Minimizing Sodium Sulfate - Sodium Carbonate Fouling in Black Liquor Evaporators and High Solids Concentrators

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Abstract

Fouling of heat transfer surfaces in black liquor evaporators and high solids concentrators by Na_2CO_3 and Na_2SO_4 salt scales continues to be problematic in many kraft pulp mills. This is in spite of the considerable gains made in the past fifteen years in understanding the processes that lead to fouling by Na_2CO_3 and Na_2SO_4. Today's challenges for controlling Na_2CO_3 - Na_2SO_4 fouling arise from a lack of understanding of how to apply the available crystallization knowledge to the conditions that lead to fouling and the crystallization process itself to minimizing fouling.

This paper reviews briefly the concentration-driven crystallization process in black liquor evaporators and high solids concentrators, and when and how that causes fouling. Most of the paper deals with scale control through managing black liquor and liquor cycle chemistry, and through controlling crystallization behavior and where it occurs within the evaporator-concentrator set. A new tool developed for configuration of liquor chemistry-dependent concentration and flow sequencing in black liquor evaporators and concentrators is introduced. Summaries of two case studies of control of Na_2CO_3 - Na_2SO_4 fouling in real mill situations are presented.

Introduction

Fouling of black liquor evaporators and high solids concentrators by sodium carbonate and sulfate deposits has plagued black liquor evaporators since product liquor solids content began to exceed the solubility limits of these salts. Prior to the 1980s, most black liquors were relatively rich in sodium sulfate, and the fouling problems were mainly attributed to burkeite. Burkeite is a double salt of sodium sulfate and sodium carbonate, with a nominal composition of $2Na_2SO_4 \cdot Na_2CO_3$, although the sulfate to carbonate mole ratio can vary from 1.4 to 2.2 (Green and Frattali, 1946). Grace and coworkers investigated the chemistry and fouling characteristics of burkeite fouling (Grace, 1976, Frederick and Grace, 1981). Grace brought into use the term *critical solids content* to describe the lowest dry solids content of black liquor where suspended sodium salts are in equilibrium with the solution phase, i.e. the dry solids content at the solubility limit of the sodium salts in black liquor. Their work led to evaporator modifications and liquor cycle chemistry improvements that largely eliminated burkeite fouling in black liquor evaporators.

With increases in sulfate reduction and decreases in sulfur inputs to the recovery cycle, the sodium carbonate to sodium sulfate ratio in many black liquors has increased over

time. High solids concentrators have come into use, replacing direct contact evaporators and the early flow-enhanced LTV concentrators. By the 1990s, high solids concentrators capable of concentrating black liquor to 75-80 percent dry solids content were installed and operating. Many of these concentrators encountered sodium salt fouling problems that could not be mitigated with methods used to manage burkeite scales.

In early 1997, it was recognized that the fouling problems in high solids concentrators were crystallization related, and that crystallization of sodium salts from black liquors was not well enough understood to solve concentrator fouling problems (Shi and Rousseau, 1999, 2001; Shi et al., 2001; Shi, 2002). In subsequent investigations, Shi and Rousseau (2003) identified a new crystalline species, sodium sulfate dicarbonate that appeared to be responsible for evaporator fouling with sodium carbonate-rich black liquors. In further investigations, the solubility and crystallization characteristics of sodium sulfate dicarbonate were measured and modeled, and its propensity to foul was demonstrated through pilot evaporator studies (Shi and Rousseau, 1999, 2001, 2003; Shi et al., 2001, 2003; Euhus, 2003a, 2003b; Frederick et al., 2004; Soemardji et al., 2004; Verrill and Frederick, 2005a, 2005b, 2005c; Bayaudri et al, 2006a, 2006b, 2006c; DeMartini and Verrill, 2007; Bialik, 2008; Bialik et al., 2007, 2008; Gourdon et al., 2008; Gourdon, 2009). The term *metastable limit*, which defines the onset of crystallization from crystal-free black liquor, replaced the term *critical solids content* as the defining point for the onset of fouling in high solids concentrators.[1] This work led to guidelines for minimizing dicarbonate scales in evaporators and high solids concentrators. Application of those guidelines alone has been less than successful in eliminating dicarbonate fouling in many high solids black liquor concentrators.

Objectives

The objectives of this paper are:

1. To review the concentration-driven crystallization process in black liquor evaporators and high solids concentrators with respect to sodium carbonate - sodium sulfate fouling.
2. To introduce a new method for evaluating conditions that lead to sodium carbonate - sodium sulfate fouling, and those that do not.
3. To evaluate options for minimizing or eliminating sodium carbonate - sodium sulfate fouling through control of liquor cycle chemistry.
4. To demonstrate control methods using data from various kraft pulp mills that are plagued with sodium carbonate - sodium sulfate fouling.

Sodium Salt Solubility, Crystallization, and Fouling

Evaporators are fouled by Na_2CO_3 and Na_2SO_4 when these salts crystallize from black liquor as it is concentrated. Na_2CO_3 and Na_2SO_4 are the least soluble salts in black liquor. They begin to crystallize when black liquor is concentrated to 45-55% dry solids content (Grace, 1976).

[1] Crystallization of burkeite and dicarbonate occur sequentially in some black liquors. In these liquors, two distinctly different metastable limits are encountered.

Different combinations of Na_2CO_3 and Na_2SO_4 crystallize when black liquor is concentrated to and above the solubility limit of the salts. They include:

1. Burkeite: its nominal composition is $2Na_2SO_4 \cdot Na_2CO_3$ but its composition can range from 1.4 to 2.2 moles of sulfate per mole of carbonate (Green & Frattali, 1946).
2. Sodium sulfate dicarbonate: commonly referred to as dicarbonate, it has a nominal composition of $2Na_2CO_3 \cdot Na_2SO_4$ but whose composition can range from 1.2 to 2.6 moles of carbonate per mole of sulfate (Shi and Rousseau, 2003; Frederick et al., 2004).
3. Sodium carbonate: crystallizes as anhydrous sodium carbonate (Na_2CO_3) above 109^{o}C, and as sodium carbonate monohydrate ($Na_2CO_3 \cdot H_2O$) below that temperature (Shi, 2002; Bayuadri et al, 2006a).

Crystals of a uniquely different fourth double salt, sodium sulfate carbonate with a stoichiometry $Na_2CO_3 \cdot Na_2SO_4$, were identified in one case (DeMartini and Verrill, 2007). It is not clear whether the 1:1 species was a stable double salt or a metastable form created by solution mediated recrystallization, where a nonequilibrium crystalline solid such as sodium sulfate is dissolved and recrystallized as e.g. the 1:1 double salt sodium sulfate carbonate. The occurrence of sodium sulfate carbonate in other black liquors has not been reported in the literature.

The stoichiometric ratios of sodium carbonate and sodium sulfate in burkeite and dicarbonate that are crystallized are related directly to the ratios of sodium carbonate and sodium sulfate in solution. The relationship is illustrated in Figure 1 for both kraft black liquors and aqueous solutions of sodium carbonate and sodium sulfate (adapted from Shi, 2002). The values along the horizontal and vertical axes are the mole ratio of $Na_2CO_3/(Na_2CO_3+Na_2SO_4)$ in the solution and crystalline phase respectively. Figure 1 is divided into four regions that correspond to crystallization of sodium sulfate (leftmost), burkeite (second from left), dicarbonate (second from right), and sodium carbonate (rightmost). The compositions of black liquors containing mole ratios of $Na_2CO_3/(Na_2CO_3+Na_2SO_4)$ from 0.4 to 0.93 were reported in one survey of black liquor evaporators (Schmidl & Frederick, 1998).

Definition: we define the symbol ***x*** as the mole ratio of $Na_2CO_3/(Na_2CO_3+Na_2SO_4)$: in solution, and ***y*** as the ratio in crystalline solids. This follows the convention used by Shi (2002).

When crystallization starts at a solution composition with ***x*** less than 0.89, the composition of black liquor moves to the right along the ***x*** axis as water is removed by evaporation and progressive crystallization depletes both carbonate and sulfate from the black liquor. The composition of the crystals produced also changes as water is evaporated and the solution composition changes with a sudden shift from burkeite to dicarbonate when the border between those regions is reached.

The vertical border between the dicarbonate and sodium carbonate regions in Figure 1 has a special significance. When ***x*** in black liquor reaches or falls at a value of 0.89, then dicarbonate and Na_2CO_3 crystallize in ratios that maintain a non-changing solution composition (Shi 2002; Frederick et al, 2004). This location is referred to an invariant

point. Movement along the horizontal axis can be in either direction, depending upon which side of ***x*** = 0.89 the solution begins. Black liquors very rich in sodium carbonate will crystallize sodium carbonate and move leftward along the ***x***-axis until the mole ratio in solution drops to the invariant composition. ***x*** = 0.89 is the location of the invariant point and corresponds to a Na_2CO_3/Na_2SO_4 mass ratio of 6.0 (Shi, 2002; Frederick et al., 2004; Soemardji et al., 2004).

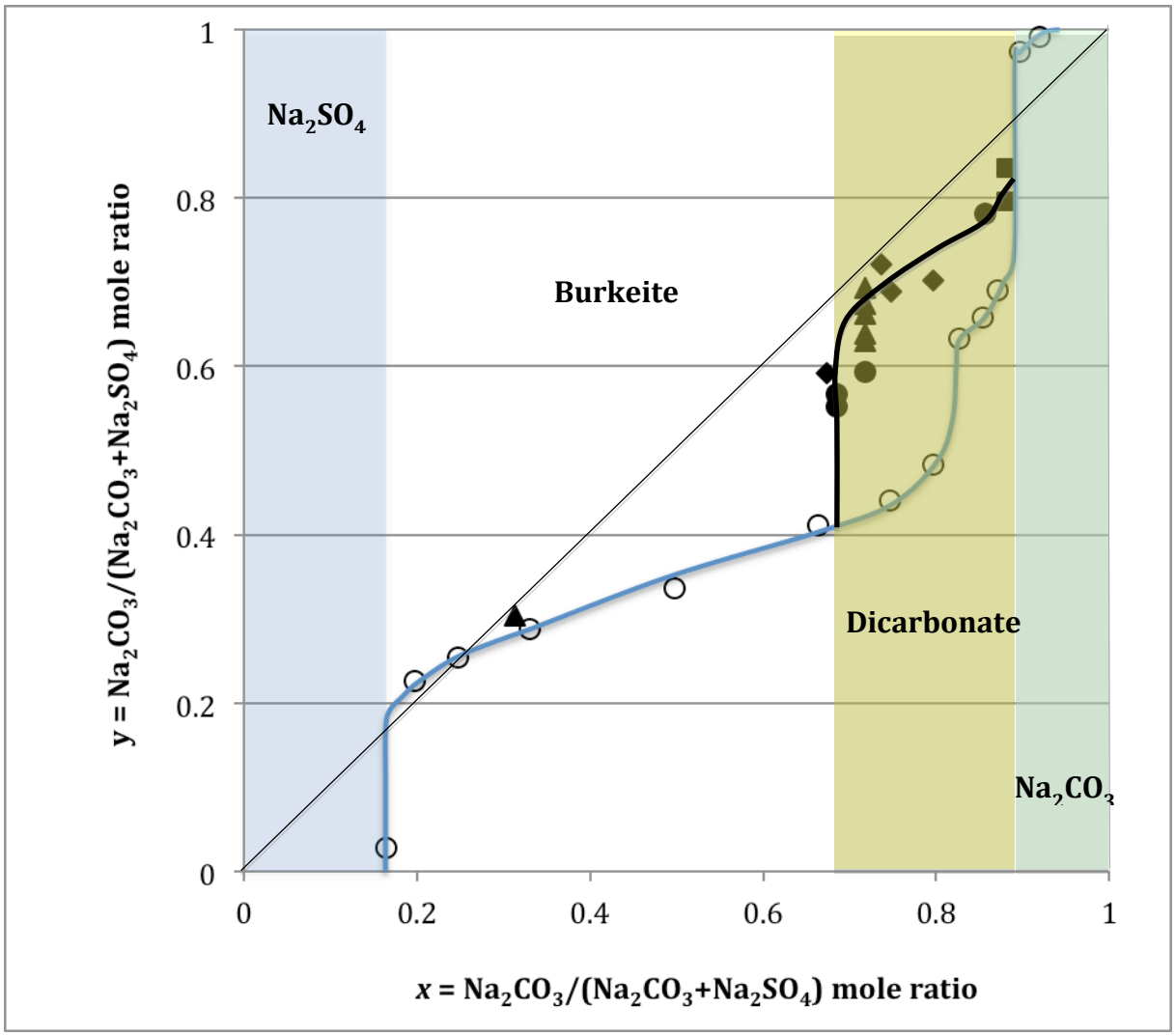


Figure 1. Stability diagram for sodium carbonate – sodium sulfate in crystals and in solution for aqueous solutions (blue line and open circles) and black liquor (black line and filled symbols). The filled colored regions denote crystal types in black liquor. The diagram is applicable from 239°F to 293°F (115°F to 145°C).

Dicarbonate Characteristics

Dicarbonate crystallizes from black liquor as many very fine particles generated in massive, spontaneous nucleation events. The individual dicarbonate particles that nucleate spontaneously are initially sub-micron in diameter. They grow to about 10 microns and agglomerate into aggregates, the same way that they form scale. Individual dicarbonate particles remain much smaller than burkeite particles that nucleate and grow more slowly (See Figure 2). These small dicarbonate particles grow slowly after nucleation (Shi, 2002; Euhus, 2003).

Verrill and coworkers (2005) found ~1 mm dicarbonate nodules, shown in Figure 3, in the sump of a tubular, falling film evaporator. No other evidence of fine dicarbonate particles or agglomerates continuing to grow in suspension in black liquor has been reported. Figure 4 shows very slow crystal growth following the massive nucleation and fine particle agglomeration of dicarbonate from a solution of pure salts in water. Dicarbonate crystal growth on suspended crystals would be necessary to prevent black liquors in the dicarbonate crystallization region to supersaturate and repeatedly initiate massive nucleation events. Dicarbonate crystals do not grow on either burkeite or sodium carbonate crystals (*Shi et al., 2001; Shi, 2002; Bayuadri, 2006*).

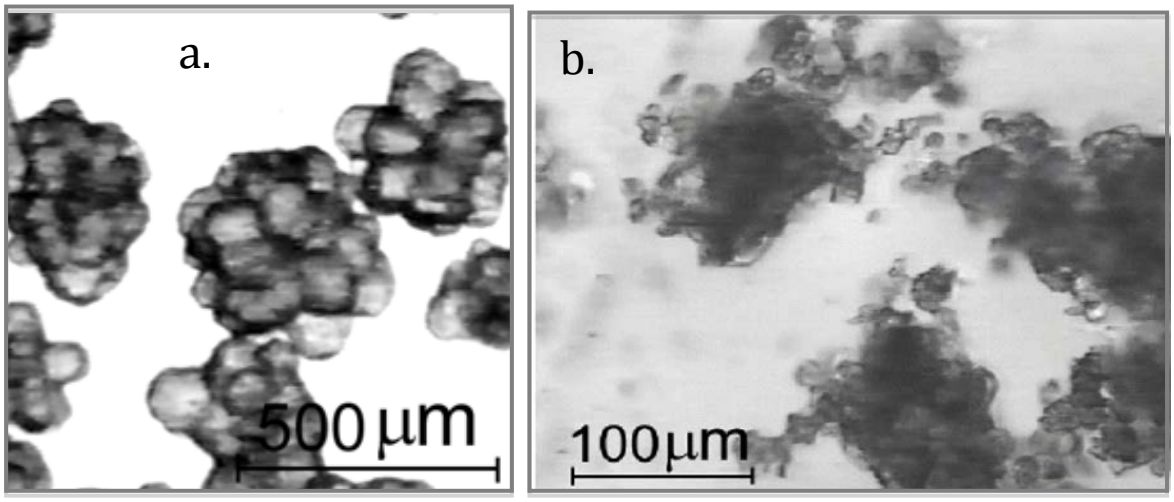


Figure 2. Crystals of (a) burkeite and (b) dicarbonate (Na_2CO_3/ Na_2SO_4 mass ratio of 3.7:1). From Shi et al. (2001) and Shi (2002).



Figure 3. Dicarbonate nodules containing 95 wt. % Na_2CO_3+Na_2SO_4 collected from the sump of a tubular, falling-film evaporator. From Verrill et al., 2005

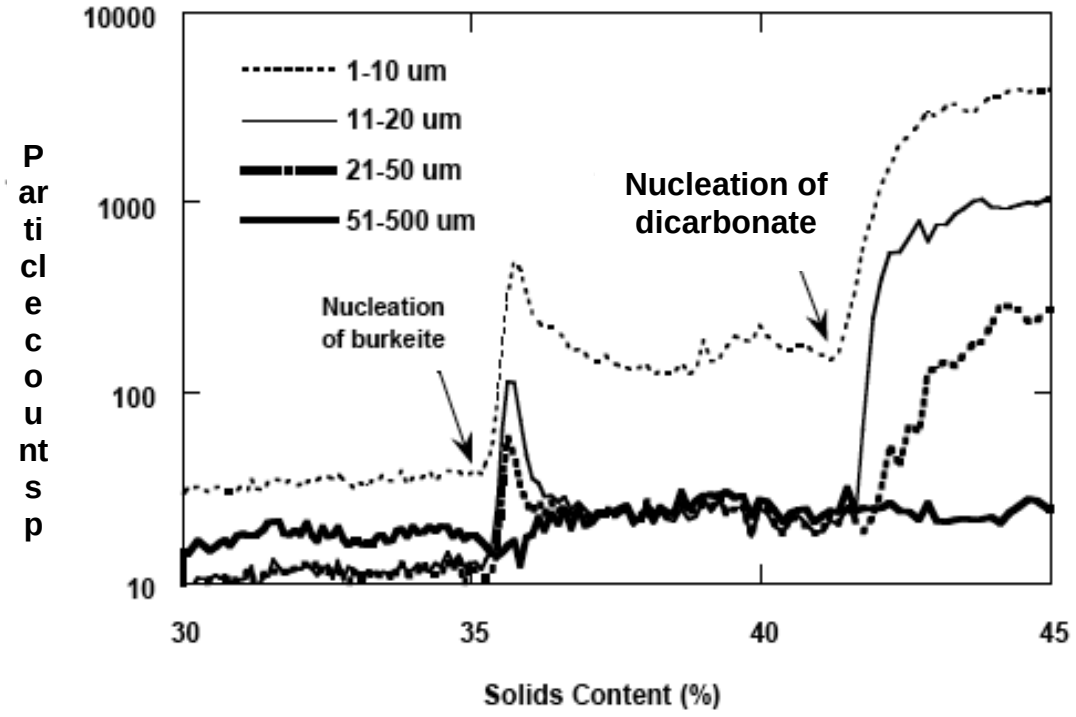


Figure 4. Crystal growth and agglomeration following nucleation events for burkeite and dicarbonate (adapted from Shi, 2002).

Conditions for Dicarbonate Fouling

Dicarbonate can form in black liquor concentrators only under these conditions:

1. The black liquor temperature exceeds 239°F. (The temperature of black liquor in high solids concentrators is normally between 250°F and 280°F (121°C and 138°C)).
2. The concentrations of sodium carbonate and sodium sulfate in black liquor exceed their solubility limit.
3. ***x*** exceeds the minimum stability limit for dicarbonate. The value for that limit in black liquor is 0.68 as shown in Figure 1. It corresponds to a Na_2CO_3/Na_2SO_4 mass ratio equal to 1.59.

Sodium Carbonate Characteristics

Na_2CO_3 crystallizes from black liquor when ***x*** > 0.89. It co-crystallizes from black liquor along with dicarbonate at the invariant point for sodium carbonate and dicarbonate. Sodium carbonate solutions supersaturate when concentrated by evaporation, but crystals nucleate and grow to large, regular-shaped ones (Figure 5).

The type of crystals produced by crystallization near the invariant point for sodium carbonate and dicarbonate depends upon from which side the invariant point is approached. When ***x*** is initially below 0.89, dicarbonate agglomerates are crystallized first, and then Na_2CO_3 crystallizes on the dicarbonate agglomerates when the invariant composition in solution is reached (see Figure 5a). However, when ***x*** is initially above 0.89, Na_2CO_3 crystallizes first until the carbonate content in solution decreases enough to reach the invariant point, and both dicarbonate agglomerates and sodium carbonate crystals are produced separately (see Figure 5b).

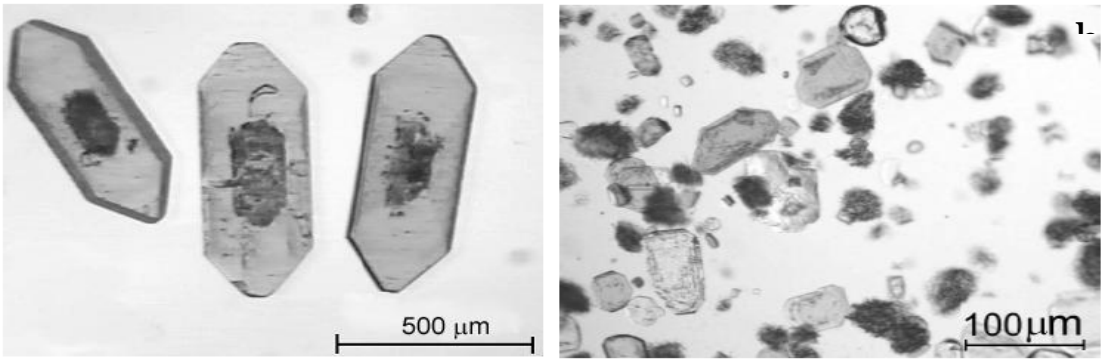


Figure 5. Crystallization of dicarbonate and Na_2CO_3 beginning on opposite sides of the dicarbonate - sodium carbonate invariant point: (a) from a solution with an initial Na_2CO_3/Na_2SO_4 mass ratio of 5.2 where dicarbonate crystallized first and $Na_2CO_3 \cdot H_2O$ crystallized over it; (b) from a solution with an initial Na_2CO_3/Na_2SO_4 mass ratio of 6.7 where $Na_2CO_3 \cdot H_2O$ and dicarbonate crystallized as separate crystals. From Shi, 2002.

Dicarbonate Fouling: A New Paradigm

The information on dicarbonate and sodium carbonate crystallization, along with empirical knowledge of fouling in black liquor concentrator bodies, form the basis for a new paradigm for dicarbonate fouling. We know that dicarbonate crystals and agglomerates are small and prone to fouling heat transfer surfaces (Euhus, 2003; Euhus et al., 2003; Gourdon et al., 2008, 2010). We also know that there is apparently no effective mechanism for relief of supersaturation other than another cycle of massive nucleation of dicarbonate and fouling.

1. The available empirical knowledge of fouling in black liquor concentrator bodies is that, while many are fouled by dicarbonate, other concentrator bodies operate with manageable fouling rates as long as they are running well above the dicarbonate metastable limit, e.g., making 70% dry solids content product from 50% dry solids content feed. We also know that recycling concentrator product liquor helps to stabilize the crystallization (there are successful examples of this applied both continuously and after boilouts), suggesting some crystal growth is occurring or another mechanism is in play.
2. The temperature of black liquor must be 115^{o}C or higher for dicarbonate to crystallize from black liquor.
3. We believe there are two different paths that black liquors with high ratios of sodium carbonate to sodium sulfate follow when they are concentrated to high dry solids content. When $\boldsymbol{x}$ is initially above 0.89, Na_2CO_3 crystallizes first until the invariant point is reached, then both dicarbonate agglomerates and sodium carbonate crystals are produced (see Figure 5b). However, when black liquor concentration approaches the dicarbonate – sodium carbonate invariant point from below the invariant point (from $\boldsymbol{x} < 0.89$), dicarbonate crystallizes first and can foul until the invariant composition is reached. From there on, both dicarbonate and Na_2CO_3 crystallize, with Na_2CO_3 crystals growing on the dicarbonate agglomerates (see Figure 5a). Under this condition, crystals may be produced with dicarbonate cores encapsulated in sodium carbonate. We believe that encapsulation of dicarbonate agglomerates in sodium carbonate crystals would reduce dicarbonate fouling.
4. Under other evaporator conditions for black liquors with high ratios of sodium carbonate to sodium sulfate, the liquors are not concentrated to high enough dry solids content to reach the invariant point where dicarbonate and sodium carbonate co-crystallize. Under these conditions, concentrator bodies are fouled by dicarbonate during massive nucleation events. These massive nucleation events occur repeatedly. Fouling of concentrator body heat transfer surfaces appears to proceed continuously, although it may actually proceed by deposition of layers of scale cyclically at frequent intervals.
5. We know that black liquors with a low initial ratio of sodium carbonate to sodium sulfate crystallize burkeite but may never reach a condition where they transition to dicarbonate crystallization. These liquors crystallize burkeite and do not foul

high solids concentrator bodies nearly as rapidly as do burkeite or Na_2CO_3 (Gourdon, 2009).

Estimating Solubility of and Crystal Phase Transitions for Burkeite and Dicarbonate in Black Liquor

The solubility of sodium carbonate and sodium sulfate and the transitions between crystal phases can be calculated using this information:

1. Mass balance closure of species (Na^+, CO_3^{2-}, and SO_4^{2-}) in the system.
2. Charge balance closure for Na^+, CO_3^{2-}, and SO_4^{2-}.
3. Equilibrium constraint(s) for the applicable chemical equilibrium (burkeite or dicarbonate) involved.

BLFoul™ is a proprietary software package and tool created for estimating solubility of and crystal phase transitions for burkeite and dicarbonate in black liquor. Empirical correlations are used for stoichiometric parameters in the equilibrium relationships for dicarbonate and burkeite, e.g. γ in:

$$K_i = [Na^+]^6[CO_3^{2-}]^{\gamma}[SO_4^{2-}]^{3-\gamma} \quad (1)$$

BLFoul™ was developed at Table Mountain Consulting, LLC. It was used to predict at what dry black liquor solids content dicarbonate crystallization would begin, and where the invariant point for co-crystallization of dicarbonate and Na_2CO_3 would occur. It has been used in calculations to generate results presented throughout this paper. It will be referred to throughout the paper as "the burkeite-dicarbonate solubility model."

Predictions of black liquor dry solids content at the solubility limits for burkeite and dicarbonate and at the invariant point were made using black liquor data from Schmidl and Frederick (1998) and from a few other sources. The sodium carbonate, sodium sulfate, and total sodium content of the black liquors evaluated are shown in Table 1. The fourth and fifth columns contain the calculated dry black liquor solids contents at the onset of dicarbonate crystallization, and for the onset of co-crystallization of dicarbonate + sodium carbonate (their invariant point). In some cases where one or the other crystal phases never occurred; in those cases, a label of "never" is entered in Table 1.

The results in Table 1 show that dicarbonate crystallization begins anywhere between 40% and 63% dry black liquor solids content, but generally begins at lower dry solids contents for higher sodium carbonate content. Dicarbonate never crystallizes by itself from black liquors with very high carbonate contents and low sulfate contents (liquors 16 and 17) that only co-crystallize dicarbonate and Na_2CO_3, or for liquors with much higher sulfate contents than carbonate content (liquor 8) that only crystallize burkeite.

Co-crystallization of dicarbonate and Na_2CO_3 will occur with seven of the twenty-seven black liquors in Table 1. The invariant point for these seven black liquors is predicted to occur over a range of dry black liquor solids from 45% to 60%. The dry black liquor solids content at the onset of co-crystallization decreases with increasing Na_2CO_3/Na_2SO_4 mass ratio in black liquor solids.

Table 1. Predicted dry solids content at which crystallization of dicarbonate alone begins, and where co-crystallization of dicarbonate + sodium carbonate begins for black liquors from 27 kraft mills. Results are for concentration of the black liquors up to 80% total dry solids content. All calculations were for a liquor temperature of 120^{o}C.

Black liquor number	Na_2CO_3, wt-% dry BL solids	Na_2SO_4, wt-% dry BL solids	Total Na, wt-% dry BL solids	Na_2CO_3/ Na_2SO_4 mass ratio	Na_2CO_3/Na_2CO_3+ Na_2SO_4 mole ratio)	Grace's critical solids	Onset of burkeite crystallization	Onset of dicarbonate crystallization	Onset of dicarbonate + Na_2CO_3 crys.
1	4.50	4.13	19.5	1.09	0.593	54.0%	49.9%	s	never
2	4.59	4.24	18.6	1.08	0.592	54.9%	50.6%	55.6%	never
3	4.77	5.49	17.1	0.87	0.538	55.8%	50.5%	59.7%	never
4	6.35	2.47	14.0	2.57	0.775	60.3%	never	51.5%	never
5	6.44	3.24	16.6	1.99	0.727	56.7%	never	48.2%	never
6	6.88	5.62	17.0	1.22	0.621	54.6%	49.4%	52.9%	never
7	7.06	3.02	17.8	2.34	0.758	55.0%	never	46.5%	never
8	7.50	14.61	18.2	0.51	0.417	50.9%	42.8%	never	never
9	8.21	2.23	19.3	3.68	0.831	53.1%	never	45.5%	54.1%
10	8.47	3.70	15.4	2.29	0.754	56.6%	never	47.2%	never
11	9.00	2.25	20.1	4.00	0.843	51.7%	never	44.1%	51.0%
12	9.88	2.19	19.4	4.51	0.858	52.1%	never	44.2%	48.8%
13	9.88	3.92	18.2	4.51	0.858	52.7%	never	43.5%	never
14	10.06	6.93	20.2	1.45	0.660	40.0%	never	39.6%	never
15	10.06	9.20	20.1	1.09	0.594	48.9%	42.9%	48.7%	never
16	10.15	0.89	17.3	11.40	0.939	55.1%	never	never	outside range
17	10.85	1.58	17.9	6.87	0.902	53.7%	never	never	outside range
18	11.47	4.42	19.5	2.60	0.777	50.5%	never	43.1%	never
19	11.47	5.00	18.5	2.29	0.754	51.4%	never	41.7%	never
20	11.47	10.38	18.2	1.11	0.597	50.9%	43.5%	49.5%	never
21	11.74	5.28	20.1	2.22	0.749	49.5%	never	40.0%	never
22	12.27	1.94	16.5	6.32	0.894	54.4%	never	46.0%	always
23	14.47	2.97	18.8	4.87	0.867	50.8%	never	41.8%	45.5%
24	14.47	4.11	17.5	3.52	0.825	52.0%	never	42.0%	54.5%
25	6.95	1.87	14.4	3.72	0.833	59.8%	never	51.7%	60.2%
26	7.70	3.68	20.0	2.09	0.737	51.8%	never	43.3%	never
27	10.14	3.25	20.0	3.12	0.807	50.8%	never	42.4%	57.8%

Validity of Predictions from the Burkeite-Dicarbonate Solubility Model

Since the mid 1970s, the standard for predicting the dry black liquor solids content at the onset of crystallization from black liquor has been Grace's "critical solids" correlation (Grace, 1975). Grace developed "a general correlation for Na_2CO_3-Na_2SO_4 solubility in black liquor by using the data of Green and Frattali and correcting it for the effect of liquor solids content." He reported a mean deviation of -0.6% and a standard deviation of 7.4% between his model and experimental solubility data.

To test the validity of results from the burkeite-dicarbonate solubility model, values of the dry black liquor solids content at the onset of burkeite and dicarbonate crystallization were calculated for the 27 black liquors whose compositions are listed in Table 1. The predicted values are compared with predictions of the onset of first crystallization using Grace's method (1976). The results, plotted in Figure 6, show that, when compared with Grace's method, the burkeite-dicarbonate solubility model under predicted the dry black liquor solids content at the onset of crystallization of burkeite and dicarbonate for 20 of the 27 black liquors. The predictions for the onset of carbonate crystallization from the burkeite-dicarbonate solubility model agreed well with the critical solids predictions for the six black liquors where burkeite crystallization occurred before dicarbonate crystallization. The predictions are on average about 18% lower than those from Grace's method for the onset of burkeite values for seven of the black liquors. It predicts on average about 13% too low for the onset of dicarbonate value for twenty of the black liquors.

At least two factors could account for the consistently low predictions for the dry black liquor solids content at the onset of burkeite and dicarbonate crystallization. First, the calculated results from the burkeite-dicarbonate solubility model correspond to the solubility limits of the two crystal species in black liquor. However, the onset of crystallization occurs not at the solubility limit but instead at the metastable limit for burkeite and dicarbonate. Shi and coworkers measured the metastable limit for burkeite to be 15% above its solubility limit in aqueous solutions, and 5.6% above for anhydrous Na_2CO_3, both at 120^{o}C (Shi and Rousseau, 2001). Verrill and coworkers (2005) measured the metastable limit for dicarbonate in black liquor to be equivalent to 7% of total black liquor solids at 115^{o}C and 5% at 134^{o}C. The difference between the solubility limit and the metastable limit for burkeite accounts for more than 75% of the difference between the dry black liquor solids predictions from the Grace method and those from the burkeite-dicarbonate solubility model. For dicarbonate, the difference between the solubility limit and the metastable limit accounts for half of the difference between the Grace method predictions and those from the burkeite-dicarbonate solubility model.

A second factor is how the activities of sodium, carbonate, and sulfate ions change as black liquor is concentrated (Bialik, 2008). The activities of carbonate and sulfate ions decrease with increasing ionic strength, so they decrease as black liquor is concentrated. If the stability constants used in the burkeite-dicarbonate solubility model were adjusted for differences in activity coefficients at higher black liquor concentrations, then the predicted dry black liquor solids content at onset of crystallization of burkeite and dicarbonate would be higher. Unfortunately, data or estimation procedures that are valid at the high ionic strengths in concentrated black liquors are not available (Bialik, 2008; Bialik et al., 2007, 2008).

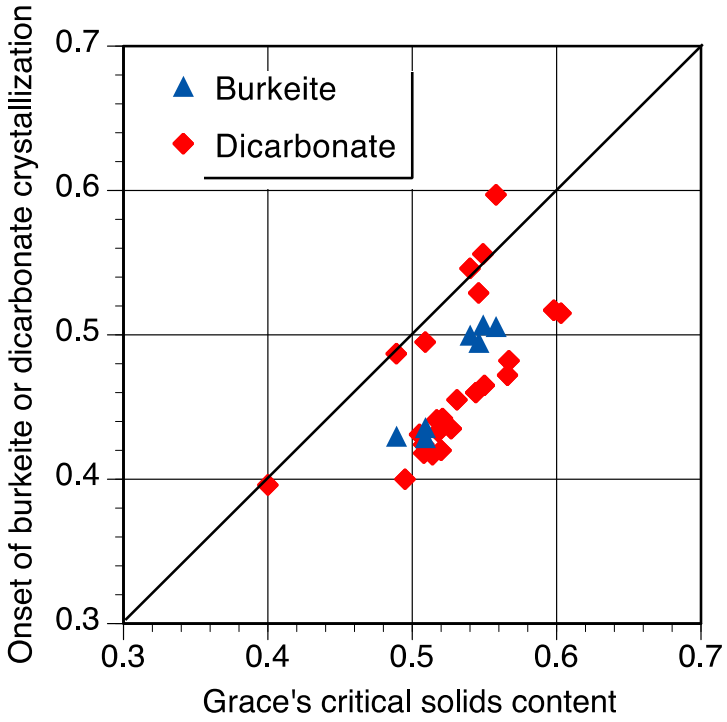


Figure 6. A plot of the dry black liquor solids mass fraction at the onset of crystallization of burkeite and dicarbonate predicted by the burkeite-dicarbonate solubility model versus predictions of dry black liquor solids content at Grace's critical solids content.

Practical Application

Figure 7 is a map that shows where dicarbonate begins to crystallize as black liquor is concentrated, for a given contents of sodium carbonate and sodium sulfate in dry black liquor solids. The numbers next to each data point are the dry black liquor solids contents at which dicarbonate begins to crystallize. A letter N indicates that dicarbonate did not crystallize at these conditions. The solid red line is the boundary between the burkeite and dicarbonate crystallization regions. The dashed red line is the boundary between the dicarbonate crystallization region and the region where dicarbonate and sodium carbonate co-crystallize. This map can be used to predict whether dicarbonate scale would be likely to occur, based on a mill's black liquor composition.

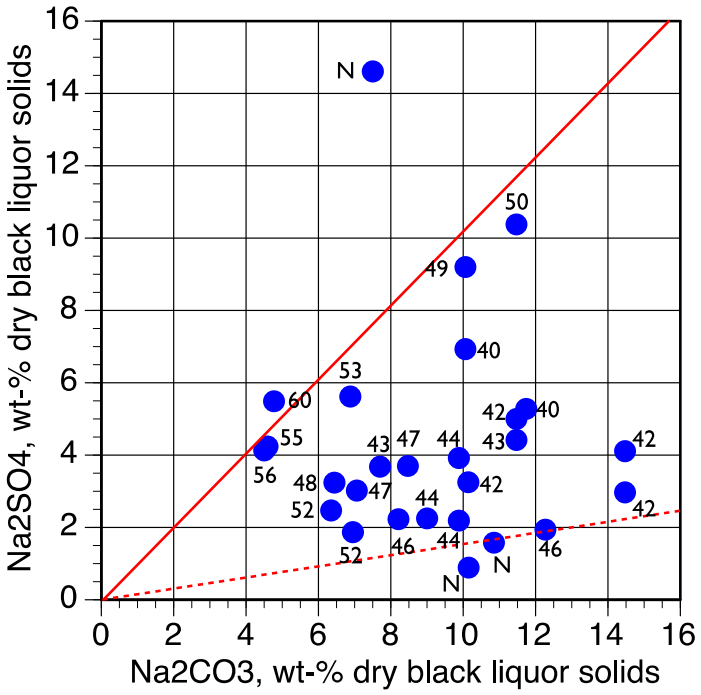


Figure 7. Map of regions of crystallization of burkeite and dicarbonate, and co-crystallization of dicarbonate and sodium carbonate from black liquor at 120°C. Numbers beside each data point are the wt-% dry black liquor solids content at the onset of dicarbonate crystallization as calculated by the burkeite-dicarbonate solubility model. The letter N indicates that the dry liquor solids were either too rich or too lacking in Na_2SO_4 for dicarbonate to crystallize during concentration of black liquor.

Example 1. Where is dicarbonate scale expected to be problematic in each of three high solids concentrators, with black liquor compositions and product liquor dry solids content shown.

Input data for analysis:

Case	A	B	C
Na_2CO_3, wt-% bls	7.70	6.95	10.14
Na_2SO_4, wt-% bls	3.70	1.87	3.25
Total Na, wt-% bls	20.0	14.4	20.0
Wt-% bl solids entering concentrator(s)	45	48	41
Wt-% bl solids in concentrator product	68	75	73

Analysis:

Case	A	B	C
Na_2CO_3,/Na_2SO_4 weight ratio in bls	2.08	3.72	3.12
Na_2CO_3,/(Na_2CO_3,+Na_2SO_4) mole ratio in bls	0.736	0.833	0.807
Solubility limit for dicarbonate, wt-% bls	43.3	51.5	42.4
Wt-% bls at metastable limit (for onset of crystallization)	46.4	55.1	45.4
Invariant point for dicarbonate + Na_2CO_3 crystallization, wt-% bls	> 80	60.2	57.8

Conclusions for Cases A-C:

Case A: dicarbonate crystallization and fouling will be severe throughout the concentrator bodies.

Case B: dicarbonate crystallization and fouling will be severe in concentrator bodies that operate between 55% and 60% dry solids content. In bodies that operate above 60% dry solids content, fouling may occur but will be less severe.

Case C: dicarbonate crystallization and fouling will be severe in concentrator bodies that operate between 45% and 58% dry solids content. In bodies that operate above 58% dry solids content, fouling may occur but will be less severe.

Example 2. Can sodium sulfate be added to black liquor to decrease the Na_2CO_3 to Na_2SO_4 mass ratio and eliminate dicarbonate fouling?

There are sources of sodium sulfate in a pulp mill that could be used for this purpose without increasing the dead load in the liquor cycle. One is electrostatic precipitator ash that contains from more than 60% to nearly 100% sodium sulfate (Frederick and coworkers, 2004). Another source is ClO_2 generator effluent.

In this example we evaluate the impact of adding ClO_2 generator saltcake to black liquor in order to control concentrator fouling.

Basis:

Black liquor that contains sodium carbonate and sodium sulfate in a weight ratio greater than 1.6 and less than 6.0 will potentially cause dicarbonate fouling when concentrated. Dicarbonate crystallization by itself in black liquor concentrators can foul them severely.

The concentrator in this case is a 3-body falling-film unit, receiving 45 wt-% ds black liquor, and concentrating it to 68%.

Without ClO_2 saltcake addition:

- The mill's black liquor contains 7.70 wt-% Na_2CO_3, 3.70 wt-% Na_2SO_4, and 20.00% total Na
- Before any crystallization the dissolved black liquor solids contain sodium carbonate and sodium sulfate in a weight ratio of 2.08 (***x*** = 0.736).
- The weight ratio of dissolved sodium carbonate and sodium sulfate in the black liquor reaches 6.0 when the dry solids content is above 80%. As a result, dicarbonate will never co-crystallize with anhydrous sodium carbonate in this unit.
- With two concentrator bodies in service for evaporation and one on wash:
    - The body receiving 45% ds black liquor and producing 56% ds black liquor will foul rapidly
    - The body receiving 56% ds black liquor and producing 68% ds black liquor will also foul rapidly. None of the dicarbonate agglomerates being crystallized will be encapsulated with sodium carbonate because sodium carbonate alone never crystallizes.

With saltcake addition (195 lb saltcake/ton dry black liquor solids):

- The mill's black liquor now contains 7.02 wt-% Na_2CO_3, 12.26 wt-% Na_2SO_4, and 21.10% total Na
- Before any crystallization, the dissolved black liquor solids with sulfate added contains sodium carbonate and sodium sulfate in a weight ratio of 1.04 (***x*** = 0.582).
- The weight ratio of dissolved sodium carbonate and sodium sulfate in the black liquor reaches 1.58 (***x*** = 0.679) when the dry solids content is 68%.
- With two concentrator bodies on evaporation and one on wash, neither concentrator body that is in evaporation mode should be fouled by dicarbonate. Burkeite, not dicarbonate should be crystallizing from black liquor in both bodies.

Recommendations for Controlling Dicarbonate and Dicarbonate + $Na_2CO_3 \cdot H_2O$ Fouling

Adjusting and controlling the Na_2CO_3/Na_2SO_4 mass ratio in black liquor is one way to minimizing dicarbonate fouling by controlling black liquor chemistry. A rough guideline to avoid dicarbonate fouling is to keep the weight ratio of Na_2CO_3/Na_2SO_4 to less than 1.6. More accurate predictions for the required Na_2CO_3/Na_2SO_4 mass ratio can be made using the burkeite-dicarbonate solubility model.

Adding saltcake at an effect prior to the effect(s) that fouls may be necessary to control the Na_2CO_3/Na_2SO_4 mass ratio. Available sources of saltcake are ESP ash and ClO_2 generator effluent. ESP ash is an internal stream to the recovery cycle. Recycling it to black liquor will not increase sulfidity. Adding ClO_2 generator saltcake will increase sulfidity if it is not already being introduced to the recovery cycle.

Dry saltcake such as ESP ash need to be added far enough upstream of the concentrator so that the saltcake dissolves completely before reaching the effect where dicarbonate first crystallizes.

A thorough evaluation of Na_2CO_3/Na_2SO_4 ratio control needs to be made to verify the effectiveness in controlling dicarbonate scale in black liquor concentrators.

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Minimizing Sodium Sulfate - Sodium Carbonate Fouling in Black Liquor Evaporators and High Solids Concentrators

Jim Frederick

Table Mountain Consulting, LLC

TMC

Persistence of Black Liquor Evaporator and Concentrator Fouling

Survey (N. Am.)	Grace, 1975	Schmidl, 1998	2012
Na_2CO_3-Na_2SO_4 fouling	28%	35%	???
$CaCO_3$ fouling	30%	22%	???
No fouling	15%	4%	???
Product BL % solids range	42-62	47-80	???
Boil out frequency avg. (range)	4.1 (0.3-15)	3.3 (0.08-12)	???
Heat flux range, kW/m^2	7.9-21.8	9.8-16.0	???
ΔT range, ^oF	9.3-23.3	10.6-15.9	???
Mills pulping softwood	69%	55%	???

Background

- **1970s**: Grace identified ***burkeite*** as foulant, measured solubility behavior and defined the concept of ***"critical solids content"***
  - ➔ Burkeite was manageable by applying Grace's concepts
- **1980s**: high solids concentrators were developed

Background

- **1990s:** black liquor concentrated to 75-80% dry solids content
  - ➔ Severe fouling of high solids concentrators
  - ➔ No longer manageable by applying Grace's concepts

What changed?

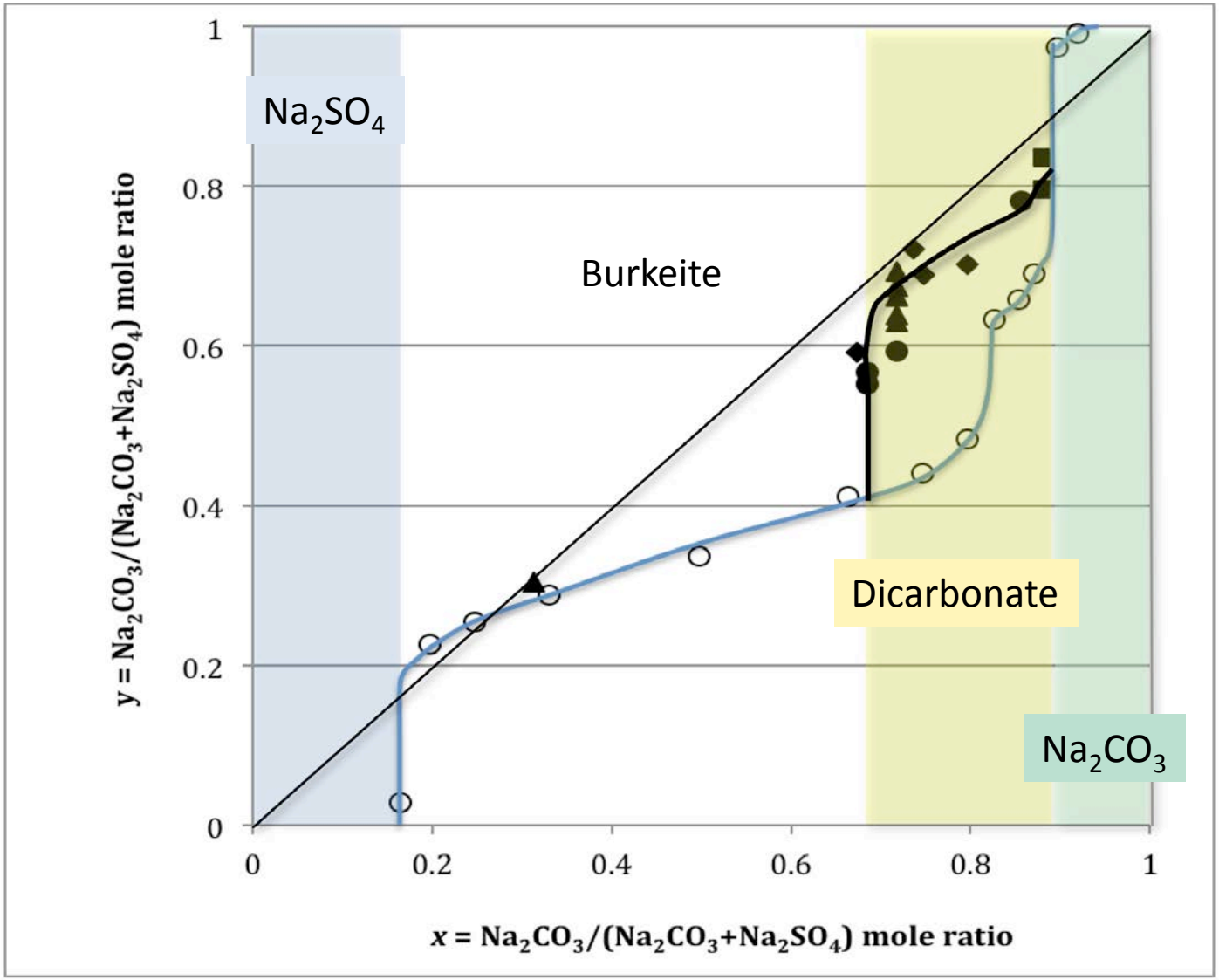
- Concentrator designs improved
- Product liquor from black liquor concentrators increased from ~65% to 75-80% dry solids content
- Na_2CO_3/Na_2SO_4 mass ratio in black liquor increased from 1-1.5 to 3-5

Dicarbonate: the New Foulant

- Shi and Rousseau discovered sodium sulfate dicarbonate, aka "***dicarbonate***"
  - Dicarbonate is $\sim 2Na_2CO_3 \bullet Na_2SO_4$
  - Burkeite is $\sim 2Na_2SO_4 \bullet Na_2CO_3$
- Pilot evaporator trials and mill measurements showed that ***dicarbonate*** is the foulant in modern black liquor concentrators

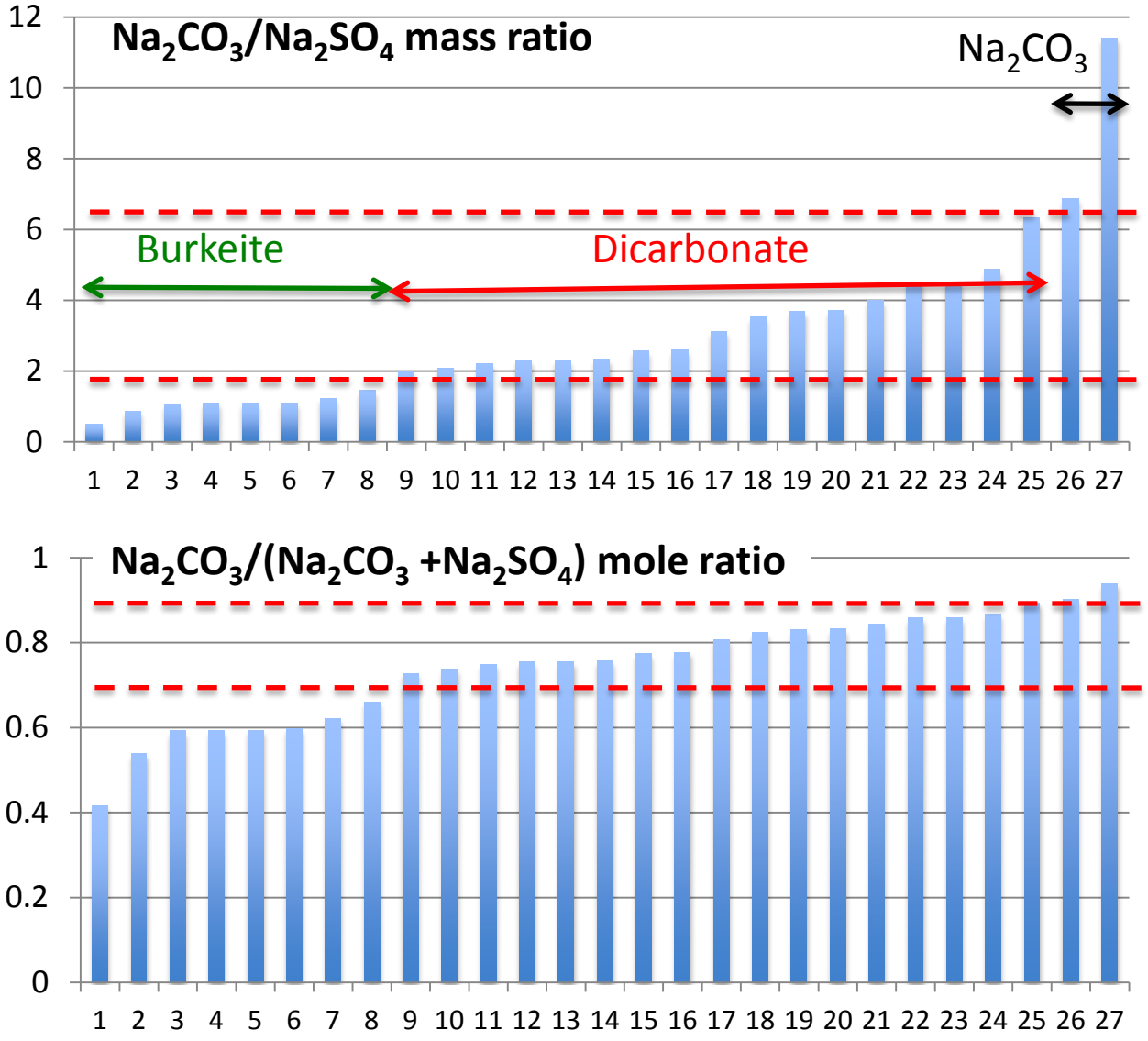
Why Dicarbonate Fouls BL Concentrators

Why Dicarbonate Fouls BL Concentrators

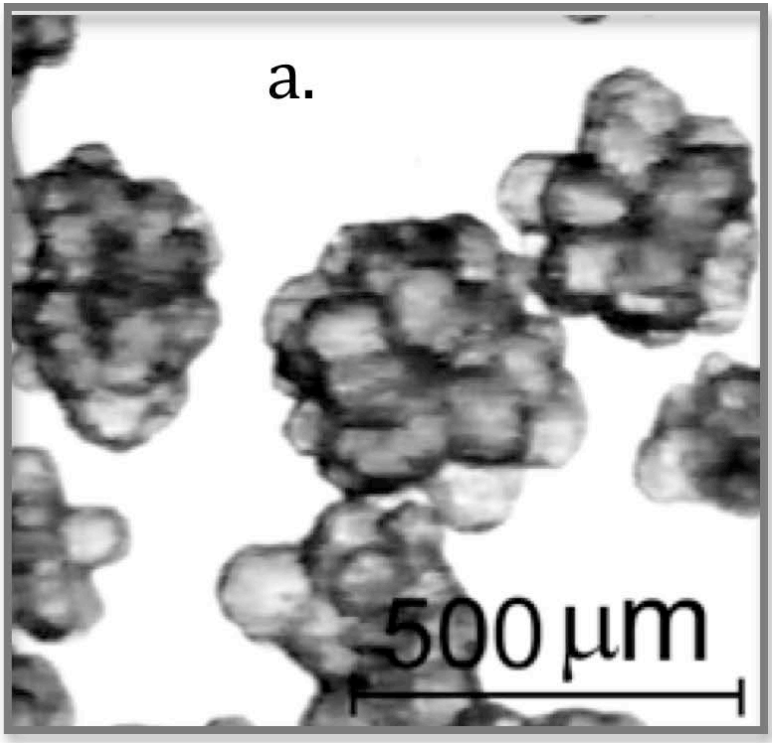


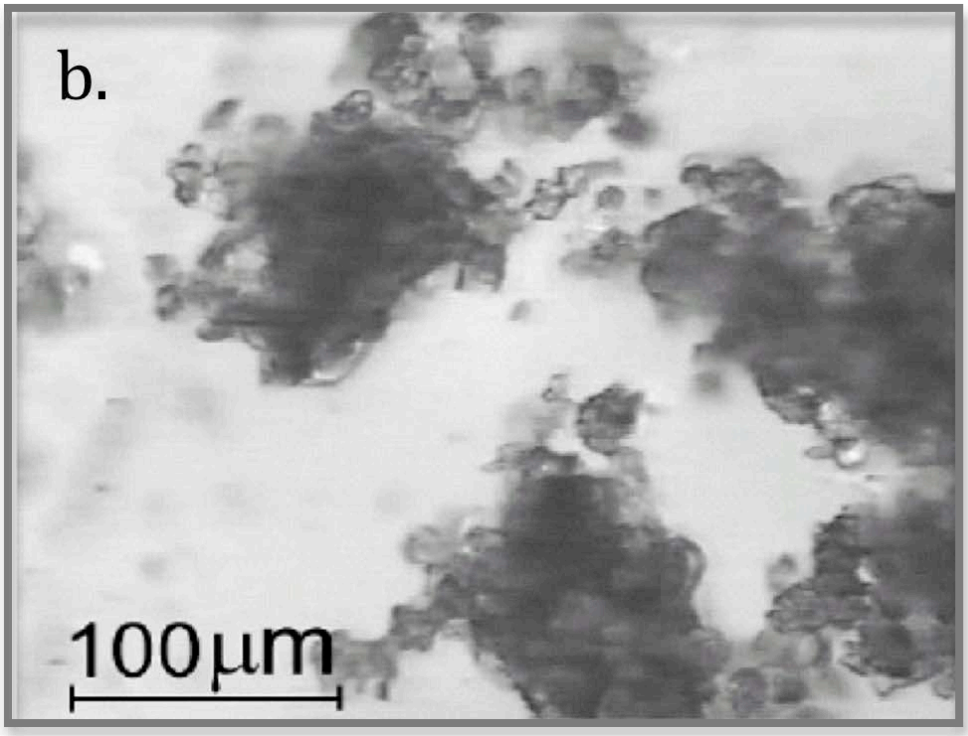
Black liquor composition data

27 N American Kraft Mills



Why Dicarbonate Fouls BL Concentrators





Burkeite: large crystals grow in bulk

Dicarbonate: small crystals nucleate rapidly, deposit on heat transfer surfaces

Crystal Nucleation Rates During Evaporation

Pilot evaporator data, semi-batch operation



From Euhus, 2003

How to Mitigate Dicarbonate Fouling

Guideline: keep the Na_2CO_3/Na_2SO_4 mass ratio in weak black liquor less than 1.6

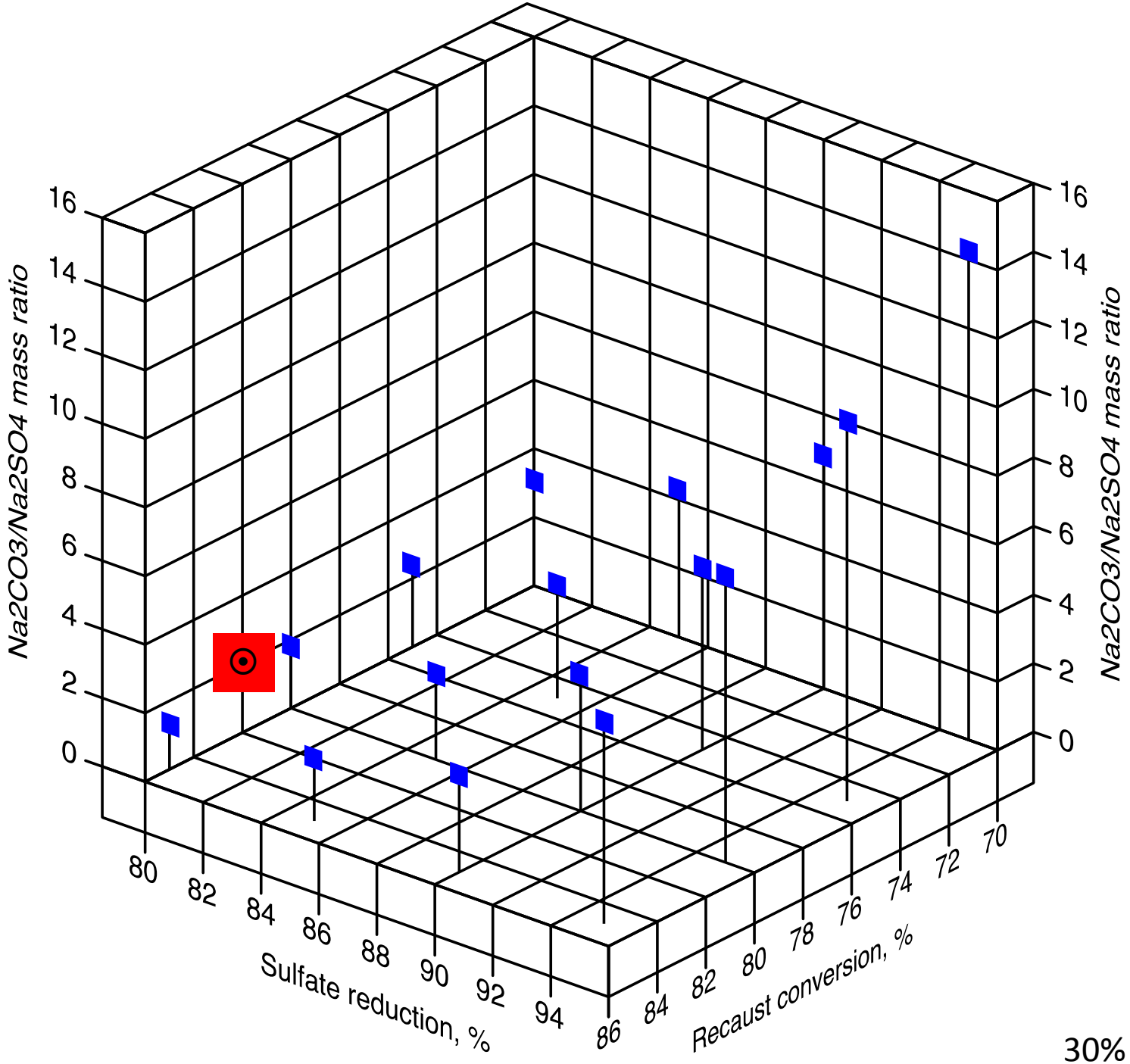
Useful Computational Tools

- ***PulpMillOpt^{TM}:*** calculates Na_2CO_3, Na_2SO_4 and their ratio in black liquor from pulp mill mass balances
- ***BLFoul^{TM}:*** calculates the black liquor solids contents at which burkeite, dicarbonate, and crystallization begin
- Both are available through ***Table Mountain Consulting LLC***

Where Crystal Transitions Occur

For black liquor concentrated to 80% dry solids content

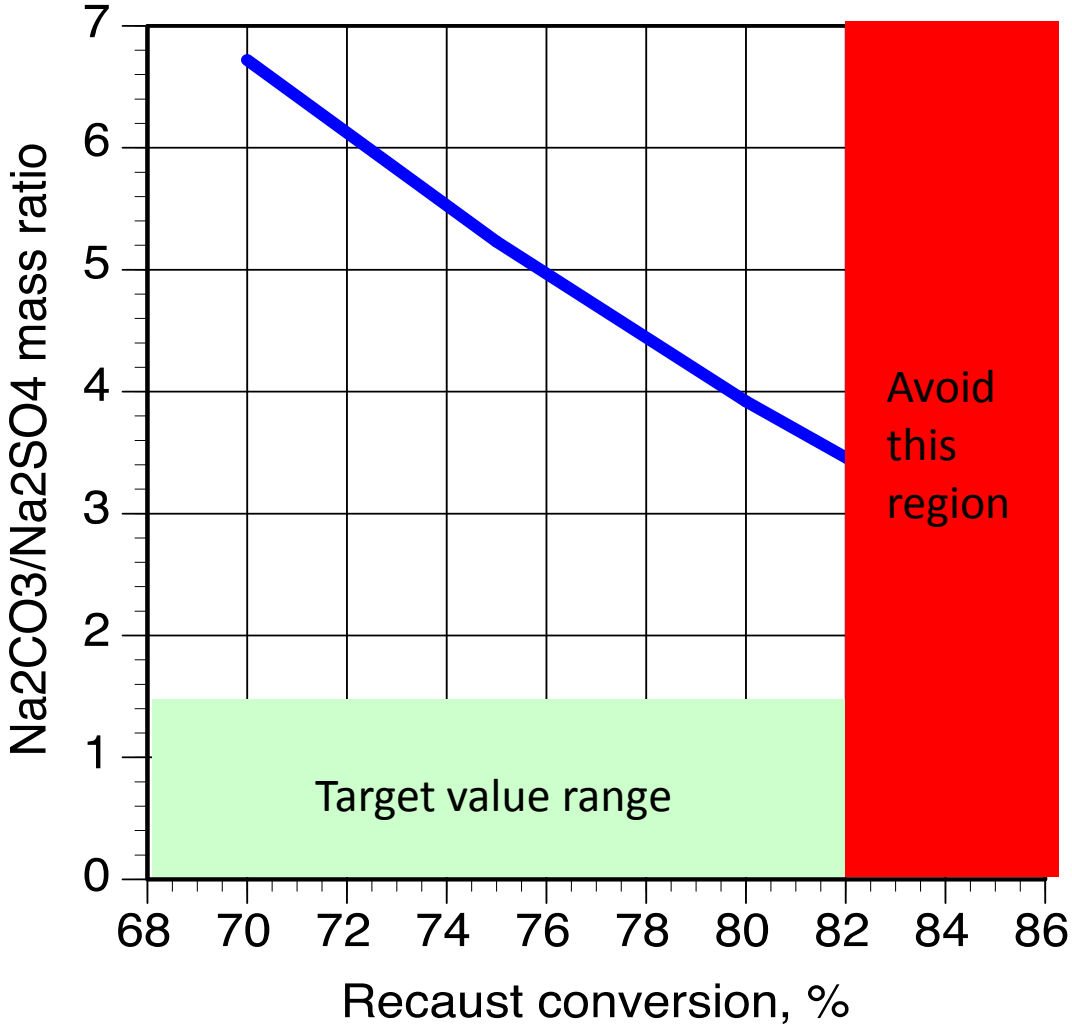
	Liquor 2	Liquor 7	Liquor 25
Na_2CO_3, wt-% bls	4.6	7.1	7.0
Na_2SO_4, wt-% bls	4.2	3.0	1.9
Mass ratio of Na_2CO_3/Na_2SO_4	1.1	2.3	3.7
% bls at onset of burkeite	51%	never	never
% bls at onset of dicarbonate	56%	50%	55%
% bls at onset of Na_2CO_3	never	never	64%



30% sulfidity

Control the Na_2CO_3/Na_2SO_4 Ratio in BLS

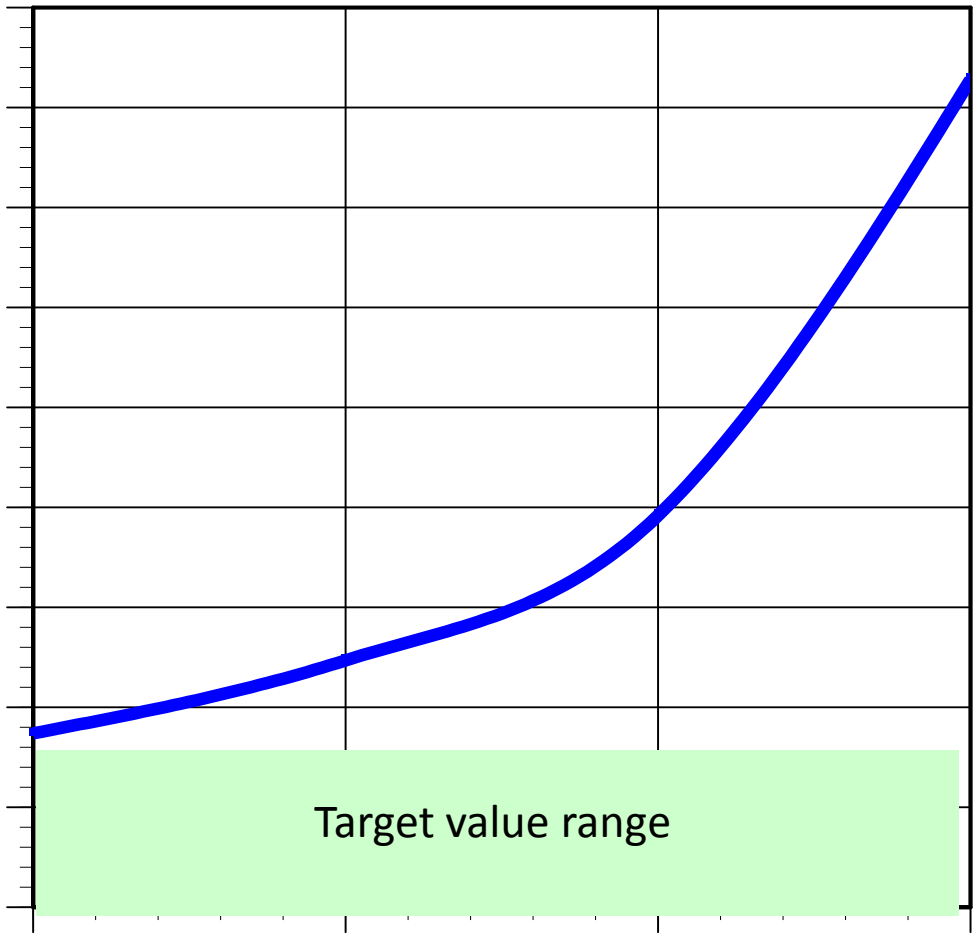
1. **Increase recaust conversion to 80-82%**



Sulfate reduction = 95%
Sulfidity = 30%
Na_2SO_4 added = 0 lb/T bls
AA/wood = 20%
Wood = southern pine

Control the Na_2CO_3/Na_2SO_4 Ratio in BLS

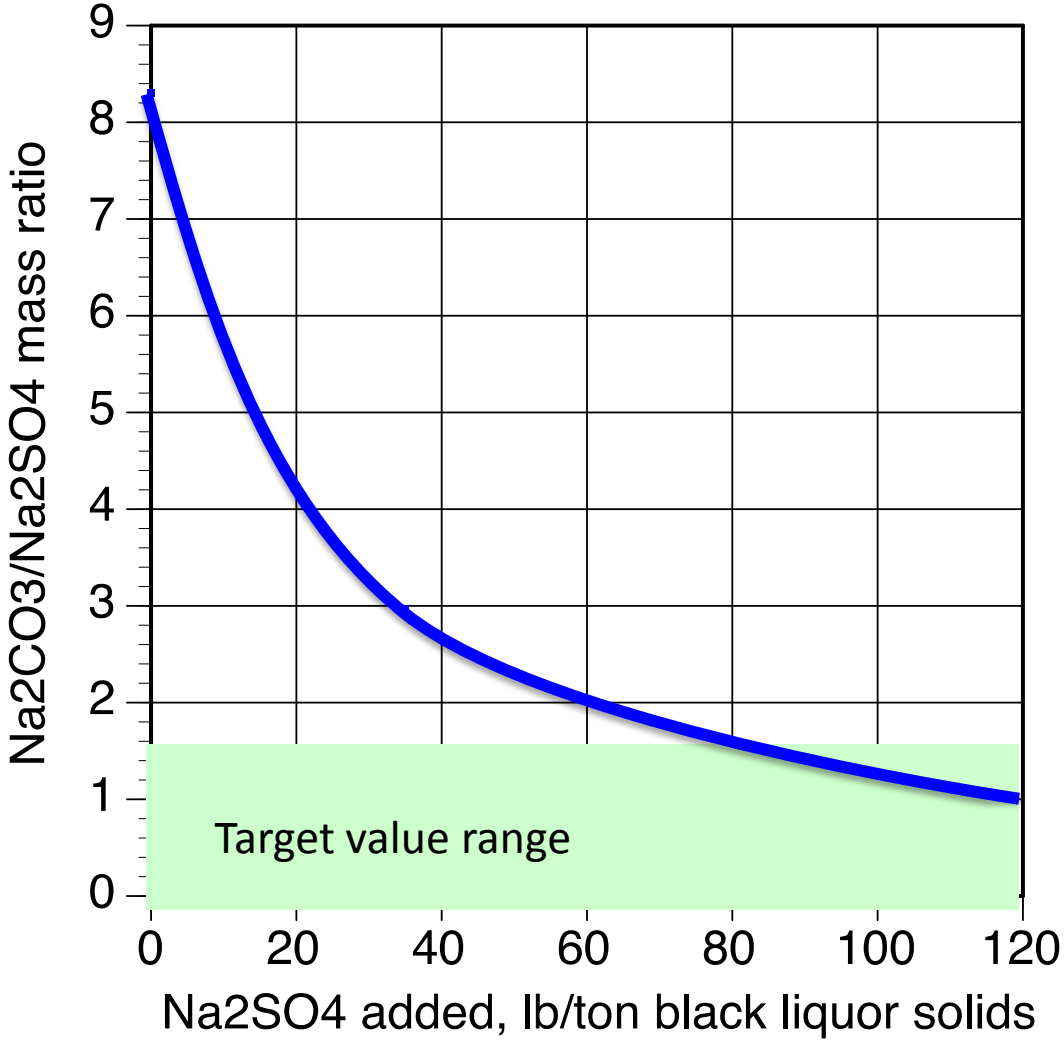
2. Reduce reduction efficiency



Recaust = 80%
Sulfidity = 30%
Na_2SO_4 added = 0 lb/T bls
AA/wood = 20%
Wood = southern pine

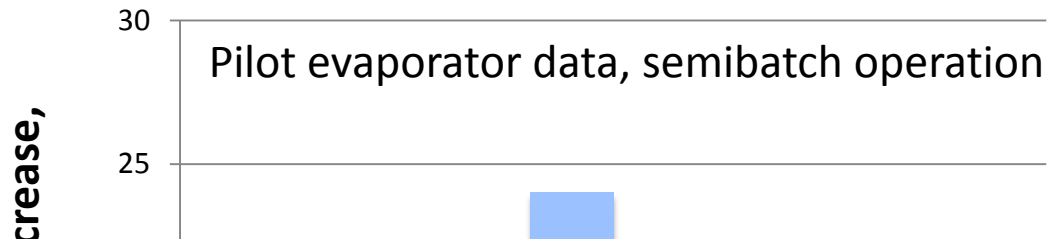
Control the Na_2CO_3/Na_2SO_4 Ratio in BLS

3. Add makeup saltcake or ESP ash (Na_2SO_4 addition)



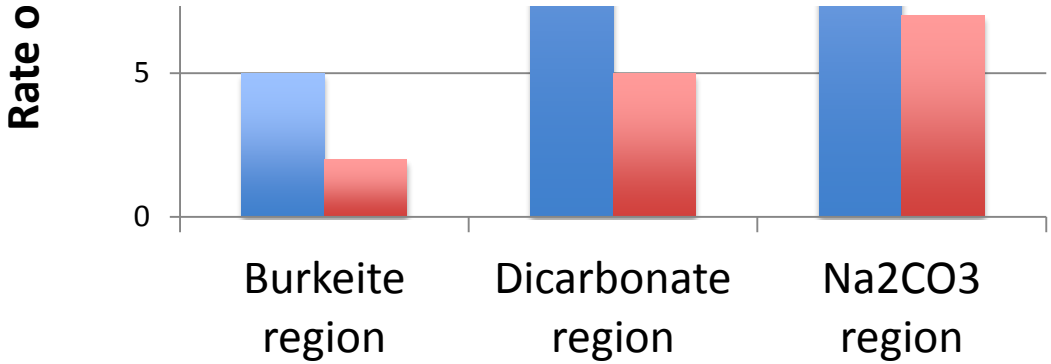
Recaust = 80%
Sulfate reduction = 95%
Sulfidity = 30%
AA/wood = 20%
Wood = southern pine

Increasing Dicarbonate Particles in Suspension



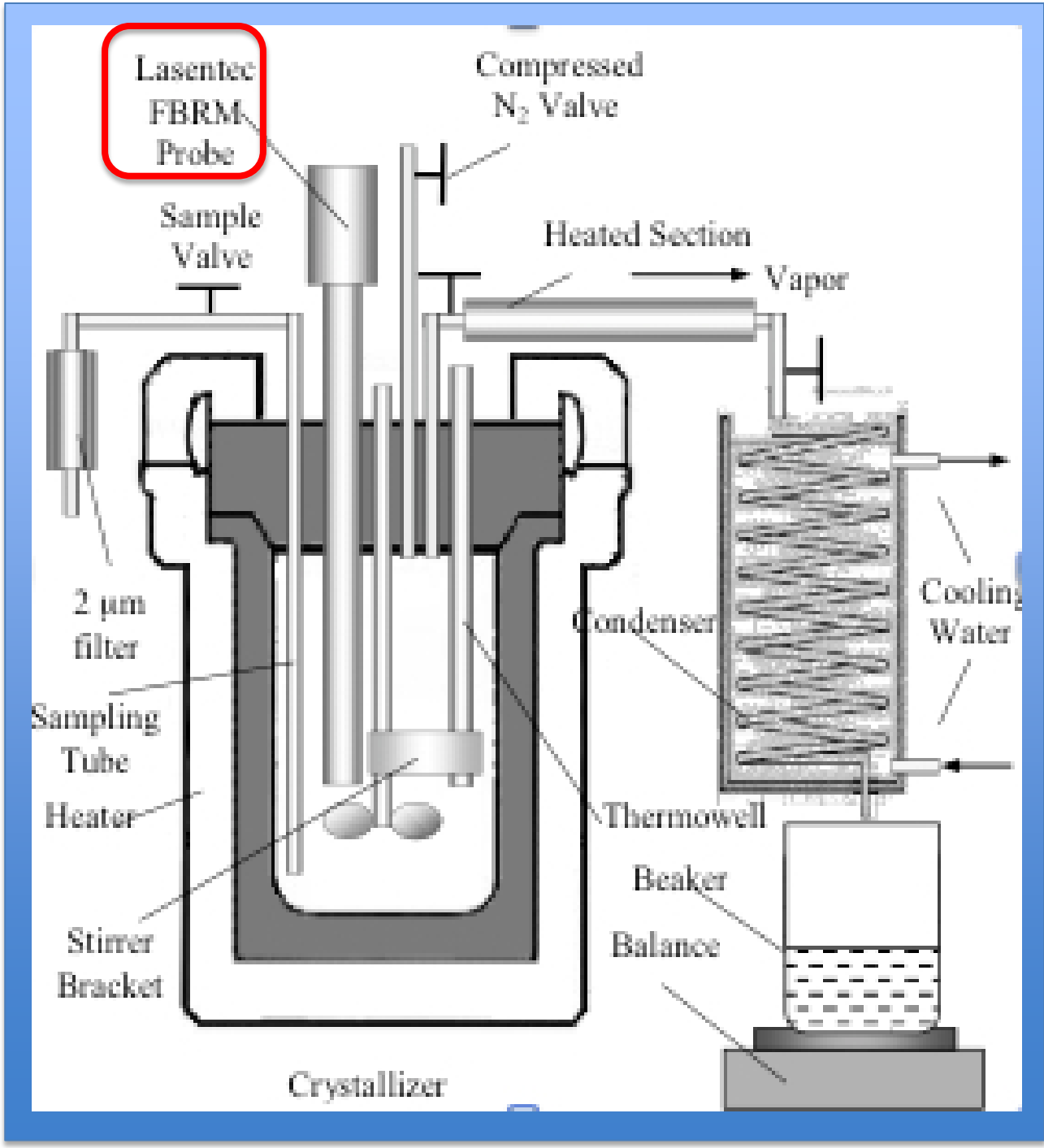
Will this work?

It remains to be evaluated.



Source: Gourdon, 2009

IPST's Batch Crystallizer with FBRM



Pilot Evaporation Plant

Chalmers University of Technology

Sweden



Recommendations for Mitigating Dicarbonate Fouling

Recommendations

- Adjust/control the Na_2CO_3/Na_2SO_4 mass ratio in black liquor solids to less than 1.6 ***before*** crystallization begins
  - Increase carbonate conversion to 80-82%
  - Let sulfate reduction decrease to 90% or less
  - Add sodium sulfate to black liquor
- Sulfate sources:
  - ClO_2 generator effluent
  - ESP ash
  - Other makeup

Recommendations

- Use existing computational tools to evaluate where transition to/from dicarbonate crystallization begins
- Optimize the suspended dicarbonate particle content in bodies that foul badly
  - No guidelines available
  - Needs to be evaluated and optimized at the lab and pilot scale

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- Georgia Tech and IPST:

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- Chalmers University of Technology (Sweden):

  M. Bialik, M. Gourdon

- Gopal Goyal who pushed me to find a better explanation than burkeite for his 1996 BL concentrator fouling

- Special recognition for ***Tom Grace***, who got us all started on BL evaporator and concentrator fouling back in 1973.

Thank you for your patience.

May fouling be the other guy's problem!

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