EVAPORATOR SCALING

Model to predict the precipitation of burkeite in the multiple-effect evaporator and techniques for controlling scaling

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ABSTRACT

The ability to predict burkeite precipitation in the evaporator train is an important consideration in the design and operation of this equipment. With knowledge of the factors affecting precipitation of burkeite and sodium carbonate, the papermaker can predict the level of black-liquor solids (BLS) at which precipitation begins. This paper presents a simple model that uses white-liquor composition and kraft digester operating parameters to predict the level of BLS (critical BLS) at which burkeite precipitation will begin. The model illustrates how critical BLS responds to changes in causticizing efficiency, to addition of spent acid (sesquisulfate) from a ClO_2 generator to weak black liquor, and to addition of makeup chemicals.

Application:

Strategies for controlling scaling in multiple-effect evaporators.

SODIUM CARBONATE–SODIUM SULFATE scales are the major form of scale in the black-liquor evaporators that are used in the kraft recovery cycle. These water-soluble inorganic scales form by crystallizing from a supersaturated solution when their concentrations exceed the solubility limit, commonly known as the critical black-liquor solids (BLS). The scale usually precipitates as burkeite ($2Na_2SO_4 \cdot Na_2CO_3$) or as a coprecipitate of burkeite and sodium carbonate (Na_2CO_3), since sodium sulfate (Na_2SO_4) is the limiting component.

The scaling caused by burkeite is concentration dependent and can be very rapid when the critical BLS is exceeded. Multiple-effect evaporators with tube heating elements [falling film or long-tube vertical (LTV) evaporator bodies] are susceptible to plugging under this condition. There is no effective way of controlling burkeite precipitation once the solubility has been reached. However, scaling can be controlled through crystallizer technology. Critical BLS can be increased by lowering the concentrations of Na_2CO_3 and Na_2SO_4 in the black liquor. The level of these components in the black liquor is regulated through control of the kraft recovery process.

The model presented here provides a method of measuring critical BLS before the black liquor is fed to the evaporators. Using this information, the evaporator operator can (a) adjust the operation to minimize scaling and (b) identify variation and causes of variation in critical BLS.

MODEL DEVELOPMENT

Burkeite solubility

Figures 1 and 2 show sodium sulfate–carbonate solubility data from the literature *(1)*. The solubility of sodium sulfate–carbonate (also known as burkeite, $2Na_2SO_4 \cdot Na_2CO_3$) is independent of temperature in the range of 100–140°C and is assumed to be unaffected by liquor organics *(1)*. The major components affecting burkeite solubility are:

- Effective sodium
- $Na_2CO_3 + Na_2SO_4$ mass-concentration ratio
- Black-liquor solids content.

Figure 1 is the general solubility relationship at a Na_2CO_3/Na_2SO_4 ratio of 80:20. Figure 2 shows correction factors for other Na_2CO_3/Na_2SO_4 ratios.

A multiple regression analysis was done on the data from Fig. 1 to develop a mathematical equation to predict BLS from a known $Na_2CO_3 + Na_2SO_4$ weight percent on solids and a known level of effective sodium. Both values can be obtained from a white-liquor analysis of Na_2CO_3, Na_2SO_4, Na_2S, and NaOH.

Effective sodium is defined *(2)* as

effective sodium, g Na/L = total sodium – $23(Na_2CO_3/53 + Na_2SO_4/71)$

The resulting equation for calculating black-liquor solids is depicted in Eq. 1.

$$BLS = 85.47 - 1.47z - 0.95w \quad (1)$$

where

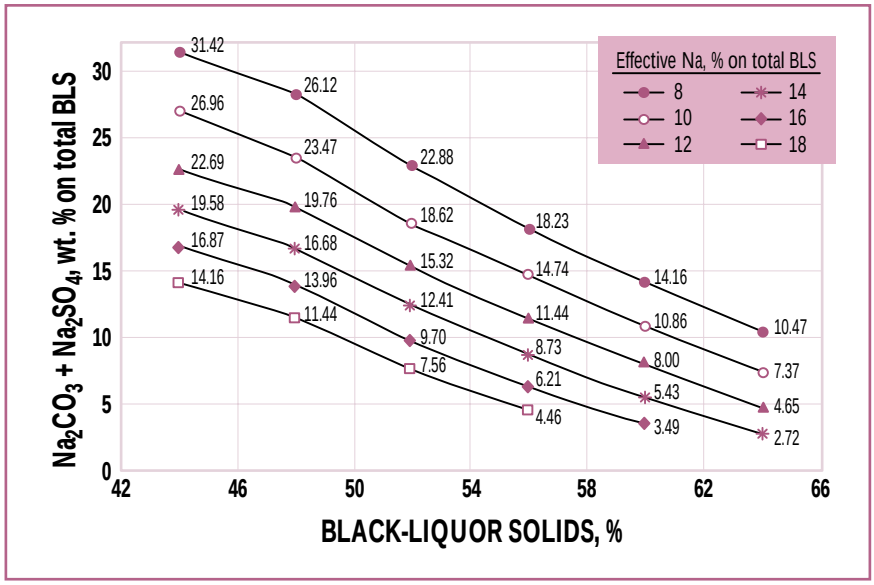
BLS = black-liquor solids content, %

z = effective sodium, % on total BLS

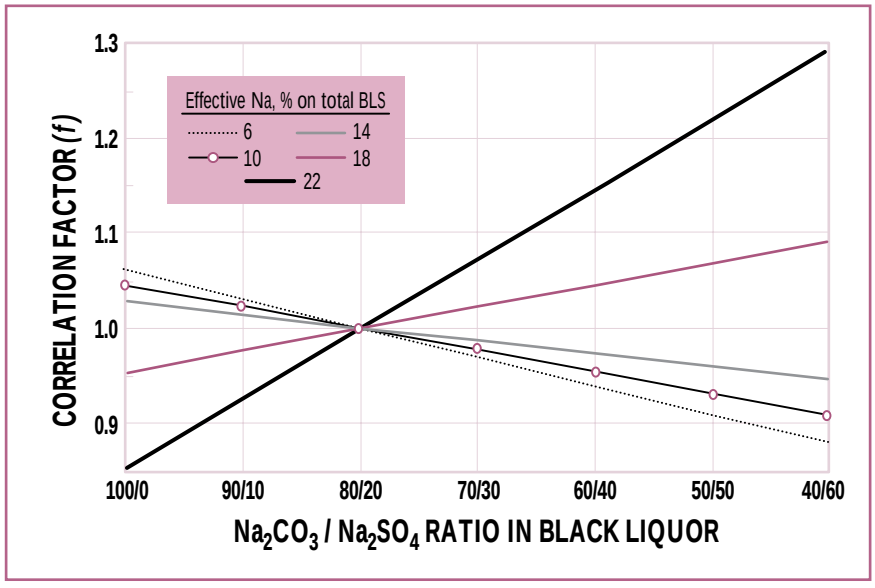
w = $Na_2CO_3 + Na_2SO_4$, wt.% on total BLS.

Figure 3 shows the resulting model overlaid on the laboratory solubility data from Fig. 1.

Modeling Fig. 2 is a bit more complicated. The relationship between the correction factor and Na_2CO_3/Na_2SO_4 ratio for a constant effective-sodium content is linear. All lines cross at a correction factor of 1.0 and a Na_2CO_3/Na_2SO_4 ratio of 80:20. (Note that Fig. 1 is based on an 80/20 ratio for Na_2CO_3/Na_2SO_4.) The cor-



1. Observed solubility of burkeite in black liquor (at Na_2CO_3/Na_2SO_4 ratio of 80:20) at six levels of effective sodium [from data developed by Grace (1)]



2. Correction factors for determining solubility of burkeite in black liquor (relative to Na_2CO_3/Na_2SO_4 ratio of 80:20) at five levels of effective sodium [from data developed by Grace (1)]

rection factors taken from Fig. 2 are used to relate critical BLS at other Na_2CO_3/Na_2SO_4 ratios to a ratio of 80:20.

The slopes and *y*-intercepts of each line in Fig. 2 change with respect to the effective-sodium content. **Figure 4** shows that the slopes of the lines in Fig. 2 are related to the effective sodium in the form of a polynomial. A nonlinear regression analysis of this relationship produced the following Eq. 2.

$$y = 5\text{x}10^{-5}x^2 - 7.7\text{x}10^{-4}x - 2\text{x}10^{-5} \quad (2)$$

where

y = slope
x = [effective sodium, (%) x BLS (%)]/[100 – BLS (%)].

Figure 5 shows that the relationship between the *y*-intercepts of the lines from Fig. 2 and the effective-sodium content is also a polynomial. The resulting equation from a nonlinear regression analysis is given as Eq. 3.

$$b = -1.0125\text{x}10^{-3}x^2 + 0.01568x + 0.99933 \quad (3)$$

where

b = *y*-intercept.

Equation 4 is derived from Eqs. 2 and 3 to calculate the correction factor shown in Fig. 2 using a known effective-sodium content and a given Na_2CO_3/Na_2SO_4 ratio.

$$f = r(5\text{ x}10^{-5}x^2 - 7.7\text{x}10^{-4}x - 2\text{x}10^{-5}) - 1.013\text{x}10^{-3}x^2 + 0.01568x + 0.9993 \quad (4)$$

where

f = correction factor
r = percent Na_2SO_4 from ratio of Na_2CO_3/Na_2SO_4 (e.g., for 80:20 ratio, r = 20).

Finally, the critical BLS—the black-liquor solids content where burkeite precipitation will begin—can be calculated from Eq. 5 using the correction factor calculated in Eq. 4 and the liquor solids content calculated in Eq. 1.

$$\text{critical BLS, \%} = [f(\text{BLS}/100)]/\{1-[(1-f)(\text{BLS}/100)]\} \quad (5)$$

Digester material balance

Modeling burkeite solubility mathematically is the first part of the overall model. However, the composition of the black liquor is still necessary data for predicting critical BLS. There is no quick and accurate method for determining black-liquor composition. However, this composition can be accurately estimated based on the

white-liquor composition, black-liquor organic/inorganic ratio, and a digester material balance. This section concentrates on the development of the material balance based on the illustration in **Fig. 6**.

The material balance around the digester is used to calculate the total solids in the black liquor feeding the evaporators. The balance is done on a per-ton ovendry (o.d.) brownstock pulp basis. The total BLS can be separated into organic solids and inorganic solids, as shown in Fig. 6.

The organic solids are the portion of the wood fed to the digester that does not result in brownstock pulp production, as shown in Eq. 7.

total BLS = organic solids + inorganic solids

$$\text{Organic solids, tons/day} = W - P \qquad (7)$$

where

W = wood charged to the digester, o.d. tons/day

P = brownstock production rate, o.d. tons/day.

The inorganic solids are assumed to originate solely from the white-liquor charge to the digester and are dependent on the ratio of effective alkali to wood [tons EA (as Na_2O)/ton o.d. wood].

$$\text{Inorganic solids, tons/day} = (TA/EA)(EA/W)\,W \qquad (8)$$

where

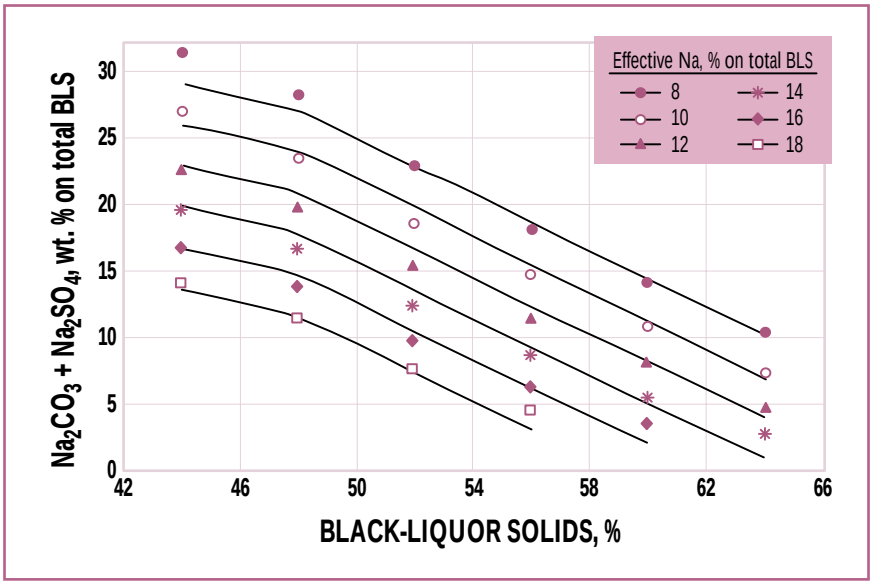
TA = total alkali, g/L (as components)

EA = effective alkali, g/L (as Na_2O)

EA/W = ratio of effective alkali to wood [tons EA (as Na_2O)/ton o.d. wood].

The definition of yield is presented in Eq. 9.

$$Y = P/W \qquad (9)$$



3. Observed vs. predicted solubility of burkeite in black liquor (at Na_2CO_3/Na_2SO_4 ratio of 80:20) at six levels of effective sodium

After solving the yield definition for W, substituting Eqs. 7 and 8, and assuming that there is 0.1 ton of water per ton of pulp produced from reactions in the digester, the material balance can be solved for total BLS.

$$\text{tons BLS/ton o.d. brownstock} = [(1/Y)-1] + [(1/Y)(TA/EA)(EA/W)] - 0.1 \qquad (10)$$

where

Y = digester yield as a fraction

$(1/Y)-1$ = tons organic solids/ton o.d. brownstock

$(1/Y)(TA/EA(EA/W)$ = tons inorganic solids/ton o.d. brownstock.

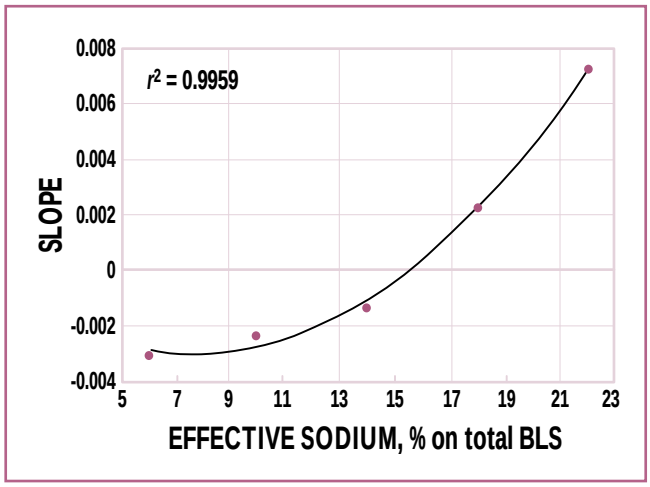
Reclaiming spent acid from ClO_2 generator

Some kraft mills reclaim sodium sesquisulfate (spent acid) from the ClO_2 generator to the weak black liquor. This spent acid is a source of inorganic solids, and after being neutralized in the black liquor, it becomes a source of sodium sulfate. Sodium sulfate is one of the scale components in burkeite.

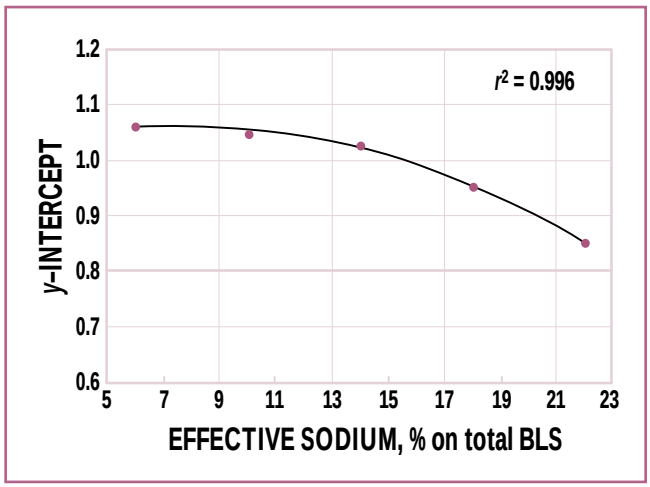
The effect of reclaiming spent acid to the weak black liquor will be added to the model. This effect is based on a ClO_2 plant (R8) producing 20 tons of spent acid per day (operating for 10 h/day). Daily production of ClO_2 would be 8 tons for a kraft mill producing 1000 tons o.d. pulp. The amount of sodium sulfate can then be calculated for a particular brownstock production rate. The model assumes that spent acid is reclaimed only during the time the ClO_2 plant is operating.

$$\text{tons } Na_2SO_4\text{/ton o.d. brownstock} = [(1.4 \text{ tons } Na_2SO_4\text{/ton } ClO_2)\,(20 \text{ tons } ClO_2\text{/day})]/(1000 \text{ tons o.d. brownstock/day}) = 0.028 \text{ tons } Na_2SO_4\text{/ton o.d. brownstock} \qquad (11)$$

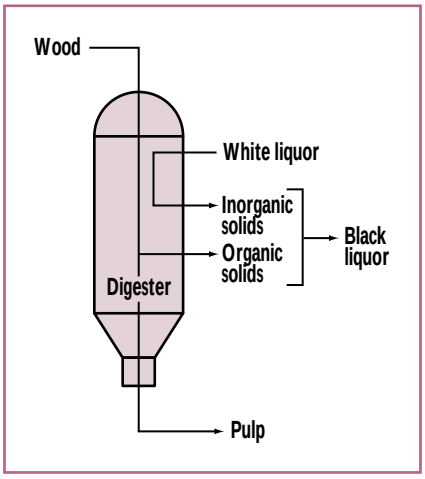
Obviously, this particular mill does not run with 100% chlorine dioxide bleaching. If it did, the ClO_2 plant would probably be operating 24 h/day and would produce even more spent acid. A mill generating ClO_2 for 24 h/day would likely produce more sodium and sulfur makeup than necessary, sewering the balance. Equation 12 is a modification of Eq. 10 that accounts for the addition of all of the spent acid that was produced during the 10 hours the ClO_2 plant was in operation.



4. Relationship between the slopes of lines in Fig. 2 and effective sodium



5. Relationship between the y-intercepts of lines in Fig. 2 and effective sodium



6. Digester material balance

Components	Effective alkali (EA), g/L (Na_2O)	Total alkali (TA), g/L (as components)	Total Na, g/L (as Na)
Na_2CO_3	20.50	35.05	15.21
Na_2SO_4	2.79	6.39	2.07
Na_2S	27.59	34.71	20.47
NaOH	72.04	92.98	53.45
	85.84*	**169.13**	**91.20**

*EA = NaOH + 1/2 Na_2S = 72.04 + 0.5(27.59) = 85.84

I. White-liquor analysis

$$\text{tons BLS/ton o.d. brownstock} = [(1/Y)–1] + [(1/Y)(TA/EA)(EA/W)] – 0.1 + 0.028 \quad (12)$$

Brownstock yield

The only unknown in Eq. 12 is the value of the brownstock yield. For the purpose of this paper, the brownstock yield is calculated using the results of black-liquor organic/inorganic ratio analysis and the organic and inorganic parameters in Eq. 12. Alternatively, the organic/inorganic ratio could be predicted on-line by evaluating its relationship to the resulting kappa number in the digester and the alkali charge (or the ratio of EA/*W*).

Equation 13 can be used to solve for the yield based on an actual measurement of organic/inorganic ratio in a black-liquor sample.

$$\text{organic solids (\%)/inorganic solids (\%)} = [(1/Y)–1]/[(1/Y)(TA/EA)(EA/W)] \quad (13)$$

The black-liquor sample used to test for the organic/inorganic ratio must be taken after the digester and before the addition of spent acid.

Sample calculation

The following sample calculation is based on an actual white-liquor analysis as shown in **Table I** and a black-liquor organic/inorganic ratio of 1.564 (61% organic, 39% inorganic). The kappa target of the digesters is 22, and EA/*W*—the ratio of tons of EA (as Na_2O) to tons of o.d. wood—is 0.199.

Calculate brownstock yield.

$$1.564 = [(1/Y)–1]/[(1/Y)(169.13/85.84)\ 0.199]$$

$$Y = 0.388 \text{ or } 38.8\%$$

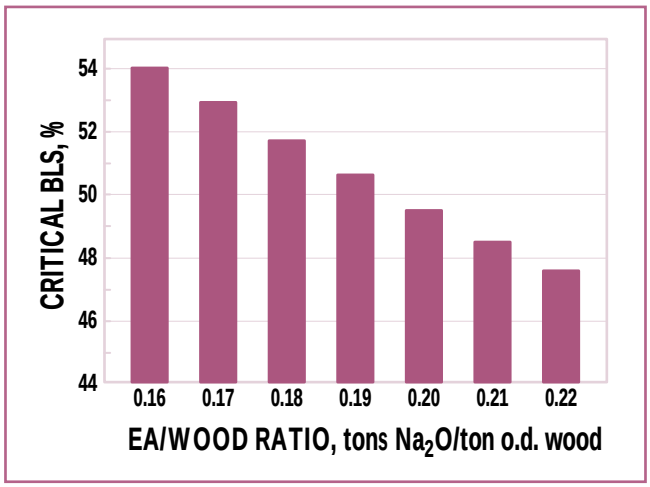
Calculate total black-liquor solids.

$$\text{tons BLS/ton o.d. brownstock} = [(1/0.388)–1] + [(1/0.388)(169.13/85.84)\ 0.199] – 0.1 + 0 = 2.489$$

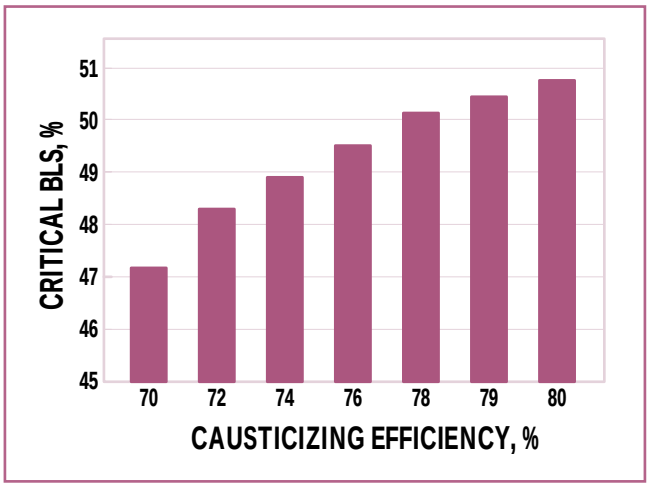
Calculate effective sodium.

$$\text{effective sodium, g Na/L} = 91.20 – \{23[(35.05/53)+(6.39/71)]\} = 73.92$$

$$\text{effective sodium, tons Na/ton o.d. brownstock} = (1/0.388)\ (73.92/85.84)\ 0.199 = 0.4417$$



7. Effect of EA/wood ratio on critical black-liquor solids



8. Effects of causticizing efficiency on critical black-liquor solids

effective sodium on total BLS, % = (0.4417/2.489) x 100% = 17.74%

Calculate weight percent of Na_2CO_3 + Na_2SO_4 on total BLS.

Na_2CO_3 + Na_2SO_4, wt.% on total BLS = {(1/0.388) [(35.05 + 6.39)/85.84] 0.199}/2.489 x 100% = 9.95%

Calculate BLS for the Na_2CO_3/Na_2SO_4 ratio of 80:20.

BLS = 85.47 – [(1.47) (17.74)] – [(0.95) (9.95)] = 49.94%

Calculate the percent contribution of Na_2SO_4 from the sum of Na_2CO_3 + Na_2SO_4

r = percent Na_2SO_4 of (Na_2CO_3 + Na_2SO_4) = [6.39/(6.39 + 35.05)] x 100% = 15.42%

Calculate the correction factor.

x = [effective sodium (%) x BLS (%)]/[100 – BLS (%)] = (17.74 x 49.94)/(100 – 49.94) = 17.70

$f = 15.42\{[5x10^{-5} (17.70)^2] – [7.7x10^{-4} (17.70)] – 2x10^{-5}\} – [1.0125x10^{-3} (17.70)^2] + [0.01568 (17.70)] + 0.9993 = 0.9907$

Calculate critical BLS.

critical BLS, % = [0.9907(49.94/100)]/{1 – [(1 – 0.9907) (49.94/100)]} x 100% = 49.71

For a mill running a 20-ton/day ClO_2 plant for 10 hours per day and reclaiming all of the spent acid produced, the critical BLS would be 47.55%.

FACTORS IN THE KRAFT RECOVERY CYCLE AFFECTING BURKEITE SOLUBILITY

There are several factors in the kraft recovery cycle that influence the solubility of burkeite in black liquor:

- Effective-alkali/wood ratio
- Causticizing efficiency
- Spent-acid addition
- Makeup chemical addition.

Each factor affects the burkeite solubility to varying degrees. The influence of each is described in the developed model.

EA/wood ratio

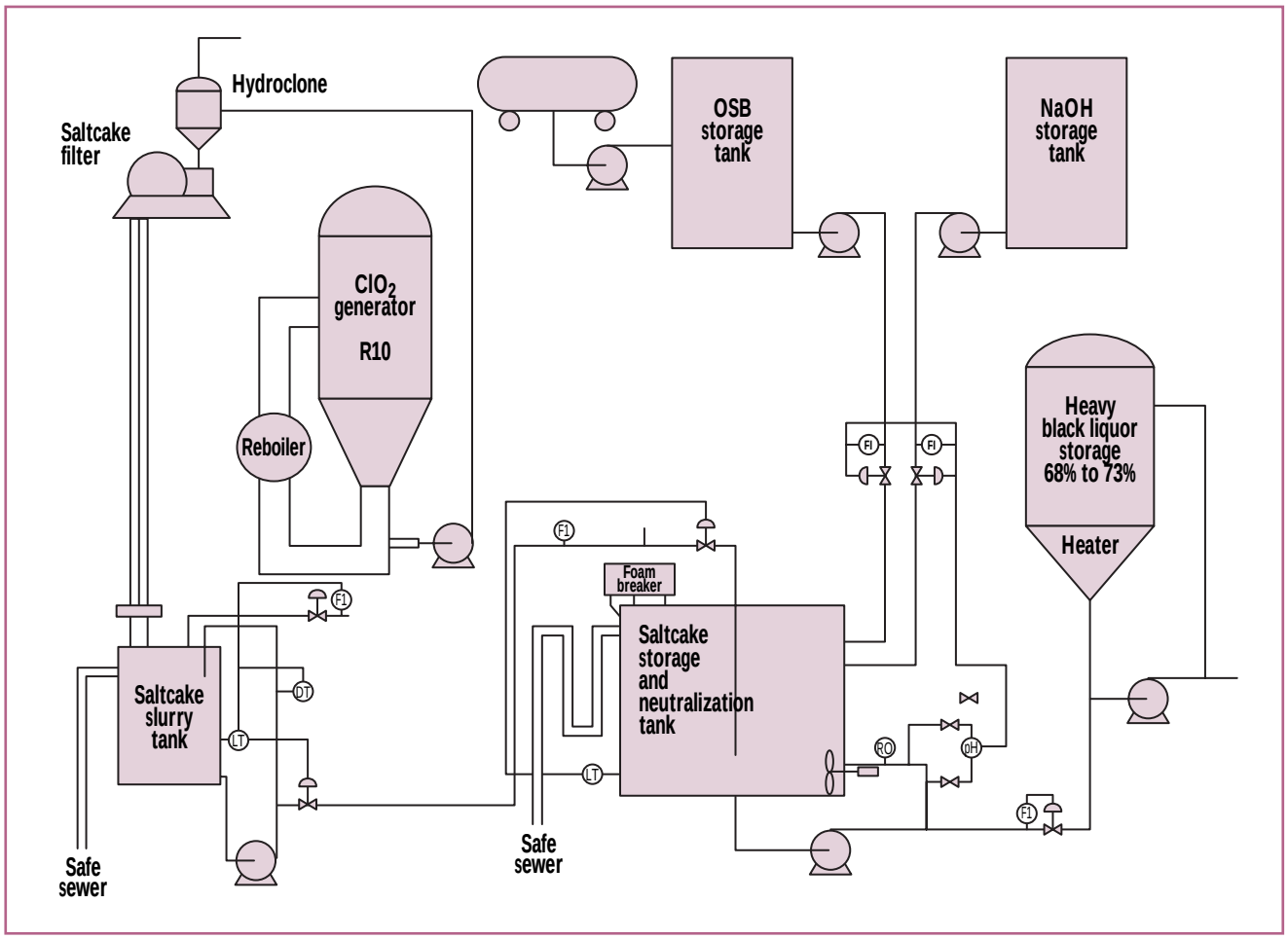
The kraft mill that provided the white-liquor sample shown in Table I is an RDH (rapid-displacement heating) design with eight digesters and a design EA/wood ratio [tons EA (as Na_2O)/ton o.d. wood] of 14.5% (0.145). The current operating EA/wood ratio is 0.195. **Figure 7** shows how the model would predict the relationship between critical BLS and the EA/wood ratio using the white-liquor analysis in Table I and assuming the brownstock yield to be steady at 38.8% (calculated based on pulp inventory and based on procedure shown in this model).

The EA/wood ratio is a pulp-production-driven parameter, and in this case it is quite high. Pulping parameters should be driven based on pulp quality and production and not by the effect on the evaporators. The evaporators should be designed to handle a variable range in burkeite solubility. In this particular case, the burkeite begins to precipitate at about 4% solids lower than it would have at design conditions. It also is important to note that the original design yield was 45%.

Causticizing efficiency

Causticizing efficiency is a measure of how efficient the causticizing area converts sodium carbonate to sodium hydroxide. A lower causticizing efficiency increases the sodium carbonate concentration in the white liquor. For the same EA/wood ratio, more sodium carbonate would be charged to the digesters and would lower the burkeite solubility in the resulting black liquor. **Figure 8** illustrates the relationship between critical BLS and causticizing efficiency using the model.

Burkeite is in the form of $2Na_2SO_4 \cdot Na_2CO_3$. However, it is a



9. Sodium sesquisulfate recovery to heavy liquor

coprecipitate with Na_2CO_3, which is the primary component that affects the critical solids level in black liquor. The exception is during addition of spent acid (or sodium sesquisulfate), which adds additional sodium sulfate to the black liquor.

Addition of spent acid from ClO_2 plant

As reported earlier, this model shows that addition of spent acid to the weak liquor (from a ClO_2 plant operating for 10 hours a day at a rate of 20 tons ClO_2 per day) drops the critical BLS from 49.71% to 47.55%. Many mills experience runnability problems because of increased burkeite scaling when spent acid is added to the weak liquor. To eliminate the additional scaling tendency, the spent acid should be added to the heavy liquor or to the suction of a crystallizer recirculating pump. There must be adequate mixing when adding the unneutralized spent acid to the heavy liquor, and addition should be at a controlled rate to avoid lignin precipitation. A better approach would be to neutralize the spent acid with caustic before adding it to the black liquor.

Figure 9 shows a potential design for the addition of spent acid to the first effect of a multiple-effect evaporator. The design permits addition of neutralized or unneutralized acid. The spent-acid percent solids is also controlled to 22% leaving the slurry tank in the ClO_2 plant. If the solids from the slurry tank are not controlled, then the evaporators could at times be adding water instead of a spent-acid slurry.

Addition of makeup chemicals

Some mills use oil-stripper bottoms (OSB) as a source of sodium makeup. OSB is a byproduct of a chemical process and has a high sodium carbonate content and high heating value. Usually, OSB is added to the weak liquor, producing an increase in sodium carbonate and a decrease in burkeite solubility. Adding the OSB to the heavy liquor and thus bypassing the multiple-effect evaporators will eliminate the additional scaling tendency. Figure 9 shows how the

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alkaline nature of the OSB can be used to neutralize the spent acid from the ClO_2 generator rather than using expensive caustic.

Adding sodium and sulfur makeup sources such as NaOH and NaSH to the white liquor increases the effective-alkali concentration of the white liquor. The result is a decrease in the ratio of total alkali to effective alkali. For an equivalent EA/wood ratio to the digester, less total alkali—and thus less sodium carbonate and sodium sulfate—will be added to the digester. The net result would be an increase in burkeite solubility. However, the overall cost of using these chemical sources would be a factor.

CONCLUSION AND RECOMMENDATIONS

This model provides a base for strategies to control burkeite scaling in multiple-effect evaporators and helps in understanding the factors affecting the critical level of black-liquor solids. There are opportunities for decreasing the burkeite scaling tendencies through improved causticizing efficiency and addition of makeup chemical sources to proper locations. The model can also be used by evaporator manufacturers to identify variations in burkeite solubility and thus design them to handle this variation.

The material balance used to develop the model must be modified for kraft mills with multiple fiber lines or for RDH and batch digester systems that use liquor-inventory management. **TJ**

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