EVAPORATOR FOULING

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INTRODUCTION

The capacity of many black liquor evaporators and most high-solids concentrators suffers from scaling or fouling of their heat-transfer surfaces. Scale and foulants on heat transfer surfaces decrease the overall heat transfer coefficients in black liquor evaporators. This decreases heat transfer and evaporation rates, and black liquor evaporation capacity.

Scaling occurs when inorganic salts crystallize or collect on heat transfer surfaces. The most prevalent types of scale in black liquor evaporators are

- Sodium carbonate and sulfate scales
- Calcium carbonate scales
- Aluminosilicate scales

Fouling is the result of organic matter (fibers, lignin, soap, AQ) collecting on or between heat transfer surfaces.

Figure 1 shows the locations in an evaporator set where fouling occurs due to various mechanisms.

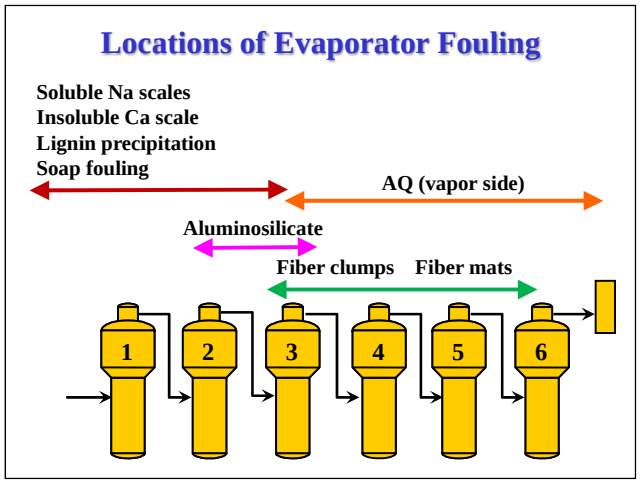


Figure 1. Locations where different types of scaling and fouling occur in black liquor evaporators.

EVAPORATOR SCALING AND FOULING MECHNISMS

The characteristics of soluble sodium salt scales are presented in **Figure 2**. Black liquor contains sodium sulfate (Na_2SO_4), and sodium carbonate (Na_2CO_3). As liquor dry solids increase, the concentration of these chemicals also increases, until their solubility limit is exceeded [1]. They then crystallize as solid salts from the liquor and can deposit on heat transfer surfaces of the evaporator. The scale they produce eventually reduces the rate of heat transfer and evaporation in the bodies. These sodium salt scale deposits are soluble in water or weak black liquor so they can be removed by boiling out the evaporator bodies. For this reason, these scales are also referred to as *soluble scales*.

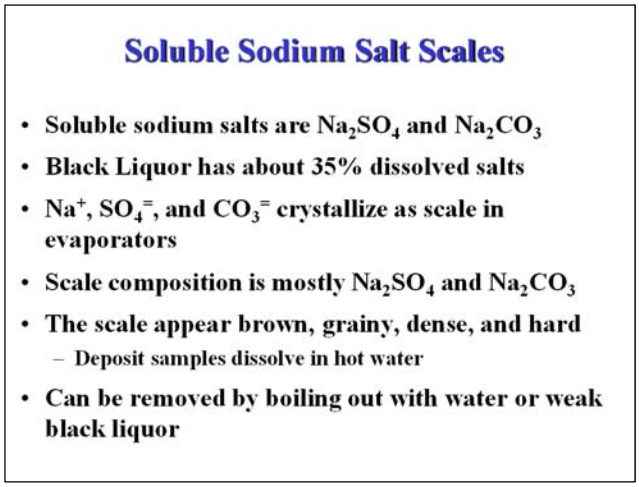


Figure 2. The characteristics of soluble sodium salt scales.

Figure 3 shows an example of severe soluble scale fouling on a 2" OD evaporator tube.



Figure 3. Severe soluble scale fouling inside a 2" OD evaporator tube.

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 Na_2SO_4 and one mole of Na_2CO_3. The other is a carbonate-rich compound that contains 2 moles or more of Na_2CO_3 per mole of Na_2SO_4. It is named sodium sulfate dicarbonate but is commonly referred to as dicarbonate [1]. Dicarbonate is the more prevalent of the two sodium salt scales in black liquor evaporators and concentrators. 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.

Figure 4 is a scale composition map that shows two important aspects of 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.

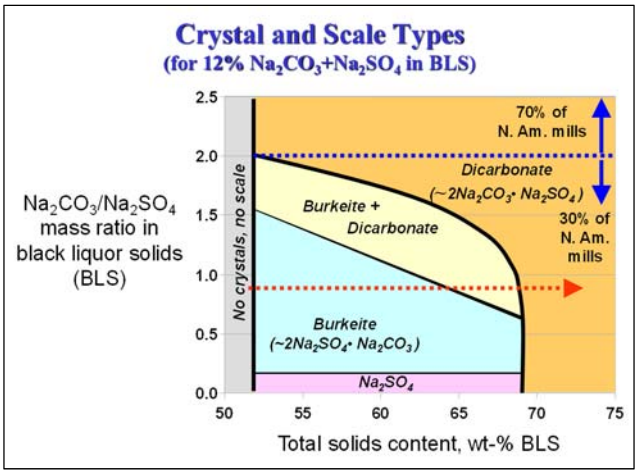


Figure 4. A scale composition map for Burkeite and dicarbonate.

The second important point from Figure 4 is that, as evaporation of black liquor proceeds, the salts being crystallized 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 in solution become richer in carbonate.

To control sodium salt scales in black liquor evaporators, we must know whether Burkeite, dicarbonate, or both are crystallizing. Past and recent data from 31 different kraft pulp mills indicate that, in 30% of these mills, Burkeite or a mixture of Burkeite and dicarbonate crystallized first as the liquor is concentrated, but eventually dicarbonate crystallized. In the other 70% of the mills tested, dicarbonate crystallized first [10].

Sodium salt scales also contain interstitial 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 important to know when crystallization begins, and when the transition from Burkeite to dicarbonate crystallization occurs. **Figure 5** summarizes some of the general characteristics of Na_2SO_4 and Na_2CO_3 salt crystallization. Below their solubility limit, all of the sodium salts are completely dissolved. As the solid content increases past this point, super-saturation develops and eventually the crystallization point is reached. At this point, the sodium salts begin to crystallize and can deposit as scale on the evaporator heat transfer surfaces.

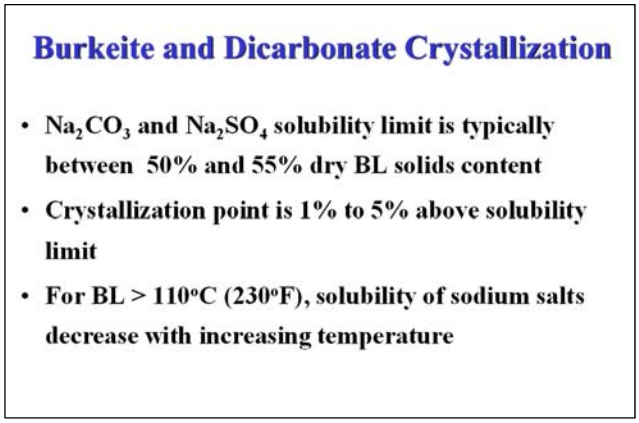


Figure 5. Crystallization characteristics of Burkeite and dicarbonate.

The total sodium content in black liquor is typically near 20%. The Na_2SO_4 and Na_2CO_3 contents are frequently between 3 and 6 wt-% and 5 to 8 wt-%, respectively, of BLS. The crystallization point is defined as the black liquor solids concentration at which crystallization begins. It is usually between 50% and 55% black liquor dry solids content.

Figure 6 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].

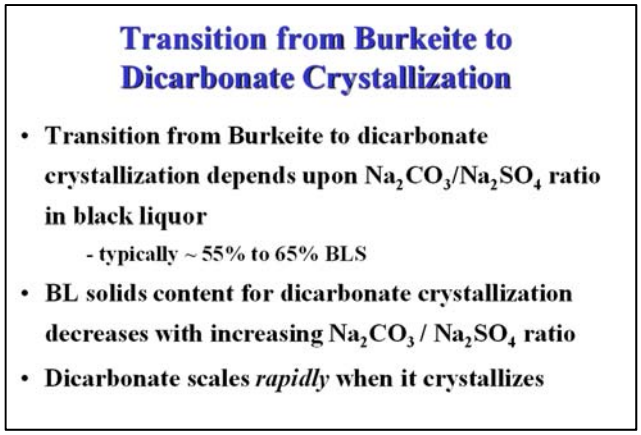


Figure 6. Factors that control transition from Burkeite to dicarbonate crystallization.

LTV evaporators have traditionally been susceptible to fouling by Burkeite. **Figure 7** shows the various ways to reduce soluble scale formation in LTV evaporators. Reducing the content of each of the components that lower the solubility limit and crystallization point is the basic approach to controlling this problem. Note that each of the three (Na_2SO_4, Na_2CO_3 and total Na) is controlled by mill operations outside of the evaporator area. An operating approach that can reduce soluble sodium salt scaling is to operate the evaporators with product dry solids content about 2 to 3% below the solubility limit.

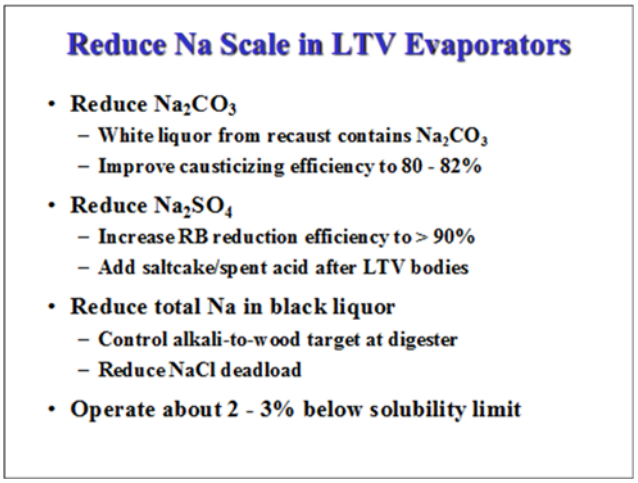


Figure 7. Actions to reduce soluble sodium salt scaling.

The situation in black liquor concentrators is slightly different. All concentrators operate well above the solubility limit of sodium carbonate/sodium sulfate double salts, so those 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 fine submicron crystals that agglomerate in suspension and on heat transfer surfaces. Spontaneous nucleation is rapid, and dicarbonate rapidly fouls heat transfer surfaces when it happens.

A second example is one where the concentrators are started up with about 65 wt% black liquor which contains dicarbonate crystals. As black liquor is concentrated, supersaturation is relieved by crystal growth on the already-present dicarbonate crystals. No significant supersaturation occurs, and massive nucleation events are avoided. Dicarbonate fouling is avoided or at last minimized.

Falling-film evaporators and concentrators are not particularly susceptible to Burkeite fouling, but are to dicarbonate fouling. **Figure 8** shows the characteristics of sodium salt scales in these units.



Figure 8. Soluble Na salt scales in falling film evaporators and concentrators.

Falling film evaporator bodies operate best at a steady product solids concentration level, either well above or just below a point of salt crystallization. Fluctuating solids concentration levels that cause a body to "swing" through a crystallization point can increase dramatically fouling and plugging rates by creating periodic massive nucleation events. Dicarbonate fouling on heat transfer surfaces is minimized when suspended dicarbonate crystals are present in the liquor.

Figure 9. summarizes how to reduce sodium salt fouling in falling film black liquor concentrators [10].

Reducing Na Scale in FF Concentrators

- **Avoid operating any body at the crystallization point of dicarbonate; preferable to operate above it**
- **Long residence time in concentrator**
- **Operate with high dicarbonate crystal concentration**
  - **Use high liquor recirculation rates**
- **Operate with low ΔT and low heat flux**
- **Start up with product liquor**
- **Distribute liquor uniformly on heater surfaces**
- **Operate to avoid upsets or changing conditions**

Figure 9. Reducing sodium salt scale in FF concentrators.

In Figure 10, the initially horizontal but later decreasing curves show the amounts of dissolved Na_2CO_3 and Na_2SO_4 in the system at any point during the evaporation process. The dissolved Na_2CO_3 content drops faster once dicarbonate begins to crystallize.

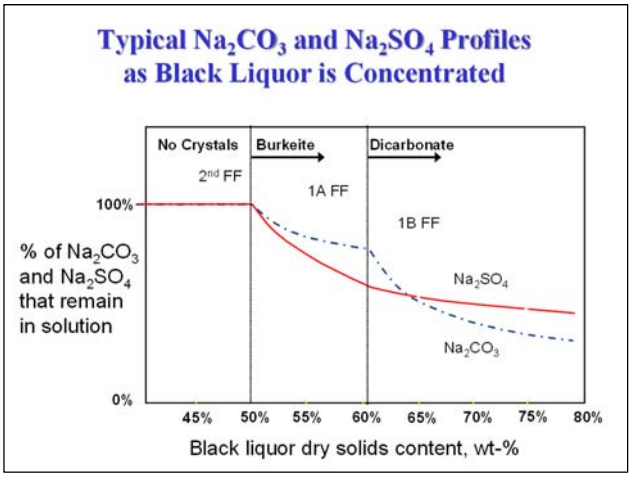


Figure 10. Typical Na_2CO_3 and Na_2SO_4 profiles as dry solids content increases during BL concentration.

Black liquor concentrators act as batch crystallizers with constant black liquor flow through each effect. The total amounts of sodium sulfate and sodium carbonate in each do not change very much with time. However, the relative amounts of each of Na^+, $CO_3^=$, $SO_4^=$, Burkeite and dicarbonate changes with time because crystallization is not always a steady process during startup. Here are two important examples.

1. In the first, the concentrators are started up on 50% dry solids content black liquor. This liquor contains no dicarbonate crystals as shown in Figure 10. As the black liquor is concentrated, no dicarbonate crystals are there to relieve supersaturation. The black liquor becomes supersaturated with Na_2CO_3 and Na_2SO_4 until it reaches a stability limit for supersaturation. At that point a massive crystallization event occurs, relieving supersaturation and generating a large amount of very fine crystals. These crystals collect rapidly on heat transfer (and other) surfaces, causing rapid scaling.

2. The second case is one where the concentrators are started up with black liquor recycled from a downstream concentrator body or storage tank – for example with black liquor at 65wt% total solids content. Liquor at these conditions contains dicarbonate crystals, enough to prevent supersaturation from building up, and to prevent massive crystallization and scaling events. Concentrators operated this way will not encounter rapid, periodic dicarbonate scaling.

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, super-saturation 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.

Since the product solids content from the 1B body in Figure 10 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 dicarbonate 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.

$CaCO_3$ Scales

Calcium scale in evaporators is usually $CaCO_3$, which is nearly insoluble in water or alkaline solutions. At higher dry solids levels, where the sodium salts are more concentrated, $CaCO_3$ can co-precipitate with Na_2CO_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.

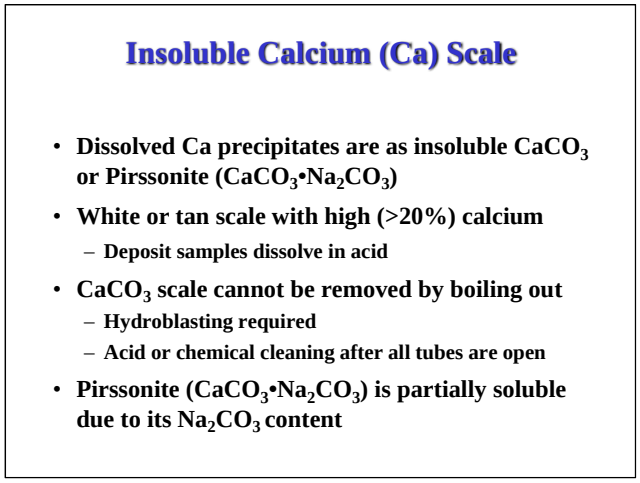


Figure 11. $CaCO_3$ and Pirssonite scales.

Figure 12 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 ($CO_3^{=}$) content. However, some of the organic matter in black liquor forms soluble complexes with Ca. This 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 and bark. Ca also comes from mill water with a high hardness (Ca) level, but Ca from this source does not contribute to Ca scale in black liquor evaporators.

Figure 13 shows a schematic diagram of the calcium deposition mechanism. Calcium is released when the Ca-organic complexes dissociate at higher temperatures [3]. It precipitates as either $CaCO_3$ or pirssonite. Both are very insoluble in black liquor and form insoluble deposits on the heat transfer surfaces of evaporators.

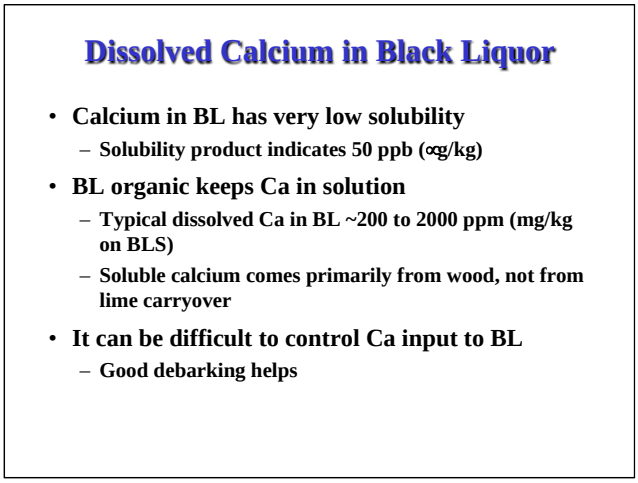


Figure 12. Why dissolved Ca is higher in black liquor than in water.

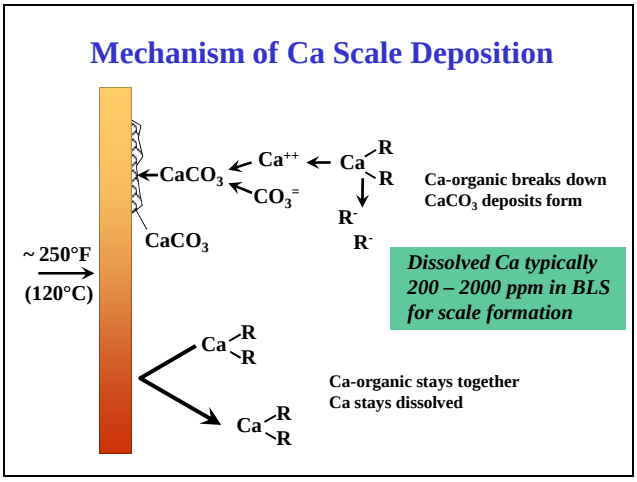


Figure 13. The mechanism by which calcium in black liquor is converted to scale.

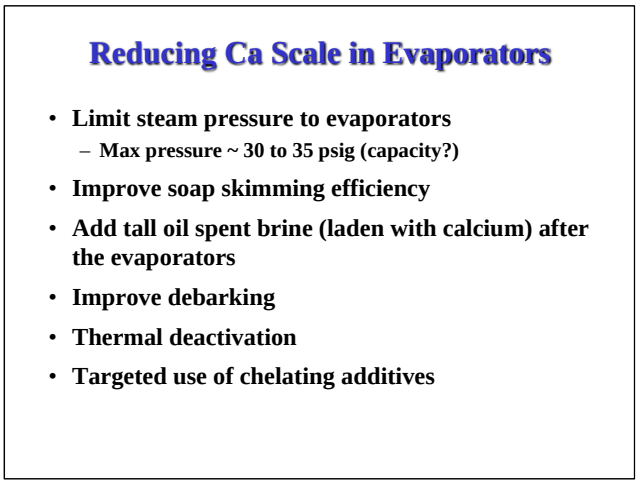


Figure 14. Reducing Ca scale in BL evaporators.

Mills with displacement batch pulping often have much more severe problems with $CaCO_3$ 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 the high temperature in a digester that reduces its fouling tendency [4].

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 2nd effect. This latter approach routes the black liquor from the 3rd effect to the 1st effect, and back to the 2nd effect. The steam temperature in the 2nd effect is lower so the surface temperatures are also lower; avoiding the temperatures that cause the release of dissolved calcium. However, the 1st effect still has the high steam temperature and will be prone to calcium scaling, since it is not dependent on percent black liquor solids content.

Figure 15 shows information about aluminosilicate scaling, and **Figure 16** tells how to control them. Al-Si scales do not occur frequently, but are problematic when they do. 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. The preferred approach is to identify and eliminate the source of high Al into the liquor cycle.

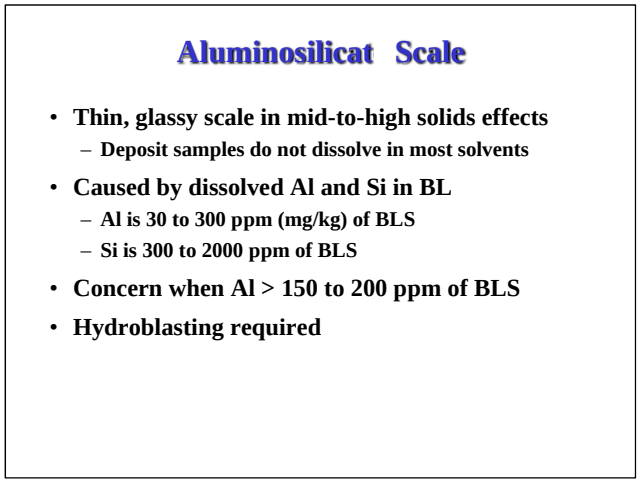


Figure 15. Characteristics of Aluminosilicate Scaling.

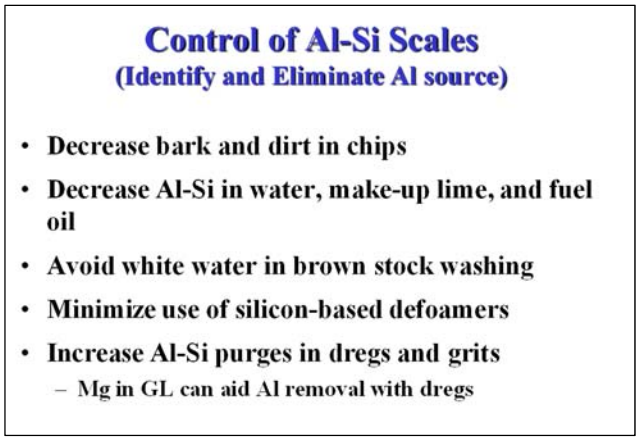


Figure 16. Controlling Al-Si scales.

Figure 17 presents information on fouling due to fiber in black liquor and 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 that way. 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. Fiber is not a primary scaling agent, but it can incorporate itself into scale deposits, and can form fiber clumps in evaporator tubes. Fiber accelerates other scaling mechanisms by plugging evaporator tubes and disrupting liquor distribution in falling film evaporators and concentrators. The only remedy for soap and fiber contributing to fouling is better soap and fiber removal.

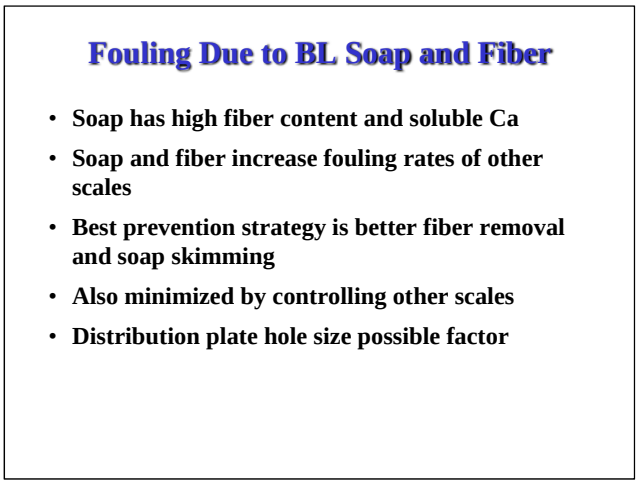


Figure 17. How BL soap and fiber contributes to evaporator fouling.

Lignin can precipitate on heat transfer surfaces when the pH of black liquor is too low. 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 **Figure 18**.

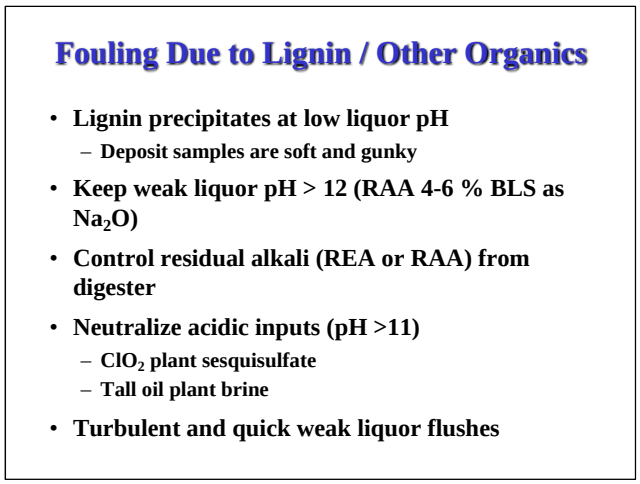


Figure 18. Fouling due to lignin and other organics.

Appendix 1. CLEANING EVAPORATORS

Figure 19 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 $CaCO_3$, 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 hydroblasting to remove the bulk of the deposits.

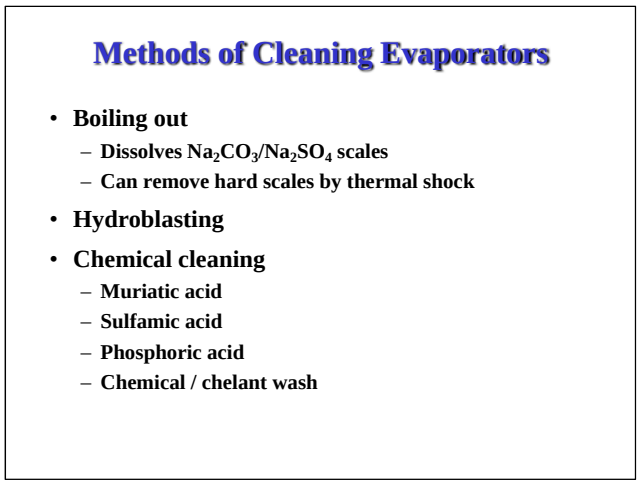


Figure 19. Methods of cleaning BL evaporators.

Figure 20 summarizes the procedures for cleaning black liquor evaporators by boiling them out.

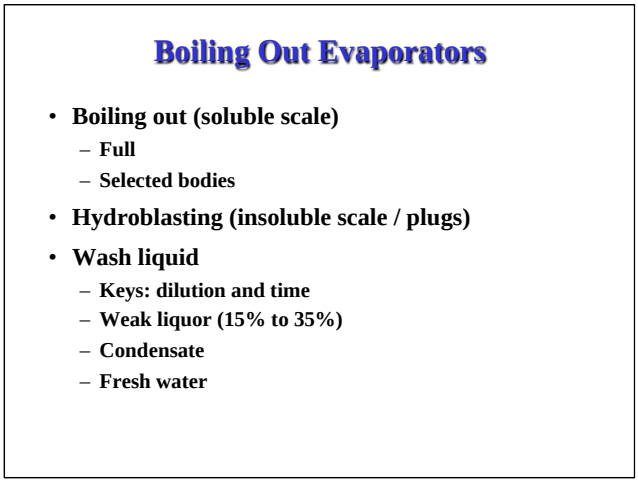


Figure 20. Boiling out evaporators.

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 **Figure 21**.

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 Na^+, $CO_3^=$, 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 **Figure 21**.

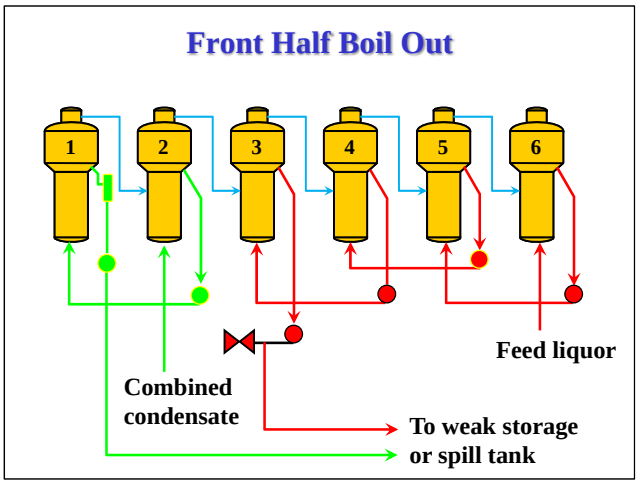


Figure 21. Configuration for a front half boil out.

Shortcut procedures as shown in **Figure 22** are often employed for evaporator boils to increase time on line for the equipment. With shortcut procedures, the minimum dry

solids content reached rarely drops below the solubility limit of ~53% and the duration of the boil is insufficient to dissolve any soluble scale deposits. A dry solids content units of at least 10% less than the solubility limit should be used. *It is better to wash for longer once per day than follow a shortcut procedure each shift.* Figure 23 contains guidelines for conducting effective boil outs.

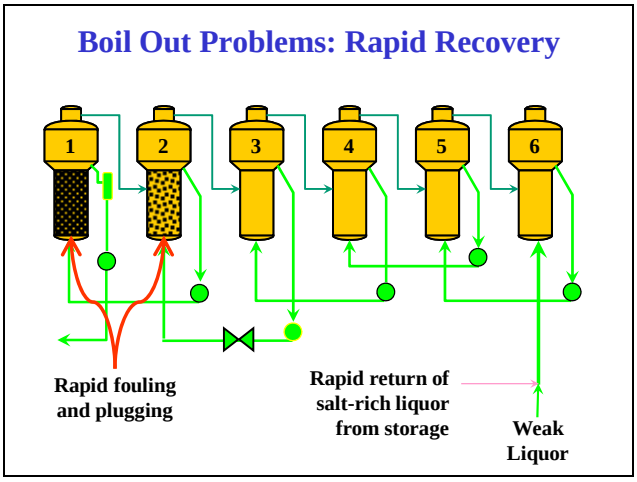


Figure 22. Boil out configuration for rapid recovery.

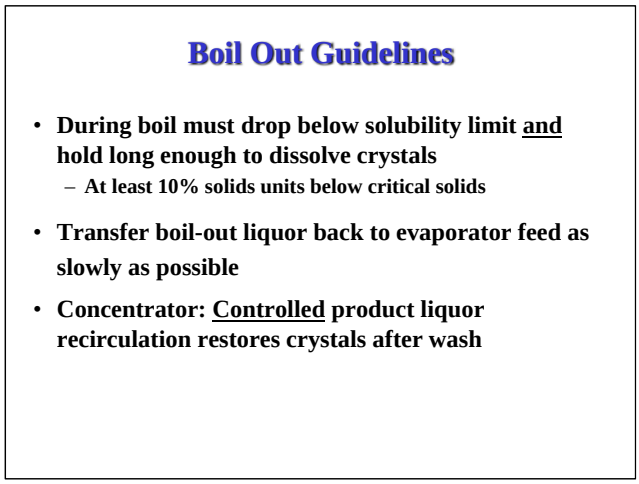


Figure 23. Guidelines for conducting effective boil outs.

Concentrator washes with weak liquor are common in falling film and forced circulation units. Steam continues to be supplied, but product solids content is limited to 30% - 35% to ensure effective washing.

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 are better, and sometimes 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 and concentrator operation and fouling can be found in references 7, 8, 9 and 10.

Slides 24 and 25 summarize the implications of black liquor fouling on evaporator and concentrator operation.

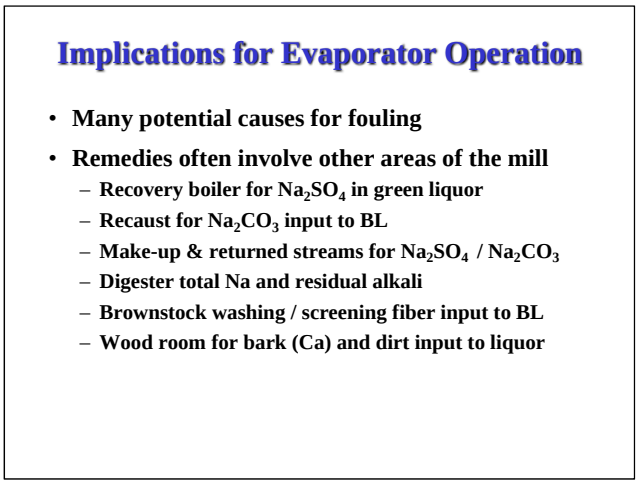


Figure 24. Implications for evaporator operation (1/2).

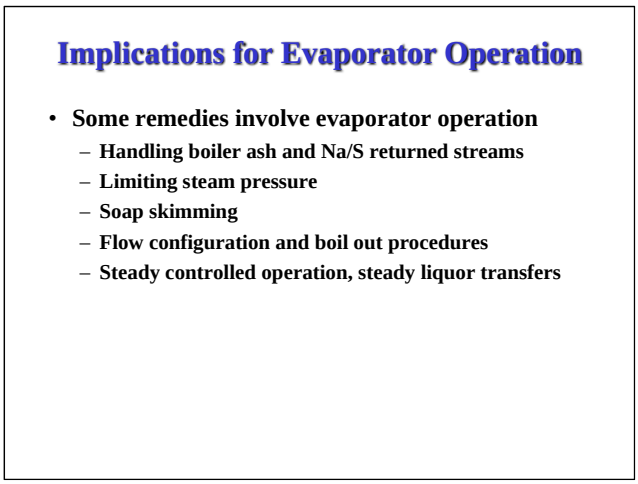


Figure 25. Implications for evaporator operation (2/2).

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