

# EVAPORATOR FOULING

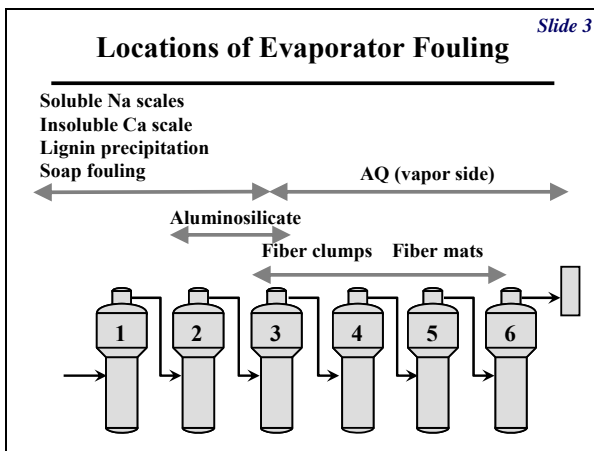
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## INTRODUCTION

Slide 1 and Slide 2 contain the title and outline of the talk.

Slide 3 shows the locations of an evaporator set where fouling occurs due to various mechanisms.



## EVAPORATOR SCALING AND FOULING MECHANISMS

The characteristics of soluble sodium salt scales are presented in Slide 4. Black liquor contains sodium,  $\text{Na}^+$ , sulfate,  $\text{SO}_4^-$ , and carbonate,  $\text{CO}_3^-$ . As liquor dry solids increase, the concentration of these materials also increases, until their solubility limit is exceeded [1]. Salts then crystallize from the liquor and can deposit on the heat transfer surfaces of the evaporator. The scale produced eventually reduces the rate of heat transfer and evaporation in the effect. These sodium scale deposits are soluble in water or weak black liquor so they can be removed by boiling out the effect.

Slide 4

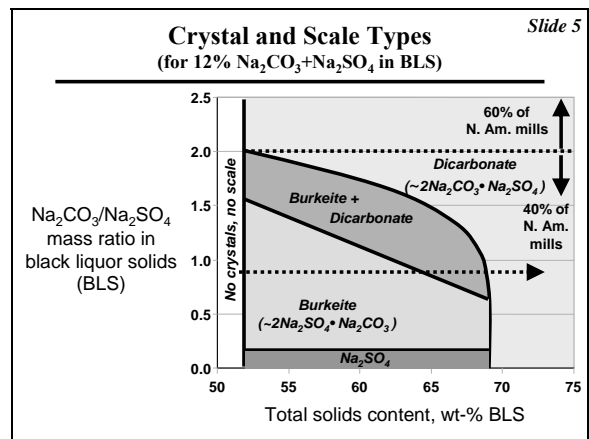
### Soluble Sodium (Na) Scales

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- BL contains about 35% dissolved salts
- Salts can precipitate as scale in evaporators
- $\text{Na}^+$ ,  $\text{SO}_4^-$  and  $\text{CO}_3^-$  cause scaling
- Scale composition mostly  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$
- Appear brown, grainy, dense, and hard
  - Deposit samples dissolve in hot water
- Can be removed by boiling out

Two different types of sodium salt scales have been identified in black liquor evaporators. One is a sulfate-rich compound called burkeite. Burkeite is a double salt that contains approximately 2 moles of  $\text{Na}_2\text{SO}_4$  and one mole of  $\text{Na}_2\text{CO}_3$ . The other is a carbonate-rich compound that contains approximately 2 moles of  $\text{Na}_2\text{CO}_3$  and one mole of  $\text{Na}_2\text{SO}_4$ . It is referred to as dicarbonate [1]. The compositions of each of these two compounds can vary. The scales produced when they crystallize from black liquor behave very differently in evaporators and concentrators.

Slide 5 is a scale composition map that shows two important aspects burkeite and dicarbonate. One is that either may crystallize from black liquor, or they may crystallize simultaneously. Which of them crystallizes depends upon the ratio of carbonate to sulfate in the black liquor. At higher ratios, dicarbonate crystallizes as black liquor is concentrated, while at lower ratios, burkeite crystallizes. There is an intermediate composition range where both can crystallize simultaneously.



The second important point from Slide 5 is that, as evaporation of black liquor proceeds, the crystals produced can change from burkeite to dicarbonate. This happens because burkeite is sulfate-rich. As burkeite

crystallizes, sulfate is removed from solution faster than carbonate, and the dissolved salts remaining become richer in carbonate.

To control sodium salt scales in black liquor evaporators, we must know whether burkeite, dicarbonate, or both are crystallizing. Recent data from 29 different kraft pulp mills indicate that, in 40% of these mills, burkeite or a mixture of burkeite and dicarbonate crystallize first as the liquor is concentrated, but dicarbonate may eventually be crystallized. In the other 60% of the mills, dicarbonate crystallizes first.

Sodium salt scales also contain organic matter that can be up to half of the total weight of the deposit, and is an important contributor to the fouling characteristics of the deposit.

To control sodium salt scaling, it is also important to know when crystallization begins, and when the transition from burkeite to dicarbonate occurs. **Slide 6** summarizes some of the general characteristics of  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$  salt crystallization. The solubility limit corresponds to the "critical solids content." Below the critical solids content, all of the sodium salts are completely dissolved. As the solids increases past this point, supersaturation develops and eventually the crystallization point is reached. At this point, the sodium salts begin to precipitate and can deposit as scale on the evaporator heat transfer surfaces.

### Onset of Crystallization

Slide 6

- Below critical solids all Na salts are dissolved
- Critical solids typically ~ 50% and 55%
- Crystallization point 1-5% above critical solids
- First salt depends on  $\text{CO}_3 / \text{SO}_4$  ratio in BL
  - Low ratios: Burkeite ( $\sim 2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ )
  - High ratios: Dicarbonate ( $\sim 2\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$ )
- For BL > 110°C (230°F), slight inverse solubility of salts

The total sodium content in black liquor is typically near 20%, and  $\text{Na}_2\text{SO}_4$  is frequently between 3 and 6 wt% of BLS, so the critical solids is usually between 50% and 55% black liquor dry solids.

**Slide 7** summarizes the factors that control when the transition from burkeite to dicarbonate crystallization occurs. This transition is more difficult to predict, and advanced calculation methods are required [for example see reference 2].

### Transition to Dicarbonate Crystallization

Slide 7

- Crystallization removes dissolved Na salts from BL
- If burkeite first, two  $\text{Na}_2\text{SO}_4$  removed per  $\text{Na}_2\text{CO}_3$
- When  $\text{Na}_2\text{SO}_4$  depleted, burkeite can't form
- Solids content at onset decreases with increasing  $\text{CO}_3 / \text{SO}_4$  ratio in black liquor

LTV evaporators have been susceptible to fouling by burkeite. **Slide 8** shows the various ways to reduce soluble scale formation in LTV black liquor evaporators. Reducing the content of each of the components that lower the critical solids is the basic approach to controlling this problem. Note that each of the three ( $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$  and total Na) is controlled by mill operations outside of the evaporator area. The operating approach within the evaporator area that can reduce soluble sodium scaling is to operate the evaporators with product dry solids about 2 to 3% below the critical solids.

### Reduce Na Scale in LTV Evaporators

Slide 8

- Reduce  $\text{Na}_2\text{CO}_3$ 
  - White liquor from recaust contains  $\text{Na}_2\text{CO}_3$
  - Improve causticizing efficiency, 80 - 82%
- Reduce  $\text{Na}_2\text{SO}_4$ 
  - Increase RB reduction efficiency, > 90%
  - Add saltcake/spent acid after LTV bodies
- Reduce total Na in black liquor
  - Control AA-to-wood target at digester
  - Reduce NaCl deadload
- Operate about 2 - 3% below critical solids

The situation in black liquor concentrators is slightly different. All concentrators operate well above the critical solids so sodium compounds are always going to crystallize as water is evaporated from black liquor. The approaches to avoiding scaling are (a) to encourage the sodium salts to crystallize on the suspended crystals instead of on the heat transfer surfaces, and (b) to avoid massive nucleation events that produce very fine crystals that agglomerate on heat transfer surfaces.

Falling-film evaporators and concentrators are not particularly susceptible to burkeite fouling, but are to dicarbonate fouling. **Slide 9** shows the characteristics of sodium salt scales in these units.

*Slide 9*

### Soluble Na Scale in FF Evaporators and Concentrators

- Falling film evaporators are *not* susceptible to burkeite scale
- Concentrators typically operate where dicarbonate fouling can occur
- All concentrators are crystallizers
  - Want crystallization on suspended solids, not heater surface
  - Dicarbonate crystallizes only on dicarbonate
- Tools being developed to determine *where* in concentrator dicarbonate crystals will form

Falling film evaporator effects operate best at a steady product solids level, either well above or just below a point of salt crystallization. Fluctuating solids levels that cause an effect to “swing” through crystallization points can dramatically increase fouling and plugging rates by creating periodic massive nucleation events. Dicarbonate fouling on heat transfer surfaces can be minimized if there are suspended crystals present in the liquor.

**Slide 10** summarizes how to reduce sodium salt fouling in black liquor concentrators.

*Slide 10*

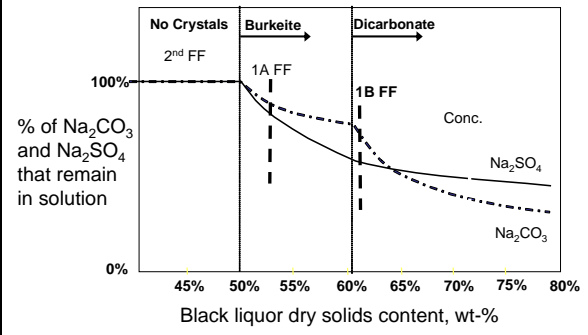
### Reducing Na Scale in FF Concentrators

- Operate with solids profile that avoids running any effect at the crystallization point of dicarbonate; preferable to operate above it.
- Start up with product liquor
- Use high liquor recirculation rates
- Long residence time in concentrator
- Distribute liquor uniformly on heater surfaces
- Operate to avoid upset conditions
  - Slow, ramped changes in operation
  - Minimize changes in black liquor composition

A situation expected to suffer from dicarbonate scaling is illustrated in **Slide 11**.

*Slide 11*

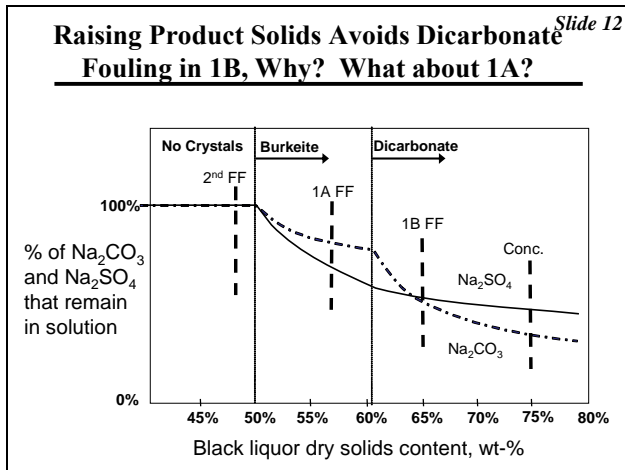
### Evaporator Configuration Where Dicarbonate Fouling Will Occur in 1B, Why?



The initially horizontal but later decreasing curves show the amounts of dissolved  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SO}_4$  in the system at any point during the evaporation process. The vertical, dashed lines mark the product solids concentration of black liquor exiting the various bodies of a hypothetical falling-film evaporator and forced circulation concentrator. In this illustration, the transition from burkeite to dicarbonate crystallization occurs in the 1B falling-film body. The crystal population in body 1B contains mainly burkeite and very little dicarbonate. Dicarbonate will not crystallize on burkeite crystals, and there are insufficient dicarbonate crystals to relieve supersaturation. Body 1B will foul when supersaturation reaches the crystallization point and a massive nucleation event occurs.

Our understanding of crystallization during black liquor evaporation suggests that operating an effect well above a crystallization point can help reduce episodes of surface fouling and tube plugging by maintaining a stable population of suspended salt crystals. In this case, supersaturation is kept low by slow growth of the suspended crystals and the chance of nucleation of a large number of new fine particles is minimized. It is the fine particles that can more easily “stick” to the tube surface and foul the evaporator.

This improved mode of operation is illustrated in **Slide 12**.



Since the product solids content from the 1B body is well above the transition point from burkeite to dicarbonate crystallization, there will be a substantial population of dicarbonate crystals in the liquor. Dicarbonate will be able to crystallize on the suspended crystals. The high degree of supersaturation needed for primary nucleation and subsequent fouling will never be reached.

To make the elevated solids content strategy work, it is essential to maintain suspended crystals in the falling-film effects at all times. A means to start up on recirculated product liquor after on-line washes and off-line boil outs will be needed. This provides a population of “seed” crystals to prevent high supersaturation from developing when the evaporator is recovering from a wash or boil out. It also helps to stabilize crystallization by maintaining the highest practical liquor volume in the falling-film effect sump and increasing the recirculation rate.

Concentrator design plays a major role in avoiding Na scaling, but there are two steps that can be taken with existing concentrators that help: ensure that liquor distribution is uniform, and start up the concentrator on stored product liquor that contains the same sodium salt crystals that will be produced during evaporation. Accumulation of flakes of scale and fiber can cause poor liquor distribution and increased Na scaling. Fiber control will be discussed later in this section.

**Slide 13** describes insoluble calcium scales. Calcium scale in evaporators is usually  $\text{CaCO}_3$ , which is nearly insoluble in water or alkaline solutions. At higher dry solids levels, where the sodium salts are more concentrated,  $\text{CaCO}_3$  can co-precipitate with  $\text{Na}_2\text{CO}_3$  as the double salt, pirssonite. Pirssonite is partially soluble in water, so calcium deposits are often not as severe a problem in concentrators as in evaporators.

Slide 13

### Insoluble Calcium (Ca) Scale

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- Dissolved Ca precipitates as insoluble  $\text{CaCO}_3$  or Pirssonite ( $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3$ )
- White or tan scale with high (>20%) calcium
  - Deposit samples dissolve in acid
- $\text{CaCO}_3$  scale cannot be removed by boiling out
  - Hydroblasting required
  - Acid or chemical cleaning after
- Pirssonite is partially soluble due to its  $\text{Na}_2\text{CO}_3$

**Slide 14** shows why dissolved Ca is higher in black liquor than would be expected from its solubility product. Calcium would normally precipitate immediately in black liquor due to the high carbonate ( $\text{CO}_3^{2-}$ ) content. However, the organics in black liquor allow much higher levels of calcium to stay dissolved. It is difficult to limit Ca levels in black liquor because most of it comes from the wood chips.

Slide 14

### Dissolved Calcium in BL

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- Calcium in BL has very low solubility
  - Solubility product indicates ~ 50 ppb ( $\mu\text{g}/\text{Kg}$ )
- BL organics keep Ca in solution
  - Typical dissolved Ca in BL ~ 200 to 2000 ppm ( $\text{mg}/\text{Kg}$  on BLS)
  - Soluble Ca is from wood, not lime carryover
- Difficult to control Ca input to black liquor
  - Good debarking helps

**Slide 15** describes the mechanism by which calcium in black liquor is converted to scale.

**Slide 16** shows a schematic diagram of the calcium deposition mechanism. Calcium is released when the organics break down at higher temperatures [3]. It precipitates as either  $\text{CaCO}_3$  or pirssonite. Both are very insoluble and form insoluble deposits on the heat transfer surfaces of evaporators.

Slide 15

### Mechanism For Ca Precipitation

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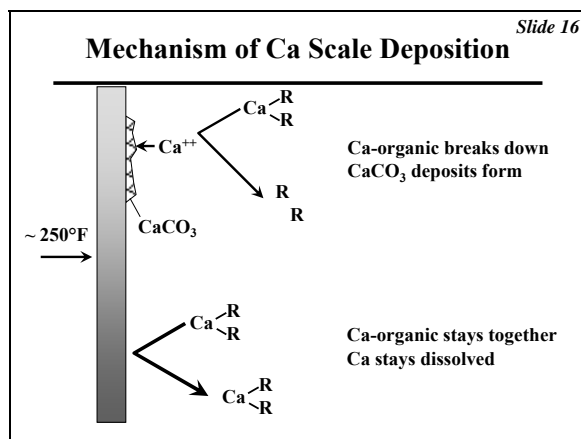
- **High temperatures break down organic**
  - Occurs near heat transfer surfaces
  - $\text{Ca}^{2+}$  is released, combines with  $\text{CO}_3^{2-}$  → deposits on surfaces
- **Typically occurs at ~ 250°F (120°C)**
  - Can occur at 220°F (104°C) in displacement batch pulping liquors

Slide 17

### Reducing Ca Scale in Evaporators

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- **Limit steam pressure to evaporators**
  - Max pressure ~ 30 to 35 psig (capacity?)
- **Improve soap skimming efficiency**
  - Soap contains high soluble calcium
- **Add tall oil spent brine (laden with calcium) after the evaporators**
- **Improve debarking**
- **Thermal deactivation**



**Slide 18** shows information about aluminosilica scaling. Al-Si scales do not occur frequently, but are problematic when they do.

Slide 18

### Aluminosilicate Scale

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- **Thin, glassy scale in mid-to-high solids effects**
  - Deposit samples do not dissolve in most solvents
- **Caused by dissolved Al and Si in BL**
  - Al is 30 to 300 ppm (mg/Kg) of BLS
  - Si is 300 to 2000 ppm of BLS
- **Concern when Al > 150 to 200 ppm of BLS**
- **Hydroblasting required**

Mills with displacement batch pulping often have much more severe problems with  $\text{CaCO}_3$  fouling in their evaporators. In these mills, the fouling occurs at lower temperatures, sometimes where the product liquor temperature is below 212°F (100°C). The reason is that soluble calcium-organic-bound calcium is extracted from wood chips by weak black liquor, which never is subjected to high temperature in a digester which reduces its fouling tendency [4].

**Slide 17** shows methods for controlling calcium scales in evaporators.

It is possible to keep the temperature of the heat transfer surfaces below the level that causes organic break down by limiting the input steam pressure to less than 35 psig, or by re-plumbing the evaporator set so that the product black liquor comes from the 2<sup>nd</sup> effect. This latter approach routes the black liquor from the 3<sup>rd</sup> effect to the 1<sup>st</sup> effect, and back to the 2<sup>nd</sup> effect. The steam temperature in the 2<sup>nd</sup> effect is lower so the surface temperatures are also lower; avoiding the temperatures that cause the release of dissolved calcium.

**Slide 19** shows the basic approaches to control this type of scale by limiting the content of Al in the black liquor. Several methods are listed on the slide. There is good data to show that magnesium in the green liquor can help reduce the Al content [5], and there have been schemes to add Mg to green liquor to promote Al removal.

Slide 19

### Control of Al-Si scales Which may apply to your mill?

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- **Decrease bark and dirt in chips**
- **Decrease Al-Si in water and make-up lime**
- **Avoid white water in brown stock washing**
- **Minimize use of silicon-based defoamers**
- **Increase Al-Si purges in dregs and grits**
  - Mg in GL can aid Al removal with dregs

**Slide 20** presents information on fouling due to black liquor soap. Soap by itself does not precipitate as a deposit, but can be incorporated in soluble and insoluble scales and contribute to fouling. Soap also contains higher concentrations of both dissolved calcium and fiber than the rest of the black liquor, so it can contribute to insoluble Ca scaling and to fouling due to fiber. The only remedy is better soap removal.

*Slide 20*

**Fouling Due to BL Soap**

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- **Soap can be incorporated into other scales**
  - Deposit samples have slippery appearance
- **Contains high fiber content and soluble Ca**
- **Can increase fouling rates**
- **Controlled by controlling other scales**
- **Only remedy is better soap skimming**

Fiber is also not a primary scaling agent. **Slide 21** describes how fiber can plug evaporator tubes. **Slide 22** describes how fiber can disrupt the liquor flow on the distributors of falling film evaporators and concentrators.

*Slide 21*

**Fouling Due to Fiber Plugs**

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- **Fiber can form mats in low-solids effects**
  - Heavier than weak liquor
  - Concentrates in stagnant areas
- **Calcium carbonate can deposit on fiber in mid-solids effects, forming clumps**
- **Dislodged mats and clumps can plug tubes**
  - Fiber is obvious in magnified deposit samples

*Slide 22*

**Fiber Fouling in Falling Film Units**

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- **Clumps stick in distributor plate openings**
- **Causes poor liquor distribution**
- **Only remedy is fiber removal from liquor**
- **Install and maintain fiber filter**
  - Target < 100 ppm fiber in BL streams to evaps

Fiber accelerates other scaling mechanisms by plugging evaporator tubes and disrupting liquor distribution in falling film evaporators and concentrators. The only remedy is better fiber removal from the liquor.

Fouling due to lignin precipitation is dependent on the pH of the black liquor. The pH for lignin precipitation increases with the level of dry solids, but the pH of the liquor increases as well. In general, a good target for weak black liquor pH is above 12, and several ways of controlling liquor pH are listed in **Slide 23**.

*Slide 23*

**Fouling Due to Lignin**

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- **Lignin precipitates at low liquor pH**
  - Deposit samples are soft and gunky
- **Maintain weak liquor pH > 12**
- **Control residual EA from digester**
- **Neutralize acidic inputs**
  - ClO<sub>2</sub> plant sesquisulfate
  - Tall oil plant brine
- **Add caustic or white liquor**

## CLEANING EVAPORATORS

**Slide 24** presents the various methods for cleaning black liquor evaporators. Boiling out is the most common method when soluble or partially soluble scales are present. Hydroblasting is the most common technique when insoluble scale builds up on the heat transfer surfaces. Because insoluble deposits have a large component of CaCO<sub>3</sub>, acid cleaning can be used to dissolve them, and more recently chemical cleaning has been used for the same purpose. These latter techniques only work well after hydro-blasting to remove the bulk of the deposits.

*Slide 24*

### Cleaning Evaporators

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- **Boiling out**
  - Dissolves Na scales
  - Removes hard scales by thermal shock
- **Hydroblasting**
- **Chemical cleaning**
  - Muriatic acid
  - Sulfamic acid
  - Chemical / chelant wash

**Slide 25** summarizes the procedure for cleaning black liquor evaporators by boiling them out.

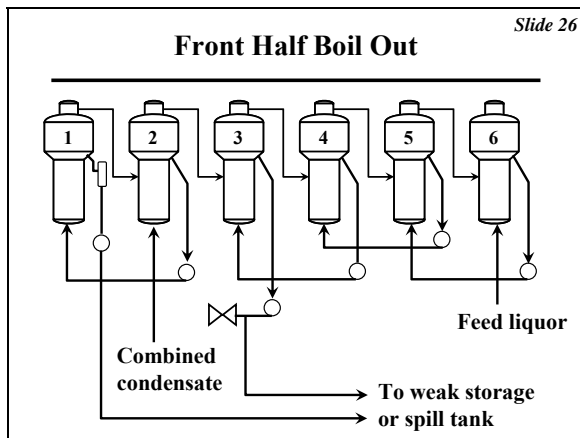
*Slide 25*

### Boiling Out Evaporators

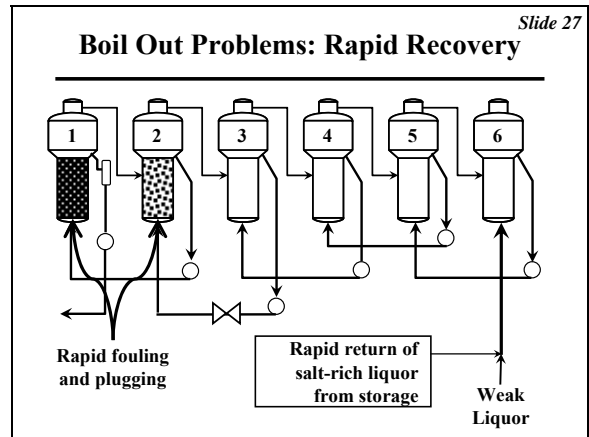
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- **Boil out procedures**
  - Full
  - Front half (1st and 2nd effect)
  - Back half
- **Wash liquid**
  - Weak liquor (15% to 35%)
  - Condensate
  - Fresh water

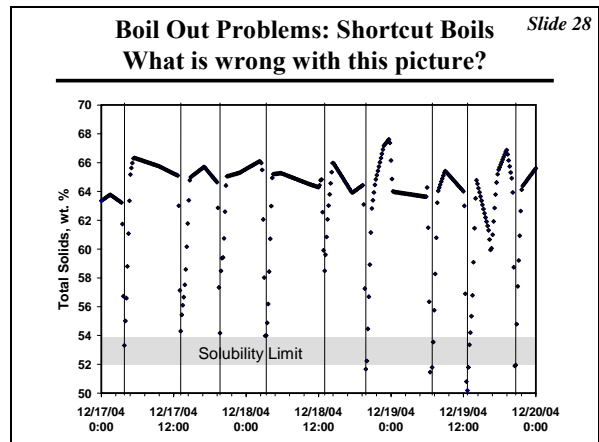
For a full boil out, combined condensate, weak liquor, or water can be used. During the boil out the evaporators are not working at full capacity, and the boil out results in additional water that must be evaporated. An approach to reducing the impact of boiling out on overall evaporator throughput is to boil out only the portion of the set that is fouled. One such arrangement is shown in **Slide 26**.



During a boil out the dilute boil-out liquor is transferred to a spill or boil-out tank and then typically pumped back to the weak liquor system that feeds the evaporator. Because it contains dissolved scale and deposits, the boil-out liquor is richer in  $\text{Na}^+$ ,  $\text{CO}_3^-$ , and other scale species, than the normal feed liquor [6]. It is important to transfer this waste stream back to the evaporator feed as slowly as possible to avoid recurrent massive nucleation and rapid fouling events, as shown in **Slide 27**.



Shortcut procedures are often employed for evaporator boils to increase time on line for the equipment. **Slide 28** presents mill data for a series of rapid boils in a falling film evaporator operating at about 65% total solids content. The minimum solids reached rarely drops below the critical solids content of ~53% and the duration of the boil is insufficient to dissolve any soluble scale deposits. In this situation it would be better to wash for longer once per day than follow a shortcut procedure each shift.



**Slide 29** provides guidelines for conducting effective boil outs.

## Boil Out Guidelines

Slide 29

- Transfer boil-out liquor back to evaporator feed as slowly as possible
- During boil must drop below solubility limit and hold long enough to dissolve crystals
- Controlled product liquor recirculation may restore crystal population after boils

## Implications for Evaporator Operation

Slide 31

- Some remedies involve evaporator operation
  - Handling boiler ash and Na/S waste streams
  - Limiting steam pressure
  - Soap skimming
  - Flow configuration, boil out procedures
  - Steady controlled operation, steady liquor transfers

### SUMMARY

Due to the variety of mechanisms for scaling and fouling of evaporators, they work best when they are operated in a steady manner. Steady feed and steady transfer of liquor between the effects allows them to avoid some of the conditions that promote rapid surface fouling. The most effective ways to mitigate recurrent soluble scale fouling can be counter-intuitive, e.g., higher product solids is better, and less frequent washing is better. It may be difficult to overcome operating culture to implement such strategies; therefore, hard piping changes or automated procedures are sometimes the only way to solve these problems. More information on evaporator operation and fouling can be found in references 7 and 8.

Slides 30 and 31 summarize the implications of black liquor fouling on evaporator operation.

## Implications for Evaporator Operation

Slide 30

- Many potential causes for fouling
- Remedies often involve other areas of the mill
  - Recovery boiler for Na<sub>2</sub>SO<sub>4</sub> input to BL
  - Recast for Na<sub>2</sub>CO<sub>3</sub> input to BL
  - Digester for total Na and residual EA
  - Brownstock washing / screening fiber input to BL
  - Wood room for bark (Ca) and dirt input to liquor

### ACKNOWLEDGEMENT

Appreciation is expressed to Christopher L. Verrill, International Paper, author of the 2007 manuscript, which was the starting point for this 2008 revision.

### FURTHER READING

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