the control of soluble scale in high solids black liquor concentrators.

PRINCIPLES OF CRYSTALLIZATION

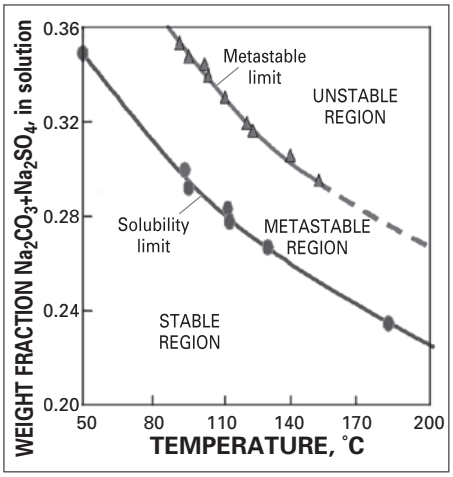
Crystals can form and grow either in suspension or as scales on surfaces. When solvent is evaporated, the concentration of the dissolved material may eventually reach its solubility, a thermodynamic limit to the amount of solute that can be dissolved at equilibrium. The solubility depends on the specific solute(s) and solvent and on temperature. A solid phase of a well-defined composition coexists with the solution when the total concentration exceeds the solubility limit.

In practice, however, the solute concentration can exceed the solubility limit. Such a solution is referred to as being "supersaturated." The difference between the actual solute concentration and the solubility is a measure of the supersaturation. One property of supersaturated solutions is that crystals and crystalline deposits will grow in them, whereas they will not grow in saturated solutions.

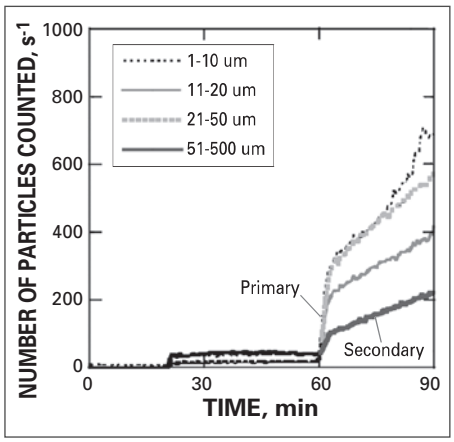
While a supersaturated solution is not thermodynamically stable, supersaturation can be maintained up to a certain limit, referred to as the "metastable limit." When a solution is concentrated to the metastable limit, the primary nucleation of crystals occurs spontaneously. The metastable limit is not a thermodynamic value and can depend on the rate of solvent removal or the presence of dissolved species or suspended particles other than the species that crystallizes [3].

Figure 1 illustrates the solubility and metastable limits for solutions of Na_2CO_3 and Na_2SO_4 in water. The region between the solubility and metastable limits is known as the "metastable zone." Solutions whose concentrations fall within the metastable zone will support the growth of crystals or crystalline deposits that already exist but will not produce new crystals by primary nucleation.

New crystals are formed by either *primary* or *secondary* nucleation. Primary nucleation occurs when the metastable limit is exceeded. At that point, large numbers of small crystals form very rapidly, and the dissolved solute concentration



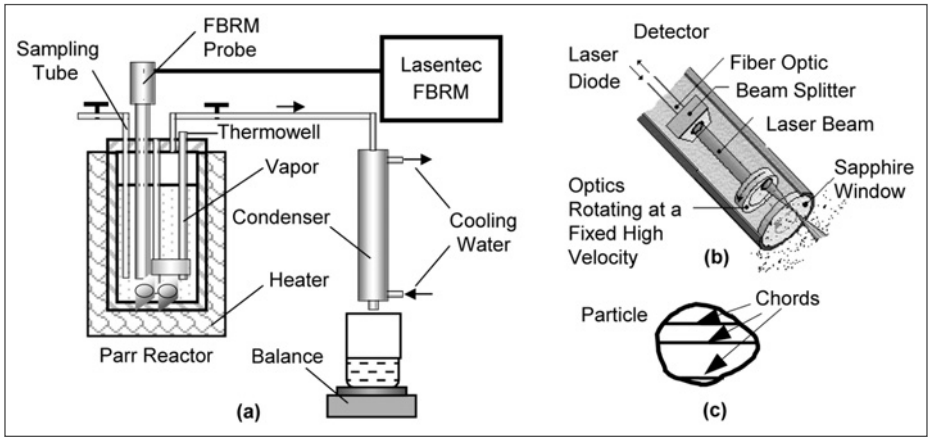
1. The solubility and metastable limits vs. temperature for the system of Na_2CO_3–Na_2SO_4 in water. The mole ratio of Na_2CO_3 to Na_2SO_4 is 1:2 in the system [4].



2. Particles counted per second in four apparent size ranges vs. time during the evaporation of water from an aqueous solution of Na_2SO_4 [5].

typically drops below the metastable limit. Secondary nucleation results from crystal collisions; it produces crystals more slowly and more steadily.

Figure 2 shows where these two nucleation events occurred during the evaporation of water from a solution of Na_2SO_4 in water. The rapid increases in the slopes of the particle concentrations that began at 60 min are the result of primary heterogeneous nucleation that produced a large number of small crystals. The primary nucleation event ended after about 3 min. The subsequent slower increase in the number of crystals is the result of secondary nucleation.



3. Apparatus used for the bench-scale evaporation experiments [5].

Once crystals or crystalline deposits are formed, they will continue to grow as long as the solution remains supersaturated. They will not grow in saturated solutions and will redissolve, often slowly, in a solution in which the concentration is below the solubility limit.

EXPERIMENTAL MEASUREMENTS

Evaporative crystallization experiments

Evaporative crystallization experiments were carried out in a batch crystallizer (**Fig. 3**, Frame A) constructed from a 1 L Parr bomb reactor. A stainless-steel propeller was used as a mixer. A PID-controlled electrical heating mantle provided the energy to increase the system temperature and evaporate water. The evaporated water left the crystallizer through a control valve, and the vapor was condensed, collected, and weighed. A computer recorded the temperature of the crystallizer contents and the mass of condensate were recorded as functions of run time.

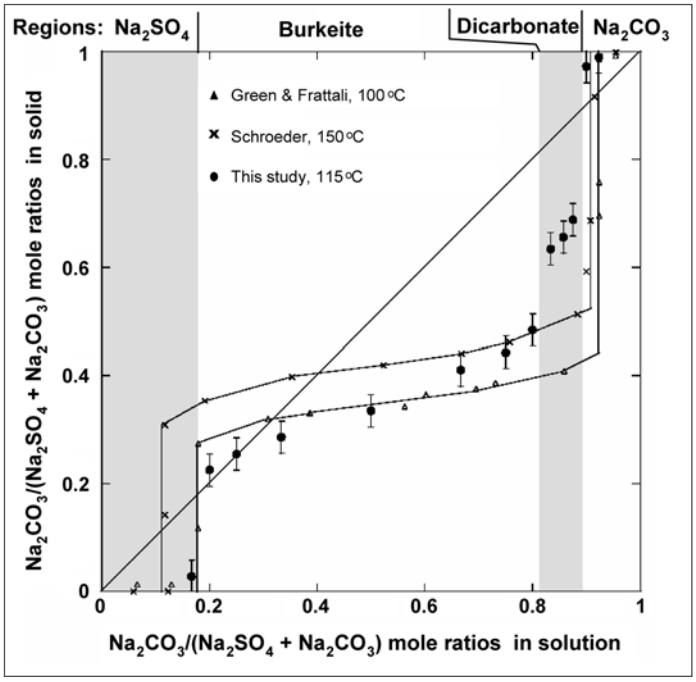
Aqueous solutions of Na_2CO_3 and Na_2SO_4 were prepared by dissolving commercially available A.C.S.-grade salts in distilled water to produce 1000 g of solution with a salt mass fraction of 0.28. The solution was initially kept at 35–50°C for about 30 min to make sure the solids were dissolved completely. The solution was then heated to 115°C, at which temperature it was evaporated at a constant rate. The rates of evaporation for different experiments ranged from 3.2 g to 4.5 g of water per minute. The sizes of crystals formed were monitored by a Lasentec® Focused Beam Reflectance Measurement (FBRM) D600L system (Fig. 3b). Detailed information about the Lasentec device can be found elsewhere [6].

The same equipment and procedure was used in experiments involving black-liquor evaporation, except that solution preparation was not necessary and the temperature of evaporation was higher (130°C).

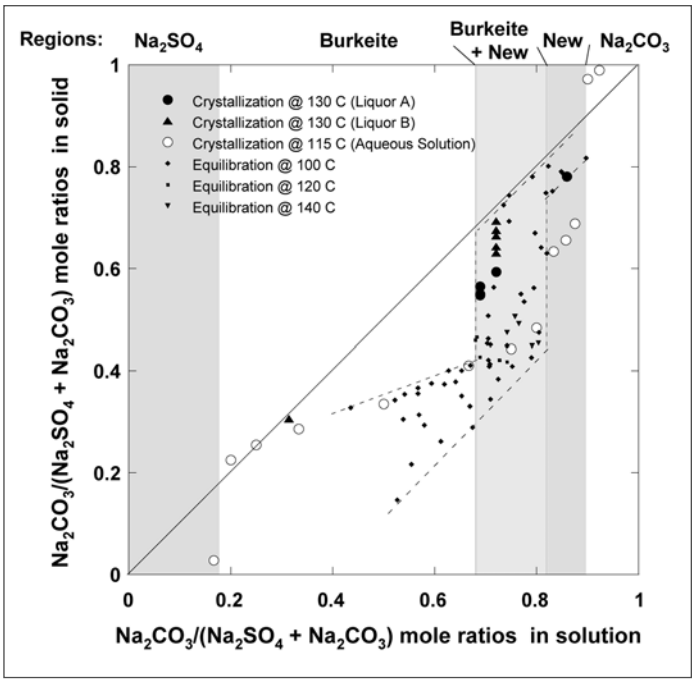
The FBRM unit actually measures the dimension of that part of a particle that is in the line of the laser beam. As indicated in Fig. 3c, this dimension may be the maximum dimension of the particle (the diameter for a spherical particle), or it may be a smaller dimension (the length of a chord smaller than the diameter for a spherical particle). When the dimensions of a large number of particles are measured with this device, the distribution recorded is actually a chord length distribution, not the distribution of the largest dimensions of the particles. For the purpose of clarity, we refer to the measured chord length distributions as "apparent particle size distributions."

Heat transfer fouling measurements

We took heat transfer measurements for both black liquor and aqueous solutions of Na_2CO_3 and Na_2SO_4 to evaluate the relationship between fouling and crystallization behavior. These measurements were made in a steam-heated, pilot-scale, falling-film, dimple-plate evaporator that was instrumented for temperature, pressure, and heat flux measurements. The evaporator was equipped with a second FBRM system to measure the apparent particle size distribution continuously during evaporation. The experiments



4. Compositions of the crystals formed as a function of the solution composition for the Na_2CO_3–Na_2SO_4–H_2O system. The regions where each solid species was first crystallized are indicated at the top of the figure [14].



6. Comparison of the crystals compositions obtained from black liquor crystallization at 130°C, aqueous solution crystallization at 115°C, and Grace's equilibrium data [11] at 100°, 120°, and 140°C [14].

were conducted in semi-batch mode, so that liquor-side condensate but no liquor was removed during each run. A more detailed description of the evaporation equipment and experimental procedure is available from Euhus *et al*. [7].

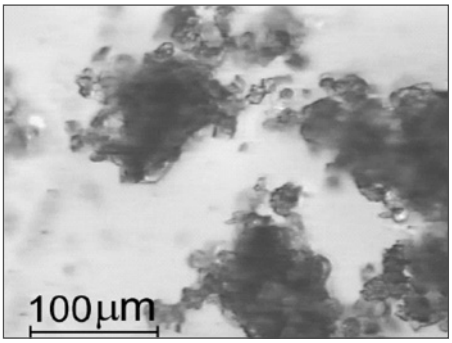
CRYSTAL PHASES

Crystallization from aqueous solutions

The solubility behavior of the Na_2CO_3–Na_2SO_4-H_2O system has been characterized in several studies [8–10]. Burkeite, Na_2SO_4, and Na_2CO_3 or Na_2CO_3•H_2O were reported in these studies as the three crystalline phases that existed in equilibrium in the temperature range 100–150°C. Burkeite is known to vary in composition, from about 1:1.4 to 1:2.2 moles Na_2CO_3 per mole Na_2SO_4.The range of composition is attributable to the similar radii of SO_4 and CO_3 ions; this similarity allows them to substitute for each other in the burkeite crystal lattice [10]. Other, more soluble sodium salts have essentially no effect on the equilibrium behavior other than through the expected common ion effect of sodium, in either aqueous solutions of sodium salts or in black liquor [10, 11].

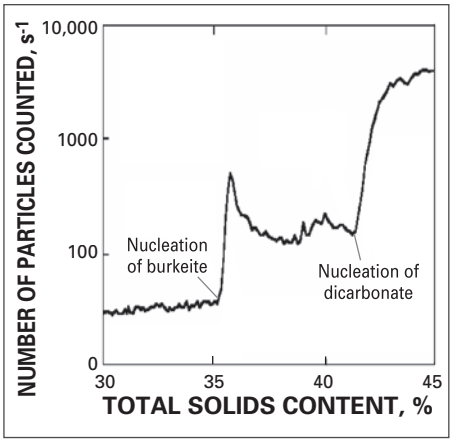
In the previous studies cited, equilibrium was approached by mixing more Na_2CO_3 and Na_2SO_4 with water than would be soluble in it and allowing the system to equilibrate. During evaporation, however, the solubility limit is approached from below saturation. In our work, the composition of the first crystals produced was measured during evaporative crystallization with aqueous solutions of sodium carbonate and sodium sulfate in molar ratios ranging from 1:5 to 12:1.The compositions of the crystals are shown in **Fig. 4**, together with equilibrium data obtained by Green and Frattali at 100°C [10] and by Schroeder *et al*. at 150°C [9].

Two important new findings are evident in Fig. 4.The first is that the compositions of the crystals produced by evaporative crystallization differ from those obtained in the earlier equilibrium studies. The second is that a previously unidentified crystalline phase was predominant for solutions of sodium carbonate and sodium sulfate in the composition range of $0.833 < x < 0.889$ for x as Na_2CO_3. This new crystalline phase was identified as a double salt with a composition that was nominally 2 Na_2CO_3•Na_2SO_4, but this composition varied with the ratio of Na_2CO_3 to Na_2SO_4 in solution from 1.6 Na_2CO_3•Na_2SO_4 to 2.2 Na_2CO_3•Na_2SO_4.

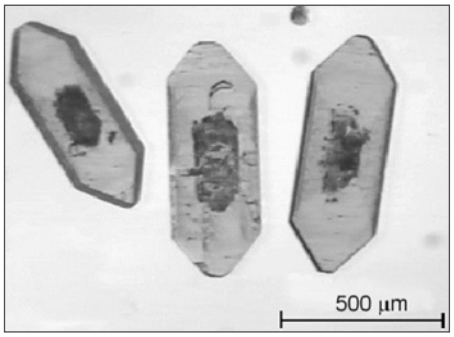


5. Crystals of dicarbonate from solutions with a carbonate-sulfate molar ratio of 5:1.

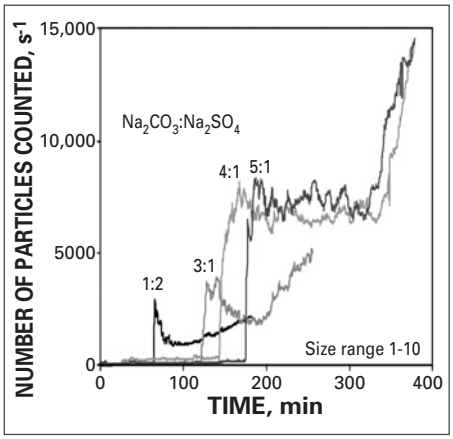
This newly identified double salt is referred to as "dicarbonate" here. The individual crystals formed during primary nucleation of this double salt are very small, less than 10 mm, and they agglomerate rapidly (**Fig. 5**). Other researchers [9, 12, 13] have speculated about the possible formation of double salts other than burkeite in the Na_2CO_3–Na_2SO_4–H_2O system. Prior to our



7. Number of 1–10 µm crystals in suspension during the evaporation of an aqueous solution containing sodium carbonate and sodium sulfate in a molar ratio of 3:1. Two nucleation events are seen, the nucleation of burkeite and of dicarbonate [16].



8. Sodium carbonate monohydrate (the larger, well-defined crystals) formed later than the $2Na_2CO_3 \cdot Na_2SO_4$ crystals from solutions of sodium carbonate and sodium sulfate in a molar ratio of 7:1. The cores of the crystals are agglomerates of dicarbonate crystals [16].



9. The number of 1–10 µm crystals in suspension during the evaporation of solutions of sodium carbonate and sodium sulfate at different molar ratios.

study, however, there have been no conclusive results reported about any other solid species present in the Na_2CO_3–Na_2SO_4–H_2O system.

Crystallization from black liquor

Similar crystallization experiments were carried out with black liquor at 130°C. Those results are shown in **Fig. 6**. Also included are the aqueous solution and crystal composition data from Fig. 4, along with Grace's equilibration data for Na_2CO_3 and Na_2SO_4 in black liquor [11]. In Fig. 6, there is an additional composition region, $0.68 < x < 0.82$ for x as Na_2CO_3, where both burkeite and dicarbonate were found in the crystal phase. The other composition regions are the same as in Fig. 4.

The regions where dicarbonate or both burkeite and dicarbonate are found in the crystalline phase is important for industrial black liquor evaporators. Data collected during a 1998 survey of black liquor evaporator fouling [15] indicate that about 60% of these evaporators have a black liquor composition that falls within the composition range of $0.68 < x < 0.89$ for x as Na_2CO_3. The compositions of the dissolved sodium salts in all of the liquors in that survey would move into that composition range when concentrated to about 70% total solids content.

NUCLEATION AND CRYSTAL GROWTH

During the evaporation of water from sodium carbonate and sodium sulfate solutions, more than one solid phase could be crystallized as the solution composition changes during crystallization. Solutions whose compositions are initially in the burkeite crystallization region shift toward and ultimately into the dicarbonate crystallization region as crystallization proceeds. This shift occurs because the mole ratio of Na_2SO_4/Na_2CO_3 in burkeite crystals always exceeds 1, so more Na_2SO_4 than Na_2CO_3 is depleted from the solution when burkeite crystallizes.

The data in **Fig. 7** are for an aqueous solution of Na_2CO_3 and Na_2SO_4 having a composition that was initially in the burkeite crystallization region, or a Na_2CO_3/Na_2SO_4 mole ratio of 3:1. During the evaporation of water, two primary nucleation events were observed: the nucleation of burkeite beginning at a total solids content just above 35%, followed by the nucleation of dicarbonate at a total solids content of 42%. In both cases, numerous fine crystals were created abruptly, but the number of fine crystals was about five times greater when dicarbonate crystallized.

Solutions with compositions initially in the dicarbonate crystallization region produce crystals that are enriched in sulfate compared with the solution. As dicarbonate crystals are produced, the composition of the solution shifts toward the Na_2CO_3 crystallization region. Once the solution composition has reached the boundary of the Na_2CO_3 crystallization region, however, both dicarbonate and Na_2CO_3 crystallize to maintain a nonchanging solution composition [16]. For a solution with an original composition in the dicarbonate crystallization region (Na_2CO_3/Na_2SO_4 mole ratio of 7:1), dicarbonate crystallized, producing small crystals that agglomerated. At the boundary, sodium carbonate monohydrate crystallized on the $2Na_2CO_3 \cdot Na_2SO_4$ crystal agglomerates (**Fig. 8**), revealing an affinity of sodium carbonate monohydrate for the $2Na_2CO_3 \cdot Na_2SO_4$ crystals.

The amount of fine crystals produced during a primary nucleation event depends on the ratio of Na_2CO_3 to Na_2SO_4 in the system, as **Fig. 9** shows. For solutions initially in the burkeite crystallization region, the number of small crystals produced when burkeite nucleates increases as the ratio of Na_2CO_3 to Na_2SO_4 increases. In Fig. 9, the initial total salt concentrations were the same in each experiment, and the evaporation rates were approximately the same. The longer time to achieve primary nucleation with increasing ratios indicates that the degree of supersaturation required for nucleation increased with increasing ratios of Na_2CO_3 to Na_2SO_4.

A second major nucleation event occurs at about 330 min into the evaporation run in the solutions that have a ratio of Na_2CO_3 to Na_2SO_4 of 4:1 or 5:1. This second event corresponds to the

nucleation of dicarbonate. The amount of fine crystals produced during these nucleation events is about the same as produced during the primary nucleation of burkeite.

EFFECTS OF CALCIUM ON THE SOLID SPECIES

We discovered that a small amount of calcium ion acts as a nucleation inhibitor for both burkeite and dicarbonate crystals. When nucleation was inhibited, higher levels of supersaturation developed before primary nucleation occurred, and many more crystals were produced upon nucleation. Conversely, when the calcium ions were removed by sequestration with EDTA, primary nucleation occurred at lower total concentrations of Na_2CO_3 and Na_2SO_4 in the burkeite, dicarbonate, and Na_2CO_3 crystallization regions, and fewer crystals were produced during nucleation.

Figure 10 illustrates the impact of calcium ion on the nucleation of burkeite and dicarbonate as water evaporates from black liquor. When no calcium was added, the primary nucleation of burkeite occurred at about 55% total solids content, and it did not produce many small crystals. A second nucleation event, during which dicarbonate began to crystallize, occurred at about 68% total solids content and produced a large number of small crystals. When 100 ppm $CaCO_3$ was added to the liquor, relatively few small crystals were produced when the black liquor was concentrated to the same total solids content.

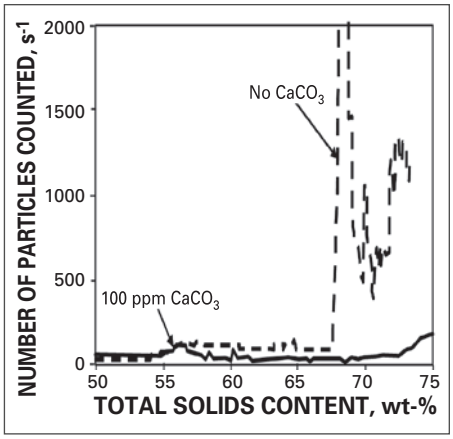
SCALING CHARACTERISTICS

In this work, we have identified two mechanisms by which soluble-scale deposits form during black liquor evaporation. They are (a) the agglomeration of fine crystals on heat transfer surfaces after primary nucleation and (b) crystal growth from a supersaturated solution below the metastable limit. These two scale deposition processes have different characteristics. However, both can contribute to scaling within the same evaporator effect, with the agglomeration of fine particles on a heat transfer surface serving as a scale initiation mechanism and with scale growth continuing via the supersaturation-driven growth of crystals on the scale surface.

The primary nucleation of dicarbonate crystals from black liquor causes heat transfer surfaces to foul rapidly. The metastable limit for sodium salts in aqueous solutions and in black liquor can be more than 10% higher than the solubility limit. This level of developed supersaturation is unusually high compared with most other solutions. It means that a large amount of potential scale is produced during a nucleation event—about 10 tons/day for a mill that produces 1000 a.d. tons of pulp per day. The fine crystals produced during nucleation agglomerate rapidly. In semi-batch pilot evaporator trials, where black liquor was concentrated to above the point at which the primary nucleation of $2Na_2CO_3 \cdot Na_2SO_4$ crystals occurred, the heat transfer surface always began to foul rapidly just before the onset of primary nucleation.

The primary nucleation of burkeite crystals from black liquor did not cause the rapid fouling of heat transfer surfaces in pilot evaporator experiments. In bench-scale experiments, burkeite scale did deposit, during nucleation, on surfaces where $CaCO_3$ scale had been deposited previously. However the surfaces where this deposition occurred were unheated surfaces. It has been observed that calcium carbonate and burkeite scales are sometimes present simultaneously in the samples of black-liquor scales, with calcium mostly concentrated on the side of the scale attached to the heat-transfer surfaces [14] That observation suggests that calcium scale formed first, followed by an overlay of burkeite scales. However, our experiments showed that calcium carbonate does not provide a nucleation or growth template for burkeite on heat transfer surfaces.

Once crystals or crystal nuclei are attached to a heat-transfer surface, scale will grow as long as there is some level of supersaturation in the liquor. The rate of scale growth depends on the degree of supersaturation, the total surface area of suspended crystals, and the crystallization kinetics of the particular crystal being grown. An important unknown is the mechanism by which scales are initiated on a clean heat-transfer surface. The importance of surface nucleation *per se* has not yet been established.



10. Primary nucleation of burkeite and dicarbonate from black liquor with (a) no $CaCO_3$ added and (b) 100 ppm $CaCO_3$ added, based on dry black liquor solids [17].

IMPLICATIONS TO SCALE CONTROL

From a practical perspective, three questions must be answered when designing or optimizing black liquor concentrators to minimize Na_2CO_3–Na_2SO_4 scales:

- When will fouling occur?
- Where will fouling occur?
- How can fouling be avoided or minimized?

According to our results, the black liquor solids content at which Na_2CO_3 and Na_2SO_4 begin to foul concentrators depends both on the amounts of Na_2CO_3 and Na_2SO_4 in the liquor and on their ratio. One condition for the onset of dicarbonate crystallization during evaporation is that the mole ratio of $Na_2CO_3/(Na_2CO_3 + Na_2SO_4)$ in solution falls between 0.68 and 0.89. In some mills, the black liquor composition is in this range before sodium salts begin to crystallize. In these mills, dicarbonate fouling of black liquor concentrators may begin when the black liquor is concentrated to 50–55% solids content.

In other mills, the black liquor composition is outside of this range before crystallization begins. However, the crystallization of burkeite removes more sulfate than carbonate. As burkeite crystallizes, the composition of the dissolved sodium salts shifts toward this range and eventually shifts into it. The liquor solids content where the transition from burkeite to dicarbonate crystallization

(and scaling) occurs depends mainly on two factors: (a) the ratio of carbonate to sulfate in the liquor *before* the onset of burkeite crystallization and (b) the total amount of sulfate and carbonate in the liquor. The relationship between solubility, liquor composition, and temperature must be known in order for us to predict accurately where dicarbonate crystallization will begin. This relationship is currently under investigation.

To minimize dicarbonate fouling in black liquor concentrators, it is important to (a) minimize the total amount of Na_2CO_3 + Na_2SO_4 in black liquor and (b) keep the ratio of Na_2CO_3 to Na_2SO_4 low. A good target for this ratio is no greater than a mass ratio of 2. Control of the Na_2CO_3 and Na_2SO_4 content in black liquor is achieved through good operation and good control of the recausticizing plant (to minimize carbonate) and the recovery boiler (to achieve high sulfate reduction), as well as by the proper management of recovery boiler ash recycling, makeup chemicals, and the input of waste streams. The optimization of these areas to achieve the desired black liquor composition is specific to each mill.

Other operating measures may also help. For example, our work showed that burkeite crystals are not good surfaces on which to grow dicarbonate crystals. It may therefore be important to operate the black liquor concentrators so that there is an adequate supply of dicarbonate crystals in those effects where dicarbonate is crystallizing. This means that the solids content of the product liquor from those effects must be well above the solids content where dicarbonate begins to crystallize, not just barely above it. This option for controlling dicarbonate scale, as well as other options based on the application of our results via conventional crystallizer design and optimization practices, needs to be evaluated in pilot- and full-scale trials.

KEY REMAINING QUESTIONS

The guidelines set out in the preceding section are based on the implicit assumption that black liquor evaporation, the crystallization of sodium salts, and fouling are steady state processes that proceed continuously and steadily. This assumption is of course not totally valid, for at least two reasons. First, evaporation is subject to throughput changes, black liquor composition changes, different amounts of heat conducted across different areas of the surface, and other upsets. Second, crystallization processes themselves can operate unsteadily but within bounds—for example, in a limit cycle. One important question is, how stable is the crystallization process within each effect? Is crystallization cyclic in some effects, so that the crystal population oscillates, and do nucleation events and fouling occur periodically?

A second important question is, can crystal nucleation or growth inhibitors prevent dicarbonate scaling? The effectiveness of calcium and other ions in suppressing primary nucleation, which was established in our work, suggests that this approach may be successful but that further development and evaluation is needed. **TJ**

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INSIGHTS FROM THE AUTHORS

Fouling of black liquor evaporators is a costly problem in the pulp and paper industry. However, it is one that can be resolved through better understanding of the crystallization behavior of the materials that foul the heat transfer surfaces.

This work represents the first real effort to relate the crystallization of sodium sulfate and sodium carbonate to the fouling of black liquor evaporators. The most surprising finding was the tremendous impact of calcium ion on the crystallization behavior and the fouling rate.

It was difficult to measure the onset of crystallization and difficult to measure changes in the size distribution of the crystals that were being formed. We overcame this problem by adapting a laser-based device originally developed for on-line measurements with slurries to the more challenging environment of black liquor evaporators.

It is possible for mills to reduce the fouling of the heat transfer surfaces and increase the capacity of black liquor evaporators by controlling crystallization. The strategy is to cause Na_2SO_4 and Na_2CO_4 to crystallize in suspension and not on heat transfer surfaces. This approach will need to be evaluated through pilot-plant and mill evaporator trials.

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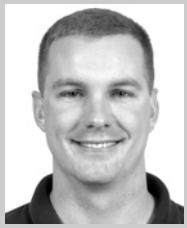

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