CONTROLLING SOLUBLE SCALE DEPOSITION IN BLACK LIQUOR EVAPORATORS AND HIGH SOLIDS CONCENTRATORS

1. A Tool for Solving Soluble Scale Problems

Project F016-02

Report 1

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

May 1999

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CONTROLLING SOLUBLE SCALE DEPOSITION IN BLACK LIQUOR EVAPORATORS AND HIGH SOLIDS CONCENTRATORS

1. A Tool for Solving Soluble Scale Problems

Project F016-02

Report 1

A Progress Report

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

By

W. Schmidl and J. Frederick

May 1999

1. Soluble Scale Fouling in Evaporators

The fouling of kraft black liquor evaporators by the deposition of soluble scale has been an ongoing problem that has recently become more pronounced. The problem is seen particularly in the product effect of falling film sets and in high solids concentrators as process changes throughout the mill have impacted the evaporator system. Changes in pulping chemistry, sub-optimal performance of the causticizing plant, the recycling of bleach plant effluent and electrostatic precipitator ash to black liquor, and overall mill closure have all impacted the liquor chemistry. In addition, evaporator systems are being pushed to achieve a higher solids throughput and higher product solids to meet recovery boiler operating requirements. The resulting higher heat transfer rates can increase soluble scale deposition.

Soluble scale is a mixture of Na_2CO_3 and Na_2SO_4 in varying proportions including the distinct compound burkeite, $2Na_2SO_4 \bullet Na_2CO_3$. Since black liquor has relatively high concentrations of Na_2CO_3 and Na_2SO_4, it is inevitable that the solubility limit for the dissolved salts will be exceeded as black liquor is concentrated to high solids. This results in precipitation in the bulk solution, and/or on the heat transfer surfaces, reducing the overall heat transfer coefficient. Soluble scales are generally the most commonly encountered scale, and their occurrence is a concentration-driven event; temperature has only a moderate effect on solubility. Controlling the concentrations of carbonate and sulfate in the liquor is important in minimizing the occurrence and severity of this scaling problem.

The generally accepted guidelines for minimizing soluble scale deposition in operating evaporators has been to operate LTV sets to produce liquor with a discharge solids of one to two percent below the solubility limit for Na_2CO_3 and Na_2SO_4. Falling film (FF) evaporators are designed to minimize scaling which allows them to operate past the solubility limit. They are run with liquor recirculation rates that are high enough to keep the precipitates suspended in solution, acting as seed crystals to promote additional precipitation in the bulk solution, rather than deposition on the heat transfer surfaces [1]. In spite of their design advantages, falling film sets are increasingly experiencing frequent and sometimes severe soluble scale fouling.

2. Solubility and Critical Solids

Pioneering work by Grace at IPST in the 1970s showed that soluble scaling in LTV evaporators always occurred when black liquor was concentrated above the solubility limit of Na_2CO_3 and Na_2SO_4. Grace called this point the "critical solids" for soluble scale formation, and he developed a method for calculating it based on the Na_2CO_3, Na_2SO_4, and total sodium content of the black liquor solids [2]. We refer to this point as the ***First Critical Solids*** for reasons that will become apparent later in this report.

Grace's work was focused on the problem of soluble scales in climbing film, LTV evaporators. It showed that, to prevent soluble scaling, these evaporators must not operate above the first critical solids. With the advent of falling film evaporators, the soluble scale problem went away – at least for a while. Falling film evaporators operate with recirculated product liquor. In effects where the product solids exceeds the first critical solids for Na_2CO_3 and Na_2SO_4, fine particles of precipitated sodium salts are recirculated with it. These fine particles act as sites for further precipitation of Na_2CO_3 and Na_2SO_4. As long as sufficient seed crystals are available and the rate of precipitation of Na_2CO_3 and Na_2SO_4 is not too high, then falling film evaporators operate without major soluble scale problems.

Most black liquors contain more Na_2CO_3 than Na_2SO_4 – typically 2/1 to 4/1 on a mass basis. As these liquors are concentrated further – above the first critical solids point – two moles of Na_2SO_4 are precipitated for every mole of Na_2CO_3, thus rapidly depleting the dissolved Na_2SO_4 and leaving the liquor rich in dissolved Na_2CO_3. Eventually, a ***Second Critical Solids*** point is reached where Na_2CO_3 co-precipitates with Burkeite. This point can vary widely based on the composition of the liquor. Also, the

rate of precipitation at solids contents above the second critical solids point is significantly higher than below it.

When the second critical solids point is exceeded in a falling film evaporator or concentrator effect, soluble scale fouling is very likely to occur. The remainder of this report deals mainly with diagnosing where the transition will occur in a falling-film evaporator train or effect, and how to alleviate the problem.

3. Predicting Solubility Behavior

Grace's method to calculate the first critical solids has been available to the industry since the mid-1970s, and has been widely used to determine upper limits on the target product solids from LTV evaporators. It is easily applied, and only requires knowledge of the Na_2CO_3, Na_2SO_4, and total sodium concentrations in black liquor solids [2]. Typically, first critical solids values are in the range of 45-55 wt.% of total solids content. Limitations of Grace's method are that it does not account for any organic binding of sodium, treats all anions except sulfate and carbonate as equivalent to hydroxide ion, and assumes a temperature independent solubility behavior. As a result, it under predicts the first critical solids value at relatively low inorganic concentrations. It also predicts too high values at temperatures well above 100°C [3].

The prediction of the second critical solids, and a more accurate prediction of the first critical solids, requires a more rigorous approach to predicting solubility behavior, based on aqueous solution thermodynamics, that calculates the most thermodynamically stable composition for both the solution phase and the solid phase.

A chemical equilibrium simulator called NAELS (Nonideal Aqueous ELectrolyte Systems) has been used to predict the first and second critical solids points [3]. NAELS accounts for precipitation of inorganic salts in a thermodynamically rigorous way, for solutions even more concentrated than black liquor at firing solids. It also deals with organic binding of sodium and the temperature dependence of solubility behavior. NAELS can predict the first critical solids to within +/- 10% (on a relative basis) of Grace's measured first critical solids [3].

To solve practical evaporator fouling problems, simulations are run for actual mill liquor compositions and operating temperatures. Typically, the total sodium, potassium, Na_2CO_3, Na_2SO_4, residual active (or effective) alkali, and NaCl content of the black liquor are specified. Calculations are made at increasing total solids contents from 40 to 85 wt.%. The first critical solids is then easily determined as the point here a solid phase (normally burkeite) first appears. The second critical solids point is where Na_2CO_3 begins to co-precipitate with burkeite as the dissolved Na_2SO_4 is depleted.

4. Verification

The first critical solids point has been verified experimentally by Grace [4], but the second critical solids point has not. As part of ongoing research here at IPST, we are conducting solubility experiments on these same aqueous systems, and on black liquors, in order to verify the location of the second critical solids point, and to generate additional data with which to improve the NAELS thermodynamic database.

5. Application of NAELS to Solving Evaporator Problems

5.1 Union Camp Corporation--Eastover, SC

The #2 evaporator at the Eastover mill is a tube-type falling film set that has been plagued with soluble scale fouling. The fouling occurred primarily in the first (product) effect, but also in the second effect, and in the lower solids side of the high solids concentrator (HSC) which is fed the product liquor from the first effect. The HSC is operated as a forced circulation crystallizing evaporator. The target product solids out of the 2nd effect, 1st effect, and the HSC (low side) are 45, 54, and 61.5 wt.%, respectively.

To address the aspect of soluble scale fouling, simulations were run to determine the first and second critical solids points and their locations relative to the target product solids for the three units mentioned above. Four liquor compositions were simulated: a "best" liquor (low carbonate and sulfate content), an "average" liquor, a "worst" liquor (high carbonate and sulfate content), and an "average" liquor with added electrostatic precipitator ash (6.2 kg ash/kg virgin liquor) which is rich in Na_2SO_4. These examples are intended to demonstrate the effect of widely varying, but realistic, liquor compositions on the locations of the critical solids points, and how these data are applied to an evaporator operating strategy.

The Na_2CO_3 + Na_2SO_4 solubility curves for the four liquor compositions are presented in Figure 1. For each curve, as the total solids is increased, two break points are apparent: the first critical solids point where burkeite begins to precipitate, and the second critical solids point where burkeite and Na_2CO_3 co-precipitate. The total sodium, Na_2CO_3, and Na_2SO_4 content of the four liquors are shown in Table I, along with the corresponding calculated critical solids values. These data demonstrate that the critical solids are very sensitive to the total sodium, Na_2CO_3, and Na_2SO_4 concentrations in the black liquors.

Table I. Union Camp--Eastover, SC: liquor compositions and calculated first and second critical solids at 260°F (127°C).

Liquor	Liquor Composition, wt.%			1st Critical Solids, wt.%	2nd Critical Solids, wt.%
	Total Na^+	Na_2CO_3	Na_2SO_4		
"Best" Liquor (A)	18	10.6	4.44	51.0	56.5
"Average" Liquor (B)	20	14.1	5.91	47.1	53.2
"Ave." Liquor+Ppt. Ash (C)	20.72	13.3	11.4	42.8	57.4
"Worst" Liquor (D)	21	17.7	8.87	43.3	51.8

In Figure 2, the slopes of the solubility curves are plotted against the total dried solids. Presented in this manner, the curves represent the normalized incremental precipitation rate as a function of total solids. This quite dramatically illustrates how the liquor composition affects the magnitude of the changes in the crystallization load that occur at the first and second critical solids points. Significantly more salt precipitates above the second critical solids point than below it, and it precipitates at a higher rate.

As discussed earlier, the desirable operating region for falling film evaporators is below the second critical solids point. However, the second critical solids point can shift quite dramatically with changes in liquor composition. To minimize soluble scale formation, it is important to control the Na_2CO_3 and Na_2SO_4 content of the black liquor – both the average concentration and the variation with time.

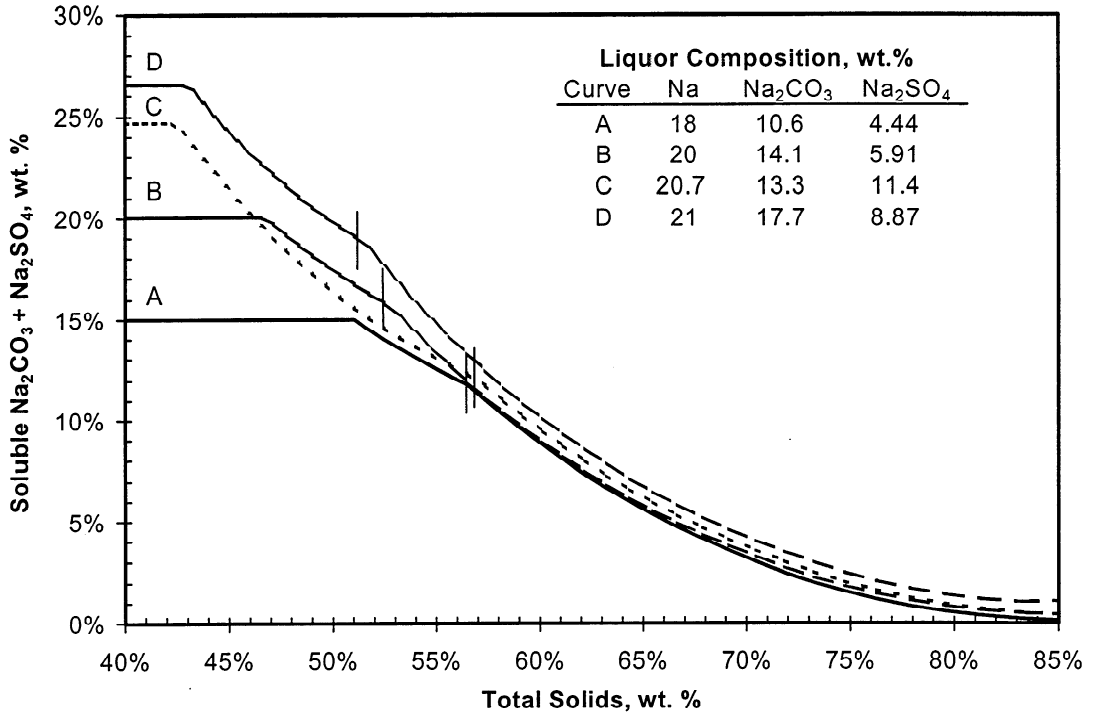

Figure 1. Union Camp--Eastover, SC: Solubility curves for Na_2CO_3 + Na_2SO_4 for the four liquor compositions in Table I.

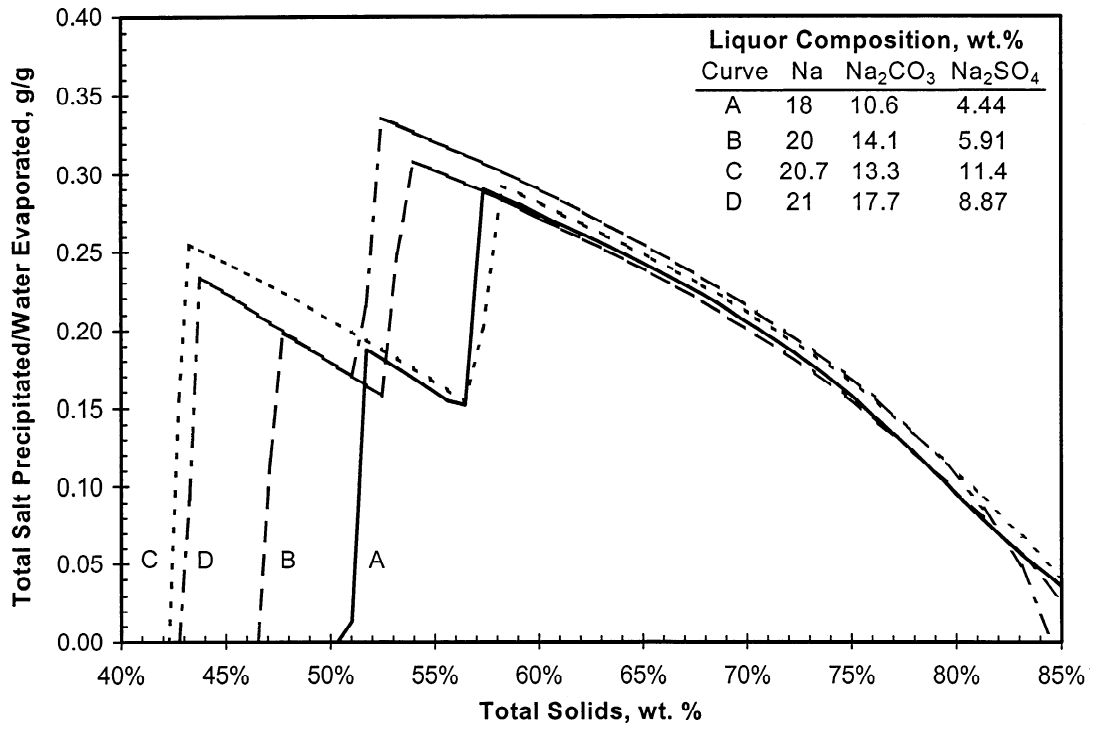

Figure 2. Union Camp--Eastover, SC: Sodium salt precipitation rate (as kg precipitate formed per kg water removed) for the four liquor compositions in Table I.

Curve C in Figure 2 shows the impact of adding precipitator ash (mainly Na_2SO_4) to black liquor. Adding extra sulfate lowers the first critical solids point and raises the second critical solids point. There are two advantages to adding precipitator ash to black liquor that is above its first critical solids point. One is the increase in the second critical solids point. The other is an increase in the total surface area of the suspended solids, providing more surface area for precipitation of sodium salts in suspension.

For the Union Camp/Eastover case, comparing the calculated second critical solids values to the target product solids for each of the three effects immediately points out potential problems. In order to produce 54 wt.% liquor, both critical solids transitions fall within the first effect for the "average" liquor (B) composition. For the "worst" liquor (D) composition, the first critical solids transition occurs in the second effect, and the second critical solids transition occurs within the first effect. In both of these cases, soluble scale deposition will occur in the first effect, which is unable to handle the more rapid Na_2CO_3 deposition above the second critical solids transition. The second critical solids point for Liquor A ("best" composition) occurs in the low solids side of the HSC, transferring the scaling problem to the HSC.

When the first effect is off line for boil-out, the product solids concentration from the second effect is increased to 54%. This moves the second critical solids point into the second effect, causing it to scale.

Liquor C, which contains added ESP catch, represents the practice of recycling electrostatic precipitator ash from the recovery boiler to the evaporators. When added to black liquor at the proper point, it can provide seed crystals for bulk crystallization in the evaporator or concentrator. It must, however, be added to the black liquor above its first critical solids point. If added at a lower concentration, it would dissolve in the black liquor and then precipitate again as the liquor is concentrated. The higher inorganic load in the liquor can, by itself, lead to scaling. In the Union Camp/Eastover example, if 6.2 kg ESP catch (Na_2SO_4) per 100 kg of black liquor solids[1] is added to 45 wt.% total solids black liquor, about half of the added ash would dissolve and the first critical solids point would decrease to 42.8 wt.%.

These simulation results suggest that the best approach to minimizing soluble scale fouling is to reduce the total carbonate and sulfate content of the liquor, and increase the ratio of sulfate to carbonate, if possible. Adding ESP catch to black liquor will be beneficial if it is added to the liquor above its first critical solids point.

5.2 Potlatch Corporation--Cloquet, MN

Potlatch Corporation's Cloquet, MN, mill has a HPD six-effect tube-type falling film evaporator and high solids concentrator (HSC) which is run as a forced circulation crystallizing evaporator. The evaporator feeds the HSC, which then discharges liquor to a flash tank that feeds the recovery boiler. The product liquor exits the first effect at 59 wt.% solids, and then exits the HSC at 65 wt.% solids. As part of a major capital expansion program, the mill installed a tube type falling film "superconcentrator" in 1998 to produce 80 wt.% solids liquor for firing in a new recovery boiler. When the evaporation plant is fully operational, the product liquor will exit the first effect at 65 wt.% solids, the HSC at 70 wt.% solids, and the superconcentrator at 80 wt.% solids. However, the first effect and HSC have had a long term problem with soluble scale fouling, and the mill has occasionally run the first effect to produce 65 wt.% solids liquor and bypassed the HSC entirely. In order to better understand the underlying solubility issues and predict the occurrence of this scaling, the mill chose to simulate the solubility behavior of these salts for the first effect and HSC operating conditions.

[1] This corresponds to a precipitator catch equivalent to 10% of the sodium in the black liquor.

Potlatch was interested in evaluating two possible operating scenarios for their multiple effect evaporator and HSC. In Case One, the concentrator is offline, and the evaporator produces 65 wt.% solids product black liquor out of the first effect. In Case Two, the first effect produces liquor at 59 wt.% solids, and the concentrator then further concentrates this liquor to 65 wt.% solids. The operating conditions for the two cases and a simplified black liquor composition are summarized in Table II below:

Table II. Potlatch Corporation--Cloquet, MN: black liquor simulation conditions.

Black Liquor Composition (wt.% of solids)	**Case One First Effect**	**Case Two A: First Effect**	**Case Two B: Concentrator**
Na^+ 19.6 CO_3^{2-} 6.06 OH^- 2.33 SO_4^{2-} 2.01 Cl^- 0.43 S^{2-} 1.19	65% product solids	59.2% product solids	64.9% product solids
	T = 256°F	T = 231.1°F	T = 239.9°F
	P = 22.3 psia	P = 21.4 psia	P = 25.3 psia

In Case Two, because both the first effect and the concentrator operate at different temperatures and pressures, the conditions in each unit were simulated as Cases 2A, and 2B, respectively. Since the liquor composition is the same for all three cases, the simulations would identify the effect of temperature on solubility, which should not be significant. The solubility plots for the Potlatch black liquor have not been included because they are materially similar to those in Figure 1 except that, because the starting compositions are identical, all three curves are co-linear until the first critical solids point is reached. The critical solids values have been calculated, however, and are presented in Table III.

Table III. Potlatch Corporation--Cloquet, MN: black liquor calculated critical solids.

Case No.	**Temperature, °F (°C)**	**1st Critical Solids, wt.%**	**2nd Critical Solids, wt.%**
1	256 (124)	52.2	54.2
2A	231 (111)	52.6	56.8
2B	240 (116)	52.5	56.1

The solubility behavior for this liquor identifies a serious operational problem. For both Cases One and Two, the first evaporator effect will be operating past the second critical solids transition in order to produce liquor with a discharge solids of 65 wt.% (Case One), or 59 wt.% (Case Two). This is an undesirable region to be operating in because tube falling film evaporators are generally not able to handle the second critical solids transition without suffering from significant scaling.

These results suggest that, for this liquor composition, the first effect should be operated to produce liquor at about 55 wt.% solids, and the concentrator should be operated to increase the liquor product solids to 65 wt.%. The concentrator should be better able to handle the crystallization load from the second critical solids transition than the first effect, but a 10 wt.% increase in liquor solids may be difficult to achieve because of evaporation rate limitations of the unit, liquor throughput requirements, the inherent liquor boiling point rise, and the available steam supply. In addition, the target firing solids (~ 68 wt.%) must be maintained to satisfy the recovery boiler operating requirements. These parameters must also be taken into account when evaluating the overall operating strategies.

A more effective option would be to reduce the Na_2CO_3 content of the black liquor, which is much higher than most. Sodium carbonate in black liquor often indicates poor recaust efficiency – if so, then reducing the Na_2CO_3 content would mean improving the recaust operation. Other possible sources of Na_2CO_3 are O_2 delignification and use of alkaline scrubber solutions as chemical makeup in the pulp mill.

The ideal scenario is for the Cloquet mill to implement process changes that reduce the total carbonate and sulfate content of the liquor, and increase the ratio of sulfate to carbonate. These compositional changes would reduce the overall crystallization load in the liquor, and shift both critical solids points to higher values.

5.3 Summary

Ideally, mills attempt to maintain a constant liquor composition. In reality, however, process upsets, changing production requirements, and other problems can, and do, cause significant fluctuations in liquor chemistry. The range of compositions represented by the "best" and "worst" liquors in the Union Camp example is not that great and can easily be experienced by any mill. This can wreak havoc with evaporator control schemes and performance. In order to maintain a constant product liquor solids for firing, the first effect of a falling film set can easily cross into the second critical solids operating region leading to significant scaling. In addition, most mills have LTV rising film multiple-effect evaporator sets that evaporate liquor to just below the first critical solids point (their practical operating limit), and their performance would be severely impacted because the first critical solids point can fluctuate significantly as well with changes in liquor chemistry. Mills continuously monitor liquor solids contents at various points in the evaporation process, and periodically measure the basic inorganic composition. Therefore, these types of calculations, while presented for two mills here, represent a valuable methodology that can be implemented to identify desirable and undesirable evaporator operating regions for any mill.

6. For assistance in analyzing a falling film evaporator or high solids concentrator:

Contact Wolfgang Schmidl or Jim Frederick at the Institute of Paper Science and Technology. Their contact information is

Wolfgang Schmidl
Phone: 404-894-1083
Fax: 404-894-5752
Email: wolfgang.schmidl@ipst.edu

Jim Frederick
Phone: 404-894-5303
Fax: 404-894-5752
Email: jim.frederick@ipst.edu

7. References

1. Venkatesh, V., and X.N. Nguyen, "Evaporation and Concentration of Black Liquor", ch. 2 in Chemical Recovery in the Alkaline Pulping Processes, 3rd ed., ed. R.P. Green, and G. Hough. TAPPI Press, Atlanta, 1992, pp. 5-35.

2. Grace, T.M., "A Survey of Evaporator Scaling in the Alkaline Pulp Industry", Institute of Paper Chemistry Project 3234, Report One (September 22, 1975).

3. Golike, G.P., Q. Pu, K.L. Holman, K.R. Carlson, P.C. Wollwage, H.G. Folster, and S. Rankin, "NAELS: A New Method for Calculating Equilibrium Solubility of Burkeite and Sodium Carbonate in Black Liquor", Proceedings of the 1998 TAPPI International Chemical Recovery Conference, TAPPI Press, Atlanta, 1998, pp. 403-418.

4. Grace, T.M., "Solubility Limits in Black Liquor", Institute of Paper Chemistry Project 3136, Report One (February 22, 1974).