Black Liquor Evaporation

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ORGANIZATION OF THIS BOOK

This book contains five chapters including Chapter 1, the Introduction.

The content of Chapter 2, Evaporation Fundamentals, includes basic information on evaporation equipment. It includes sections on the design and analysis of black liquor evaporators and concentrators, and on flow characteristics and heat transfer in different types of evaporators. It includes a section on troubleshooting when evaporator performance is below design expectations. It also includes sections on tall oil soap recovery, removal of fiber from black liquor, and condensate stripping. A section on methanol purification is included, and another on collecting and burning of noncondensible gases.

Chapter 3 is an up-to-date summary of the composition and physicochemical characteristics of black liquor. Data on black liquor viscosity are presented, and the relationship between liquor composition, pulping conditions, and viscosity is presented. Data for other properties such as heating value, thermal conductivity, and surface tension are included.

Chapter 4 deals with the causes of scaling of black liquor evaporators and concentrators, and how to minimize scaling.

Chapter 5 discusses research needs for further development of black liquor evaporators. Water removal alternatives coupled with conventional evaporation technologies are considered.

1 INTRODUCTION

Black liquor is an important co-product of kraft pulping. It contains almost all the spent inorganic pulping chemicals along with wood components extracted during pulping. The wood components include lignin, hemicellulose, sugars from cellulose and hemicellulose degradation, the sodium salts of organic acids, various extractives, and minor inorganic components of wood. Weak black liquor is collected as filtrate from brownstock washers at a dry solids content between 14 wt% and 18 wt%. It must be concentrated to between 65 wt% and 85 wt% dry solids content to be fired in a recovery boiler. 4 to 5 tons of water must be evaporated per air-dry ton of pulp produced.

The main function of an evaporation plant is to remove water from black liquor, concentrating to a dry solids content acceptable for firing in a recovery boiler. Other separations also take place in the evaporation plant. They include skimming of tall oil soap, and stripping of methanol, and TRS removal. Makeup chemicals such as chlorine dioxide generator effluent, spent acid from tall oil acidulation, recovery boiler ash, and dust collected in electrostatic precipitators may be added to black liquor at different points in the evaporator set. Noncondensible gases which contain TRS, methanol, turpentine, and other volatile organic compounds must be removed from the evaporator set. Methanol and turpentine, which have economic value, are recovered. The others are burned.

Evaporation of water from black liquor is a heat driven process. Water is evaporated as fast as heat can be transferred to the black liquor. Evaporators and high solids concentrators are heated by process steam. The overall driving force for heat transfer is the difference between the saturation temperature of the steam and the black liquor temperature in the last evaporator effect. Black liquor evaporators and concentrators are configured as multiple units (effects) in series. Live steam enters the first effect, vapor from the first effect provides heat to the second effect, and so forth until vapor from the last effect is condensed in a surface condenser. The use of multiple effects reduces the energy cost for concentrating black liquor. Black liquor concentrators may be an integral part of the evaporator set, or may be a stand-alone set. Modern multiple effect evaporator sets are designed with six to eight effects.

Earlier, black liquor was concentrated to 48 - 52 wt% dry solids content in steam heated evaporators and then to 65 wt% dry solids content in direct contact evaporators. In direct contact evaporators, flue gas from the recovery boiler heated the black liquor and removed the water that was evaporated. Direct contact evaporators acted as a heat sink for the recovery boiler flue gas. This evaporation process was used through the 1970s in North America and some other countries, while in Sweden, indirect contact evaporation developed and implemented to produce higher dry solids content black liquors. In the 1980s, high solids concentrators began to replace direct contact evaporators, and concentrator technology was subsequently developed to produce 80 wt% or higher dry solids content black liquor. Today, high dry solids concentrators have replaced nearly all direct contact evaporators.

Evaporator capacity limitations are common problems in alkaline pulp mills. Capacity limitations can arise from high black liquor viscosity, evaporator scaling, too low a vacuum in the surface condenser, ineffective NCG removal from one or more effects, steam or liquor leaks, or other causes.

Scaling of evaporator and concentrator heat transfer surfaces is a serious operating problem in many sets. Liquor-side heat transfer surfaces may be scaled by sodium carbonate/sulfate scales calcium carbonate scales, sodium oxalate scales, or aluminosilicate scales. Organic matter such as tall oil soap or precipitated lignin may foul heat transfer surfaces. Evaporator tubes may become plugged by fiber, often together with organic or inorganic deposits.

2 EVAPORATION FUNDAMENTALS

2.1 EVAPORATOR HARDWARE

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Configuration of Black Liquor Evaporators and Concentrators

The terminology used to describe black liquor evaporators and their configuration can be confusing when they are first encountered. The terminology reviewed here describes the components and configuration of black liquor evaporators and concentrators.

Black liquor evaporators and concentrators are configured from individual units, connected in series or parallel configurations. An *evaporator body* is a single evaporator unit that includes one heating element and one flash chamber. It is the basic building block of multiple effect evaporators and concentrators.

An *evaporator effect* consists of one or more evaporator bodies with liquor boiling at the same pressure. Several bodies may be linked together in different configurations. Two or more bodies are often operated as a single evaporator effect, with a common steam supply to them and sequential black liquor flow through them. Figure 2.1 shows two evaporator bodies, A and B, linked to form one evaporator effect with a common steam supply to each body. Black liquor is fed to Body B, from there to Body A, and finally is withdrawn from Body A as concentrated product.

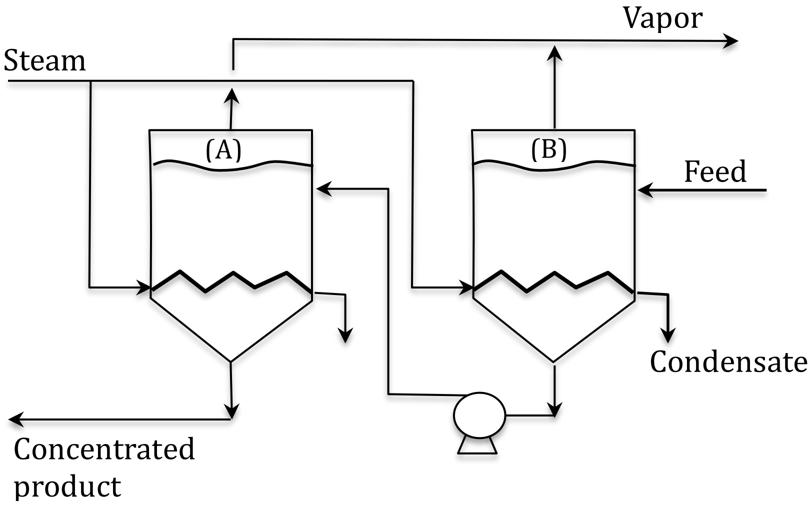

Figure 2.1. Diagram of a single evaporator effect consisting of two bodies, A and B.

A *multiple-effect evaporator set* consists of more than one evaporator effect in which the vapor from one effect is used as the heating medium for the next lower pressure effect. Figure 2.2 illustrates the steam, liquor, and vapor flow sequence for a counter-flow, 3-body, 3-effect evaporator.

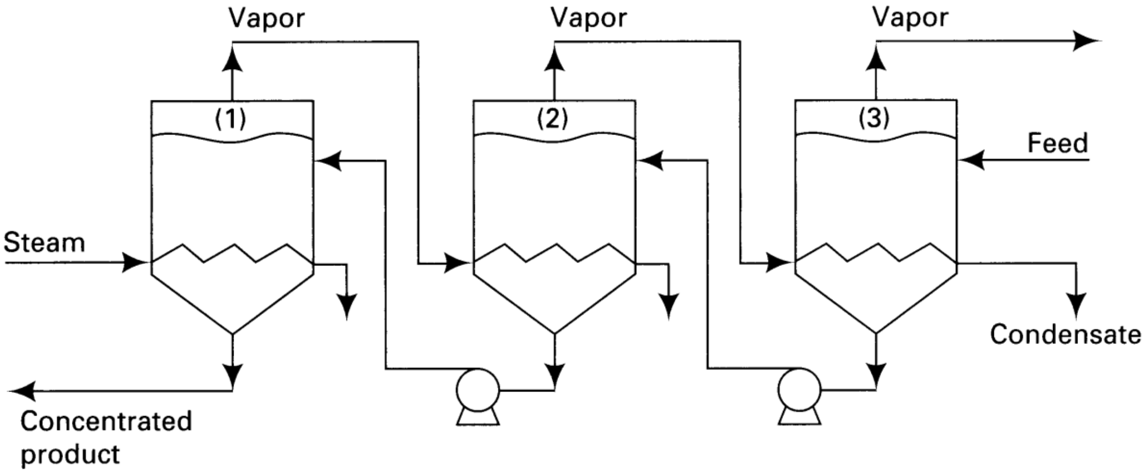

Figure 2.2. The steam, liquor, and vapor flow sequence for a counter-flow, 3-body, 3-effect black liquor concentrator.

2.2 EVAPORATOR EQUIPMENT

Concentration of black liquor became an essential operation with the development of kraft pulp mills. Evaporation plays an important role in recovering pulping chemicals and producing steam and electricity for mill consumption or resale. This section deals with the types of black liquor evaporators that are in common use and operation in today's kraft pulp mills. These include rising film long tube vertical (LTV) evaporators, falling film evaporators, forced circulation evaporators, and direct contact evaporators.

2.2.1 Long Tube Vertical (LTV) Evaporators

Long tube vertical (LTV), or rising film, evaporators (Figure 2.3) were the standard black liquor evaporators for decades, and many older mills still employ them [1]. Figure 2.4 is a more detailed diagram of an LTV evaporator, showing it many components. They consist of a tube bundle with tubes spaced and held in place by a tube sheet. Black liquor enters each evaporator body below the bottom tube sheet and exits through a port near the bottom of the vapor head. The product liquor may be removed from the liquor recirculation line if black liquor recirculation is a feature of the particular LTV unit.

Figure 2.3. Photo of one body of an installed rising film evaporator.

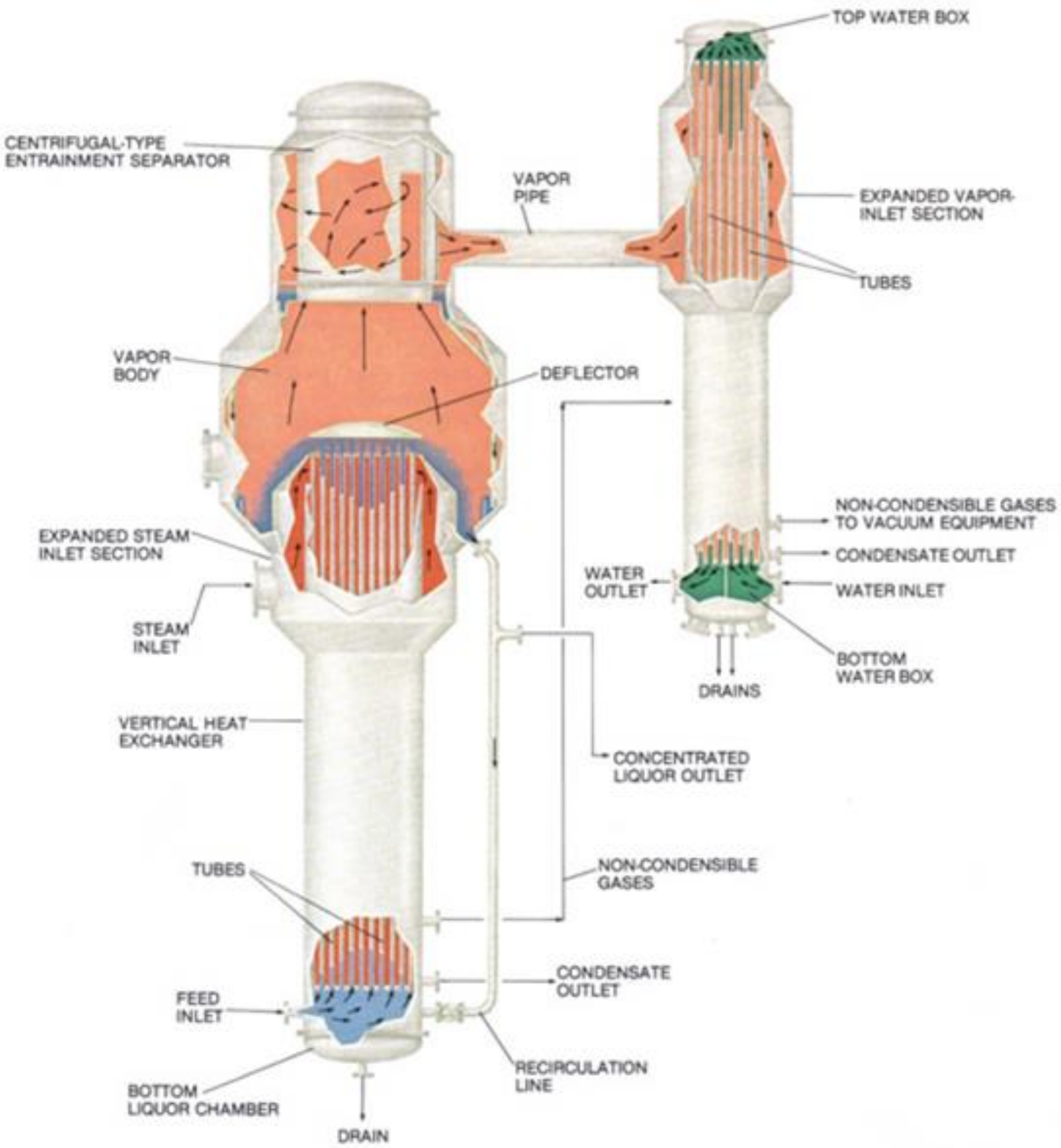

Figure 2.4. Components of an LTV evaporator.

The tubes and tubesheets (Figure 2.5) are made of 18 BWG 304 SS.

The tube bundle is enclosed in a steam shell where either primary steam or vapor from a previous effect condenses to heat liquor within the tubes, driving evaporation. Black liquor is propelled upward within the tubes by the rising vapor generated.

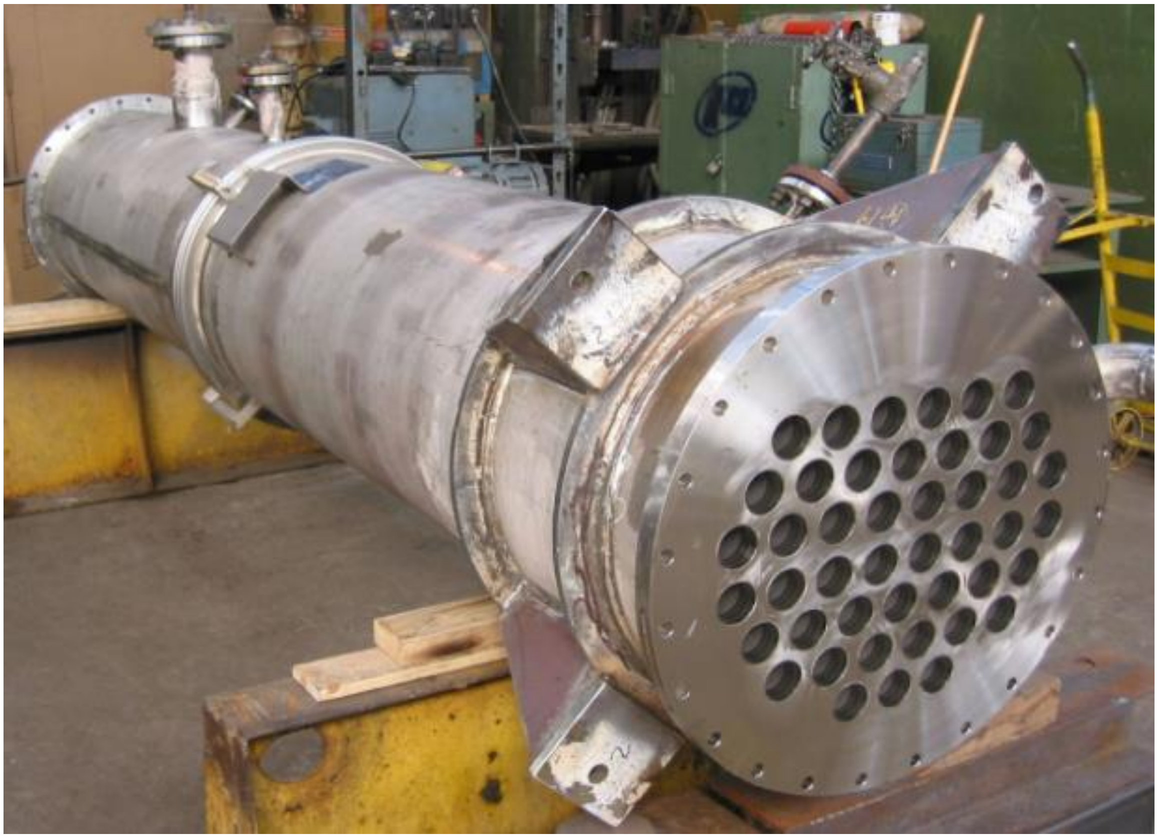

Figure 2.5. Evaporator tube bundle and tubesheet. Tube diameter is 5 cm (2 in.).

The heating element is a shell and tube heat exchanger, consisting of 5 cm (2 in) OD tubes, typically 7.2 m to 9.0 m (24 ft to 30 ft) in length (Table 2.1). Black liquor entering each effect is usually below its boiling point at the pressure within the effect. It flows into the bottom liquor chamber and then upward into the evaporator tubes. Steam condensing on the outside of the tubes heats the liquor. The lower section of the tube bundle acts as a preheat section, heating the liquor to its boiling point. The liquor temperature increases as the liquor rises upward in the tubes, and the pressure decreases. Evaporation begins at the height within the tubes where the vapor pressure of water in the black liquor equals the local system pressure and the upward flow becomes two phase [1].

The rate of heat transfer to black liquor in the lower, subcooled region of the tubes is poor. Long subcooled regions have to be avoided because the heat transfer rate is so low in them that it limits the overall evaporation rate in the body. Heat transfer rates increase by an order of magnitude from the preheat section to the boiling region within the tubes. Heat exchangers between effects are used to bring liquor temperatures entering an effect to within 10°C (18°F) of the boiling temperature within that effect.

Vapor and concentrated black liquor exit each body from the top of the tubes into a vapor dome that separates black liquor from vapor. The vapor dome material is normally carbon steel, and is protected with stainless steel in areas where the black liquor concentration exceeds 25 wt% dry solids content.

The vapor dome contains an umbrella or deflector located directly above the top tube sheet. It acts as the first stage of liquor and vapor separation. It must completely shield the tube sheet from product liquor flowing back into the tubes from above. A second stage of vapor-liquid separation (a demister) in the vapor dome is necessary to separate fine black liquor droplets from the exiting vapor.

The operating pressure for the first effect of most LTV evaporators is from 6 to 7 bar (75-90 psig).

Evaporator effects may be equipped with either an internal liquor heater or an afterheater, and sometimes both. These heaters are dedicated sections of tubes designed to heat liquor only. No boiling should take place in them.

Crystallization fouling and high liquor viscosity limit the ability of LTV evaporators to produce concentrated black liquor at dry solids contents above 48 wt% to 52 wt% [2]. Liquor recirculation is sometimes used to improve operation in effects operated near or at the onset of sodium salt crystallization from black liquor.

LTV evaporators have poor turndown ratios and that makes it difficult for them to operate with black liquor throughput less than 70% of design capacity. This is because rising vapor within the tubes is necessary to propel the black liquor upward, thinning the liquor film at the tube walls, and generate high heat transfer rates. The ΔT per effect must be at least 7°C to 8°C (12°F to 15°F) for them to operate well. At lower throughput rates, the overall ΔT required to achieve the target product dry solids content is too small to meet the minimum ΔT per effect. As a result, two-phase flow is not sustained and the flow regime becomes single-phase flow, heat transfer rates drop by an order of magnitude, and required evaporation rates are not met. The advantages and disadvantages of rising film LTV evaporators are summarized in Table 2.2.

Table 2.1. LTV Characteristics

Tube dimensions:

Length: 7.4 m (28 ft), the current industry standard. 6-10 m (20-33 ft.) tubes were used earlier.
OD: 5.0 cm (2.0 inches)
Wall thickness: 18 BWG (1.24 mm)
Metallurgy: 304 SS

Table 2.2. Advantages and disadvantages of rising film LTV evaporators

Advantages of LTVs:

- Simple design
- Minimal control requirement
- Low operating horsepower

Disadvantages of LTVs

- Requires large ΔT (7-8°C; 12-15°F) for each effect
- Poor turndown ratio
- Product dry solids content is limited to 48-52 wt% dry solids content because of severe sodium salt scaling

- Cannot process black liquors with unusually high viscosity in the first and second effects

2.2.2 Falling Film Evaporators, Tube-Types

Falling film evaporators have replaced LTV evaporators as the industry standard for new installations since the 1970s. Falling film evaporators consist of a heating element, a vapor-liquor separator, a liquor sump, a liquor recirculation line and pump, and a liquor flow distribution device (Figure 2.6). With tube bundles as heating elements, black liquor flows downward, either on the inside or outside of the tube. Both types are used to concentrate black liquor in kraft pulp mills; one installation is shown in Figure 2.7. Uniform liquor distribution on the heat transfer surface is critical with either type, to maintain a continuous liquor film along the entire length of the heat transfer surface. This avoids dry areas and deposits of black liquor solids along the heat transfer surface.

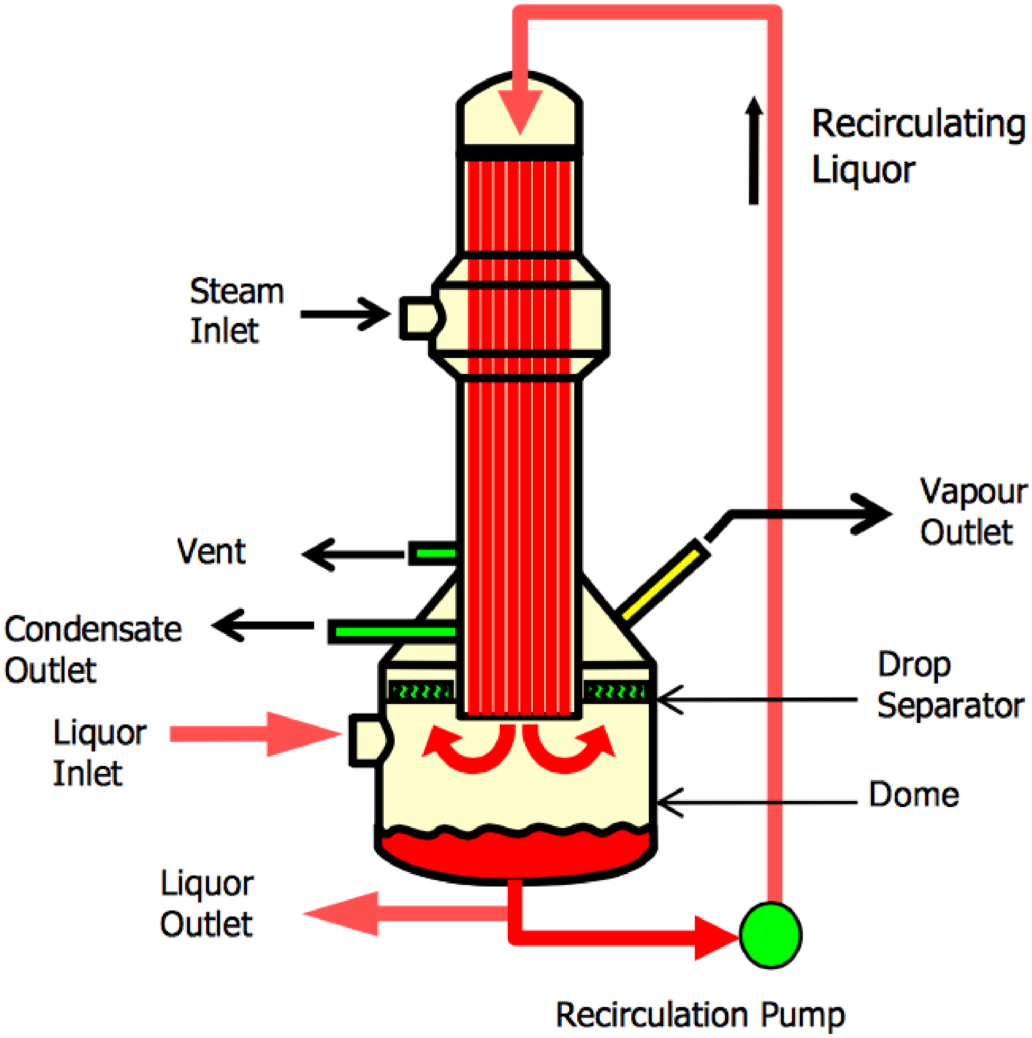

Figure 2.6. Diagram of a tube type falling film evaporator [1].

Falling film evaporators provide higher heat transfer rates, especially at higher liquor concentrations, than do rising film evaporators. These heat transfer rates are listed in Table 2.3. Liquor recirculation helps to minimize crystallization fouling by providing suspended crystals in the liquor as more favorable crystallization sites than heat transfer surfaces. The crystals grow by relieving supersaturation of Na_2CO_3 and Na_2SO_4 in black liquor. This minimizes their tendency to deposit as scale on heat transfer surfaces. Falling film evaporators are suited for handling viscous liquids [3].

A high rate of recirculation-to-feed liquor flow rates, typically about 20, improves the overall rate of heat transfer by eliminating the long subcooled region encountered in LTV evaporators.

Figure 2.7. Photo of a falling film evaporator set installation. (Photograph courtesy of Valmet Inc.)

Table 2.3. Heat Transfer Rates with a Pilot Tube-Type Falling Film Evaporator with Black Liquor on the outside of the Tubes

Evaporator type	Dry BL solids, wt%	Heat flux, W/m^2	ΔT, ^{o}C
Pilot falling film, BL outside of tubes	43.9	10,570	5.3
	55.9	9,400	6.2
	61.5	8,670	6.0
	67.0	8,300	6.2
	72.5	7,630	7.0
	78.6	4,800	8.0
	84.9	3,500	25.0

2.2.3 Falling Film Evaporators with Lamella-Type Heating Surfaces

The heating elements are sometimes referred to as dimple plates because of their appearance. They are comprised of two sheets of stainless steel welded together at their perimeters and tack welded together at points across the sheets. Once welded, the plate unit is inflated with pressurized nitrogen to open up the steam or vapor space between them. Figure 2.8 is an illustration of these heating elements. Detailed characteristics of these evaporators as well as their advantages and disadvantages are listed in Tables 2.4 and 2.5.

The plates are arranged in a header as a bank of plates. The bank of plates is the heating element for a body, and the outer shell acts as a combination vapor dome and liquor sump. Liquor is circulated by pumping from the sump area to a distribution tray located above the plates. The liquor flowing over the plates is heated by the condensing vapor inside the plates. Heat transferred from the condensing vapor to the black liquor evaporates water from it.

The heating elements are arranged in three or four separate sections within a common vapor body. Each section has a separate liquor circulation pump. With this arrangement, one section can be taken offline and washed to remove scale while the remaining sections are in operation.

When employed as concentrators, these falling film units are fed black liquor at nominally 50 wt% dry solids content. They produce product liquor at 68 wt% to 75 wt% dry solids content after flashing of the concentrator product liquor.

Condensate segregation and stripping and is accomplished by using sections of the heating elements as countercurrent strippers for volatile organic species. This is discussed in more detail in Section 2.6.3.

Table 2.4. Characteristics of Lamella-Type Falling Film Evaporators

- Plate dimensions: 1.2 m x 6.0 m (4 ft x 20 ft)
- Constructed in banks of plates
- Liquor distribution trays above the plates ensure that liquor is distributed uniformly on the plates and not between them.
- Steam condenses on the inside of the elements

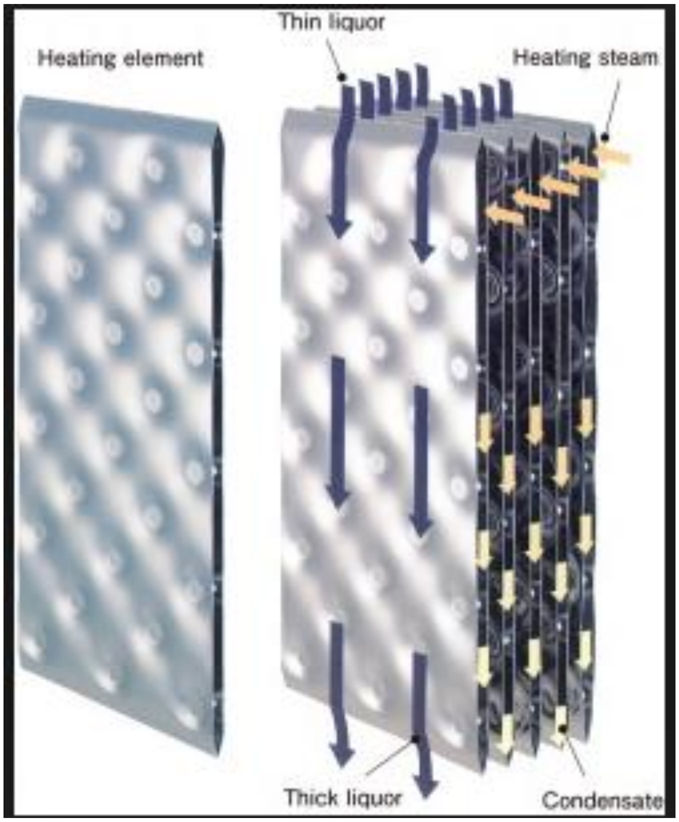

Figure 2.8. Illustration of heat transfer elements for lamella-type heating units for a falling film evaporator.

Table 2.5. Advantages and Disadvantages of Lamella-Type Evaporators

Advantages of lamella-type evaporators:

- Suitable for viscous liquids
- Minimal scaling problems
- Low pressure drop
- Excellent turndown capability / can operate at low ΔT
- Can achieve >75 wt% dry solids content product liquor

Disadvantages of lamella-type evaporators:

- Plate repair is costly and difficult
- Liquor distribution tray is susceptible to plugging with fiber, scale, etc.

- Operation relies on extensive level control of liquids
- Black liquor foams easily at liquor dry solids content of less than 18%

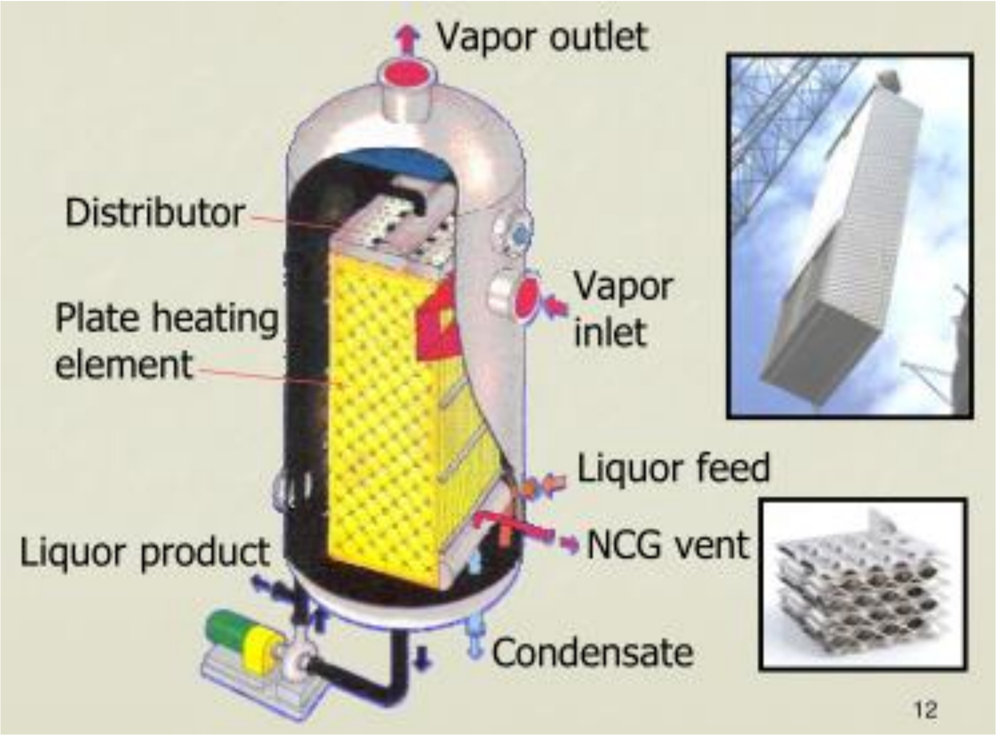

Figure 2.9. Illustration of an evaporator body with lamella-type heating elements.

2.3 CONCENTRATOR EQUIPMENT

Black liquor concentrators differ from black liquor evaporators in two important aspects: (a) They process black liquor at higher dry solids content and therefore at higher viscosity and temperatures. (b) They are de facto crystallizers as well as evaporators as they concentrate black liquor to above the total dry solids content where Na_2CO_3 and Na_2SO_4 crystallize from solution. The viscosity of black liquor at 80 wt% dry solids content is from 10^3 to10^4 mPa-s (10^3 to 10^4 cP) at 100°C and 10^2 to 10^3 mPa-s (10^2 to 10^3 cP) at 130°C. Sodium salts begin to crystallize from black liquor when it is concentrated to 50% dry solids content or higher. Either burkeite or dicarbonate will crystallize first, depending on the ratio of Na_2CO_3 to Na_2SO_4 dissolved in the black liquor. Dicarbonate is more aggressive in scaling and its scaling is more difficult to control. Black liquors in today's kraft pulp mills are richer in Na_2CO_3 relative to Na_2SO_4 than they were 30 or more years ago. As a result, dicarbonate scaling has become much more prevalent than Burkeite scaling [4]. Evaporator fouling and how to minimize it is discussed in detail in Chapter 4.

2.3.1 Lamella-Type Falling Film Concentrators

These are similar to the lamella-type falling-film evaporators in most respects. There is no differentiation between "evaporator" effects and "concentrator" effects in single, 7- or 8-effect sets that consist of one or the other type of falling film effects.

2.3.2 Falling Film Concentrators with Tubular Heating Surfaces

Tube-type falling film concentrators consist of a bundle of vertical tubes with a liquor distributor at the top and a vapor body and liquor sump below the tubes. They are designed either for black liquor to flow downward inside the tubes with steam condensing on the outside of the tubes, or for black liquor to flow down the outside of the tubes and steam within the tubes. Liquor recirculated from the sump is mixed with feed liquor in a ratio of about 20:1. The black liquor mixture is pumped to the distributor plate. The distributor plate delivers the black liquor either to the inside of the tubes where it flows downward as a thin film on the inside surfaces of the tubes, or downward as a liquor film on the outer tube surfaces. The distributor plate is designed to provide a uniform flow of liquor to each tube. This is essential to avoid liquor drying on the surface of some of the tubes. Black liquor flows from the bottom of the tubes and into the liquor sump. Condensate is collected from near the bottom of the steam shell.

2.3.3 Black Liquor Inside Tubes

Falling film tube-type evaporators look much like an LTV that has been turned upside down, but they operate much differently. Black liquor flows down the inside of the tube surface from the top of the tubes. The liquor is distributed to each tube by passing through a distribution tray. Some evaporators, however, use a special splash plate instead of the distribution plate. After evaporation, the black liquor is collected in the lower sump area and is circulated by pump to the top tube sheet. The size of the circulation pump is based on the number of tubes in the heating element. A circulation flow of 15 to 27 L/min (4 to 7 gal/min) per tube is normal. Advantages and disadvantages of these evaporators are outlined in Table 2.6.

The tubes used in the falling film design are normally 5.1 cm (2.0 inch) in outside diameter, 18 BWG, and 304 type ERW (Electric resistance welding) stainless steel. Tube lengths vary by manufacturer from 8.4 to 15m (28 to 50 ft).

Vapor enters the heating element section and condenses on the outside of the tube surface. Energy is transferred through the tube wall to the black liquor. Vapor flows downward, concurrent with the black liquor. It leaves the lower sump and flows to the shell side of the next effect.

Table 2.6. Advantages and Disadvantages of Tube-Type Evaporators with Black Liquor inside Tubes

Advantages of tube-type falling film evaporators with black liquor inside of tubes:

- Suitable for viscous liquids to 300 mPa-s (300 cP)
- Minimal scaling problems
- Low pressure drop
- No head-induced boiling point elevation
- High heat transfer rates at low ΔT
- Excellent turndown capability / can operate at very low ΔT
- Can achieve > 75 wt% dry solids content product liquor
- Low liquor residence time due to thin liquor film on tube walls
- No particle accumulation areas

Disadvantages of tube-type evaporators with black liquor inside of tubes:

- Requires a liquor recirculation pump
- Performance is sensitive to liquor flow distribution
- Limited to low ΔT (high ΔT would disrupt film)
- Liquor distribution tray is susceptible to plugging with fiber, scale, etc.
- Operation relies on extensive level control of liquids
- Foams easily at liquor dry solids content of 18% or less

Figure 2.10 shows a tube-type evaporator with liquor flowing on the inside of the heat transfer tubes and internal vapor segregation to minimize environmental impact. The black liquor flow sequence and the vapor flow sequence are as follows.

1. Black liquor flow sequence:
    a. Black liquor enters at the bottom of the unit, into the liquor sump where it mixes with the more concentrated liquor in the sump.
    b. Black liquor in the sump is circulated to the liquor distribution plate above the upper tube sheet.
    c. The distribution plate distributes liquor into the top of each of the evaporator tubes.
    d. Liquor flows downward as a falling film on the inside of the tubes, where it is heated by steam condensing on the outside of the tubes. Water is evaporated from the liquor by convective boiling of the black liquor films within the tubes.
    e. Vapor and liquor are separated primarily in the lower liquor compartment. Final removal of remaining smaller liquor droplets is performed as the vapor exits via horizontal flow type droplet separators and flows to the next (higher number) effect.

2. Vapor and condensate flow sequence:
    a. Vapor from the previous effect enters near the bottom of the heating shell. It rises and most of it is condensed on the evaporator tubes, heating the liquor and evaporating water from it within the tubes.
    b. As the condensate runs down the outside of the evaporator tubes, it is in contact with the up-flowing vapor where it becomes increasingly depleted in volatile organic species such as methanol. It therefore exits from the bottom of the heating shell as a relatively much cleaner condensate.

c. A small fraction of the vapor entering the heating shell is not condensed at this point. The remaining vapor, enriched in methanol, flows into an inner cylinder at the center of the evaporator and condenses on separate evaporator tubes (the “foul zone”) inside the inner cylinder, heating the liquor in those tubes and evaporating water from it within the tubes.

d. The relatively smaller flow of foul condensate collected within the inner cylinder exits the effect in a separate pipe via the bottom of the inner cylinder.

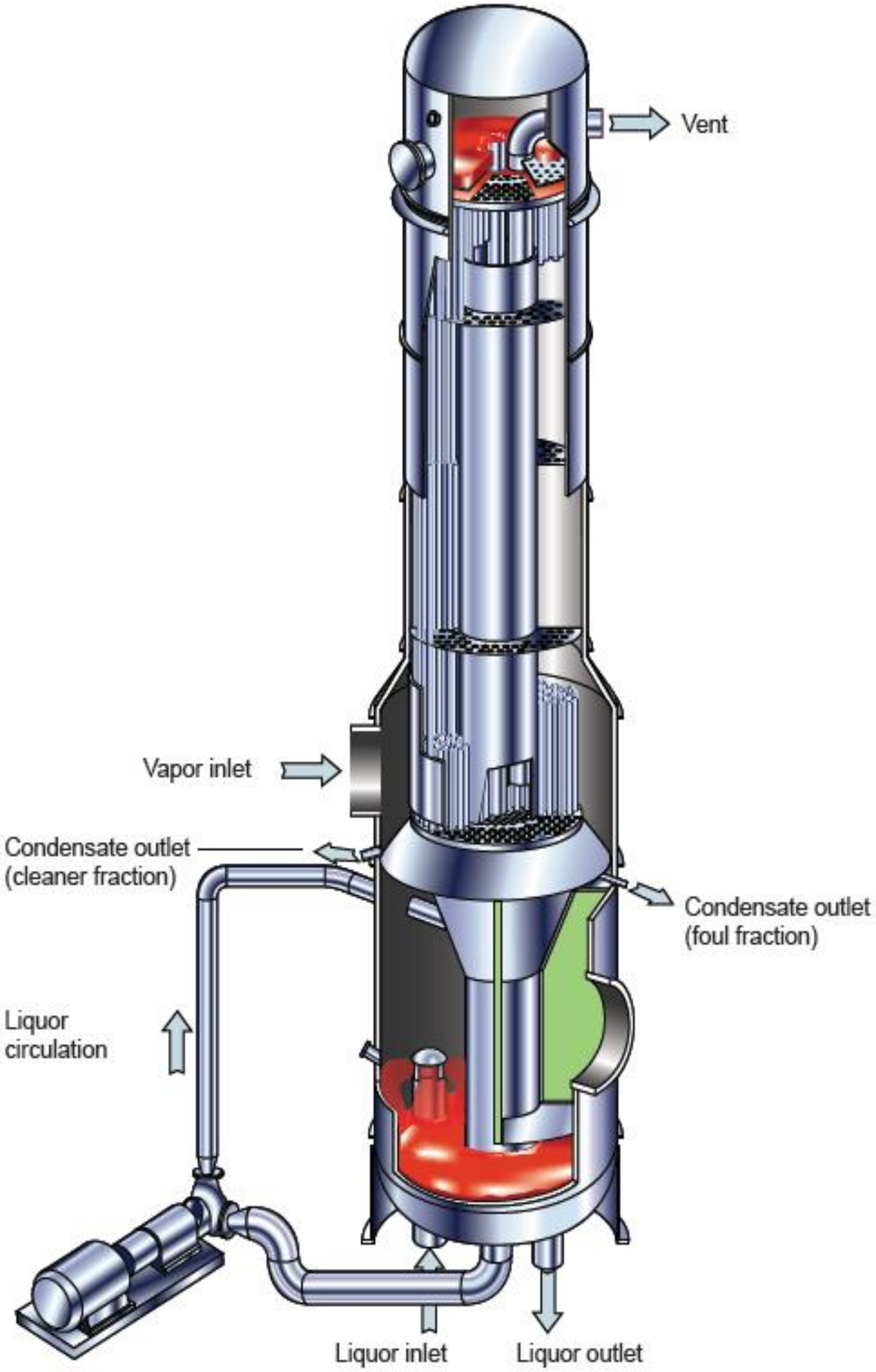

Figure 2.10. Diagram of a tube-type falling film black liquor evaporator with liquor on the inside of the tubes and with internal vapor separation. (Illustration courtesy of Valmet Inc.)

3. TUBEL™ (Tube-Element) evaporator
    a. Black liquor enters at the bottom of the unit, into the liquor sump, where it mixes with the more concentrated liquor in the sump.
    b. Black liquor from the sump is circulated, via a liquor distributor, to the liquor distribution plate above the tube elements.
    c. The distribution plate distributes liquor onto the external surface of the tube elements.
    d. Liquor flows downward as a falling film on the outside of the tubes where it is heated by steam condensing on the inside of the tubes. Water is evaporated from the liquor by convective boiling of the black liquor films on the outer tube surfaces.
    e. Vapor and liquor are separated in the sump. Final removal of remaining smaller liquor droplets is performed as the vapor exits at the top of the evaporator, via horizontal flow type droplet separators, and flows to the next (higher number) effect.

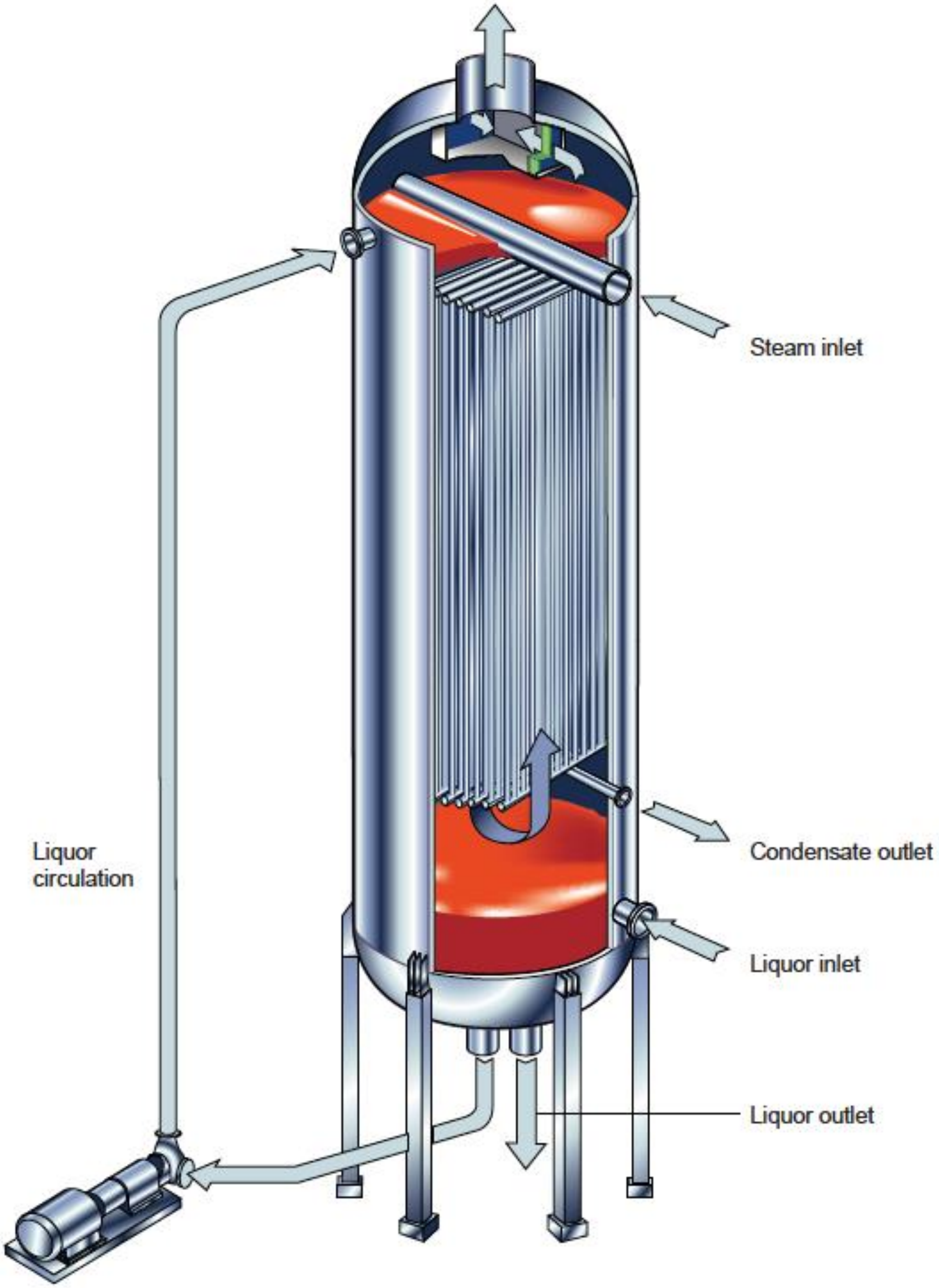

Figure 2.11. Diagram of a TUBEL black liquor evaporator with liquor on the outside of tubes. (Illustration courtesy of Valmet Inc.)

2.4 FORCED CIRCULATION CONCENTRATORS

Forced circulation concentrators were developed to minimize the crystallization scaling that has plagued LTV evaporators. They consist of heating elements, a flash tank, and large liquor recirculation pumps. The pressure within the heat exchangers is maintained high enough to prevent boiling within them. This minimizes crystallization and scaling of the heat transfer surfaces. Liquor to be concentrated is pumped into a much larger stream of recirculated liquor. The combined liquor stream is circulated at high velocity through the concentrator tubes to reduce its viscosity through shear thinning and to enhance heat transfer rates. The hot liquor is flashed in the vapor head (flash tank) of the concentrator. Flashing concentrates the black liquor. Sodium salts crystallize mainly in the vapor head rather in the heat exchangers, and are removed with the concentrated product liquor. The vapor generated passes through mist eliminators before flowing to another effect or separate evaporator unit.

Forced circulation evaporators are designed with two heat exchanger loops connected to a common vapor body as shown in Figures 2.12 and 2.13. This allows for on-line washing of one heat exchanger while the concentrator remains in operation with the other heat exchanger online.

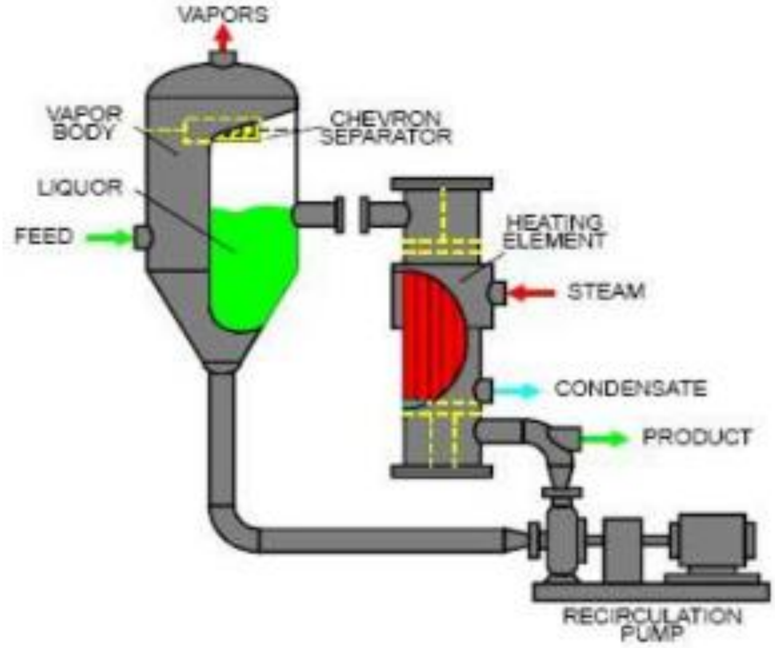

Figure 2.12. Diagram of a forced circulation concentrator with a heat exchange loop [5].

Figure 2.13. Photo of a forced circulation concentrator with two heat exchange loops [5].

2.5 DIRECT-CONTACT EVAPORATION

This is older technology used to concentrate black liquor prior to the late 1960s, before indirectly heated black liquor concentrators became the standard. Direct-contact evaporators utilize hot flue gas from a recovery boiler as the heat source for evaporation. Black liquor at about 50 wt% dry solids content is contacted directly by flue gas exiting the recovery boiler, concentrating it to about 65 wt% dry solids content. Under typical conditions, heat removed from the flue gas to increase the black liquor solids content from 50 wt% to 65 wt% dry solids results in a 140°C (250°F) drop in flue gas temperature [6]. The upper dry solids content limit for direct contact evaporators is imposed by the viscosity of black liquor above 65 wt% dry solids content. Direct contact evaporators operate at atmospheric pressure so the temperature of the black liquor cannot exceed boiling point of the black liquor at atmospheric pressure, typically 115°C.

Early on, direct contact evaporators were a major source of TRS emissions from kraft pulp mills. When hot acidic flue gas contacts black liquor, H_2S and other TRS species are released into the flue gas. Through the installation of black liquor oxidation (BLOX) technology, TRS emissions limits were met by oxidizing the TRS compounds in black liquor to sodium thiosulfate and other non-odorous compounds. This reduced TRS emissions to less than 100 ppm. With difficulty in meeting decreasing TRS emissions limits, many pulp mills converted from conventional recovery boilers and BLOX technology to modern recovery boilers that can operate with nearly undetectable TRS emissions.

Two types of direct-contact evaporators have been commonly used. One is the cascade evaporator illustrated in Figure 2.14. Liquor is lifted by rotating bundles of tubes held between two circular endplates. The tube bundle rotates through the black liquor tank at about 6 rpm. Hot flue gas flows across and between the tubes before exiting to the recovery boiler stack. Black liquor at about 50 wt% dry solids content flows continuously into the liquor tank through which the tube bundle rotates. Concentrated black liquor at about 65 wt% dry solids content is removed continuously from the tank through a screen to remove lumps.

Another type of direct contact evaporator is the cyclone evaporator illustrated in Figure 2.15. The cyclone itself is a cylindrical vessel with a conical bottom. Hot flue gas enters the cyclone through a tangential inlet near the bottom of the vessel. It flows in a helical path to the top of the vessel, and exits through a concentric outlet port. Black liquor droplets at about 50 wt% dry solids content are sprayed across the flue gas inlet. Evaporation occurs as droplets are heated by the hotter flue gas. The cooled flue gas exits through the top of the vessel. The inertia of the black liquor droplets carries them to the vessel wall where they collect as a liquid film and flow downward along the wall to the conical bottom and into a black liquor sump below it. Additional black liquor is recirculated from the sump to maintain a continuously wetted vessel wall and prevent liquor dryout on the vessel walls.

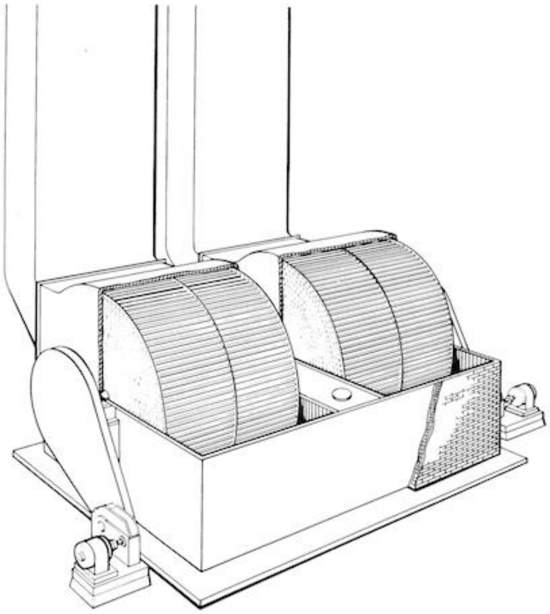

Figure 2.14. Cascade evaporator [7].

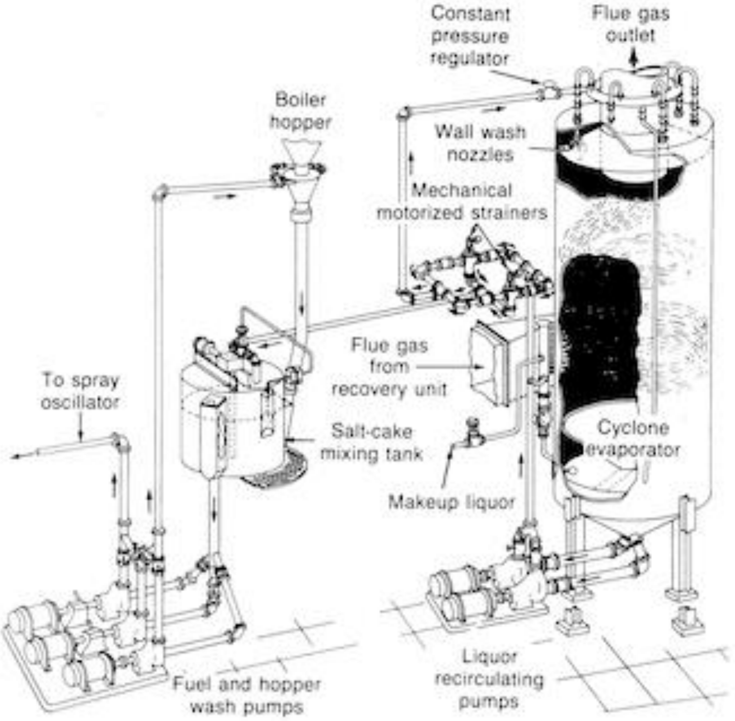

Figure 2.15. Cyclone evaporator [7].

2.6 MULTIPLE-EFFECT EVAPORATOR CONCEPTS AND EVAPORATOR CONFIGURATIONS

Black liquor evaporators use steam as a heating medium for heat transfer devices to evaporate water from black liquor. The water evaporated has about the same heat content as the steam used to evaporate it. The vapor generated is used as the heating medium for a second, lower pressure effect. When several effects are linked into multiple-effect evaporators, only the first effect receives live steam. The downstream effects are each heated by vapor generated in the previous effect. The pressure of the steam or vapor decreases from the effect where it is generated to the next effect where it condenses. This cascading of heat continues until the pressure of the vapor generated in the last effect drops to about 75 kPa (22 in Hg vacuum). Vapor exiting the last effect is condensed in a sub-atmospheric pressure condenser. With proper design, evaporator effects are linked together with heat cascading from higher pressure effects to lower pressure ones. Reuse of heat in this way multiplies the total amount of evaporation accomplished by the evaporator set per kg of live steam to the first effect. A six-effect evaporator set may evaporate between 4.5 and 5.0 kg of water per kg of live steam. The ratio of the mass of water evaporated to mass of live steam used is commonly referred to as steam economy. Typically the steam economy for an evaporator set will be between 0.7 and 0.9 times the number of evaporator effects. A 6-effect evaporator set would operate with a steam economy between 4.2 and 5.4. The impact of operating parameters on steam economy is discussed in the material and energy balances section of this chapter.

Figure 2.16. A multiple effect evaporator set.

Many configurations of black liquor evaporators and concentrators have been used with the intent of improving both overall capacity and steam economy. A 6-effect black liquor evaporator set producing 50 wt% dry solids black liquor and a separate black liquor concentrator producing 65 wt% dry solids content product liquor was an early configuration. The number of effects in black liquor evaporators evolved to the current use of a 9-effect set. Black liquor concentrators became partially integrated with the evaporator set, with vapor from both a concentrator effect and an evaporator effect combined to drive the next lower pressure effect. Eventually, full integration of concentrator and evaporator trains came into use. The first one or two effects became the “concentrator” section of the combined set, concentrating black liquor from 50 wt% to as high as 80 wt% dry solids content.

2.6.1 Steam Consumption

In an average Swedish non-integrated market pulp mill, the evaporation plant, including the stripper, accounts for one third of the total steam consumption. The total steam consumption in this average pulp mill is 15.5 GJ/ADt, (14.7×10^6 Btu/ADt) of which 5.1 GJ/ADt (4.8×10^6 Btu/ADt)) is consumed by the evaporation plant [7].

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3 DESIGN PRINCIPLES AND ANALYSIS FOR BLACK LIQUOR EVAPORATION

3.1 DESIGN PRINCIPLES AND ANALYSIS FOR BLACK LIQUOR EVAPORATION

W. J. Frederick

3.2 BLACK LIQUOR EVAPORATOR MASS & ENERGY BALANCES

H. Jeff Empie

Mass and energy balances form the basis for designing, evaluating, and troubleshooting multiple effect evaporator sets. They account for all mass and energy entering and leaving an evaporator set. They can also be applied to subunits such as a single body, a single effect, multiple connected effects, flash tanks, the surface condenser, etc. They must be constructed carefully so as to be error-free if they are to be of value. Accurate information on the design and operating conditions of an operating evaporator set or sets must be obtained before undertaking mass and energy balance calculations. Reliable estimates must be made for use in design of a new evaporator set. The balance calculations are relatively straightforward for a single line evaporator set (Figure 1), but become more complicated when evaporator, concentrator, and pre-evaporator units are interconnected.

The data required to perform these calculations are:

- ***Definition of the calculation basis***: this is normally the throughput rate of dry black liquor solids;
- ***Reference conditions:*** temperature (normally 0°C/32°F) and pressure (normally 1.013 bar/14.7 psia)
- Temperature and dry solids content of weak black liquor feed

    - Temperature and dry solids content of evaporator product liquor
    - Pressure and temperature of live steam to the first evaporator effect
    - Pressure drops from effect i vapor head to effect i+1 steam shell
    - Vapor pressure in the condensate side of the surface condenser
    - Heat transfer area in each effect, the surface condenser, and any intermediate liquor heaters
- Heat transfer coefficients for each evaporator body, intermediate liquor heaters, and the surface condenser
- Input or output flow rates of any process streams such as tall oil soap that are input or removed after the weak liquor feed point and before the product liquor storage tank, and their temperatures and compositions
- Steam and NCG purge rates, temperatures and pressures

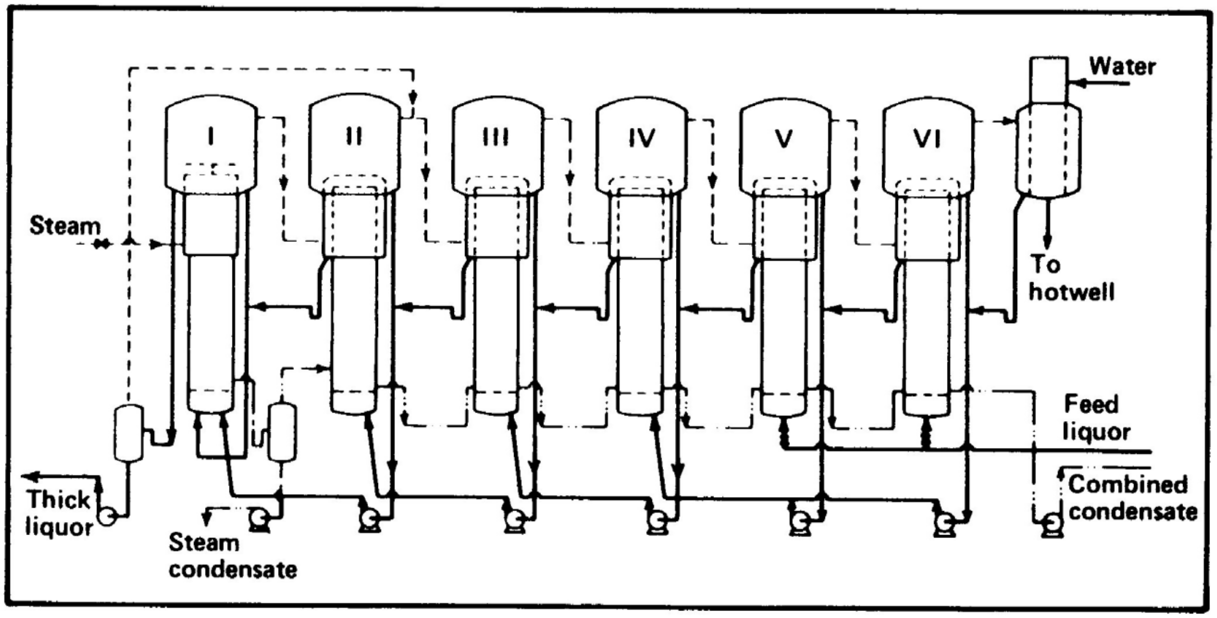

Figure 1. 6-effect evaporator, numbered to correspond to the example presented here [1].

Mass and energy balances are calculated for each evaporator effect and liquor heater, flash tank, etc. for the overall evaporator set.

Mass and Energy Balance Calculation Procedure [2]

A. Introduction

Black liquor evaporation is accomplished in both rising film (LTV) and falling film (FF) multiple-effect evaporators whereby sensible heat is transferred to the black liquor, followed by latent heat transfer at boiling. This is accomplished by condensing steam or vapor on one side of a tubular or flat plate heat transfer surface. For saturated steam or vapor, the condensation temperature is fixed by the pressure in the shell or vapor chamber of the heat exchanger. This temperature remains essentially constant over all of the heat transfer surface in the effect. On the other hand, as heat from the condensing steam is absorbed by the liquor, its temperature rises until the boiling point is reached and evaporation commences. In multiple-effect systems, the vapor generated is used in the next effect as the heat source for evaporation in that unit. This can be viewed as a reuse of the latent heat of vaporization of water.

B. Mass and Energy Effect Balances for Single Effect

Calculation of fundamental mass and energy balances for an evaporator effect must recognize that the steam side and liquor side have to be dealt with separately because the two never come into direct contact with each other. Referring to Figure 2 (shown here as a LTV unit) and using the nomenclature below, the mass balances are straightforward (valid for FF unit also). Taking first the shell (steam) side and then the tube (liquor) side:

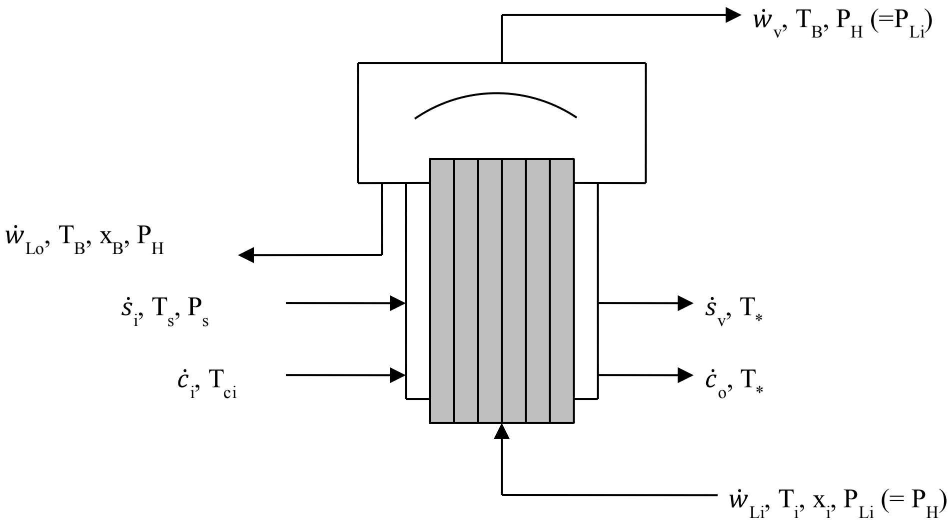

Figure 2. Single Effect.

Using the following nomenclature:

P_{Li} = black liquor pressure in

P_H = pump head pressure (= P_{Li})

P_s = steam pressure

P_{ref} = reference pressure

$\dot{w}_{Li}$ = weak BL flow rate in

$\dot{w}_{Lo}$ = concentrated BL flow rate out

$\dot{w}_v$ = vapor flow rate out

$\dot{s}_i$ = steam rate in

$\dot{s}_v$ = vent loss

$\dot{c}_i$ = condensate rate in

$\dot{c}_o$ = condensate rate out

x_i = wt. fraction black liquor solids (BLS) in

x_o = wt. fraction BLS out

T = saturation temperature at P_s

T_B = BL boiling point @ P_H

T_{ci} = condensate temperature in

T_s = steam temperature in

T_i = BL inlet temperature

T_{cond} = temperature of final condenser

c_{pw} = specific heat of condensate

c_{ps} = specific heat of steam

c_{pLi} = specific heat of black liquor in

c_{pLo} = specific heat of black liquor out

λ_B = heat of vaporization @ P_{ref}

λ_s = heat of vaporization @ P_s

$\dot{q}_T$ = heat transfer rate to BL

$\dot{q}_L$ = heat lost

BPR = black liquor boiling point rise

Mass Balances:

Shell (steam) side: $\dot{s}_i + \dot{c}_i = \dot{c}_o + \dot{s}_v$ (1)

Liquor side: (total) $\dot{w}_{Li} = \dot{w}_{Lo} + \dot{w}_v$ (2)

(BL solids) $\dot{w}_{Li}\, x_i = \dot{w}_{Lo}\, x_o$ (3)

Energy Balances:

Shell (steam) side:

$$\dot{c}_i\, c_{pw}\,(T_{ci} - T^*) + \dot{s}_i\,[c_{ps}(T_s - T^*) + \lambda_s] - \dot{s}_v\,\lambda_s = \dot{q}_T + \dot{q}_L \qquad (4)$$

$\dot{s}_v$ and $\dot{q}_L \approx 0$. Additionally, the sensible heat of vapor is small ($c_{ps} \approx \frac{1}{2}\, c_{pw}$, $T_s \approx T^*$) and can be neglected. With these substitutions, Eq. (4) becomes:

$$\dot{c}_i\, c_{pw}\,(T_{ci} - T^*) + \dot{s}_i\,\lambda_s = \dot{q}_T \qquad (5)$$

Liquor Side:

$$\dot{w}_{Li}\, c_{pLi}\, (T_i - T_{ref}) - \dot{w}_{Lo}\, c_{pLo}\, (T_B - T_{ref})$$
$$- \dot{w}_v\, [c_{ps}(T_B - T_{ref}) + \lambda_B] + \dot{q}_T = 0 \qquad (6)$$

But: $c_{ps}(T_B - T_{ref}) << \lambda_B$ and

$$\dot{w}_{Lo} = \dot{w}_{Li} - \dot{w}_v$$

Hence Eq. (6) becomes:

$$\dot{w}_{Li}\, c_{pLi}\, (T_i - T_{ref}) - (\dot{w}_{Li} - \dot{w}_v)\, c_{pLo}\, (T_B - T_{ref})$$
$$- \dot{w}_v\, \lambda_B + \dot{q}_T = 0 \qquad (7)$$

If the energy balance reference temperature is chosen to be at the boiling point of the black liquor, then $T_B = T_{ref}$, which forces λ_B to be evaluated at the liquor boiling temperature, T_B, and the saturation pressure, P_B (= P_{ref}). With these substitutions, Eq. (7) simplifies to:

$$\dot{w}_{Li}\, c_{pLi}\, (T_B - T_i) + \dot{w}_v\, \lambda_B = \dot{q}_T \qquad (8)$$

Balance Eqs. (5) and (8) can be used to help diagnose the operating performance of an individual effect based on measurable operating variables. These variables are the steam (vapor) temperature, pressure, and feed rate for an effect as well as the black liquor feed rate, temperature and total solids content, and liquor product rate, temperature and total solids content. Black liquor physical properties, namely specific gravity and heat capacity, are calculated from standard correlations included in Chapter 3. Latent heat of vaporization and specific volume for water at saturation conditions are derived from the standard Steam Tables. One practical example of diagnosing operating performance might involve calculating the Steam Economy (weight of water evaporated per weight of steam (vapor) used) of an individual effect. This should normally fall in the range of 0.75 to 0.95. A calculated value greater than 1.0 is generally an indication that the feed liquor temperature to that effect is too high and flashing is occurring as the liquor enters the effect in question; a value lower than this range would indicate the feed temperature is too low or that significant fouling is occurring. This type of analysis can be carried out using a spreadsheet calculation.

C. Mass and Energy Balance Coupling between Effects

Design of a multiple effect evaporator set requires computing mass and energy balances for all the effects, along with the rates of heat transfer in each. This is difficult because all of the intermediate stream temperatures and pressures are not known apriori. Instead the balances are coupled between the effects and must be solved for by trial and error. The governing balances for the jth and (j-1)th effects are shown below in Figure 2.

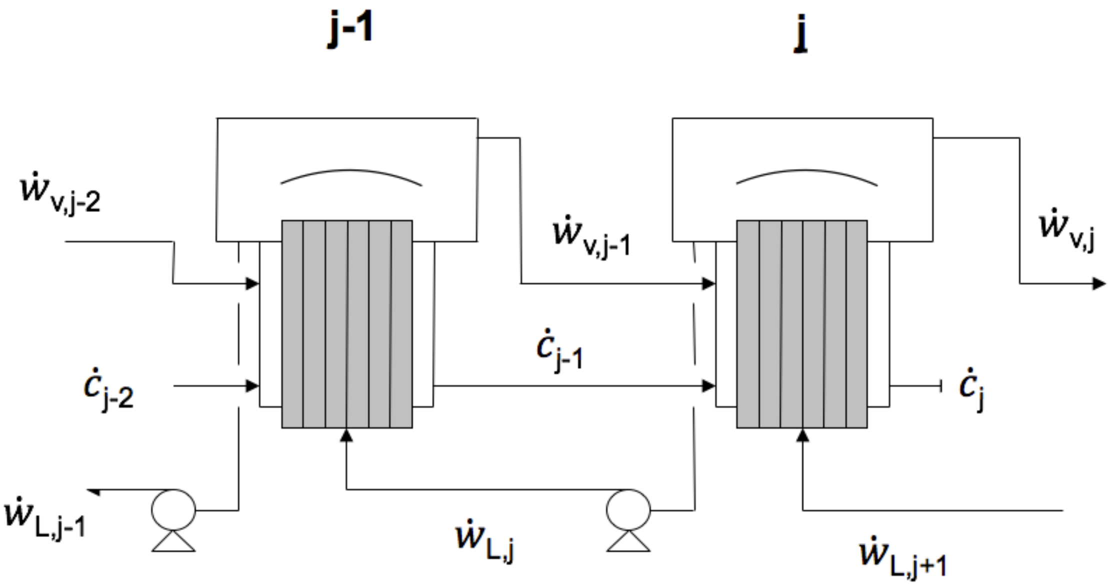

Figure 2. Coupling between Effects.

Applying Eq. (8) to the (j – 1)th effect BL side:

$$\dot{q}_{j-1} = \dot{w}_{L,j}\, c_{PLj}\, (T_{B,j-1} - T_{B,j}) + \dot{w}_{V,j-1\; j-1} \tag{9}$$

Applying Eq. (5) to the jth effect steam side:

$$\dot{q}_{j} = c_{j-1}\, c_{PW}\, (T_{j-1} - T_{j}) + \dot{w}_{V,j-1\; j-1} \tag{10}$$

Eliminating $\dot{w}_{V,j-1\; j-1}$ from these two equations:

$$\dot{q}_{j-1} - \dot{w}_{L,j}\, c_{PLj}(T_{B,j-1} - T_{B,j}) = \dot{q}_{j} - c_{j-1}\, c_{PW}\, (T_{j-1} - T_{j})$$

or

$$\dot{q}_{j} = \dot{q}_{j-1} + c_{j-1}\, c_{PW}\, (T_{j-1} - T_{j}) - \dot{w}_{Lj}\, c_{PLj}(T_{Bj-1} - T_{B\,j}) \tag{11}$$

From Eq. (11), we see that the heat duty in any effect equals the heat duty in the preceding effect with two sensible heat corrections:

- $\dot{q}_j$ reduced by the sensible heat demand of the BL in the jth effect
- $\dot{q}_j$ increased by the sensible heat in the condensate from the (j-1)th effect

In the common backward flow MEE configuration, BL sensible heat is more important at low number (i.e. high T) effects (because of higher BPR at higher BL concentration), while the condensate term is more important in the high number effects where c_j gets large. Thus $\dot{q}_j$ starts out high and decreases, then increases. In general, $\dot{q}_j = \dot{q}_{avg} \pm$ 20%.

The $\dot{q}_j$'s are determined by heat balances which are coupled with heat transfer rates from steam/vapor to liquor. The rate of heat transfer, $\dot{q}$, is traditionally expressed as:

$$\dot{q} = U\ A\ \Delta T_d$$

where U is the overall heat transfer coefficient and A is the surface area for heat transfer. ΔT_d is the temperature driving force for heat transfer calculated. By convention, it is defined as the difference between the steam condensation temperature and the product black liquor boiling temperature. The overall temperature difference between the steam and liquor flows in an effect is variable and difficult to predict. In a multiple effect system, the mass and energy balances along with the heat transfer rate equations ($\dot{q}_j = U_j\ A_j\ T_j$) specify the entire system. However, this system is subject to the temperature constraint:

$$T_j = T_s - T_{cond} - BPR_j \qquad (12)$$

This involves a trial and error calculation so that the individual mass and energy balances, which need temperature and pressure specified to evaluate enthalpies and black liquor boiling points, can be rigorously satisfied.

The boiling point rise (BPR) is a key factor because the vapor generated from boiling black liquor at T_B and P_H becomes the heat source for the next effect, condensing at the boiling temperature of water at that pressure. This temperature difference between the vapor generation temperature and water condensation temperature is the BPR [Note the definition of BPR: $BP_{BL} - BP_{water}$ at a given pressure] and is therefore lost for driving heat transfer in the next effect. This BPR temperature loss is experienced in each effect not fed with fresh steam. Hence, the overall temperature driving force for the multiple effect evaporator system, T_o (= T_j), is diminished by the sum of the individual effect BPRs as given by Eq. (12).

D. Optimizing Operation

Optimum multiple effect evaporator operation involves a tradeoff between capacity and steam economy. Increasing the number of effects raises the steam economy, but a (N+1)-effect system with the same total heat transfer surface area as an N-effect system will have a lower evaporation capacity. This is because the T_o is decreased by the higher BPR losses (c.f. Eq. (12)) with the (N+1)-effect system. This can be shown quantitatively by calculating the $\dot{q}_T$ for (N+1)- vs. N-effect systems with the same total surface area (A). Assuming constant and equal U-values (U_o),

$$\dot{q}_{N+1} = U_o\, T_{o,N+1}\; A_j\, /(N+1) = (U_o\; A_j\,)\; T_{o,N+1}/(N+1)$$

$$\dot{q}_N = U_o\, T_{o,N}\; A_j\, /(N) = (U_o\; A_j\,)\; T_{o,N}\,/(N)$$

But

$$T_{o,N+1} = T_s - T_{cond} - \sum_{j=1}^{N+1} BPR_j$$

Therefore $T_{o,N+1} < T_{o,N}$, which forces $\dot{q}_{N+1} < \dot{q}_N$.

One final concept of importance concerns maintaining an even distribution of heat duties in each effect in a multiple-effect system. To illustrate the impact of this, we define a Heat Duty Distribution Factor, γ_j, as

$$\gamma_j = \dot{q}_j\, /\dot{q}_{avg}$$

where $\quad \dot{q}_{avg} = \dot{q}_{Total}\, /\, N = \text{constant}$

Therefore: $\quad \gamma_j = N\, \dot{q}_j\, /\, \dot{q}_{Total}$

Note: $\quad \dot{q}_{avg} = \dot{q}_j\, /\, \gamma_j = \qquad \text{constant}$

Therefore: $\quad \dot{q}_{avg} = U_j\, A_j\, T_j\, /\, \gamma_j = U_1\, A_1\, T_1\, /\, \gamma_1 = U_2\, A_2\, T_2\, /\, \gamma_2 = \cdots \qquad (13)$

which makes: $T_2 = [U_1 A_1 T_1 / U_2 A_2] [\gamma_2 / \gamma_1]$

But:

$$T_o = \sum_{j=1}^{N} T_j$$
$$= T_1 + [U_1 A_1 T_1 / U_2 A_2] [\gamma_2 / \gamma_1] + [U_1 A_1 T_1 / U_3 A_3] [\gamma_3 / \gamma_1] + \cdots$$
$$= [U_1 A_1 T_1 / \gamma_1] [\gamma_1 / U_1 A_1 + \gamma_2 / U_2 A_2 + \gamma_3 / U_3 A_3 + \cdots + \gamma_N / U_N A_N]$$

Therefore:

$$\dot{q}_{\text{Total}} = N\, \dot{q}_{\text{avg}} = N\, \dot{q}_j / \gamma_j$$

$$= [N\, U_1 A_1 \Delta T_1] / \gamma_1 = N\, T_o / [\gamma_1 / U_1 A_1 + \cdots + \gamma_N / U_N A_N] \qquad (14)$$

$$\dot{q}_{\text{Total}} = [N\, (T_s - T_{\text{cond}} - \sum_{j=1}^{N} BPR_j) / \sum_{j=1}^{N} (\gamma_j / U_j A_j)] \qquad (15)$$

Eq. (15) implies that the capacity of the multiple-effect unit determined by $\dot{q}_{\text{Total}}$ is a function of not only N, BPR_j, T_s, T_{cond}, U_j, and A_j, but also the Heat Duty Distribution Factors (γ_j).

From Eqs.(13 and 14):

$$\Delta T_j / \Delta T_o = (\gamma_j / U_j A_j) / \sum_{j=1}^{N} (\gamma_j / U_j A_j) \qquad (16)$$

The important implication of Eq. (16) is that the ratio of the heat transfer resistance of an individual effect to the total resistance for the multiple effect system is the same ratio of the ΔT for the individual effect (ΔT_j) to the total ΔT for the system (ΔT_o). Hence, a relatively large individual resistance can be totally controlling for the system. This implies that we should keep the individual resistances approximately equal and that higher surface area should be employed in effects where the U-value is low. This would generally apply to higher solids effects where liquor viscosity is higher and scaling is more prevalent.

E. A Complete Mass and Energy Balance for an LTV Evaporator Set

The following tables contain a set of data required for a complete mass and energy balance for an LTV evaporator set, and results of the balance calculations [3].

Table 1. Input Data for Mass and Energy Balance Calculations for a 6-effect Evaporator Set.

Feed rate: 5.823 kg/s dry black liquor solids

Feed dry solids content: 13.9 wt%

Product liquor dry solids content: 52.0 wt%

Steam conditions to the first effect: 3.185 bar, 135.6 ^{o}C

Surface condenser vapor pressure and saturation temperature: 100.4 mm Hg, 51.7 ^{o}C.

Table 2. Heat Transfer Surface Areas and Heat Transfer Coefficients by Effect.

Effect #	A, m^2	U, J/m^2 s K
IA	409	981
IB	409	1230
II	818	2229
III	818	2186
IV	818	1792

V	818	1363
VI	818	1076

Table 3. Data Set for Mass and Energy Balance Calculations for a 6-effect LTV Black Liquor Evaporator Set; Example Heat Balance [3]

Effect	Flash tank	IA	IB	II	III	IV	V
Steam pressure, bar		3.19	3.19	1.66	1.22	0.72	0.4
mm Hg vacuum						211	41
Steam temperature, °C		135.6	135.6	114.4	102.2	91.1	79.
T, °C		13.3	14.4	7.2	7.2	8.3	9.
Liquor temperature, °C	111.1	122.2	121.1	107.2	95.0	82.8	70.
Boiling point rise, °C	7.8	7.2	6.1	3.9	2.8	1.7	1.
Saturated vapor temperature, °C	103.3	115.0	115.0	103.3	91.1	80.6	68.
Vapor pressure, bar		1.69	1.69	1.14	0.75	0.47	0.2
mm Hg vacuum					188	396	54
Heat of vaporization, kJ/kg		2217	2217	2249	2277	2307	233
Pressure drop between effects, bar		0.028	0.028	0.041	0.030	0.020	0.02
mm Hg					23	15	1
Next effect vapor pressure, bar		1.66	1.66	1.10	0.72	0.45	0.2
mm Hg vacuum					165	381	53
Feed rate, kg/s	11.42	13.83	17.11	22.54	27.67	31.88	20.9
Discharge rate, kg/s	11.24	11.42	13.83	17.11	22.54	27.67	16.4
Total dry solids content in, wt%	51.2	42.3	34.2	25.9	21.1	18.3	13.

Total dry solids content out, wt%	52.0	51.2	42.3	34.2	25.9	21.1	17.
Condensate, kg/s	0.18	2.42	3.28	5.42	5.13	4.21	4.5

Table 4. Mass and Energy Balance Calculations for a 6-effect LTV Black Liquor Evaporator Set; Example Heat Balance [3]

	Heat Flow Rate, kJ/s	Heat of Vaporization, kJ/kg	Evaporation Rate, kg/s
Steam to 1A	5,402		
Heating feed to IA			
(13.98 kg/s)(122.2-121.1^{o}C)(3.31 kJ/kgK)	50.9		
Evaporation 1A	5,352	2,217	2.41
Steam to 1B	8,090		
Heating feed to IB			
(17.11 kg/s)(13.9C)(3.45)	821		
Evaporation IB	7,270	2,217	3.28
From IA	5,352		
Steam condensate flash from IA, IB			
(2.570+3.868)kg/s (20.56C)(4.18kJ/kgK)	553		

Heat to II	13,175		
Heating feed to II			
(22.54 kg/s)(12.2C)(3.53 kJ/kgK)	971		
Evaporation II	12,204	2,249	5.43
Condensate flash from II	318		
Flash liquor from IA	171		
Heat to III	12,694		
Heating feed to III	1,229		
(27.67 kg/s)(12.2C)(3.64 kJ/kgK)			
Evaporation III	11,692	2,277	5.13
Condensate flash from III	537		
Heat to IV	12,229		
Heating feed from V	789		
(16.44 kg/s)(12.8C)(3.75kJ/kgK)			
Heating feed from VI	1,708		
(15.31kg/s)(29.4C)(3.79kJ/kgK)			
Evaporation VI	9,732	2,307	4.22
Condensate flash from V, VI	815		
Heat to V	10,546		

Feed flash to V	89.8		
(20.98 kg/s)(1.1C)(3.89kJ/kgK)			
Evaporation V	10,636	2,338	4.55
Condensate flash	1,117		
Heat to IV	11,754		
Feed flash to VI	1453		
(20.98 kg/s)(17.8C)(3.89kJ/kgK)			
Evaporation VI	13,206	2,379	5.55
Total evaporation			30.57
Live steam consumed			6.44
Steam economy			4.75

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3.3 EVAPORATOR CAPACITY AND STEAM ECONOMY

The black liquor processing capacity of an evaporator set is equivalent to the rate at which it can remove water from black liquor. The capacity for water removal is equivalent to the rate at which heat is transferred from steam to the black liquor, or

CAPACITY = HEAT TRANSFER RATE

Defining capacity is that simple. Evaporator designers and operators must know this relationship and know how to apply it. Applying it, however, is often more difficult than defining it. The next sections of this chapter deal with how to apply it.

Steam economy and evaporation capacity (or rate) are two important factors that are considered when designing black liquor evaporators and concentrators. New evaporator installations are designed to match a pulp mill's requirement for concentrating the volume of black liquor generated to the desired total dry solids content for firing. Meeting the pulp mill's evaporation demand today is a greater challenge with older evaporator sets that were likely designed for different weak black liquor feed rates and feed dry solids contents, total evaporation loads and product dry solids contents, and black liquor streams with different physical properties. Existing older evaporator sets often need to be optimized to meet new black liquor processing requirements. Optimization alone of an existing evaporation plant may not be sufficient to meet current or future mill needs, so that hardware to increase evaporation capacity may need to be installed. Changes in collection of methanol and turpentine as high value products, and management of NCGs and condensates must be dealt with as well.

The factors that impact steam economy and capacity of multiple effect black liquor evaporators are [1]:

Steam economy (in decreasing importance):

- Number of effects
- Feed liquor temperature
- Steam pressure to first effect
- Dry black liquor solids content of the feed and product liquors from the evaporator set
- The number of stages of liquor and condensate flash, and the temperature of the discharged liquor and condensate
- The liquor flow sequence within the evaporator set

Capacity (evaporation rate):

- Total heat transfer surface area
- Available temperature drop
- Overall heat transfer coefficients in each effect

The capacity of an evaporator set is determined by the complicated interaction of these variables. This issue is discussed in more detail later in this section.

3.4 FLOW CHARACTERISTICS IN EVAPORATORS AND CONCENTRATORS

The amount of heat transfer surface required in an evaporator set depends in part on the flow behavior black liquor in contact with the heat transfer surface. Evaporator bodies are designed for one of these three types of flow:

- Climbing (rising) film
- Falling film
- Forced circulation

The first two types operate with vertical, two-phase flow. In these units, water is evaporated mainly by convective boiling as the liquor is heated. Vapor is generated along the liquor flow path, with evaporation taking place at the liquid-vapor interface.

Forced circulation evaporators operate with single-phase flow. The pressure in forced circulation evaporators is kept high enough to prevent boiling within the heating element. Vapor is generated when the hot liquor flashes as it enters a vapor head through a pressure reduction valve.

The rates of heat transfer evaporation are determined in part by the vapor-liquor flow behavior. Vapor and liquid flows are coupled through the momentum of each phase as vapor and liquid move together through the heating element of the evaporator. In climbing film LTV evaporators, for example, the vapor generated during evaporation pushes and drags black liquor upward to the exit of the evaporator tubes, operating against the effect of gravity that pulls it back downward. Similarly, the liquor acts as a drag on rising bubbles and slugs of vapor, shaping and compressing them and creating distinctive flow patterns within the two-phase flow. Boiling increases the total vapor flow rate from zero at the tube entrance. The geometry of the flow as imposed by the flow conduit or surface also plays a role.

The mass ratio of vapor to liquid flowing upward in the heat transfer tubes of a typical climbing film LTV evaporator is between 0.15 and 0.32 (Table 1). The vapor to liquid volume ratios are much higher, from more than 500 in the 1st effect to more than 20,000 in the 6th effect (Table 1). These values reflect the huge change in specific volume of water vapor from the high-pressure conditions in the first effect to the sub-atmospheric conditions in the 6th effect. These are the ratio of volumetric flow rates for vapor and black liquor exiting the tubes for each of the six effects in a 6-effect climbing-film LTV evaporator:

Table 1. Mass Flow and Volume Flow Ratios for Vapor and Black Liquor in each of the Six Effects of a Typical LTV Evaporator Set.

Effect #	6	5	4	3	2	1
Pressure, bar	0.13	0.27	0.46	0.72	1.08	1.64
Liquor in, kg BLS/kg BL	0.139	0.183	0.211	0.259	0.342	0.423
Liquor out, kg BLS/kg BL	0.183	0.211	0.259	0.342	0.423	0.512
Flow rate ratios at tube exit:						
Vapor to BL volume ratio, m^3/m^3	21,000	4,230	3,310	2,390	1,020	544
Vapor to BL mass ratio, kg/kg	0.317	0.153	0.227	0.320	0.237	0.210

Flow regime maps for multiphase flow (vapor-liquid flow) are useful representations for flow visualization. They have been used as tools to better understand a variety of 2-phase and multi-phase flow applications [2, 3].

Flow maps are approximations. The boundaries represent transitions between regions. The actual boundary locations change with tube diameter and with variables such as surface roughness, and, for multicomponent fluids, even small differences in composition. Although viscosity is included as a variable within the correlations, most were developed from data for lower viscosity fluids. Even with these limitations, flow maps can be useful in understanding flow behavior in convective heat transfer equipment such as black liquor evaporators.

A flow regime map for vertical flow of black liquor and vapor under one set of conditions is illustrated in Figure 1. The flow regime boundaries are plotted on axes of the superficial vapor momentum flux versus the superficial liquid momentum flux, which are defined as

$$\text{Superficial vapor momentum flux} = [G\,x]^2/\rho_g$$

Superficial liquid momentum flux $=[G(1-x)]^2\rho_l$

where:

G = mass velocity
x = vapor quality
ρ = density.

The boundaries between regions of the map were calculated using correlations for each vertical flow in conduits as developed by Hewitt and Roberts [7] and included in Collier [5]. Figure 4 shows that black liquor flow falls within the churn region in climbing film LTV evaporators. Lavery observed this same slug-churn flow behavior with black liquor in a pilot LTV evaporator [4].

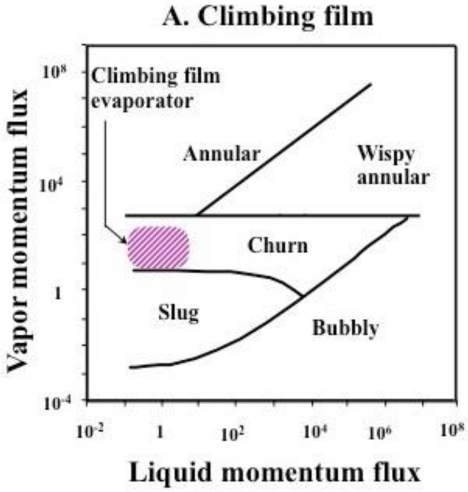

Figure 1. Flow map for black liquor in a climbing film LTV evaporator for black liquor at 50 wt% dry solids content, 100°C.

3.5 DESCRIPTIONS OF FLOW PATTERNS IN VERTICAL, CO-CURRENT VAPOR-LIQUID FLOW

The five flow patterns illustrated in Figure 2 are encountered in two-phase vertical upward co-current flow in LTV evaporators, vertical tubes boilers, and other similar devices. The flow patterns are described here.

Bubbly flow: the vapor bubbles, much smaller than the tube diameter, are distributed as discrete bubbles in a continuous liquid phase.

Slug flow: bubbles are nearly the diameter of the tubes that contain them. A slowly descending film of liquid separates the bubbles from the tube wall.

Churn flow: formed when large bubbles in slug flow begin to break down. The vapor flows in a chaotic manner through the liquid that is mainly displaced to the tube wall. The flow has an oscillatory character.

Wispy annular flow: the liquid forms a thick film on the tube wall, with a considerable amount of liquid entrained as droplets in the center core. The droplets agglomerate into long, irregular filaments.

Annular flow: a liquid film forms at the tube wall, with a central vapor core. Large amplitude coherent waves appear on the liquid film surface. Continuous breakup of the waves generates entrained droplets in the central core flow.

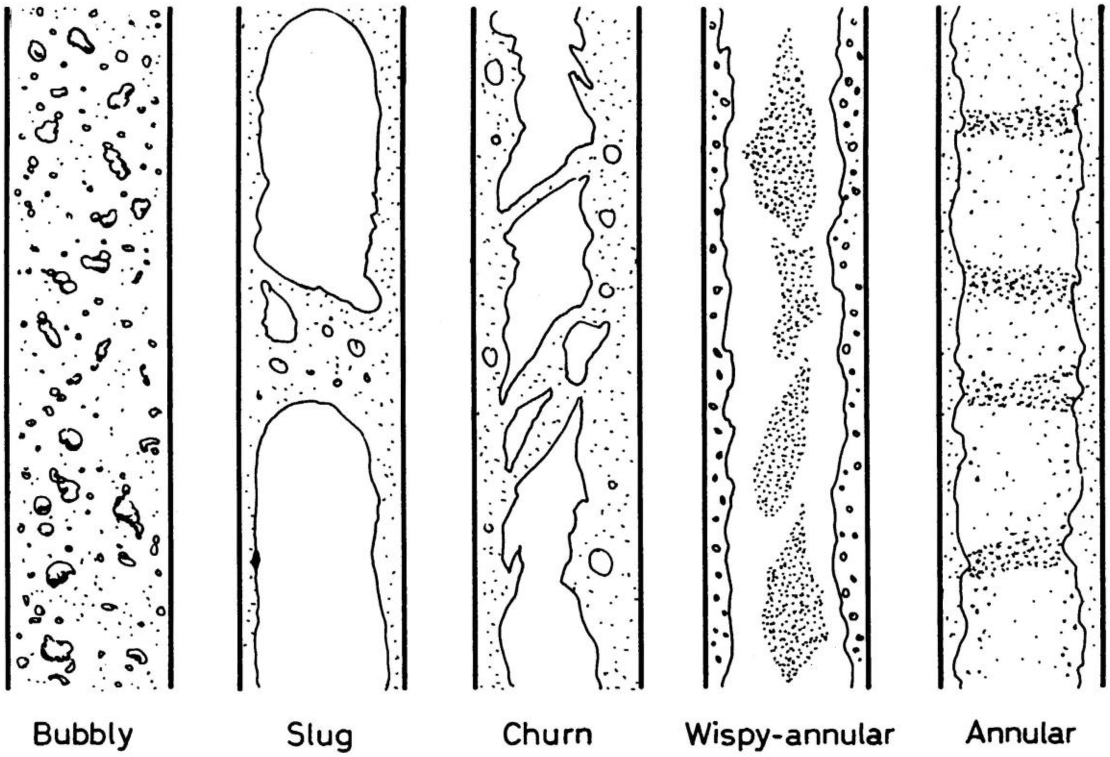

Figure 2. Flow patterns in rising film two phase flow [5].

The range of void fractions, measured experimentally with air-water systems [3] are:

Bubbly flow: 0.057-0.20

Slug flow: 0.28-0.54

Froth flow: 0.43-0.7

Falling film flow: 0.80-0.94

Annular flow: 0.81-0.94

3.5.1 Climbing Film LTV Evaporators

Liquor enters an LTV body from a liquor plenum in the bottom. Flow is single phase liquid for the first meter or more, until the liquor begins to boil and generate vapor.

The rising vapor pushes and drags black liquor upward with it. This transports the liquor to the top of the tube and into the vapor head at the top of the tube bundle. There, liquor and vapor are separated.

Two-phase flow in a climbing film evaporator is chaotic. Liquor is transported upward in the center of the tube and gravity pulls it downward along the tube wall, creating a large back flow. Large slugs of vapor formed from coalescing vapor bubbles rise unsteadily, creating an unstable, chaotic flow. As heat is transferred, the vapor content increases in each tube. Then the liquor and vapor exit the top of the tube as if they are burped out. The tube then refills with liquid, mainly by back flow of liquor collected in the vapor head. Different tubes within the tube bundle eject liquor at different times and cyclic pressure fluctuations for each tube have been observed. Two important consequences are that the flow pattern within any one tube is unsteady and the liquor concentration within a tube varies with time. As a result, tubes that begin to plug with scale will plug faster than adjacent clean tubes because the liquor eject-refill cycle in the scaling tubes is hindered.

Heat transfer in climbing film LTVs is from the tube walls to the liquor adjacent to the walls. The evaporation mechanism is convective boiling, with water evaporating from the liquor-vapor interface of liquor on the tube walls.

The flow map in Figure 1 shows the regions of flow for two-phase vertical up flow in climbing film LTV black liquor evaporators. The axes represent the superficial momentum fluxes for the vapor and liquid respectively, with superficial velocities calculated for the vapor only or liquid only as their respective volumetric flow rates divided by the tube cross section. The solid lines in the map are boundaries between different flow regions [5]. The boundaries in Figure 1 were calculated specifically for black liquor at 100°C, 50 wt% dry solids content [6]. Flow maps can be created for other vapor-liquid systems using the method developed by Hewitt and Roberts [5, 7].

The flow region for black liquor in climbing film LTVs lies in the churn flow region at low liquor superficial velocities and moderate vapor superficial velocities. This slug-churn flow behavior has been observed in a pilot LTV evaporator [4].

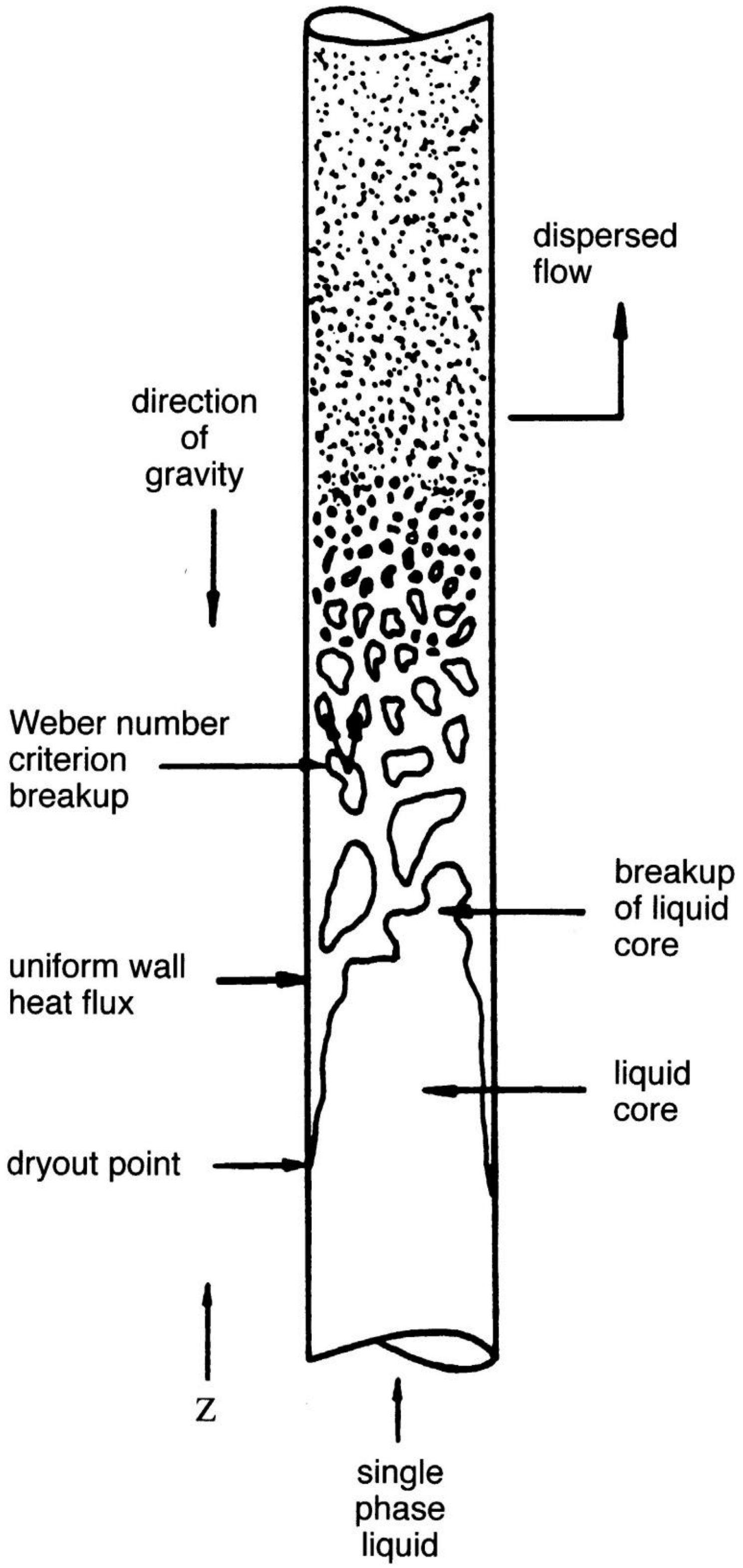

Figure 3. Flow regimes in a rising film evaporator tube [5].

3.5.2 Vertical Downflow Inside Tubes

Here, gravity acts in the same direction as the black liquor flow. When liquid and vapor both flow downward, flow is not chaotic. Downflow in black liquor evaporators is either falling film or annular, depending on the ratio of vapor to liquid volumetric flow rates, liquor velocity, and viscosity. Higher liquor velocity and vapor-to-liquid volumetric flow rate ratio move the flow pattern more toward annular flow.

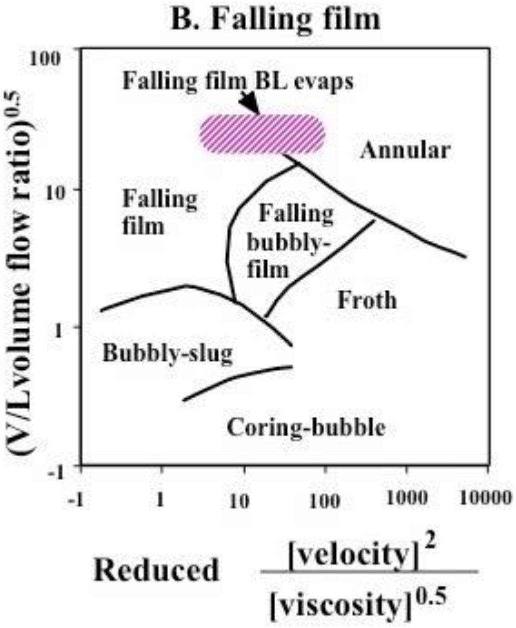

Figure 4. Flow map for black liquor inside a tube in a falling film evaporator.

3.5.3 Vertical Downflow over Tube Heating Elements

The flow of black liquor downward on the outside of vertical tubes is complex. Figure 5 shows the appearance of a black liquor film in downflow near the top of a tube (left) and near the bottom of the tube (right). These photos were taken for black liquor flowing on the outside of a tubular heat transfer surface in a pilot falling film black liquor evaporator. The range of Reynolds numbers ($Re_f = 4\Gamma_z/\mu_f$) in these measurements was from 2,000 to 56,000, where 5,000 represents the transition from wavy laminar to turbulent flow for viscous liquids in downflow on the outside of tubes [8]. This transitional Reynolds is three times higher than the accepted value of 1,600 based on measurements with low viscosity liquids.

The flow pattern of the black liquor falling film in the reported observations was smooth but wavy near the top of the tube. It became increasingly more chaotic along the tube length. One example is shown in Figure 5. The chaotic flow characteristic became more pronounced at the highest viscosities. Bubble formation was not seen in the film, indicating an absence of nucleate boiling.

No dry out of the black liquor film was observed except in runs at the highest black liquor viscosity (570 Pa-s).

Even though the viscosity was very different in the different experiments, from 0.0015 Pa-s to 0.57 Pa-s, the hydrodynamics behavior was similar and did not deviate much from that in Figure 5.

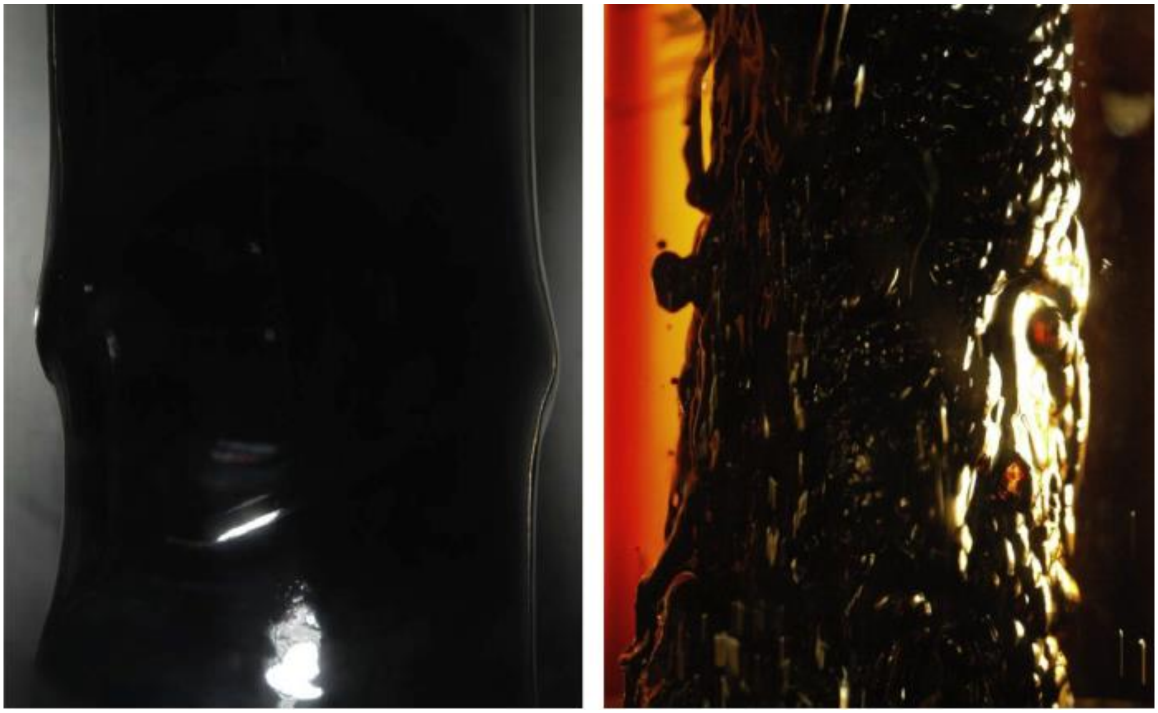

Figure 5. Hydrodynamic behavior of a black liquor falling film at q = 7700, Re = 230, and Pr = 209 (left) near the top of the evaporator tube, 0.3 m below the black liquor inlet, and (right) near the bottom of the tube, 4 m below the black liquor inlet [9].

3.5.4 Vertical Downflow over Plate Heating Elements

Evaporation from liquid films destabilizes the films flowing downward over heated, vertical surfaces at all Reynolds numbers [10, 11]. The instantaneous vaporization rate is greater at the troughs in the film rather than at the crests of surface waves since the film is thinner at the troughs. This creates thin spots in the film within the troughs. The vapor leaving perpendicular to the surface exerts a reactive pressure on the liquid. It is larger at the troughs than at the crests, which therefore tends to increase the wave amplitude [11].

The rupture into rivulets of a thin liquid film flowing down a vertical surface is assumed to occur when both the continuous film and the rivulets carry the same mass flow and total (surface plus kinetic) energy and when, moreover, the latter exhibits a local minimum in the rivulet configuration.

On cooled surfaces, liquid films are not inherently unstable and only becomes so at a critical Reynolds Number.

3.5.5 Design Procedure

Design Basis and Input Variables

The design basis for an evaporator set is the amount of water to be evaporated per hour from the black liquor processed, i.e.

$$\dot{m}_w = \dot{m}_{bls}\,(1/x_{out} - 1/x_{in}) \tag{1}$$

Other values that need to be specified for designing an evaporator set are:

- Number of effects
- Steam pressure to 1st effect (P_{stm})
- Steam temperature to first effect, if superheated (T_{stm})
- Mass flow rate of black liquor solids ($\dot{m}_{bls}$)
- Dry solids mass fraction of black liquor feed (x_{in})
- Dry solids mass fraction of black liquor product (x_{out})
- Temperature of cooling water to condenser for last effect vapor (T_{cw})

Calculation of the Required Heat Transfer Area

q_{tot}, the amount of heat transferred, is calculated from an energy balance around the evaporator unit. It depends upon the amount of water to be evaporated, the entering and exiting black liquor conditions, and exiting condensate conditions.

The overall thermal driving force, ΔT_o, is calculated from the saturation temperature of steam to the first effect ($T_{sat}(P_{stm})$) and the temperature of coolant (T_{cw}) in the vapor condenser following the last effect:

$$\Delta T_o = T_{sat,stm} - T_{cw} \tag{2}$$

The overall available thermal driving force is ΔT_o minus the sum of the boiling point rise for each effect, or

$$\Delta T_{avail} = \Delta T_o - \Sigma(BPR_i) \tag{3}$$

Heat transfer coefficients for each effect must be provided. Evaporator suppliers have proprietary data that they use in designing evaporator sets. For preliminary design estimates, values of heat transfer coefficients can be estimated using the correlations in Section 2.4 of this book.

ΔT_{avail} apportions itself among the evaporator effects to the evaporation requirements (heat demand) of each effect. The evaporator designer and operator are not able to specify the distribution of ΔT_i between effects.

The heat transfer areas for each effect is calculated as

$$A_i = \dot{q}_i/U_i\Delta T_i \tag{4}$$

For initial calculations, $q_i = q_{tot}/n$ and $\Delta T_i = \Delta T_{avail}/n$. $\dot{q}_i$ and ΔT_i will adjust themselves to correct values during iterative calculations.

Liquor Recirculation Rate

In forced circulation evaporators:

- The tube velocity is determined by a tradeoff between pumping cost and maintenance cost (tube erosion, fouling/scaling).
- The liquor recirculation to feed ratio is selected to maintain the desired temperature in the heat exchangers, control crystallization rate and location, and maintain the desired liquid velocity in the tubes.
- The operating pressure is high enough to prevent vaporization, which minimizes crystallization scaling of the heat exchangers.
- The pressure drop through the heat exchangers is depends upon the flow rate through the tubes and the viscosity of the black liquor. It may be set by optimization of capital vs operating cost for the evaporator set.

Flow Distribution

It is important that the flow of black liquor to each heat transfer tube in a tube-type falling film evaporator is nearly equal. This balances the rate of heat transfer for each tube and prevents dryout on the tube surface for those tubes receiving too little liquor. If the liquor loading is too low in some tubes, the flow of black liquor may be insufficient to initially completely wet the tube surface or to maintain a fully wetted surface during evaporation (Figures 6 and 7). Under these conditions, the liquor film breaks down. Rivulets of liquor flow down the tube surface, with dry regions interspersed between them. Heat transfer to the liquor is reduced and dry regions are subject to scaling and fouling.

Liquid films flowing down a metal surface can wet the surface completely if certain criteria are met. For a liquid to initially wet the inside of a falling film evaporator tube, the liquor loading must exceed a minimum liquid loading given by

$$\Gamma_{min} = C_{w,i} (\mu \text{ sg } \sigma^3)^{0.2}$$

where:

Γ_{min} = minimum tube loading, kg/s-m, for complete surface wetting
μ = liquor viscosity at process conditions, cP
sg = liquor specific gravity
σ = liquor surface tension, dyne/cm
$C_{w,i}$ = initial wetting constant = 0.00806 kg/s-m (19.5 lb/hr-ft)

The same correlation applies the liquid loading to maintain a wetted surface during evaporator operation except the value of the wetting constant changes. The wetting constant becomes $C_{w,ss}$ = steady state wetting constant = 0.000992 kg/s-m (2.4 lb/hr-ft). The ratio of the initial to steady state wetting constants show that the minimum tube loading during startup needs to be at least 8 times the minimum loading during steady state operation.

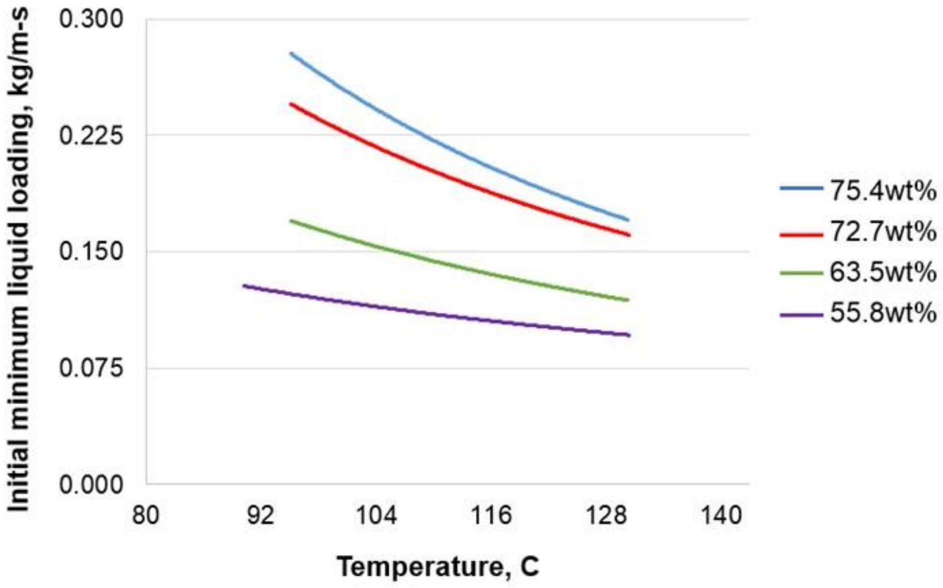

Figure 6. Minimum initial liquid loading (Γ_{min}) to establish complete wetting of tube surface versus dry black liquor solids content and liquor temperature. Data sets are for different black liquor dry solids contents.

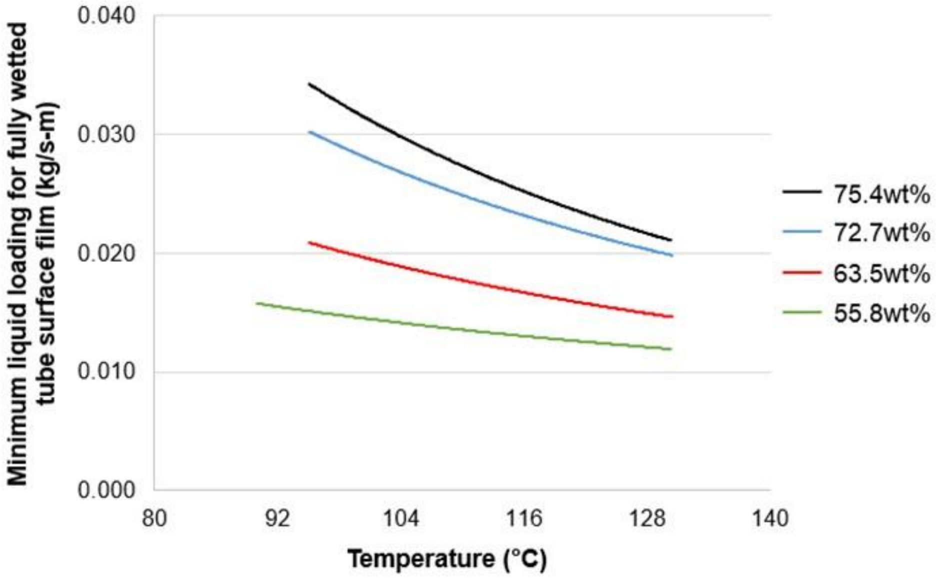

Figure 7. Minimum liquid loading (Γ_{min}) to maintain complete wetting of tube surface versus dry black liquor solids content and liquor temperature. Data sets are for different black liquor dry solids contents.

Nucleate boiling occurring at the tube surface can cause liquor film rupture and film breakdown. This can be avoided by operating with low ΔTs. Recommended ΔTs for tube type falling film evaporators are ΔT < 6 °C -7°C (11 °C -13°C).

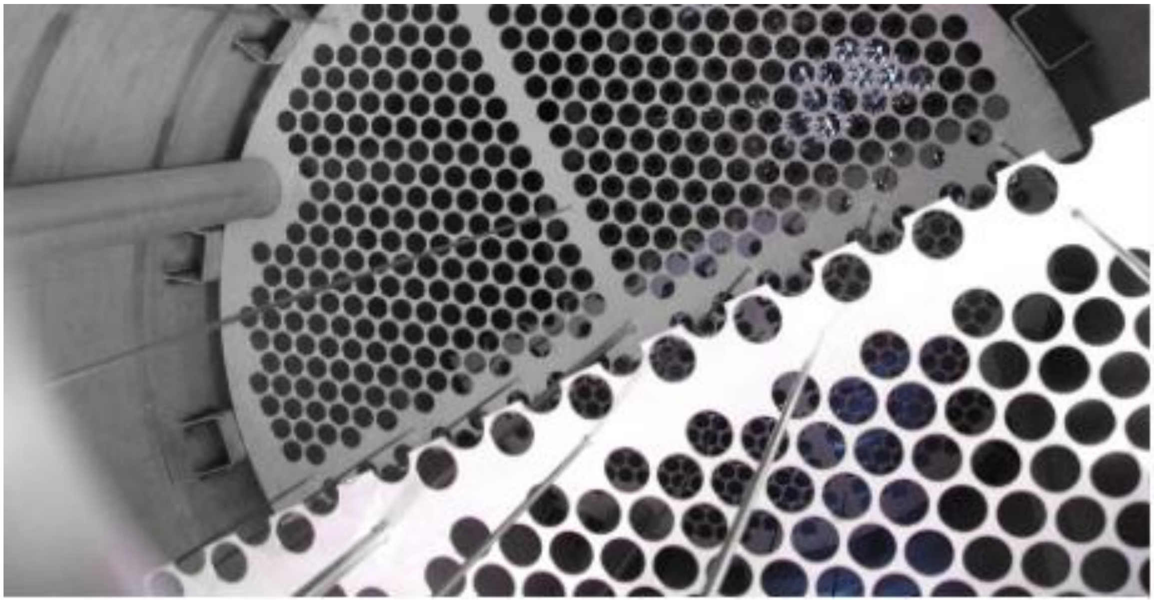

Figure 8. A distributor plate for tube type falling film evaporators for black liquor and other liquids [12].

3.5.6 Flow Distributors in Black Liquor Falling Film Evaporators

The two most common types of flow distributors in black liquor falling film evaporators are drilled distribution plates and spray nozzles. Distribution plates (Figure 8) can either be the width of the top liquor box (for tube units) or smaller with a weir wall (for tubes or plates). On a tube unit, the liquor is directed through the drilled holes in the distribution plate and down onto the tube sheet between the tubes. It overflows into the tubes to form a black liquor film in each tube. The same concept is used with a plate unit, except the liquor is evenly distributed over the top line of the plate.

Spray nozzles are used in instances where the liquor properties cause issues with distribution plate plugging or prevention of even black liquor distribution. The downside of spray nozzles is that some of the liquor is sprayed into the tube and does not adhere to the tube wall until it is part of the way down the tube. This is generally a minor issue when compared to the performance of that body with one using a drilled distribution plate.

Important design considerations for falling film evaporators include:

- Fluid distribution in tubes
- Fluid distribution across the tube sheet
- Film breakdown wetting limits
- Lower ΔT limit for nucleate boiling
- Pressure drop along the liquor flow path

3.5.7 References

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3.6 HEAT TRANSFER IN BLACK LIQUOR EVAPORATORS

W. J. Frederick

The rate of heat transfer in black liquor evaporators determines the rate of evaporation and therefore the capacity to support a mill's pulp production rate. In this section, factors that determine evaporation rate are considered.

The overall rate of heat transfer in a steam-driven heat exchanger or evaporator body is set by $\dot{q}$ = U A ΔT where U is the overall heat transfer coefficient, A is the heat transfer area, and $\Delta T = T_{sat,stm} - T_{BL}$ is the temperature driving force.

To estimate $\dot{q}$, we need values for U, $T_{sat,stm}$, and T_{BL}. Evaluating ΔT for the individual evaporator effects in a multiple effect evaporator set is not straightforward because of the coupling of steam and vapor pressures and black liquor temperatures between effects. Evaluation of the distribution of ΔTs involves iterative calculations for the set. Since U_i can depend on ΔT_i, the calculation procedure is complicated when done manually. For an approximate and rapid manual calculation procedure, refer to Ulrich [1]. Process simulation software greatly accelerates the calculations.

Evaluating ΔT for Individual Evaporator Effects

Evaluating ΔT for single evaporator body or a heat exchanger is complicated by the type of hardware, the flow configuration on both sides of the heat transfer device, and any change of phase that occurs on either side of it. Here are ΔT definitions for different cases.

a. For single phase flow on both sides of the exchanger (Figures 1 and 2), e.g. heat exchange between black liquor and hot water:

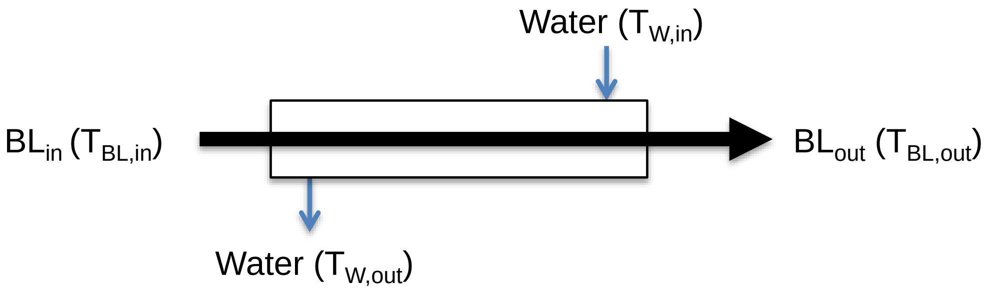

Figure 1. Simplified diagram of a single pass heat exchanger with single passes on both the tube and shell side.

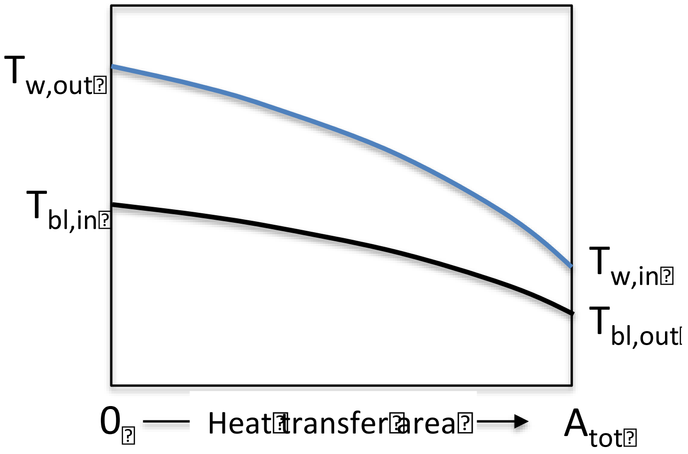

Figure 2. Temperature profiles for both the liquor and coolant (water) sides of the heat exchanger in Figure 1.

In this case, a log-mean temperature difference (LMTD or ΔT_{LM}) is used to calculate the overall rate of heat transfer in the heat exchanger:

$$\Delta T_{LM} = (\Delta T_{out} - \Delta T_{in})/\ln(\Delta T_{out}/\Delta T_{in}) \quad (1)$$

$$\text{where } \Delta T_{out} = T_{BL,out} - T_{w,in} \text{ and } \Delta T_{in} = T_{BL,in} - T_{w,out} \quad (2)$$

Multi-pass heat exchangers for similar applications require a correction factor (F) be applied to ΔT_{LM}. F is evaluated for configuration-specific equations or published charts [2, 3]. Figure 3 contains an F-factor chart for a single shell, double tube pass heat exchanger. Similar charts are available for many shell and tube configurations.

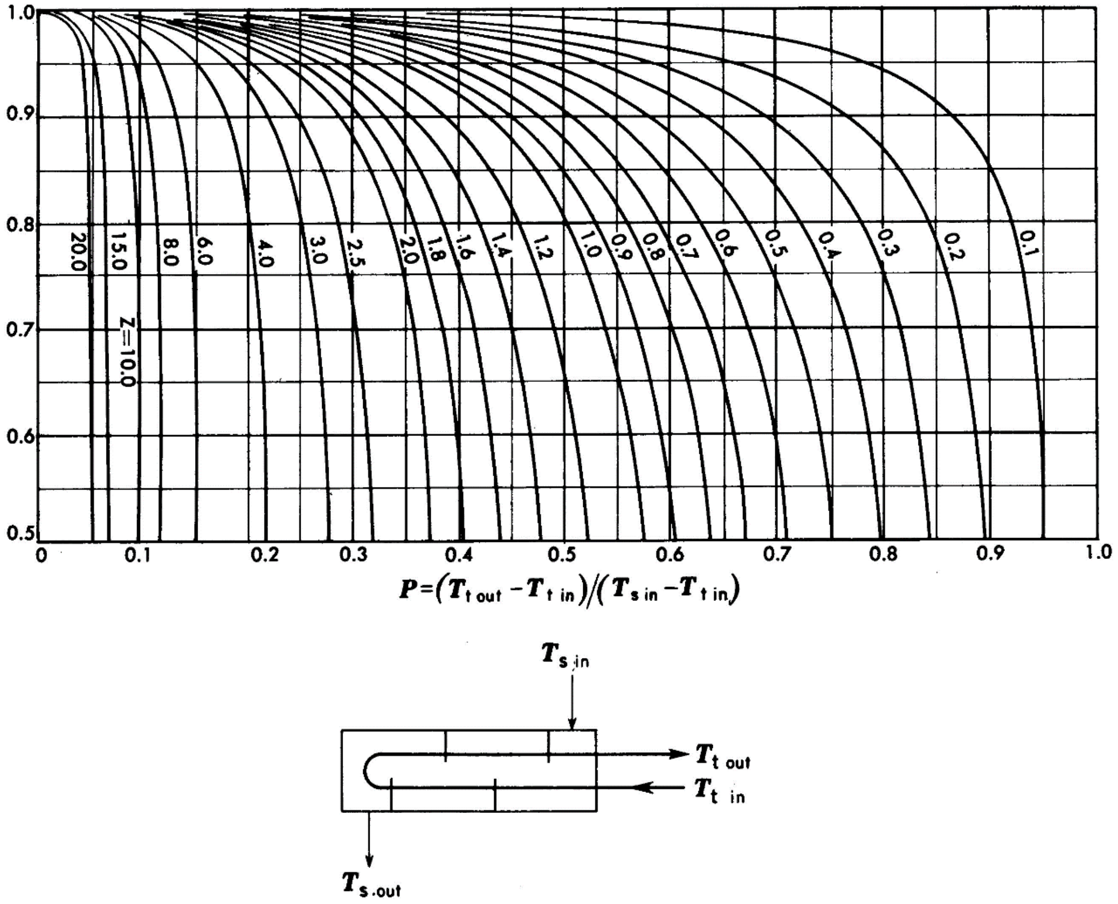

Figure 3. Correction factor (F) to counter-flow ΔT_{LM} for heat exchangers with one shell pass and two or multiple of two, tube passes [4].

b. For LTV evaporators with vertical 2-phase flow, the vertical black liquor temperature is controlled by the pressure in the evaporator body and the changing boiling point rise of the liquor as it moves up the tube. In the subcooled region, the liquor temperature profile is determined by the entering liquor temperature and the ratio of heat transfer rate ($\dot{q}$) to liquor thermal mass flow rate ($\dot{m}\,c_p$). Above the onset of two-phase flow, the local temperature depends mainly upon cooling by evaporation as well as the local pressure and boiling point elevation of the black liquor. Figure 4 shows two typical black liquor temperature profiles in rising film LTV evaporators. ΔT_{LM} is not applicable to these types of temperature profiles. By convention, the ΔT used is the difference between the saturated steam temperature ($T_{s,stm}$) and the temperature of the black liquor exiting the heat transfer region ($T_{BL,exit}$), so that

$$\Delta T_{LTV} = T_{s,stm} - T_{BL,exit} \tag{3}$$

c. For falling film and forced circulation evaporators, the ratio of recirculated to feed black liquor is high, typically about 20:1, the boiling point rise change is small through the unit, and the black liquor temperature is controlled mainly by the pressure for the unit. While a log-mean ΔT is applicable for these types of evaporators, a simple temperature difference between the saturated steam and black liquor exiting the unit gives approximately the same result, so

$$\Delta T_{FF} = T_{s,stm} - T_{BL,exit} \tag{4}$$

$$\Delta T_{FC} = T_{s,stm} - T_{BL,exit} \tag{5}$$

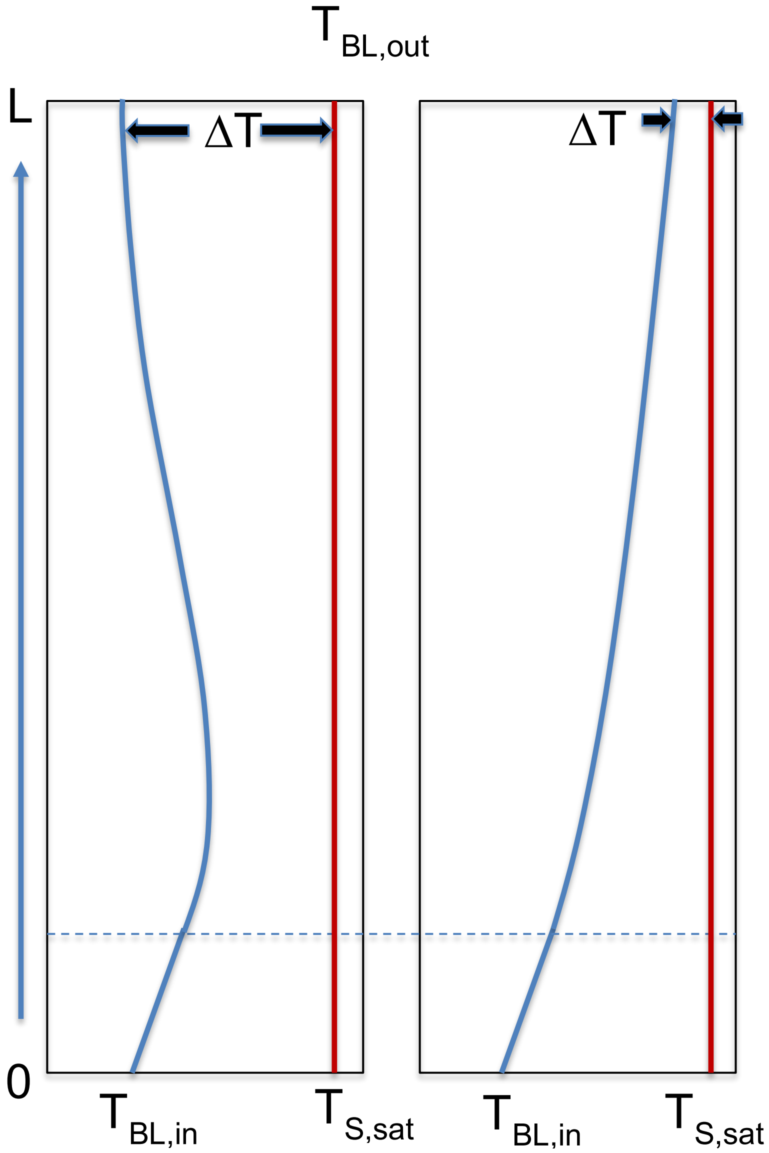

Figure 4. Vertical temperature profiles for black liquor in LTV evaporators.

Different temperature profiles are also possible:

- At a given location, liquor temperature increases with the rate of heat transfer. However, the liquor temperature decreases with evaporation and pressure decreases as the liquor moves up in the tube.

- The left figure is for black liquor at low dry solids content, where the BPR does not increase rapidly as water is evaporated.
- The right figure is for high dry solids black liquor, where the BPR increases rapidly as water is removed.

In summary, the definition of ∆T is different between LTV evaporators and other types. The values of heat transfer coefficients (U) calculated for each different type of evaporator will differ from each other because of the differences in how ∆Ts are defined. U values obtained from one type of evaporator should not be used with other types of evaporators even when they are processing the same black liquor.

Estimating Heat Transfer Coefficients for Black Liquor Evaporators

Methods for estimating heat transfer coefficients in two-phase flow have been developed over the past six decades. However, most were based on data for low viscosity liquids such as water, light hydrocarbons, and alcohols. They do not predict accurately heat transfer coefficients with more viscous fluids such as black liquor [5]. Only a few correlations have been developed specifically for black liquor or other viscous liquids. The estimation methods for heat transfer coefficients with black liquor in the heating elements of different types of black liquor evaporators are summarized here.

Terminology for Dimensionless Heat Transfer Correlations

Heat transfer coefficient are normally correlated using dimensional variables for heat transfer coefficients, flow behavior, fluid properties, and equipment dimensions. These include:

1. The Nusselt number for the heat transfer coefficient
    1. For single phase flow in a tube: Nu = hD/k

    2. For falling liquid film heat transfer on a surface: $Nu_f = h_{TP}\,\delta / k_f$
2. The Reynolds number for flow behavior
    1. For single phase flow in a tube: $Re = DV\rho/\mu$
    2. For falling liquid film on a surface: $Re_f = 4\Gamma/\mu$
3. The Prandtl number for fluid properties: $Pr = c_p\,\mu/k$

Heat transfer coefficient correlations for convective flow heat transfer normally take the form of:

$$Nu = K\,Re^a\,Pr^b \tag{6}$$

The values of K, a, and b are obtained by fitting Eq. (6) to experimental data. These parameter values are not universally constant but change depending on system characteristics flow regime change from laminar to turbulent and system geometry.

Heat transfer coefficients depend strongly on fluid viscosity to the reciprocal of the power of 0.4 ($h \propto 1/\mu^{0.4}$). The viscosity of black liquor increases from 1 cP to 10^4 cP when black liquor is concentrated from a dry solids content of 15 wt% to 80 wt%. With this significant change in viscosity, h decreases by a factor of 40. Because of their strong viscosity dependence, heat transfer correlations developed from low viscosity fluid data do not give accurate estimates of heat transfer coefficients for black liquor [1].

The standard definition for Nu in falling film heat transfer is

$$Nu = (h/k)(\nu^2/g)^{1/3} \tag{7}$$

Correlations are valid in certain flow regime (laminar, wavy-laminar, or turbulent), as characterized by the Reynolds (Re) number. The Reynolds number for falling film flow is:

$$\mathrm{Re} = 4G/\mu \tag{8}$$

Nusselt number correlations usually take on a different form in each different flow regime. Table 1 contains examples of some different forms. Various reported values for K, P1, and P2 are included. Most of the experimentally based correlations were developed from experiments where the evaporated fluid flowed on the outside surface of a vertical tube. The equation proposed by Nusselt (1916), however, was derived analytically.

The Re number at the transition from laminar flow with capillary or roll waves to turbulent flow [6] is

$$\mathrm{Re}_{\mathrm{trans}} = 5800\,\mathrm{Pr}^{-1.06} \tag{9}$$

The Kapitza number ($\mathrm{Ka} = \sigma/\rho(g\sin\beta)^{1/3}\nu^{4/3}$), an indicator of the hydrodynamic wave regime in falling liquid films, is included in some correlations.

Table 1. Nusselt Number Expressions for Falling Film Flow on Surfaces [5]

Flow regimes	Nusselt number relationship
Laminar flow with no ripples	$Nu = K\,Re^{P1}$
Laminar flow with capillary or roll waves	$Nu = K\,Re^{P1}$
Transition[a]	$Nu = (Nu^{n}_{ripples} + Nu^{n}_{turbulent})^{1/n}$
Turbulent	$Nu = K\,Re^{P1}\,Pr^{P2}$

[a] Values for n of 2, 5, and 6 have been used in the transition flow correlation.

Three Nu versus Re correlations for the laminar with ripples vertical flow regime from other researchers [5] all give very similar results. Combining three of those correlations into one equation, gives:

$$Nu_{l\text{-}t} = 1.20\,Re^{-0.298}$$

This correlation is valid for the Prandtl number range $2 < Pr < 8$.

A correlation for turbulent vertical flow, developed using a similar approach, is

$$Nu_{t} = 0.0123\,Re^{0.321}\,Pr^{0.559}$$

This correlation is valid approximately for the range $10^4 < Re < 10^5$ and $1 < Pr < 50$.

Convective Heat Transfer Correlations for Black Liquor

The next three subsections present heat transfer correlations for black liquor in both single- and two-phase flow in climbing film evaporators, falling film evaporators, and forced circulation concentrators [7].

For single-phase laminar flow in a circular cross section tube:

$$\mathrm{Nu_{lam}} = (6.488^3 + 0.517^3(\mathrm{f\,Re}))(\mathrm{Re\,Pr\,D/x}) \tag{10}$$

where $\mathrm{f} = (1.82 \log_{10} (\mathrm{Re}) - 1.64)^{-2}$

For single-phase turbulent flow in a tube:

$$Nu_{turb} = \frac{f/8\,(Re-1000)Pr}{1+12.7\sqrt{f/8}(Pr^{2/3}-1)}\left\{1 + \ 1/3\,(d_h/x)^{2/3}\right\} \tag{11}$$

Replace Re with Re* in Eqs. (10) and (11), where

$$\mathrm{Re^*} = [\mathrm{Re}^2 + \mathrm{Gr}/2.5]^{0.5} \tag{12}$$

and

$$\mathrm{Gr} = \mathrm{g}\,\beta\,(\mathrm{T_s} - T_\infty)\,\mathrm{D}^3/\nu^2 \tag{13}$$

where:

g = acceleration due to Earth's gravity

β = volumetric thermal expansion coefficient (equal to approximately $1/T$, for ideal gases, where T is absolute temperature)

T_s = surface temperature

T_∞ = bulk liquor temperature

L = characteristic length

D = diameter

ν = kinematic viscosity

Subcooled Flow Boiling Heat Transfer

Subcooled flow boiling occurs when the wall temperature is high enough to support bubble growth at the tube wall, but the bulk temperature remains below saturation. For subcooled flow, the two phase heat transfer coefficient (h_{tp}) is the sum of contributions from nucleate boiling (h_{nb}) and forced convection (h_{fc}):

$$h_{tp} = h_{fc} F + h_{nb} S \tag{14}$$

The parameter F accounts for the increase in liquid velocity due to the expansion of liquid to vapor. h_{fc} in Equation 14 is obtained from either Eqs. (10) or (11). The two phase Reynolds number for the liquid phase is

$$Re_{tp} = Re\,(1-\dot{x})\,F^{1.25} \tag{15}$$

where $\dot{x}$ is the vapor mass quality

$$\dot{x} = \dot{m}_{vap}/(\dot{m}_{vap} + \dot{m}_{liq}) \tag{16}$$

S accounts for the lower effective superheat in the region of bubble formation, which suppresses nucleate boiling.

F and S are given by:

$$F = 1 \text{ for } 1/X_{tt} \leq 0.1 \tag{17}$$

$$F = 2.35\,(1/X_{tt} + 0.213)^{0.736} \text{ for } 1/X_{tt} > 0.1 \tag{18}$$

$$S = 1/(1 + 2.53\text{x}10^{-6}\,Re_{tp}^{1.17}) \tag{19}$$

X_{tt} is the Martinelli parameter, a dimensionless number used in internal two-phase flow calculations. It expresses the liquid fraction of a flowing fluid as $X_{tt} = (\dot{m}_l/\dot{m}_g)(\rho_g/\rho_l)^{0.5}$. Its main application is in two-phase pressure drop and boiling/condensing heat transfer calculations. It is calculated as

$$X_{tt} = ((1-\dot{X})/\dot{X})^{0.9}\,(\rho_v/\rho_l)^{0.5}\,(\mu_l/\mu_v)^{0.1} \tag{20}$$

Determination of Flow Quality

Flow quality ($\dot{X}$) is the ratio of vapor mass flow rate to the total mass flow rate. For the subcooled fluid,

$$\dot{X} = \mathrm{Ph} - \mathrm{Ph}_n \exp\{(\mathrm{Ph}/\mathrm{Ph}_n)-1\} \tag{21}$$

where Ph, the phase change number, at the transition from region B to C is shown in Figure 5.

$$\mathrm{Ph} = (h_{tp} - h_1^*)/\Delta h_v \tag{22}$$

$$\mathrm{Ph}_n = -\mathrm{Bo}/\{(4.55/\mathrm{Pe})^2 + 0.00652\}^{0.5} \tag{23}$$

where Pe = Péclet (Re Sc) and Sc is the Schmidt number ($\mu/\rho D$).

$$\mathrm{Bo} = \dot{q}/\dot{m}\,\Delta h_v \tag{24}$$

The phase number and Boiling number (Bo) are related by

$$\mathrm{Ph} = -4\mathrm{Bo}\,\{\Delta L/D)\,(R/(1+R) \tag{25}$$

R is the radius ratio (D_i/D_o) and ΔL is a characteristic length.

Figure 5 shows the different regions encountered over a length of tube with uniform heat flux to a subcooled liquid. In region A, the surface temperature is highest but then is cooled by the onset and continuation of subcooled boiling.

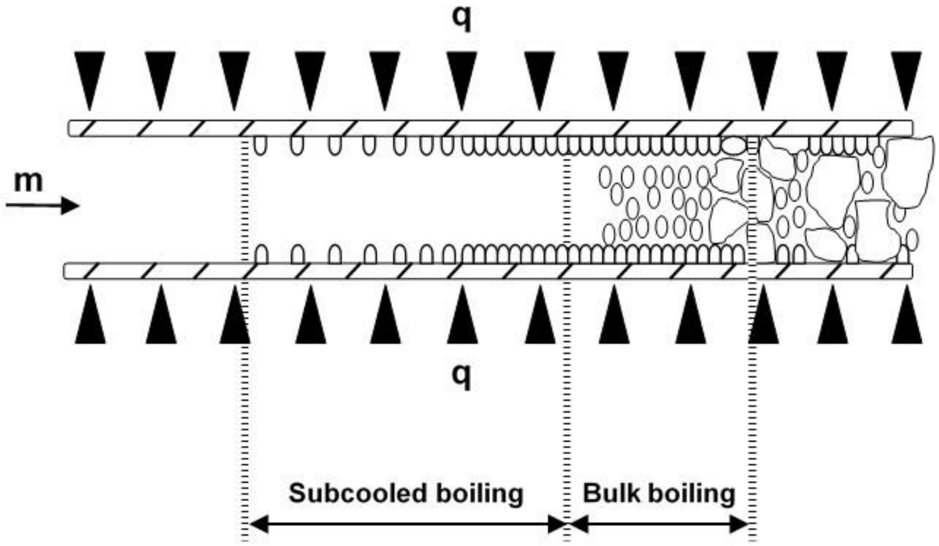

Figure 5. Transition region from single phase convective heat transfer to bulk boiling in flow in a tube [7].

Nucleate Boiling Heat Transfer

For saturated nucleate boiling:

$$h_{nb}/h_o = (\dot{q}_{nb}/\dot{q}_o)^{Np}\, F_p \tag{26}$$

$$N_p = 0.9 - 0.3(P/P_c)^{0.15} \tag{27}$$

$$F_p = 2.55(P/Pc)^{0.27} + [9.0 + \{1/(1-(P/Pc)^2)\}][P/Pc]^2 \tag{28}$$

The reference heat transfer coefficient (h_o) is calculated from Eq. (18):

$$Nu = 0.0871(\dot{q}\, d_B/\lambda_1\, T_{sat})^{0.674}\, (\rho_v/\rho_l)^{0.156}\, (\Delta h_v\, d_B{}^2/a_e{}^2)^{0.371}\, (a_l{}^2\, \rho_l/\sigma\, d_B)^{0.350}\, Pr_l{}^{-0.162} \tag{29}$$

$$a_l = \lambda_l/\rho_l C_{p,l} \quad (30)$$

The range of the reference heat transfer coefficient is from 3400 to 4400 W/m^{2}K [7].

The Nusselt number in Eq. (29) is

$$Nu = h_o d_B/\lambda_l \quad (31)$$

The bubble diameter (d_B) is estimated from

$$d_B = 0.0146\, \beta\, [2\sigma/g(\rho_l - \rho_v)]^{0.5} \quad (32)$$

Eq. (14) suggests that

$$\dot{q} = \dot{q}_{fc} + \dot{q}_b \quad (33)$$

For Eq. (33) to be valid, the nucleate boiling heat transfer coefficient (h_{nb}) must be redefined as

$$h_{nb} = \dot{q}_b/(T_s - T_{sat}) \quad (34)$$

Eq. (33) must hold for subcooled boiling, so

$$h_{sb} = h_{nb}\, \{(T_s - T_{sat})/(T_s - T_b)\} \quad (35)$$

Falling Film Heat Transfer, Black Liquor on Outside of Tubes

Many researchers have proposed correlations for heat transfer coefficients in falling film evaporators by evaporating solution on the outside of the tubes. Many were developed for turbulent flow, but most were developed for Prandtl numbers less than 20. The Prandtl number for black liquor, which has a higher viscosity than simpler liquids, exceeds 50 as it is concentrated and can be as high as 500**Error! Bookmark not defined.**.

The conventional form of correlations for falling film heat transfer correlations is

$$\mathrm{Nu} = K\,\mathrm{Re}^{a}\,\mathrm{Pr}^{b} \tag{36}$$

where :

Nu is defined as $(h/k)\,(\nu^2/g)^{1/3}$
Re is defined as $4\Gamma/\mu$
Pr is defined as $c_p\,\mu/k$

Johansson presented a straightforward correlation for heat transfer coefficients in black liquor falling film evaporators with the liquor on the outside of heat transfer tubes. The correlation is in the form of Eq. (36). The constants K, a, and b for black liquor were determined from extensive experimental data obtained using a research evaporator described by Johansson [5] and others [8, 9]. Their values based on the black liquor used and other operating parameters (q range, ΔT range, etc.) are $K = 201$, $a = 0.26 \pm 0.12$, and $b = -0.41 \pm 0.05$. With these constants, the correlation becomes

$$\mathrm{Nu} = 201\,\mathrm{Re}^{0.26}\,\mathrm{Pr}^{-0.41} \tag{37}$$

The correlations presented here are for turbulent flow of the black liquor film down the outside surface of the tubes. The Reynolds number at the transition from wavy-laminar flow to turbulent flow is

$$Re_{trans} = 5800\,Pr^{-1.06} \tag{38}$$

The range of conditions for data on which the correlation is based are

- Black liquor temperature in the pilot evaporator: 50-60°C and 110-120°F
- Black liquor dry solids content: 35-51 wt%
- Black liquor rheology: all of the pilot evaporator data was taken at conditions where black liquor behaves as a Newtonian fluid

Wetting of Heat Transfer Surfaces by Falling Black Liquor Films [10]

Falling film evaporators are used extensively in the food industry for their ability to process heat sensitive liquids. A coherent liquid film is required to maintain heat transfer efficiency and minimize fouling. It is likely that most evaporator fouling occurs after film breakdown as the substance within the evaporator dries out. The minimum flow rate required to maintain a film is known as the minimum wetting rate, which is defined as the minimum mass flow rate per unit circumference. In the work by Morison and coworkers [10], minimum wetting rates were determined in a 1 m long, 48 mm internal diameter, vertical stainless steel tube. Water and aqueous solutions of glycerol, alcohol, and calcium chloride were used. These substances were chosen so as to give a wide range of properties such as viscosity (0.5-39 mPa s; 0.5-39 cP), density (950-1410 kg/m^3; 59-88 lb/ft^3), surface tension (35-90 mN/m; 35-90 dyne/cm), and contact angle (64-98°). In a separate set of experiments, the minimum flow rate required to distribute liquid and completely wet the top of industrial evaporator tubes was measured using a range of sucrose solutions.

The tube wetting results obtained fitted a dimensionless power law relationship well. Surface tension and contact angle had a strong influence on the wetting rate, but viscosity and density were found to have very little effect. The minimum flow rates for distribution were found to nearly always exceed the minimum wetting flow rate to maintain rates, showing that more attention needs to be given to distributor design.

The flow rate to initiate or maintain a continuous film wetting the heat transfer surface is [11, 12]

$$\Gamma_{min} = C_w\,(\mu_l\, s_l\, \sigma^3)^{0.2} \tag{39}$$

C_w = 19.5 for initial surface wetting while C_w = 2.4 to maintain a wet surface.

In Eq. (39), Γ_{min} = [lb/hr-ft], μ_l = [cP], σ = [dyne/cm], and s = specific gravity.

Nucleation Film Destruction

Nucleate boiling that generates vapor bubbles can occur at the surface if the wall ΔT is too high. These bubbles disrupt falling liquid films on heat transfer surfaces. As a rule, the wall ΔT should not exceed 25°C (45°F) to avoid film disruption. Falling film evaporators for black liquor are designed with much lower wall ΔTs, about 5°C (9°F), so that nucleation does not break down black liquor films in falling film evaporators.

3.6.1 References

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3.7 EVAPORATOR AND CONCENTRATOR DESIGN CONSIDERATIONS FOR TROUBLESHOOTING

David T. Clay

The main performance targets for evaporator performance when evaluated at the pulp mill level are to:

- Meet or exceed the evaporation rate commensurate with the mill's pulp production rate.
- Produce a high dry solids content black liquor to maximize high pressure steam generation for power generation.
- Minimize the environmental impact of evaporation and associated operations including tall oil soap recovery.

Operationally these targets are met through design of the evaporator set, design of the evaporator operating and control strategies, and scheduling and maintenance for maximum on-line availability.

Higher product dry solids content increases the recovery boiler steam generation per mass of black liquor solids fired. Dry solids content is therefore a key operating parameter. Temperatures of warm water from surface condensers and clean process condensates from evaporator and concentrator sets are two other key operating parameters. Warm water temperature targets that are sustained year-round enable minimum low pressure steam use for water heating, e.g., in the pulp mill, bleach plant, recausticizing area, and paper machines.

Evaporator and concentrator designs are based principally on a specific water removal rate. The dry product solids content and the water temperature from the surface condenser are also specified for the design of black liquor evaporators and concentrators. The number of effects, number of bodies, and their configuration are determined by economic optimization of capital and operating costs within constraints imposed by the pulp mill operations. Maximum use is made of clean process condensate, either directly as warm/hot water or indirectly by recovering its useable energy. Best practice designs enable the owner's staff to sustain these design configurations and operating targets over the life of the set. The intent of this section is to present a design approach that enables rapid identification of conditions that cause the above three key energy parameters of the evaporator/concentrator set and its steam use to deviate from their targets. See section 2.3 for more detailed information on evaporator design.

3.7.1 Design of Evaporation Systems

Evaporator and concentrator suppliers design and build sets based on specifications developed by owners or their engineering representative. The specifications define expected conditions that the set must meet. Traditionally, once the set has met these specifications as confirmed by performance tests, the supplier's obligations are met. The owner on the other hand is now charged with sustaining the specified performance. It is therefore in the owner's long term interest to ensure that sufficient control and monitoring tools are included in the original design to sustain performance. A recommended evaporator test procedure including process parameters to measure is available for use by owners and suppliers [2].

Control tools are included in evaporator design to sustain short-term performance. Product liquor dry solids content can be controlled by varying the steam supply to the set. There are several different control strategies for dry product solids content that are successful. However, many mills continue to use steam pressure as the control parameter and manually adjust the set point to meet the product solids content target. Warm water temperature from the surface condenser can be controlled by varying the cooling water flow rate. This in turn gives stable vacuum control, which is essential for good evaporation system operation. Both percent dry product solids content and warm water temperature can be measured directly, controlled, and evaluated against their respective targets.

Table 1. Basic Operation Instrumentation

Evaporator parameter	Control & Monitor	Monitor & Alarm
Weak black liquor feed flow rate	Yes	
Percent WBL feed solids content		Yes
Product solids flow rate		Yes
Percent product solids content via BPR	Yes	
Final concentrator effect vapor pressure	Yes	
Product liquor final flash tank pressure	Yes	
Steam pressure and flow rate capability	Yes	
Steam temperature after desuperheater	Yes	
Vacuum in surface condenser		Yes
Surface condenser water temperature in & out	Yes	
Clean steam condensate conductivity		Yes
Combined process condensate(s) flow rate		Yes
Combined process condensate(s) conductivity		Yes
Foul condensate flow rate		Yes
Foul condensate conductivity		Yes
Levels in some vessels, tanks, or stand-pipes	Yes	Yes
Amps used by some pump motors		Yes

Clean process condensate quality and temperature can be measured directly. Target values are included in the set design. They cannot be controlled directly because they depend upon numerous other upstream operating conditions. The overall steam economy of an evaporation system is also not controlled directly. These operating conditions include both parameter changes such as feed liquor flow rate and temperature, as well as operating practices, e.g., selection of the flash tank vapor sink and bypassing of liquor heaters.

Significant differences related to instrumentation can be included in original evaporation system designs. Table 1 shows current minimum instrumentation for evaporator and concentrator systems operation recommended by the author.

These instrumentation and control functions enable the evaporation system to meet typical owner specifications related to black liquor processing. However, these functions are not sufficient to determine the cause of problems if one of the specifications is not met. Practices and instrumentation recommended for troubleshooting to identify the cause of problems are discussed in the next sections.

Upon commissioning of a new or upgraded evaporator and concentrator system, the mass and energy balances for the design case(s) and the performance test(s) are delivered to the owner. The latter become the commercially-clean desired condition(s) that defines best performance.

Evaporator and concentrator designs are based on either measured or assumed physical and chemical characteristics of the black liquor to be processed. Chapter 3 contains a complete list of the black liquor properties of interest and ranges of values for each. The specific properties measured depend on the supplier and the owner's specifications. In either case the physical and chemical characteristics that are included in the design basis are to be understood by both the supplier and the owner.

3.7.2 Troubleshooting Evaporation Systems

Evaporator/concentrator systems consist of a series of bodies interconnected through numerous vapor ducts and pipes. Overall performance of the set can be assessed by measuring the product dry solids content, warm water outlet temperature, and condensate conductivity and temperature. However, determining why one or more of these parameters is not meeting target specifications requires that performance of individual bodies be determined. Since there can be from five to eleven bodies configured as five to eight effects in a set, the first step is to identify where the problem is located. Design of the set needs to include tools that will rapidly identify which body(s) is not performing as designed.

The fundamental starting point for troubleshooting is to define both the current set of operating conditions and a desired set of operating conditions. The latter can either be an acceptable set of operating conditions, conditions during the system acceptance tests, or the design specifications. The first troubleshooting objective is to identify what has changed between these two sets of conditions. Definition of the current and prior conditions ideally would include not only available operating data, but also mass and energy balances. In cases where the design and/or desirable condition balances are not available, an evaporator supplier or another capable firm can be used to estimate the original design balances.

Since black liquor is a complex solution of water, inorganic salts, organic salts, and free organics along with suspended solids, other pulp mill processes will influence its chemical composition. This means that changes in other areas of the mill may contribute to an evaporator and concentrator problem. A comparison of physical and chemical characteristics of the liquor at current and prior conditions may be needed, especially if heat transfer surface fouling is a potential cause of the problem. One example is a significant decrease in causticizing conversion which can lead to increased evaporator and concentratior fouling.

Potential changes in operating procedures or personnel also need to be considered. Potential issues in these areas need to be recognized and the design executed to minimize their likelihood. Differences in boil out procedures and nonuniformity in operation between shifts are examples where personnel and procedures can contribute to operational problems.

3.7.3 Design Principles for Troubleshooting Evaporation Systems

When evaporator and concentrator issues occur there are typically limited knowledgeable resources at the mill, especially at mills that traditionally have not had problems in these areas. Mill operations and technical staffs have been reduced significantly over the last twenty-five years. Best practice evaporator/concentrator design will include tools for monitoring and troubleshooting that are useful to both operations and technical personnel. Instrumentation in addition to those needed for operation is required. Table 2 below lists these instruments and the subsequent discussion will highlight their use in troubleshooting operating problems. Data from the recommended additional instruments for troubleshooting are applied in one or more design principles that are noted in Table 2.

Table 2. Troubleshooting Instrumentation: Additions to Basic Operation Instrumentation

	Applied in Principle No.
Temperature Monitoring:	
Weak black liquor feed	3&4
Liquor from each bodies	1&3
Liquor to & from internal & external heaters	2&3
Liquor to / from soap skimmer	3&4
Liquor from intermediate flash tanks	3&4
Product liquor from final flash tank	3&4
Combined condensate(s)	4
Foul condensate	4
Steam temperature at flowmeter	3
Steam condensate from final flash tank	3&4
NCG from surface condenser & pre-cooler	4
Pressure Monitoring:	
Over liquor in each body or exiting vapor duct	1 &3
Over product liquor in final flash tank	3&4
Vapor pressure in final steam flash tank	3&4
Vacuum in surface condenser(s)	2&3
Pressure / vacuum in hotwell or outlet of after-condenser	3&4
Percent Solids Monitoring with Meter:	
Product liquor from final flash	3&4
Feed weak black liquor	3&4
Flow Monitoring	
Liquor flow from soap skimmer	4
Water flow(s) to surface condenser	4

Principle 1

Evaporator and concentrator systems designed for troubleshooting incorporate measurements and calculations that display, trend, and archive Δ T and BPR values for each body.

The classic individual body performance parameter is the temperature difference (Δ T) between the saturated vapor temperature on one side of the heating surface and the outlet liquor temperature on the other side. The saturated vapor temperature is calculated from the corresponding measured vapor pressure. Table 3 shows some values of corresponding pairs of steam pressures and saturated steam temperatures.

Table 3. Steam Pressures and Saturated Temperatures

P, bar	T, ^{o}C	P, psig	T, ^{o}F
1.5	111.4	7.1	232.5
2.0	120.2	14.3	248.4
3.0	133.5	28.8	272.4
5.0	151.9	57.8	305.3
7.5	167.8	94.1	334.0
10.0	179.9	130.3	355.8

$$\Delta T_n = T_{n-1,vapor, sat} - T_{n, bl, out} \qquad (1)$$

where: $\Delta T_n = \Delta T$ in body n.

n is a body and n-1 is the higher temperature body supplying vapor to body n.

Note: If the body contains a forced circulation heater, see Principle 2.

A high ΔT compared to a design or desired condition implies poor heat transfer in a body. This may be the result of heat transfer fouling or several other conditions. High ΔT screening of individual bodies is the first-level approach to identify the body or bodies that have the problem.

The boiling point rise (BPR) of liquor within a body can also be calculated from the difference between the liquor temperature in the body and the saturated vapor temperature over the liquor in the same body.

$$\mathrm{BPR}_n = T_{n,bl} - T_{n,vapor,\, sat} \tag{2}$$

where:

BPR_n = boiling point rise of black liquor in body n.

Boiling point rise is mainly a function of dry solids content. It can be used to estimate dry solids content deviations for a specific body. A lower BPR compared to a desired condition, when adjacent bodies are not lower, indicates a possible condensate leak into the black liquor. Since the BPR is relatively low at low dry solids content, it is difficult to use this as a definitive indication of condensate leaks in bodies where the dry solids contents are below 30%.

Both the ΔT and the BPR calculations require saturated vapor temperatures. Accurate pressure measurements in either the vapor space over the liquor or in the exiting vapor duct, coupled with calculations to determine the saturated vapor temperature, are required. Steam tables are sufficiently accurate for black liquor applications. Direct measurement of vapor temperature over the liquor has potential for high temperature errors of superheat and contact with carryover liquor. These errors can be reduced by locating the temperature sensor at the condensation destination for the vapor, e.g., heat-supply side of the subsequent effect. Any ΔT due to pressure drop through the vapor ducts needs to be accounted for to determine the actual vapor temperature in the upstream effect.

Principle 2

Evaporator and concentrator systems designed for troubleshooting incorporate measurements and calculations that display curent values and trends, and they archive the ΔT_{LM} and approach temperatures for each internal heater, external heater, and surface condenser.

The applicable ΔT in these heat exchangers is the log-mean ΔT, or ΔT_{LM}. These heat exchangers involve a condensing vapor heating a liquid stream, either liquor or water on the other side of the heat transfer surface. It is calculated by:

$$\Delta T_{LM} = (A - B) / \ln(A/B) \quad (3)$$

where:

$A = T_{vapor, sat} - T_{liquid, in}$
$B = T_{vapor, sat} - T_{liquid, out}$
T_v = saturated temperature of condensing inlet vapor
T_l = temperature of liquid
ln = natural logarithm

This is also the appropriate equation to use for forced circulation concentrator bodies that have fully flooded heat exchangers with recirculating black liquor. Use of ΔT_{LM} corresponds to the use of ΔT in Principle 1. The inlet approach temperature for these heat exchangers is important since internal vapors and liquids are the heating sources and sinks, respectively. Their temperatures vary with process and heat transfer surface conditions. The inlet approach ΔT is calculated by:

$$\text{inlet approach } \Delta T = T_v - T_{l,in} \quad (4)$$

Inlet approach ΔT is a useful tool to identify if a low outlet liquid temperature is due to a low inlet vapor temperature and not the result of heat transfer surface fouling. Tracking the inlet approach ΔT for a surface condenser will also give an early alert to fouling, if the value increases continuously.

Principle 3

Evaporator and concentrator systems designed for troubleshooting incorporate measurements of the key energy-related parameters necessary for completing performance mass and energy balances.

Mass and energy balances provide predictions of liquor and vapor flow rates, energy flow rates, and dry black liquor solids content to and from bodies. Heat transfer coefficients, which are measures of heat transfer performance, are also calculated for each body. These reflect more accurately the heat transfer performance condition of a body, since they are less dependent on the evaporation rate, steam flow rate, and liquor flow rate than on the Δ T. The overall heat transfer coefficient (U_i) for body i is calculated by:

$$U_i = \dot{q}_i / (A_i \Delta T_i) \qquad (5)$$

where:

$\dot{q}_i$ = rate of heat transferred in body i

A_i = heat transfer surface area for body i

ΔT_i = either Δ T or ΔT_{LM} for body i as noted in Principles 1 & 2

The energy transferred between bodies is a result of the mass and energy balance, which enables the heat transfer coefficients (U_i's) to be determined for each body. Balances are not necessary to calculate an estimate of the heat transfer coefficients (U_i's) for bodies or heaters supplied with steam for which flow and pressure are measured. These calculations are readily done in the owner's DCS system:

$$\dot{q}_{s,i} = \dot{m}_{s,i} h_{vs,I} \qquad (6)$$

where:

$\dot{q}_{s,i}$ = rate of heat transferred from steam or vapor in body i

$\dot{m}_{s,i}$ = mass flow rate of steam or vapor into body i

$h_{vs,i}$ = heat of vaporization of steam in body i

The overall steam economy of the set is calculated from the evaporator set mass and energy balances using Eq. (7). It can also be determined by calculations readily done in the owner's DCS systems. Use the steam flow rate and calculate the evaporation rate using the weak liquor inlet flow rate and dry solids content in the feed and product liquor streams:

$$SE = \dot{V}_{wbl}\ x_{wbl}\ (1/x_{wbl} - 1/x_{hbl}) / \dot{m}_s \qquad (7)$$

where: SE = steam economy

$\dot{V}_{wbi}$ = volumetric flow rate of weak black liquor

ρ_{wbl} = density of weak black liquor

x_{wbl} = fraction of solids in weak black liquor feed

x_{hbl} = fraction of solids in heavy black liquor product

Cross-checks can also be done if the product flow rate is measured and/or if all condensate flow rates are measured.

A valuable function of a mass and energy balance is that the consistency of data for a given test can be checked. This is typically done overall by either comparing the calculated steam flow rate versus the measured flow rate or the calculated weak black liquor flow rate versus the measured flow rate. The author judges an acceptable performance balance as one that predicts the measured value within 5%. This also assumes that the owner's instrumentation values used are sufficiently accurate. U and SE estimates using direct measurements can be cross-checked against mass and energy balance values to determine the accuracy of these rapid estimation methods.

Principle 4

Evaporator and concentrator systems designed for troubleshooting incorporate measurement, display values and trends, and give access to archival feed and product parameters. These can be used to ensure stream characteristics do not exceed their expected ranges.

Characteristics of inlet streams to evaporator and concentrator bodies, be they external or internal to the evaporator set, have the potential to upset the system if their characteristics are outside of acceptable ranges. For all parameters listed in Table 2, these can be measured directly. Examples showing the value of some of these parameters are:

- High weak black liquor temperature that resulted in high condensate conductivity and condensate sewering.
- Erratic flow from a soap skimmer resulting in high dry product solids content and fouling of the product body.
- Partially flooded NCG line following an after-condenser that resulted in less vacuum at its discharge and lower throughput for an evaporator set.

Principle 5

Evaporator and concentrator systems designed for troubleshooting incorporate sampling stations and/or ports for black liquor and condensate sampling from each body.

Table 3. Sampling Station and Port Locations

	Basic Operation	Troubleshooting
Sampling stations for feed and product liquor	Yes	
Sampling ports for liquor from each body		Yes
Sampling ports for condensates from each body		Yes
Level glasses or gauges for condensate in each body	Yes	
Ports for pressure / vacuum measurement in each vessel	Yes	
Ports for vacuum ahead of each ejector or vacuum pump	Yes	

Ports for pressure drop across demisters		Yes
Ports for pressure drop across recirculating liquor orifices		Yes
Ports for discharge pressure from pumps	Yes	
Ports for dP across surface condenser water-side		Yes
Ports for dP across vacuum system condenser(s) water-side		Yes

Manual sampling and testing of process streams is essential for a well operating evaporator and concentrator system. In some cases sampling and testing is used to obtain actual reported parameter values while in others it is used for cross-checks on instrumentation values. In either case safe and effective sampling stations are incorporated into the design. Additionally, sample ports are placed at locations where samples may be needed for consistent operation or to troubleshoot future problems. Table 3 shows a list of suggested sampling stations and ports.

Examples showing the value of some of these sampling stations and ports are:

- Liquor sampling between bodies to screen for low U's and tube leaks that cause low evaporation capacity. This is important for facilities not having mass and energy balance capability.
- Prevention of high condensate level in a body that results in poor heat transfer performance. This averts lower evaporation rate and therefore limited black liquor throughput.
- Prevention of low water-side pressure drop in a surface condenser due to a baffle door inadvertently being left open. This averts poor heat transfer and lower vacuum that contributes to lower evaporation rate and therefore limited black liquor throughput.

Practical Considerations

The extent to which owners specify and/or suppliers require additional instrumentation for troubleshooting depends on many factors. These include capital and human resources, instrumentation philosophy, and maintenance philosophy. In the event that minimal or no instrumentation for troubleshooting is chosen, owners typically rely on outside experts to troubleshoot and resolve evaporator and concentrator problems.

In some cases additional instruments for troubleshooting are included in the design, but owner human resources are not available to use them effectively. However, these instruments will aid outside experts in identifying and resolving the problem. A potential problem with this approach is that instrument maintenance and calibration may be insufficient due to infrequent use. Consequently, reliable and accurate information may not be readily available when needed.

Several owners, suppliers, or outside experts have the capability to remotely access evaporator and concentrator data information systems. Remote access capability allows those experienced in evaporator and concentrator technology to regularly monitor and/or rapidly assist facilities where technical and operations staff have limited experience and/or resources in this area. Additionally, it is used to spot potential instrumentation or operational issues, which, when corrected minimize the likelihood of performance degradation.

3.7.4 Industry Examples

The following industry examples are intended to illustrate use of the instrumentation suggested for inclusion in the design of evaporator and concentrator systems for troubleshooting purposes.

Example 1 Surface Condenser Fouling

Problem

The weak black liquor flow rate through a six-effect multiple-effect evaporator had dropped below the minimum acceptable rate for the set.

Observations

Operators noticed that a significant decrease in surface condenser vacuum had recently occurred. Outside testers found a low heat transfer coefficient for the surface condenser and a high NCG temperature from the surface condenser. Outlet water temperature remained essentially unchanged.

Key Measurements

NCG temperature from the surface condenser

Water temperatures in and out of the surface condenser

Measurements required for a performance mass and energy balance

Resolution

Cause Location. Water-side of tubes was fouled significantly.

Cause Clarification. Higher NCG outlet temperature implied fouling rather than an air leak.

Learning. Monitor NCG outlet temperature as an early warning of surface condenser fouling.

Example 2 Vacuum System Leak

Problem

A six-effect multiple-effect evaporator was periodically venting through a regulated PV-breaker.

Observations

Operations noticed periodic cycling of numerous evaporator process parameters including vacuum, outlet water temperature, body liquor temperatures, percent product solids, and steam flow.

Key Measurements

Surface condenser vacuum trends

Other parameters that were observed cycling with the vacuum

Resolution

Cause Location. Condensate line from main surface condenser to hotwell had a hole in it.

Cause Clarification. Corrosion through the down-leg allowed air to be periodically introduced when the condensate level was below the opening.

Learnings. Compare trends of multiple process parameters to identify patterns and dependencies.

Example 3 Lower Concentrator Product Solids

Problem

A single-effect concentrator integrated into a multiple-effect evaporator was only able to make dry product solids content at 5% solids below the desired target.

Observations

Operations had steam pressures of both the concentrator and the evaporator at maximum values.

Operations noted inlet weak liquor dry solids content was in an acceptable range.

Outside testers measured process parameters required for a performance mass and energy balance.

Key Measurements

Steam pressure

Those parameters required for a performance mass and energy balance

Calculation of heat transfer coefficients for each body

Resolution

Cause Location. Entire evaporator and concentrator system

Cause Clarification. Comparison of measured heat transfer coefficients with those from design showed the system as configured was operating at maximum conditions. That is, to achieve an increase in dry product solids content, the concentrators needed to operate at lower black liquor throughput or add additional heat transfer area to sustain target dry product solids content.

Learnings. Maximum liquor throughput and energy-related performance of a well maintained and instrumented evaporator and concentrator set can be determined. These can be used to justify improvements to achieve target throughput and performance.

Additional Examples

Troubleshooting approaches to problems in black liquor evaporators that are accompanied with examples and practical solutions are available in the literature [3, 4, 5, 6, 7, and 8].

3.7.5 Conclusions

Two instrument groups are defined for design of evaporator and concentrator systems. These are 1) those required for basic operation and 2) those used primarily to troubleshoot operating problems. The primary focus of the later group is to improve the effectiveness of troubleshooting operational problems. The main objective of troubleshooting instruments is to define individual body performance. Five design principles were defined for identifying instruments used for troubleshooting. The extent to which troubleshooting instruments are included in the design is based on owner specifications and suppler requirements. Industrial examples are used to illustrate the value of troubleshooting instruments to guide, confirm, and/or assist in resolving operational problems.

3.7.6 References

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4

4 AUXILIARY PROCESSES

4.1 TALL OIL SOAP RECOVERY

C. Douglas Foran

Tall oil soap is a mixture of saponified resin and fatty acids and neutral, unsaponifiable compounds generated by kraft pulping primarily of softwoods. The acids and neutral compounds are extracted during pulping and are saponified by NaOH in the kraft liquor. The soap produced is also referred to as "black liquor soap". Tall oil soap is completely soluble in black liquor at dry liquor solids contents less than 10 wt%. At higher dry solids contents, it separates, eventually becoming a low-density phase that floats on black liquor. Soap has economic value as the third most abundant byproduct from kraft pulp mills, but, if not managed properly, it can have a large negative impact on the evaporation capacity of black liquor evaporators.

This section deals with those aspects of tall oil soap that impact black liquor evaporators. For a broader understanding of tall oil and tall oil soap, its origins, its chemistry and physical characteristics, and its management and recovery in kraft pulp mills, please refer to the publication by Drew and Propst [1] and the more recent publications by Foran [2, 3, 4].

4.1.1 Soap Quantities and Characteristics

Tall oil is a natural product of pines and other softwoods. The amount and composition differs with wood species and geographic region. The values in Table 1 illustrate the tall oil content of different North American wood species.

Table 1. Typical Tall Oil Content of Different Wood Species [5, 6]

Wood Species	Location	Typical tall oil content, kg /ton OD Wood
Longleaf	Southeastern U.S.	43.5
Slash	Southeastern U.S.	41.5
Loblolly	Southeastern U.S.	35.5
Shortleaf	Southeastern U.S.	34.5
Spruce	Southeastern U.S.	31.0
Lodgepole	Interior British Columbia	23.8
Ponderosa	Interior British Columbia	15.5
White spruce	Interior British Columbia	6.2

The values in Table 2 show that tall oil yields from pulping differ widely for different geographic regions in the northern hemisphere. The higher yields are from regions where pine species are the main softwoods pulped. The lower values in the Pacific Northwest and Canada reflect the lower tall oil content of Douglas fir, a major pulpwood source in these regions.

Table 2. Typical Tall Oil Soap Recovery after Pulping of Softwoods by Region in the U.S., Canada, and Nordic Countries

Region	Tall Oil, kg /ton OD Wood
Southwestern U.S	31.5
Coastal, Southern U.S	26
Piedmont, Southern U.S	24
Canada	11.5

Pacific Northwestern U.S.	7.5
Finland	19.5
Sweden	25

Differences in tall oil quality for different regions are shown in Table 3. Tall oil from pines across the southern U.S. has higher acid and saponification numbers, higher resin acid content, and lower neutral (unsaponifiable) content.

Table 3. Composition of Crude Tall Oil by Region

	Southeastern U.S.	Northern U.S. and Canada	Nordic Countries
Acid number[a]	165	135	132
Saponification number[b]	172	166	142
Resin acids, %	40	30	23
Fatty acids, %	50	55	57
Unsaponifiables, %	8	15	20

[a] The number of milliequivalents of potassium hydroxide to neutralize one gram of tall oil.

[b] the number of milliequivalents of sulfuric acid required to neutralize one gram of tall oil that has been saponified with potassium hydroxide.

Tall oil consists of a mixture of fatty and rosin acids, fatty and rosin acid esters, and neutral components and includes hundreds of different compounds. Representative compounds are shown in Figure 1; more are included in Sjostrom (1993) [7]. The predominance of a given constituent varies with tree species, pulping chemistry, and genetic factors. The fatty acids are predominantly oleic and linoleic acids with small quantities of linolenic, stearic, and palmitic acids. The rosin acids are monocarboxylic diterpene acids having a general formula $C_{20}H_{30}O_2$. The predominant rosin acids are abietic and dehydroabietic acids, although numerous distinctive isomers occur. Both abietic and dehydroabietic acids contain three six-membered rings. Dehydroabietic acid contains one aromatic ring, and thus differs from abietic acid, which contains three unsaturated rings. The neutral fraction, often called unsaponifiables, is a mixture of a variety of substances including phytosterols, fatty and wax alcohols, terpenes, and hydrocarbons [8].

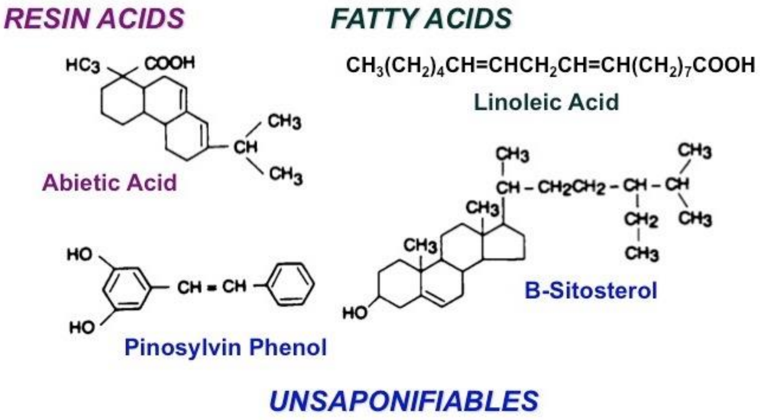

Figure 1. Examples of resin and fatty acids and unsaponifiable species found in tall oil.

Not all of the tall oil in wood is recovered from black liquor after pulping. The quantity of tall oil soap recovered by a given mill varies according to wood species, season of the year, and wood storage practices. The quantity of tall oil available from several southeastern U.S. wood species has been determined by solvent extraction (Table 2) [6]. This method tends to overstate the true soap availability but is valid for assessing the amount of soap in different wood species by the same method.

4.1.2 Solubility of Soap

The solubility of soap in black liquor depends on several factors including the fatty acid to resin acid ratio in the soap, the residual effective alkali of the black liquor, and temperature. In mixed liquors, the ratio of hardwood to softwood liquor solids also impacts soap solubility. The curves in Figure 2 show how the solubility of tall oil in black liquor changes with dry solids content at three different temperatures. It shows that the solubility is a minimum near 30 wt% dry black liquor solids content. Its solubility is substantially higher at lower dry solids content and increases with temperature in that region.

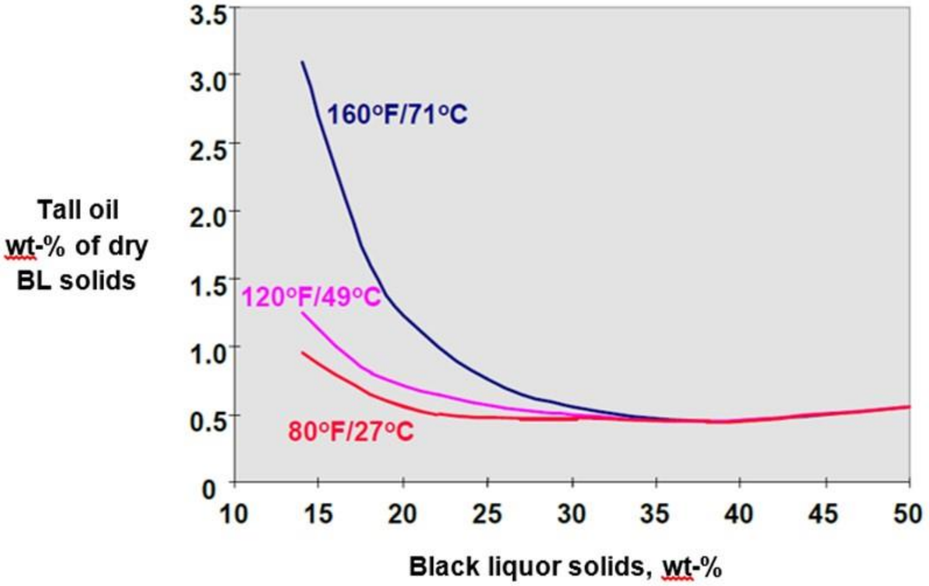

Figure 2. Solubility of tall oil in black liquor at different dry solids content and temperatures.

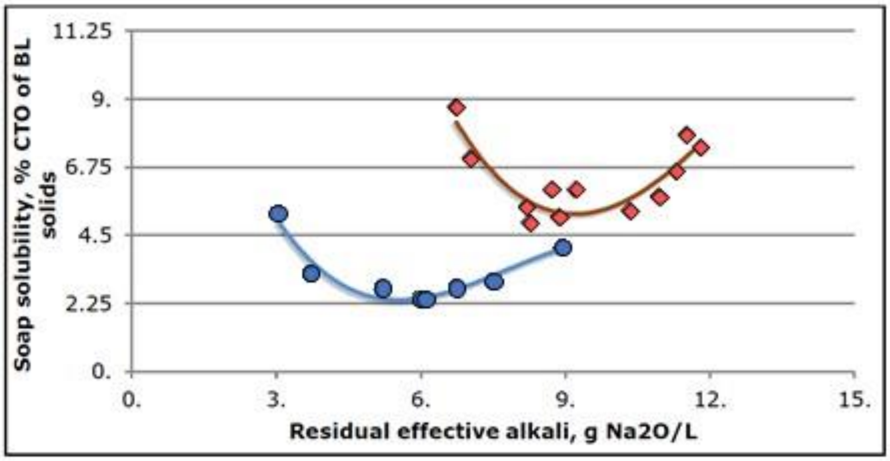

Figure 3. Impact of residual effective alkali on the solubility of CTO. Circles represent data for a fatty acid:resin acid ratio (FA:RA) of 5. Diamonds are for FA:RA <2.

Residual effective alkali (REA) content of the black liquor has a marked effect on the minimum solubility of soap in black liquor. For good recovery it should be kept above 6 g/l as Na_2O. The combined effect of lower effective alkali content and fatty acid:resin ratio on soap solubility is illustrated in Figure 3.

4.1.3 Physicochemical Characteristics of Soap

Soap is completely soluble in black liquor at dry solids contents below about 10%. At higher dry solids contents, the extractives in black liquor may be in several different states in black liquor, including true solution, micellar solution, liquid crystalline phases, and, eventually, neat soap. Most of these colloidal states occur simultaneously. The aggregative state of the soap depends on the concentration of the dispersed soap as well as on the salt content and dry solids content of the liquor.

As water is evaporated from weak black liquor, the chemical environment of the soap changes continuously. The salt concentration in the liquor increases, causing a natural salting out of any organic matter present. The fatty acid and rosin acid salts form micelles that solubilize the neutral fraction of the extractives.

The *critical micelle (micelleization) concentration (CMC)* is defined as the concentration of surfactants above which micelles form, and additional surfactants added to the system form micelles. Micelle formation from soap components in black liquor indicates the onset of phase separation. It depends on a number of factors. These include salt concentration, fatty to rosin acid ratio, and temperature. As the salt concentration increases, the CMC decreases; i.e., the soap is less soluble. The onset and separation path of the soap is dependent on many variables such as wood species, dissolved solids content of the liquor, temperature, and residual effective alkali concentration [1, 9, 10].

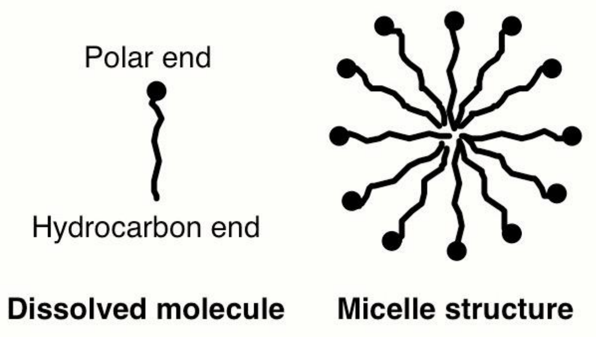

Figure 4. Representations of a single soap molecule (left) and soap molecules aggregated in a micelle structure (right).

Black liquor soap separates from black liquor at various points in the pulping process. It separates as a lamellar liquid crystalline phase [11]. This phase-separated material may be observed floating in pulp washer vats, at the surface of filtrate and weak black liquor tanks, and in large amounts at the foam tower and black liquor soap skimmer. The black liquor soap skimmings are collected from various locations and are pooled together in a central holding tank where they are held prior to acidulation.

4.1.4 Why Should the Tall Oil Soap Be Removed?

Tall oil soap should be recovered from black liquor to:

- Improve evaporator operation.
- Reduce effluent toxicity.
- Improve recovery boiler operation.
- Reduce caustic room load.
- Reduce accidents due to slips and falls.
- Be sold as a valuable byproduct of the alkaline pulping operation.

Soap in the liquor contributes significantly to liquor carryover in the evaporator effects. This is particularly true in the weak liquor effects in falling film evaporators. The liquor carryover is essentially that of a foam. Several observations about this foam are:

- The foam is generated shortly after liquor boiling begins to occur.
- The foam contains water vapor and some TRS.
- Foam liquor carryover will occur if the height of a column of foam is taller than the height of the vapor space in the evaporator.

Tall oil soap recovery is usually somewhat lower than what is available in the wood due to wood storage practices and differences in operating practices.

4.1.5 How Soap Hurts Black Liquor Evaporators

- Foaming
- Soap-fiber plugs
- Ca transport leading to $CaCO_3$ scales
- Soap inclusions in Na salt scales
- Other negative impacts of soap

The negative impact of soap on heat transfer performance and evaporation rate is shown in Figures 5 through 7. These data are from pilot studies of black liquor evaporation [12]. Similar results were reported by Grace (1975) [13].

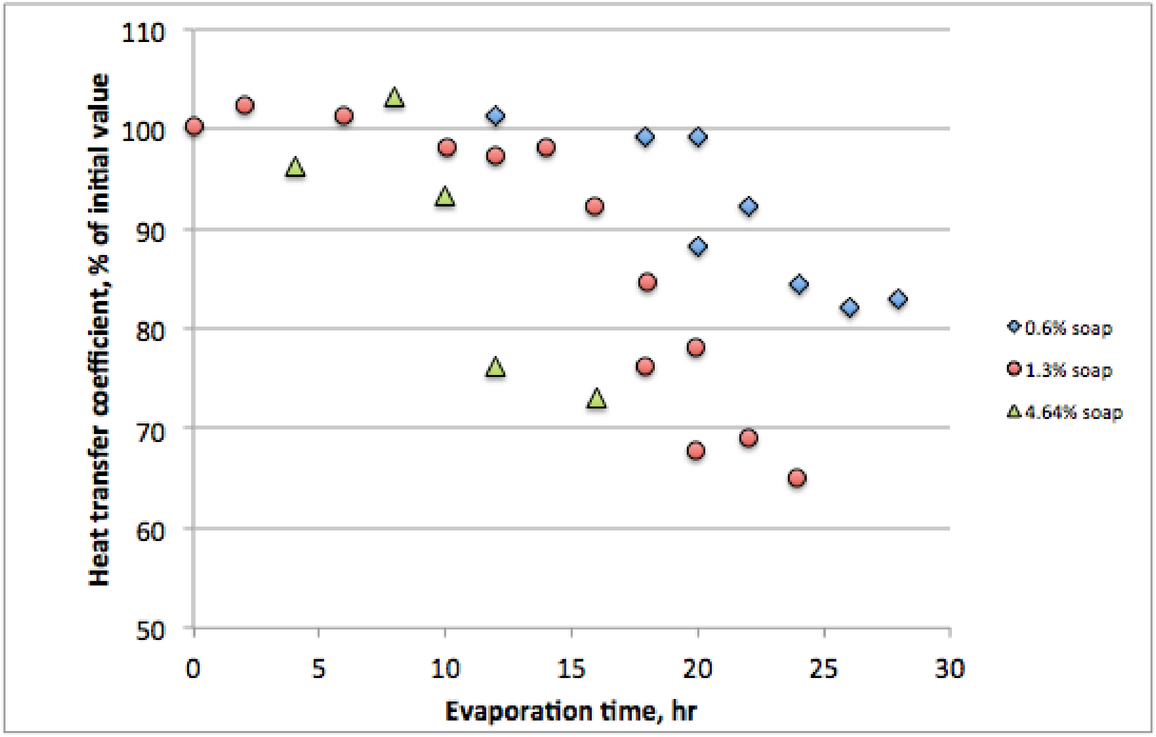

Figure 5. Impact of soap content in black liquor on evaporator heat transfer coefficient loss [12].

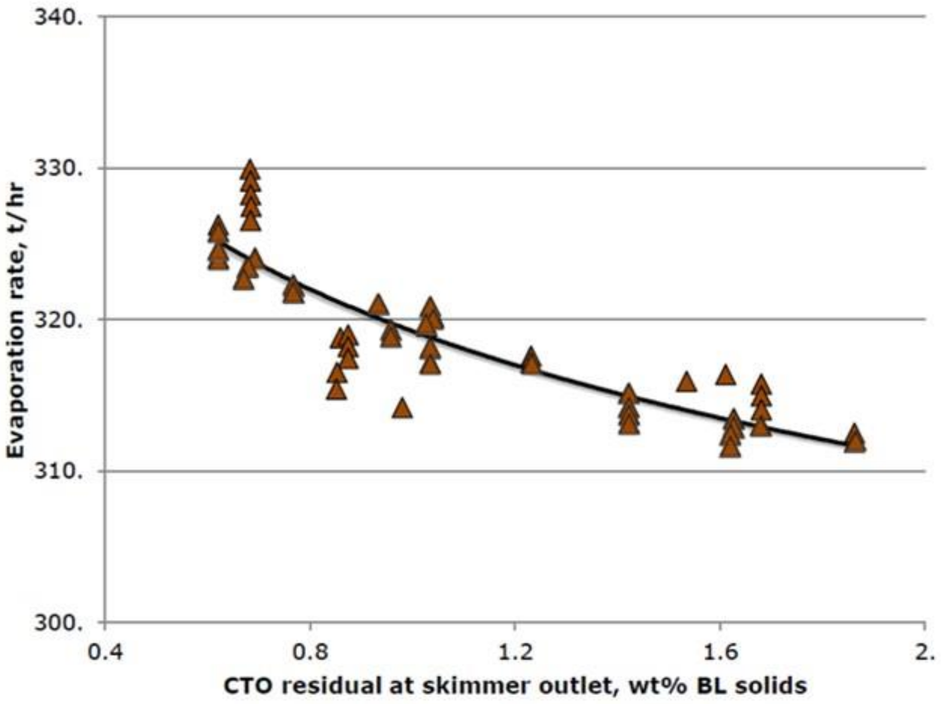

Figure 6. Evaporation rate versus CTO in black liquor; data from a full-scale LTV evaporator [12].

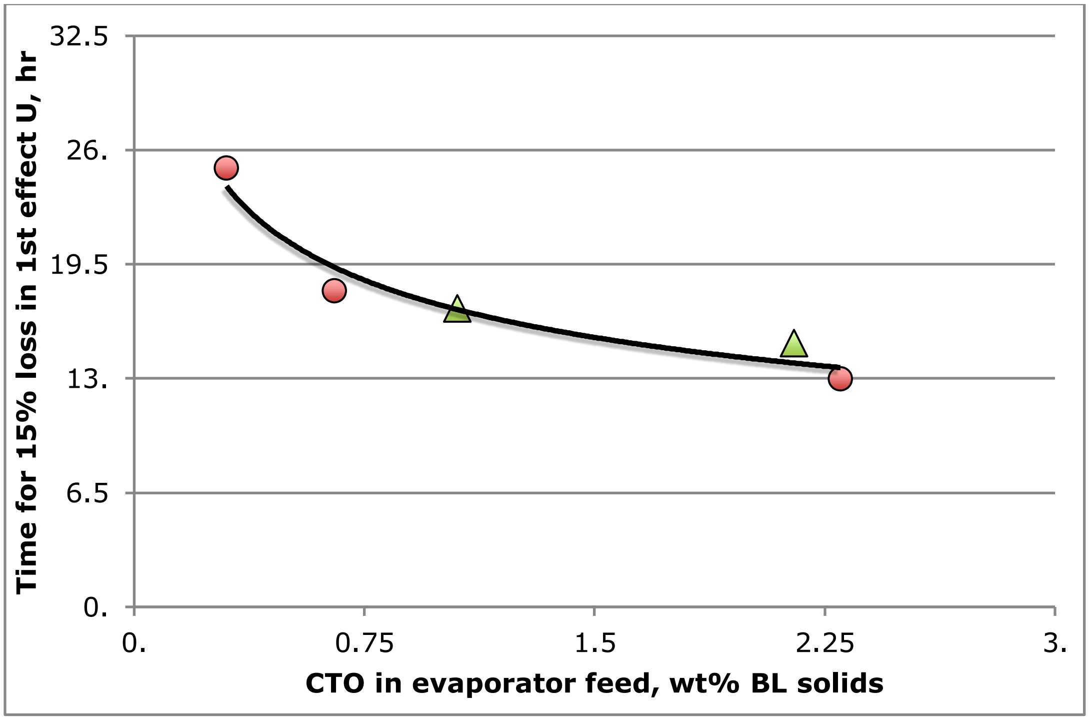

Figure 7. Time for a 15% decrease in first effect overall heat transfer coefficient (U) in hr versus CTO in black liquor feed to evaporators. Mill evaporator (Δ), pilot evaporator (O) [12].

4.1.6 How Much Tall Oil Soap Is Present and Recoverable?

The amount of CTO in wood chips depends upon the species of wood, where it was grown, when it was harvested, and the storage conditions to which it has been subjected. After pulping, more than 90% the crude tall oil (CTO) in the wood chips remains as tall oil soap in the cooked chips. Most of it is removed during brownstock washing but 10% to 15% remains with the brownstock after washing. Other soap losses also occur. 50% to 75% of the CTO originally in the wood chips is recovered as tall oil soap. Detailed tall oil soap recovery values are presented in Table 4.

Table 4. Tall Oil Recovery from Brown Stock [2]

	Bleached Canada, kg CTO/ADT	Bleached SE US, kg CTO/ADT	Linerboard SE US, kg CTO/ADT
CTO in wood chips	27	61	59
CTO lost on pulp	4	6	9
CTO lost to sewers	2	1	2
CTO lost with black liquor	9	8	5
Recoverable CTO	13 (48%)	46 (75%)	43 (73%)

4.1.7 Soap Recovery

Soap removal from weak liquor before evaporation is increasingly important. Typically 40% to 80% of the soap recovered evolves in the weak liquor system.

Soap solubility begins to decrease beyond about 10% dry BL solids content. It becomes increasing less soluble as water is removed by evaporation. The solubility of tall oil soap decreases to a minimum of 3 kg soap/t to 8 kg soap/t BL solids as the black liquor dry solids content is increased. The minimum solubility at 60°C is reached at 27% to30 % dry solids content. Soap separation is optimum at that dry solids content at a temperature near 60°C. After skimming, the concentration of soap in softwood black liquor varies from 30-50 kg/t black liquor solids [2].

As soap becomes insoluble, it separates from solution as a liquid crystal phase [11]. The liquid crystals coagulate into large clumps that float on black liquor. These clumps appear on the surface of black liquor in the weak black liquor storage tanks and soap skimmer, and to a less extent on black liquor in the heavy storage tanks. Soap removal begins in the washer filtrate tanks (Figure 8). An operating soap skimmer is shown in Figure 9.

Most of the soap is removed from the surface of the weak liquor storage tanks and the soap skimmer. Additional soap is removed from the heavy liquor storage tanks. These tanks are designed to have a uniform and low enough black liquor down-flow velocity to allow the lower density soap to rise against it and reach the tank surface. Soap is skimmed off from the liquor surface, collected, and sent to the acidulation plant for purification and acidification to tall oil. From the foam tank, the soapy, high solids black liquor should be pumped continuously to the weak liquor storage tank. It should never be recycled back to the washing system.

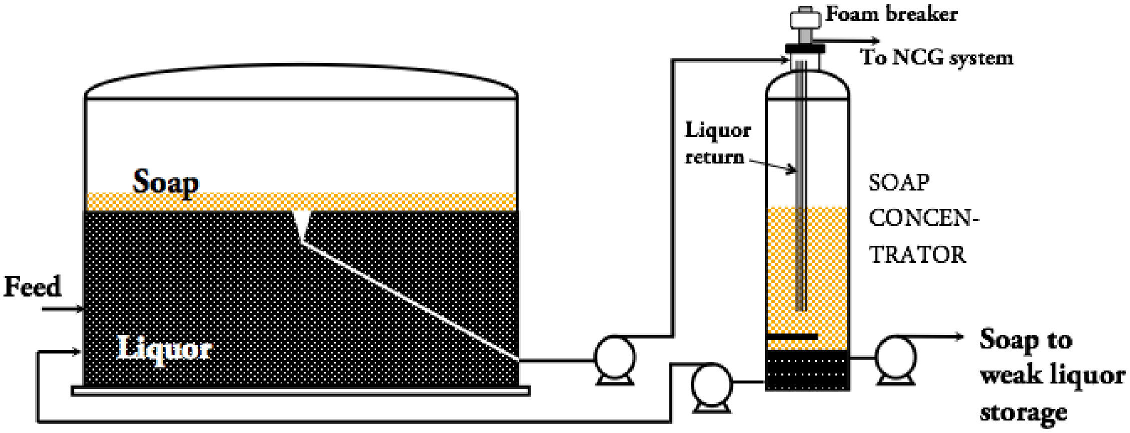

Figure 8. First stage liquor tank and foam tank arrangement.

Figure 9. Photo of a soap skimmer installation [14].

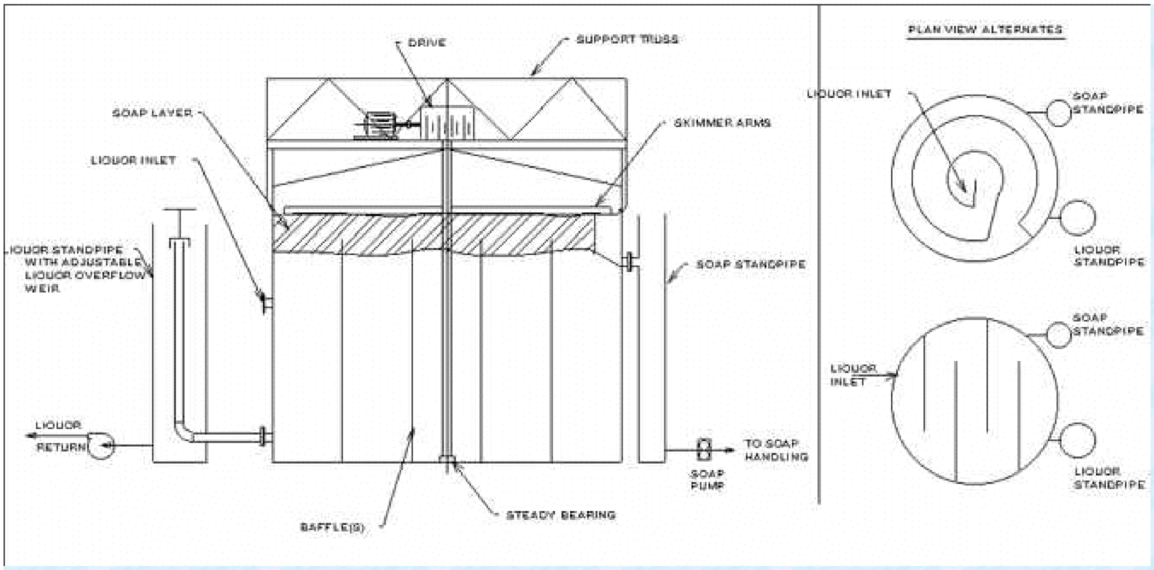

Figure 10. Diagram of a black liquor soap skimmer, showing two alternatives for baffling [14].

4.1.8 Foam Control [14]

The fatty and resin acids in tall oil soap are ionic surfactants. They create foam and are more stable as foams at lower pH when they are present in their free acid (unsaponified) form. As the concentration of black liquor is increased, all of the fatty and resin acids become neutralized (saponified) and no longer foam. These soap components are completely saponified at a dry black liquor solids content of 18% to 20%. At lower dry solids content, foaming can be a significant problem in weak black liquor tanks and in the lower dry solids content end of evaporator sets. Foam in black liquor evaporator bodies causes excessive entrainment of black liquor and contamination of vapor and evaporator condensate [15].

Serious foam problems can occur in several locations. These include the first filtrate tank, from weak liquor in storage, and evaporators. In addition, liquor entrained in soap can be carried over into the vapor head, contaminating vapor to the next effect and condensate from that effect.

Foam in First Filtrate Tank

When pressure builds up in the first filtrate tank due to foam accumulation, the pressure can be relieved through a foam breaker. The foam breaker is installed on the side of the filtrate tank at a level 30 to 60 cm above the liquor level. The internals of the filtrate tank frequently require modification so that the incoming liquor and air from the washer are discharged in a seal pot that facilitates separation of the air from the liquor. The liquor to be used in pulp dilution is withdrawn from the bottom of the tank. The excess liquid destined to the evaporators is overflowed into a funnel and discharge pipe that establishes liquor level in the tank. The foam layer is established on the top of the liquor and above the discharge funnel. It is above this liquor level that the foam nozzle leading to the foam breaker is located. Broken foam from the foam breaker can be flushed with a side stream of overflow liquor from the transfer pump on the weak liquor storage tank.

Soap Accumulation on Weak Liquor in Storage

When soap separates from weak liquor in storage, a layer of soap accumulates on top the liquor. In extreme cases, weak liquor tanks have become filled with soap and a false liquor inventory is indicated. As liquor inventory is depleted, soap can be pumped to the evaporators. This usually results in fouled evaporators that require washout.

To control this problem, the soap layer can be withdrawn either through a floating soap skimmer or through drawdown pipe nozzles. In cases where severe soap accumulations are encountered, the use of two or more weak liquor storage tanks is recommended to maintain a constant liquor level. As soap is accumulated, it overflows into a soap concentrator. The concentrated soap is then pumped to the soap handling or soap storage system. Liquor enters the first tank near the top to facilitate soap separation. A second inlet at the bottom of the tank is provided when the liquor inventory in the first storage tank is required.

Removal of Soap in the Evaporators

The most common method of soap recovery is skimming of liquor at 23 to 28 percent solids. This is accomplished at an intermediate stage of evaporation. The sizing of a soap skimming tank is dependent upon the rate of rise of soap in liquor. Typically, the rate of rise for soap is assumed to be 1 meter per hour when actual data is not available. The skim tank should also be baffled to elongate the flow of liquor through the tank and minimize short-circuiting. A liquor depth of about 3 meters is recommended, with a 0.6 meter soap layer accumulation on the liquor surface. The tank baffles extend into the mid-level of the soap. The skim rake and drive are supported by a truss system across the tank top. The skim rake moves the soap to a launderer. Removed soap flows into a soap concentrator for removal of entrained air. The deaerated soap then enters a small tank where some liquor is drained and soap accumulates for transfer to soap storage. A special overflow weir is recommended for use in maintaining a constant liquor level in the skim tank.

Black Liquor Entrained in Soap

Foam is air bubbles surrounded by a film of fatty or resin acids in the liquor system. When the bubbles are broken, some weak black liquor remains with the soap.

The handling of foam and soap requires first the removal of air from the foam, and second the removal of liquor from soap. Soap collected by flotation usually contains 12% to 15% weak black liquor. Upon acidification, the alkali content of the black liquor must be neutralized prior to saponification of the soap. Removal of the excess liquor prior to acidification reduces the acid requirement. A tank dedicated to liquor/soap separation, fitted with a rake system, is used to remove liquor from soap. In this system, the rake system consists of fingers that provide a path for the liquor to flow downward through the soap into the bottom of the tank where liquor accumulates. Periodically the liquor is pumped to storage. At the top of the tank, a skim arm pushes the soap to a launderer and then it is transferred with a soap pump to soap storage.

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4.2 FIBER REMOVAL

W. J. Frederick

Brown stock washer face wires and continuous digester extraction screens permit a fraction of fine fibers and other suspended solids to pass through with the filtered black liquor. In batch pulp mills, weak black liquor fiber filters are sometimes employed to remove and recover of these fibers. They also act as safeguards from unexpected high fiber loads that can occur when extraction screens or face wires of brown stock washers are damaged mechanically or through wear.

Fiber filters reduce costs by reclaiming valuable fiber product. However, these savings do not usually justify their installation. They are employed in situations to prevent fiber plugging in black liquor evaporators and heat exchangers. Fiber plugs by themselves or in combination with inorganic deposits and crystals can block flow in evaporator tubes and channels between heating panels, reducing evaporation capacity. Fiber filters, when properly operated and maintained, increase evaporation capacity and reduce the cost of cleaning evaporators to remove fiber plugs. Their cost may be justified based on increased evaporation capacity in evaporator-limited pulp mills and decreased evaporator cleaning costs.

The fiber content of weak black liquor before filtration is often 150-200 ppm. It should be 5-25 ppm after the liquor is filtered [1].

4.2.1 Drum Filters

Working Principle

A drum filter consists of a horizontal rotating perforated drum covered with a fine mesh facing wire. Liquor pumped into the vat inlet overflows into the drum trough and filters through to the interior of the drum. The filtered liquor is discharged from the inside of the drum, and the separated fibers and other solids are carried on the outside of the drum over the outlet weir into the reject outlet. The drum is submerged on the inlet side.

Fiber collected on the wire is blown off by a low-pressure steam shower that acts through a perforated deck. The shower pipe is placed along the inside face of the drum. With a shower pipe above the doctor, the fibers are flushed from the doctor into a tank.

Fiber filters are automated to operate periodically to control the filter vat level.

Figure 1. A drum type black liquor fiber filter. (Courtesy of Valmet Inc.)

4.2.2 Design [2]

Basis: Black liquor fiber filters are designed to process weak black liquor containing up to 600 mg/L of fiber loading. Filtered liquor typically contains less than 20 to 50 mg/L of fiber.

The filters (Figure 2) consist of a vat, a mesh-covered drum, flushing and wire cleaning pipes, drive equipment, and level control instrumentation. The drum is mounted in a vat and is totally enclosed within a hood that prevents uncontrolled escape of noxious fumes. The upper part of the hood is equipped with inspection covers on both the front and back sides. A doctor is fastened to the vat at the fiber discharge side.

The drum consists of a shaft and a perforated plate with a wire cloth stretched onto it. The direction of the shower from the flushing pipe to flush the doctor is adjustable. The wire cleaning pipe is led to the drum through the vat wall. The cleaning pipe can be turned slightly in relation to the vat.

Drum type fiber filters collect most of the fine fibers in weak black liquor. An 80 or 100 mesh fabric can be used. A 100 mesh wire may also remove a large amount of other suspended solids such as inorganic crystals and resin particles that may blind filter cloths.

The drum, vat, and hood are made of type 304, 316 L, or 254 SMO stainless steel [3].

Typical drum parameters:

Diameter: 0.8 to 1.4 m
Length: 1.0 to 3.0 m
Drum rotation speed: 5 rpm
Drive power: 0.22 to 0.75 kW

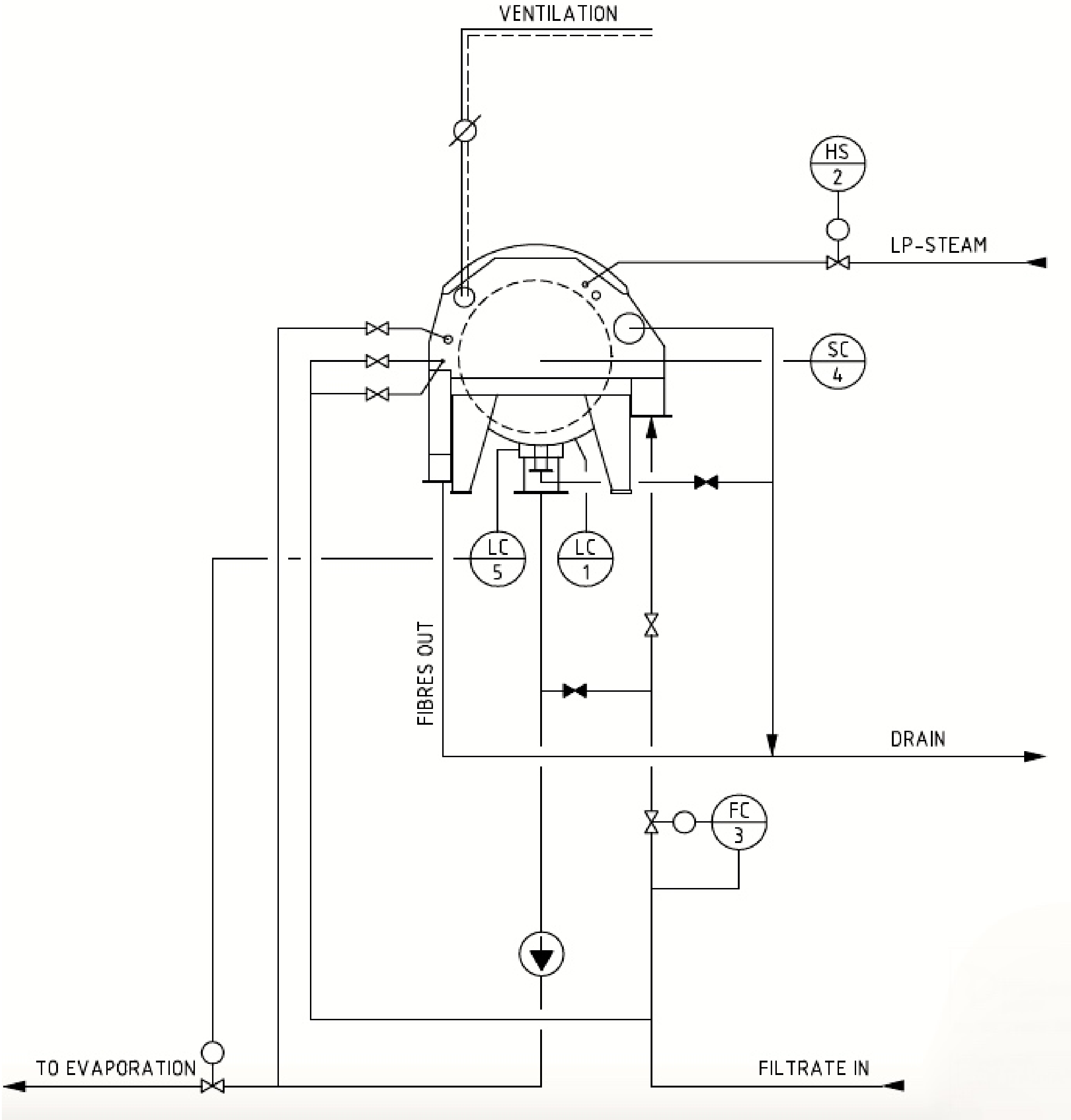

Figure 2. Flow diagram for a drum black liquor fiber filter. (Courtesy of Valmet Inc.)

4.2.3 Basket Fiber Filters

Basket fiber filters, as shown in Figures 3 through 5, consist of a rotating basket with small holes or slots (>100 microns) through which black liquor passes. Fibers removed are collected on the outside of the drum. Pneumatic cake discharge is achieved by a pulse of gas behind the cake. The blow-back shoe is fitted with close clearances to the machined inside surface of the cylinder, sealing off vacuum or pressure at the point of cake discharge. Pressurized units operate up to 5 bar pressure on the inlet side. The open area on the drum is up to 14% of the drum area.

Materials of construction: 316L stainless steel or equivalent
Basket surface area: 0.8 or 1.3 m^2
Basket rotation speed: 1000-1500 rpm
Drive power: 75 kW

4.2.4 Who should have responsibility for operating the fiber filters?

This is an important question. Under pulp mill operation, it is easy to take the fiber filters offline when a problem occurs with the stock washers. Taking the fiber filter offline at this point will send a large flow of fibers to the evaporation plant, creating potentially severe fiber plugging in the evaporators. If the evaporator operators control the fiber filter, they will be able to recycle the high fiber-containing filtrate stream to the filtrate tank until the problem is resolved. In this way, fiber plugging of evaporators is avoided.

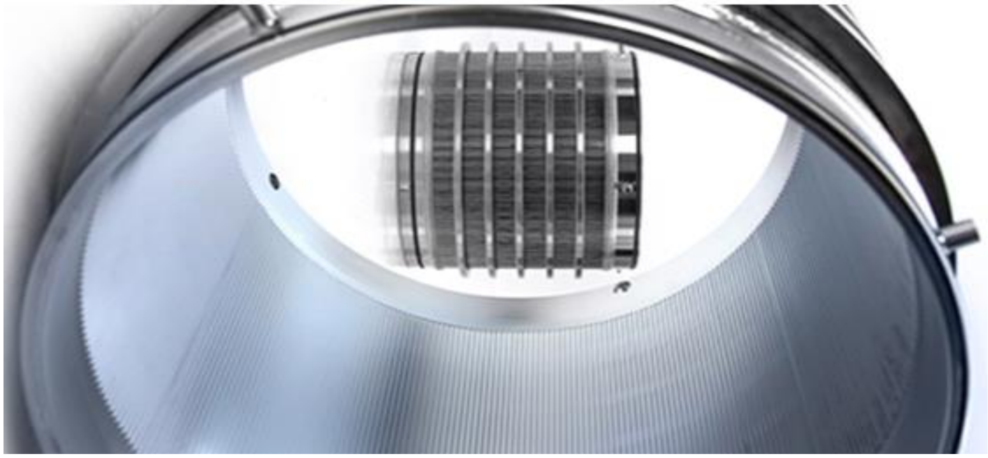

Figure 3. Slot screen fiber filter basket.

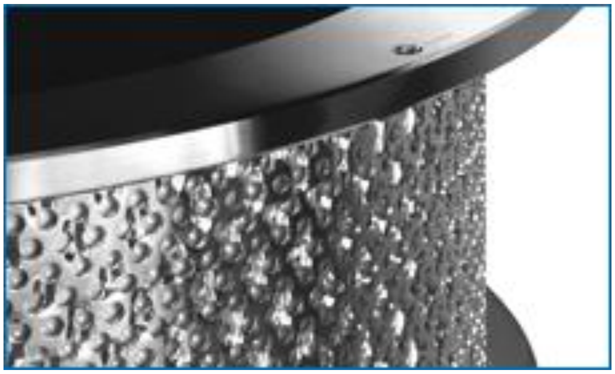

Figure 4. Andritz screen basket for a pressurized weak black liquor fiber filter [4].

Figure 5. Valmet LiquorScreen installation. (Courtesy of Valmet Inc.)

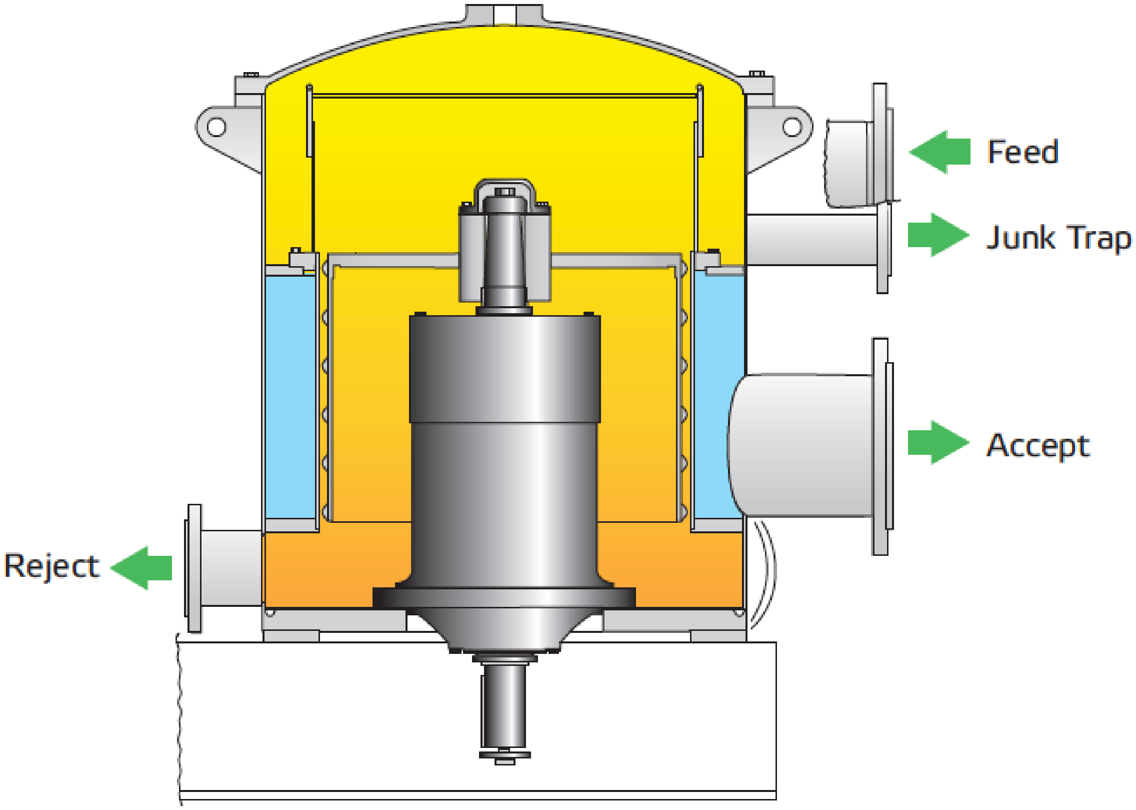

Figure 6. Valmet pressurized liquor screen. (Courtesy of Valmet Inc.)

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4.3 CONDENSATE SEGREGATION

Ben Lin, P.Eng.

Foul condensate stripping is energy intensive when BOD (biological oxygen demand) removal is required; for high efficiency removal, the steam usage is 20% by weight of the foul condensate to be stripped. For example, a 1000 L/min stripper operated at high efficiency for BOD stripping will use about 12,000 kg/h. Reducing the steam consumption will reduce stripping efficiency.

Methanol is typically used as a surrogate for BOD as it typically makes up a very large fraction (80 to 90%) of the BOD in foul condensate. At 20% steaming rates, methanol removal is greater than 90% and TRS removal is over 99%.

Contaminated condensates are generated in a number of locations in the mill. Two of the major areas are the digester area and the multiple effect evaporator systems. If the mill were to strip all of the contaminated condensate generated in these two locations, the system would be prohibitive from both an equipment and operation cost perspective.

4.3.1 Principles of Condensate Segregation

In order to minimize the amount of condensate that needs to be stripped, condensing equipment is typically partitioned into first and second condensing stages. The result is the formation of two types of condensates. The first type, from the first stage, is a “contaminated” condensate that contains some methanol and very little TRS. The second type of condensate from the second stage, “foul” condensate, is highly contaminated in both methanol and TRS and must be treated by stripping. The process which separates these two types of condensate is called condensate segregation.

The main contaminants, methanol and TRS, have a much higher volatility than water. If a water vapour stream containing these components is allowed to condense in series on two distinct surfaces, a larger percent of the more volatile components will carry on to the second surface. The technical term for this phenomenon is differential condensation.

The amount of separation is a function of the percent of the vapour that is condensed on the second surface. For example, referring to Figure 1, if 5% is condensed on the second surface, then approximately 65% of the inlet methanol in the vapour will be carried to the second surface. If the separation is increased to 15% blow through to the second surface, the percent of methanol carried through will be approximately 80%. In this way a large fraction of the methanol can be captured in a relatively small stream.

Because the TRS components are much more volatile than methanol, the amount of separation will be significantly higher. At the 5% and 15% condensed amount on the secondary surface, depending on the composition of the TRS mixture, about 95% and 99% of the TRS will be contained in the foul condensate portion, respectively.

Separation can also occur when part of the liquid is flashed. For example, referring to Figure 1, if 5% of the liquid is vapourized, then approximately 30% of the inlet methanol in the liquid will also be vapourized. If the flash is increased to 15% of the liquid, the percent of methanol carried in the vapour will be approximately 55%. The technical term for this phenomenon is continuous flash distillation.

The theoretical amount of methanol separated is based on a pure methanol-water system. In practice, because kraft mill condensates are multi-component in nature, methanol separation efficiencies may be slightly reduced.

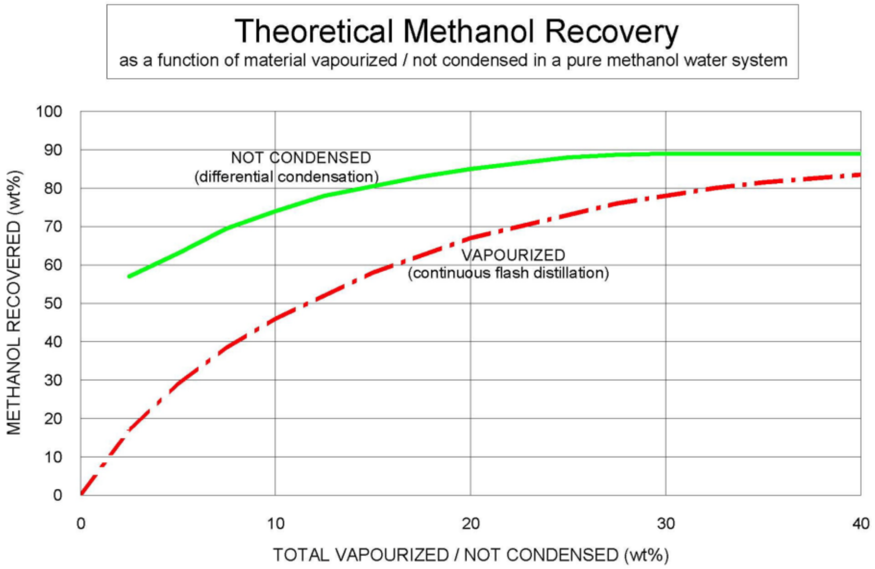

Figure 1. Theoretical methanol recovery diagram.

4.3.2 Evaporator Condensate Segregation

It is well documented that a large fraction of the TRS and methanol is flashed off in the first two stages of weak black liquor evaporation. For example, in the first liquor flash of a typical evaporator plant, about 15% of the total liquid is flashed off; the flash vapour will contain about 60% of the total methanol that was in the black liquor. Of the remaining 40% methanol in the black liquor, 60% of this (i.e. 60% of 40% or 25% of the initial total) will be removed in the second liquor flash; therefore, 60% plus 25% or 85% of the initial methanol in the black liquor will be contained in the condensate from the first two liquor flashes.

The condensing vapour from the first two liquor flashes is typically segregated. This means these vessels are partitioned into first and second condensing stages typically containing 85% and 15% of the heat transfer surface, respectively. To continue our example, about 80% of the methanol from the first liquor flash (containing 60% of the methanol) will be recovered in the foul condensate fraction, i.e about 48% of the total methanol. Additionally, 80% of the methanol from the second liquor flash containing

25% of the methanol will be recovered in the foul condensate fraction, i.e. about 20%. Therefore, for this segregation system collecting 15% of the condensate from the first two liquor flashes, about 48% plus 20%, or 68%, of the methanol contained in the black liquor can be captured in a very small foul condensate stream.

To apply the theory behind condensate segregation, Table 1 lists condensate segregation design features and equipment included for a typical new installation and for a retrofit of an older evaporator set.

Table 1. Evaporator Condensate Segregation Equipment

Equipment	New System	Retrofit Existing System
Weak liquor feed	No split feeding of liquor, all liquor fed to penultimate effect	No split feeding of liquor, all liquor fed to penultimate effect
Last effect	Minimum last 15% of condensing surface segregated for foul condensate	Add external liquor heater, size limited to about 5% condensing
Surface condenser	Minimum last 15% of condensing surface segregated for foul condensate	Add secondary surface condenser in series after existing primary surface condenser; size for minimum 15% of vapour
NCG venting	Last two or more heater bodies vent to foul side of surface condenser	Last two or more heater bodies vent to secondary surface condenser
Vacuum system	Two stage with indirect intercondenser and aftercondenser	Two stage with indirect intercondenser and aftercondenser
Condensate flash tanks	Segregated flash areas inside effects for combined (process) and contaminated condensates for polishing	Add flash tanks on combined (process) and contaminated condensates for polishing

4.3.3 Digester Condensate Segregation

The principles of condensate segregation can be applied by having a primary flash steam condenser perform 85% of the heat duty and using a secondary condenser to condense about 15% of the flash vapours. After segregation, only the foul condensates from the secondary condenser should be stripped.

The benefits of segregating the digester condensates include:

- Reduced foul condensate loading to the stripper.
- Reduced foul condensate loading for turpentine decanting (as turpentine is also very volatile and 99+% will be contained in the secondary condensate).
- Improved heat recovery, i.e. instead of heating cold mill water, 87°C (105°F) warm water can be heated to 85 to 88°C (185 to 190°F) in the primary condenser.

4.3.4 Kraft Mill Condensates

In general, there are three types of kraft mill condensates: combined (or process), contaminated, and foul (Table 2).

Table 2. Types of Kraft Mill Condensates Mill Condensates

	Combined (Process) Condensates	Contaminated Condensates	Foul Condensates
Typical TRS concentrations	40 ppm	150 ppm	600 ppm
Typical methanol concentrations	100 ppm	500 ppm	3000 ppm
Typical volumetric flow rates	8000 L/min	4000 L/min	1500 L/min

Combined condensates are the cleanest and has the largest volume of the three. Combined condensates are often reused at brown stock washing and/or at recausticizing without any further treatment. Typical combined condensates include:

- The front end of the evaporators, i.e. the 2nd effect through to the next to last effect of the evaporator plant.
- Stripped condensate. The cleaned condensate from a foul condensate stripping system. Requirements: minimum 20% stripping steam.

- Primary flash steam condenser. The condensates from the first condenser of a two stage digester condensing system. Requirements: primary condenser must be operated at a vent temperature of no less than 99 °C (210°F); in this case the mill would have a single condenser and send all of the condensate to stripping.

Contaminated condensates are in between combined and foul condensates in contaminant concentration. These condensates are generally too odourous for reuse in the mill and are usually used for level controlled makeup to the stripper feed tank. Typical contaminated condensates include:

- The condensates from the primary split of the last effect of the evaporators. Requirements: the liquor feed effect is to the second effect; up to 85% is condensed on the primary surface.
- The condensates from the primary split of the surface condenser. Requirements: up to 85% of the vapour is condensed in the primary surface.

Foul condensates are the most odourous condensates and have the highest BOD concentrations found in the kraft mill. Sending to secondary treatment without in-plant treatment such as steam stripping will result in higher odour and BOD loading at the water treament plants. Typical foul condensates include those from the back end of the evaporator such as segregated portions from the first two (and sometimes three) liquor flashes:

- The condensates from the secondary split of the last effect of the evaporator. Requirements: 15 to 25% of the vapour is condensed in the secondary surface.
- If the last effect is not segregated, then the condensates from an external liquor heater off the last evaporator effect. This is not as effective as segregating the last effect surface area as listed above because liquor heating duty limits the vapour condensed to about 5%.

- The condensates from the secondary split of the evaporator surface condenser or a secondary surface condenser. Requirements: 15 to 25% of the vapour is condensed.
- Evaporator vacuum system. Condensates from the two stage vacuum system. Requirements: indirect precooler, intercondenser, and aftercondenser.
- Secondary flash steam turpentine condenser. The condensates from the second condenser of a two stage condensing system. The condensates are first sent to turpentine decanting. Requirements: primary condenser must be operated at a vent temperature of no less than 210°F.
- NCG/SOG line drains. Line drains from the NCG and SOG headers are collected and pumped to the stripper feed tank.
- Turpentine storage tank padding water. If a mill collects 1136 L/day (300 US gallons/day of turpentine), then the padding water flow will be 0.76 L/min (0.2 gal/min).

4.3.5 References

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4.4 THE BASICS AND PRACTICE OF FOUL CONDENSATE STRIPPING

Ben Lin, P.Eng.

Foul condensates from the digesters and evaporators contain reduced sulfur gas and organic compounds, such as methanol (MeOH) and turpentine, which contribute greatly to pulp mill water pollution in the form of Biochemical Oxygen Demand (BOD) and toxicity as well as air pollution in the form of Volatile Organic Compounds (VOC) and odor.

For this reason, foul condensates are collected and treated by stripping, using either air or steam, to remove the pollutants. In many cases, the pollutants can be used economically as a fossil fuel substitute.

This section covers the condensates that are collected, various stripping methods, types of stripping columns, basic stripping theory, operating problems, the latest operating procedures, and disposal of the stripper off gas (SOG) which contains the pollutants removed.

The Cluster Rules resulting from the Clean Air Act Amendments (CAAA) of 1990 require the collection and treatment of "kraft process condensates", better known as foul condensates or combined condensates.

Steam stripping is one of the treatments accepted by the Environmental Protection Agency (EPA). The others are hard piping to biological treatment, reusing the condensates in a process where the vents are collected and incinerated, or any other process that can meet the required removal efficiencies.

Although the rules allow various methods of determining removal efficiencies, bleached mills have to collect selected condensates and treat them to destroy 10.2 pounds of methanol (MeOH) per oven dry ton of pulp (ODTP) (5.1 kilograms per oven dry mectric ton of pulp). Unbleached mills will have to destroy 6.6 pounds per ODTP (3.3 kg/metric ton).

Most mills built or upgraded since 1980 have had a condensate stripping system installed as an integral part of the overall mill process. Many older mills have now added a foul condensate stripper to meet the new EPA Cluster Rule.

Table 1. Typical Pollutant Loads in Foul Condensates Based on Unbleached Digester Production of a Bleached Kraft Mill

Source		**Total Flow**		**MeOH**		**Turpentine**		**TRS**	
		kg/tonne	lb/tonne	kg/t	lb/t	kg/t	lb/t	kg/t	lb/t
Batch Digester Mill (Softwood)	Digester accumulator overflow	1125	2250	4.0	8.0	0.50	1.0	0.20	0.40
	Turpentine decanter underflow	250	500	1.5	3.0	0.50	1.0	0.15	0.30
	Total evaporator condensate	7000	14,000	4.2	8.4	0.25	0.5	1.00	2.00
Continuous Digester Mill (Softwood)	Turpentine decanter underflow	450	900	2.5	5.0	0.50	1.0	0.12	0.24
	Total evaporator condensate	8000	16,000	7.5	15.0	0.50	1.0	1.20	2.40

4.4.1 Why strip foul condensates?

The prime reason for stripping foul condensates is pollution control. Foul condensates can contain 14 to 20 lb (7 to 10 kg) of BOD, 2 to 4 lb (1 to 2 kg) of turpentine, and 2 to 4 lb (1 to 2 kg) of TRS per ton (tonne) of pulp (Table 1).

If these foul condensates are untreated, they cannot be reused in the mill and are therefore sewered, putting a high load of BOD and toxicity into the secondary treatment system and frequently causing air pollution problems; as the TRS and MeOH is released to the atmosphere by flashing off from open sewers.

By collecting these foul condensates and stripping them, most of the pollutants can be removed and burned, reducing the pollution load to the air and to the secondary treatment system.

In most cases, the stripped condensates can be reused in the mill for such purposes as brown stock washing and make-up water in the recaust area. Thus, stripping also has the potential to reduce the total mill water demand [1]. Stripping is an integral part of the effluent free mill development.

Fortunately, the stripped compounds are easily burned. Heat of combustion values for stripper overheads in the order of 500,000 KJ/tonne (475,000 BTU/Ton) of pulp have been reported (Table 2).

These stripper overheads can be transported as a gas or condensed and transported as a liquid. They can then be used to replace fossil fuel in lime kilns, boilers and incinerators. In most cases, the net heat released by burning these pollutants is greater than the heat energy required to operate the stripper. As a result, they can be used to help economically justify installing the stripping system.

Table 2. Heating Values of Pollutants

Pollutant	Net Heat of Combustion kJ/kg	 Btu/lb
MeOH	21,580	9066
Alpha-pinene	40,890	17,200
H_2S	15,620	6565
CH_3SH	26,690	11,212
CH_3SCH_3	31,580	13,268
CH_3SSCH_3	24,150	10,148

4.4.2 What condensates are stripped?

The Cluster Rule requires collection and treatment of the condensates from the digester system, turpentine recovery system, evaporator systems, HVLC (dilute NCG) collection system, and LVHC (concentrated NCG) system.

Batch Digester Blow Steam Condensate

The condensates from condensed blow steam are rich in methanol and TRS. In order for these pollutants to be collected, however, the blow steam system must function correctly. If the blow steam system is undersized or operated incorrectly, much blow steam is vented with much of the methanol and TRS vented as well.

In some mills, fresh water is added to the accumulator to keep the bottom temperature low. This dilution of the blow steam condensate makes collection of these condensates undesirable.

In a modern blow steam condensing system, the direct contact primary condenser is followed by an indirect secondary/tertiary condenser. It has been found that up to 80%

of the pollutants can be “segregated” into the 10% to 15% of condensed blow steam that comes from the secondary/tertiary condenser. This concentration of the pollutants in a smaller flow greatly improves the efficiency and economics of stripping.

The Cluster Rule will allow the treatment of only the segregated stream, provided that at least 65% of the methanol in all the blow steam condensates is contained in the segregated stream.

Batch Digester Relief Steam

During a batch cook, non-condensable gases (NCG) are vented from the digester. The NCG contains considerable amounts of steam, MeOH, and frequently turpentine. This steam must be condensed in order to collect the NCG. The condensates formed must be collected and treated. As above, this condensation can be done in two stages with only the rich or segregated stream collected and treated, providing at least 65% of the methanol in the relief gas is in the segregated stream.

Continuous Digester Flash Steam

With continuous cooking, hot, pressurized liquor is removed from the digester continuously and flashed to atmospheric pressure. Again, the flash steam contains considerable amounts of NCG, MeOH, and turpentine. This steam must be condensed and the condensate subsequently treated as are condensates from batch digesters.

Turpentine Decanter Underflow

In softwood mills, batch digester relief and continuous digester flash steam condensates go to a turpentine recovery system. The underflow from the turpentine decanter is a relatively low flow that is rich in methanol, turpentine, and TRS, making a foul condensate that is a prime candidate for stripping.

Evaporator Condensates

The combined foul condensates from the multiple effect evaporators contain methanol, turpentine, and TRS removed from black liquor during evaporation. The evaporators, in effect, act as strippers to remove these pollutants from the black liquor.

It has been found that most of the pollutants (80%+) will collect in the condensates of the effects and condensers following the effects where the weak black liquor is fed. For example, if weak black liquor is fed to effects 5 and 6 of a six-effect evaporator, the pollutants will be found in the condensates from the 6th effect and the surface condenser. The Cluster Rule allows splitting out such condensates for treatment, thus reducing the amount of evaporator condensate to be treated by about two thirds.

In modern multiple effect evaporators, especially those of the falling film design that have been supplied since 1980, the majority of the pollutants can be collected in 15% or less of the total condensate. This is primarily done by using two-stage condensing with internal condensate segregation. This, as mentioned above, greatly reduces the condensate to be treated, and thus improves the efficiency and economics of stripping.

In general, there will be four condensate streams generated in a modern falling film evaporator. The first is clean steam condensate from the first effect. The second is combined condensates from the middle effects with a 100 ppm concentration range of methanol. The third stream is contaminated condensates from the lean steam of segregated condensates from the feed effects with a 1000 ppm concentration range of methanol. The final stream is foul condensates from the rich stream of segregated condensates with a 5000 ppm concentration range of methanol.

The Cluster Rule will allow segregation of condensates, providing that 65% or more of the methanol in all the evaporator condensates is in the segregated stream.

NCG System Condensates

The condensates formed in NCG systems, although small in volume, are very concentrated in methanol and TRS compounds, which contribute to odors in the mill area if drained into open sewers. The Cluster Rules may require collection and treatment of these condensates.

4.4.3 Methods of Stripping

There are two methods of stripping used in kraft pulp mills today. One uses air and the other uses steam. Both of these methods can be further subdivided into two types of strippers; stripping for TRS only and stripping for methanol (BOD). TRS is easily stripped whereas MeOH is more difficult, consequently making the latter systems bigger and more complex. Furthermore, the new Cluster Rules will not accept air stripping or stripping for TRS only.

Air Stripping for TRS

This is the most basic form of stripping and is generally used to remove TRS from condensates so that they do not create odor problems in the secondary treatment system (Figure 1). In this case, the foul condensates are stripped by air moving counter-currently in a stripper column.

About 3% to 5 weight % of air on condensate is required. Higher air ratios may be necessary if the TRS concentration is high to ensure that the stripped gases are well below the Lower Explosive Limit (LEL) in the overheads.

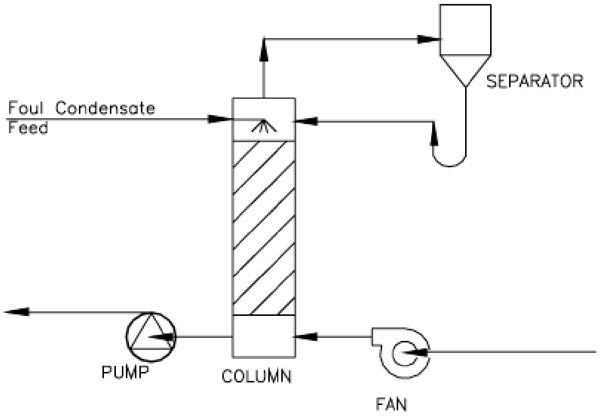

Figure 1. Air Stripper for TRS

The two factors that have the greatest effect on air stripper efficiency are temperature and pH (Figure 2). A pH of seven or less and a condensate temperature of 50 °C (120 °F) or more are required for good stripping efficiency. Disposal of the high volume of warm moist overheads is the major disadvantage of this system.

Disposal is usually done by burning in a boiler, kiln, or incinerator. The major advantages of this system are its simplicity and low cost.

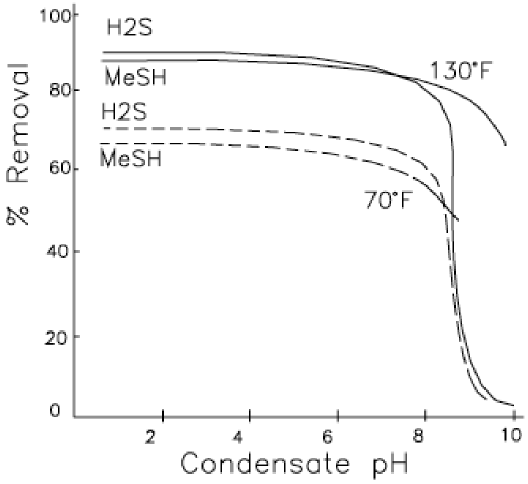

Figure 2. Air stripper efficiency.

Air Stripping for BOD

This system is similar to air stripping for TRS except that much higher quantities of air are required, in the range of 16 wt% to 20 wt% air on condensate. Temperature is also very important where temperatures in excess of 70°C (160°F) are required for good efficiency. This form of stripping is not practical and is not practiced.

Steam Stripping for TRS

This system is similar to the air stripper except that two heat exchangers are added to the system (Figure 3). It is necessary to preheat the foul condensate before stripping, otherwise the stripping steam would be condensed by the cold condensate. This preheating is done by heat exchanging with the hot stripped condensate.

The second heat exchanger is used to condense the steam out of the stripped TRS gas before it is incinerated. The condensate is returned to the top of the stripping column. About 3 wt% to 5 wt% of steam is required on condensate.

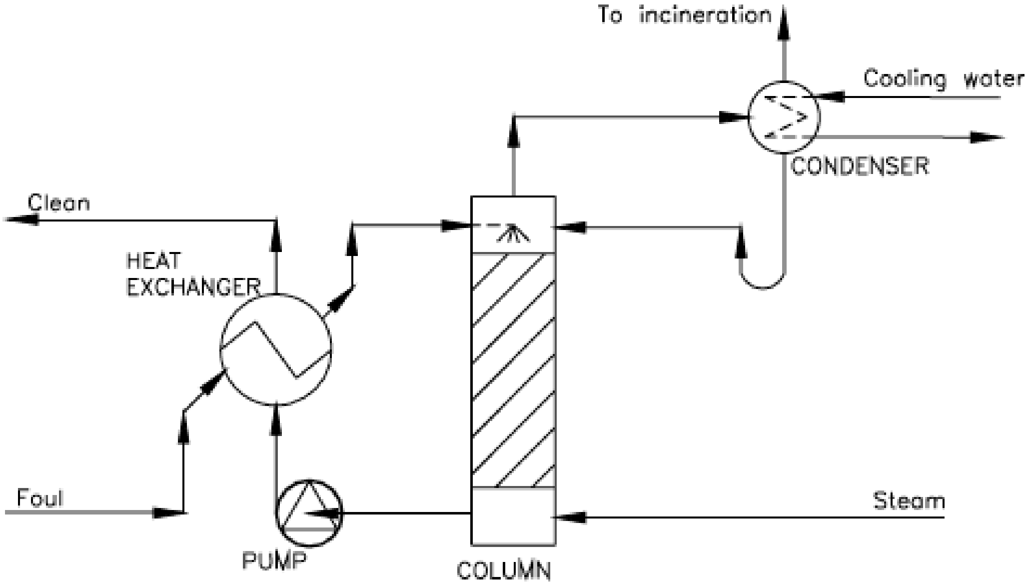

Figure 3. Steam stripper for TRS.

As with air stripping, efficiency is pH dependent. Despite the disadvantage of higher capital and operating cost, disposal of the overheads is much simpler. Operating costs can be reduced if some use can be made of the hot water generated in the overhead condenser.

Steam Stripping for BOD [2]

This system is similar to the steam stripper for TRS except that the overhead condenser becomes a reflux condenser and the top of the column becomes a distillation column to concentrate the methanol (Figure 4).

The steam requirement increases to 15 wt% to 20 wt% steam on condensate (Figure 5).

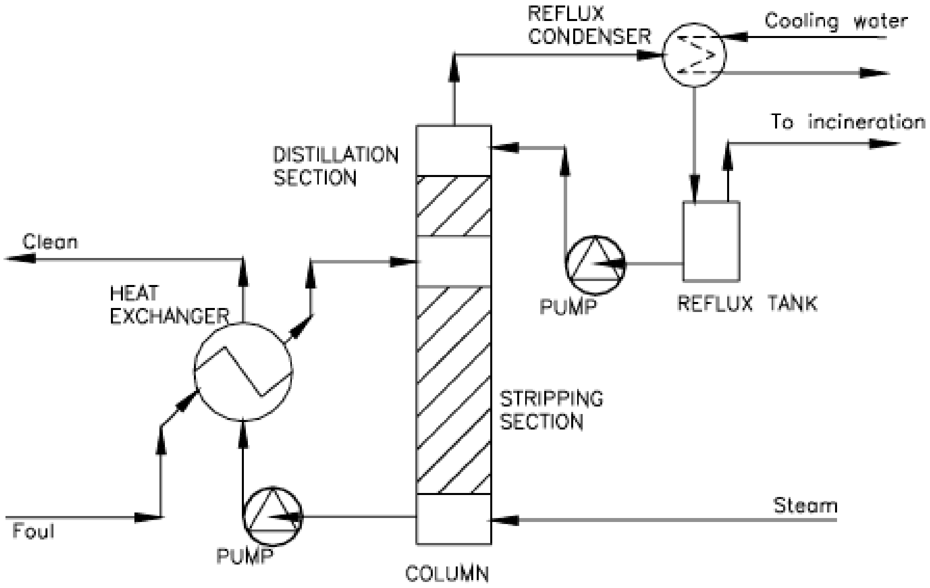

Figure 4. Steam stripping for BOD.

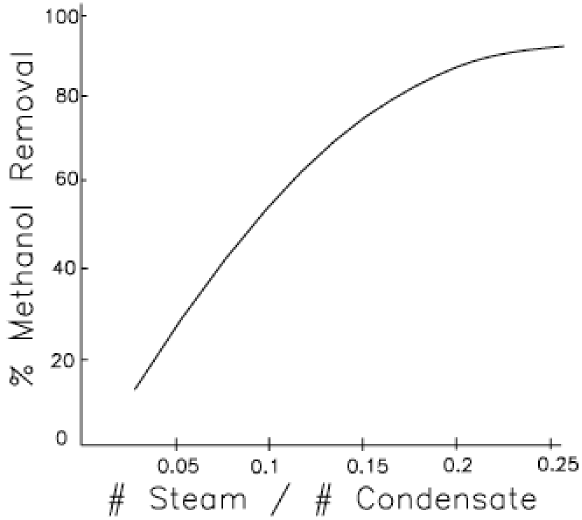

Figure 5. Distillation Efficiency.

These systems have the advantage of high efficiency, producing an overhead that is usable as a fuel. The major disadvantages are high capital and operating costs. The operating costs can be reduced if some use of the heat from the reflux condenser can be found such as preheating boiler feed water or making clean hot water for a bleach plant.

The reflux tank shown in Figure 4 is optional, and many systems do not have them. Instead, the reflux condenser is positioned above the column, and reflux flows by gravity back to the column.

There are examples of this type of stripping system at the mills in Palatka, FL. and Brunswick, GA.

4.4.4 Types of Columns

In general, two types of columns are used for stripping; packed columns and valve tray columns.

Packed columns are generally cheaper, especially for small diameter columns. Packing material is either stainless steel pall rings or corrosion resistant plastic saddles. The disadvantages of packed columns are poor turndown ratio and plugging of the packing by fibers carried in the condensate.

Valve tray columns are an advanced form of a bubble cap tray column. They have the advantages of maintaining high efficiency over a wide operating range, a constant pressure drop at varying vapor load rates, and self-cleaning of the trays. These advantages normally offset the higher capital cost of the valve tray column.

As a general rule, packed columns are used for TRS strippers and very small BOD strippers while valve tray columns are used for large BOD strippers. The valve tray column has become the standard under the Cluster Rule.

4.4.5 Integrated Columns

In order to reduce the capital and operating costs of steam type BOD strippers, they are normally integrated into a set of multiple effect evaporators. There are two basic ways to do this.

Fully Integrated

The stripping column is placed between two effects, usually the 1st and 2nd effects. Steam from the 1st effect is run through the stripper and then condensed in the 2nd effect. The 2nd effect is the reflux condenser, saving this capital cost. The stripping steam is essentially free.

Figure 6 is a schematic depicting a fully integrated stripping system.

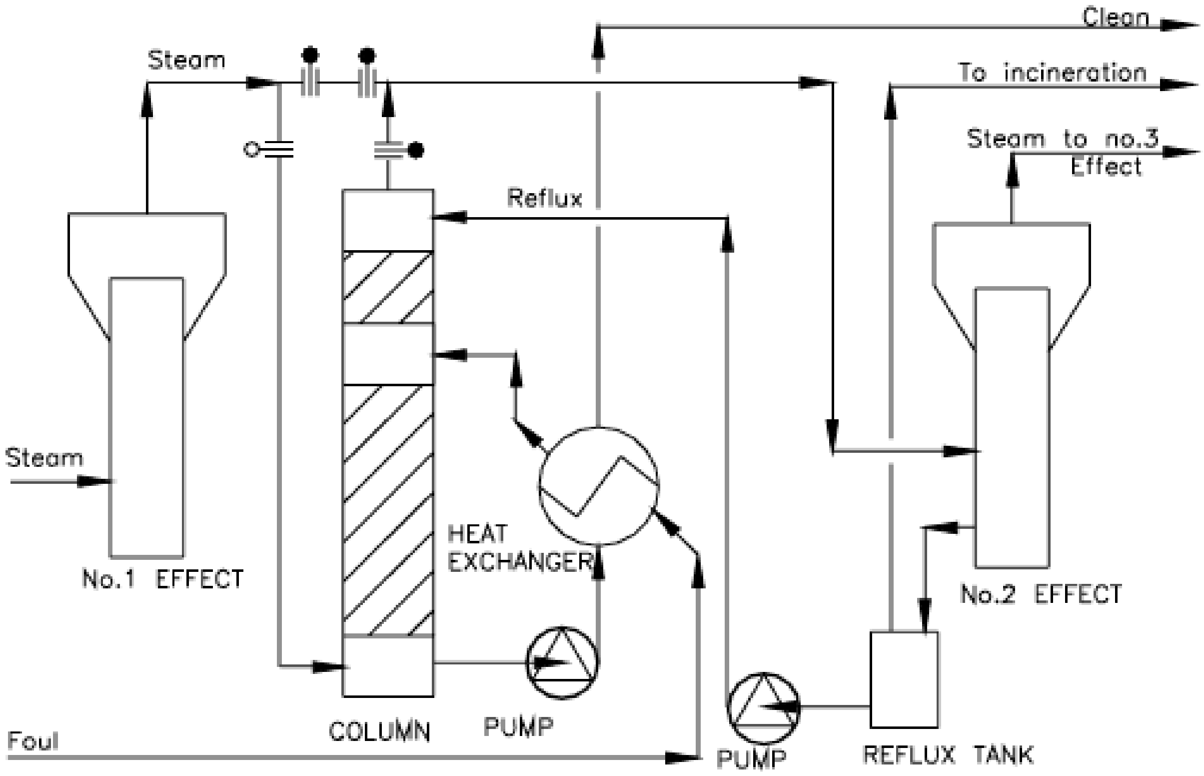

Figure 6. Fully integrated column.

However, there is an efficiency loss of about 12% in the evaporators when the column is fully integrated. In a system of this type, for every kJ or BTU lost by integration, two or more kJ or BTUs are returned by the heat value from burning the stripped BOD.

This type of full integration with respect to the evaporators can be used when a stripper is integrated into an existing mill and where condensate flows are high compared to the relative size of the evaporators.

Partially Integrated

In the case of a new mill with reduced foul condensate flows and where the stripper is part of the initial evaporator design, only partial integration is required.

In this case, only part of the evaporator steam flow is used for stripping and the overheads are condensed in either an external preheater or in a dedicated internal section of a subsequent evaporator effect. Such systems have a much better energy return than fully integrated systems.

There is an example of this type of stripper at the mill in Leaf River, MS.

Figure 7 is an illustration of a partially integrated stripping system.

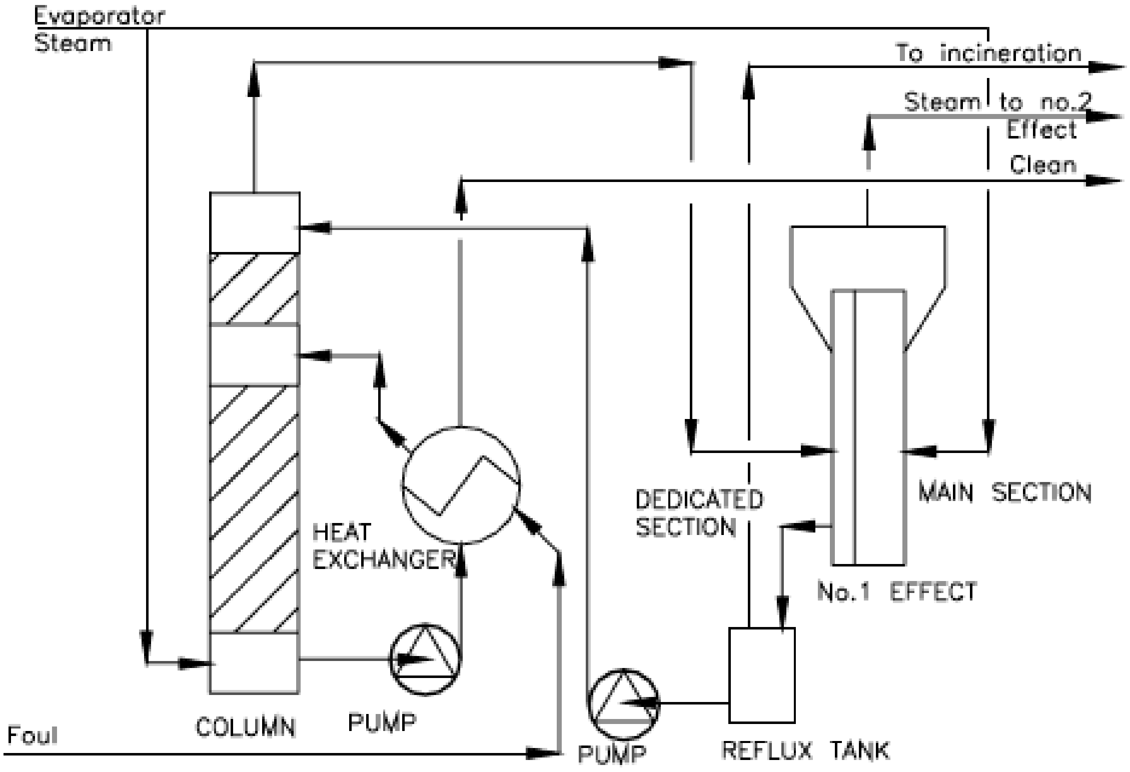

Figure 7. Partially integrated column.

4.4.6 Column Operation

Stripping columns are generally easy to operate although control schemes for strippers integrated into evaporators can be complex due to their interdependence on evaporator operation. Some problems in column operation are as follows:

Foaming

Liquor in the foul condensate can cause the condensate to foam when air or steam is blown through it. This results in a flooded column where the condensate is carried out at the top of the column and steam or air flow is stopped.

This problem is handled by measuring the conductivity of the foul condensate. A high conductivity indicates the presence of liquor and the condensate can be dumped before it gets to the column.

This problem will show up as loss of steam flow to the stripper, or high level in the reflux tank.

At worst, the foam will carry through the stripper off gas (SOG) system and into the incineration point, where it may extinguish the flame or cause other damage.

Unstable Operation

In steam strippers, where steam use is controlled and based on condensate flow, every change in flow upsets the system for several minutes. In a continuous change situation, such as a case in which the condensate feed flow is based on level control of a foul condensate storage tank, the system remains unstable. Therefore, flow changes should be made on a stepwise basis and made as seldom as possible. In the case of an integrated column, the evaporators used should be run as smoothly as possible.

If a mill has more than one set of evaporators, the set with the stripper should carry a constant base load while the other set takes up the production rate changes. Unstable operation can also cause problems if the stripper gas is burned in a kiln or an incinerator. Rapid changes in MeOH load can upset the heat balance in the kiln or incinerator.

Unstable operation will result in low stripping efficiency.

Steam Collapse

Once the column is started up, it is full of steam. If enough cold condensate enters the column, it will condense the steam where it enters the column, causing an almost instantaneous high vacuum in the top of the column.

The hot condensate in the bottom of the column will boil rapidly, almost exploding. This sudden upward rush will buckle trays, pop them out of their hold down clips, or carry packing out of the column.

Such a situation can happen on a start-up, when there is insufficient hot condensate in the bottom of the column to preheat the foul condensate. Great care must be taken to avoid such situations. Start-ups should be done very slowly.

Loss of trays results in loss of stripping efficiency.

Control of Contaminant Removal

Condensing in the reflux condenser must be controlled to maximise contaminant removal while minimising steam loss. At this point in the process, the system is a very complex, two-phase multi-component system, mainly made up of water, methanol, reduced sulfur gases, and turpentine with several other compounds such as ethanol and acetone in lesser quantities.

Good control depends on a combination of pressure and temperature control in the reflux condenser. More details are provided below in the Reflux Control section.

Fiber

The foul condensates tend to contain pulp fibers. These fibers can plug packed columns and heat exchangers, especially plate-type heat exchangers. Fortunately, valve tray columns are self-cleaning.

The handling of fiber can be done in two ways. The first is to install a good fiber filter before the heat exchanger. The second is to design the system to pass the fiber through, using valve trays and heat exchangers with wide gaps or large diameter tubes.

This problem normally shows up as loss of flow through the heat exchangers, especially plate-type heat exchangers.

Plugging of Heat Exchangers

Several mills have experienced a scale build-up on the stripped condensate side of the heat exchanger. The reason for this is still not clear, and the scale is very difficult to remove. For this reason, the stripped condensate should go through the tube side of the heat exchanger to facilitate mechanical cleaning.

Attempts to chemically remove the scale have been tried, but with mixed success. Chemical cleaning should be done before the tubes become too badly scaled.

This problem usually shows up as loss of flow of the stripper bottoms, or an excessively high level in the bottom of the stripper.

Turpentine in Storage Tank

As there is turpentine in the condensates, there is a tendency for the turpentine to decant in the storage tank, and collect on top of the condensates. If this happens and the storage tank is pulled down, it is possible to send a slug of turpentine to the stripper.

The turpentine will easily strip. As a result, the turpentine will go through the SOG system and cause problems at the incineration point, usually a high temperature trip.

There are several means to avoid the turpentine build up in the storage tank. The first is to send the turpentine decanter underflow, which can be rich in turpentine, directly to the suction of the stripper feed pump. The second method is to make sure there is agitation in the tank to prevent the turpentine decanting. This can be done by making the incoming condensate lines tangential, recirculating feed condensate back to the tank, or by adding an internal agitator.

Skimming the turpentine can also be done. This can either be done periodically, returning the turpentine to the turpentine recovery system, or by continuously skimming the turpentine into the stripper feed condensate.

4.4.7 Reflux Control

As mentioned above, good control of the reflux cycle is required to operate the stripper efficiently, both with respect to contaminant removal and heat recovery.

For any given operating pressure and any desired stripper off gas (SOG) concentration, there is fixed equilibrium temperature. Operating at the proper equilibrium temperature and pressure is necessary in order to control the overhead composition.

Furthermore, operating at the proper equilibrium conditions will ensure removal of the turpenes and red oils with the SOG where they can be burned. If the reflux condensate is allowed to sub cool, the red oils will separate out and build up in the reflux cycle until they give control problems.

The concentration of methanol in the SOG is a compromise between stripping efficiency and heat recovery. At higher methanol concentrations, heat recovery improves but stripping efficiency declines. At lower methanol concentrations, stripping efficiency improves but heat recovery declines. The generally accepted optimum methanol concentration in the overheads is 50% by weight.

In a non-integrated stripper, it is possible to control both the pressure and the temperature. Two methods of doing this are shown in Figures 8A and 8B.

With an integrated stripper, the evaporator operation will fix the stripping temperature. Thus it is necessary to control the operating pressure based on this temperature.

Temperature control is done by controlling the cooling water flow to the reflux condenser. Pressure control is done by controlling the back pressure on the SOG line.

In the scheme shown in Figure 8A, the temperature of the reflux condensate is measured rather than the gas, which gives faster response to temperature changes. This assumes that the condensate is not sub-cooled and is at the equilibrium temperature. The condenser is mounted horizontally in order to minimize sub-cooling of the condensate. This scheme works well at design conditions but sub-cooling tends to occur at reduced operating rates.

In the scheme shown in Figure 8B, gas temperature is measured directly. Vapor from the reflux condenser is bubbled through the condensate in the reflux tank, which ensures that liquid and gas phases are in equilibrium. This gives better control, but at a capital cost penalty.

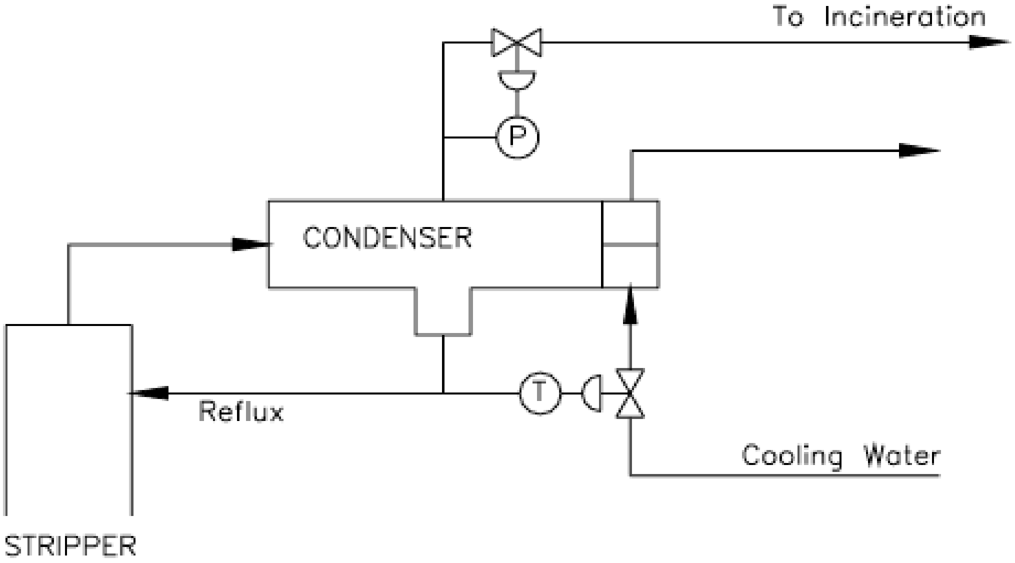

Figure 8A. Reflux control.

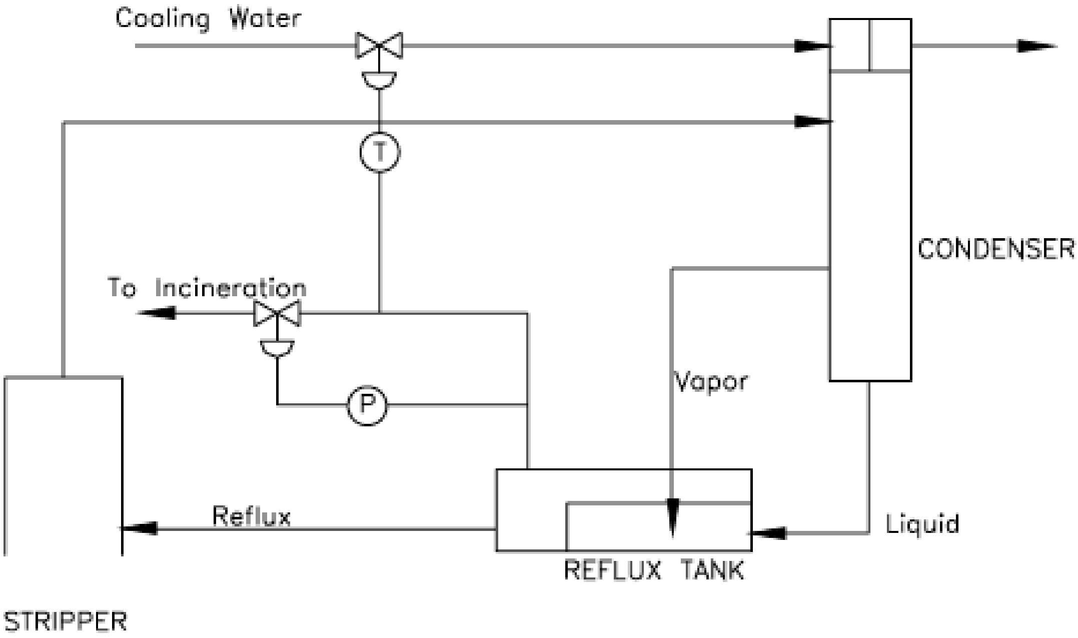

Figure 8B. Reflux control.

4.4.8 Transport and Disposal of Contaminants

Once the contaminants have been stripped out of the condensate and removed from the system, they must be disposed of. The most common way to do this is to carry them in gaseous form and burn them directly in a kiln, boiler, or separate incinerator. The system for transport is almost identical to a concentrated, or low volume high concentration (LVHC) non-condensable gas (NCG) system. The system is shown in Figure 9.

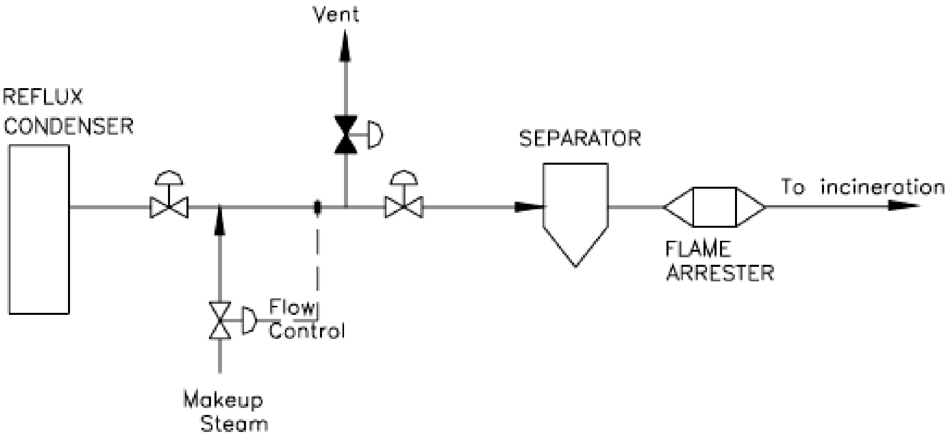

Figure 9. Stripper off gas system.

The major difference with a concentrated NCG system is that the stripper gas system requires makeup steam to ensure purging of the entire system on start-up and a minimum velocity in the entire line at all times. This is done by measuring the line velocity near the incineration point and adding makeup steam, as necessary, near the pressure control valve at the stripper. The stripper gas system should be operating, with SOG going to incineration, before any foul condensate is sent to the stripper.

The advantages of burning stripper overheads are low cost, simple operation, and recovery of the high fuel value of the contaminants.

The major disadvantage is that if this stream is ever vented, it will create a severe odor problem in the local area very quickly.

It is also possible to collect the contaminants as a liquid by use of an extra condenser. This allows for storage of the contaminants as a liquid, which can be used for fuel or be further refined for recovery of the chemicals.

In the past, the liquid MeOH collected fell under Resource Conservation and Recovery Act (RCRA) rules classifying it as a hazardous waste, making this form of collection virtually illegal. The Cluster Rule reclassifies this liquid methanol as a “clean fuel”, which therefore allows it to be collected and stored as a liquid.

In most cases, the SOG will be further rectified to increase the methanol concentration to 85% to 90% by weight.

4.4.9 Proper Operation Procedures

The following procedures have been recently developed to reduce the possibility of steam collapse and to eliminate venting of SOG during start-up and shutdown.

The stripper should be started up with steam. Once the stripper is fully heated and all air purged out of the system by cracking open the back pressure control valve, feeding of condensate can begin. At a minimum steam flow of about 20% of design, start with a condensate flow of about 10% of design.

After five minutes, increase condensate flow to 20% of design. Both condensate and steam flow should continue to increase in 10% increments every five minutes until the full operating rate is achieved.

The slow start-up will prevent damage to the trays due to steam collapse and give the incineration point time to adjust to the changing fuel load from the methanol in the SOG.

As mentioned before, any changes in operating rate should be made in small increments (maximum 10%) and as seldom as possible.

For planned shutdowns, condensate and steam flow should be reduced slowly until 20% of design is reached. At this point, the condensate flow should be stopped while the steam flow is left on.

The SOG should continue to be sent to incineration until the back-pressure control valve is closed. At this point steam flow to the stripper can be stopped and the SOG system, which now contains no pollutants, can be shut down.

In the emergency shutdown situation, such as when the fire goes out at the kiln or incinerator, it is necessary to vent the gases coming off the column.

To virtually eliminate this venting, condensate flow to the column should be stopped immediately and at the same time the pressure control valve at the column should be closed. However, steam flow should remain unchanged.

This will keep the system in thermal balance, which is especially important if integrated into the evaporator. It will also speed up the restart of the system. As before, on the restart, the condensate flow must be brought on slowly.

4.4.10 Conclusion

The Cluster Rule requires collection and treatment of foul condensates to reduce Kraft Pulp Mill pollution. The stripping of foul condensates is a good in-plant method of doing this. BOD, toxicity, and odor can be reduced by stripping. In most cases, the pollutants can be converted to a usable fuel, giving an economic return on investment.

4.4.11 Acknowledgement

This paper was originally authored by Mr. Tom Burgess. He had been the instructor for the TAPPI Kraft Recovery Short course since 1986 before retiring in 2005.

4.4.12 References

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4.5 METHANOL PURIFICATION

Ben Lin, P.Eng.

4.5.1 Methanol Formation

Methanol is formed as a by-product of the kraft pulping process; in the digester, the hydroxyl ion reacts with a lignin methoxyl group:

$$\text{Lignin-OCH}_3 + \text{OH}^- \Rightarrow \text{CH}_3\text{OH} + \text{lignin-O}^-$$

The amount of methanol produced is dependent on:

- Wood species: in general lignin methoxyl groups are more numerous in hardwoods than softwoods. Therefore more methanol is formed from pulping of hardwoods.
- Hydroxide concentration: higher alkali charge will produce more methanol.
- Temperature: higher cooking temperatures will produce more methanol.
- Time: longer cooking times will produce more methanol.

Some methanol is also formed from the acid-catalyzed methanol elimination from hemi-cellulose while naturally occurring methanol is freed from the biomass at the start of pulping.

Estimates are provided in Table 1 for methanol formation in the digester when producing bleachable grade kraft pulp from various softwoods and hardwoods [1].

Table 1. Methanol Formation in Kraft Pulping.

Wood Species	Methanol Formation, kg/ADT Pulp
Western Hemlock	6.6
Douglas Fir	7.5
White Spruce	8.2
Southern Pine	8.4
Aspen	8.6
Birch	9.9
Maple	10.2
Oak	11.5
Bass	11.8
Sweetgum	13.5

4.5.2 Methanol Capture

In a continuous mill, the methanol leaves the digester with the extraction liquor or with the brown stock. Methanol is relatively volatile compared to water; therefore, a large fraction will tend to flash-off in the extraction liquor flash tanks and collect in the flash steam condenser foul condensate. In a batch mill, a large fraction of the methanol will leave the digester with the relief steam and collect up in the relief steam condenser foul condensate. Additional methanol is captured in the foul condensate from the blow heat recovery system.

Some methanol will be carried away by the digester Concentrated Noncondensible Gas (CNCG) collection system and some will be lost to the Dilute NonCondensible Gas (DNCG) system during brown stock washing. The methanol that is captured in the washing filtrate will eventually end up in the weak black liquor feed to the evaporators. Depending on the level of condensate segregation, anywhere from 50% to 90% of the methanol in the weak liquor can be captured in the evaporator foul condensate, with the remainder lost to the combined condensate and the CNCG vent.

Up to 80% of the methanol formed in the digester will end up in the foul condensate. In a well operated stripping system, up to 95% of the methanol will be removed from the foul condensate and captured in the SOG, with up to 90% of this recovered as purified methanol. Overall, up to about 70% of the methanol formed in the digester can be recovered as purified methanol.

4.5.3 Process Overview

Methanol is produced as a byproduct of the kraft pulping process. A large fraction of this methanol is recovered in the foul condensate steam stripping system. The stripper off gas (SOG) is condensed to produce a crude methanol solution, which is upgraded to minimum 99.85 wt% in the methanol purification system (Figure 1). Methanol purification is based on the unit operation of distillation, including two separate stages. In the first "topping" stage, the compounds more volatile than methanol, such as H_2S and ammonia, are removed in the vapor phase while the methanol, water, and other less volatile compounds remain in the bottoms. In the second "rectification" stage, the purified methanol is recovered from near the top of the column while the water and other less volatile compounds are removed in the bottoms.

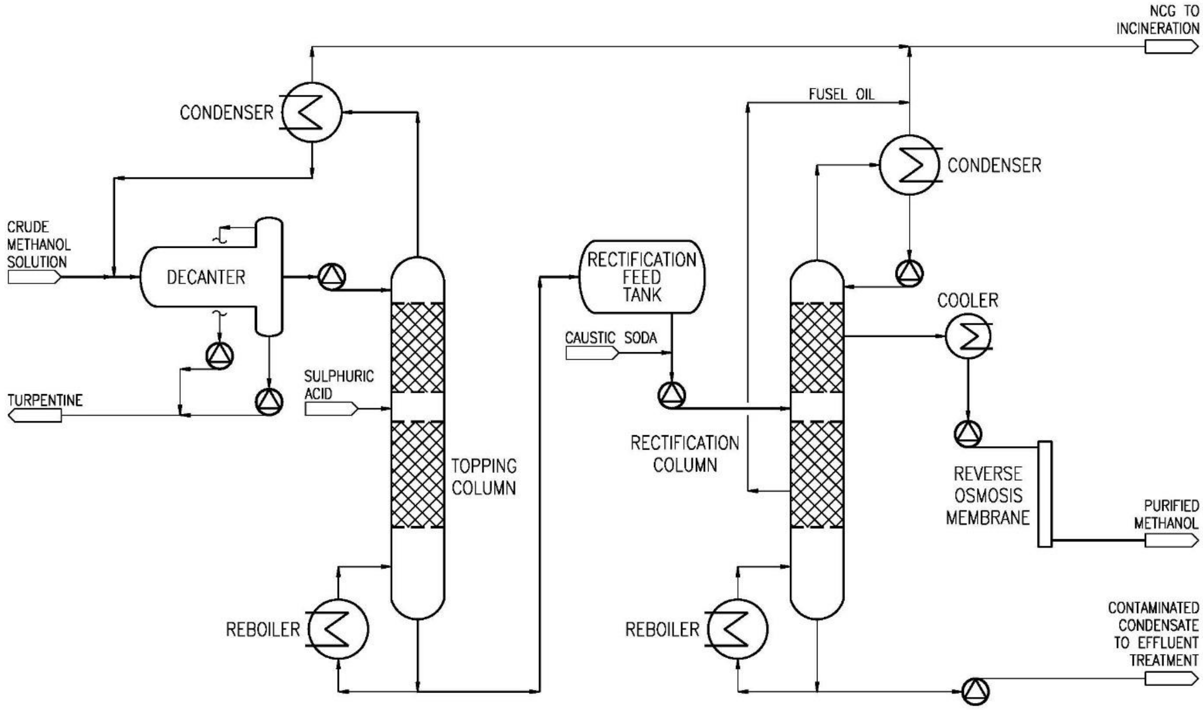

Figure 1. Methanol Purification System Process Flow Diagram [2].

There are numerous methanol purification systems in service around the world and their operation is well understood, but this process had not previously been applied to this feed stream. Recovery of methanol from kraft pulping condensates has several unique characteristics that inhibit separation by distillation:

- Azeotropes of methanol and organic contaminants
- Immiscibility of terpenes
- Dissociation of hydrogen sulphide and methyl mercaptan
- Ammonia reacting to produce ammonium sulphate (fouling)

Each of these issues are dealt with in today's designs for methanol purification plants.

4.5.4 Modular Construction

A Methanol Purification System can be constructed as conventional chemical plants or can be built and supplied in modular form (Figure 2). In the latter case, all equipment, inter-connecting piping, hand valves, instruments, control valves, insulation, and access stairways and ladders are supplied pre-assembled on steel skids. Figure 2 depicts a modular methanol purification system.

Figure 2. Methanol Purification System Modules [1].

4.5.5 Process Description

The presence of azeotropes between methanol and some organic contaminants require that the SOG generated in the stripping system be no higher than 40 wt% methanol to ensure separation of the contaminants in the topping system. Effective distillation requires a consistent feed stream; therefore, the SOG quantity as well as quality must be stable. In some cases, this requirement will necessitate upgrades to the stripping system.

The SOG is condensed and stored as a crude methanol solution. Typically about one hour of retention is recommended; this gives operational flexibility and provides volume to homogenize the feed flow to the methanol purification system.

Topping System

The crude feed solution is composed mainly of methanol and water, but it also contains over 150 different inorganic and organic "impurities" including various terpenes and aliphatic alcohols and ketones, along with many sulfur and nitrogen compounds. The topping column is designed to strip out the "low boilers" and noncondensibles, including the odorous total reduced sulfur (TRS) compounds, ammonia, and some ethers, ketones, and aldehydes.

The crude methanol solution is first introduced to the red oils (turpentine) decanter for separation and removal of terpenes. From there it is pumped to the top of the topping column, where it flows down through the packing countercurrent to the stripping steam, thereby driving off the volatile constituents to be removed from the less volatile constituents (methanol, water, etc.). Heat is added to the topping column via an integral bayonet type steam reboiler. The overhead vapors from the column are condensed in the topping reflux condenser with the heat recovered into cooling water. The low boilers and noncondensibles from the reflux condenser are vented to the NCG system while the reflux condensate is drained to the decanter.

Contaminants produced during the kraft pulping of wood include the ionisable sulfur compounds, hydrogen sulphide, and methyl mercaptan. The removal of these compounds by distillation is directly related to the pH of the liquid phase in the column. For example, at a pH above about 6, hydrogen sulfide begins to dissociate, and at a pH above about 9, this occurs with methyl mercaptan (Figure 3). In their dissociated form, these compounds do not exert a vapor pressure and therefore cannot be removed by distillation.

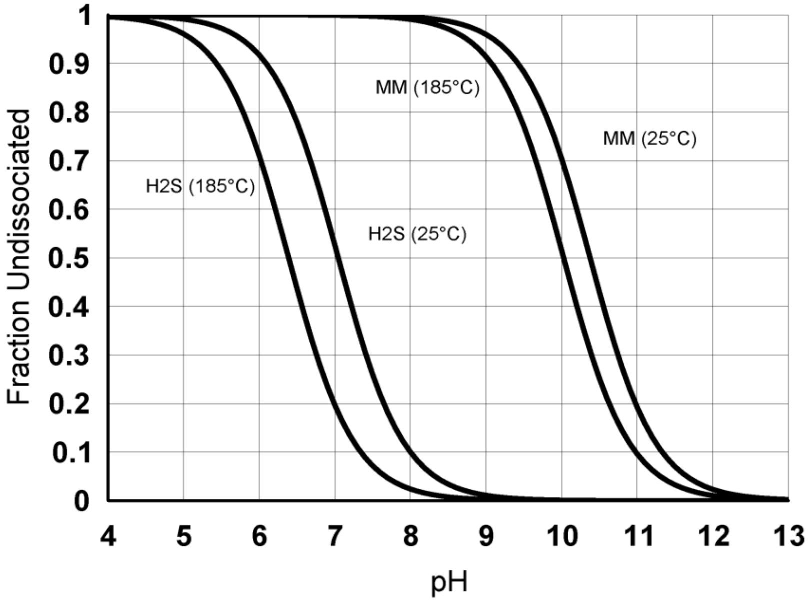

Figure 3. Dissociation of Hydrogen Sulphide and Methyl Mercaptan.

The pH of condensed SOG is typically slightly alkaline at about 9 to 10. To ensure that 4.175ionisable sulfur compounds are removed, sulfuric acid is added to the topping column. Due to the presence of ammonia, the acid cannot simply be added to the liquid feed to the column as it will react with ammonia and produce ammonium sulfate.

Ammonium sulfate is very soluble in water (about 0.7 kg dissolved per kg water at 25°C (77°F) and 1.0 kg per kg at 100°C (212°F)), but essentially insoluble in methanol. To ensure that no ammonium sulfate forms, potentially fouling the topping column, the sulfuric acid is added at the mid-point of the column; the top section of the column is therefore used to strip out the highly volatile ammonia before is has a chance to react with the acid.

Sufficient acid is added to lower the pH to between 5 and 6, thereby releasing the newly undissociated hydrogen sulfide and methyl mercaptan. They are stripped out in the bottom section and then must rise up through the top section of the column. These gases, when reabsorbed, are weak acids and will cause a slight decrease in the pH in the top section of the column, but no ammonium sulphate precipitate will form due to lack of any sulfate ions in solution.

Red Oils Decanting

Terpenes, naturally present in wood, are extracted during kraft pulping. Due to their extremely high relative volatility, they will be stripped from stock and liquor streams and collected in foul condensate. Those not decanted in the turpentine recovery system will make their way to the stripping system and subsequently into the SOG. The mixture of terpene compounds is referred to as turpentine, or crude sulphate turpentine, or, when heavily contaminated with TRS compounds, "red oils", due to their distinctive red hue. The terpenes are almost totally immiscible in the methanol solution; therefore a red oils decanter is required. If turpentine is disposed of through incineration, then the red oils can be pumped to the turpentine recovery system. If turpentine is sold, the red oils should be processed separately as their high TRS content will degrade the quality of regular turpentine.

Rectification System

The underflow from the topping column flows by gravity to the rectification feed tank. This tank is sized for one hour of retention; therefore, it provides operational flexibility by separating the topping system and rectification system processes. The tank also provides volume to homogenize the methanol solution feed flow to rectification.

The methanol solution from the feed tank is pumped to the rectification column and flows down through the stripping section countercurrent to the stripping steam, thereby driving off the volatile constituent (methanol) to be removed from the less volatile constituents (water, ethanol, etc). This column is designed to separate the water and other "high boilers" into the underflow, and methanol vapor into the overhead vapor flow. Heat is added to the rectification column via an integral bayonet type steam reboiler.

“Intermediate boilers,” those with boiling points between methanol and water and referred to as “fusel oils,” are drawn off from the bottoms column below the methanol solution introduction point. The fusel oils include some higher alcohols (primarily ethanol) and higher ketones (primarily methyl ethyl ketone). They are combined with the underflow from the column, but can in the future be recovered separately if desired. Typically a fusel oil flow sacrificing about 2% to 3% of the methanol must be bled off to ensure that the methanol product remains free of ethanol contamination. The contaminated condensate from the rectification column is pumped away to effluent treatment.

The vapor from the top of the stripping section passes up to the rectification section. Vapor from the top of the column is condensed in the rectification reflux condenser, with low boilers and noncondensables (not removed in the topping column) vented to the NCG system. The heat introduced by the reboiler steam is recovered into cooling water in the rectification reflux condenser. The reflux condensate is pumped back to the rectification column.

Methanol Product

The methanol product is drawn off slightly below the top of the column. The methanol is withdrawn in sufficient quantity to maintain the temperature profile (and therefore methanol concentration) in the column. The methanol is cooled and then pumped through a reverse osmosis (RO) membrane for final polishing. The 99.85 wt% methanol product is then directed to storage. If necessary, the methanol product can also be recycled back to the stripper feed tank, crude methanol tank, rectification feed tank, or disposed of through incineration in a boiler or the lime kiln.

Methanol at a purity level of 99.85 wt% can be worth over five times as much as a traded commodity than in crude form as a combustion fuel displacing light fuel oil or natural gas [3]. Typically about 30% to 40% of the methanol produced at a bleached kraft mill can be used internally for production of chlorine dioxide (ClO_2), with the balance for external sale.

4.5.6 References

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4.6 COLLECTING AND BURNING NONCONDENSIBLE GASES

Ben Lin, P.Eng.

In order to meet stringent air quality requirements in kraft pulp mills, it is necessary to collect noncondensible gases (NCG) containing volatile organic compounds (VOC) and total reduced sulfur (TRS) from various emission sources into one or several systems for disposal by chemical modification or incineration.

The VOCs typically in the highest concentrations include methanol and the terpenes while the TRS compounds most commonly encountered include hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide (CH_3SCH_3), and dimethyl disulfide (CH_3SSCH_3). These later compounds are noxious and have very low thresholds of odor detectability.

TRS are generated in pulp digesters when wood is cooked with kraft white liquor. TRS can also be generated in direct contact evaporators, turpentine systems, strippers, brown stock washers, liquor storage tanks, recovery boilers, and lime kilns. TRS gases that are emitted are contained in gases referred to as noncondensible gases.

NCG collection and treatment systems successfully contain and chemically convert the malodorous gases released during the operation of a kraft pulp mill. A well designed system will collect all odorous streams from the mill and deliver the gases to the point of treatment under controlled temperature and pressure conditions.

Attempts to collect and burn NCG were first tried in the late 1950's. The initial systems collected the gases in pipelines, using fans as motivators to transport the gases. These systems usually diluted the gases with air to bring the TRS concentrations below their lower explosive limits. This was not always successful, especially with concentrated gases coming from digesters and evaporators, and many early systems experienced fires or explosions.

In the early 1970's, a system was developed in Sweden that kept the NCG undiluted and that used steam ejectors as motivators. This system has virtually eliminated explosions in NCG systems and is now the accepted method for handling NCG.

NCG also contains other pollutants, such as turpentine and methanol, which are classified as Hazardous Air Pollutants (HAPs). Environmental Regulations also require the collection and destruction of HAPs.

The steam ejector based NCG systems have been so successful and reliable that the Environmental Regulations in the United States require all kraft mills to have NCG systems and to operate them at 99% uptime.

4.6.1 Composition of NCG

NCG can be broken down into four separate categories depending upon composition. These are: Concentrated NCG (low volume high concentration (LVHC)); Dilute NCG (high volume low concentration, (HVLC)); chip bin gases; and stripper off gases (SOG).

Table 1 shows a typical analysis for concentrated NCG. These gases come from blow heat recovery systems, turpentine recovery systems, continuous digester flash steam condensers, evaporator vacuum systems, and hotwells. The actual composition will vary widely from system to system and from time to time within the same system.

Table 1. Concentrated NCG Typical Analysis at Normal Operation

Source	TRS, vol%			O_2, vol%		
	Min	Avg	Max	Min	Avg	Max
Batch Digester	20	50	70	0.5	2.0	5.0

Continuous Digester	12	60	80	1.0	3.0	10.0
Turpentine (Batch)	0.1	2.0	10	4.0	12.0	20.0
Evaporator	1.0	60	70	1.0	5.0	8.0
Combined	10	50	65	2.0	3.0	6.0

Note: The balance of the gas is nitrogen.

It should be noted that in concentrated NCG, the TRS gases and HAPs make up only about 50% of the volume. The largest component of NCG is air, which has been depleted of 50% or more of its oxygen.

Although some air enters the system by dissolving in white and black liquors and then stripping back out of them, most air enters through leaks in the system. The oxygen is depleted by reacting with reducing agents, such as Na_2S, in the liquors that it contacts. The data shown in Table 1 are for a “tight” system.

4.6.2 Properties of NCG

Corrosivity

NCG, especially concentrated NCG, are highly corrosive to carbon steel. These gases are normally saturated with water vapor, such that condensation occurs in the collection system. Some of the TRS gases, especially H_2S and CH_3SH are acidic and will absorb in the condensate formed. The combination of this acidic condensate, along with the oxygen present in the NCG, can be very corrosive to carbon steel. Therefore, carbon steel should be avoided in NCG collection systems.

Other components of NCG, especially turpentine and methanol, are very strong solvents and can dissolve or soften plastics or resin in fiberglass reinforced plastic (FRP) piping.

Therefore, plastics or FRP should also be avoided in NCG collection systems. Furthermore, FRP should be avoided because of potential failure during a fire started by NCG ignition.

Stainless steel of the 300 series, typically 304 or 316, has proven to be corrosion resistant to NCG and is the preferred material of construction for NCG systems.

Toxicity

NCG are highly toxic and are responsible for deaths and injuries in the pulp and paper industry. The toxicity of hydrogen sulfide is well known. At 20 ppm it causes irritation of the eyes and respiratory tract. Thirty minutes of exposure at 500 ppm causes severe sickness. Exposure at 1000 ppm for 30 minutes is fatal. The other components of NCG are similarly toxic. TRS concentration in concentrated NCG is 100,000 ppm or greater.

Because these gases are toxic, great care must be taken in the design and construction of systems to handle these gases. Gas leaks, especially in enclosed areas, must be avoided. Adequate venting must also be provided, such that when there is an upset condition causing the gases to vent, the gases are released in a safe area and in a safe manner. Vent stacks should be as high as possible and clear of any buildings, platforms, and ladders where personnel may travel and well clear of any ventilation air intakes.

Explosivity

TRS, methanol, and turpentine are flammable in the presence of sufficient oxygen, and, if contained in a pipeline or vessel, can be explosive. Table 2 shows the combustion properties of the main components of NCG.

Table 2. Combustion Properties of NCG in Air

	Explosive Limits			
	Lower, Vol %	Upper, Vol %,	Flame Speed, ft/s (m/s)	Auto Ignition Temp, °F (°C)
H_2S	4.3	45.0		500 (260)
CH_3SH	3.9	21.8	1.8 (0.55)	
CH_3SCH_3	2.2	19.7		400 (206)
CH_3SSCH_3	1.1	8.0		572 (300)
α-pinene[a]	0.8	6.0	12 (3.7)	487 (253)
Methanol	6.7	36.5	1.5 (0.50)	867 (464)

[a]

[a] Source: Courty et al., 2012.

The Lower Explosive Limit (LEL) is the lowest concentration of gas by percent volume, that, when mixed with air, will burn. Below the LEL, there is an insufficient supply of combustible material to sustain combustion.

Similarly, the Upper Explosive Limit (UEL) is the highest concentration of gas, that, when mixed with air, will burn. At higher concentrations there is insufficient oxygen to sustain combustion.

Unfortunately, the terms LEL and UEL only explain the situation in theoretical terms. In reality, TRS gases, as emitted, are mixed with air that has most of its oxygen depleted such that the gases are not explosive. Figure 1 illustrates this situation.

It is based on some test data and the assumption that mixed TRS gases, which also contain other combustibles such as MeOH and turpentine, are flammable over the range of 2% to 50% for all combustibles. The exact shape of this curve has not been determined, and will vary depending on the TRS components present.

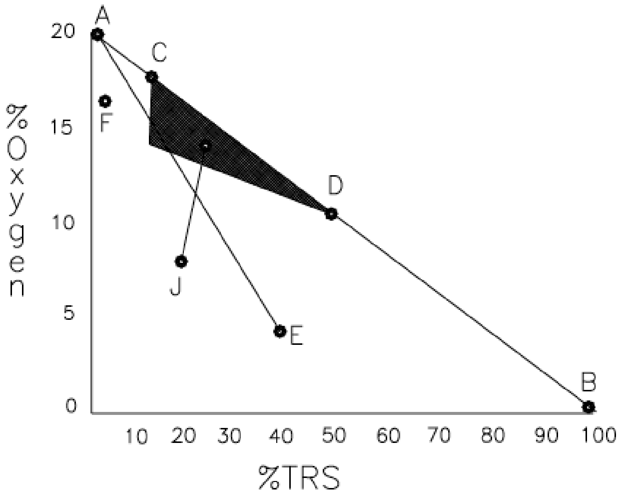

Figure 1. Explosive range of NCG.

Point A on Figure 1 is the pure air case with 21% oxygen and 0% combustible. Point B is the pure combustible case with 100% combustible and 0% oxygen. The two points, C and D, on line AB represent the LEL and UEL respectively.

The shaded area under CD represents the range of mixtures that are explosive. Point E represents a typical concentrated NCG mixture, which is well outside the explosive range. However, as air is added, the mixture moves along Line AE towards Point A. At some point, if enough air is added, the gases will enter the explosive range.

In the past, attempts were made to reduce concentrated NCG below the explosive limit by diluting by a factor of 20 to 1 with air. As a result the mixture ended up at Point F, which is outside the explosive range.

However, if the system was underdesigned-, or if an upset occurred which reduced this dilution ratio, the gases would end up in the explosive range. At this point, if an ignition source were present, such as a spark from a fan, then an explosion would occur.

The explosive range for the mixture of combustibles that make up NCG has been estimated to be 2% to 50%, but this will vary greatly from mill to mill, depending on the composition of the waste gases.

Another characteristic of flammable gases is flame propagation speed. This is a measure of how fast the flame will travel through the pipeline or vessel once a fire is started (Table 2).

The flame propagation speed for sulfur gases is relatively slow. However, the flame propagation speed for turpentine is fast. The value reported in Table 2 for turpentine was reported in 2012 and is currently being disputed by some experts in the field who claim the speed is much slower.

Regardless, explosions caused by TRS are usually minor, with minimum damage, while explosions caused by turpentine can be catastrophic.

It should be noted that the flame propagation speeds listed in Table 2 are based on pure compounds in pure air.

It should also be noted that while NCG systems are designed to handle the flame propagation speed of TRS, it is not practical to design against the flame propagation speed of turpentine. For this reason, it is very important to minimize the amount of turpentine entering the NCG system.

The auto ignition temperatures for the combustibles are as low as 206 °C, so care must be taken to ensure the NCG does not contact any surfaces above this temperature.

4.6.3 Ignition Sources

Before an explosion can occur, three things must be present. The first two, namely a combustible material (TRS) and sufficient oxygen, have already been discussed. The final item is an ignition source.

Fans have traditionally provided an ignition source for NCG system fires. This could be from static sparks, hot spots on the casing if rubbed by the impeller, a hot impeller shaft due to a bearing failure, or sparks created by foreign material hitting the impeller.

Another potential cause of fire is welding. Welding torches have ignited many NCG fires. Lines and vessels containing NCG should be clearly labeled so that they are not accidentally touched by welding flames or arcs.

If welding is necessary, all lines or vessels thought to contain NCG should be thoroughly purged and then checked for combustibles before welding is permitted. Care must also be taken to ensure that welding sparks are not drawn in through vacuum relief devices.

As TRS is known to adsorb onto and then desorb from metal walls, welding should be done immediately after purging and testing for combustibles.

Static electricity can also provide a spark to ignite NCG. All lines and vessels containing NCG must be properly grounded. Otherwise, a static charge may build up, eventually leading to a spark or static discharge. Several explosions have been traced to this mechanism.

Turpentine can provide a second mechanism for static discharge. If sufficient turpentine vapor enters an NCG system, such as during loss of water flow to a turpentine condenser, then some of that turpentine will condense in the piping along with the water vapor also present.

As water and turpentine are immiscible, they will decant in the pipeline. At this point, if the interface between the two immiscible liquids is subjected to a shear force, the friction between the two liquids can generate a static spark, which will ignite the turpentine.

Such a shear force can occur if these liquids enter a fan or if they cascade from a horizontal pipe run down a vertical pipe run. As before, several explosions have been credited to this mechanism.

4.6.4 Concentrated NCG (Low Volume High Concentration) Systems

Concentrated NCG come from two types of sources, continuous and batch. Continuous sources are:

- Continuous digesters
- Flash steam condensers
- Turpentine recovery systems
- Evaporator seal tank and vacuum systems
- Pressurized heavy liquor storage tanks
- Foul condensate storage tanks

- Stripping systems when operated in TRS mode only

Batch sources are:

- Digester relief condensing systems
- Blow heat recovery systems

The volumes of gases to be collected vary greatly from mill to mill and from time to time within each mill. Table 3 shows the expected ranges of concentrated NCG flow from various sources. It is always best to design on actual test data. If this is not available, then conservative values should be used. Line sizes should be chosen to give a low pressure drop (0.4 to 1.0 inches w.c. per 100 ft. of pipe) at peak flow conditions.

Table 3. Concentrated NCG Volumes

Source	Concentrated NCG Volume	
	ft^3/T Pulp	m^3/t Pulp
Batch Digester	100 - 200	2.6 - 5.2
Continuous Digester	150 - 300	3.9 - 7.7
Turpentine System (Batch)	40 - 80	1.0 - 2.0
Evaporators	50 - 200	1.3 - 5.2

Note: Volumes are actual at 60 °C (140 °F) and saturated with H_2O.

Collected NCG are typically at 60 °C (140 °F) or cooler. If the gases are hotter than this, then consideration should be given to cooling them before transporting them.

The concentrated NCG, Point E on Figure 1, are normally outside the explosive range due to lack of oxygen. Therefore, the system should be designed to prevent ingress of air into the system. This is done by sealing all parts of the system to make them airtight.

However, a sealed system can be exposed to high pressure or vacuum under upset conditions. Most storage tanks or evaporator hotwells are not designed to withstand pressure or vacuum. Therefore they must be protected by both pressure and vacuum relieving devices in order to prevent damage to the vessel during upset conditions.

Keeping the NCG outside the explosive range will insure a safe system at most times. However, during upset conditions, especially during start-ups and shutdowns, it is possible for air to enter the system, creating a potentially explosive mixture.

For this reason, it is necessary to eliminate all possible ignition sources during the design and operation of the system. Hence, steam ejectors, rather than fans, should be used to motivate the gases. The CNCG system collects the most concentrated emitters into a relatively small system. The design of the CNCG header incorporates a number of safety design features including use of steam ejectors, flame arresters, rupture disks, high gas velocities, sloping of lines in the direction of flow, and low point drains.

Since the vacuum that an ejector pulls varies inversely with gas flow, it is possible to pull a high vacuum under low flow conditions. In that case, a vacuum breaker could open, allowing air into the system. To overcome this problem, a pressure controller is used on the ejector suction.

Steam ejectors have other advantages. It is possible to size the ejector and the piping downstream of the ejector, such that the steam flow to the ejector insures a line velocity greater than the flame propagation speed of TRS gases, even under low NCG flow conditions.

It should be noted again that it is impractical to design against the flame propagation speed of turpentine. However, steam is an inert gas, and it is possible to design the ejector such that the steam flow will dilute the NCG to a point outside the explosive range.

If, for some reason the NCG coming to the ejector is in the explosive range, Point I, the steam flow will dilute the resulting steam-NCG mixture to Point J, which is outside the explosive range (Figure 1).

For the reasons discussed above, it is necessary to keep the steam in the system from condensing. This requires that all steam lines, and all NCG lines after the ejector be properly insulated to insure the steam does not condense.

If a condenser or scrubber is used after the ejector and the steam does condense, then some other means of ensuring line velocity and dilution should be provided. If not, then the NCG will burn back into the transport line whenever the gases get into the explosive range.

Even if care is taken to keep the gases outside the explosive range and remove ignition sources, there is still a remote possibility that a fire may occur.

To protect against this, flame arresters should be used at several points throughout the system in order to prevent the spread of a fire and to minimize pipeline and equipment damage. As a general rule, flame arresters should be placed at each NCG source and incineration point.

To prevent damage from an explosion in the NCG line, line size rupture discs have been used on the NCG line. Typically, rupture discs have been placed at approximately 100 ft. (30 m) intervals on extended NCG lines. Care must be used when placing the rupture discs to insure that the gases are vented in a safe location if a disc ruptures.

However, because the rupture discs are subject to mechanical failure due to fatigue rather than explosions, some mills are removing them and some new installations are built without rupture discs on the transport lines.

The collection of NCG from continuous sources is relatively straightforward (Figure 2). Care must be taken to insure that the vessels from which the gases are being collected are airtight and properly sealed. Each vessel should be protected by a pressure/vacuum breaker and by a flame arrester.

Special attention must be given to overflow lines on these vessels. Overflow lines must be sealed to insure that during an upset condition, pressure or vacuum is relieved through the pressure/vacuum breaker rather than through the overflow line.

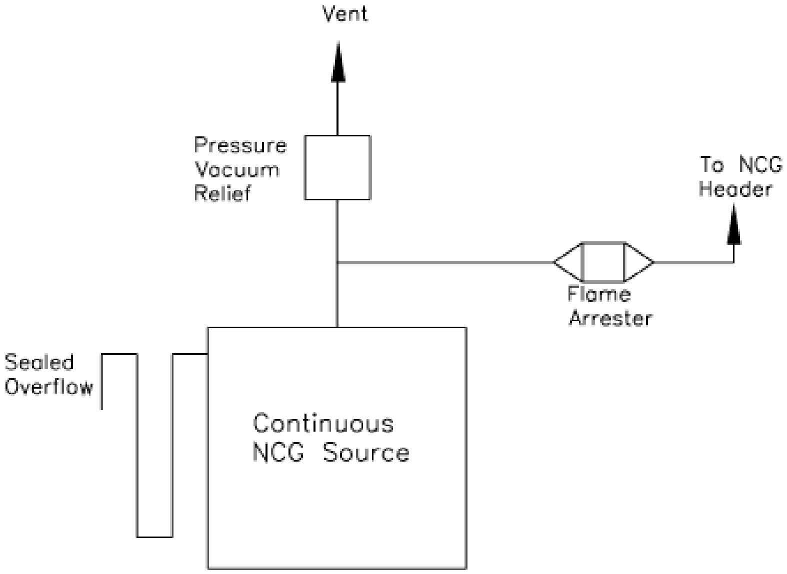

Figure 2. NCG Collection–Continuous source.

The collection of NCG from batch digesters is much more difficult due to the cyclical nature of the gas flow. Between blows, there is virtually no NCG flow. At the start of a blow, there is a momentary high flow. As the blow progresses, this flow drops off until it reaches zero flow at the end of the blow. In many cases, there is another small peak flow at the end of the blow when the digester blows clean.

In the past, these variations in flow were smoothed out using a gas holder of either a diaphragm or invertedbell- type. These gas holders were expensive to build and troublesome to maintain. In modern NCG systems, gas holders are no longer required except in rare situations.

Blow steam condensing systems should be operated under positive pressure at all times to prevent ingress of air into the system. If air gets into the accumulator and condensers, it becomes part of the NCG to be collected. The result is a very high NCG flow and a decrease in condenser efficiency at the start of the blow, invariably leading to venting of steam and NCG (Figure 3).

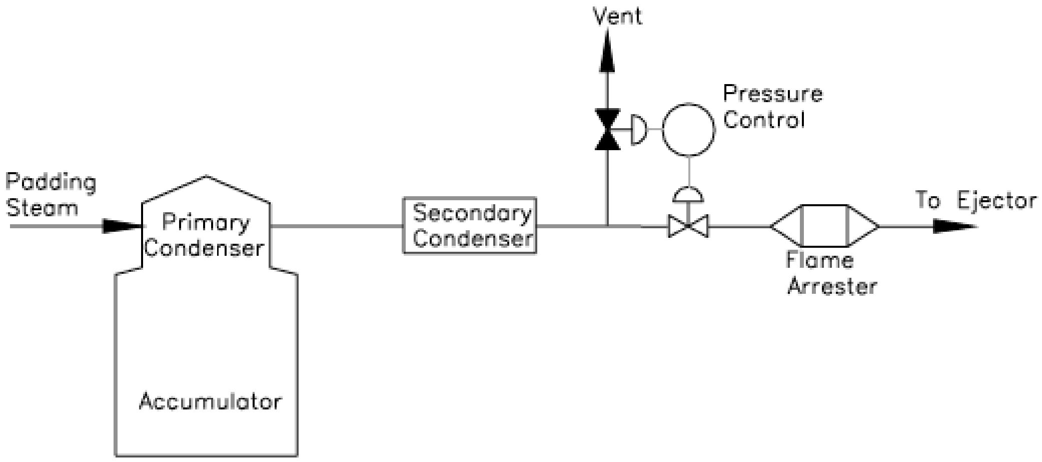

Figure 3. NCG Collection–Batch Gases.

Pressure is maintained in the system by use of pressure control on the NCG discharge line from the condensers or by pressure control between the primary and secondary condensers. More steam is also added to the accumulator, blow tank, or condensers between blows to keep the pressure and temperature up.

It is essential that the blow steam condensing system be properly sized and operated. If this is not done, very little NCG from the batch digesters will be collected.

Pressure relief is also required on the NCG line. This will prevent large quantities of steam from entering the NCG system and overloading the ejector system if the blow steam condensing system fails.

Batch gases must be kept separate from continuous NCG sources until it passes downstream of the ejectors. If this is not done, the pressure swings in the batch gas line will upset the smooth flow of the continuous gases, causing frequent venting of the continuous gases.

Figure 4 shows a concentrated NCG transport system.

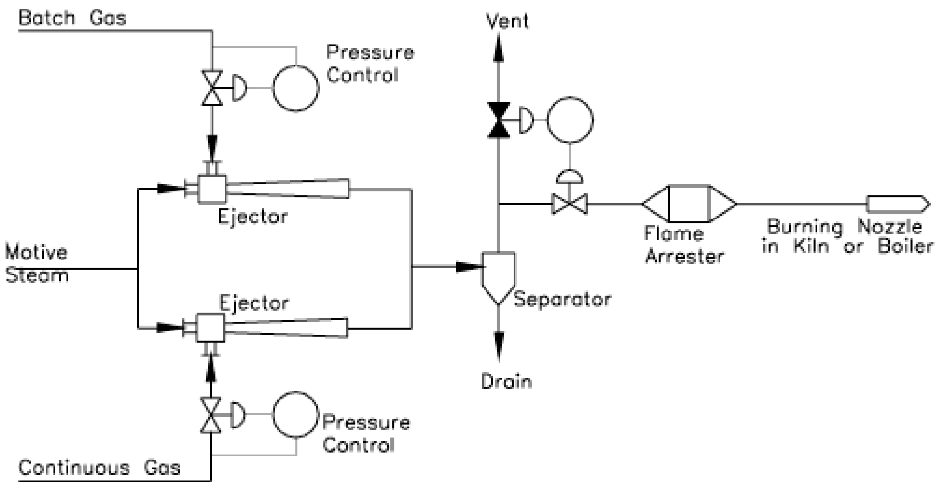

Figure 4. LVHC NCG Transport.

4.6.5 Piping Design and Layout

The flame speed of the combustibles is around 0.5 m/s; all NCG transport piping is designed for velocities greater than 5 m/s to ensure the flame at the incineration point cannot travel back through the piping. NCG piping design takes into account the volume of gases at each point of the system to ensure gas velocities will be above the flame propagation speed. Proper selection of gas velocities combined with mechanical safety devices and an extensive interlock system provide for safe operation of these systems.

Consideration in the design of NCG systems must be given to the condensates that form in the lines. The NCG are normally saturated with water vapor and some water will condense in the lines. Therefore, NCG piping is designed with a slope in the direction of flow to facilitate the removal of condensate and all low points have sealed drains to prevent plugging, foul condensate accumulation, and two phase bidirectional flow.

Sloping of NCG lines in the direction of flow is important to prevent condensate hang up, "black tar" accumulation, and pressure fluctuations in the system. Black tar is commonly found in CNCG lines. It is the result of the condensation and accumulation of pitches, resins, terpenes, and other organic material carried with the NCG.

Low point drains and separators are also required. The condensates formed are very foul and should be collected and treated.

Special attention needs to be paid to the layout and positioning of block valves at the incineration point on both the NCG lines and the steam purge lines.

Any condensate that collects behind these valves will be injected into the incineration device when the valve is opened. This condensate will be instantly vaporized when it gets into the incineration device and could result in a minor explosion, damaging the equipment.

Attention must also be paid to the condensate collection system. It must be designed so that it can never be pressurized. If it does become pressurized, condensate can be pumped back up the collection lines and into the incineration device, possibly leading to an explosion.

The motivating steam ejectors should be as close to the point of incineration as possible. A separator or mist eliminator is used after the ejector to remove any water droplets or condensate before the gases are injected into the incineration point.

The NCG then goes through a final flame arrester and into the kiln, boiler, or incinerator for destruction. If the kiln, boiler, or incinerator is not available for incineration, the gases should be safely vented upstream of the incineration point.

The final consideration is vent lines. From time to time it will be necessary to vent the gases to atmosphere. All vent lines should be made as high as possible and should release the gases straight up and away from buildings and platforms.

Vent lines should not terminate in elbows or have caps on the discharge. Water build-up in the vent line, due to rainfall or condensate, can be removed through sealed drain lines.

4.6.6 Scrubbing NCG

Some mills have found it advantageous to scrub the TRS from the NCG before the gases are burned. Scrubbing the TRS may be necessary to reduce SO_2 emissions if the NCG are burned in a boiler or an incinerator. In mills where NCG are burned in lime kilns, the

SO_2 formed may contribute to ring formation in the kiln. Scrubbing the NCG may alleviate this problem.

Scrubbing is normally done in packed columns or spray columns, using either a caustic solution or white liquor for scrubbing. The polar sulfur gases, H_2S and CH_3SH, are easily and almost totally removed from the NCG by a chemical reaction, while the non-polar gases, CH_3SCH_3 and CH_3SSCH_3, are not removed.

In most cases, hot white liquor is used for scrubbing. However, the NCG is heated up and must be sent to a gas cooler to reduce the gas volume and reduce condensation in the line following the scrubber.

To avoid the cooler, some mills have used cooled white liquor for scrubbing. However, the heat exchanger used to cool the white liquor is often subject to severe scaling.

There are also specialized chemicals on the market that are designed to scavenge the TRS from NCG. These have proven very effective. They have been successfully used as a backup for TRS reduction when incineration is not available. However, their high cost excludes their use on a continuous basis.

Depending on the scrubbing media used,and the NCG streams scrubbed, overall TRS removal efficiencies from as low as 40% to as high as 99% have been reported, although overall TRS removal of about 65% is typical.

4.6.7 Dilute NCG (High Volumne, Low Concentration) Systems

DNCG sources generally include:

- Diffusion washer
- Brown stock washer

- Knotter hood
- Screen hood
- Decker washer
- Black liquor oxidizer
- Soap skimmer
- Sewer vent
- Fiberline tankage: filtrate, stock, knot, screen feed, screen rejects, refiner feed
- Evaporation tankage: black liquor, spill, soap, tall oil
- Recovery tankage: precipitator mix and chemical ash mix tanks

Historically, sources from the lime kiln and causticizing areas were not collected due to low TRS concentrations, although it is becoming more common to include these in the DNCG system as there is typically some hydrogen sulphide present.

The recovery boiler smelt dissolving tank vent gases are a special source due to the high particulate loadings and are usually dealt with in a separate system. New or rebuilt recovery boilers usually include a venturi and cyclone, followed by a cooler, scrubber, fan and heater to treat these gases so they can be injected into the recovery boiler as combustion air.

As with concentrated NCG, the total volume of dilute NCG to be handled varies greatly. Flows of between 10,000 to 30,000 ft^3 per ton (300 to 900 m^3 /tonne) of pulp are typical.

Brown stock washer hoods on vacuum drum washers are the largest single source of dilute NCG. It is necessary to properly seal the washer hoods to the vats and to train operators to always keep the inspection doors closed. Suppliers are developing better fitting hoods to keep the washer hood gases to a minimum. Design volumes are now about 1000 ft^3/min (cfm) per drum.

Recirculating seal tank vents back to the washer hoods in order to reduce volumes has been successfully done. This reduces the volume to be collected here by about half.

Similarly, air for air doctors should be taken from the hood, thus recirculating this air and further reducing the volume.

Pressure washers and diffusion washers have much lower volumes of gas to handle.

Large, flat top storage tanks are another problem. In most cases, they were never designed to take any pressure or vacuum. When they are tied into a collection system, they will be subjected to either a pressure or a vacuum (or both from time to time). Safe design here is a real challenge.

Because NCG collection systems are designed to provide up to about 10 kPa (1.5 psia) draft, it is possible to expose source tankage to vacuums that are considerably higher than design. Additionally, the age and condition of the tankage must be considered. Tanks that were previously free to vent to atmosphere will be very confined. Confined vapor spaces in tanks are susceptible to vapor collapse either slowly through radiation loss or quickly through liquid spray. Vapor collapse will result in tank implosion.

To safeguard against tank collapse, high volume mechanical vacuum breakers are required at each tank not designed for full vacuum. Water sealed vacuum breakers have been used in these applications but are slower to respond due to their higher inertia. In addition, pressure relief devices are used to protect tankage from over pressurization where there is a possibility of freezing, thus plugging the overflow.

Gases in this category are normally outside the explosive range due to low concentration of TRS (see point F on Figure 1). Dilute NCG systems are normally designed to run at 25% of the LEL or less. Frequently they are diluted with air to ensure they are well below the LEL. Dilute NCG are normally collected and transported in a common pipeline, and motivated with a fan.

As with concentrated NCG, these gases are normally collected at 60 °C (140 °F) or cooler. In instances where dilute NCG are hot and saturated with moisture, coolers are used to reduce their volume and moisture before the fan.

Heaters can be used to raise the dilute NCG above the saturation temperature and thus dry them out. Generally, they are heated to a point where they are at 50% relative humidity. Having a dry gas is necessary if the gas will eventually go through mild steel equipment, such as forced draft fans, at the incineration point.

Under no circumstances should concentrated NCG be added to dilute NCG, especially a concentrated NCG stream that may contain considerable quantities of turpentine vapor.

As in the case of concentrated NCG systems, the pipelines for dilute NCG systems should be properly sloped and drained. A moisture separator should be installed upstream of the fan suction.

Many mills monitor the concentration of combustibles in the dilute NCG system to ensure that the gases are always well below the LEL. If the combustible concentration rises above 50% of the LEL during system upsets, then the system is vented or shut down until the problem is corrected.

A system for handling dilute NCG is depicted in Figure 5.

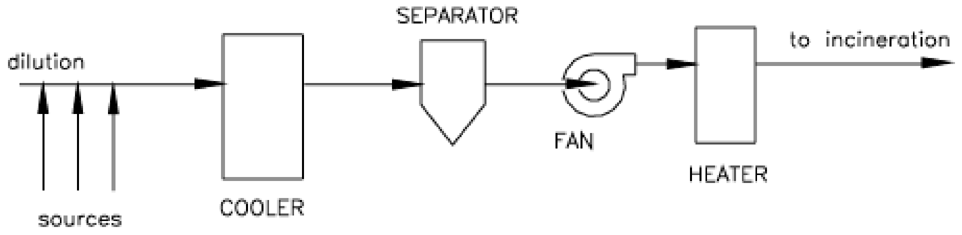

Figure 5. HVLC System.

4.6.8 Chip Bin Gas Systems

Chip bin NCG (and more recently ImpBin™ NCG) has historically been defined as a high volume, low concentration source and collected with other DNCG sources. The majority of the time, these gases are emitted as a dilute DNCG source, but it can at times, reach combustibles levels (turpentine and TRS) that are in the explosive range. Therefore, it is common to install a dedicated system for this source.

In the United States, the Environmental Regulations require the NCG from chip bins to be collected if flash steam is used for steaming. Collection is not required if fresh steam is used for steaming.

Collection of chip bin NCG is illustrated in Figure 6. Chips are steamed in the chip bin to remove air before they enter the steaming vessel. This steam can drive volatile compounds, such as turpenes, out of the chips. This situation is aggravated when too much steam is used, or if the steam breaks through the chips due to low chip bin level.

In any case, large quantities of turpentine vapor may be present in chip bin gas. One kraft mill in the southern United States that pulps pine has reported recovering up to 2 lb. of turpentine per ton (1kg/tonne) of pulp from chip bin gas.

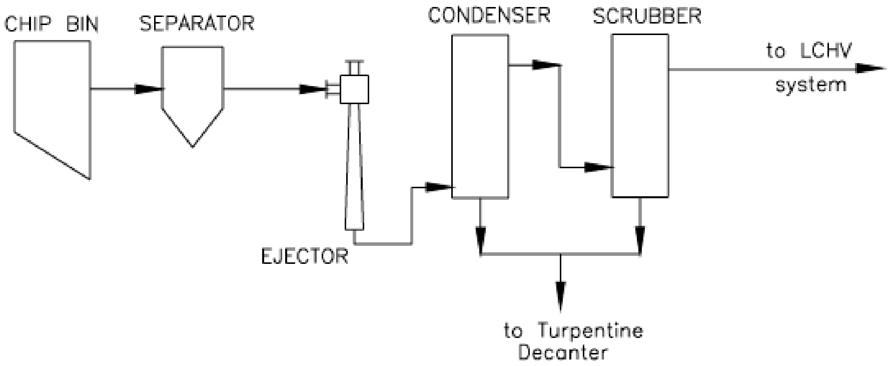

Figure 6. Chip Bin System.

The majority of time the chip bin gases are emitted as a dilute NCG source, i.e. essentially air with trace amounts of combustibles (TRS, methanol, etc); the combustibles originate from the low pressure feeder which is typically vented back to the chip bin. However, chip bin vents may also have momentary situations with high combustible concentrations; this may occur due to pockets of foul gas forming in the bin which then break through the chip pile causing a surge in flow and combustibles in the vent gases. This situation is exacerbated when contaminated steam from the extraction liquor flash tanks (a CNCG source) is used for pre-steaming.

In the case of softwood mills, the vent stream may also contain high turpentine vapor loadings due to stripping from the raw chips. In locations where a high proportion of softwood is used in the wood supply, turpentine liberated in the chip bin and carried out with the NCG becomes a safety concern if introduced into the main DNCG collection header.

The chip bin typically requires pressure and vacuum protection; fast acting mechanical type devices are the preferred technology. The vent gases from the chip bin are first passed through a cyclone separator to remove any entrained fibre; the cone of the cyclone is flushed with hot water or filtrate to prevent fibre hang-up. The gases are then passed through an indirect contact cooler, similar in design to the DNCG cooler, to cool and dehumidify the gases ahead of collection. For softwood mills, due to potentially high turpentine levels, a direct contact turpentine scrubber is included after the cooler.

Due to the transitory nature of chip bin NCG and because the concentration of combustibles in these gases can exceed the lower explosive limit (LEL), the design philosophy for collecting this source has been changing and the chip bin is now typically collected in a separate dedicated NCG system designed very similar to a CNCG system as described above; a steam ejector, moisture separator, flame arrester, and rupture disk are supplied for each incineration point.

The concerns over the transitory nature of chip bin NCG are exacerbated with the recent change in design where the chip bin and impregnation vessel have been combined into what is referred to as an ImpBin™. In this design, the hot extraction black liquor is flashed directly into the chips; therefore, the chance of introducing what is CNCG source (extraction liquor flash) into the ImpBin™ vent gases is exacerbated. For mills that include an ImpBin™, the installation of a dedicated ImpBin™ NCG system is mandatory.

Proper treatment of chip bin gas includes cooling, condensing, and scrubbing to remove as much turpentine as possible. A typical system will include a separator to remove chip fines, followed by an indirect cooler/condenser and a packed column scrubber using cold water.

At temperatures as low as 87 °F (30 °C) and atmospheric pressure, the vapor pressure of the alpha-pinene fraction of turpentine is high enough to create an explosive mixture. Therefore, dilution air must be added to ensure a safe mixture is being transported.

The use of cold water to recover turpentine can cause the temperature of the condensate going to the decanter to be too low for good decanting. In this case, it may be necessary to reheat the condensate before it goes to the decanter.

4.6.9 Stripper Off Gas (SOG) Systems

Some mills treat their odorous foul condensate in a steam stripping column, producing SOG, Stripper Off Gas. This effectively reduces the odour originating from downstream effluent treatment systems where the odorous compounds may be stripped out during aeration. In the case of a stripping system designed to target TRS removal only, the SOG consists mainly of noncondensables and is added to the CNCG collection system.

The steam stripping system can also be designed for removal of volatile condensables, mainly methanol, but also turpentine and other organics, to reduce the BOD, or Biological Oxygen Demand, loading to the effluent treatment system. The stripping column will then include a rectification system and a reflux condenser and use a higher steaming rate.

In most cases, the stripper off gas is removed as a mixture of 50% methanol and 50% water by weight at about 210 °F (99 °C). This stream, due to its high temperature and water content, must be transported separately in a concentrated NCG system (Figure 7). For a BOD stripper, the SOG cannot be added to the CNCG system and is transported to the incineration point in a separate dedicated system.

The stripper typically runs under pressure, so an ejector is not required for motivation. It is necessary to insulate and heat trace the gas line in order to prevent condensation.

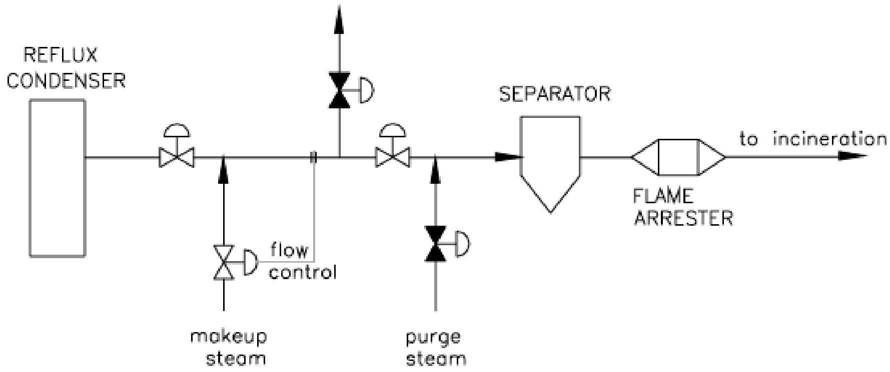

Figure 7. Stripper Gas System.

It is necessary to steam purge the entire line to remove all air before any methanol rich gas is introduced. This is done by a steam makeup line.

Steam is added at the stripper pressure control valve on flow control by measuring the flow at the incineration end of the line. This ensures a minimum velocity in the line during start-up, shutdown, and low flow conditions.

As an alternative to incineration of SOG as a gaseous stream, it can be passed through a condenser to produce a liquid methanol solution, referred to as SOL, Stripper Off Liquid. The SOL can then either be fired directly, or it can be passed through a second steam stripping column to rectify it up to 90+wt% methanol.

The SOL can then be used in the lime kiln displacing fossil fuel or as a support fuel when firing CNCG in the recovery boiler or dedicated incinerator. With installation of a methanol purification system, it is possible to produce grade "AA" (99.85%) methanol from SOG for use in CLO_2 production or for external sale.

4.6.10 Burning NCG

Several options are available to treat the NCG including incineration, scrubbing, biofiltration, gas phase oxidation, and adsorption. Unfortunately, other than incineration, no other alternatives have been shown to have high enough efficiency or reliability. That said, CNCG scrubbing is commonly used for pre-treatment ahead of incineration.

The most effective means of treating waste gases is by thermal oxidation. Minimum incineration temperatures in the combustion zone are required to achieve and maintain this oxidation, for kraft mills this temperature is typically 850°C. The incineration system thermally converts the organic vapors and TRS contained in the NCG to water vapor, carbon dioxide, and sulfur dioxide. Thermal oxidation of some of the substances requires turbulent mixing, which is accomplished through relatively high pressure drops, gas inlet design, and the overall geometry of the incineration device.

In order for the TRS and HAPs in NCG to be properly destroyed by combustion, three conditions must be met. These are:

- Temperature of 1600 °F (871 °C)
- Residence time of 0.75 sec.
- Excess oxygen (O_2) content of 3-4%

These should be considered basic conditions and if any of them are exceeded, the others can be reduced. That is, if the temperature is higher than 1600 °F (871 °C), then reducing retention time and/or lowering excess oxygen content will still provide good destruction. For example, some new, high efficiency kilns are capable of meeting TRS emissions at excess oxygen content as low as 2%.

Options for thermal oxidation in a kraft mill include the recovery boiler, power boiler, lime kiln, or a waste gas incinerator. The most popular disposal point for CNCG, SOG and SOL is incineration in the lime kiln, with incineration in the recovery boiler, power boiler and dedicated incinerator also practiced. DNCG has traditionally been fired in the power boiler, although recently the recovery boiler appears to have become the number one choice. Dedicated incinerators have also been used for DNCG treatment, but because these can be high in operating costs, they are more often used as a secondary disposal point.

Lime Kiln

The lime kiln has traditionally been the first choice for burning NCG. It has the advantage that most of the SO_2 formed is absorbed on the lime mud and returned to the liquor cycle.

In many mills, the lime kilns are overloaded and have low levels of excess O_2. An overloaded kiln is not very effective at TRS destruction.

Modern high efficiency kilns are designed to run at about 0.5% excess oxygen. This is normally not enough O_2 to completely destroy TRS.

CNCG can be fired in the lime kiln in a dedicated port on the main burner or preferably in a dedicated injection nozzle. This nozzle must be cooled in order to prevent pre-ignition of the gases while still in the nozzle. In addition, during NCG system shut down, with the kiln operating, the cooling jacket prevents heat damage to the nozzle.

Air, steam, and water have all been successfully used as cooling media. NCG can also be injected through a dedicated port in the main fuel burner of the kiln.

The dedicated firing gun has many advantages over burning in a main burner. The avoidance of burning the CNCG in a main burner allows the main fuel to burn more efficiently because the waste gases do not interfere by "grabbing" oxygen and starving the main flame. Also, it is important that any impurities contained in the waste gases do not have a chance to foul the main burner and result in fewer unscheduled shutdowns and less maintenance on the main burner.

SOL is burned in the lime kiln using a dedicated air or steam atomized injection nozzle. SOL is a heat contributor and will result in primary fuel savings.

When incinerating NCG in the kiln, a large fraction of the SO_2 formed in the burning of NCG is expected to be absorbed in the reburned lime as calcium sulphate. The remaining SO_2 passes to the primary dust chamber and scrubber where SO_2 can also be absorbed.

Kiln ringing, balling, and dusting can be minimized by maintaining high mud solids of at least 70% and minimizing soda content in the mud. Removal of TRS by upstream alkaline absorption, such as scrubbing with white liquor, is also helpful. Since SO_2 will acidify the lime mud at the back of the kiln, it is important to ensure that the lime mud is well washed and the sulphides removed; acidification will result in the formation of H_2S and this will be seen in the lime kiln vent flue gases.

The dilute NCG are not normally burned in the lime kiln due to their large volume. If burned in the kiln, they are used as primary air and introduced either on the suction or discharge of the forced draft (F.D.) fan. However, in most cases, the volume of dilute NCG is larger than the kiln primary air flow, and thus the kiln cannot be used.

Power Boilers

Firing of CNCG, DNCG, Chip Bin NCG, and SOG or SOL in the power boiler is being done at many mills around the world. In the case of DNCG, the flow added to the power boiler effectively displaces normal combustion air requirements. Similar to the recovery boiler and unlike kiln or incinerator burning however, the heat generated during firing is not wasted but is recovered as steam.

Boiler incineration of NCG will probably not reduce boiler natural gas requirements. Because of the additional moisture introduced with the NCG, fuel consumption may in fact increase. However, those NCG sources with relatively high TRS/organic contents will be net heat contributors.

In order to avoid TRS leakage into the boiler area, the point of NCG entry must be carefully selected. CNCG, Chip Bin NCG, and SOG is typically fired through dedicated injection nozzles located near the fossil fuel burners while possible admission points for DNCG include the natural gas burners, under/over grate plenums, or directly through the boiler wall. Admission points may be a combination of one or more of these alternatives.

The NCG flow may be split into two or more parallel lines before entering the boiler. This is done to balance the flow of NCG into the boiler. However, if this is done, great care must be taken to ensure a balance of flow to each nozzle in order to prevent flame backs due to low gas velocity on one side.

Ideally, the preferred entry point should be into an area of high temperature and turbulence in the boiler. Because of the huge volumes of boilers, residence times are not an issue and are expected to be far in excess of the standard 0.75 to one second residence time.

For DNCG, the use of natural gas burners as an admission point will typically require either adding one or more new units as required or replacing the existing natural gas burners. The new gas burners would be equal to the existing units except they would use DNCG for combustion air. Since this method would require continuous consumption of natural gas, operating costs may be high unless the boiler is operated with one burner on natural gas at all times.

The use of grate plenums for DNCG entry is practiced by most mills. Since the existing air ducts are not air tight and are therefore susceptible to leakage, modifications must be made to ducting to seal all joints tight. DNCG leakage of even small quantities will produce an odour nuisance in the local area.

The small quantities of TRS gases are converted to sulfur dioxide as byproduct. The SO_2 is lost in the flue gas and cannot be economically recovered. Provided the prevailing flue gas temperatures are kept above the "acid condensation" temperature of about 150 °C, the additional sulfur dioxide loading in the flue gas is not expected to affect corrosion rates in the boiler. However, in situations where flue gas scrubbing or heat recovery is practiced, the additional sulfur dioxide will cause a drop in the prevailing pH. In these specific cases, accelerated corrosion in the stack may be quite pronounced.

Studies have shown that considerable amounts of SO_2 are absorbed on the ash from coal or bark if either of these fuels are used in the boiler. This can reduce the SO_2 emitted from the burning of NCG.

Recovery Boilers

The recovery boiler is theoretically the best place to destroy NCG, as the sulfur gases are destroyed and recovered as Na_2S in the smelt.

However, due to the nature of the recovery boiler, its importance in the recovery cycle, and the potential for catastrophic explosion due to water entering the unit during operation or explosive gas build-up during shut down, the recovery boiler is generally not used as a place to burn NCG.

The Black Liquor Recovery Boiler Advisory Committee (BLRBAC) has recently published “Recommended Good Practice for the Thermal Oxidation of Waste Streams in a Black Liquor Recovery Boiler”. It is available on the BLRBAC Website, www.blrbac.com.

New mills are burning concentrated NCG in recovery boilers successfully. With respect to dilute NCG, several mills are now doing this and there is a trend towards accepting this practice.

DNCG consists of 99+% air and therefore simply displaces combustion air in a boiler. It is typically introduced to a recovery boiler at the secondary air level, displacing combustion air volume supplied by the secondary air fan. It can also be introduced at the tertiary air level, but the available volume to be displaced is lower and the potential to recover the sulfur into the smelt bed is reduced, instead venting with the flue gases as sulfur dioxide.

For DNCG incineration in recovery or power boilers, the DNCG must not simply be added into an existing air manifold and mixed with combustion air. Instead it must be introduced directly into the combustion chamber. This typically takes the form of multiple nozzles at dedicated ports or penetrating the manifold.

Incinerators

A special dedicated incinerator is a proven and reliable method for disposal of NCG gases. Despite its potentially high capital and operating costs, the incinerator has become more popular, primarily because it is independent of other operating equipment. The incinerator has a virtually unlimited turndown capability, being able to burn various waste sources in any flow range from almost zero to one hundred percent.

The dedicated incinerator consists of a cylindrically shaped, horizontal or vertical vessel made of refractory lined steel. The design of the vessel is to provide efficient gas mixing with sufficient retention time.

The incinerator is typically sized to handle malodorous gases from the CNCG, Chip Bin NCG and DNCG collection systems, SOG or SOL from the foul condensate stripping system, and crude sulphate turpentine (CST) from the turpentine recovery system. CNCG and SOG are admitted through dedicated ports in the auxiliary burner, while SOL and turpentine are introduced through dedicated air or steam atomizing nozzles. To maximize efficiency, DNCG is used as primary combustion air for the auxiliary burner, with the balance introduced into the main chamber.

Waste Heat Boiler

If DNCG is burned alone, fossil fuel requirements can be extremely high and heat recovery can be practiced to minimize usage. If the incinerator is to be used for a backup incineration point, then heat recovery equipment is typically not installed. The two main types of heat recovery are DNCG preheating using the flue gases or steam production via a waste heat boiler.

For DNCG preheating, the DNCG is passed through a heat exchanger in counterflow to the hot flue gases. Care must be taken to ensure the flue gases are not cooled to below the acid dew point or corrosion will become a concern. The acid dew point is typically about 150°C, so the flue gases are cooled to no less than 200°C. For an incinerator operating at 850°C, the DNCG can be preheated up to about 600°C.

For steam production the hot flue gases are directed to a fire-tube waste heat boiler. The boiler is typically a horizontal shell and tube heat exchanger with the hot flue gases passing through the tubes. Again it is imperative that the flue gases from the heat exchanger remain above the acid dew point temperature. Boiler feed water is fed to the shell side and the steam produced rises to a steam drum located above the boiler. Heat recovery is limited to about 80% with the recovered heat in the form of 400 kPa(g) (58 psig) steam.

Other mills have installed incinerators without heat recovery and use this system as a backup to the power or recovery boiler. Fossil fuel requirements are high when the system is in use, but with good availability of the main incineration point, the occasional use of the incinerator with its high fuel consumption is not a concern.

Incinerator Flue Gas Conditioning

Once the flue gas leaves the incinerator or heat recovery equipment, it is either vented or cooled and scrubbed for SO_2. Available methods of flue gas conditioning include air quenching, water quenching, alkaline absorption, and water absorption.

Typically, the vent gases exiting the incinerator are scrubbed for removal of SO_2. Before scrubbing, the temperature of the vent gases is lowered by direct contact of water with the gases in a spray type cooler, or quench vessel. The vent gases first pass through a venturi throat section that promotes turbulence and mixing with water spray from several nozzles. The gases then flow to the main section of the quench vessel where they are sprayed with water once again. From here, the cooled gases flow to the absorption tower for scrubbing of the SO_2.

The absorption tower can be a spray type or a packed type tower using an alkaline solution for scrubbing of SO_2. Alkaline solutions successfully used include caustic soda, sodium carbonate, oxidized white liquor, and oxidized green liquor. Scrubbing of SO_2 with caustic provides 99+% reaction efficiency of SO_2 producing sodium sulfite and bisulfite as well as Na_2SO_3 and $NaHSO_3$.

Another byproduct of incineration is sulfuric acid mist (SAM), which can give high opacity. Some mills have added devices, such as Candle Mist Eliminators, to reduce SAM.

Stripper off gas, due to its high MeOH content, has a very high fuel value and can be used as a primary fuel for incinerators, reducing the incinerator operating cost by supplying most of the fuel requirement.

However, SOG also contains ammonia, which can give high NOx emissions from incinerators.

In some cases, if the incinerator combustion air flow is greater than the dilute NCG flow, it is possible to burn the dilute NCG in the incinerator. However, this is not normally done.

Regenerative Thermal Oxidizers

Regenerative Thermal Oxidizers (RTO) are viable devices for incinerating dilute NCG as they generally have much lower installation costs than other incineration alternatives. They also have very low operating costs and very high uptime.

Several mills are successfully using RTOs to incinerate dilute NCG. The RTOs provide 95% thermal efficiency and provides the added benefit of locating the unit in the same area as the DNCG sources, thereby saving long runs of large diameter ducting and overall installation cost.

Other Considerations

Several other factors affect the choice of an incineration point for NCG. These are usually site specific. The age, size, and operating condition of the locations available are important.

As a general rule, higher capacity of a selected location is better as the NCG will have less impact on the operation of the larger equipment.

The uptime of the equipment used to burn NCG is very important. A boiler or kiln that is off line frequently, or for long periods of time, is a poor choice. The Environmental Regulations in the United States require an uptime of 99% for burning concentrated

NCG. It is virtually impossible to do this unless there are two points for NCG incineration.

The relative locations of the NCG sources and the point of incineration is also important as this affects the length, and hence the cost, of the pipe line required to carry the gases. Generally, shorter piping runs are advantageous.

A final factor to consider is human nature. Few operating superintendents are willing to accept the responsibility of handling and burning NCG.

4.6.11 Impact

Installation and operation of NCG systems has an impact on the rest of the mill operation. The largest impact usually comes from the digester blow heat recovery system.

It is necessary for the blow heat system to collect and condense all the blow steam. Consequently, steam and methanol that was previously vented are now recovered as hot foul condensates. The recovered heat must be reused or discarded.

Many mills are now using recovered blow heat to pre-evaporate black liquor, while others install cooling towers to get rid of it. Also, the methanol collected can increase the B.O.D. load to the effluent treatment system, forcing mills to add aeration capacity or install foul condensate strippers.

Capturing and burning the reduced sulfur gases in the kiln, or scrubbing the SO_2 formed with white liquor, will increase the liquor sulfidity. This may upset the mill sulfur balance, necessitating a change in mill makeup chemicals away from saltcake and toward caustic soda or sodium carbonate.

There is a new process available that will convert the TRS in NCG directly to sulfuric acid, which can be used to cut tall oil. This will help the overall mill sulfur balance.

It may be necessary to update and improve the operations of the turpentine recovery system and multiple effect evaporators in order to make them compatible for NCG collection. For instance, the practice of bleeding air into the evaporator vacuum system in order to control vacuum is not acceptable with NCG collection.

Finally, places where NCG are burned can no longer be looked upon as production devices only. They must also be considered pollution control devices. It is not uncommon for a mill to run a kiln or a boiler strictly for the purpose of burning NCG, even when the production capacity is not needed.

4.6.12 Conclusion

In order to reduce odorous and hazardous air pollutants from kraft pulp mills, environmental regulations require that noncondensible gases containing TRS and HAPs be collected and incinerated. These gases are very corrosive, highly toxic, and if mixed with air, potentially explosive.

Consequently, great care must be taken in the design, construction, operation, and maintenance of these systems. Fortunately, the technology exists to build NCG systems that are safe, efficient, and reliable.

4.6.13 Acknowledgements

This paper was originally authored by Mr. Tom Burgess. He had been the instructor for the TAPPI Kraft Recovery Short course since 1986 before retiring in 2005.

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5 PROPERTIES RELEVANT TO EVAPORATION

W. J. Frederick

5.1 INTRODUCTION TO BLACK LIQUOR PROPERTIES

The chemical, thermal, and transport properties of black liquor directly affect the design and operation of black liquor evaporators and concentrators [1]. The properties of interest include viscosity, boiling point rise, heat capacity, surface tension, inorganic solubility, density, and thermal conductivity. Knowledge of these properties is needed to assess accurately the flow and heat transfer characteristics of black liquor. The chemical characteristics of black liquor that can influence these properties include its elemental composition, the composition of its organic and inorganic components, its residual alkali content, and the molecular weight of the organic matter that it contains.

Black liquor is a complex mixture of water, inorganic chemicals, and organic matter. Each of these components plays an important role in determining its chemical characteristics and physical properties. One of the challenges in developing broadly applicable descriptions of the properties of black liquor is that a wide range of wood species and pulping conditions are used to produce paper making fiber. Both the wood species and pulping conditions influence the relative amounts of organic and inorganic constituents in black liquor as well as the composition and molecular weight of the organic matter. Some properties of black liquor (e.g., heat capacity and density) depend on the nominal composition of the black liquor solids. These properties differ from mill to mill, but they are related directly to the charge of chemicals used in pulping or the yield and Kappa number of the pulp. Others, such as viscosity, depend on the wood species and the pulping conditions. They cannot be predicted as easily.

Another factor that impacts the chemistry and properties of black liquor in bleached kraft mills is the use of bleach plant filtrates in brownstock washing. The dissolved organic solids from oxygen delignification or alkaline extraction stages are partially oxidized compared with the organic matter in kraft black liquor. The inorganic matter contains little sulfur and may contain more chloride than kraft black liquor solids. The use of these filtrates in brownstock washing impacts the composition of the resulting black liquor and its properties.

One purpose of this chapter is to provide an understanding of how the chemical characteristics and physical properties of black liquor depend upon wood species and process conditions. The second purpose is to present the best available methods currently available for estimating these properties for process calculations.

5.2 CHEMICAL COMPOSITION OF BLACK LIQUOR

Kraft black liquor is the spent liquor from pulping of wood or other biomass with aqueous solutions of NaOH and Na_2S. It contains dissolved components from biomass, along with the spent inorganic chemicals from pulping, and water. It is the chemical composition of black liquor and the nature of the dissolved organic matter from wood that determines its physical and transport properties.

5.2.1 Black Liquor Composition

Wood contains mainly polysaccharides (cellulose and hemicellulose) and lignin, but also extractives and inorganic species. It is the larger molecules of lignin and hemicellulose extracted during pulping that play a dominant role in black liquor viscosity. The data in Table 1 are typical compositions for softwood and hardwood species in different regions of the world. Polysaccharides are the largest group of components in all wood species. Softwood species always contain more lignin than do hardwood species. Extractives, while present as minor constituents, account for 2% to 5% of most wood species.

Table 1. Lignin, Cellulose, Hemicellulose, and Extractives Content of Wood Species used for Pulp Manufacture. Values are normalized to 100% on a dry, ash-free basis [2].

Northern Softwoods

Wood species	Lignin wt%	Cellulose wt%	Hemicellulose wt%	Extractives wt%
Balsam fir	29.4	39.2	28.8	2.7
Douglas fir	29.4	38.9	26.4	5.3
Eastern hemlock	30.7	37.9	28.0	3.4
Monterey pine	27.3	37.6	33.3	1.8
Scots pine	27.8	40.1	28.6	3.5
Norway spruce	27.6	42.1	28.6	1.7
White spruce	27.6	39.6	30.7	2.1

Northern Hardwoods

Wood species	Lignin wt%	Cellulose wt%	Hemicellulose wt%	Extractives wt%
Red maple	25.5	42.2	29.0	3.2
Sugar maple	25.4	41.0	31.0	2.5
Common beech	25.1	39.9	33.7	1.2
Silver birch	22.3	41.6	32.9	3.2
Paper birch	21.9	40.2	35.2	2.7
Gray alder	25.2	38.8	31.3	4.7

Eucalyptus and Acacia

Wood species	Lignin wt%	Cellulose wt%	Hemicellulose wt%	Extractives wt%
Eucalyptus camaldulensis (River red gum)	31.8	45.8	19.5	2.8
Eucalyptus globulus (Blue gum)	22.0	51.5	25.3	1.3
Gmelinaarborea (Yemane)	26.3	47.7	21.3	4.6
Acacia Mollissima (Black wattle)	21.0	43.3	33.9	1.8

Lignin and cellulose are natural polymers, or macromolecules. In wood, lignin consists of a 3-dimensional, cross-linked network comprised mainly of phenylpropane monomer units connected by ether linkages or carbon-carbon bonds. By contrast, cellulose is a linear, crystalline polymer composed of cellobiose units. Hemicelluloses are more diverse in composition. They are composed of different five- and six-carbon sugars, particularly of glucose, mannose, xylose, rhamnose, and uronic acids.

During kraft pulping, the alkali and sulfide present in white liquor attack the lignin and polysaccharides in wood, reducing their molecular size and rendering them soluble. Fragmentation of lignin is by cleavage of both α- and β- aryl ether linkages, the predominant linkages in both hardwood and softwood lignins [3]. Both the hydroxide and hydrosulfide ions in kraft white liquor contribute to lignin degradation. Polysaccharides, on the other hand, are attacked only by the hydroxide ions. The main reactions of the polysaccharides are removal of the acetyl groups in hemicelluloses to form acetic acid, "peeling" or sequential loss of sugar units and their conversion to a mixture of hydroxy acids, random cleavage of the main polysaccharide chain, and removal of methoxyl and other groups from xylans. Tall oil and other extractives may be saponified, but are extracted without reacting further with alkali or hydrosulfide ion.

Most of the alkali in white liquor consumed in pulping is consumed in neutralizing the acidic phenolic groups in lignin and its degradation products, the organic acids formed from the polysaccharides, and the fatty and resin acids. Black liquor consists of the dissolved organic matter, dissolved cooking chemicals, and dissolved inorganic matter from the wood or impurities in the white liquor.

White liquor contains smaller amounts of sodium sulfate (Na_2SO_4), sodium thiosulfate ($Na_2S_2O_3$), sodium carbonate (Na_2CO_3), and sodium chloride (NaCl) in addition to NaOH and Na_2S. During pulping, much of the Na_2S is oxidized to $Na_2S_2O_3$, and most of the NaOH is consumed in neutralization of organic acids. The resulting inorganic salts and the sodium associated with the organic anions comprise most of the inorganic part of black liquor.

The range of heating values and elemental composition of kraft black liquors from northern hardwood and softwood species and Brazilian eucalyptus are shown in Table 2.

Table 2. Heating values and elemental composition of black liquor from pulping of five different groups of wood species, presented as averages and standard deviations [4]. The numbers in parentheses for each different group of wood species indicate the number of black liquors analyzed.

		HHV	S	C	Na	K	Cl	H	N
		MJ/kg ds	wt% dry solids						
	Average	14.09	4.65	34.36	19.45	2	0.38	3.46	0.102

Northern softwood (149)*	St. Dev.	0.69	0.91	1.91	1.57	0.92	0.23	0.23	0.041
Northern hardwood (25)	Average	13.4	4.02	33.48	19.12	2.2	0.43	3.45	0.135
	St. Dev.	0.68	0.81	1.48	1.79	0.93	0.19	0.34	0.043
Birch (36)	Average	13.38	5.23	32.3	20.47	2.17	0.38	3.35	0.131
	St. Dev.	0.64	0.95	1.43	1.43	0.63	0.24	0.18	0.047
Eucalyptus (91)	Average	14.17	4.16	34.61	19.04	2.09	0.82	3.27	0.171
	St. Dev.	0.83	1.04	1.98	1.85	1.5	0.68	0.23	0.092
Mixed tropical woods (21)	Average	14.02	3.63	35.08	19.75	2.62	1.04	3.51	0.153
	St. Dev.	0.86	0.62	2.07	2.2	1.72	0.74	0.25	0.048

*Number of black liquors analyzed for each wood category.

Acid-Base Behavior of Black Liquor

Black liquor contains several chemical species that act as buffers and influence its pH. These include:

- Sodium sulfide, which buffers the pH according to the equilibrium

$$Na_2S + H_2O \Leftrightarrow NaHS + NaOH, \quad pK = 13 - 13.5 \qquad (1)$$

- Phenolate groups on lignin, which buffer the pH according to the equilibrium

$$R\text{-}OH + NaOH \Leftrightarrow R\text{-}ONa + H_2O, \quad pK = 9.4 - 10.8 \qquad (2)$$

- Sodium carbonate, which buffers the pH according to the equilibrium

$$Na_2CO_3 + H_2O \Leftrightarrow NaHCO_3 + NaOH, \quad pK = 10.2 \qquad (3)$$

Because of these buffers, the residual alkali content of black liquor cannot be measured by direct acid-base titration. SCAN test procedures SCAN-N 33:94 and SCAN-N 31:94 are used for measuring the residual active and effective alkali content in black liquor. The residual active alkali is defined as the sum of the concentrations of hydroxide and hydrosulfide ions in black liquor, while the residual effective alkali is the hydroxide ion concentration.

5.2.2 Molecular Size and Conformation of Kraft Lignin and Polysaccharides

The size and shape of large molecules in black liquor play a dominant role in its viscosity. The weight average molecular weight of alkali lignin in black liquor is typically 10,000 to 50,000, while the number average molecular weight range is 1,000 to 5,000. These values reflect the broad distribution of molecular weights, from a few hundred to over 100,000. Over 20% of the alkali lignin in kraft black liquor can have a number average molecular weight greater than 5,000; up to 10% can be greater than 10,000. Softwood kraft black liquors contain more of the high molecular weight alkali lignin than do hardwood liquors.

The conformation and apparent size of kraft lignin molecules changes with pH. At a pH of 12.5 or higher, the phenolate moieties of alkali lignin are completely ionized and the alkali lignin molecules are soluble. In solution, they assume a compact, spherical shape. At a pH below 12.5, the phenolate groups are not completely ionized and the alkali lignin molecules are less soluble. The lignin molecules associate with each other, forming larger alkali lignin structures that behave as molecules of higher molecular weight. At pHs substantially below 11.5, alkali lignin precipitates from solution.

Polysaccharides behave quite differently from alkali lignin in black liquor. They tend to form loose, expanded random coils. The volume encompassed by polysaccharide molecules is much greater than that of lignin molecules of the same molecular weight. In the pH range normally encountered with black liquor, the polysaccharide molecules can entangle with a number of lignin and other polysaccharide molecules. By doing so, they can have a greater influence on the viscosity of black liquor than would be expected based on their molecular weight alone. This effect is more pronounced with hardwood kraft liquors, which have higher polysaccharide content than do softwood kraft liquors.

5.2.3 Extractives

The extractives in black liquor include phytosterols and saponified resin and fatty acids [2]. These extractives are removed from black liquor as crude soap as black liquor is concentrated. The saponified acids are converted to resin and fatty acids when the tall oil soap is acidulated.

Resin acids: These are tricyclic terpenoids, some of which are shown in Figure 1. They are extracted from wood during alkaline pulping.

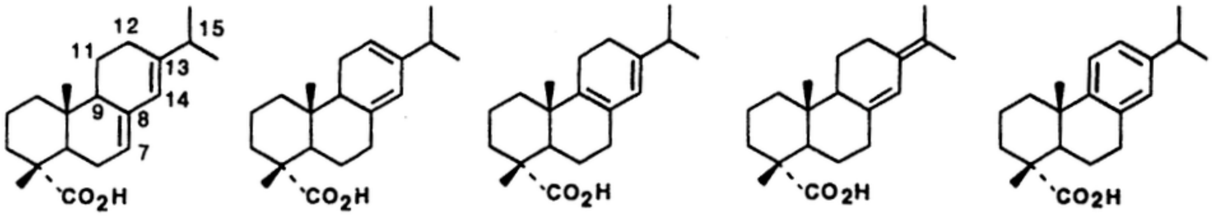

Figure 1. Common tricyclic resin acids from wood. From left to right: abietic acid, levopimaric acid, palustric acid, neoabietic acid, and dehydroabietic acid [2].

Fatty acids: These are long-chain hydrocarbons with a carboxylic acid group on one end, illustrated in Figure 2. Oleic and linoleic acid are recovered after acidulation of North American tall oil soaps, while pinolenic acid is also recovered from Nordic soaps.

Neutral species consist of high molecular weight alcohols that do not contain carboxylic acid groups and therefore are unsaponifiable. The alcoholic neutral extractives include fatty alcohols, sterols, stannols, triterpene alcohols, mono- and diterpene alcohols, and betulaprenols.

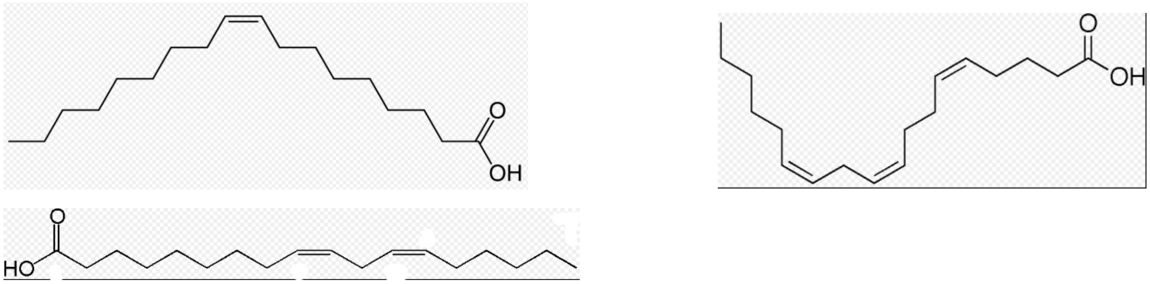

Figure 2. Oleic (top left), linoleic (bottom left), and pinolenic (right) acids that are extracted as their saponified versions (soaps) from kraft black liquor from pulping of softwoods.

Fatty and resin acids exist as their sodium salts in black liquor. These relatively long molecules have a polar, hydrophilic end where the carboxylate group is located and a neutral, hydrophobic (hydrocarbon) end. The molecules clump together to form micelles with the hydrophobic ends together in the center and are stabilized by the ionized hydrophilic groups at the outer surface. The micelles are small, 2 to 20 nm, and form a stable suspension within black liquor. The neutral species are soluble in the hydrocarbon-rich regions within the micelles.

As black liquor is concentrated, the increasing concentration of sodium ions tends to neutralize the negative charge that keeps the micelles dispersed. This causes the micelles to coalesce into a soap phase. The solubility of the soap is normally at a minimum when the dry solids content of black liquor is 25% to 28%.

5.2.4 Terpenes

Softwoods contain a number of small, neutral, and ringed structures called terpenes. They are also extractives, but are not collected with tall oil soap. They contain monoterpenes, mainly α-and β-pinenes. They are not very soluble in black liquor and are relatively volatile. Most of the terpenes are flashed when the digester is blown and/or stripped from black liquor during evaporation. They are collected from the digester and evaporator condensates as water-insoluble turpentine.

5.3 THERMAL AND TRANSPORT PROPERTIES

5.3.1 Viscosity

Viscosity is the property of a fluid that describes how easily it flows. It is formally defined as the ratio of the shear stress to the shear rate for a fluid when subjected to a shearing force.

Weak black liquor, at a dry solids content of about 15% to 18%, is quite thin, having a viscosity two or three times that of water. Its viscosity increases rapidly with dry solids content and decreases with temperature. The nature and amount of the organics molecules and their molecular weight and colloidal state are important in determining the viscosity of specific black liquors. These variables are affected by wood species pulped, the pulping conditions, and the subsequent processing conditions to which the black liquor is subjected. They vary considerably so that black liquors from two different mills, or from one mill at two different times, can have viscosities that differ by almost an order of magnitude when measured at the same dry solids content and temperature.

Newtonian Behavior

The shear rate to which black liquor is subjected can affect its viscosity. Most common fluids such as water have viscosities that are not affected by shear rate. These fluids are referred to as Newtonian fluids. For Newtonian fluids, the shear force is directly proportional to the shear rate, as shown in Eq. (4). The constant of proportionality is the Newtonian viscosity.

$$\tau = \mu \, dv/dy \quad (4)$$

where:

τ = shear stress, Pa

μ = Newtonian viscosity, Pa-s

v = velocity, m/s

y = distance from surface normal to the direction of flow, m

Black liquor, like many other polymer solutions and melts, exhibits non-Newtonian behavior under certain conditions. At low shear rates, its viscosity is independent of shear rate. At higher shear rates, however, its apparent viscosity decreases with increasing shear rate. This is referred to as shear thinning. Flow calculations with non-Newtonian fluids are often complicated. Fortunately, most black liquors exhibit Newtonian behavior at normal conditions in pulp mill operations.

Note that both *dynamic* and *kinematic* are reported for fluids. Dynamic viscosity (μ) is used in most engineering calculations and all viscosity data included in this chapter are dynamic viscosity values. The two are related as $\mu = \nu/\rho$ where ν is the kinematic viscosity and ρ is the density of black liquor.

Dynamic viscosity is reported in several different but equivalent sets of units. The relationship between them is shown in Table 3.

Table 3. Equivalent Units for Dynamic Viscosity

1 Poise = 1 dyne-second/sq centimeter

1 Pascal-second (Pa-s) = 1 Newton-second/sq meter

100 cP = 1 Poise

0.1 Pa-S = 1 Poise

1 centipoise (cP) = 1 mPa-s

Impact of Temperature and Dry Solids Content on the Viscosity of Black Liquor

Viscosity data of kraft black liquor from pulping of slash pine are presented in Figure 1 for a range of temperatures and dry solids content. These data show a rapid increase in viscosity with dry solids content, and a rapid decrease with temperature. The viscosity data follow the characteristic behavior for black liquors and many other fluids. The data in Figure 1 qualitatively are typical of all black liquors in the Newtonian behavior range.

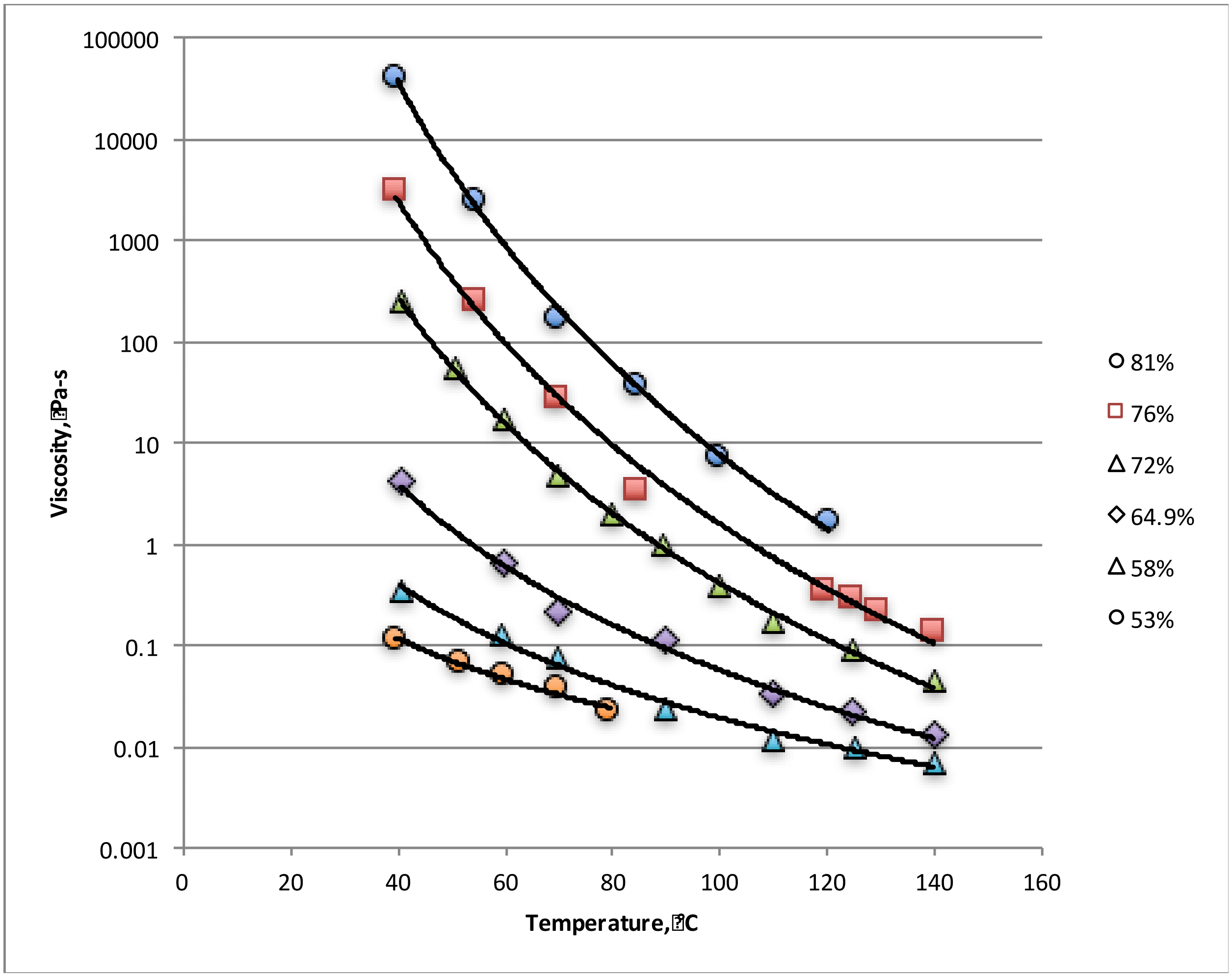

Figure 1. Viscosity versus temperature and dry solids content for a kraft black. liquor from pulping of slash pine to Kappa 107 [5].

Impact of Pulping Conditions

The viscosity of black liquor is a strong function of the Kappa number to which wood is pulped. This is illustrated in Figures 2 and 3. Both figures contain data for black liquors from pulping of slash pine to four different kappa numbers. Viscosity was measured at high dry solids content, near 76%.

In Figure 2, the viscosity versus temperature data for the two black liquors from pulping to the highest (107) and lowest (18) kappa numbers are nearly the same. The viscosities of those from pulping to the two intermediate kappa numbers (40 and 51) are also nearly the same, but differ by a factor of 50 from the black liquors from high and low Kappa pulps.

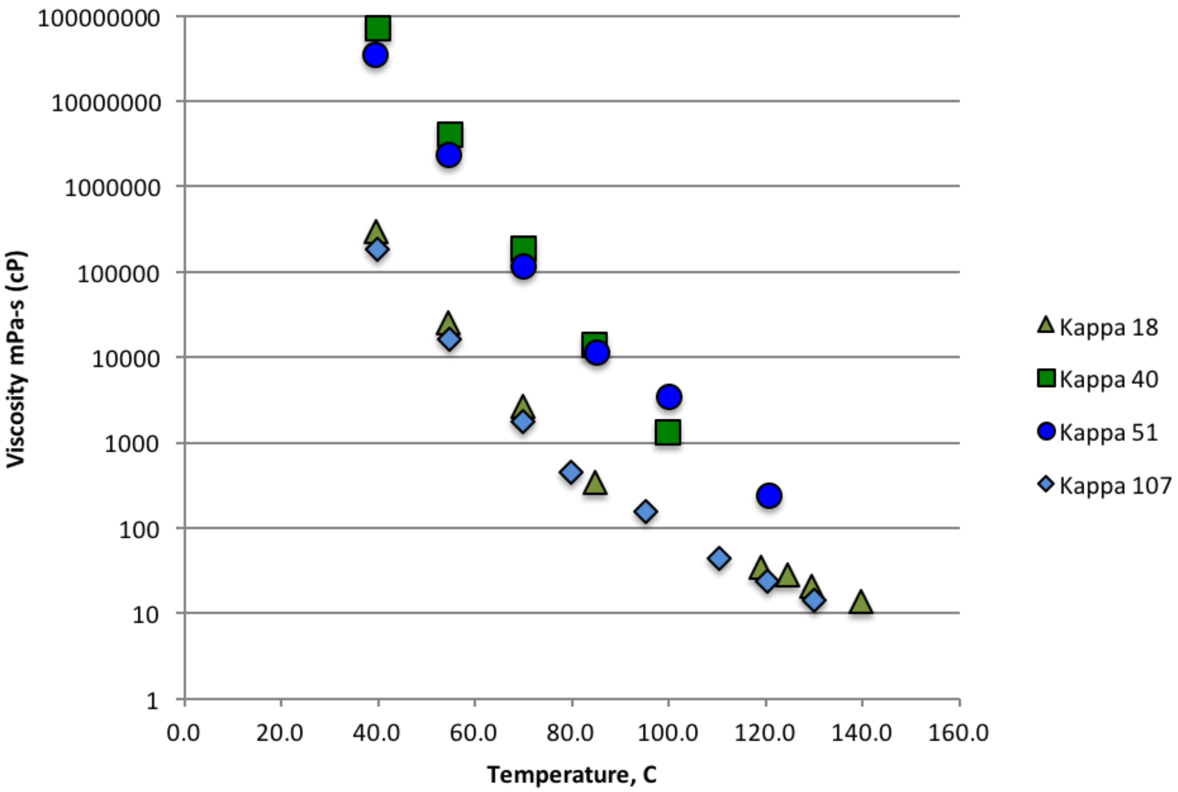

Figure 2. Viscosity versus temperature for black liquors from pulping of slash pine to the kappa numbers indicated.

Similar viscosity data, when plotted in Figure 3 versus kappa number of the pulp produced, clearly show a maximum in viscosity at intermediate kappa numbers (between 40 and 60). All viscosity measurements were made at the same temperature and dry solids content. The maximum in viscosity is attributed to differences in the length of the extracted lignin and carbohydrate molecules at different kappa numbers. Pulping to high kappa numbers extracts relatively little lignin and hemicellulose. Additionally, these are mostly the more soluble, lower molecular weight lignin. Pulping to low kappa numbers extracts most of the lignin and much of the hemicellulose in wood chips. The long pulping times required to reach low kappa numbers also shorten the length of the dissolved lignin and hemicellulose molecules. At intermediate kappa numbers, significant amounts of lignin and hemicellulose are extracted, but pulping times are not long enough for the larger, higher molecular weight molecules to be cut into shorter ones. It is the longer lignin and hemicellulose molecules in black liquor produced at intermediate kappa numbers that results in the highest viscosity black liquors in Figure 3. Differences in other composition factors such as organic to inorganic ratio, the concentrations of sodium, chloride, sulfite, and carbonate ions, and residual active alkali (REA) also contribute to differences in the viscosity of black liquor.

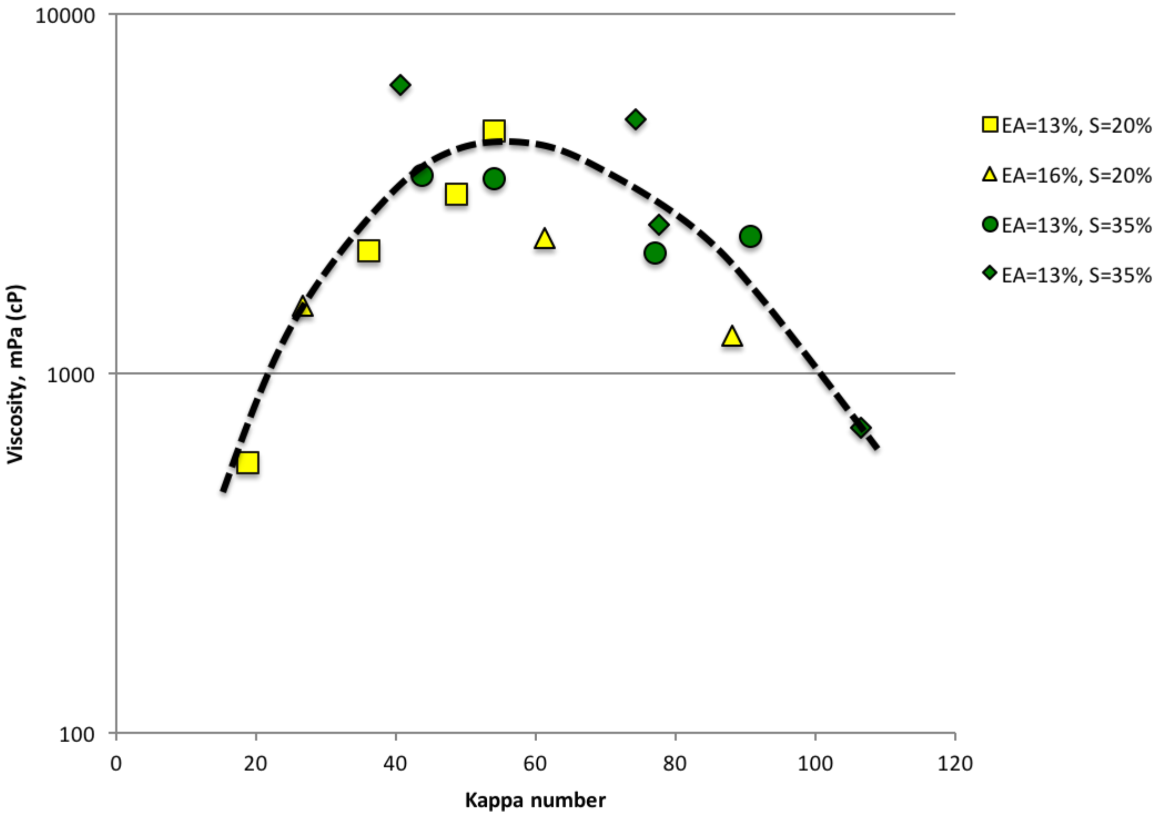

Figure 3. Viscosity of black liquors from pulping of slash pine to different kappa numbers [6]. Measurement conditions were 120ºC and 80 wt% dry solids content. EA is the effective alkali charge as wt% of dry wood and S is the sulfidity of the white liquor used in pulping.

Comparison of the Viscosity of Black Liquors from Pulping of Northern Hemisphere Woods and Eucalyptus

The viscosity versus dry black liquor solids content data shown in Figure 4 are for kraft black liquors from three different northern wood species. Viscosity data for a eucalyptus black liquor and a Nordic softwood sulfite liquor are included for comparison. The liquor-to-liquor variation in viscosity among these data increases from a factor of 2 at 45 wt% dry solids content to a factor of 10 at 70 wt% dry solids content. This much variation makes it difficult to find correlative models to predict black liquor viscosity from different wood species at the same temperature and dry black liquor solids content. Measured viscosity data from representative black liquors is essential for process design and evaluation of black liquor evaporators. Laboratory-generated liquors used for viscosity measurements must be produced at pulping conditions as closely as possible to those expected to be employed at full scale.

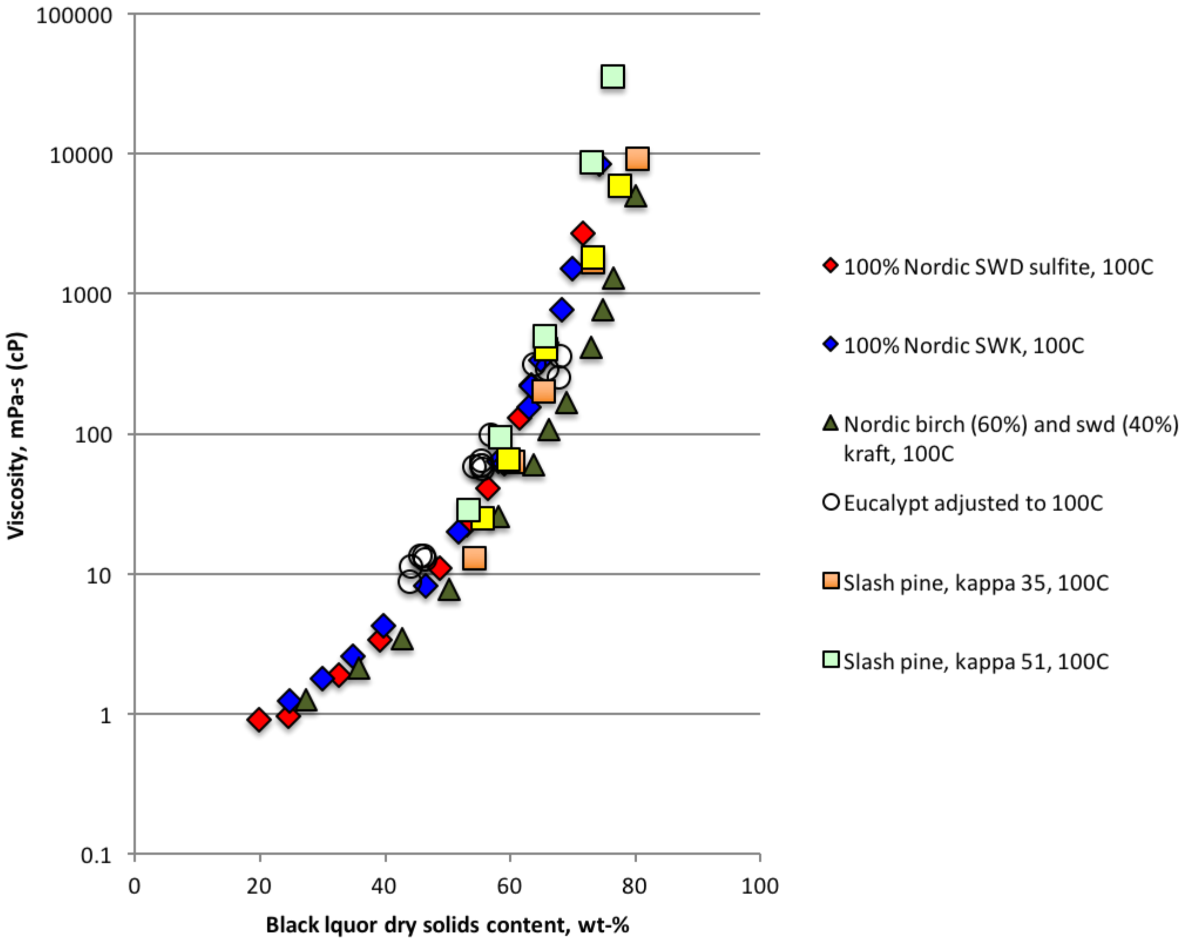

Figure 4. Viscosity of six different black liquors, measured at 100°C and 76% dry black liquor content.

Viscosity of Black Liquor from Pulping of Agricultural Residues and Other Non-Wood Raw Materials

Black liquors from pulping of these fiber sources are notoriously difficult to evaporate. The viscosity data in Figure 5 are for black liquors from bagasse, straw, and bamboo. Data for two northern softwood black liquors are included for reference. The viscosities of the non-wood black liquors in Figure 4 are a factor of 10 higher than those of the northern softwood black liquors when compared at 60 wt% dry black liquor solids. This is typical of the viscosity of those liquors.

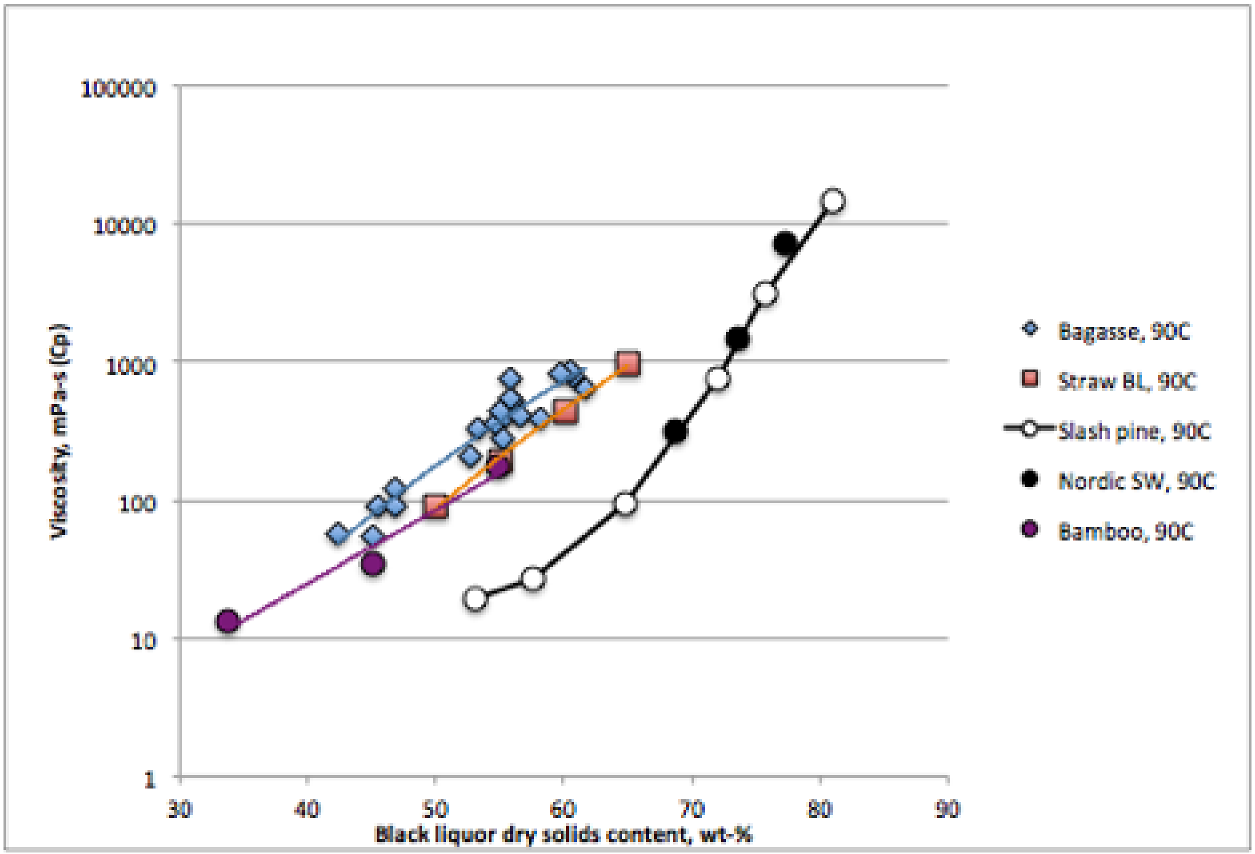

Figure 5. Comparison of viscosities of black liquor from pulping of bagasse [7, 8, 9] straw, bamboo [10, 11], and two northern softwoods.

The data in Figure 6 show how liquor temperature, dry solids content, and residual alkali content impact the viscosity of black liquor from pulping of bagasse. The impact of dry solids content and liquor temperature are as expected from other viscosity data. Differences in residual active alkali (RAA) content have a large impact on viscosity. The viscosity of bagasse black liquor decreases by a factor of 10 when the residual active alkali (RAA) is doubled. A low residual active alkali content is common for black liquors produced from pulping of non-wood fiber raw materials. This can account for the high viscosity that makes these black liquors difficult to concentrate by evaporation.

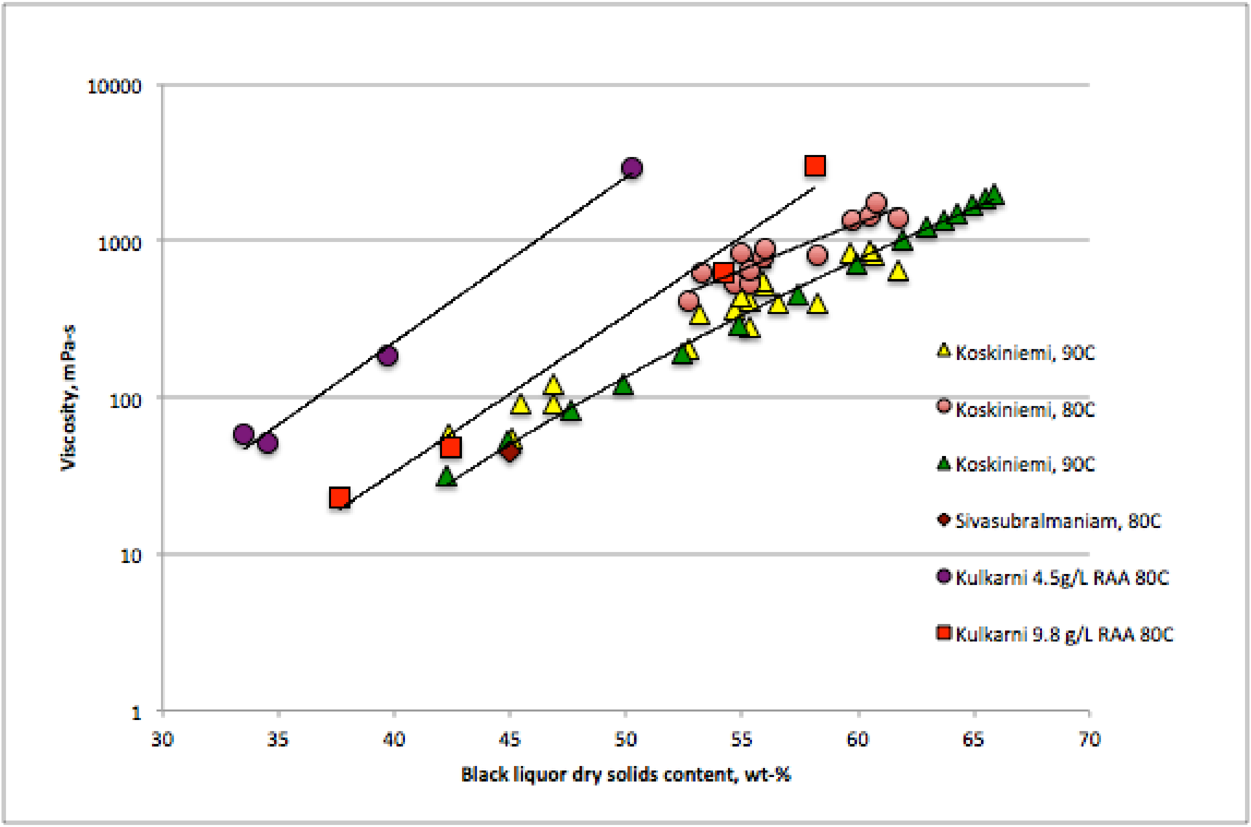

Figure 6. Viscosity of black liquor from pulping of bagasse at different conditions [6, 7, 8].

High concentrations of silica in black liquors from pulping of non-wood fiber sources increases the viscosity of these black liquors. Figure 7 shows viscosity values for a straw black liquor that contained 3.5 g/L of silica as SiO_2 as well as the same liquor after acidification to pH 9.9 and filtration which removed 93% of the silica. That amount of silica removal decreased the liquor viscosity by a factor of 3. Methods for desilification of black liquor have been developed. A critical concern is how to acidify to remove silica without precipitating lignin [12].

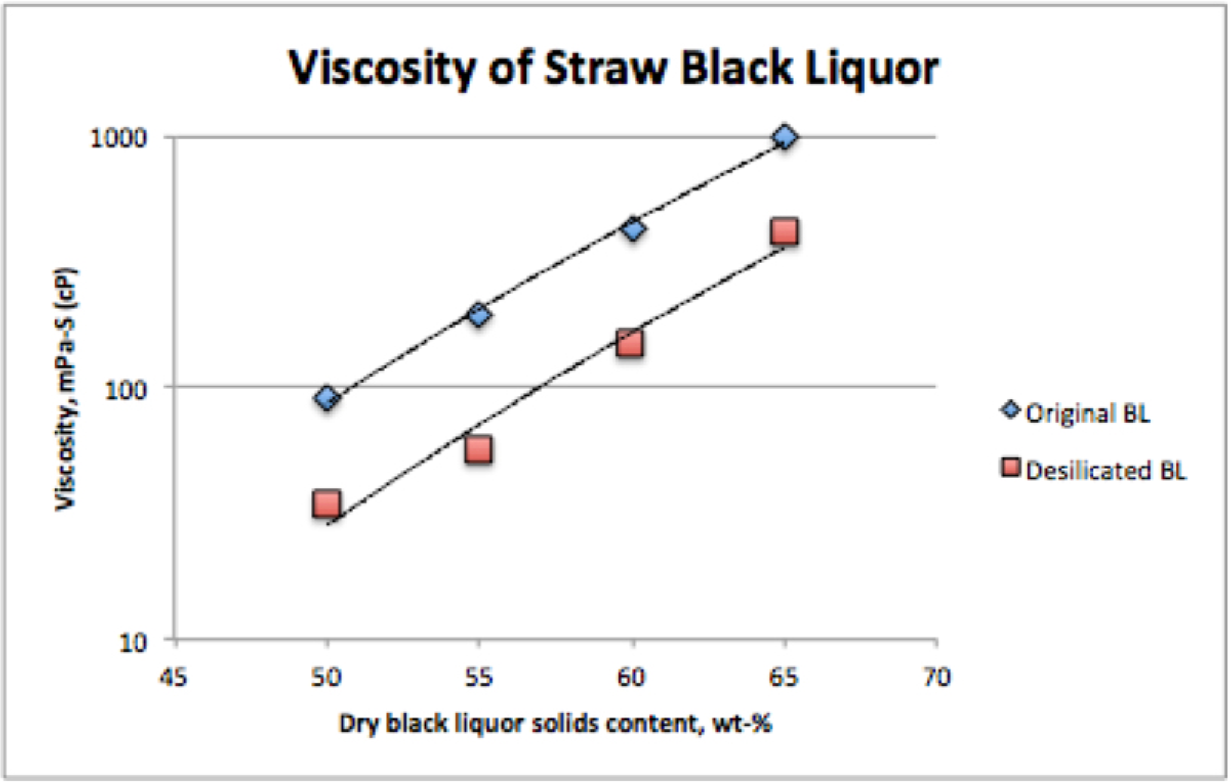

Figure 7. Impact of desilification on the viscosity of straw black liquor [6]. Viscosity measured at 125°C.

Impact of Lignin Removal

Removing lignin from black liquor decreases its viscosity. Figures 8 and 9 show the extent of viscosity reduction when lignin was precipitated from black liquor by acidification with CO_2 and then removed by filtration. The liquors used in both cases were Nordic softwood black liquors. The data in Figure 8 suggest that up to an 80% reduction in viscosity can be obtained by removing 60% of the lignin in black liquor. The data in Figure 9 are consistent with that, showing that a nearly 90% reduction in viscosity can be obtained by removing 67% of the lignin. Viscosity reductions of 20% to 70% were obtained with other black liquors, with greater viscosity reductions when more lignin was removed [13].

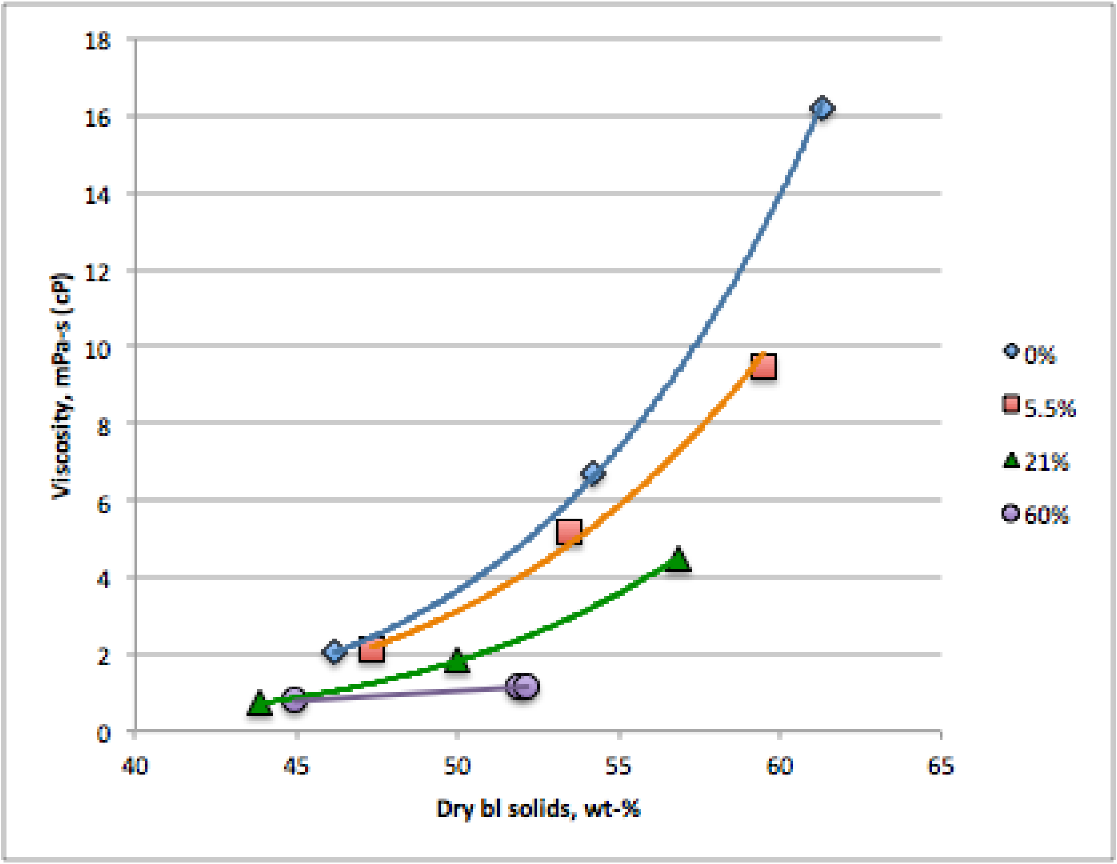

Figure 8. Viscosity at 120°C of an unmodified Nordic softwood kraft black liquor and the same liquor at three different levels of lignin removal [14].

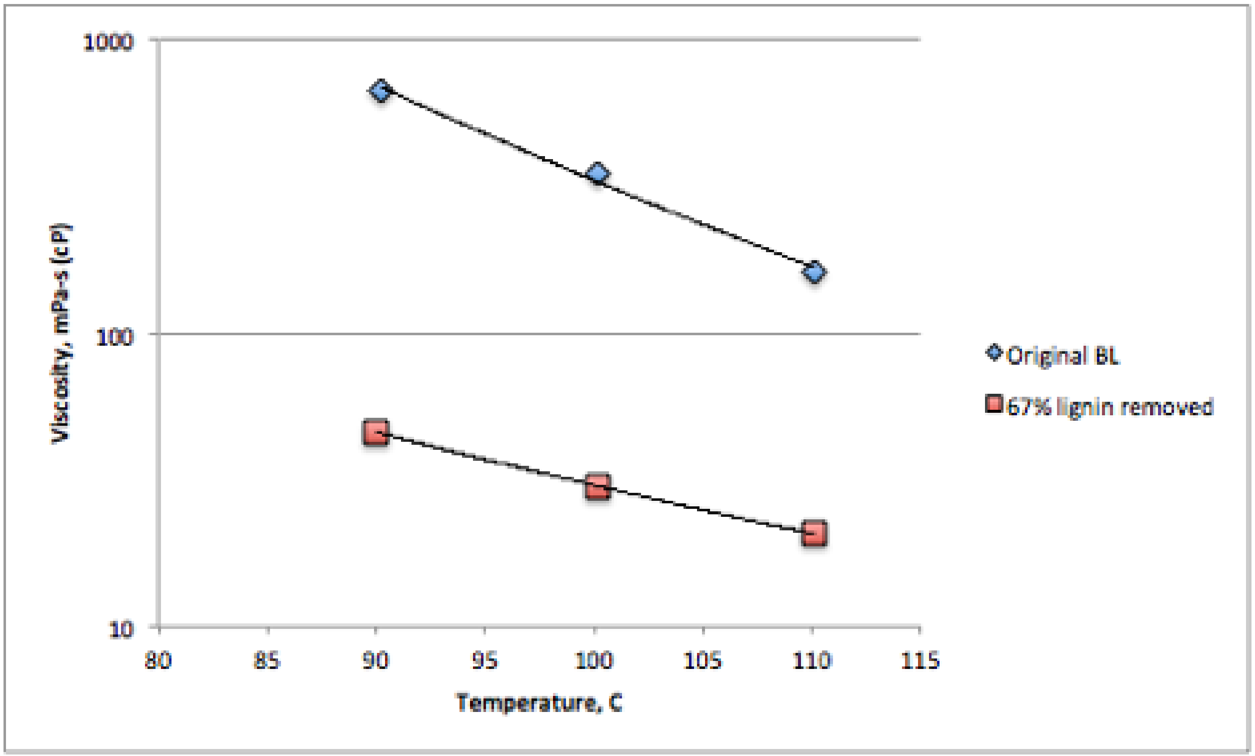

Figure 9. Viscosity of unmodified Nordic softwood kraft black liquor and the same liquor modified by removing 67% of lignin. Viscosity measured at 102°C [13].

Non-Newtonian Behavior

At normal processing conditions, black liquor almost always behaves as a Newtonian fluid, meaning that its viscosity depends only on temperature and dry solids content but not on shear rate. At very high dry solids contents or certain other conditions, however, black liquors can exhibit thixotropic or pseudoplastic behavior. These are defined as follows.

Pseudoplastic behavior is reversible shear thinning. It usually occurs because the shear forces disturb the long polymer molecule chains from their preferred conformation. Thixotropy is a characteristic which causes the apparent viscosity of a material to change from its initial value when shear is first applied to another steady value after some period of shearing. This usually occurs when polymer molecules that are initially entangled become aligned in flow, making it easier for shear layers to slip past each other. Thixotropy is similar to pseudoplasticity, but the time scale for changes in the fluid is not negligible. Both thixotropic and pseudoplastic behavior has been observed in hardwood kraft liquors including eucalyptus liquors, but not in softwood kraft liquors. The degree of pseudoplasticity correlated well with the carbohydrate content of the liquors.

Thixotropic behavior per se should not be a concern in a practical mill environment because every effort is made to keep the liquor reasonably thin (viscosity < 300 mPa-s (cP)) by maintaining a high liquor temperature and keeping it flowing. This is not the case during a shutdown or mill upset, when the extraordinarily high viscosity of thixotropic liquors can become a major concern.

Reduction of Black Liquor Viscosity by Thermal Treatment

It is possible to change the viscosity of black liquor irreversibly by heating it to temperatures above those normally encountered during evaporation. When sufficient alkali is present, thermal treatment above 140°C results in depolymerization of the high molecular weight lignin. In effect, the dissolved lignin and polysaccharides continue to be "pulped". The data in Figure 10 illustrate the effect of thermal treatment on black liquor viscosity. A commercial process for controlling black liquor viscosity is available and is in use in mills in several countries.

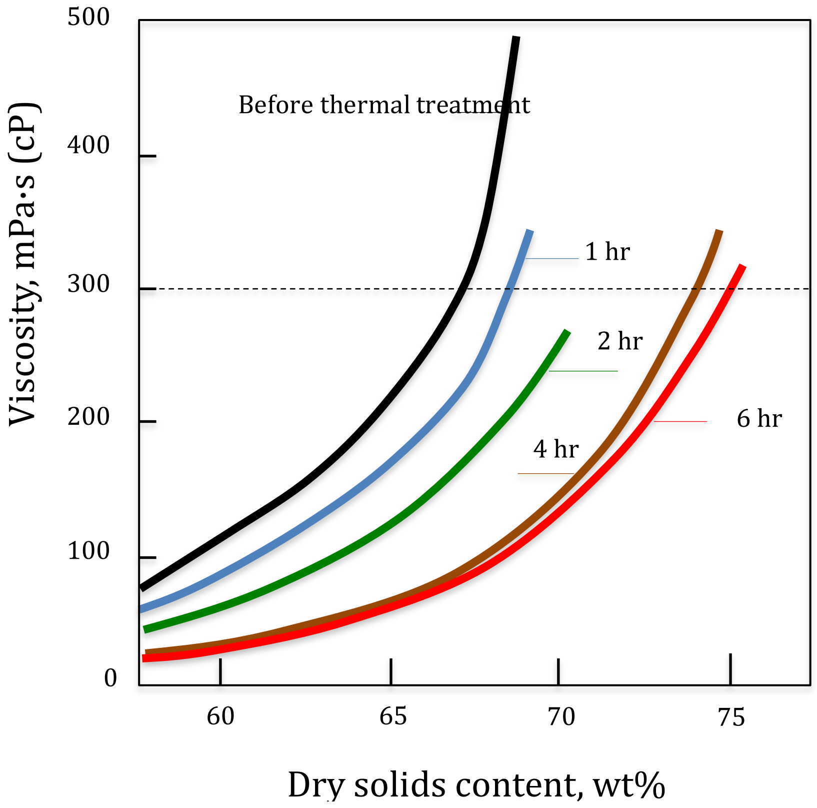

Figure 10. Impact of thermal treatment on the viscosity of a kraft black liquor [15].

Controlling Black Liquor Viscosity in the Mill Environment

From an operating point of view, the viscosity of black liquor can be controlled by temperature and alkali addition. Temperature is the normal control variable and is the most effective for liquors of normal alkali content. The effect on viscosity of changing the temperature of black liquor can be determined from the data in Figures 1, 2, and 6.

Alkali addition to either the black liquor or the digesters is effective in reducing the viscosity of black liquors with low alkali content. Adding alkali to the black liquor is easy and useful in solving short-term high viscosity problems or stabilizing viscosity after black liquor oxidation. It can be added to the weak or heavy liquor, or at the cascade evaporator. Adding alkali to black liquor before the evaporators can solve problems with poor evaporator performance associated with high liquor viscosity.

For mills with black liquor oxidation, alkali can be added before and/or after the oxidation towers if poor control of the oxidation towers creates high viscosity problems. Determining the optimal EA can be accomplished by having viscosity measurements made at varying levels of hydroxide addition.

Thermal treatment of black liquor has been used successfully to reduce the viscosity of black liquor. Removal of lignin from black liquor, a newer alternative, is being explored for that purpose.

5.3.2 Boiling Point Rise

The addition of soluble material to a liquid changes its boiling characteristics. Boiling point rise (BPR) is the difference in boiling temperature between the solution and the pure solvent when measured at the same pressure. BPR increases with solute concentration and can be as high as 27°C (49°F) for concentrated black liquor. This property is crucial to the design and performance of black liquor evaporators. Heat transfer in these units is dependent on the temperature difference between the condensing steam and the evaporating black liquor. BPR can substantially reduce the available ΔT for heat transfer.

Boiling point rise is a colligative property, proportional to the molal concentration of solute. Inorganic compounds are the dominant component in determining the BPR of black liquor. The reason for this is that they make up over 90% of the solute on a molar basis. As the dry solids content increases, the concentration of the inorganic salts in solution also increases, which increases the BPR.

Figure 11 shows a plot of BPR as a function of dry solids content from several sets of measurements using different measurement techniques [16, 17, 18, 19]. The BPR increases very rapidly with increasing solids content above 50% dry solids content. The BPR values from the four sets of measurements do not differ much even though they are from four different black liquors measured with four different methods. The small differences between the data sets are due both to composition differences in the liquors tested and in the test methods used. No single technique has been accepted as a standard for measurement of BPR.

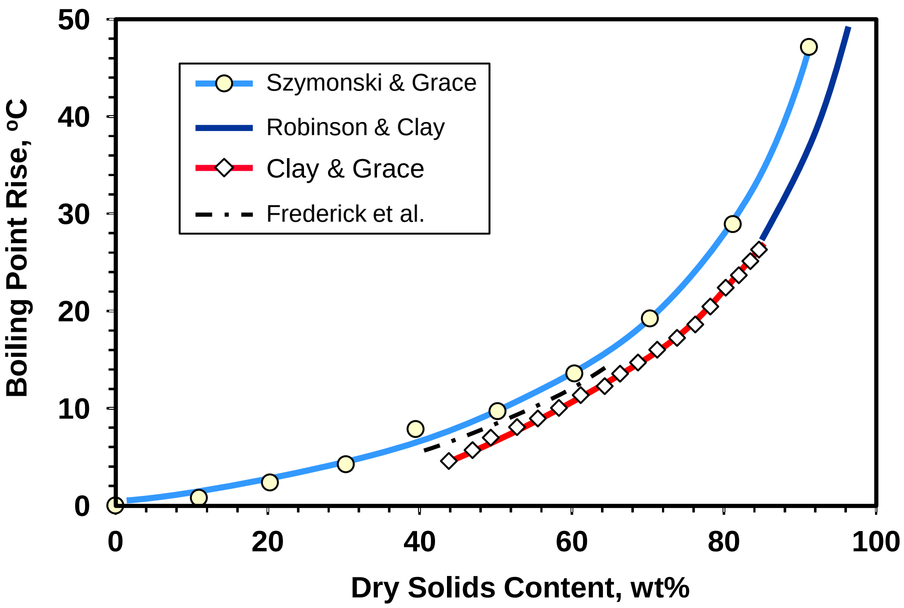

Figure 11. Black liquor boiling point rise data from various sources [15, 16, 17, 18].

One aspect of the inorganic composition which has been demonstrated to affect BPR is the solubility of Na_2CO_3 and Na_2SO_4. As will be discussed further in the following section, these two components crystallize from solution first as black liquor concentration is increased. For typical black liquors, these components begin to crystallize at about 50% dry solids content. When this occurs, the influence of concentration on BPR changes as shown in Figure 12. The BPR for two liquors is plotted as a function of the solids-to-water mass ratio (S/(100–S)) in this figure. At low concentrations the BPR is a linear function of solids-to-water ratio, although the slope is different for the two liquors. At about 50% dry solids content (solids-to-water of 1.0) the slope decreases due to the precipitation of some of the inorganic. This is further demonstrated by increasing the dry solids content of one of the liquors by adding Na_2CO_3 instead of evaporating water. At 50% dry solids content, the additional Na_2CO_3 is no longer soluble in the aqueous solution portion of the black liquor so no increase in BPR was observed. This is indicated by the horizontal line in Figure 12 [16].

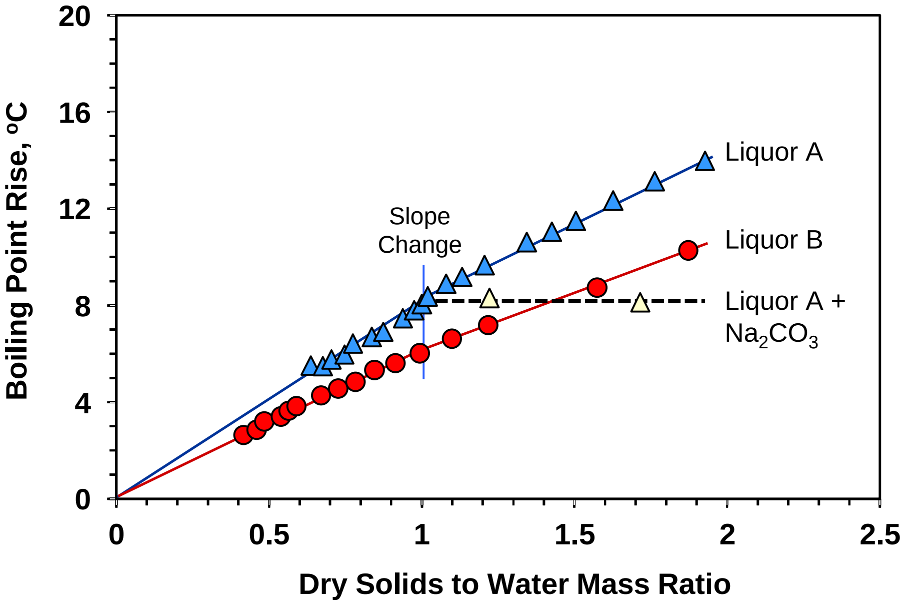

Figure 12. Boiling point rise as a function of the solids/water ratio for two black liquors [15].

The method of plotting the BPR data in Figure 12 is suggested by Raoult's law. For dilute solutions, the vapor pressure of the solvent is decreased in direct proportion to the molal concentration of solute. The boiling point increases as a result. For small changes in boiling point, the rise is directly proportional to the molality of the solute, which in turn is proportional to the ratio of dry solids content to water. The following expression can be used to estimate BPR up to 50% dry solids content:

$$\Delta T_b = \Delta T_{b50}\,(S/(100\text{-}S)) \tag{5}$$

where:

ΔT_b = boiling point rise (BPR), °C

ΔT_{b50} = boiling point rise at 50% dry solids content, °C

When no data is available, using ΔT_{b50} equal to 7.5°C (13.5°F) should result in no greater than 20% error for kraft black liquor. Above 50% total dry solids, the BPR of black liquor depends in a complex way on the solubility of the inorganic components. The upper limit on the BPR for dry solids content approaching 100 wt% is approximately 55°C (99°F).

The most accurate method of estimating boiling point rise requires measured values of heat capacity and normal boiling point versus dry solids content. These parameters must be available for the black liquor of interest. The estimates are based on standard thermodynamic calculation methods [20, 21]. This method both gives excellent agreement with experimentally measured boiling point rise curves (Figure 13**)** and can be used to estimate boiling point rise for liquors above the normal boiling point. It does, however, require extensive and accurate measurements of heat capacity and normal boiling point over the range of dry solids contents of interest.

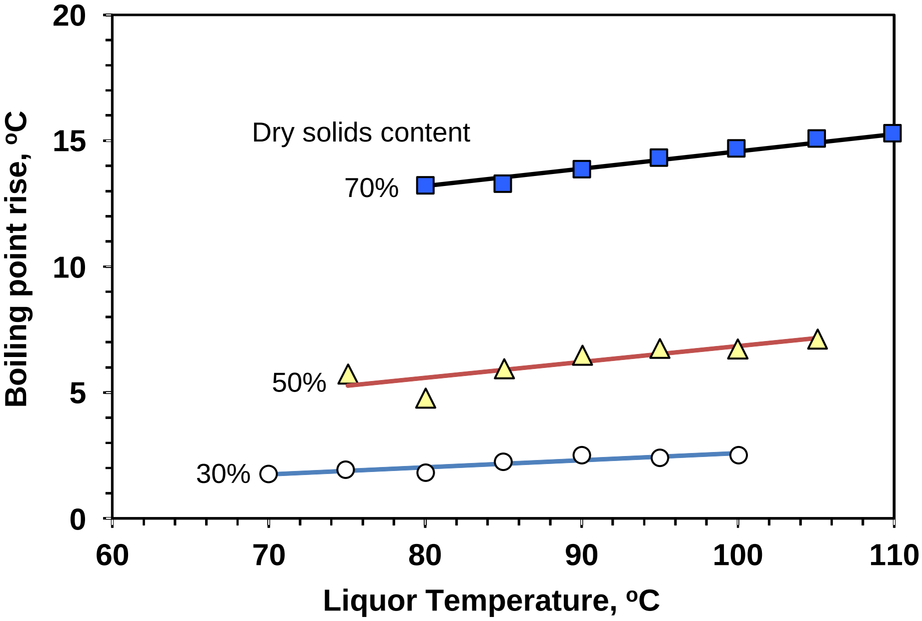

Figure 13. Comparison of experimental boiling point elevation data for black liquor (symbols) with values obtained from the vapor pressure estimations and extrapolations from Eqs. (8) and (9) (lines).

When heat capacity and normal boiling point data are not available, the data in Figure 11 can be used to estimate BPR at higher solids concentration and at atmospheric pressure. A small amount of data for one liquor is available, which shows the trends above 50% solids for pressures above atmospheric pressure. When no data at elevated pressure are available, Eq. (6) for estimating the effect of pressure on boiling point rise for dilute solutions can be used to estimate the boiling point rise for black liquor at elevated pressure. The relationship between boiling point rise, salt concentration, and the properties of water is:

$$\Delta T_{bpr} = m\, MW_w\, R\, (T_{bw})^2 / \Delta H_v \qquad (6)$$

where:

ΔT_{bpr} = boiling point rise of black liquor, °C

ΔT_{bpr} = m = molality of the solution

MW_w = molecular weight of water, 18

R = gas constant, 8.314×10^{-5} m^3 bar / mol K

T_{bw} = boiling point of pure water, K

ΔH_v = enthalpy of vaporization of water, J/kg

From this, the BPR at 50% solids for any pressure can be estimated in terms of the value at one atmosphere. The molality at 50% dry solids content is independent of pressure for particular liquors as long as the inorganic is completely dissolved, so that the value of ΔT_{bpr} at any pressure can be estimated as:

$$\Delta T_{bpr50\text{-}p} = \Delta T_{bpr50\text{-}1\,bar}\,[T^2_{bw\text{-}p}/T^2_{bw\text{-}1\,bar}]\,[\Delta H_{v\text{-}1\,bar}/\Delta H_{v\text{-}p}] \qquad (7)$$

where:

$\Delta T_{b50\text{-}p}$ = BPR at 50% dry solids content at pressure p, °C

$\Delta T_{b50\text{-}1\,atm}$ = BPR at 50% dry solids content at one atmosphere, °C

$T_{bw\text{-}p}$ = boiling point of water at pressure p, K

$T_{bw\text{-}1\,atm}$ = boiling point of water at one atmosphere = 373 K (100°C)

$\Delta H_{v\text{-}1\,atm}$ = enthalpy of vaporization of water at one atmosphere = 2,244 kJ/kg

$\Delta H_{v\text{-}p}$ = enthalpy of vaporization of water at pressure p, kJ/kg

Eq. (7) provides a method for extrapolating boiling point rise data taken at one pressure to other pressures of interest. Extrapolated values of boiling point rise based on Eq. (7) are compared with the experimental data in Figure 13. The 90°C liquor data was used as the base point at each dry solids content and the boiling point rise at other liquor temperatures was calculated using Eq. (7). The results, shown as solid lines in Figure 13, agree very well with the experimental data.

5.3.3 Solubility Limit

The inorganic matter in kraft black liquor consists mainly of a variety of sodium salts with smaller amounts of potassium salts and minor quantities of calcium, magnesium, aluminum, silicon, iron, and other metals. The solubility of the sodium and potassium salts is much greater than those of the other inorganic species. At concentrations below about 50% dry solids content, the sodium salts are completely dissolved in the aqueous portion of the liquor. When the dry solids content is increased above the 50 wt% level, salts begin to crystallize from solution. The exact concentration at which they begin to precipitate is often referred to as the “solubility limit.”

When the solubility limit of Na_2SO_4 and Na_2CO_3 is exceeded, either of three double salts of Na_2SO_4 and Na_2CO_3 may begin to crystallize (Figure 14). One of these is Burkeite, a sulfate-rich double salt with a nominal composition of 1.6 to 2.6 $Na_2SO_4 \bullet Na_2CO_3$. The second is sodium carbonate sulfate (~1.5 $Na_2CO_3 \bullet Na_2SO_4$). The third, sodium sulfate dicarbonate (referred to as dicarbonate), is richer in carbonate and has a nominal composition of 1.6 to 6.0 $Na_2CO_3 \bullet Na_2SO_4$. All of these double salts can foul heat transfer surfaces in evaporators, although Burkeite fouling is normally only a problem in older, climbing-film LTV evaporators. The specific double salt that crystallizes first depends upon the ratio of $CO_3/(CO_3+SO_4)$ *dissolved* in the black liquor. This is illustrated in Figure 6. Below a dissolved $CO_3/(CO_3+SO_4)$ mole ratio of about 0.68, Burkeite crystallizes, while at higher molar ratios any of the three others may crystallize. Between about a ratio of 0.8 to 0.9, dicarbonate will precipitate as shown in Figure 14. During evaporation, when crystallization of sulfate-rich burkeite proceeds, the molar ratio of Na_2CO_3 to Na_2SO_4 dissolved in black liquor increases and eventually dicarbonate crystallizes. The key variables that determine when Na-CO_3-SO_4 salts crystallize are the temperature and the concentration of total dissolved sodium, carbonate, and sulfate. The solubility and crystallization behavior of sodium sulfate and carbonate in black liquor is discussed in detail in Chapter 5 of this book.

Other sodium salts, including such as sodium hydroxide, sodium thiosulfate, and sodium chloride, in black liquor are more soluble than sodium carbonate and sodium sulfate. They do not crystallize during the concentration of black liquor. Sodium oxalate can crystallize during black liquor concentration. Its characteristics are discussed in Chapter 5. Inorganic salts of divalent metal ions are nearly insoluble in black liquor. They are carried through the liquor cycle as suspended solids and are removed as dregs or with purged precipitator ash. Inefficient dregs removal can result in the accumulation of these elements in the liquor and lime cycles, but they remain insoluble throughout the cycle.

Calcium, aluminum, and silicon behave differently. The total dissolved concentration of calcium in black liquor is an order of magnitude higher than would be expected based on inorganic solubility data. The reason for its higher solubility is that calcium ions form complexes with the dissolved organic matter in black liquor [22]. These organo-calcium complexes are less stable at higher temperatures. They decompose in digester liquor heaters and black liquor evaporators, releasing calcium ions that deposits as calcium carbonate on heat transfer surfaces.

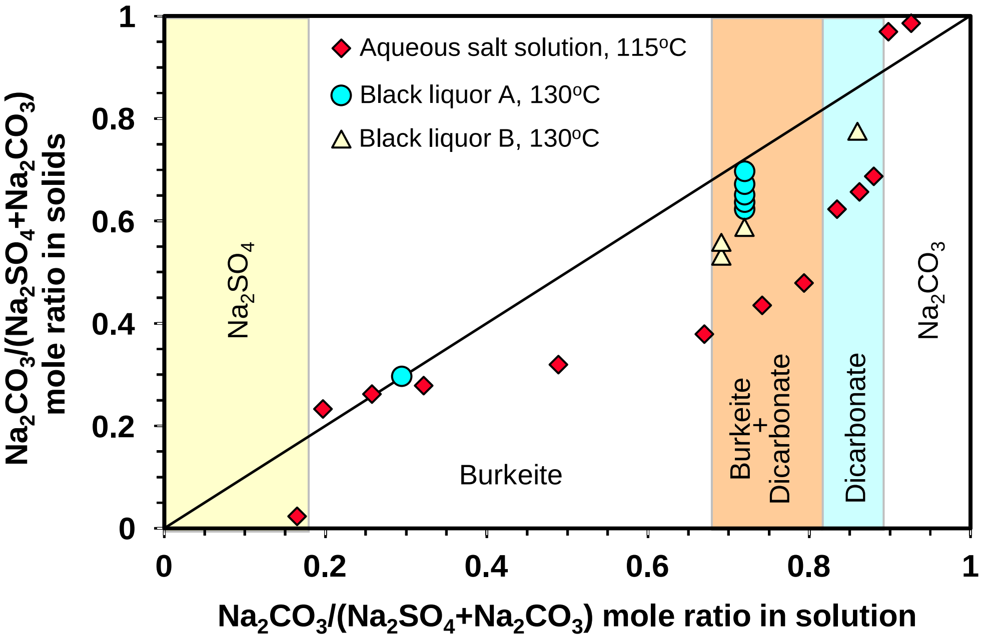

Figure 14. Relationship between the composition of crystals produced and the solution composition for Na_2CO_3 and Na_2SO_4 in water and in black liquor.

Aluminum and silicon are problematic because their solubility in green and white liquor increases with increasing pH [23, 24]. They can be removed effectively as green liquor dregs. Poor dregs removal efficiency will result in their accumulation in the liquor cycle in kraft pulp mills. However, aluminum and silicon that pass through the green liquor clarifier or filter will redissolve as the pH increases during causticizing. Because the lowest pH in the liquor cycle occurs in the black liquor evaporators, aluminosilicates will precipitate in the evaporators if aluminum and silicon are allowed to accumulate in the liquor cycle. Efficient dregs removal is the most effective way to control aluminosilcate scales in black liquor evaporators.

5.3.4 Density

The density of black liquor is important in the calculation of flow characteristics and static heads. At very low dry solids contents the density is close to that of water at the same temperature. At higher dry solids contents the density depends on the organic and inorganic material that constitute the solids. The density of most organic matter, including the lignin and carbohydrates in black liquor, is close to that of water while that for the inorganic matter is nearly twice that of water. As a result, the inorganic matter has the stronger effect on the density of black liquor. The apparent density of black liquor can also be affected by entrained air. This air enters the liquor during various processing stages including black liquor oxidation. It is not an inherent constituent of the liquor, but can affect the apparent density both in operation and in laboratory testing.

Some data for the density of various spent pulping liquors is shown in Figure 15. The specific gravities are calculated at 25°C (77°F) based on the density of water at 16°C (60°F). The specific gravity is very nearly a linear function of the dry solids content of the liquor for each type of liquor.

The slopes of the specific gravity versus dry solids content data in Figure 15 depend on the inorganic content of the individual liquors. These slopes correlate well with the inorganic content (expressed as ash equivalent) of the dry solids as shown in Figure 16. The inorganic content was obtained by ashing in oxygen rather than by the sulfated ash technique. Although the composition of the inorganic is changed by this process, the result is a direct measure of the inorganic content of the liquor. The excellent correlation between inorganic content and the specific gravity slope for the four pulping processes indicated the dominant role of inorganic matter in black liquor density.

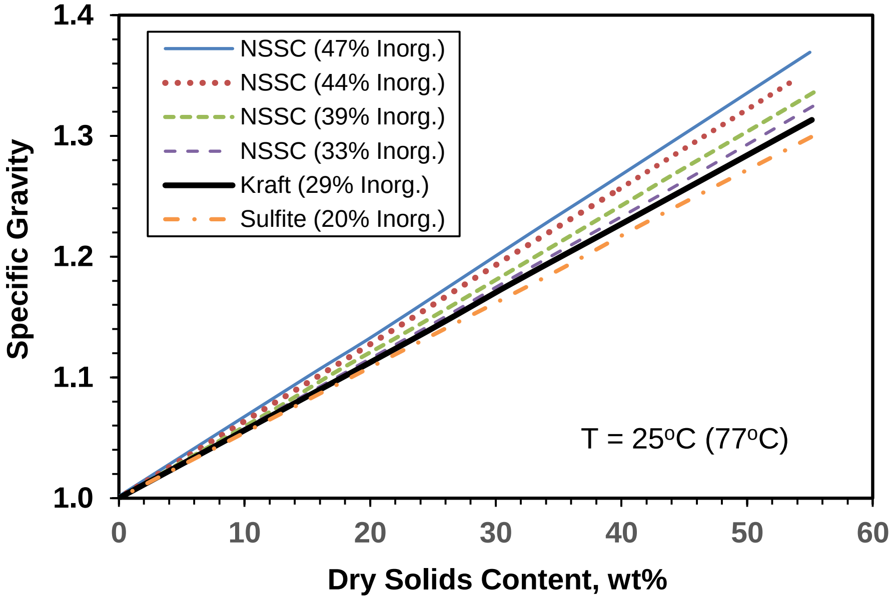

Figure 15. Specific gravity of typical spent pulping liquors [25].

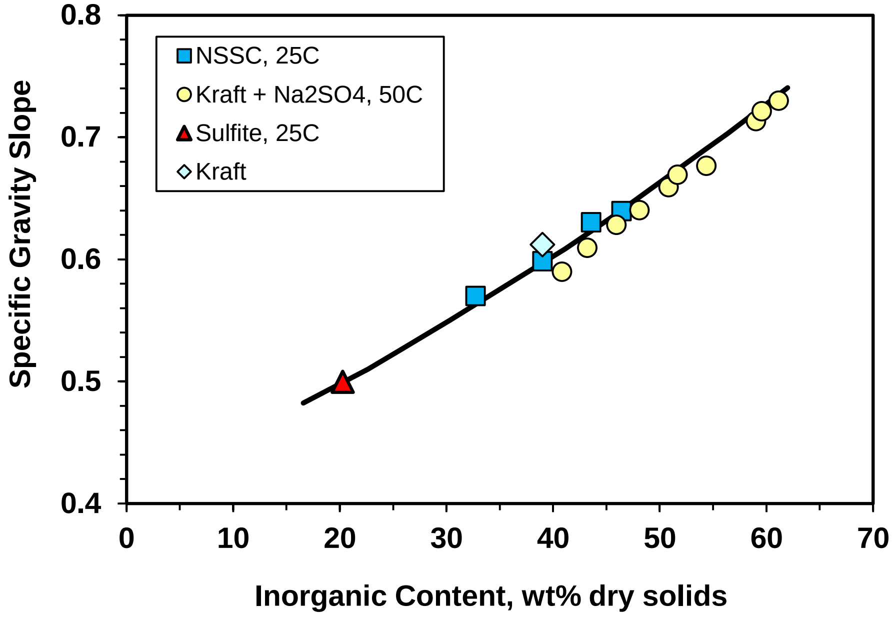

Figure 16. Slopes of specific gravity as a function of inorganic content for four spent pulping liquors [16].

A correlation that predicts the density of black liquors at 25ºC and dry solids contents up to 50% is [26]:

$$\rho_{25} = 997 + 649\,S \tag{8}$$

where:

ρ_{25} = black liquor density at 25°C, kg/m^3

S = black liquor dry solids mass fraction

The inorganic content of the liquor solids has the predominant effect on the density. Eq. (8) predicts a higher specific gravity than indicated in Figure 15 because it represents the density of degassed black liquor.

The characteristic behavior of black liquor density is shown in Figure 17 at dry solids contents up to 100%. At 25^{o}C, density is a linear function of dry solids content up to 65%. At higher dry solids content, the density first increases more rapidly with dry solids content (to about 80% dry solids content) and then increases much more slowly until it reaches the final density of dry black liquor solids. The change in slope near 65% dry solids content is associated with the shift from a water-continuous phase to a polymer-continuous phase, while the second transition may be due to change in plasticization (by water) of the glassy polymer continuous phase.

The effect of temperature on black liquor density can be estimated from Eq. (9) for the temperature range of 20°C to 100°C and dry solids contents up to 65%.

$$\rho_T/\rho_{25} = 1 - 3.69\text{x}10^{-4}\,(T\text{-}25) - 1.94\text{x}10^{-6}\,(T\text{-}25)^2 \tag{9}$$

where:

ρ_T = black liquor density at temperature T, kg/m^3

T = temperature, ^{o}C

For dry solids contents above 65%, the data in Figure 17 provides an estimate currently available for the density of black liquor at 25°C to 30°C.

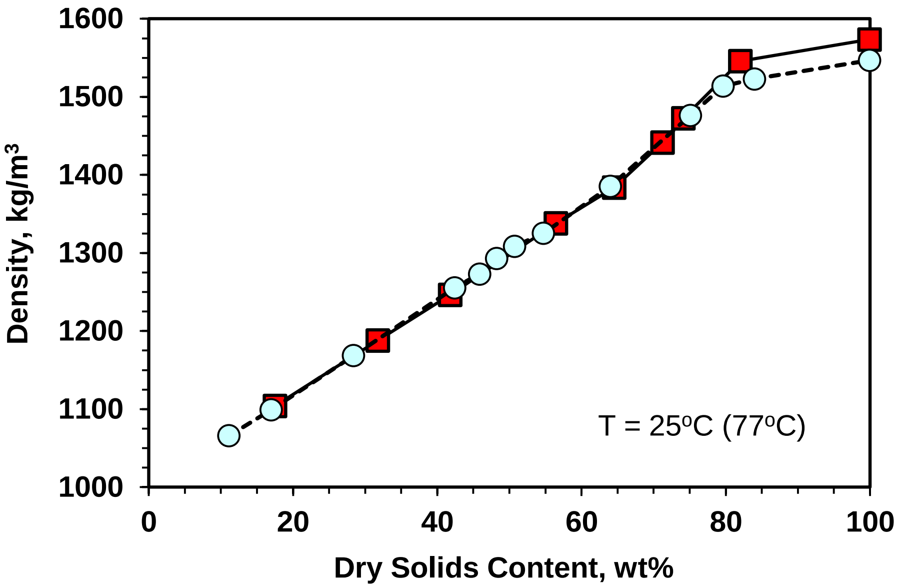

Figure 17. Density versus dry solids content for two North American kraft black liquors at 25°C [17].

5.3.5 Enthalpy and Heat Capacity

Enthalpy data for black liquor is needed to estimate the preheat requirements during evaporation. It can also be used with normal boiling point data to estimate the boiling point rise of concentrated black liquor.

Heat capacity

Figure 18 contains heat capacity data from three sources. The heat capacities of most organic and inorganic matter typical of black liquor are about half the value for water. As the dry solids content increases from zero, the heat capacity falls approximately linearly from the value for pure water to a value about half that of water. Considering the differences in wood species and test methods, the data agree well. The data from Masse et al. is far more detailed and shows an important feature of heat capacity for black liquor, which is the small deviation from a linear dependence on dry solids content between 40% and 100%.

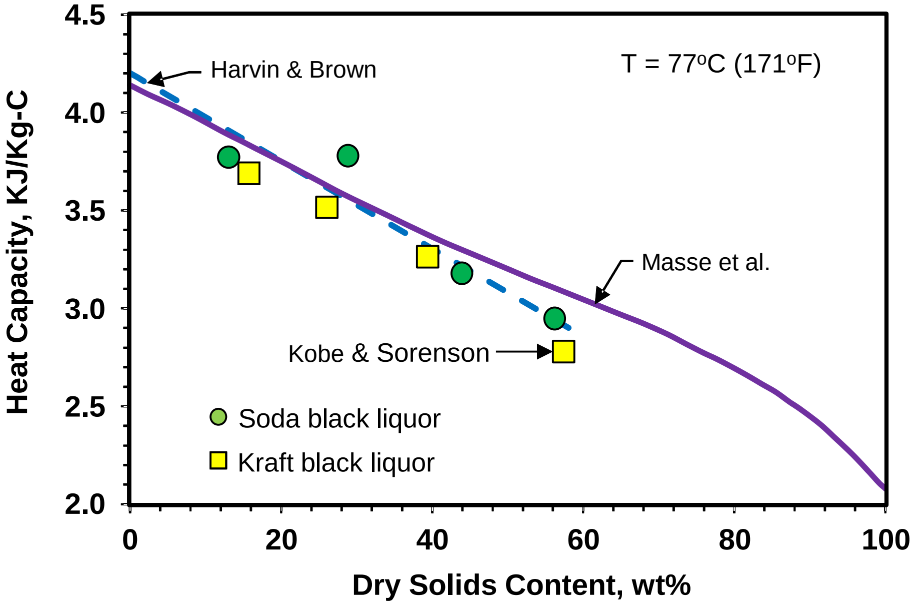

Figure 18. Comparison of heat capacity data for black liquor at 77°C [27, 28, 29].

A linear mixing rule for water and black liquor solids works for estimating the heat capacity of black liquor below 50% dry solids content. However, the character of black liquor changes substantially above about 50% solids. At low solids, black liquor is a mixture of an aqueous solution of inorganic salts, sugar acids, and colloidal material, with water as the continuous phase. Above 50% dry solids content, some inorganic salts begin to crystallize from the aqueous phase where the organic matter eventually becomes the continuous phase. A mixing rule that incorporates an excess property function accounts for the departure of the heat capacity of black liquor versus dry solids content from that of an ideal mixture [20]. The general form of the expression is:

$$Cp_{bl} = (1\text{-}S)\, Cp_W + (S)\, Cp_S + Cp_E \qquad (10)$$

where:

Cp_{bl} = heat capacity of black liquor, J/kg°C

Cp_W = heat capacity of water, 4216 J/kg°C (1.008 Btu/lb$_m$°F)

Cp_S = heat capacity of black liquor solids, J/kg°C

Cp_E = excess heat capacity, J/kg°C

S = dry solids mass fraction

T = temperature, °C

The heat capacity of dry black liquor solids changes with both temperature and composition. Typically, the heat capacity at 60°C falls within 10% of 1950 J/kg°C (0.46 Btu/lbm°F) and at 105°C within 10% of 2160 J/kg°C (0.51 Btu/lbm°F). An equation that describes the temperature dependence of the heat capacity of dry black liquor solids is:

$$Cp_s = 1684 + 4.47\,T \quad \pm 8\% \text{ for T in °C} \tag{11}$$

An equation for the excess heat capacity term is:

$$Cp_E = (4930 - 29\,T)(1 - S)(S)^{3.2} \tag{12}$$

The constants in Eqs. (11) and (12) are based on Cp data for several black liquors. They and Eq. (10) predict the heat capacity for these liquors within 3%.

Heat of Dilution

Heat effects due to dilution arise because the forces of attraction between dissimilar molecules differ from those between similar molecules. The heat effect can be either exothermic or endothermic.

Heats of dilution data for black liquors diluted from 80% to 1.7% dry solids content are shown in Figure 19. The heat effect is exothermic, with a magnitude of about 150 kJ/kg black liquor solids for dilution from 80% solids to infinite dilution. This is a significant energy release, equivalent to the energy required to increase the temperature of black liquor at 50% dry solids content by 20°C.

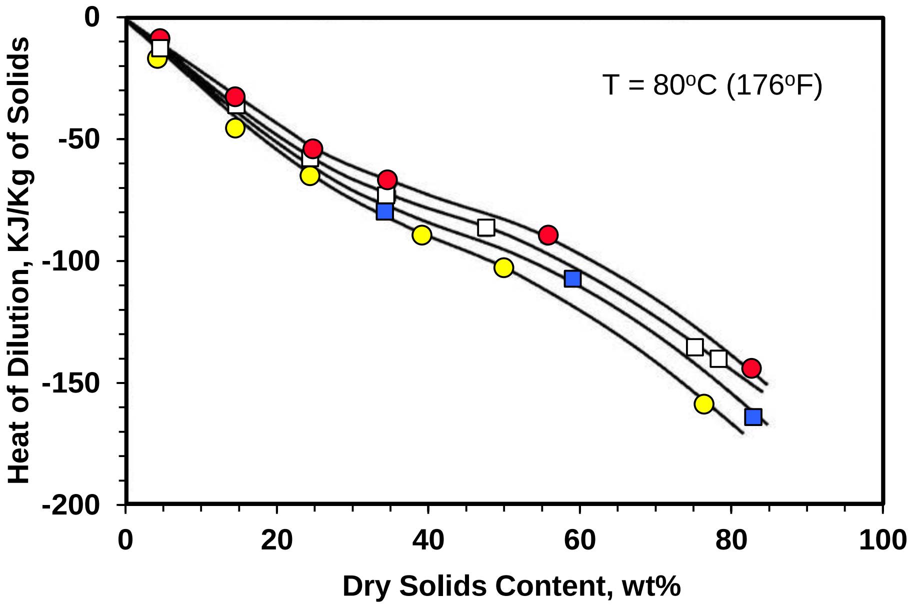

Figure 19. Heat of dilution data for four kraft black liquors from 80% dry solids content to infinite dilution at 80°C [13].

Enthalpy

The enthalpy of any solution, relative to an arbitrary reference state, can be calculated from heat capacity and heat of dilution data. The enthalpy of black liquor at 80°C, relative to water at 0°C, and dry solids contents from 0% to 80%, can be calculated from Eq. (20).

$$H_s = (1\text{-}S)\, H_w - (S)\, Q^{\infty} \qquad (13)$$

where:

H_s = the enthalpy of black liquor at 80°C and dry solids content S

H_{aw} = the enthalpy of water at 80°C relative to 0°C

Q^{∞} = the heat of dilution per unit mass of solids at 80°C from solids S to infinite dilution

Figure 20 contains enthalpy-concentration data for a kraft black liquor. The enthalpy values were calculated using Eq. (20) and a measured heat of dilution for the liquor. They increase with increasing temperature and with decreasing dry solids content.

They are less sensitive to dry solids content at higher dry solids content and lower temperatures. For different black liquors, the enthalpy at fixed temperature and dry solids content can vary by more than 20 kJ/kg. Enthalpy-concentration data for a variety of kraft black liquors are available [14].

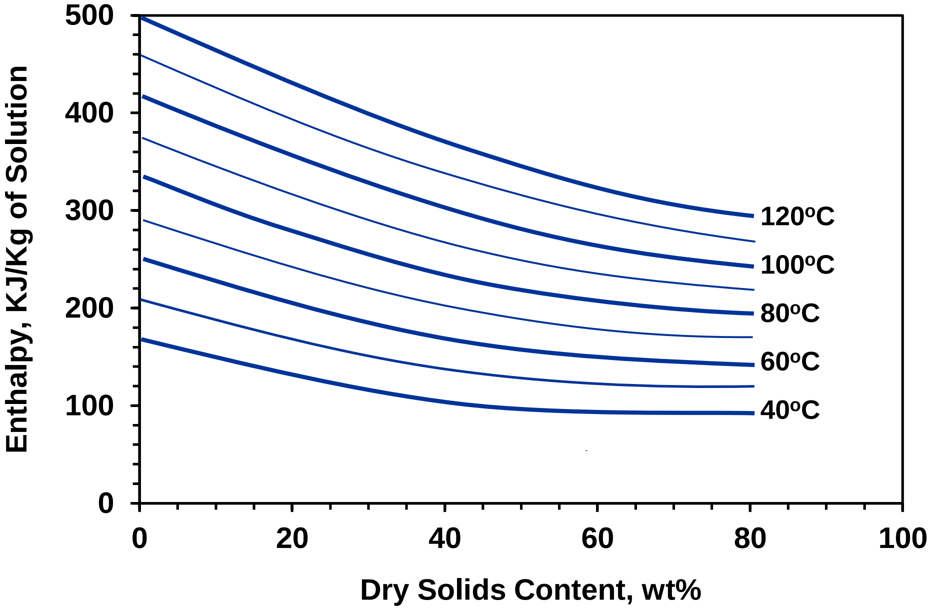

Figure 20. Enthalpy-concentration data for a kraft black liquor [13].

5.3.6 Surface Tension

Surface tension is the property of a liquid that tries to minimize its surface area. This property is responsible for the rise of a liquid in a capillary and for the break-up of fluid filaments into spherical droplets during spray formation.

The surface tension of pure liquids depends on its temperature, while for solutions it depends also on the nature of the dissolved compounds. The surface tension of water is unusually high. At 20°C it is 72.8 dynes/cm (72.8×10^3N/m). It decreases linearly with temperature to a value of 58.9 dynes/cm (58.9×10^3N/m) at 100°C. Inorganic compounds increase the surface tension when dissolved in water, although this effect is mild within the range of concentrations found in black liquor. Of the main inorganic constituents in black liquor, NaOH has the strongest effect on the surface tension of water, increasing it approximately 1% for each 1 wt% NaOH in solution. Organic surfactants such as tall oil soap decrease the surface tension of water by a factor of two to three. This effect of surfactants on surface tension is very non-linear with concentration, and larger quantities of organic matter in water have only a very small additional effect on surface tension.

An important factor in both measurement of surface tension and its impact on mill operation is the time factor for the surfactant concentration to equilibrate at a gas-liquid interface. When a liquid surface is formed, the concentration of the surface-active molecules at the liquid surface increases compared to that in the bulk liquid. Surface-active molecules are usually large and the time needed for them to diffuse to a newly formed liquid surface can be long. Most surface tension measurement techniques measure the *static* surface tension. In these measurements, the liquid surface is formed long enough before the measurement that the surface-active molecules have reached their equilibrium concentration at the surface. A method for measuring *dynamic* surface tension is available [30]. With this method, the surface tension can be measured within 0.1 second of the time after which a surface is formed.

The effect of dry solids content on surface tension for five kraft black liquors is shown in Figure 21 at temperatures from 22°C to 90°C. The general pattern for the effect of solids is clear. Surface tension falls rapidly with increasing dry solids content to a value between 40% and 60% of that of pure water. The surface tension may go through a flat minimum between 15% and 40% solids.

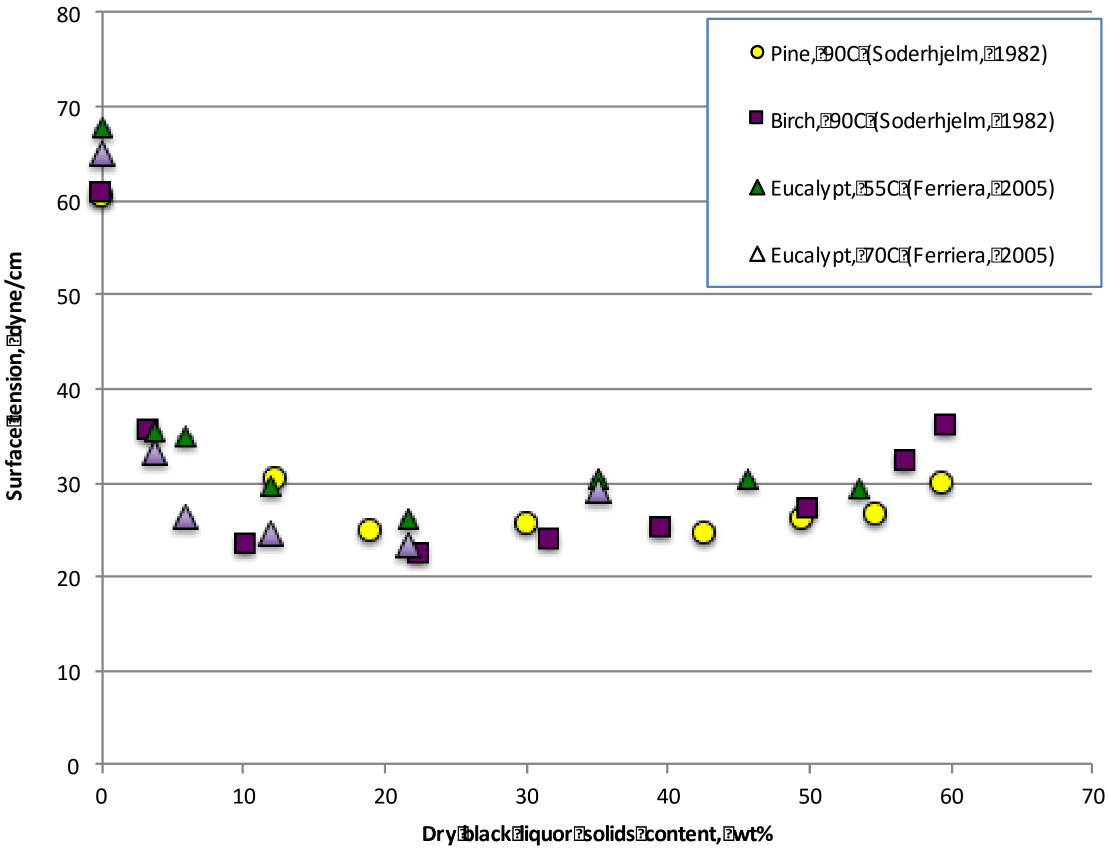

Figure 21. Effect of dry solids content on black liquor surface tension [31, 32].

The effect of temperature on the surface tension of black liquor is about the same as for pure water.

The exact composition of the organic portion of black liquor undoubtedly influences measured results. Tall oil and turpentine are agents that depress the surface tension of black liquor. Beyond this, there is little data on the effect of liquor composition on surface tension.

During spraying, black liquor droplets form in a millisecond time frame where dynamic surface tension is the more important one. Immediately after a new surface is formed, the dynamic surface tension of black liquor is higher than the static value measured at longer times. The change in surface tension with time after a surface is formed is shown in Figure 22 for one liquor. At low to moderate dry solids content, the dynamic surface tension of black liquor approaches that of water. At dry solids contents above 50 wt%, the *apparent* surface tension increases with increasing dry solids content as suggested by the data in Figure 21. At these dry solids contents, the apparent surface tension data reflects the effects of liquor viscosity as well on the apparent (or measured) surface tension changes. Note that water is not the continuous phase above 50 wt% dry solids content, and the dynamic surface tension may depend on the composition of the organic matter as well as the effect of viscosity.

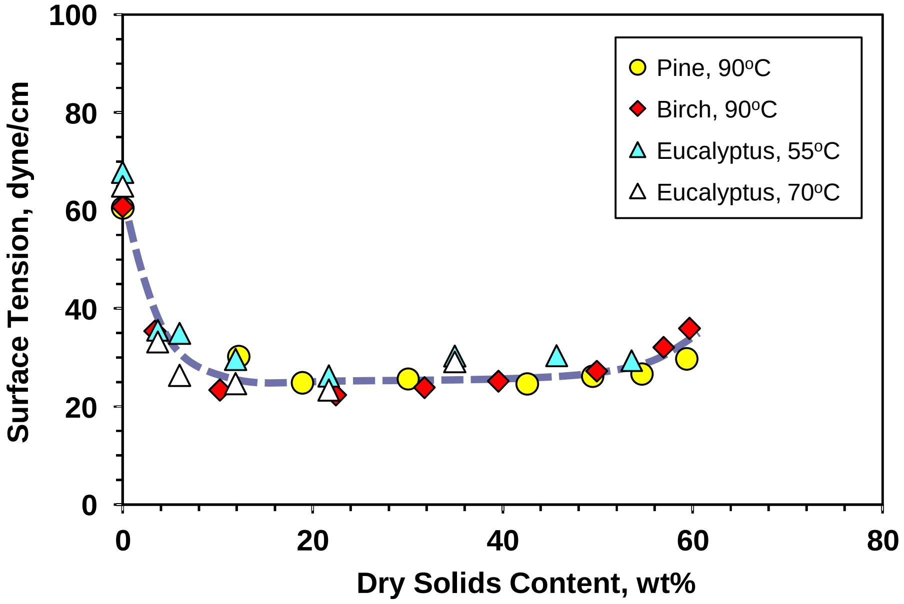

Figure 22. Time to reach equilibrium surface tension after the formation of new black liquor surface [33].

5.3.7 Thermal Conductivity

Thermal conductivity is the property of a material that characterizes its ability to conduct heat. It is important in calculations of heat transfer rates during black liquor evaporation and in assessing the heat transfer within droplets as they dry and devolatilize under high temperature furnace conditions.

The data available on the thermal conductivity of black liquor is quite limited. Figure 23 shows the effect of dry solids content (up to 55%) and temperature (up to 100°C) for one kraft black liquor. The thermal conductivity decreases with increasing dry solids content and increases with increasing temperature.

Figure 24 compares thermal conductivity data for a second kraft black liquor with interpolated and extrapolated values from Figure 23. There is essentially no difference in thermal conductivity between these two liquors.

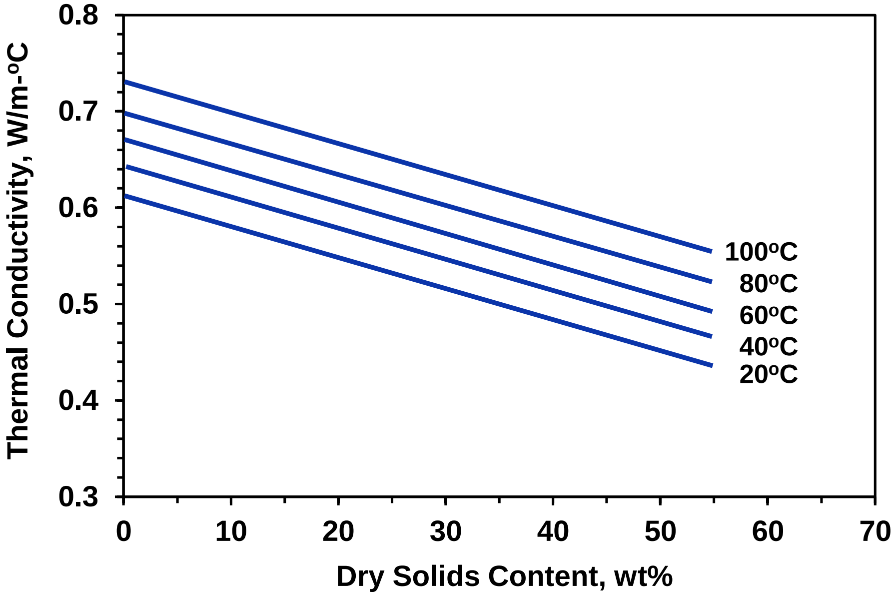

Figure 23. Thermal conductivity of a kraft black liquor [34].

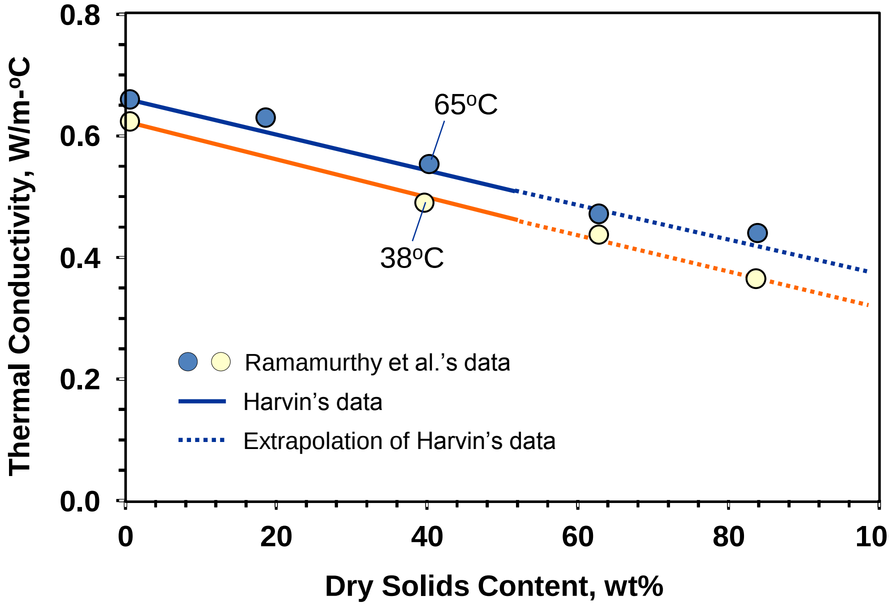

Figure 24. Thermal conductivity versus dry solids content for two kraft black liquors [35].

An empirical equation which fits the data in Figure 24 within ±4% is:

$$k = 1.44\mathrm{x}10^{-3}\ T - 0.335\ S + 0.58 \qquad (13)$$

where

k = thermal conductivity, W/m°C

S = dry solids mass fraction

T = temperature, °C

Equation 13 can be used with confidence over the range of dry solids contents 0% to 82% and temperatures from 20°C to 100°C. Extrapolation to higher temperatures is probably valid as well, although there is no data available with which to test this.

The general pattern of Figures 23 and 24 is reasonable. Dissolved inorganic matter changes the thermal conductivity of water only slightly, while organic matter typically has a thermal conductivity about half that of water. Thermal conductivity of the liquor would then be expected to fall from the value for water to approximately half that value as the dry solids content is increased. Beyond this, there is too little data to assess the effects of black liquor composition.

5.4 SUMMARY

Black liquor is a complex mixture of materials. The variety of raw materials and diverse pulping practices result in a very wide range of chemical and physical characteristics of black liquor. This has made chemical characterization and determination of physical properties a difficult task. Procedures are available for measuring key chemical constituents such as dry solids content, sulfide content, residual active or effective alkali, other major inorganic species, and trace metals. Data are available for a variety of mill and laboratory liquors, and at least a reasonable understanding of the important liquor properties is available. In some cases the results have been comprehensive enough to draw general conclusions about black liquor and to yield estimating procedures useful in mill practice.

Some of the properties of black liquor can now be estimated with reasonable confidence using only a very small amount of data for a specific liquor or mill operation. Liquor density, surface tension, and heat capacity fall in this category. Particular mill conditions can change each of these properties, but the range of variation is not very wide, and relatively easy means are available to estimate them for any particular mill condition.

There are three other properties for which there is sufficient data for identifying general levels and trends as a function of liquor state. These are viscosity, boiling point rise, and the solubility of the main inorganic components. Although general information is available for each of these, all three are sensitive to liquor composition. Also, all have an important impact on the design and operation of evaporators. Measurement procedures for each of these properties are relatively complex and have not been reduced to routine mill procedures.

In a category by itself is the thermal conductivity of black liquor. The small amount of data available on thermal conductivity of two black liquors suggests that liquor-to-liquor differences may be small. Although this data is reasonable, it does not cover a range of liquors which would allow the data to be used with confidence. The values reported might be adequate to estimate the range of thermal conductivity for gross heat transfer calculations, but would not be adequate for estimating heat transfer coefficients in evaporators which now must be obtained empirically. More data and analysis is need on the thermal conductivity of black liquor.

Nearly all of the published data on the properties of black liquor are based on measurements of liquors produced from North American or northern European wood species. Data on South American and Asian wood species such as eucalyptus are becoming more available, but more data for those species are needed.

5.5 NOMENCLATURE

Cp = heat capacity of black liquor, J/kg°C
Cp_E = excess heat capacity, J/kg°C
Cp_s = heat capacity of black liquor solids, J/kg°C
Cp_w = heat capacity of water, J/kg°C
H_s = enthalpy of black liquor at 80°C and dry solids content S
H_w = enthalpy of water at 80°C relative to 0°C
ΔH_v = enthalpy of vaporization of water, J/kg
$\Delta H_{v\text{-}1\ atm}$ = enthalpy of vaporization of water at one atmosphere = 2244 kJ/kg
$\Delta H_{v\text{-}p}$ = enthalpy of vaporization of water at pressure p, kJ/kg
k = thermal conductivity, W/m°C
m = molality, mol/kg water
MW_w = molecular weight of water = 18
Na_{bls} = wt% sodium in black liquor solids, %

Q^T = heat of dilution per unit mass of solids at 80°C from dry solids content S to infinite dilution

R = ideal gas constant, 8.2x10^2 atm m^3/kmole K

S = black liquor dry solids mass fraction

sulfidity = liquor sulfidity based on AA, %

T = temperature, K

T^* = arbitrary reference temperature = 373K

T_{bw} = boiling point of pure water, K

$T_{bw\text{-}1\ atm}$ = boiling point of water at one atmosphere = 373 K (100°C)

$T_{bw\text{-}p}$ = boiling point of water at pressure p, K

ΔT_b = boiling point rise (BPR), °C

ΔT_{b50} = boiling point rise at 50% dry solids content, °C

$\Delta T_{b50\text{-}1\ atm}$ = BPR at 50 wt% solids at one atmosphere, °C

$\Delta T_{b50\text{-}p}$ = BPR at 50 wt% solids at pressure p, °C

v = velocity, m/s

y = distance from surface, m

μ = viscosity, Pa-s

ρ = black liquor density, kg/m^3

τ = shear stress, Pa

<u>Subscripts</u>

bl = black liquor

w = water

T = temperature

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6 SCALING AND FOULING IN BLACK LIQOUR EVAPORATORS

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Nikolai DeMartini

6.1 INTRODUCTION

The greatest capacity limiting and operational problem for black liquor evaporators is scaling and fouling of heat transfer surfaces. Results from two historic surveys of black liquor evaporator scaling and fouling have shown the range of scale and foulant types, along with the frequency of each. These results are presented in Table 1. They show that scaling and fouling problems increased with time from 1973 to 1997, but that the distributions of types of scaling and fouling changed relatively little except for sodium carbonate- sulfate scales. No more recent survey has been undertaken in the 20-year period from 1997 to present.

Table 6.1. Distribution of scale and foulant types in black liquor evaporators in North America in 1973 and 1997.

Number of kraft and soda pulp mills responding	43	25
	Number if evaporator sets reporting this problem	
Type of scale or deposit	1973 survey	1997 survey
Na_2CO_3-Na_2SO_4	19 (30%)	18 (39%)
$CaCO_3$ and Pirssonite	20 (31%)	12 (26%)
Aluminum silicate	9 (14%)	4 (9%)
Sodium oxalate	-	1 (2%)
Fiber, soap, other organics	6 (9%)	9 (20%)
No scale or fouling	10 (16%)	2 (4%)
Total reporting scales or foulants	54	44

Table 6.2. Locations of scales and deposits in black liquor evaporators as reported in the 1997 survey.

Scaling location	Range of dry black liquor solids content, wt%	Number of mills reporting scales and deposits
Evaporator effects (Traditional effects excluding integrated concentrator units)	<30	3
	31-40	3
	41-50	10
	51-60	7
Concentrator effects (Separate unit or integrated 1st effect of evaporator train.	51-60	5
	61-70	10
	71-80	2
Total		40

Each type of scale has its own unique cause. Sodium salt scales are deposited because the solubility limit for Na_2CO_3 and Na_2SO_4 are exceeded, and double salts containing them are crystallized on heat transfer surfaces. Calcium scales are deposited because organocalcium complexes are decomposed near heat transfer surfaces, and the calcium ion released reacts with carbonate ions to produce calcium carbonate or Pirssonite deposits on heat transfer surfaces. Aluminosilicate scales are deposited when thee solubility of limit aluminate and silicate species is exceeded. Sodium oxalate crystallizes from solution onto heat transfer surfaces when its solubility limit is exceeded.

Fouling by lignin occurs when the alkali content of black liquor is too low for lignin to remain in solution. Soap deposits occur when the concentration of soap in black liquor exceeds substantially its solubility limit and is not removed effectively from black liquor. Fouling by fiber is the result of inefficient removal by black liquor fiber filters.

Regardless of the type of scale or foulant, they often limit evaporator capacity when they occur. The cost of each depends upon the loss in pulp production due to loss in evaporator capacity, and the cost of cleaning of evaporators and concentrators to remove scale and deposits.

Minimizing the impact of scale and foulants is key to achieving and maintaining evaporation capacity. Both evaporation plant design and liquor cycle chemistry play important roles. For For example, limiting species responsible for fouling from the pulp mill chemical cycle is an effective way to eliminate scaling by aluminosilicates. Designing concentrators as crystallizing evaporators can reduce Na_2CO_3-Na_2SO_4 fouling in these units.

Important: remember, not all scaling and fouling problems are solved in the evaporation plant. Often, they require changes elsewhere in the mill. Improving causticizing conversion is one example. Proper control of residual alkali in black liquor is another. Minimizing aluminum input to the recovery cycle is a third.

This chapter addresses both the chemistry of pulp mill liquor cycle as it impacts scaling and fouling in black liquor evaporators and concentrators. It also addresses certain aspects of process design that can impact scaling and fouling. Scale- and foulant-specific methods of evaporator cleaning are reviewed.

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6.2 SODIUM CARBONATE-SULFATE SCALES IN BLACK LIQUOR EVAPORATORS AND CONCENTRATORS

Black liquor concentrators not only evaporate water; they also act as crystallizers, producing 100 to 200 kg of sodium salt (Na_2CO_3+Na_2SO_4) crystals per ODt pulp. Crystallization of Na_2CO_3, and Na_2SO_4 salts can deposit scale on concentrator heat transfer surfaces, limiting evaporation capacity, plugging flow passages, and often requiring frequent cleaning of concentrators and transfer piping.

Traditionally, black liquor concentrators were designed as heat transfer devices. While this is their primary function, they can avoid serious scaling problems when they are designed and operated to accommodate evaporative crystallization as well. This section discusses some aspects of crystallization behavior as related to crystallizing evaporator design and operating practices, and how they apply to scale control in black liquor concentrators.

6.2.1 Influence of Composition on the Na-CO3-SO4 Crystals formed in Black Liquor

Inorganic scale is deposited in modern black liquor concentrators because sodium salts crystallize during evaporation of water. Scaling is primarily caused by crystallization of double salts of sodium sulfate and sodium carbonate. At least three different double salts have been identified in black liquor, Table 1. One is Burkeite which has a nominal composition of $2Na_2SO_4 \bullet Na_2CO_3$. The other well-known double salt is sodium sulfate dicarbonate, (nominally $Na_2SO_4 \bullet 2Na_2CO_3$) commonly referred to as dicarbonate. A third double salt which is not well known, but has been found in black liquor, is sodium sulfate carbonate (nominally $Na_2SO_4 \bullet 1.5Na_2CO_3$). While this salt is distinct from dicarbonate, it behaves similarly to dicarbonate with regards to fouling. Which of these double salts precipitates first depends on the ratio of dissolved carbonate to dissolved sulfate, Table 1.

Table 1. Crystals produced when black liquor is concentrated above their solubility limits.

Na_2CO_3/Na_2SO_4 mass ratio *in solution*	Crystal composition	Solid phase name (common name)
Less than 0.16	Na_2SO_4	Sodium sulfate
Between 0.16 and 1.7	1.6-2.6 $Na_2SO_4 \cdot Na_2CO_3$	Burkeite
Between 1.7 and 3.4	– $Na_2SO_4 \cdot 1.5Na_2CO_3$	Sodium sulfate carbonate
Between 3.4 and 6.7	– $Na_2SO_4 \cdot 1.6\text{-}3.0Na_2CO_3$	Sodium sulfate dicarbonate (dicarbonate)
Greater than 6.7	Na_2CO_3	Sodium carbonate

Burkeite had long been considered the source of Na_2CO_3-Na_2SO_4 scaling in black liquor evaporators (1). A few decades ago, black liquor was relatively rich in sulfate and the LTV evaporators used predominantly in those days were not designed to perform as crystallizing evaporators. When black liquor was concentrated to above the solubility limit for sulfate-rich *Burkeite*, it crystallized, scaling and plugging LTV evaporator tubes rapidly (2). Units in which Burkeite deposited as scale required frequent boilouts to maintain evaporation capacity. As the falling film technology developed, falling film, high solids concentrators replaced direct contact evaporators. These early concentrators experienced extremely high scaling rates and this reopened the study of evaporator fouling due to sodium salts. Shi (3) identified the XRD patter for the carbonate rich double salt dicarbonate. One of the important findings was that dicarbonate forms fine, micron sized crystals, Figure 1, that subsequently agglomerate in suspension and on heat transfer surfaces (4,5). One of the important features of dicarbonate is that it does not grow on existing Burkeite crystals.

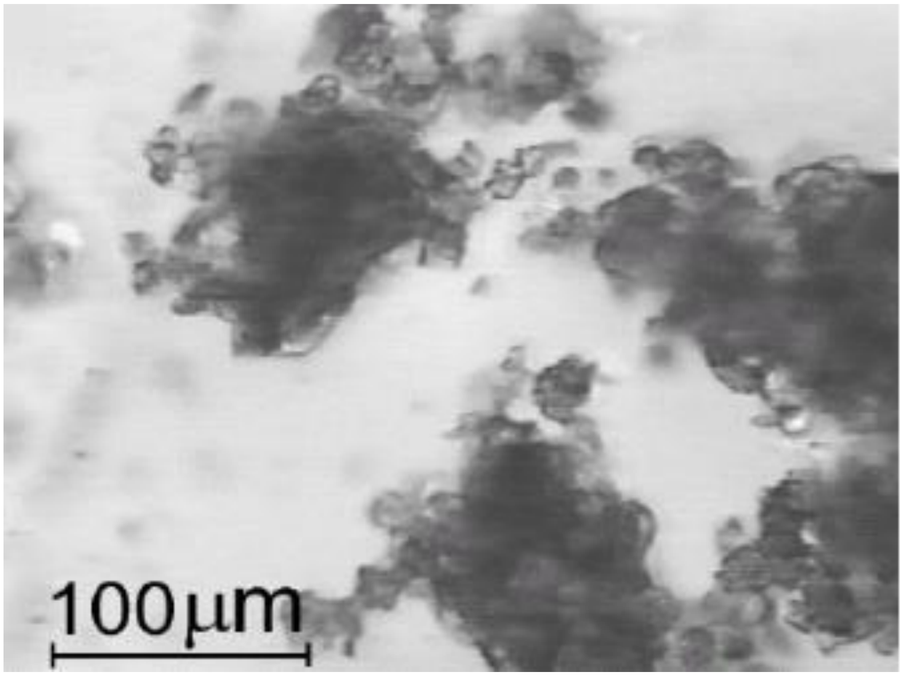

Figure 1. Crystal agglomerates of dicarbonate from a solution with a carbonate-sulfate molar ratio of 5:1. From (4).

The firing of higher solids black liquor in recovery boilers resulted in higher temperatures in the lower furnace, increasing the reduction efficiency in the recovery boiler, leading to lower sulfate concentrations in black liquor. Thus, the black liquor composition has changed over time, moving from sulfate-rich to carbonate-rich black liquor.

Figure 2 shows the Na_2CO_3/Na_2SO_4 mass ratio in 31 black liquors analyzed from 1997 through 2012. Most of the liquor samples analyzed were from the first effect or concentrator feed liquors, while some were weak or intermediate liquor samples. The 19 liquors labeled as "dicarbonate" in Figure 2, first crystallize dicarbonate as water is evaporated from them. Seven of the nine liquors labeled as "Burkeite" initially crystallize Burkeite when they are concentrated, but eventually dicarbonate crystallizes. This is because crystallization of Burkeite depletes Na_2SO_4 from solution more rapidly than it depletes Na_2CO_3. As a result, the ratio of *dissolved* Na_2CO_3/Na_2SO_4 in the liquors increases.

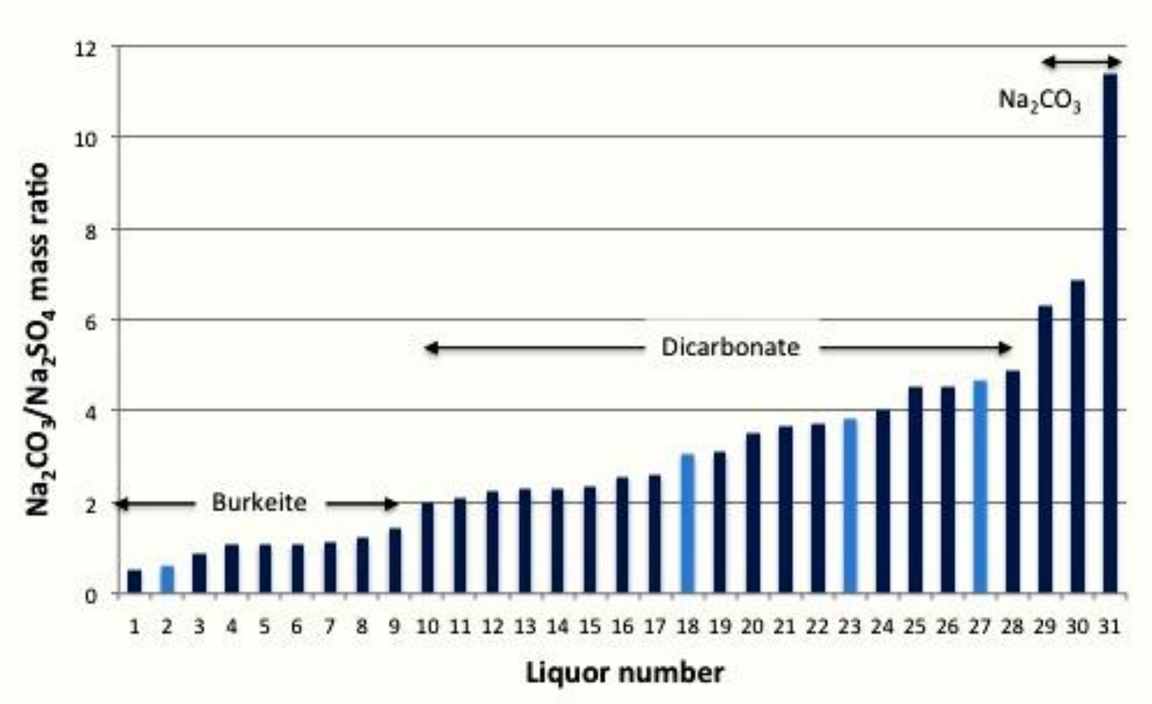

Figure 2. Na_2CO_3/Na_2SO_4 mass ratios for 31 kraft mill black liquors. The ranges marked Burkeite, dicarbonate, and $Na2CO_3$ indicate what the first salts to crystallize would be for each black liquor when concentrated to above its solubility limit. Dark blue: from Schmidl and Frederick, 1998 (6); light blue: from other black liquors analyzed more recently. The area marked "dicabonate" includes sodium sulfate carbonate which is a separate crystal species, but appears to behave in the same way as dicarbonate.

6.2.2 Solubility of Sodium Salts in Black Liquor

The solubility of Na_2CO_3+Na_2SO_4 in most black liquors is from 60 to 100 g/L at 50wt% total dry solids content. The solubility of these salts decrease with increasing sodium, carbonate and sulfate concentration (1). The solubility of these salts also decreases with increasing temperature in the temperature range relevant to black liquor evaporators (7). Their solubility changes with the ratio of Na_2CO_3 to Na_2SO_4 in black liquor as illustrated in Figure 3. The solubility limit decreases by about 4 wt-% dry solids content as the carbonate to sulfate ratio increases from 60/40 to 90/10 as shown here. Evaporator operators need to be aware of how these changes in Na_2CO_3/Na_2SO_4 ratio, total sodium content, and temperature can create or eliminate conditions for rapid dicarbonate scale deposition even when operating at constant product dry solids content. There are a number of published approaches for estimating the solubility limit (8-10). These correlations are based primarily on the data of Grace (1).

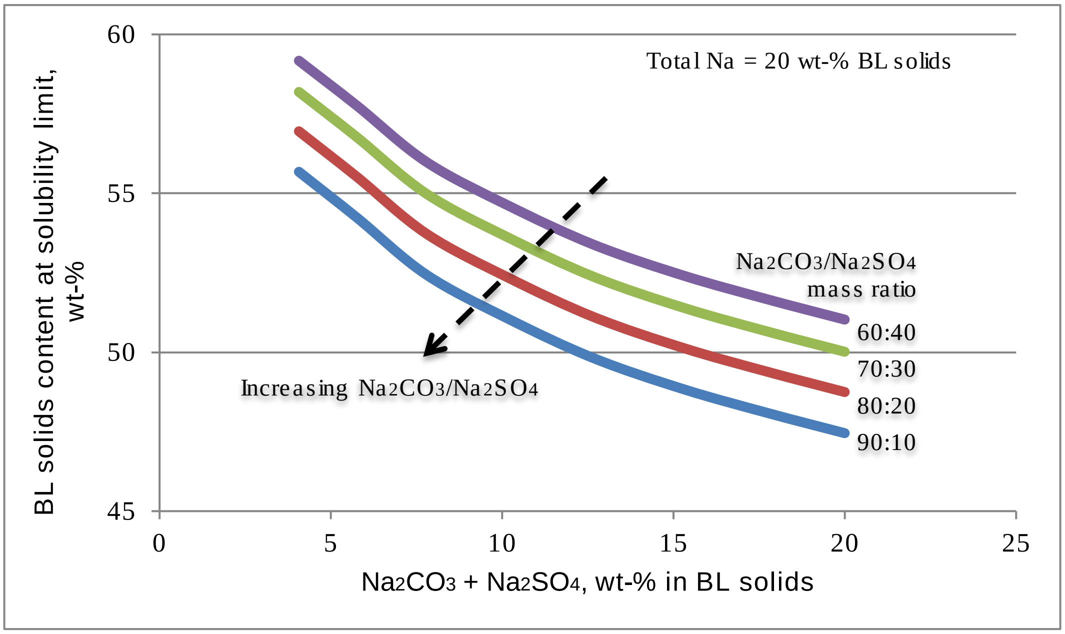

Figure 3. Black liquor solids content at the solubility limit for Na_2CO_3+Na_2SO_4 versus wt-% Na_2CO_3+Na_2SO_4 in dry black liquor solids. Based on Grace's correlation (1975).

6.2.3 Crystallization in Black Liquor Concentrators

Nucleation is the formation of a stable crystal nucleus and requires some level of supersaturation (11). For some salts, such as the sodium double salts discussed here, the level of supersaturation can be quite high. The concentration at which nucleation occurs, is called the *metastable limit*. The metastable limit depends on the salt being precipitated as well as external factors such as the solvent properties, presence of ions that inhibit the formation of a stable nucleus, degree of mixing, and defects in the equipment surfaces. This is illustrated for dicarbonate in water, Figure 4. To understand the metastable limit, consider the solution in Figure 4, starting at a salt content of 29% at 130 °C. All of the salt is soluble at those conditions. As water evaporates isothermally, the concentration of dissolved salt in solution increases above the solubility limit. In the case of these experiments, the solution reached a concentration of ~32 wt% salt content before dicarbonate precipitates.

For both Burkeite and dicarbonate the metastable limit is 5-8% higher than the solubility limit (3,12). From a practical perspective, if the metastable limit is quite high, as is the case for these sodium salts, a large amount of salt can precipitate quite rapidly once the metastable limit is exceeded. In the case of dicarbonate, the micron sized crystals agglomerate in suspension and on available surfaces. Heat transfer surfaces are scaled most rapidly by dicarbonate during spontaneous nucleation (13). It has been shown in pilot evaporator studies with a falling film, that nucleation of dicarbonate results in a scaling rate 5 times more rapid than the scaling that occurs at similar evaporative loads with a stable dicarbonate crystal population and 10 times more than during evaporation if there is a stable Burkeite crystal, Figure 5 (14). This study also showed that the scaling rate during Burkeite nucleation is about the same as scaling from Burkeite under normal evaporative crystallization. Thus, evaporators and concentrators should be operated to avoid dicarbonate nucleation events. In practice this means operating at least at least 3-4 percent dry solids above or below the solubility limit. If the heat balance in the evaporator train results in an effect operating near the dicarbonate solubility limit, the mill can help itself by decreasing the ratio of dissolved carbonate to dissolved sulfate. The can be accomplished by good control in the recausticizing plant to minimize carbonate and if possible, increasing sulfidity (15,16).

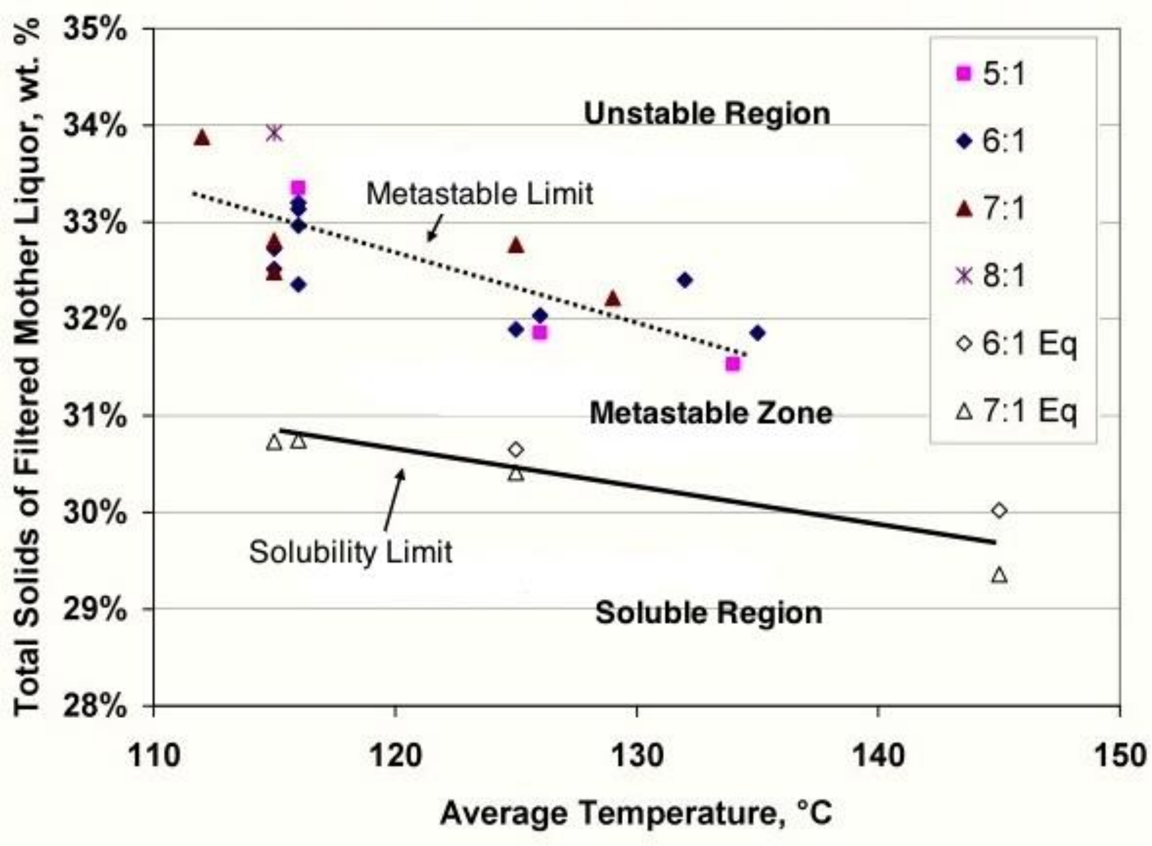

Figure 4. Dicarbonate metastable zone for aqueous solutions of Na_2CO_3 and Na_2SO_4. Symbols indicate the molar ratio of Na_2CO_3 to Na_2SO_4 (12).

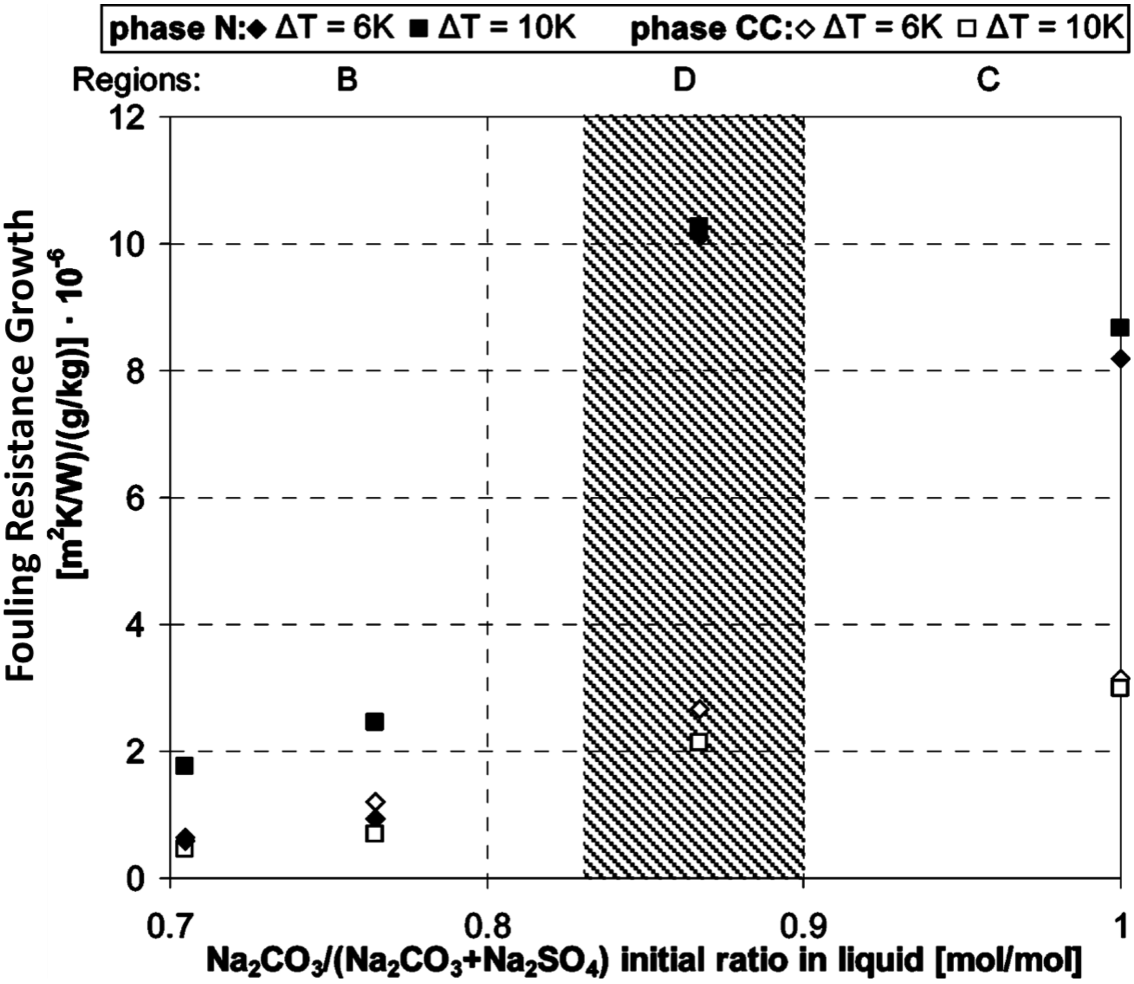

Figure 5. Average fouling resistance growth ($\Delta R/\Delta X_{c+l+s}$) during evaporation of aqueous solutions in a pilot evaporator with Na_2CO_3 and Na_2SO_4 at different initial solution compositions. Growth rates were measured during nucleation phase (N) and continuous crystallization phase (CC). Continuous crystallization refers to evaporation with crystals present. (14).

Once stable nuclei are present, precipitating salts can deposit on existing crystals. Having a higher crystal concentration in principal can reduce the degree of scaling. However, Karlsson et al. (17) did not find a correlation between the scaling rate and crystal population when the crystal concentration was between 1.5 and 6 wt % on a dry solids basis, Figure 6.

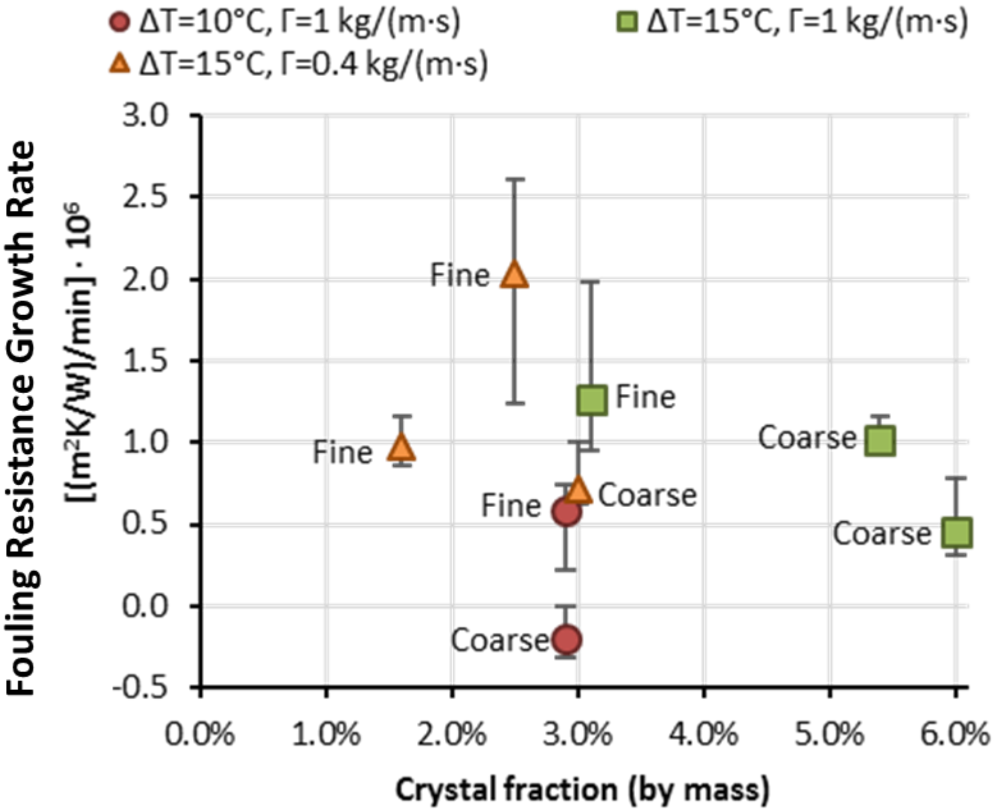

Figure 6. Fouling resistance growth rate (ΔR/Δt) due scaling to scaling during evaporation of black liquor with different crystal loads. Coarse and fine refer to the hydrocyclone operational modes used (17).

It is important to note that dicarbonate does not grow on crystals other than itself. It does not grow on Burkeite, or recovery boiler ash particles. Dicarbonate crystals must be present during concentration of black liquor to remove supersaturation and prevent spontaneous dicarbonate nucleation. Thus, you can have a nucleation event for dicarbonate, even when you have a Burkeite crystals present in the black liquor. Operation where dicarbonate crystallizes spontaneously nucleate are to be avoided to prevent rapid scaling of black liquor concentrators.

6.2.4 Critical Solids Content

"Critical solids content" is a term coined by Tom Grace (1,8) to indicate the dry solids content below which LTV evaporators should be operated. In his work, he was equating this term to the solubility limit. The term is no longer relevant but is still used in the literature, sometimes to describe the solubility limit, and at others, the metastable limit. The reader should thus be careful in this distinction.

6.2.5 Stable Operation of Crystallizing Evaporators

By definition, black liquor concentrators are crystallizing evaporators. They crystallize Na_2CO_3+Na_2SO_4 salts as water is evaporated. Crystallizing evaporators must be operated in the metastable region in Figure 3. This region is above the solubility limit and below the metastable limit where spontaneous nucleation begins (18). In crystallizing evaporators, supersaturation must be relieved by growth of suspended crystals to prevent spontaneous nucleation (12). The crystallization process is stabilized by having a well-mixed liquor volume within the concentrators and a high concentration of suspended dicarbonate crystals to relieve supersaturation.

Growth of suspended dicarbonate crystals must be sufficient to prevent the concentrations of Na_2CO_3 + Na_2SO_4 from exceeding the dicarbonate metastable limit. Crystal growth kinetic data for dicarbonate are needed to determine the mean residence time (liquor volume to feed rate ratio) required for this as well as the acceptable evaporation rate because as the black liquor flows down the heat transfer surface, it is concentrated and so the concentration at the bottom of the heat transfer surface is higher than at the top. Pilot studies with a falling film evaporator have shown that scale growth when there is a stable crystal population tends to start from near the bottom of the heat transfer surface and work its way up. To date, there is only data is available for either dicarbonate crystal growth kinetics or nucleation kinetics from either aqueous solutions of Na_2CO_3 and Na_2SO_4 or from black liquor (13). This type of data is needed to improve black liquor concentrator design.

Recirculation of liquor with suspended crystals is also practiced in other industrial crystallization operations (18). It stabilizes the crystal population within the body of an effect when the recirculated liquor contains a large concentration of suspended crystals. These crystals relieve supersaturation. The presence of stable crystals prevents the dissolved concentration of Na_2CO_3 and Na_2SO_4 from exceeding the metastable limit. This prevents nucleation of fine dicarbonate particles that foul heat transfer surfaces.

6.2.6 Design considerations for black liquor concentrators

Flow sequences in multi-effect black liquor concentrators are sometimes configured so that much of the crystallization load occurs where very few suspended dicarbonate crystals are present. This easily moves evaporation to the metastable limit, where spontaneous nucleation and fouling occur. It is therefore critical to operate those units where dicarbonate will precipitate in such a way that a stable dicarbonate crystal population is maintained. Start-up poses a significant problem because suspended dicarbonate crystals may be absent if the black liquor contains no dicarbonate crystals at startup.

The residence time for black liquor in concentrators is important in crystal growth. Black liquor must remain in a concentrator effect long enough to relieve supersaturation to well below the metastable limit for dicarbonate. The concentration of suspended dicarbonate crystals must be sufficient to provide growth area for dicarbonate crystallizing from solution. That is determined by the rate at which dicarbonate needs to be crystallized from black liquor.

The only available dicarbonate crystallization growth rate data were measured during dicarbonate crystallization from water in a pilot evaporator and reported by Euhus (13):

$$\text{Crystal growth rate} = 1.81\text{x}10^{-8}\ \text{ms}^{-1} \qquad (1)$$

This growth rate falls between $1\text{x}10^{-8}$ ms^{-1} and $5\text{x}10^{-7}$ ms^{-1}, the reported range for growth rates for a number of inorganic salts (13). We can use this information to estimate the black liquor residence time in a concentrator required to relieve supersaturation. In a typical black liquor concentrator operation, black liquor at 50% dry solids content might be concentrated to 65% dry solids content. The black liquor feed might be just below the solubility limit for dicarbonate crystallization as it enters the concentrator effect. The total concentrations of Na_2CO_3 and Na_2SO_4 based on dry black liquor solids might be

Na_2CO_3 = 7.0 wt-% dry bl solids
Na_2SO_4 = 3.0 wt-% dry bl solids

All of the Na_2CO_3+Na_2SO_4 is soluble at 50% dry solids content.

When this black liquor has been concentrated to 65% dry solids content, over 90% of the Na_2CO_3+Na_2SO_4 originally in solution will have crystallized, producing dicarbonate. The volume fraction of dicarbonate particles in the concentrator would be 0.0021 m^3 particles/m^3 black liquor. The total residence time required for black liquor in the concentrator for this amount of crystallization to occur would have been 6.0 hours.

If the feed rate to the concentrator were 25 kg/s (300 gpm) black liquor at 50% dry solids content, the total volume required for the concentrator to be able to maintain steady crystal growth conditions would have been 108,000 gal. This is impractically large for a concentrator with a feed rate of 300 gal/min at 50% dry black liquor solids content!

The most effective way to manage crystallization without huge concentrator volumes is to increase the concentration of suspended dicarbonate particles in the recirculated black liquor. This concept is the basis for a patent awarded to Olausson et al. (19). Table 2 shows the relationship between the liquor recirculation rate, the concentration ratio of particles in the recirculation to that in the product liquor if particles were not concentrated in the recirculated stream, and the residence time required for the concentrator to be able to relieve supersaturation in the black liquor within the concentrator. These values were calculated using the Euhus growth rate constant in Equation 1. It is clear that increasing the concentration of particles by a factor of at least 10 would bring the residence time requirement for the concentrator to less than an hour. This would minimize dicarbonate fouling in the high solids concentrator for the case presented here.

Table 2. The residence time required for black liquor in a high solids concentrator to relieve Na_2CO_3+Na_2SO_4 saturation during concentration of black liquor. Residence times are shown as a function of suspended dicarbonate particle concentration. [a]Calculations assuming linear crystal growth using rate equation (1).

Liquor recirculation/feed ratio	Particle concentration ratio in recirculation/feed	Particle concentration ratio in concentrator‡	Liquor residence time[a]	
			Hr	min
10	1	1	5.98	359
10	3	2.82	2.12	127
10	10	9.18	0.65	39
10	100	91.0	0.066	4
15	1	1	5.98	359
15	3	2.88	2.08	125
15	10	9.44	0.63	38
15	100	93.8	0.064	3.8
20	1	1	5.99	359
20	3	2.9	2.06	124
20	10	9.57	0.626	38
20	100	95.3	0.0628	3.8

‡ Ratio of recirculated black liquor to crystals in the concentrator without crystals from recycled black liquor

6.2.7 Controlling Dicarbonate Crystal Populations

Dicarbonate scale deposition can be reduced or eliminated by maintaining enough dicarbonate crystals in suspension and operating the concentrator within the metastable range for dicarbonate crystallization. Dicarbonate can crystallize on suspended dicarbonate crystals or on heat transfer surfaces. When the total dicarbonate crystal surface area is high, Na_2CO_3+Na_2SO_4 will grow on suspended crystals. Na_2CO_3+Na_2SO_4 supersaturation will remain low, and spontaneous nucleation of dicarbonate crystals will not occur. Growth of crystals on heat transfer surfaces will also be slow. This minimizes scale formation. It requires a large suspended dicarbonate crystal population. To maintain a large dicarbonate crystal population, the concentrator system needs to be designed using the industrial crystallizer design principles discussed here.

6.2.8 Small ΔTs Avoid Dicarbonate Scaling

Black liquor concentrators rely on small *ΔTs* and correspondingly large heat transfer surface areas to minimize rapid scaling. A higher *ΔT* will translate to a higher evaporation rate and higher rate of scaling, Figure 7. Excessively high *ΔTs* may even lead to exceeding the metastable limit, Figure 8. To avoid rapid dicarbonate scaling, the liquor temperature in a concentrator body must be low enough so that the liquor does not cross into the metastable region. This is most likely to occur with liquor adjacent to the heat transfer surface. The liquor temperature near the surface will be higher than that of the rest of the liquor within the body. It is possible for the liquor near the surface to cross the metastable limit, undergo spontaneous nucleation, and deposit dicarbonate scale on the heat transfer surface, as illustrated in Figure 8. This can be avoided with smaller *ΔTs*.

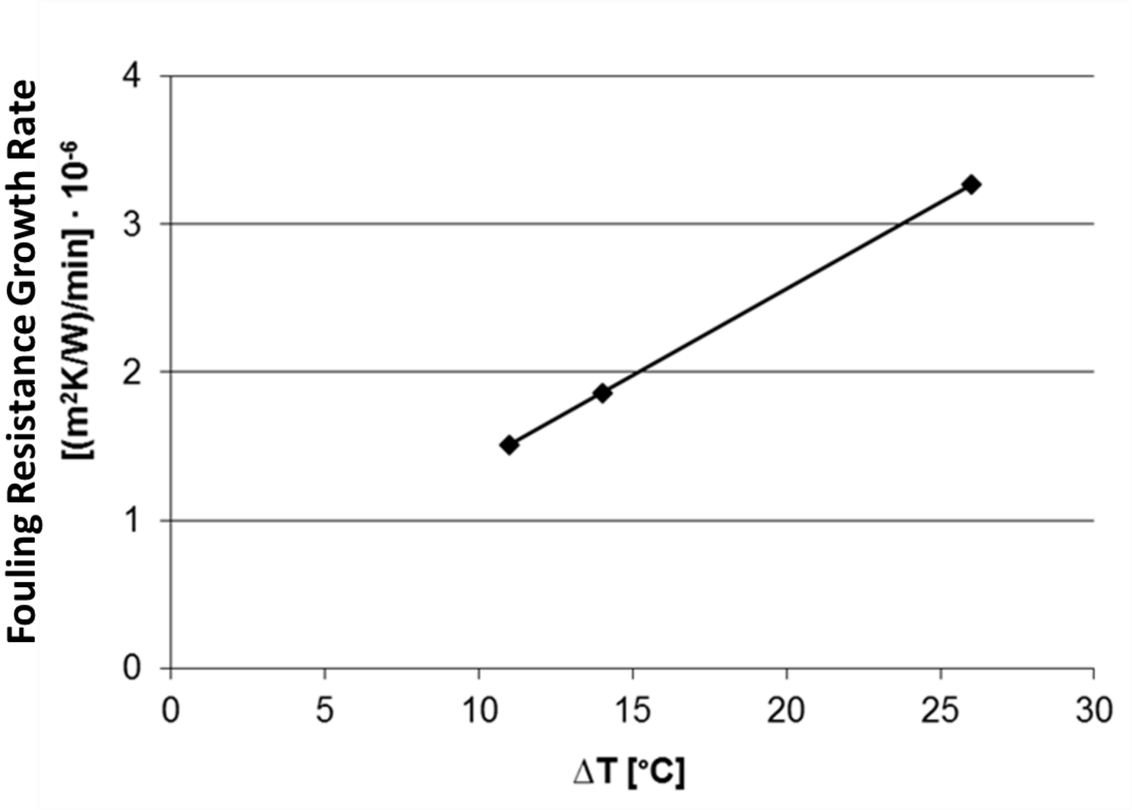

Figure 7. Change in average fouling resistance growth rate ($\Delta R_f/\Delta t$) to heat transfer (as a measure of scaling) vs ΔT in a pilot evaporator during the evaporation of water when crystals are present (20).

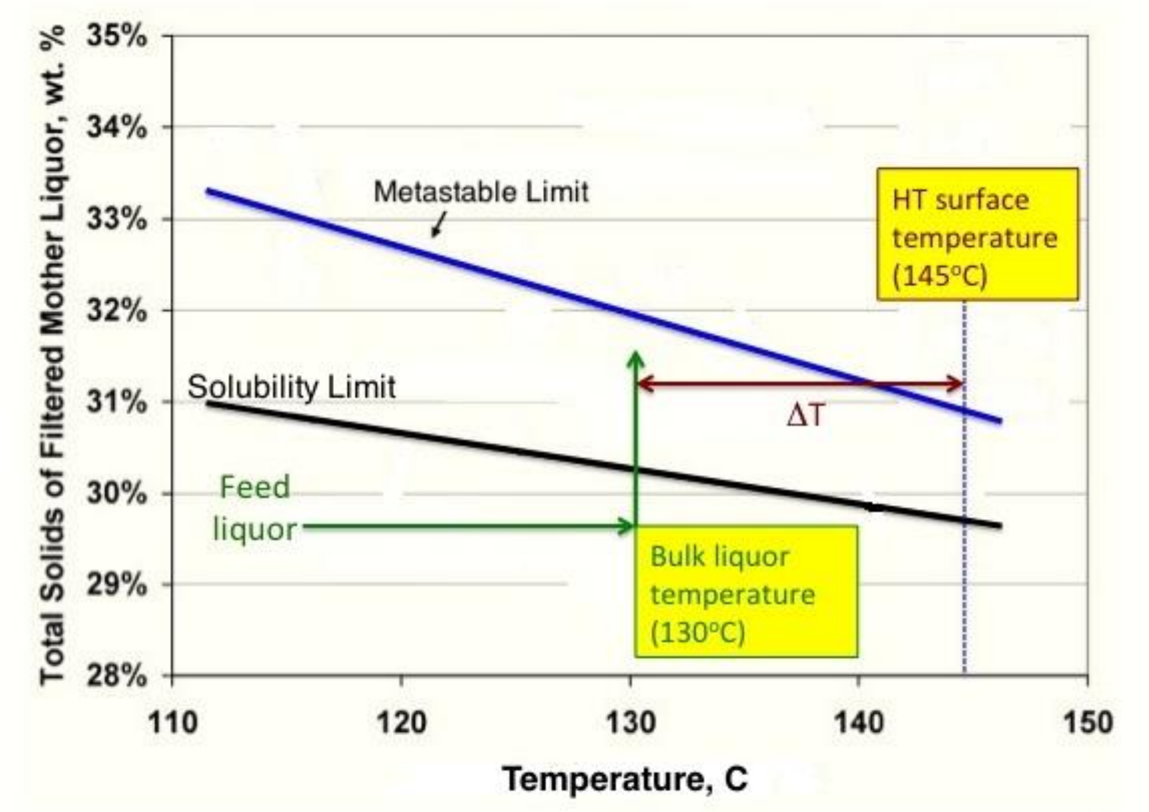

Figure 8. Impact of ΔT on spontaneous nucleation of dicarbonate near heat transfer surfaces.

6.2.9 Washing soluble scales

Karlsson et al. (21) developed a model from the dissolution of sodium salt scales during the wash cycle of a black liquor evaporator. They established that the dissolution process is diffusion controlled mass transfer. The dissolution rate (Jx) is calculated using the following equation based on film theory:

$$Jx = k(c^* - c)$$

where k is the mass transfer coefficient, c* is the solubility limit of the salts in the wash liquor and c is the concentration of the salts in the bulk wash solution. For black liquor as a wash solution, a value of k was determined to be about 50 µm/s (22). Calculations have been made for washing a concentrator effect in a Swedish mill (23). The calculations show that the wash liquor feed rate, concentration of salt in the wash liquor and evaporation rate have the largest effects. The former affects the discharge rate for dissolved salts, from the washed evaporator while the latter two affect the amount of salt that can be dissolved per unit volume of wash liquor. Thus, using a more dilute liquor for wash cycles and using a high feed rate will shorten washing times considerably. The scale will wash from the top down. This is because the wash liquor dissolves salt as it flows down the heat transfer surface and so the driving force for dissolution decreases as the wash liquor flows down.

Once an effect has been washed, the dry solids should be brought up to operational solids by recirculating higher solids black liquor. This is to repopulate the crystals to avoid a nucleation event.

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6.3 SODIUM OXALATE SCALING

Oxalate is formed during pulping [1], in oxygen delignification [2-3] and in bleaching stages [4-7]. Oxalate is present in wood as a salt with Ca or other cation. The amount formed depends on the wood species, Figure 1 [1]. For most mills, sodium oxalate precipitates in the concentrators in small quantities along with large amounts of Na-CO_3-SO_4 salts and will not create a scaling problem by itself. There have been a few published instances of sodium oxalate leading to scaling, Figures 2a and b, either in an effect operating below the solubility limit for Na-CO_3-SO_4 salts or in the high solids lines where it was found layered with other sodium salts [8]. Mills pulping hardwood, particularly tropical hardwood are the most likely to see sodium oxalate scaling.

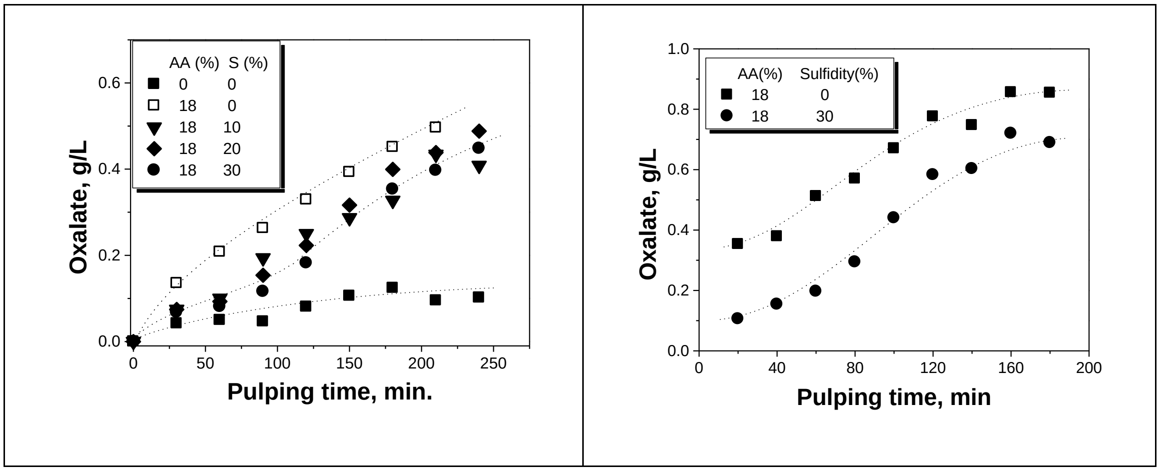

Figure 1. Oxlate formation during the batch pulping of pine (left) and acacia (right) at different sulfidities. The final pulping temperature was 170 °C, reached after 120 min. The data at 0% AA, 0% S in the figure on the left are the results for heating in water [1].

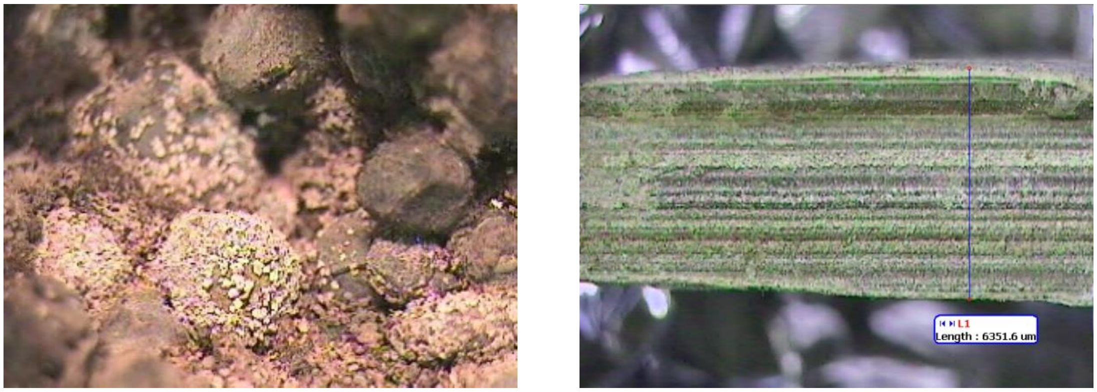

Figure 2. a) Soluble deposit plugging second-effect tubes in Mill B falling-film evaporator, diameter of individual nodules is ~5 mm; b) example stratified soluble deposit from piping handling high solids black liquor in a second mill (right), thickness of plate-like material is ~6 mm [8].

There is one published study for sodium oxalate solubility in black liquor [9]. Ulmgren derived a set of expressions for the apparent solubility product (L_s) of sodium oxalate in black liquor as a function of the sodium concentration and temperature.

$$L_S = [Na^+]^2[C_2O_4^{2-}] \quad (1)$$
$$\text{Log}\ (L_S) = 0.53-0.024[Na^+] \qquad (T = 363\ K) \quad (2)$$
$$\text{Log}\ (L_S) = 1.78 + 0.044[Na^+] - 856/T \qquad (383\ K < T < 423\ K) \quad (3)$$

In the above equations T is in Kelvin, and the concentrations of total sodium $[Na^+]$ and oxalate $[C_2O_4^{2-}]$ are in mol/L. It is important to note that at 90 °C, Ulmgren found that there was a negative correlation between the apparent solubility and the sodium concentration while between 110 and 150 °C, it was positive, thus the two equations. While more solubility data is needed to understand this, the above equations can be used to provide at least a qualitative understanding in which effects sodium oxalate precipitation might occur.

The sodium and oxalate concentrations in the weak black liquor can be measured and then extrapolated as a function of dry solids content. If the solubility lines are plotted on the same graph using equations (1) – (3), it can be seen in which effects it is expected to be soluble and in which effects it is not. This is illustrated in Figure 3 for a black liquor with a sodium concentration of 18 wt% d.s. and for two different oxalate concentrations, one at 0.2 wt% and the other at 0.4 wt% d.s. The concentration of sodium is on the x-axis and the concentration of oxalate is on the y axis. The solubility lines for 110, 125 and 150 C have been calculated using equations (1) and (2). The concentration of sodium and oxalate at 40% dry solids has been converted to mol/l by using a calculated density using the equations for estimated black liquor density provided in Chapter 3 of this book. In this figure, the concentration of oxalate and sodium is in increments of 5% dry solids content represented by the circles and triangles between 40% dry solids content (left most black circle or triangle) and 80% dry solids content (right most circle or triangle). To generate these lines for the concentration of sodium and oxalate, it is assumed that no sodium or oxalate precipitates. If we consider the dashed solubility line for sodium oxalate at 110 °C, in the case of the black liquor with 0.2 wt% oxalate (circles), the solubility limit is not reached until about 70% dry solids content. For the liquor with 0.4 wt% oxalate, the solubility limit is reached at 46% dry solids content.

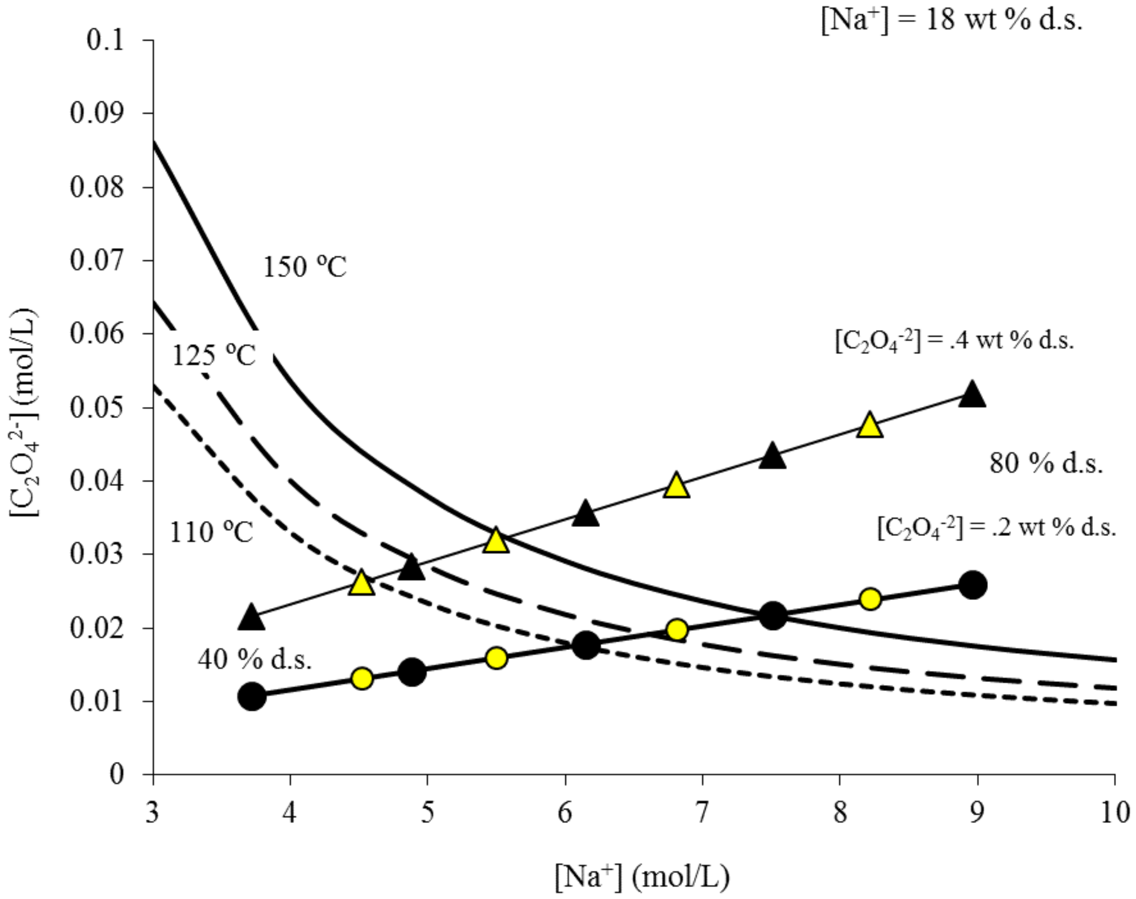

Figure 3. Solubility curves for sodium oxalate in black liquor based on equations (1) and (2) above and concentration lines for two black liquors both with a Na concentration of 18 wt% d.s. and oxalate concentrations of 0.2 wt% d.s. (circles) and 0.4 wt% d.s. (triangles). The concentration lines are made assuming no precipitation of sodium or oxalate and using a calculated black liquor density as a function of dry solids content and temperature.

Changes in sodium oxalate concentration can occur through changes in wood species pulped, or through quick recovery of wash liquor. Mills can understand the implications of changing wood species by sampling weak black liquor from the pulping of the different wood species. In the case of handling wash cycles, it is important to bring back wash liquor as slowly and evenly as possible [10]. Wash liquor is inherently concentrated in the inorganic salt being washed. As for other soluble salts, if the wash liquor is recovered quickly, the concentration of sodium or oxalate can spike causing a more significant amount of salt to precipitate, leading to more rapid scaling.

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6.4 CALCIUM CARBONATE AND PIRSSONITE SCALES

Calcium carbonate ($CaCO_3$) scales have plagued black liquor evaporators since the onset of indirect concentration of black liquor to recover and regenerate pulping chemicals. Calcium carbonate forms dense, tenacious scales with good insulating properties, effective at reducing evaporation capacity. Pirssonite, $CaCO_3 \bullet Na_2CO_3 \bullet 2H_2O$, is a Ca-based double salt that is also a source of scaling in black liquor evaporators. It deposits from black liquors with both high soluble calcium and high carbonate content. We refer to these scales collectively as “calcium-based scales.”

Figure 1 shows the compositions of calcium-based scales from evaporation of seven different kraft black liquors. Together, $CaCO_3$ and Pirssonite account for 65% to 96% of these scales. The unaccounted fraction is small quantities of salts of other minerals such as Al, Si, and Mg, and organic matter from dry black liquor solids retained within the porous scale matrix.

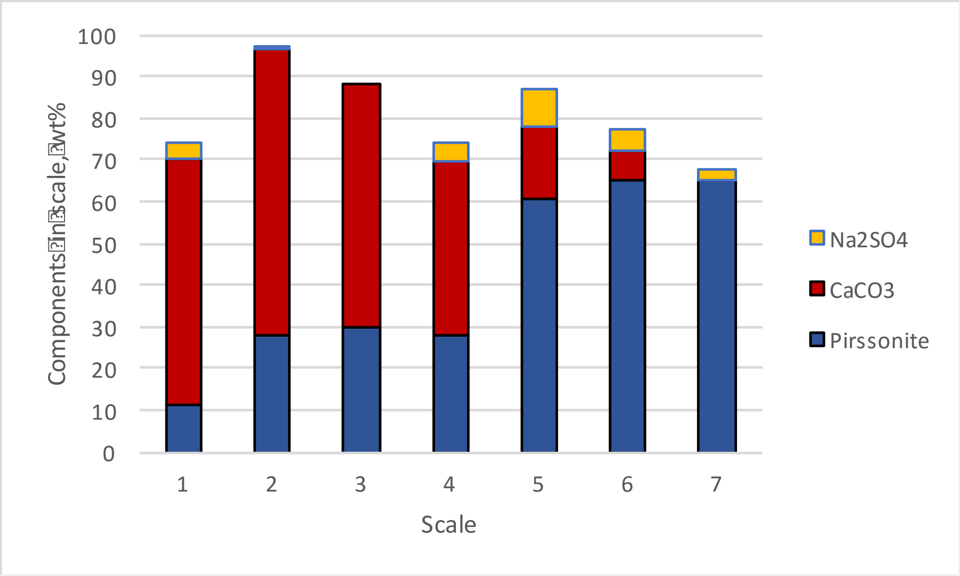

Figure 1. Inorganic chemical composition of predominantly calcium scales from seven different black liquor evaporators.

6.4.1 Where Calcium-Based Scales are a Problem

$CaCO_3$ scales are deposited at temperatures above 120°C during evaporation of black liquors from conventional kraft pulping. They impact mainly the first and second effects in multiple-effect LTV evaporators, but sometimes the 3rd effect as well. They deposit at temperatures as low as 90°C in evaporators processing black liquor from kraft displacement batch pulping such as RDH and Superbatch pulping.

6.4.2 Chemical Processes in Calcium-Based Scaling

The main source of calcium in black liquor is wood. Calcium content varies widely with wood species and with growing region. Bark contains far more calcium than do sapwood and heartwood as illustrated in Table 2 for a typical eucalyptus wood species.

Table 1. Representative values of the calcium content of various North American wood species (bark-free, OD basis).

Balsam fir	850 ppm
Eastern cottonwood	105 ppm
Eastern hemlock	950 ppm
Eastern white pine	250 ppm
Quaking aspen	950 ppm
Red maple	750 ppm
Red spruce	750 ppm
Southern red oak	300 ppm
Sweetgum	600 ppm
White ash	300 ppm
White birch	800 ppm
White oak	500 ppm

Table 2. Calcium content of Australian wood species (mg/OD kg) [1].

Species	Outer bark	Inner bark	Sapwood	Heartwood
Eucalyptus gummifera	1520 - 10,300		180 - 420	100 - 410
Radiata pine	1872	9385	900	1149

Table 3. Typical calcium content of bark and stemwood for several pulpwood species (OD basis) [1].

Wood species	Ca in stemwood, mg/OD kg	Ca in bark, mg/OD kg
Birch	430	5,900
Pine	700	4,950
Spruce	870	11,300
Alder	760	6,370
Oak	470	22,900
Eucalyptus	1000	15,200

Calcium also enters black liquor as carry-over of lime and spent acid from tall oil acidulation. Calcium is purged with green liquor dregs, pulp, and as scale. Figure 2 illustrates where calcium enters and leaves the chemical cycle of a typical kraft pulp mill.

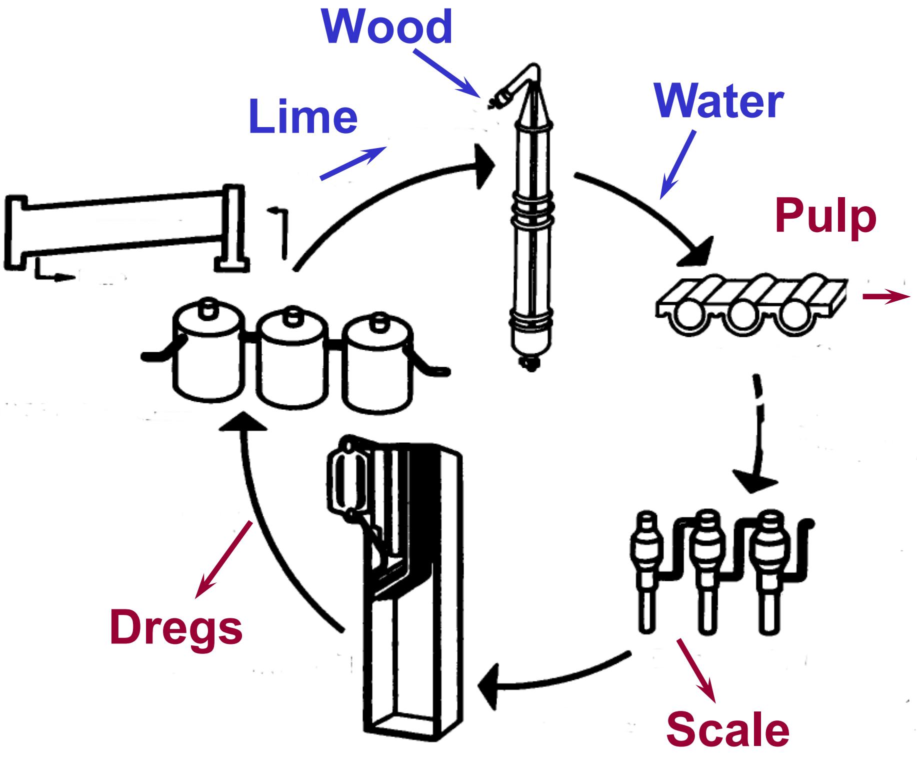

Figure 2. Sources and purges of calcium in kraft recovery cycles.

6.4.3 What is Soluble Calcium?

Inorganic calcium ions such as Ca^{2+} and $CaOH^{+}$ are nearly completely insoluble in kraft black liquor with its high carbonate content. The forms of calcium responsible for evaporator scaling are collectively referred to as “soluble calcium”. Soluble calcium is any form of calcium that is exists in solution as opposed to in the form of suspended crystals or particles. One way that calcium is solubilized in black liquor is as organocalcium complexes with organic compounds in wood. The complexation of calcium ions with chelating agents accounts for the relatively high solubility of Ca in kraft black liquors. The complexation of calcium ion with one such chelating agent, a catechol derivative, is illustrated in Figure 3. At temperatures below about 120°C the calcium complexes formed are stable, but at higher temperatures, they dissociate, releasing divalent calcium ion (Westervelt et al. [2,3]. Heating takes place at evaporator heat transfer surfaces. Divalent calcium ion, once released, reacts rapidly with the abundant carbonate ions nearby. This generates $CaCO_3$ that deposits on the heat transfer surfaces as scale. $CaCO_3$ is orders of magnitude less soluble than are other Ca compounds such as $Ca(OH)_2$ and $CaSO_4$, so Ca^{2+}, when released, forms $CaCO_3$ scale preferentially.

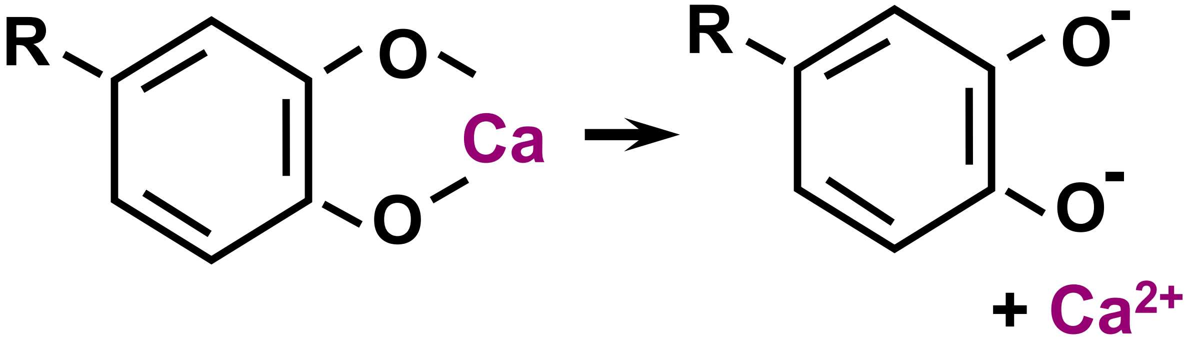

Figure 3. Dissociation of an organocalcium complex upon heating.

Some other calcium-containing compounds can contribute to calcium-based scales in black liquor evaporators. Table 4 shows the impact of adding other Ca sources to black liquor. Tall oil soap, which contains Ca-binding fatty acids, has a similar but weaker impact on $CaCO_3$ scaling than does lignin-derived organic matter in black liquor. Inorganic Ca sources such as $CaCO_3$ and $CaCl_2$ suppress Ca-based scaling. In black liquor, $CaCl_2$ is converted rapidly to crystals of $CaCO_3$. $CaCO_3$ crystals provide surfaces for $CaCO_3$ generated on which to crystallize as an alternative to heat transfer surfaces. Seeding black liquor with $CaCO_3$ particles is one way to reduce $CaCO_3$ scaling.

Table 4. Relative scaling rates of a black liquor containing Ca from different sources.

	Calcium, g/L‡	Relative scaling rate
Black liquor	1.0	1.00
+ $CaCl_2$	4.7	0.33
+ Tall oil soap	1.8	1.04
+ $CaCO_3$	0.7	0.37

‡In black liquor at 46±3% dry solids content

Figure 4 shows the behavior of calcium during one kraft pulping study. Calcium is extracted from wood, mainly as soluble calcium during pulping. The amount of soluble calcium in black liquor increases with time as the digester temperature rises and part of the wood is dissolved. Once the digester temperature approaches 150°C, however, the concentration of soluble calcium reaches a maximum of 76 mg/L (in this case), and then decreases. It continues to decrease until the soluble calcium concentration has declined to about 10 mg/L. This reduction in soluble calcium during pulping reduces greatly the calcium scaling tendency of the black liquor.

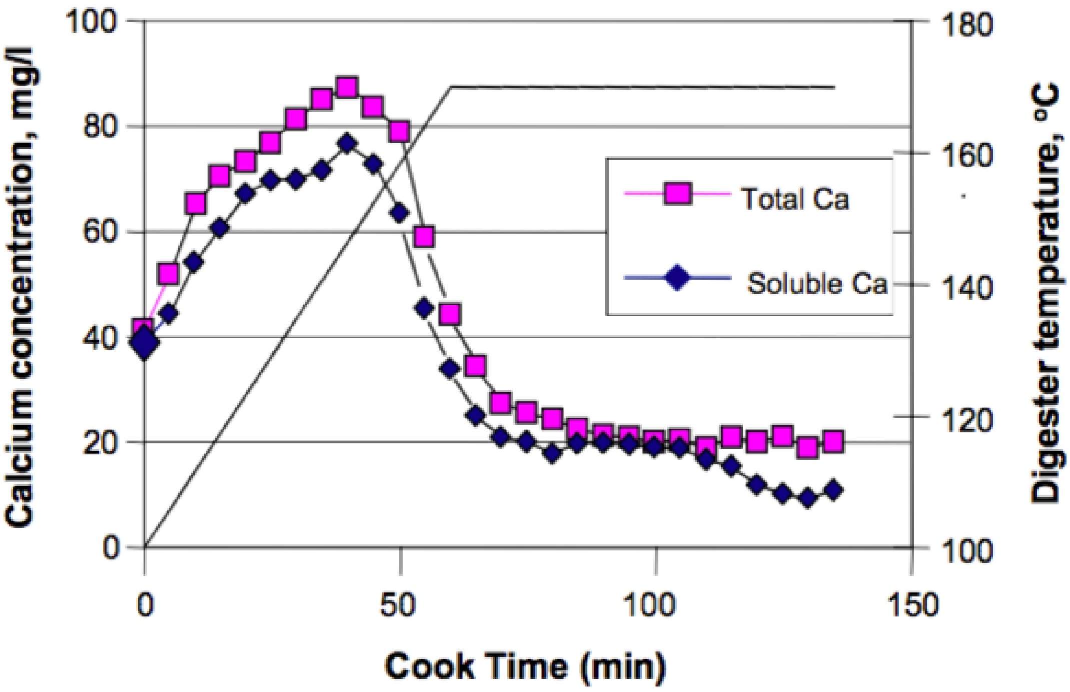

Figure 4. Total and soluble calcium profiles from conventional kraft batch pulping of aspen chips [4,5].

In conventional batch kraft pulping, about 2% of the total calcium in the wood leaves with the black liquor. About half of that is soluble calcium

6.4.4 Impact of Process Conditions on $CaCO_3$ Fouling Rate

The rate of $CaCO_3$ scaling is controlled by the rate of dissociation of organocalcium complexes that liberates free Ca ions as $CaCO_3$ scale precursors. The activation energy of this dissociation process is about 270 kJ/mol, making it clearly a chemical kinetic controlled rate process [6].

The rate of $CaCO_3$ fouling doubles for a 4-5°C increase in evaporator temperature. For a 6-effect LTV unit, this means that the $CaCO_3$ scaling rate in effect 2 would be a factor of 3 higher than in effect 3. The rate in effect 1 would be a factor of 5 higher than in effect 2.

Increasing black liquor pH reduces scaling rate because it stabilizes the organocalcium complexes that form.

The presence of tall oil soap increases scaling rate because the calcium-fatty acid compounds in soap serve as an additional organocalcium source.

6.4.5 Modified Kraft Pulping Processes.

Displacement batch cooking[1], a modified kraft pulping process, was introduced in the 1980s. The two versions are called RDH [7] and Superbatch [8]. In these processes, wood chips were direct steam preheated and then pre-impregnated with warm black liquor. Among their other attributes, these methods of chip pretreatment are effective in extracting rapidly scaling organocalcium compounds from wood.

Lansdell [9] investigated soluble calcium and calcium scaling during evaporation of black liquor from displacement batch pulping. His results showed that:

- Kraft black liquor from displacement batch pulping exhibited a calcium carbonate scaling tendency approximately four times higher than black liquor from conventional batch kraft pulping.
- In displacement batch pulping, roughly 10% of the calcium in the wood pulped went with the black liquor sent to the evaporators, and 4-7% of the calcium in the wood was extracted as soluble calcium.
- In conventional batch pulping, much less of the calcium in the wood–about 2% as total Ca, and 1% as soluble Ca, went with the black liquor.
- The soluble calcium content range for the displacement batch black liquors was 193-392 mg Ca/kg dry black liquor solids. For the conventional batch black liquor, the soluble calcium content was 44 mg Ca/kg dry black liquor solids.

The threshold soluble calcium concentration for $CaCO_3$ scale deposition in black liquor evaporators is about 200 mg Ca/kg black liquor solids [10]. These differences in soluble calcium content between conventional kraft and displacement batch pulping account for the large difference in $CaCO_3$ scale deposition between these types of black liquor.

Differences in the alkali or carbonate content of the impregnation liquor used in the displacement batch cooks changed the soluble calcium content of the spent impregnation liquor sent to the evaporators. However, these differences had too small of an impact on the soluble calcium content to be of value in reducing $CaCO_3$ scale deposition.

6.4.6 How to Control $CaCO_3$ Scaling

Controlling calcium input is an effective way to reduce calcium scaling and is often the lowest cost method. The first step in reducing calcium scaling in evaporators is to identify the sources of calcium input to black liquor. This would in principle require a Ca mass balance around the pulp mill. However, some Ca inputs and outputs, particularly lime, lime mud, dregs, and grits overwhelm other Ca flow rates that impact scaling. The important streams to consider are wood, especially if poorly debarked, tall oil soap, spent acid from soap acidulation, and free lime. Effectiveness of debarking needs a close look since bark contains anywhere from 10x to 50x as much Ca as does bark-free wood (see Table 3). Debarking is often the most important way to minimizing the input of Ca in scalable form. More effective soap removal from black liquor is also important, as are not over liming during causticizing, and neutralizing spent acid from soap acidulation.

A process solution to reduce calcium scaling is to reduce steam pressure to the first effect of an LTV set. The goal is to keep the black liquor temperature in that and downstream effects below 120°C. This alternative is a tradeoff between increased evaporation rate due to less scaling and decreased evaporation rate because of a lower thermal driving force. The optimal reduction in steam pressure depends upon how rapidly calcium scaling decreases the heat transfer and evaporation rates. It is effective in evaporators where the rate of calcium scaling is high, requiring regular acid cleanings every few days.

Employ co-current liquor and steam/vapor flow in the first two or three effects where calcium scaling is problematic. Modifying the black liquor flow sequence in an LTV evaporator set from 6-5-4-3-2-1 to 6-5-4-3-1-2 reduces the rate of calcium fouling in the first effect because the highest concentration black liquor is now at a lower temperature. Calcium scaling is more rapid from higher concentration black liquor. Evaporating water at a lower temperature from the highest concentration black liquor reduces calcium scaling rate.

Install a thermal deactivation system to reduce or eliminate soluble calcium in black liquor before it enters the hotter evaporator effects [6]. This is the heavy-duty solution when others fail to eliminate calcium scaling. Thermal deactivation converts soluble calcium to suspended $CaCO_3$ particles under controlled conditions upstream of evaporator effects that otherwise scale badly. It has reduced scaling by 50% or more in one industrial installation with treatment conditions of 162°C and 11 min residence time [11]. Thermal deactivation systems have been installed with success in reducing calcium scaling at black liquor evaporation plants world-wide.

Two options are available for thermal deactivation as shown in Figure 5. One is direct injection of steam into black liquor followed by a deactivation vessel with a residence time of 10 to 20 min. This method is effective and eliminates the capital cost for a heat exchanger, but it has high operating cost associated with high-pressure steam consumption and loss of power generation from it. A second option is to use indirect heating of indirectly heated, recirculated, black liquor from the deactivation vessel to heat the incoming black liquor. This method uses less net energy but requires capital expenditure. Energy costs for different options were reported by [10].

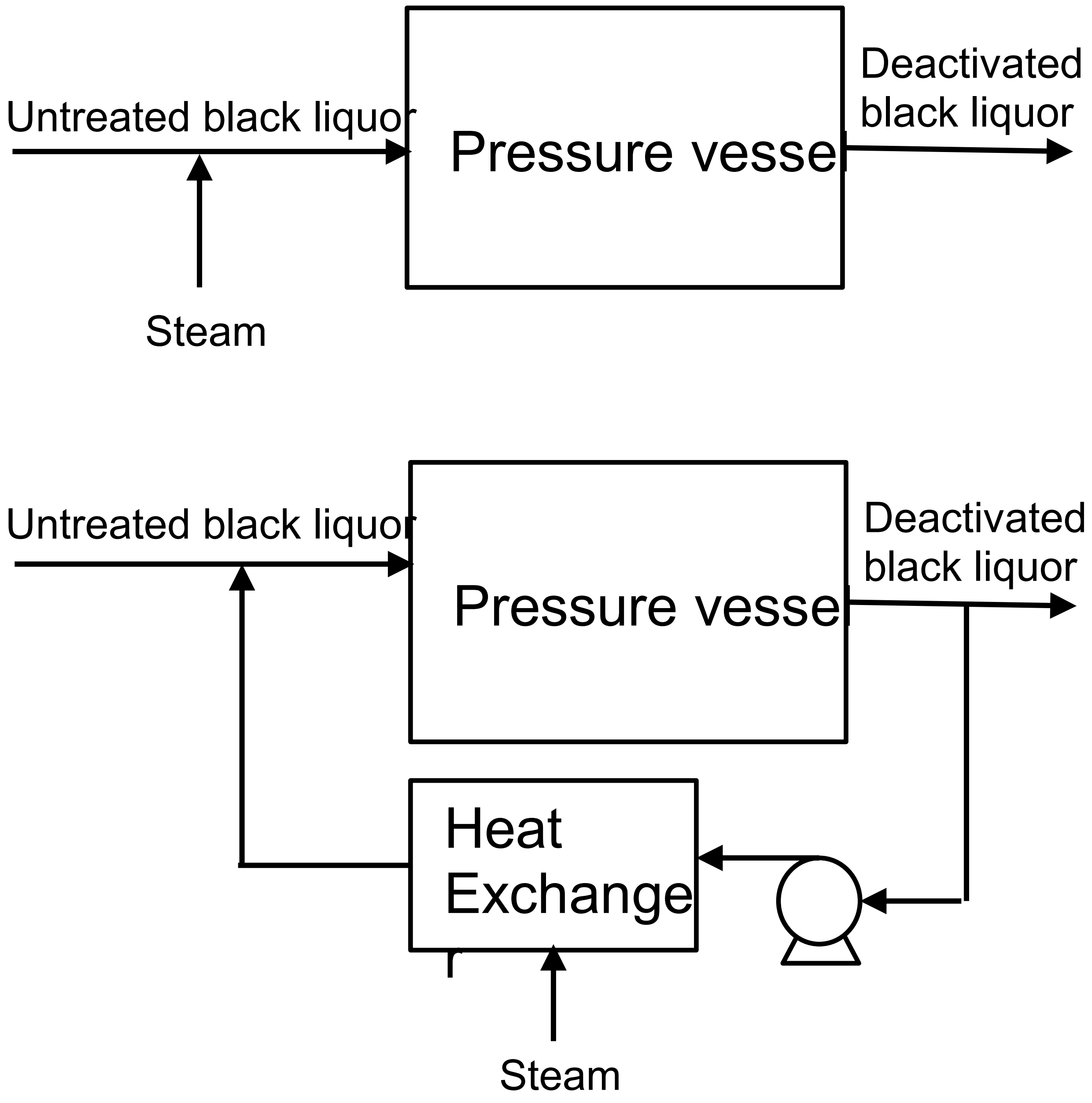

Figure 5. Options for thermal deactivation. Top: direct steam injection with no black liquor recirculation. Bottom: indirect heating with deactivated black liquor recirculation.

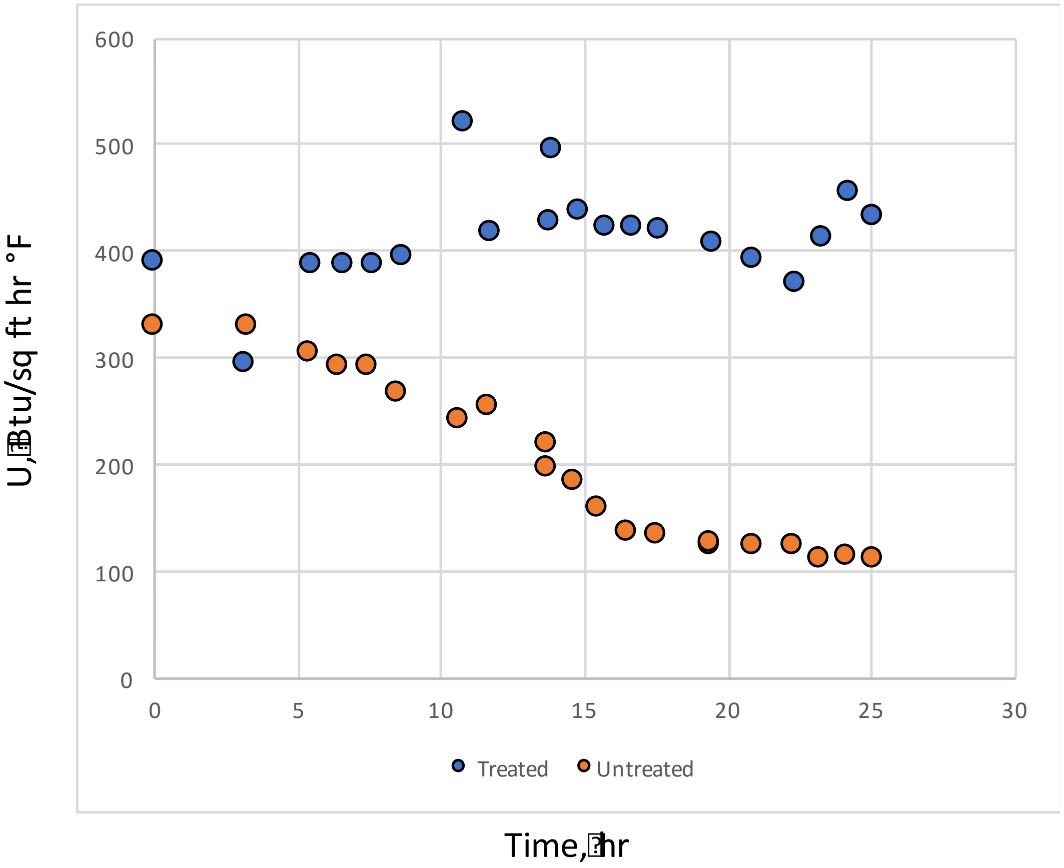

Figure 6. Heat transfer coefficients for black liquor evaporation before thermal deactivation (untreated) and after thermal deactivation (treated) [10].

Figure 7. An industrial thermal deactivation plant for a black liquor with severe calcium scaling of black liquor evaporators.

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6.5 ORGANIC FOULANTS

Organic matter in black liquor can foul evaporator heat transfer surfaces. Lignin can foul heat transfer surfaces when the residual alkali content of black liquor drops too low. This is illustrated in Figure 1. The stability limit (as pH) for lignin to remain in soluble black liquor is shown by the symbols in this figure, and the line fitted to them. As black liquor is concentrated, its residual alkali content per unit volume increases and so does its pH. But the stability limit (as pH) also increases. By 60 wt% dry solids content, the pH required for stable lignin in solution begins to exceed the pH of the black liquor at that concentration. This is when lignin begins to collect on heat transfer surfaces. The black liquor concentration where this begins depends upon the residual alkali content, with lignin remaining more stable in solution at higher pH.

To minimize lignin fouling of evaporator heat transfer, it is important to keep the black liquor pH high enough by increasing the residual alkali. Neutralizing spent acid input to black liquor must be done. Adding caustic before or after black liquor oxidation (BLOX) is also essential.

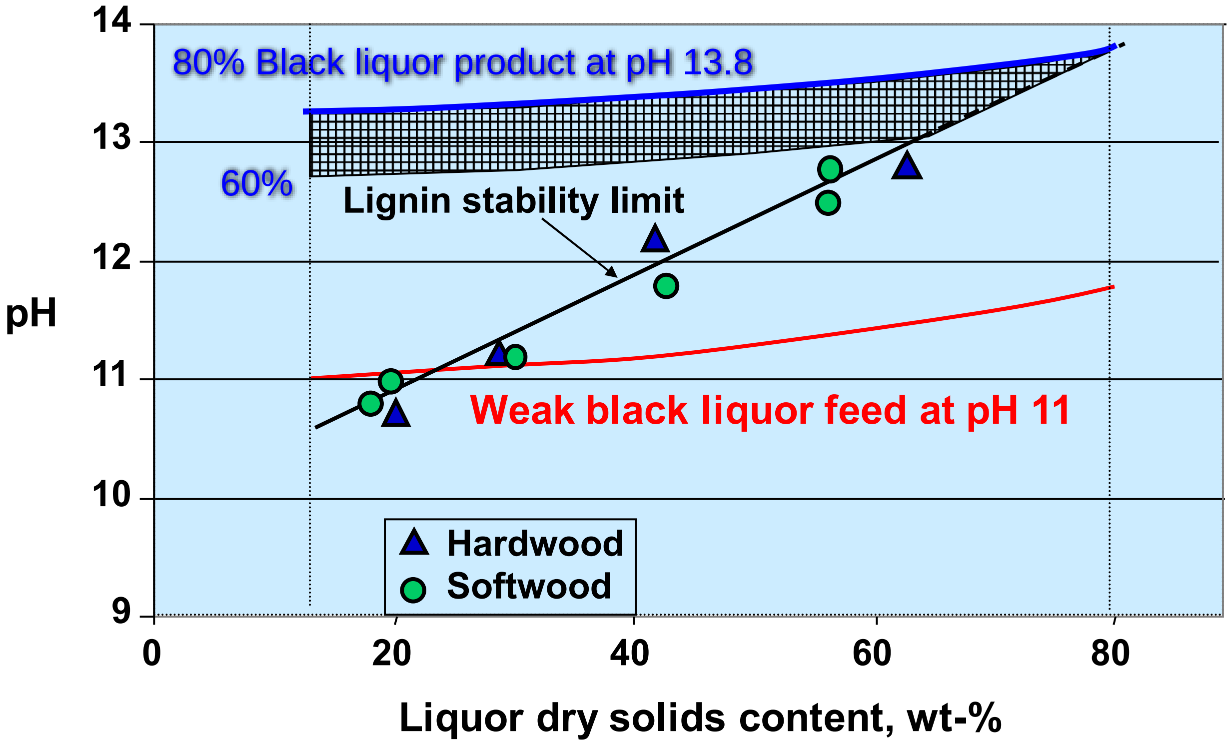

Figure 1. Stability limit map for lignin in black liquor.

Soap is another source of organic deposits on evaporator surfaces that limits evaporation capacity (Figure 2). Effective soap removal is important for several reasons, but improving pulp mill operations is the most important of them.

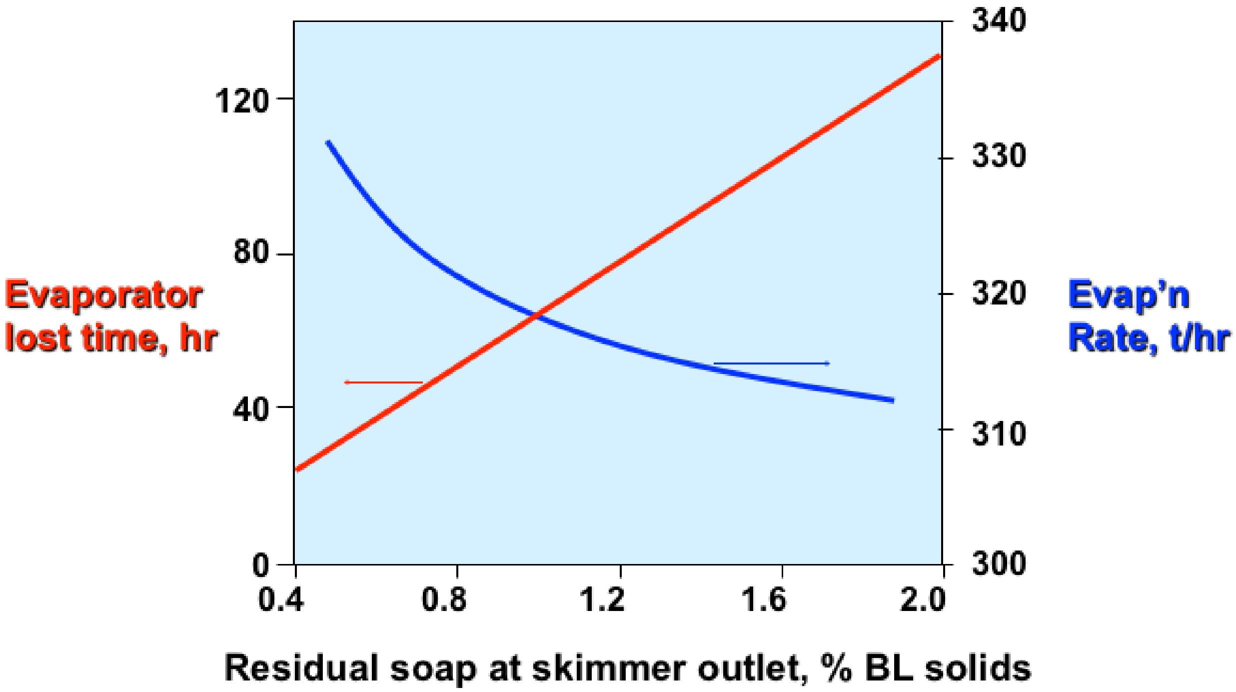

Figure 2. Decline in black liquor performance with increasing soap content in black liquor (Uloth, 1986).

Another source of evaporator capacity loss is fiber deposits and fiber plugs in tubes or passages between heat transfer plates. These can be avoided by removing fiber from weak black liquor. A maximum fiber content below 80 ppm based on dry black liquor solids is recommended. Black liquor filters are required to achieve this level. 100 mesh screens are recommended with softwood pulp liquors, and 80 mesh with hardwood pulp liquors. Fiber filters should be maintained well and not taken out of service. Soap contains 10 to 15 times the fiber content of soap-free black liquor, so effective soap removal is essential to achieve low fiber levels in black liquor.

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6.6 ALUMINOSILICATE SCALES

With increased mill closure, Al and Si levels have increased in black, green and white liquors in kraft pulp mills. When Al and Si concentrations are not controlled, aluminosilicate scales become problematic. Aluminosilicates form tough, glassy scales that are difficult to remove. Hydroblasting is required to remove them.

Figure 1. Flakes of aluminosilicate scale from a black liquor evaporator.

The components of aluminosilicate scales are sodalities and Cancrinite. They are large aluminosilicate molecules. They are synthesized in green and white liquor from Al and Si sources that enter the liquor cycle from various sources including dirt carried in with wood (as dirt), as components of makeup lime and limestone), as silicon based defoamers, and from alum in whitewater used in brownstock washing (Figure 2). Aluminum and silicon components are soluble in aqueous, alkaline liquors. Their solubility increases with increasing hydroxide ion content (Wannenmacher et al., 1995). Their solubility is lower in weak black liquor than in green or white liquor, but it can be higher in strong black liquor. There is relatively little data on the effect of temperature on their solubility. At low hydroxide concentrations, they tend to precipitate in suspension, but at higher concentrations they deposit on any available surface. The transition point for this precipitation behavior is about 0.8 mol/l NaOH (Streisel, 1987). This explains why aluminosilicate scales tend to form in the effects that process intermediate and higher dry solids content black liquors (Ulmgren, 1982).

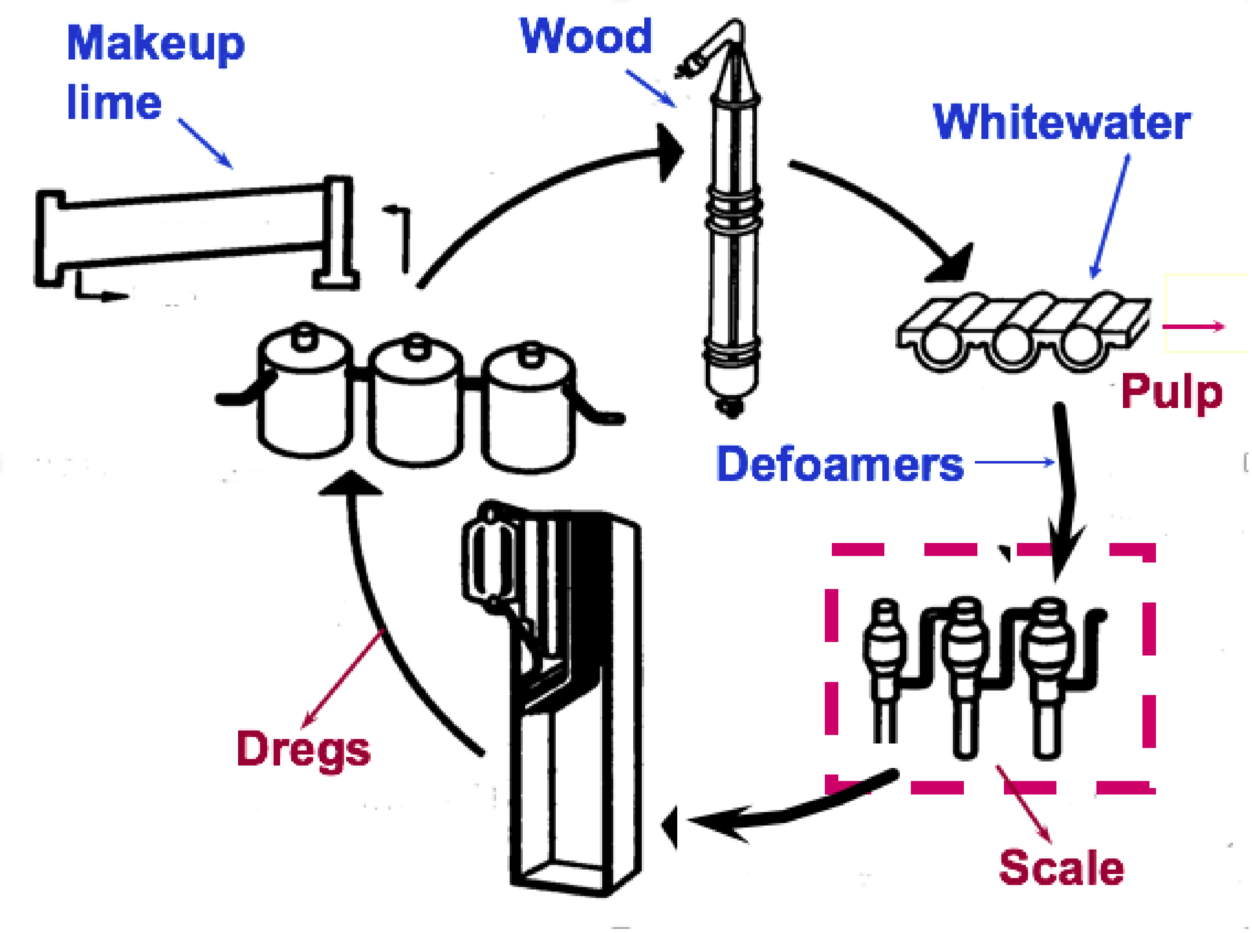

Figure 2. Sources and purges of Al and Si from kraft pulp mills.

Effective control of aluminosilicates depends upon minimizing the input of Al and Si to the black liquor, and on very effective dregs removal (Figure 3). Al and Si in dregs that are not removed in the green liquor clarifier will redissolve in the more alkaline white liquor. Mills with poor green liquor clarification have experienced serious aluminosilicate scaling problems as a result of this.

Figure 2 suggests the approach used by some mills to control aluminosilicate scales. Since the silica content in kraft pulping liquors is always much higher than the aluminum content, the aluminum content is monitored as a predictor of when aluminosilicate scales would form. For one mill, an aluminum levels above 60 ppm in the clear green liquor marked the onset of aluminosilicate scaling. When the aluminum content reached that level, it triggered action to reduce aluminum input and check the effectiveness of green liquor dregs removal. Note that 60 ppm aluminum is not a universally applicable criterion. The maximum acceptable aluminum level is different from mill to mill depending on the silica and magnesium concentrations in the liquor cycle as well. The control strategy, once developed, is applicable to any kraft mill. The critical steps are (a) defining the aluminum concentration where significant scaling begins, and (b) developing a plan to reduce Al input to control the aluminum concentration in the liquor cycle. Approaching that concentration needs (a) to trigger action to reduce Al below it. A current aluminum mass balance around the pulp mill is essential to where aluminum is entering the mill, and on how effectively dregs are removed.

6.6.1 Aluminosilicate Chemistry

In alkaline solutions, aluminate, and silicate ions combine to form complex structures such as those of hydroxysodalites and Cancrinites illustrated in Figure 3. The cage-like structures trap carbonates, sulfates, chlorides and other simple inorganic molecules in their central pores. Hydroxysodalites and Cancrinites are found in natural rock fomations. They also are commonly found in alkaline industrial solutions where they are formed synthetically from dissolved Al and Si species. They are the most prevalent components in aluminosilicate scales in black liquor evaporators.

Hydroxysodalites and Cancrinites have similar structures to zeolites but are more compact. The central pore is too small to allow inorganic ions to move easily in and out. Some ions are trapped within the central pore when hydroxysodalites and Cancrinites are formed in solution, with different compositions depending on the prevalence of other, simpler, inorganic compounds in solution. Cancrinite formed in green liquor typically have compositions of $Na_6Al_6Si_6O_{24}•2Na_2CO_3$ and $Na_6Al_6Si_6O_{24}•2Na_2SO_4$. The sodium carbonate version is the more prevalent form found in carbonate-rich green liquor. The large carbonate or sulfate ions reside within the cage structure.

Hydroxysodalite ($Na_6Al_6Si_6O_{24}•2NaOH$), rather than Cancrinites, are produced in white liquor where hydroxide content is high and carbonate is much lower than in green liquor.

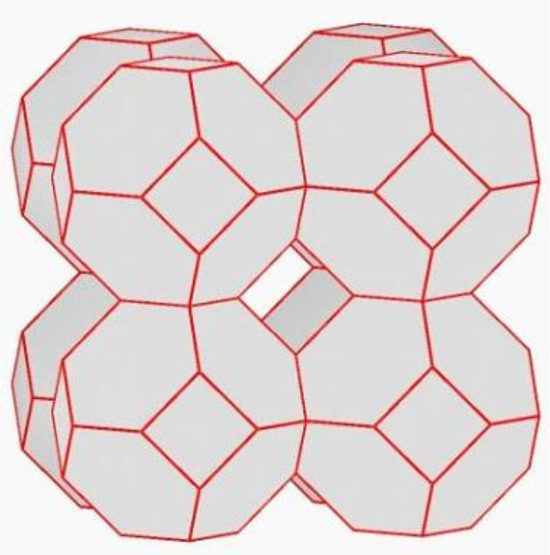

Figure 3. Cage-like structure of Cancrinite and hydroxysodalite.

6.6.2 Solubility and precipitation regions for aluminisilicates

The aluminosilicates deposited as scale in black liquor evaporators are sodalites and Cancrinites.

The solubility of the aluminosilicates increases with increasing NaOH concentration. This means that they are more soluble in white liquor than in green liquor. In black liquor, they become more soluble at higher concentrations since the alkali concentration in black liquor increases as it is concentrated. Figure 4 is a solubility map for aluminum and silicon, showing solubility limits for them in both green liquor and white liquor.

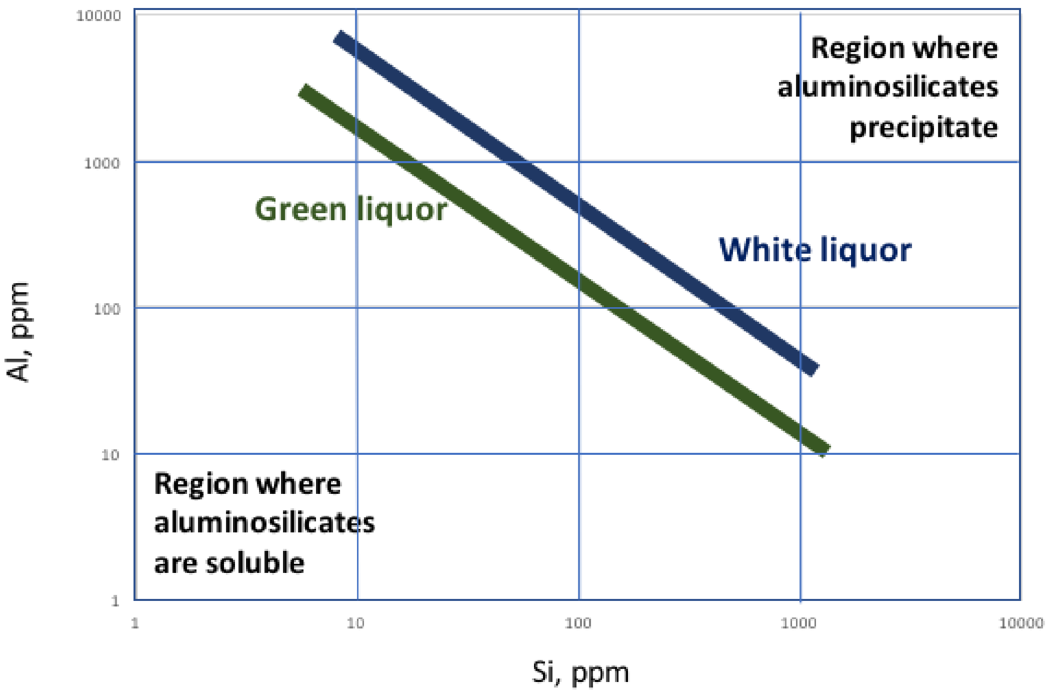

Figure 4. Solubility map for aluminum and silicon, showing their solubility limits in both green liquor and white liquor.

The low points for aluminosilicate solubility in the kraft recovery cycle are in green liquor and in intermediate dry solids content black liquor. Precipitated aluminosilicate accumulates as dregs, and dregs removal is the most important purge point of aluminosilicates from kraft pulp mills. Ineffective dregs removal creates a problem in that aluminosilicates not removed during green liquor clarification will end up dissolving in white liquor, eventually becoming a soluble component of black liquor, and contribute to aluminosilicate scaling in evaporators as black liquor is concentrated.

6.6.3 Removing Aluminosilicate Scales

Aluminosilicate scales are tough and tenacious, and difficult to remove. Hydroblasting is required to remove them.

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7 RESEARCH NEEDS IN BLACK LIQUOR EVAPORATION

W. J. Frederick

Energy efficiency is important to manufacturing industries. Pulp and paper manufacture rates third in industrial energy consumption by US industries, using 7% of industrial energy in the US.[1,2,3] Evaporation of water from kraft black liquor consumes 38% of thermal energy and 4.7% of electrical power consumed in a kraft pulp mill is used to evaporate black liquor[4] (Gilbreath, 1995).

The pulp and paper industry began employing evaporation technology as part of the first kraft pulp mills for two important reasons. One was economic: to recover spent pulping chemicals for reconversion to active pulping chemicals. The second was to avoid the major pollution problems that would result from discharging weak black liquor to rivers and lakes. A third reason, also economic, was to recover the energy value of the organic matter that was dissolved during pulping. That energy was used to generate process steam, and eventually electric power as well.

Evaporation technology has undergone major developments since the 1920s. Swedish companies led the development of the steam heated, indirect contact evaporator technology that is in practice today. Finnish companies led the development of black liquor concentrator technology to achieve up to 85 wt-% dry solids product liquor. Almost all of North America's old direct contact evaporators have been replaced. The challenges of air emissions and discharge of organic pollutants with waste water have been reduced to very low levels and meet today's stringent environmental standards.

Opportunities for Technology Enhancement

The future brings several more opportunities for more advanced evaporation technologies and enhancement of existing ones. Many of the opportunities evolve around water removal and water management in the pulp mill. One possibility is to remove water from black liquor at lower cost than is done with current evaporation technology. This means alternative ways to dewater weak black liquor prior to evaporation. The current or new black liquor evaporator/concentrator installations might concentrate black liquor from e.g. 35 wt-% dry solids content to a firing solids concentration of 80 wt-%. This could support more pulp production without installing more conventional evaporation hardware. In this scenario, more than half of the water removed from black liquor would be removed prior to the evaporators using an advanced, alternative technology.

Another alternative is to recover water and recycle it to where it is needed in the pulp mill: makeup water for green liquor production and brownstock washing are two examples. Each require an acceptable level of cleanliness to minimize contaminant-caused process problems downstream. Process water that is recovered and reused does not end up in weak black liquor, and therefore does not need to be evaporated.

A third R&D need is to define the acceptable level of contaminants in recycled process waters and to find methods to remove various contaminants to achieve the acceptable levels. Brownstock washing effectiveness, minimizing evaporator fouling, and avoiding blinding of white liquor filters are three important examples.

Lower Cost Water Removal Methods

Membrane separation methods have are interesting options for concentrating various for water removal from weak black liquor include membrane filtration[5],[6],[7],[8], freeze concentration[9], electrocoagulation[10], and others[11]. Many of these have been evaluated at least at the bench scale. Challenges to membrane separation include:

a. sufficiently high removal efficiency of non-water components
b. capability of membranes to withstand the high temperature and highly caustic environment in black liquor,

c. concentration polarization,
d. propensity to foul with inorganic matter, soap, etc.,
e. separation of small liquid molecules (e.g. methanol) from water.

A techno-economic evaluation of water removal from weak black liquor by the Agenda 2020 Technology Alliance[2], indicated that using membrane technology to concentrate weak black liquor has the potential for significant reduction in energy use when compared with current black liquor evaporation technology[12]. According to their preliminary model results, advanced systems based on membrane concentration of weak black liquor that raise the dry solids content from 15% to 30% have the potential to save as much as 1.5 million Btu fuel-based energy per ton of pulp[12]. The net energy-saving potential varies considerably from mill to mill, depending on the configuration of mill steam and power systems. For typical mills producing 2,000 air-dried tons per day of pulp there is a $2–3 million annual energy cost savings potential for integrating membrane-based black liquor concentration technology. Large-production mills with weak black liquor solids content below 15% could realize as much as $5–6 million in annual energy cost savings.

Assuming that the modeled purchased-energy reduction of 0.5 million Btu per ton could be achieved on average across all 47 million tons per year of kraft pulp produced in the United States, concentration with advanced membrane systems could reduce energy consumption nationally by 23 trillion Btu per year. The economic value of this energy saving would be $70 to $120 million per year, based on energy costs of $3 to $5 per million Btu.

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[2] The Agenda 2020 Technology Alliance is a non-profit organization, exists to identify high priority, pre-competitive technology challenges for the pulp and paper industry and to promote scientific research and development projects to address them

Given the likelihood of a viable business case for one or more membrane technologies, the Agenda 2020 Black Liquor Concentration Team has developed a research initiative to explore this option in detail.

Increasing Evaporation Rates with Existing Evaporators

Increasing evaporation rates per unit area of heat transfer surface is the holy grail of evaporation. Three effective ways of accomplishing that are

1. Reducing scaling of heat transfer surfaces,
2. Reducing black liquor viscosity, and
3. Reducing BPR

Scaling of heat transfer surfaces creates a significant capacity limitation for many black liquor evaporators and concentrators, although not for all of them. When fouling is a serious problem, evaporation capacity can often be increased by 20% or more by careful management of the chemicals in a mill's liquor cycle. Often it is possible to nearly eliminate scaling altogether by this approach. Chapter 4 addresses evaporator scaling in detail and how to deal with it for most types of scaling in black liquor evaporators and concentrators. Significant work has been done earlier to develop strategies for controlling or eliminating chemical species that contributing to scaling from black liquor. A continuing effort is needed to focus on a broad effort to optimizing liquor cycle chemistry.

The Agenda 2020 roadmap for reuse of effluents includes four proposed projects. One of them is to develop technology to effectively remove inorganic constituents (total dissolved solids and calcium) that cause scaling issues. This project has direct benefits to reducing evaporator fouling. Water reused in various areas of a kraft pulp mill with good water management cascades downward from applications requiring the cleanest water to those requiring less clean water. Bleached fiber slurries to paper machines require high quality, very clean water; so does washing of bleached fiber stock in bleach plants. The quality requirements are lower for washing of brownstock.

The quality of water for smelt dissolving can be low because green liquor clarification removes most inorganic contaminants. Al and Si are potentially problematic exceptions.

Black liquor viscosity reduction is addressed in Chapter 3. Those mills where brownstock kappa numbers are low (30) or high (90) are fortunate to have low viscosity black liquors. Those with brownstock kappa numbers in an intermediate range (~50) have much higher black liquor viscosities. The section titled *Impact of pulping conditions* in Chapter 3 explains the reasons for this unexpected viscosity behavior.

Two methods that have been effective in reducing black liquor viscosity are control of the residual alkali content and thermal treatment. Wong[13] showed that the viscosity of softwood black liquor was at a minimum at 2.0 % Na_2O REA. He reported the minimum between 1.1 and 1.5 REA for a hardwood black liquor. The viscosity went through a shallow maximum at higher REAs with the hardwood black liquor, but then decreased back to about the same minimum values at REA value of 3.4. The viscosity of bagasse black liquor decreased by a factor of 10 when its residual active alkali (RAA) was doubled[14] (see Figure 6 in Chapter 3). Overall heat transfer rates in black liquor evaporators are inversely proportional to viscosity to the 0.4 power ($\dot{q} \propto 1/\mu^{0.4}$). Decreasing the viscosity black liquor by a factor of 10 would result in an increase the rate of heat transfer by a factor of 2.5.

Viscosity versus REA for a softwood kraft black liquor. Measured at 69 wt-% dry solids content in a pressurized viscometer at 2.5 s^{-1} shear rate.

Viscosity versus REA for a hardwood kraft black liquor. Measured at 115^{o}C, 106 s^{-1} shear rate.

BPR reduction has a large effect on evaporation rate. BPR reduces the available T to drive heat transfer. 30% reduction in capacity due to BPR from 15% to 50% dry solids content. Even greater in concentrator effects. Its impact is greater at high dry solids content.

BPR is proportion to the amount of dissolved inorganic salts in black liquor (see section 3.3.2). The boiling point rise can be reduced by improving causticizing conversion and sulfate reduction, by minimizing the amounts of chloride and thiosulfate in black liquor. Other species such as sodium oxalate and sodium acetate can impact BPR in unusual situations.

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