CHAPTER 17

Kraft Spent Liquor Recovery

17.1 CHEMICAL RECOVERY

Chemical recovery is the process in which the inorganic chemicals used in pulping are recovered and regenerated for reuse. This process results in (1) recovery of the inorganic cooking chemicals, (2) generation of large amounts of heat energy by burning the organic materials derived from the wood, (3) reduction in air and water pollution by converting the waste products into useful (or at least harmless) materials, (4) regeneration of the inorganic chemicals into pulping chemicals. In summary, the recovery process for kraft pulping is (1) concentration of black liquor by evaporation; (2) combustion of strong black liquor to give the recovered inorganic chemicals in the form of smelt; the smelt, Na_2S and Na_2CO_3, dissolved in water gives green liquor; (3) preparation of the white cooking liquor from green liquor; this is done by converting the Na_2CO_3 to NaOH using $Ca(OH)_2$, which is recovered as $CaCO_3$; (4) recovery of by-products such as tall oil, energy, and turpentine; (5) regeneration of calcium carbonate, $CaCO_3$, to calcium hydroxide, $Ca(OH)_2$. Storage at all of the above steps allows the overall operation to continue even though one component requires servicing or is not operating smoothly and also accommodates surges in the system. Storage capacity of 3–24 h is common; longer down times of essential components may result in the shutdown of the entire mill. It is not uncommon, however, for a mill to ship black liquor to a nearby mill for recovery and exchange it for fresh liquor during recovery boiler rebuilding. Fig. 17.1 shows the kraft liquor recovery cycle from the point the pulp and liquor leave the blow tank to the point the liquor is ready for the green liquor clarifiers.

17.2 PULP WASHING

Pulp Washers (Brown Stock Washers)

Pulp washers are almost always drumflow or counterflow washers for separating spent pulping chemicals. Pulp washers use countercurrent flow between stages such that the pulp moves opposite in direction to the flow of wash water as described in Chapter 12, Volume 1. This design allows for the most removal of pulping chemicals (for recovery) and lignin (to reduce bleaching chemical demand or improve papermaking with brown papers) with the least amount of water. The dilution factor is a measure of the amount of water used in washing compared with the amount theoretically required to displace the liquor from the thickened pulp; it is reported as mass of water per mass of dry pulp. A low dilution factor decreases the energy requirements of the multiple-effect evaporators (MEEs). Using more washers increases removal of pulping chemicals with less water dilution but increases capital and

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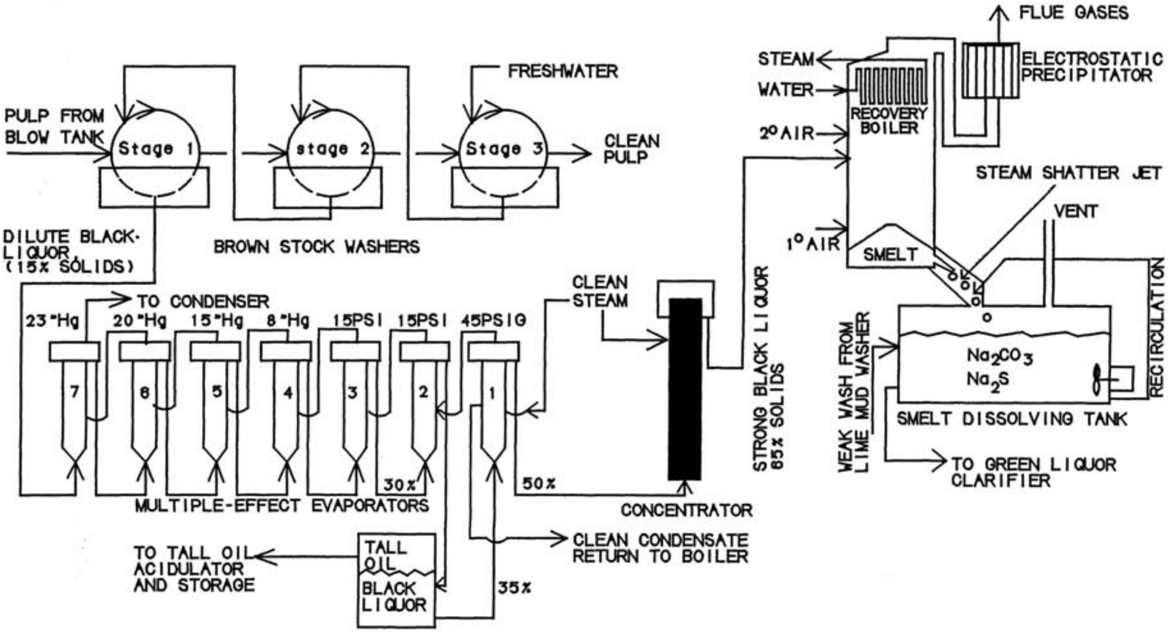

FIGURE 17.1 The liquor recovery cycle in a kraft mill before causticizing. (Not to scale and liquor storage points are not shown.)

operating costs. Usually three or four washers in series are used with about 2–3 tons of water being added to the black liquor per ton of pulp to recover over 96% of the pulping chemicals. Washing of some entrained material occurs at the repulpers (shown in Fig. 17.2) used between the washers. The two fundamental controls are drum speed and stock inlet flow rate. Soda loss in the pulp is traditionally measured as lb/ton pulp on a Na_2SO_4 basis. This alone is not a good indicator of washing efficiency because 12–15 kg/t (25–30 lb/ton) soda (as Na_2SO_4) is chemically bound to the pulp, presumably to the carboxylate groups much like an ionic exchange resin. Resinous species such as the pines tend to foam and require larger washers and filtrate tanks or the use of large amounts of defoamers. Linerboard mills often use excess paper machine white water in the brown stock washers because it is not overly contaminated with filler and additives. A *drop leg* is used to siphon the water from the washer so that a vacuum pump is not usually required. The bottom end of the drop leg goes to a filtrate storage tank that is designed to prevent air from entering the bottom end of the drop leg. The drop leg supplies a vacuum on the order of 24 kPa below atmospheric pressure (7 in. Hg below atmospheric pressure) for the first stage, 30 kPa (9 in. Hg) for the second stage, and 40 kPa (12 in. Hg) for the third stage. The overall drop leg length is about 12–14 m (40–45 ft) with 3 m (10 ft) within the filtrate tank yielding an effective length of 10 m (30–35 ft). The actual vacuum is lowered proportionally to the air bubble content of the pulp slurry. The drop leg is ideally a vertical drop. If a horizontal section is needed, it should be exactly horizontal and placed at least 7 m (22 ft) below the washer. Drop legs that are not entirely horizontal or vertical allow air to separate from the stock and rush upward, thereby accumulating and decreasing the vacuum.

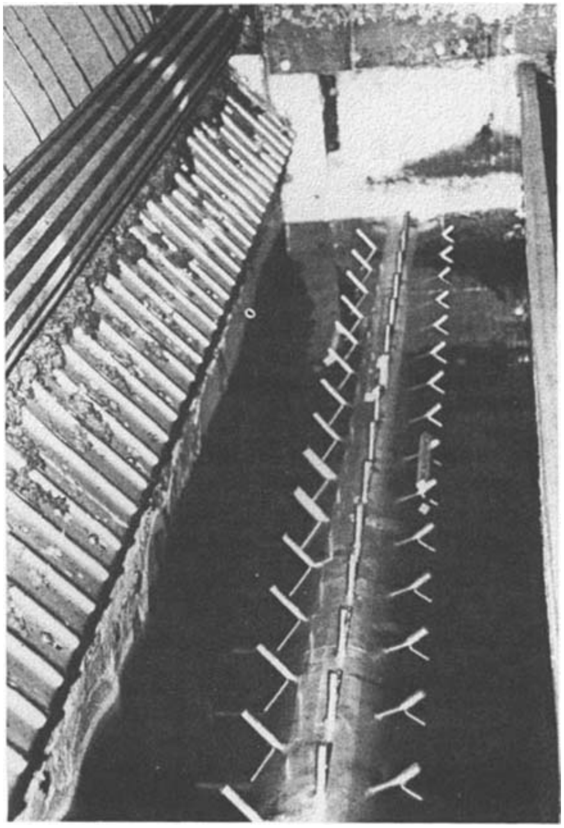

FIGURE 17.2 A repulper after a pulp washer.

17.3 LIQUOR EVAPORATION

Black Liquor Behavior During Evaporation

It is desirable to concentrate the solids of the black liquor as much as possible to make heat recovery from liquor combustion as efficient as possible, but when the black liquor reaches high solids contents, the viscosity increases drastically (Chapter 13, Volume 1). Combustion of highly concentrated black liquor leads to higher temperatures in the lower part of the furnace, which increases the rate of smelt reduction and decreases sulfur emissions. Black liquor is most often burned at 65%–73% solids content in conventional commercial systems. Some systems allow black liquor combustion at 75%–80% solids content, but only a few mills use these systems. Sometimes the viscosity of certain black liquors (e.g., from straw pulping) can be decreased by holding the concentrated black liquor at 115°C (240°F) for several hours. Like any aqueous solution, the boiling point of black liquor increases with increasing solids content. The boiling point rise (relative to water) is about 3°C (6°F) at 33% solids, 8°C (14°F) at 50% solids, 13°C (23°F) at 67% solids, 17°C (30°F) at 75% solids, and 21°C (37°F) at 80% solids. This is the overall solids content; not all of this is actually in solution because, when black liquor is concentrated above 55%, burkeite ($2Na_2SO_4 \cdot Na_2CO_3$), etc. precipitates as scale.

Multiple-Effect Evaporators

MEEs contain several units (effects) that are connected in series by vapor piping. The water vapor boiled off from the liquor in one effect acts as heating steam in the steam chest of the following effect. Most black liquor is concentrated in MEEs.

MEEs are used for black liquor processing. The term multiple effect comes from the multiple effective use of energy to perform the evaporation task. In such a configuration, live steam is condensed only in the first effect evaporator, producing vapors that are then sent to condense in a second effect where additional evaporation takes place. The process can then be repeated until reaching the last effect evaporator where the vapors produced are condensed in a condenser using cooling water. Steam generation in the kraft mill is a significant operating expense, and every effort should be made to conserve its use. The evaporation plant is by far the major consumer of that steam for the removal of water from the weak black liquor. Economic operation of the evaporator is therefore predicated on the multiple effective use of the heat available from the steam and therefore on the number of effects in the MEE.

The MEEs are a series of four to eight evaporators with indirect heating for removing water from the dilute black liquor coming from the pulp washers. Traditionally, long-tube vertical (LTV) bodies were used, but recently, falling film evaporators have also been installed. Later effects are operated under vacuum to achieve evaporation within the desired temperature range. The black liquor leaves at 50% solids. In North America, the water evaporated from the concentrated black liquor of one effect is used as steam in the previous effect. (In Europe, the operation is often partially cocurrent to avoid scaling that occurs when the hottest steam contacts the most concentrated liquor). Stated conversely, each effect acts as a surface condenser for the previous effect. Fig. 17.3 shows the arrangement of a set of evaporators. For example, 100 lb of black liquor containing 15 lb of solids and 85 lb of water is evaporated to 30 lb; with a steam economy of 5.0 it would take 14 lb of steam to remove the 70 lb of water. The steam economy is about 0.8 per effect. An overall steam economy of 4–5, depending on the number of effects, is normally good for mill operation. If this stage is a bottleneck, lower steam economy is sacrificed for higher throughput. The initial steam introduced at the first effect comes from the boiler, and its condensate is returned to the boiler. The subsequent condensates are contaminated with volatile black liquor components and are usually sent to the sewer.

$$\text{steam economy} = \frac{\text{water mass evaporated}}{\text{mass of steam used}}$$

Long-Tube Vertical Bodies

The climbing film, LTV evaporator has become the standard system for concentrating black liquor. These evaporators came into use during the 1920s and 1930s. The LTV evaporator is still the most widely used type of evaporator.

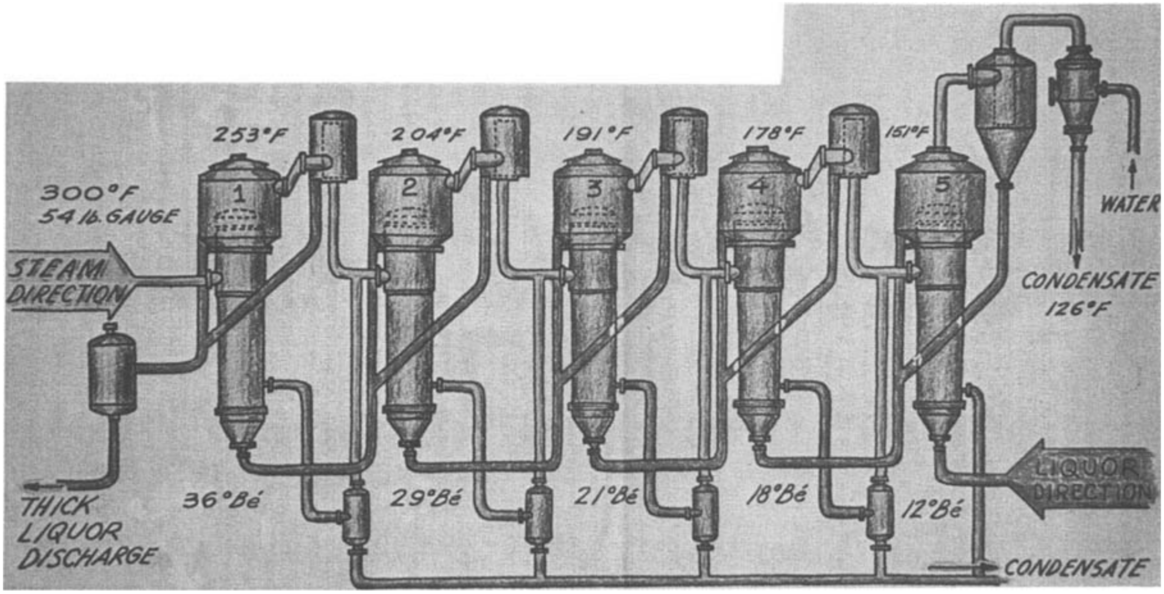

FIGURE 17.3 Five-effect black liquor concentration. *From J. Ainsworth,* Papermaking, *©1957 Thilmany Paper Co., with permission.*

Traditionally, each effect consists of a LTV evaporator (Fig. 17.4). Several LTV bodies are shown in Fig. 17.5. Black liquor rises up the heat exchanger area until it reaches the vapor dome at the top. In the vapor dome, steam flashes from the black liquor and is pulled by vacuum to the next effect as the steam source. The shell of the evaporator is usually 12.5-mm (0.5 in.) steel plate. The heat exchanger consists of 2 in. diameter tubes from 14 to 32 ft long. Stainless steel is often used in the first two effects where the liquor is warmest and most concentrated. The first effect is operated at 50 psig and 150°C (300°F), whereas the last effect is about 27 in. Hg vacuum and 46°C (115°F).

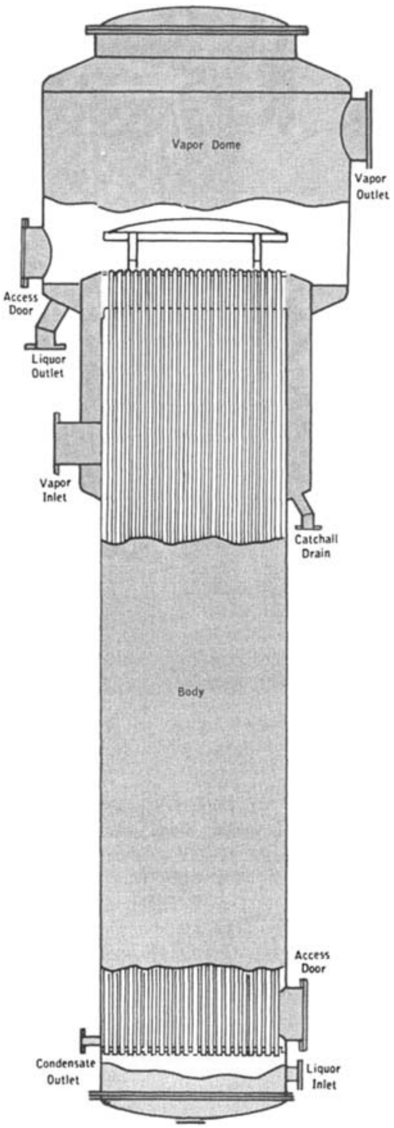

FIGURE 17.4 Long-tube vertical evaporator. *Reprinted from* Making Pulp and Paper, *©1967 Crown Zellerbach Corp., with permission.*

Falling Film Evaporators

Falling film evaporators are used much like conventional evaporators, except the mechanism of evaporation in each stage is different. These evaporators are being used in many countries to produce black liquor slurry with up to 80% solids content for firing in the recovery boiler (Vakkilainen and Holm, 2000). This evaporator design relies either on tubes or on plates as heat transfer surfaces. In tubular units, liquor is processed on the inside of the surface, whereas in plate designs, the liquor is processed on the outside of the heat transfer surface.

In each stage, steam (or sometimes hot water in the first stage) is used as the heat source and flows between stainless steel plates about 30 mm (1.25 in.) apart. Large banks of these plates are aligned radially outward in each effect. Dimples in the metal plates keep the plates a fixed distance apart and increase the strength of the metal plates. Fig. 17.6 shows a section of the plates.

The black liquor is introduced at the top of the evaporator and flows down the opposite side of the metal plates where the dimples help spread the black liquor into a thin film. The falling film plate design allows for selective condensation of the vapors boiled from the black liquor of previous effects. About 65% of the methanol and BOD is concentrated in 6% of the overall condensate stream in the upper portion of the plates to give *foul condensate segregation.* The remaining condensate is collected from the lower

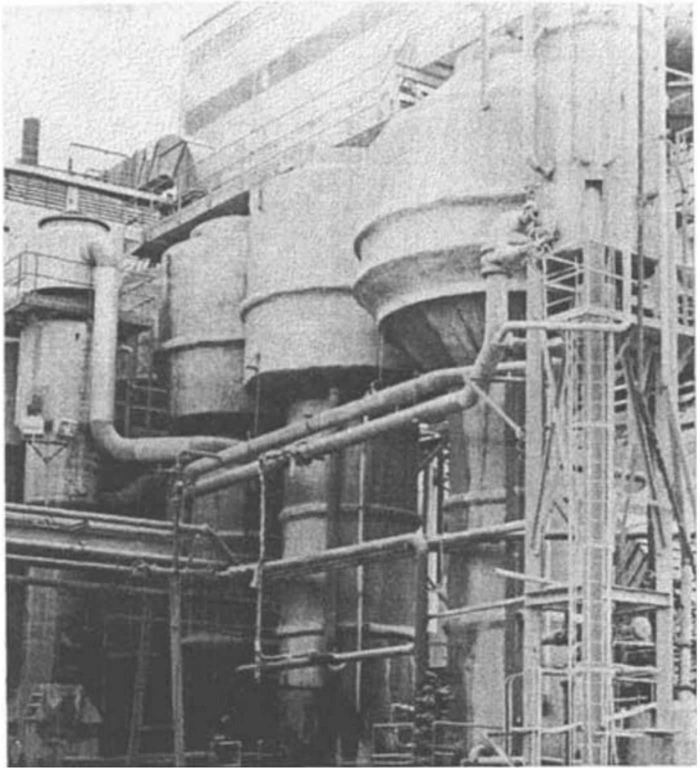

FIGURE 17.5 A series of long-tube vertical bodies (the multiple-effect evaporators).

portion of the plates and is suitable for brown stock washing.

Falling film plate evaporators are less subject to fouling than LTV and require boilouts much less often. They also operate at a lower overall vacuum than conventional evaporators with the last stage operating at 26 in. Hg. Black liquor must be recirculated within each stage. For example, the fourth stage of one operation uses 10,000 gal/min recirculation with a liquor feed of 900 gal/min at 14% solids and an outlet of 450 gal/min at 26% solids. Some of the fourth effect concentrated liquor can be used to concentrate the infeed of the third effect because liquor at low to intermediate concentrations tends to foam, a big problem with large recirculation rates. Falling film evaporators can be used in conjunction with blow heat recovery at mills using batch digesters because lower temperature gradients are required. The steam discharged during blowing is used to heat large quantities of water. The hot water is then used in liquor evaporation until the next digester blow reheats it. This provides a leveling effect for the intermittent heat generation of blowing with batch digesters.

Direct Contact (Cascade) Evaporator

The direct contact evaporator is a chamber where black liquor of 50% solids content directly contacts the hot flue gases from the recovery furnace. The final black liquor concentration is 65%–70% solids. This method is now obsolete because high sulfur emissions result as the hot CO_2-containing flue gases strip sulfide from the

FIGURE 17.6 A small section of a falling film evaporator plate (wood-grain table background).

black liquor. Also, indirect concentrators allow higher energy recoveries. A few mills that have recovery boilers installed before the early 1960s still use this method. This process, before being replaced by concentrators, required partial *black liquor oxidation.* In this process, the black liquor enters a chamber where it is mixed with air (or oxygen) to convert reduced sulfides, such as $(CH_3)_2S$ and S^{2-}, to oxidized forms of sulfur and thereby minimize sulfur emissions (Chapter 15, Volume 2). The reason this is required is that the CO_2 in the flue gases exists as the acid H_2CO_3, which lowers the pH of black liquor, stripping H_2S from it. This process is not necessary with indirect concentrators because the pH of the black liquor remains high before combustion. Three types of direct contact evaporators have been used:

- Cascade evaporators (CE)
- Cyclone evaporators (B&W)
- Venturi scrubbers (B&W)

Concentrators, Indirect Concentrators

Indirect concentrators (used in so-called *low odor recovery boilers)* are forced circulation or falling film steam heated evaporators used to concentrate black liquor in the range where burkeite precipitates as scale. Because concentrators are more energy efficient and environmentally sound than direct contact evaporators, they have largely replaced direct contact evaporators since their introduction in the mid-1960s. The final solids content of the black liquor is about 65%−70% with a fuel value of 14−16 MJ/kg (6000−7000 Btu/lb) compared with coal that is 32 MJ/kg (14,000 Btu/lb). Although a very high solids content in black liquor is desired to increase combustion efficiency, the viscosity increases quickly with solids contents above 65% −70%, and the black liquor becomes too thick to pump even at elevated temperatures.

Tall Oil

Tall oil is a by-product mixture of saponified fatty acids (30%−60%), resin acids (40%−60%, including mostly abietic and pimaric acids), and unsaponifiables (5%−10%) derived from the wood extractives of softwoods. Crude tall oil is isolated from acidified skimming of partially concentrated black liquor. It is collected and refined at special plants. The refined products are sold commercially for soaps, rosin size, etc. Typically, 30−50 kg/t (60−100 lbs/ton) on pulp may be recovered from highly resinous species representing about 30%−70% recovery. It is recovered from mills pulping resinous species such as the southern pines. The pulp and paper industry recovers about 450,000 tons of crude tall oil annually.

Turpentine

Turpentine is a mixture of volatile extractives (monoterpenes) collected during digester heating. In batch digesters, most of it is collected before the digester temperature reaches 132°C (270°F). It is collected from the digester relief gases and sold for solvents and limited disinfectants used in household pine oil cleaners. Because terpenes are volatile, the recovery can decrease by 50% with outside chip storage of a few weeks. It is often standard practice at mills recovering turpentine to use a portion of green (fresh) wood chips in the digester feed to reduce turpentine loss, while the balance is used from chips rotated in inventory. Fresh wood of loblolly and short leaf pines yield about 6—12 L/t (1.5—3 gal/ton) air dry pulp, whereas slash and longleaf pine yield 10—18 L/t (2.5—4.5 gal/ton). The US pulp industry recovers about 30 million gallons of turpentine annually.

Kraft Lignin

Some black liquor is recovered by acidification and used as dispersants, phenol-formaldehyde adhesive extenders, and binders in printing inks. For example, Indulin is Westvaco's trade name for kraft lignins of various grades. Dimethylsulfoxide (DMSO, a solvent and controversial healing remedy) can also be recovered from kraft lignin. However, kraft lignin is not isolated and marketed to the same degree that lignosulfonates from sulfite pulping methods have been. Calcium lignosulfonates were a waste problem, which were marketed as a "solution in search of a problem."

17.4 RECOVERY BOILER

Recovery Boiler or Recovery Furnace

The development of the recovery boiler by Tomlinson in conjunction with Babcock & Wilcox in the early 1930s led to the predominance of the kraft process. Fig. 17.7 shows a typical recovery boiler design, while Fig. 17.8 compares two types of boilers with widespread use. Fig. 17.9 shows a recovery boiler building at a brown paper mill. The purpose of the recovery boiler is to recover the inorganic chemicals as smelt (sodium carbonate and sodium sulfide), burn the organic chemicals so they are not discharged from the mill as pollutants, and recover the heat of combustion in the form of steam. The latter is accomplished by large numbers of carbon steel tubes filled with circulating water or steam to recover heat from the walls of the recovery boiler and the flue gases. Fig. 17.10 shows some banks of tubes to be installed into a recovery boiler.

In Finland and Sweden, the outer surfaces of these tubes are clad with stainless steel to greatly increase their life. Some recovery boilers in the United States are equipped with stainless steel clad tubes as well, but it is not a widespread practice. Combustion Engineering has used a "chromizing" process where chromium is incorporated "in" the surface to produce a stainless steel—like surface. The recovery boiler or furnace burns the concentrated black liquor by spraying it into the furnace through side openings (Plate 17.1). The water evaporates, and the organic materials removed from the wood form a char and then burn. There are three zones: The upper section is the *oxidizing zone*, the middle section (where the black liquor is injected) is the *drying zone*, and the bottom section is the *reducing zone* where, in a bottom bed of char, the sulfur compounds are converted to Na_2S. The remaining NaOH and sodium salts of organic acids are converted to Na_2CO_3. These sulfur- and sodium-based inorganic materials leave as molten slag that is directed to the green liquor dissolving tank (Plate 17.2). Because of the possible adverse reaction of molten smelt with water, all recovery boilers have an *emergency shutdown procedure* in the event of trouble! The recovery

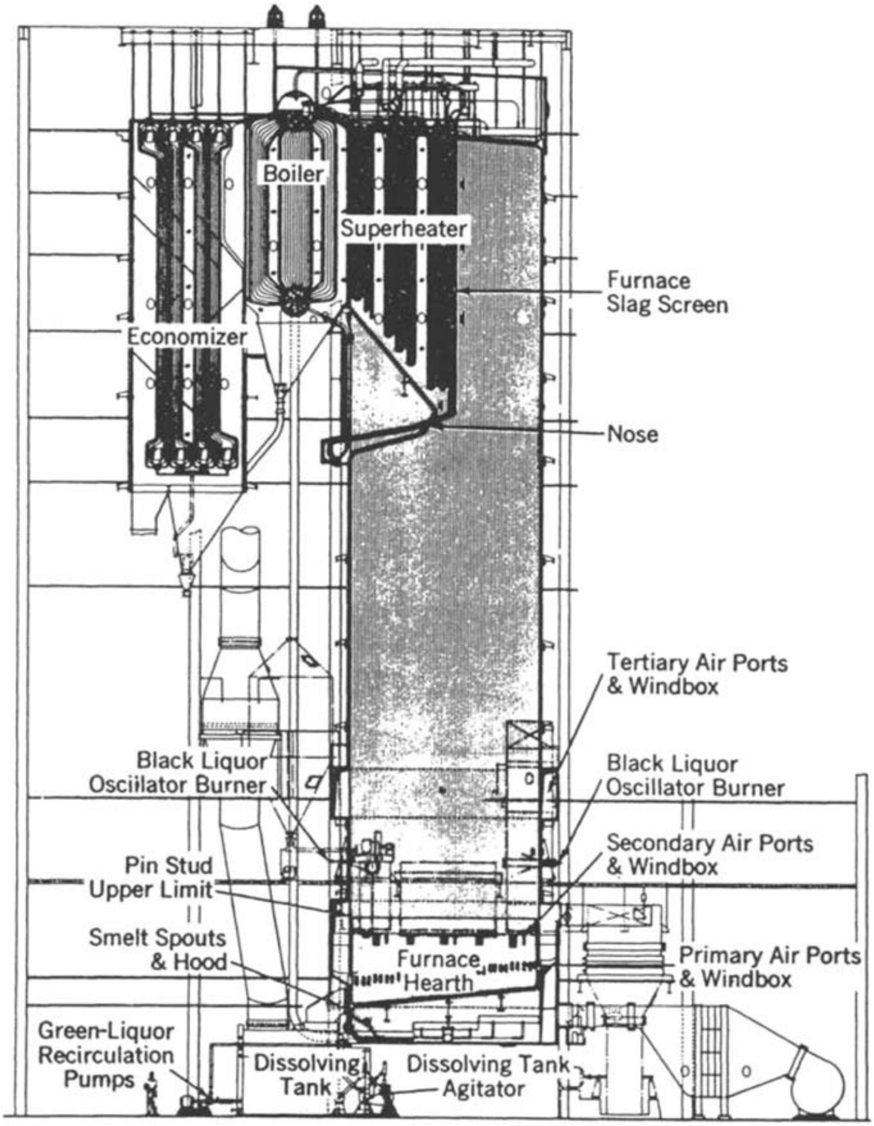

FIGURE 17.7 Kraft recovery boiler from Babcock & Wilcox. *From Stultz, Steven and Kitto, John B (1992).*

boiler is the largest, single, most expensive piece of equipment in a kraft mill costing over $100 million; hence, in many mills the recovery boiler limits the maximum production. The newest recovery boilers may support 2500–3000 tons of pulp production per day. The overall chemical reactions in the recovery boiler in addition to combustion are: conversion of sodium salts:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

reduction of makeup chemical:

$$Na_2SO_4 + 4C \rightleftarrows Na_2S + 4CO$$

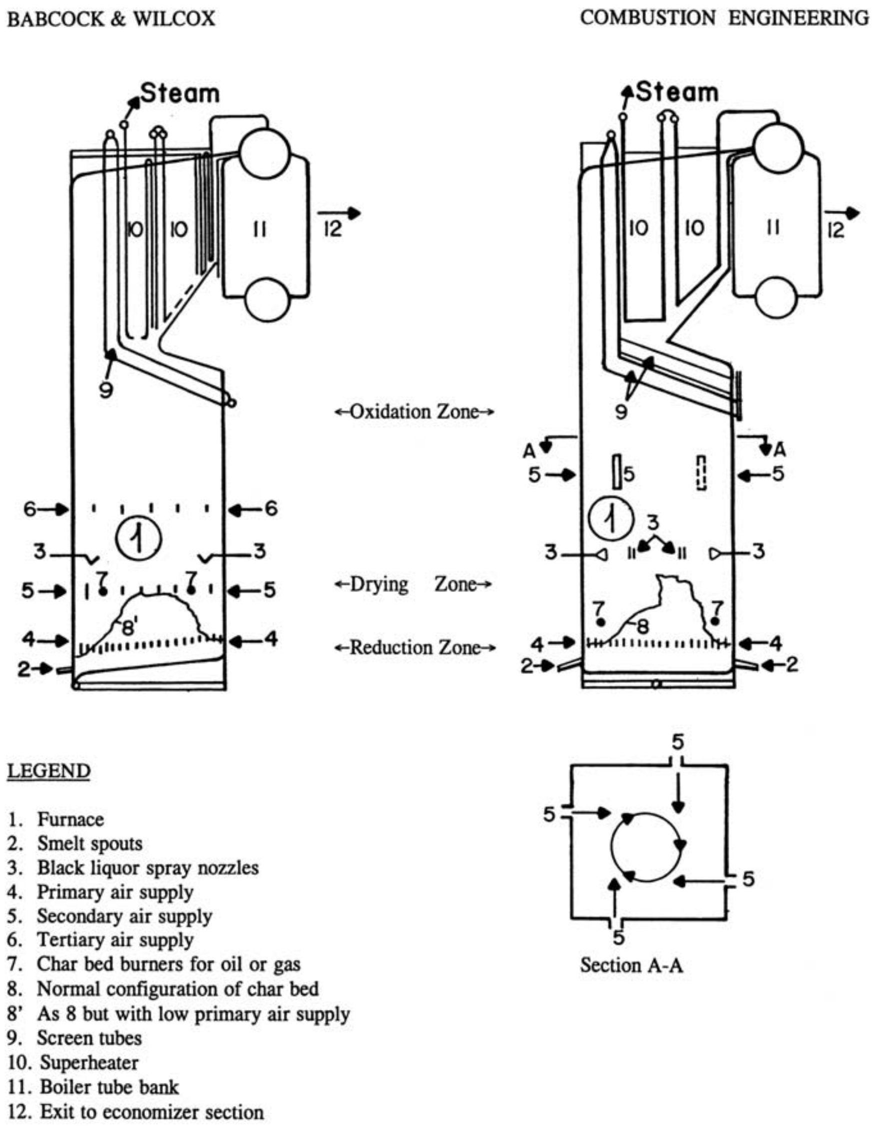

FIGURE 17.8 Principal design and air distribution of two recovery boiler designs. *From Stultz, Steven and Kitto, John B (1992).*

The lower zone is deficient in oxygen, so reduction reactions occur. This allows the sulfur in the smelt to occur as Na_2S and not $Na_2S_2O_3$ or Na_2SO_4, which would be unsuitable for fresh liquor. About 40%–50% of the air required for combustion is added by forced draft fans at the primary vents at the bottom of the recovery boiler. The primary air supply is preheated to 150°C (300°F) and bums the organic compounds, leaving smelt, but maintains reduction conditions. The upper zone begins above the region of secondary air supply and has about 10%–20% excess air above that required for complete combustion of the organic materials. The

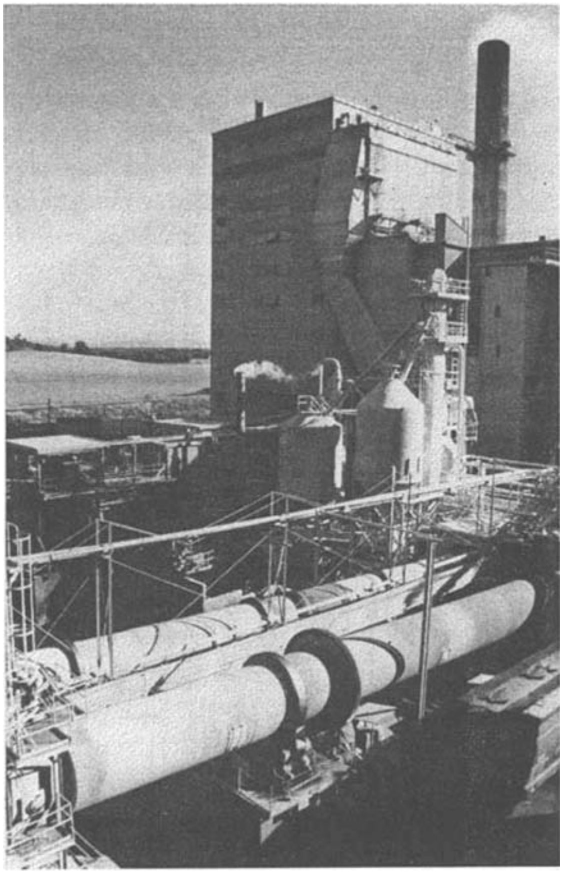

FIGURE 17.9 Kraft recovery boiler in the background and two limekilns in the foreground.

top zone must be under oxidative conditions to prevent carbon monoxide emissions. The flue gases are drawn away from the recovery boiler at the exit of the electrostatic precipitator; this maintains an air pressure below ambient so that gases will be sucked into the boiler in the vicinity of the black liquor nozzles to improve the safety of the operation. Some example reactions in each zone are:

Oxidation zone:

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

$$Na_2S + 2O_2 \rightarrow Na_2SO_4$$

$$H_2S + 1\tfrac{1}{2}O_2 \rightarrow SO_2 + H_2O$$

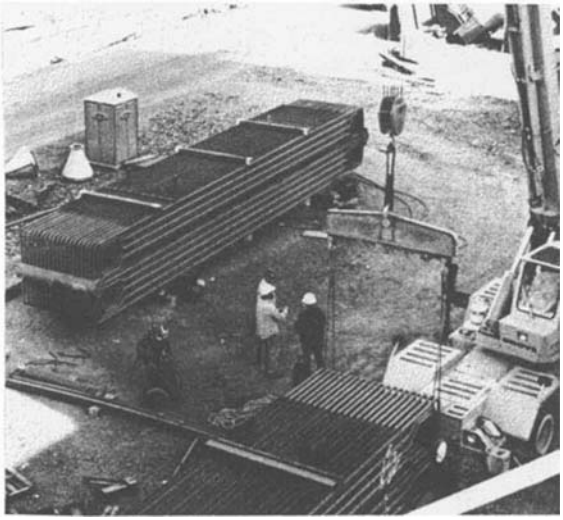

FIGURE 17.10 A small portion of the heat recovery tubes to install in a recovery boiler rebuild.

Drying zone:

$$\text{Organics} \rightarrow C + CO + H_2$$

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

Reduction zone:

$$\text{Orgaincs} \rightarrow C + CO + H_2$$

$$2C + O_2 \rightarrow 2CO$$

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$$

$$C + H_2O \rightarrow CO + H_2$$

The low secondary air supply of the B&W boilers is placed about 2 m (6 ft) above the primary air supply. This air acts as secondary air along the walls of the boiler, but as primary air in the char bed and, therefore, controls the height of the bed. Additional secondary air is needed; it is called tertiary air. (By definition all nonprimary air is secondary air.) In the CE boilers a tangential air supply is used to produce a rotary movement of the furnace gases (EPA, 1976).

The maximum combustion temperature occurs between the plane of black liquor entry and plane of secondary air entrance. Firing black liquor at 65% solids leads to a maximum

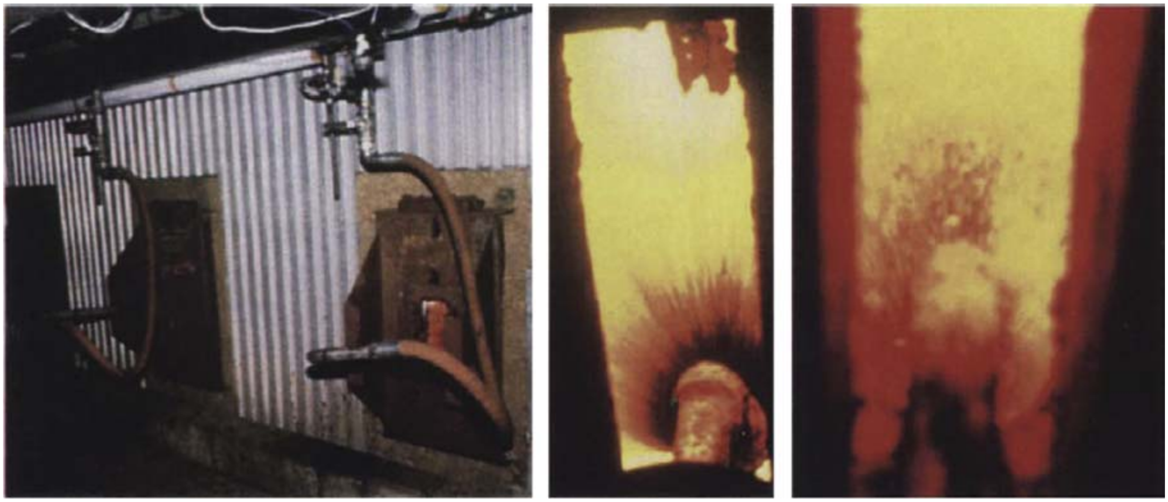

PLATE 17.1 Some black liquor guns of a kraft recovery boiler. The inserts show the liquor being fired into the furnace.

PLATE 17.2 Several views of smelt flowing from the bottom of a kraft recovery boiler.

combustion temperature of 2000–2400°F, whereas combustion at 70% solids leads to combustion temperatures greater than 2500°F. Cameras are used to monitor the appearance, size, and position of the char bed at the bottom of the recovery boiler to properly control liquor combustion.

Heat Recovery

The maximum temperature in the recovery boiler is about 1100–1300°C (2000–2400°F) for black liquor burned at 65% solids. The heat of combustion of the organic materials is transferred to tubes filled with water in several areas:

in the walls of the recovery boiler, in the *boiler* section, and in the *economizer* section. The economizer section is a final set of tubes (from the point of view of the exhaust gases, but the first tubes the water travels through) used in more recent recovery boilers to warm water for various processes. The *thermal efficiency*, defined below, is the proportion of heat recovered as steam and is about 60%. Most of the heat loss occurs as steam in the flue gases from water in the black liquor.

$$\text{thermal efficiency} = \frac{\text{heat to steam}}{\text{total heat input}}$$

The minimum temperature of the exhaust gases is 130°C (265°F) to prevent condensation of corrosive materials and to insure the exhaust will go upward beyond the smokestack. The combustion gases cool by radiation to about 870°C (1600°F) before entering the convection heating tubes. Temperatures above this, which might result by overloading the recovery boiler, do not allow complete combustion of the organics, which causes fouling of the screens and superheater tubes by tacky soot particles. The flue gases are cooled to about 450°C (850°F) after the boiler and to 160°C (320°F) after the economizer. (With direct contact evaporation, the flue gases leave the economizer section at 400°C.) About 6000–7000 kg/t (12,000–14,000 lb/ton) steam on pulp are produced by the recovery boiler.

Cogeneration

Cogeneration is the process of producing electricity from steam (or other hot gases) and using the waste heat as steam in chemical processes. In contrast, a stand-alone power-producing plant typically converts less than 40% of the heat energy of fuel (coal, natural gas, nuclear, etc.) into electricity. The remaining heat is simply lost to the heat sink; the heat sink lowers T_{cold} to increase the efficiency and is usually a large body of water where the effects of thermal pollution must be considered. The *Carnot cycle*, which predicts the maximum possible efficiency for the conversion of heat to work, of a heat engine is:

$$e_{\text{rev}} = 1 - T_{\text{cold}}/T_{\text{hot}} = (T_{\text{hot}} - T_{\text{cold}})/T_{\text{hot}}$$

where T is expressed in an absolute temperature scale such as Kelvin, T_{hot} is the temperature of the steam entering the turbine, and T_{cold} is the temperature of the steam exiting the turbine. Because pulp mills (both chemical and most mechanical) can use the steam coming out of the turbine and would produce steam in any case, these mills can essentially convert heat energy into electricity with over 80% efficiency. Surprisingly, many pulp mills do not cogenerate. This is particularly true in the northwestern United States where electric companies and relatively cheap hydroelectricity have discouraged this.

Electrostatic Precipitators (Cottrell)

Electrostatic precipitators (ESP, Fig. 17.11) consist of chambers filled with metal plates, charged with high DC voltage (30,000–80,000 V) through which exhaust gases from the recovery furnace pass. The chambers remove solid materials (particulates) in the gas stream that acquire a charge from the high voltage and collect on the plates, thereby

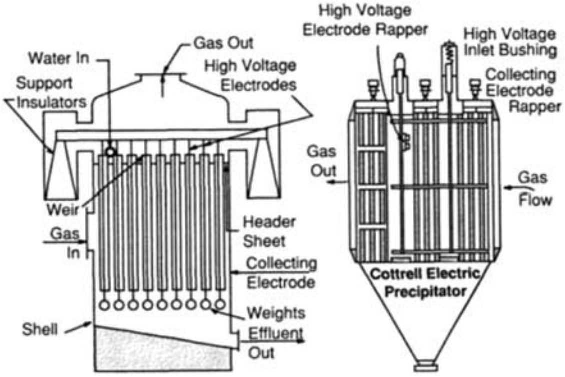

FIGURE 17.11 Cottrell electrostatic precipitator. *Redrawn from J. Ainsworth,* Papermaking, *1957 Thilmany Paper Co., with permission.*

purifying the stream before it is discharged into the atmosphere. Removal of over 99% of the particulates over 0.1/μm can be achieved. The current required is on the order of 500 mA/1000 m^2 (50 mA/1000 ft^2) of plate area. Rapping the plates with a shock wave dislodges the particulates into a collecting tray placed below them. Much of the material collected is sodium sulfate and sodium carbonate, typically 5–20 kg (10–40 lb) per ton pulp, which is returned to the recovery boiler. Electrostatic precipitators are now used on many new limekilns as well.

17.5 COOKING LIQUOR REGENERATION—THE CAUSTICIZING PROCESS

Chemical Recovery

The chemical recovery cycle is summarized in Fig. 17.12. Inorganic pulping chemicals are recovered from the furnace as a molten smelt (Na_2CO_3 and Na_2S) that falls to the bottom of the furnace. These are dissolved in water to give green liquor. The combination of molten smelt and large quantities of water in the heat exchanger tubes make recovery boilers potentially explosive, a critical concern at all times. The green liquor is treated with $Ca(OH)_2$ to regenerate the NaOH. The $CaCO_3$ that is formed must go through the limekiln to generate CaO that is later dissolved in water to regenerate $Ca(OH)_2$.

Green Liquor (Dissolving) Tank

Water (from the dregs washer) fills the green liquor dissolving tank, which is located below the kraft recovery furnace, where the molten slag is added through the smelt spout to form green liquor (mainly Na_2CO_3 and Na_2S). A *steam shatter jet* and recirculated green liquor impinges on the smelt stream to break it into small pieces. If the steam shatter jet fails, major explosions

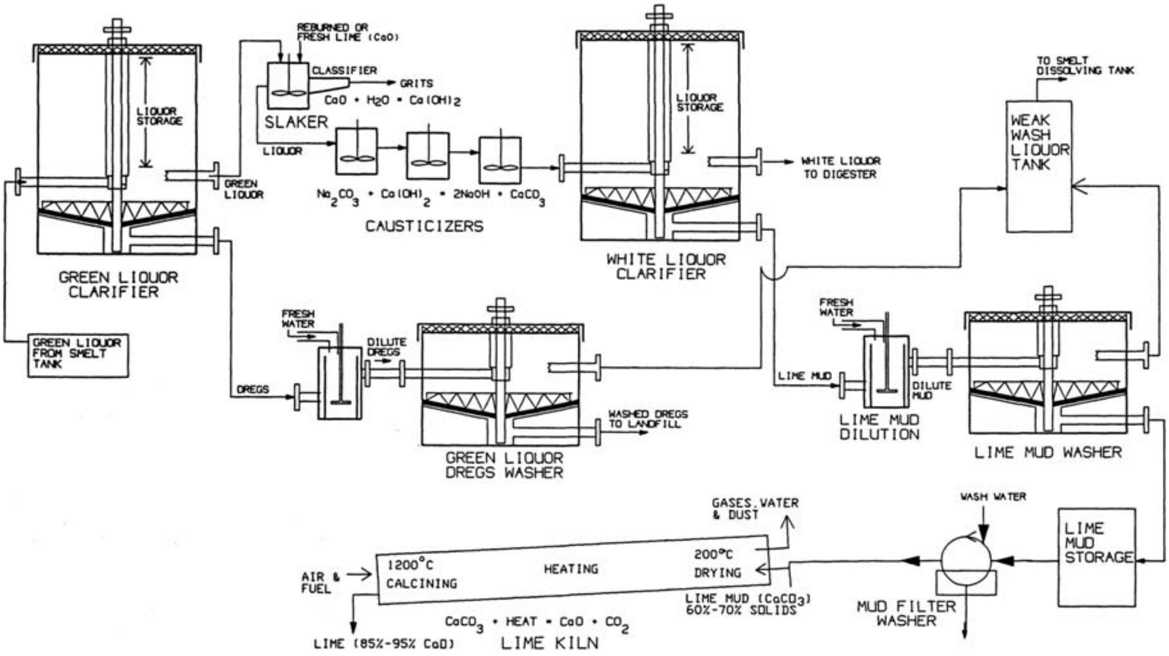

FIGURE 17.12 A summary of the causticizing process of a kraft mill.

become probable. The green liquor then goes to the green liquor clarifier tank. The density of the green liquor at this point is used as a process control variable of green liquor concentration.

Green Liquor Clarifier

The green liquor clarifier is a settling tank used to remove *dregs* by sedimentation before the green liquor is recausticized as shown in Fig. 17.13. It can also serve as a storage tank for green liquor and should provide at least 12 h supply of green liquor. Since the mid-1960s, single-compartment clarifiers have been used in place of the older multicompartment clarifiers. Overflow rates on the order of 0.6 m/h (2 ft/h) and retention times over 2 h are used. The dregs settle to the bottom where rakes move them to the outlet. If green liquor clarification is not used or is inadequate, these inert materials build up in the lime, decreasing the *lime availability.* The green liquor clarifier/storage unit should be insulated to limit heat loss of the green liquor coming from the smelt dissolving tank at 85–95°C (185–205°F). Most mills now use polymeric additives to help green liquor clarification.

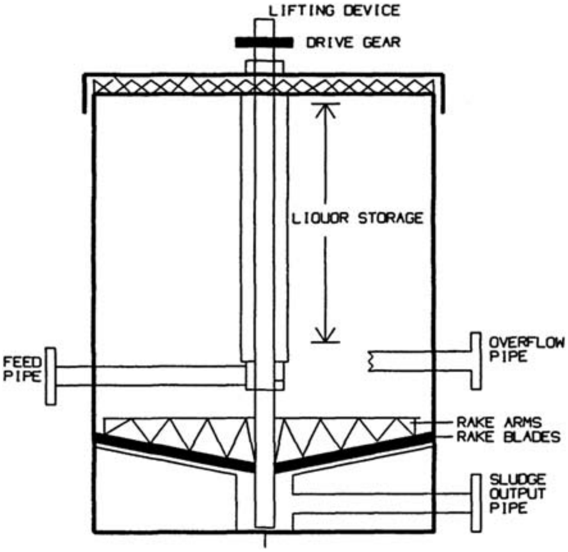

FIGURE 17.13 A single-compartment gravity sedimentation (settling) clarifier and storage unit suitable for green or white liquor.

Green Liquor Dregs and Dregs Washer

The green liquor dregs are undissolved materials in the green liquor. The dregs are about 0.1% of the liquor and consist of carbon (50% or more) and foreign materials (mainly insoluble metal carbonates, sulfates, sulfides, hydroxides, and, especially from nonwood fibers, silicates) to give a black bulky material. Incomplete combustion of organic materials in the recovery boiler can lead to inert carbon particles that leave with the smelt and greatly increase the amount of dregs. The metal salts arise from nonprocess elements (impurities) of the wood and corrosion products of the processing equipment, particularly from the recovery boiler. Improvements in the design of the recovery boiler have decreased the dregs yield to less than 4 kg/t (8 lb/ton) pulp. The dregs are washed in a dregs washer, often a drum filter or sedimentation washer (Fig. 17.14) where about 90%–95% of the sodium chemicals are removed, of which there is about 1–4 kg (2–9 lb) (Na_2O basis) per ton of pulp in the dregs before the washers.

Slaker

The slaker is a chemical reactor in which lime is mixed with green liquor (Fig. 17.15). The reaction temperature is 99–105°C (210–220°F). Using a high temperature and lime directly from the kiln gives a lime mud that settles well. The lime, CaO, forms slaked lime, $Ca(OH)_2$, and much of the causticizing reaction occurs here where the retention time is 10–15 min. These two chemical equations are shown below:

Slaking reaction:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

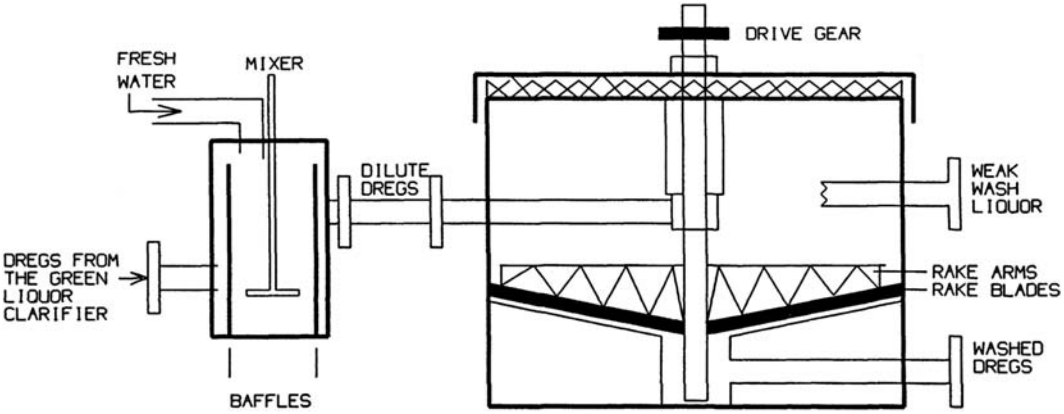

FIGURE 17.14 Sedimentation type green liquor dregs washer.

Causticizing reaction:

$$Ca(OH)_2 + Na_2CO_3 \rightleftarrows 2NaOH + CaCO_3(s)$$

Grits (large, unreactive lime particles and insoluble impurities corresponding to about 0.5%–2% of the lime feed) are removed here by the *classifier*, which uses a raking action. The grits are often sent to landfills although a few mills will send them through a ball mill and use them to neutralize the acid effluent of the bleach plant. The extent of the causticizing reaction (and therefore the causticizing efficiency in the white liquor) depends on the concentration of the initial Na_2CO_3 and the amount of lime used. With concentrations below 16% of actual chemical, the theoretical conversion is over 90%. At concentrations above this, the theoretical conversion drops off quickly. It is desired to have about 1% excess lime. Much more than this increases the turbidity of the white liquor and decreases the filtration rates of the lime mud. Commercially, about 75%–85% of the ultimate level of conversion is achieved in the agitator section of the slaker. The causticity efficiency should be 3%–4% below the equilibrium value to avoid excess liming.

Causticizers

The causticizers are two to four continuous flow, stirred reactors that are used to complete the causticizing reaction (Fig. 17.16). The contents are stirred with a pitched blade turbine at 70–80 rpm. The liquor/lime slurry flows through them in series with a total retention time of 1.5–2.5 h. The internal surfaces must be stainless steel or another corrosion resistant material.

White Liquor Clarifier

The white liquor clarifiers are settling tanks (gravity sedimentation) used to remove the lime mud ($CaCO_3$) from the white liquor. The clarified liquor should have turbidity below 100 ppm. The lime mud leaves with a solids content above 35% to minimize entrained soda that is removed in the lime mud washer. Like the green liquor clarifiers, white liquor clarifiers with single compartments with at least 12 h storage (see Fig. 17.13) are now much more common than the multicompartment clarifiers. Poor lime settling may be a result of excess lime to the slaker (more than 1% excess), a low lime availability (below 80%–85% that is indicative of a high level of contaminants because of inadequate removal of dregs and/or grits or incomplete slaking due to overloading the limekiln), a high percentage of low reactivity unburned fresh lime (i.e., purchased lime that has not been through a limekiln or is aged),

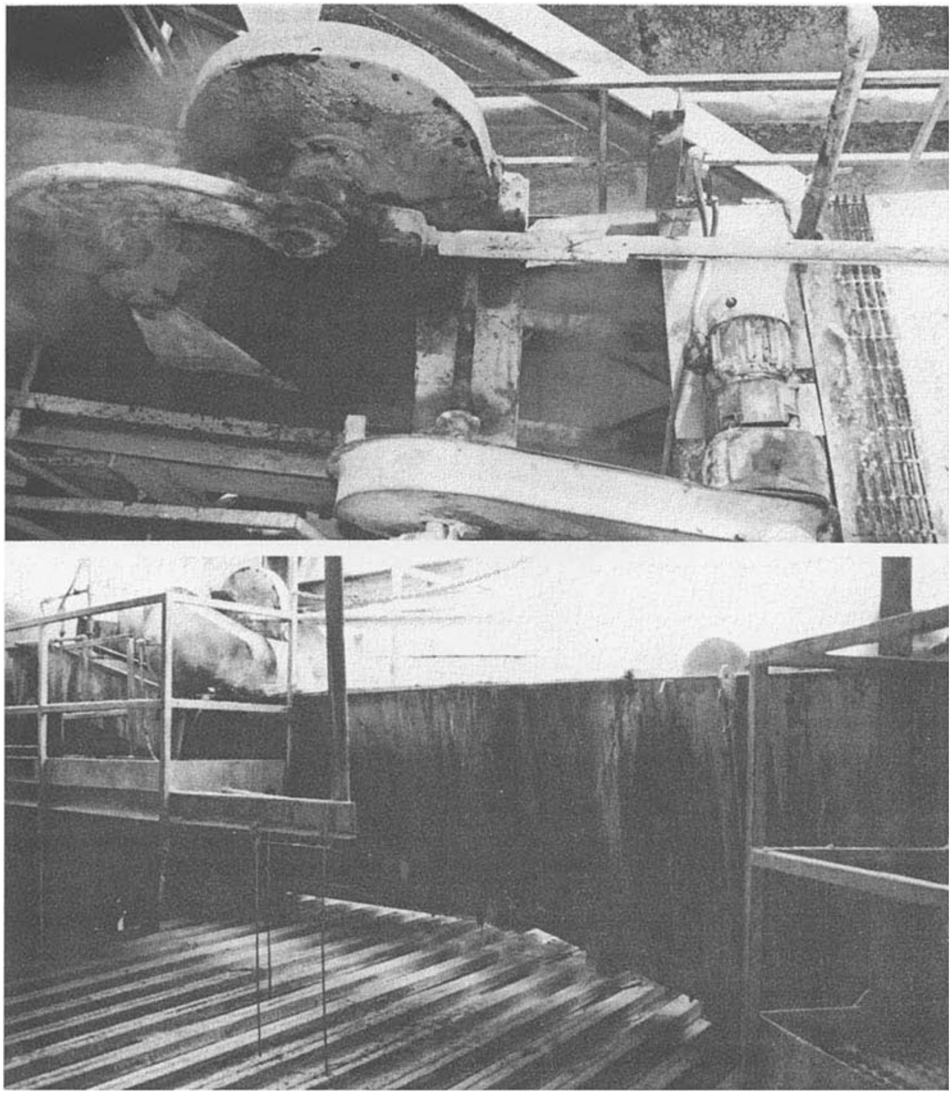

FIGURE 17.15 The top (top) and side (bottom) views of a slaker.

or inadequate white liquor clarification or clarifier operation. Lime burned at too low a temperature gives much mud of high viscosity; lime burned at too high a temperature gives a slow causticizing reaction and a slow settling lime mud with entrained alkali. Polymeric additives are often used to help white liquor clarification.

White Liquor Pressure Filters

Recently, some mills have been installing white liquor pressure filters after the white liquor clarifiers to supply additional clarification. Typically the filters have polypropylene filter tubes through which the white liquor flows under a pressure of 140–210 kPa (20–30 psig)

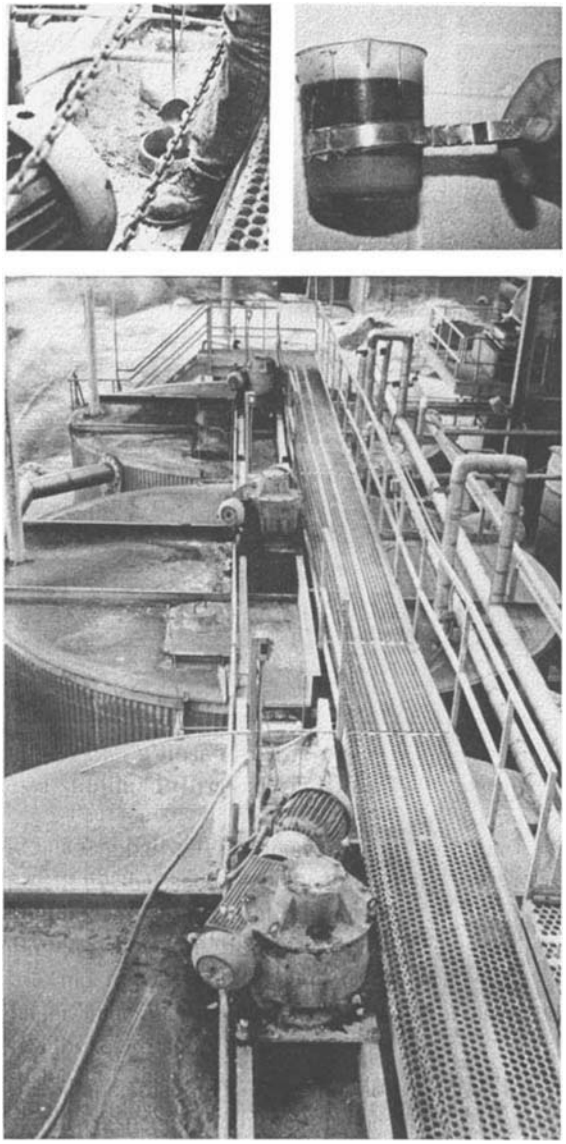

FIGURE 17.16 The causticizers (bottom). Top: The left insert shows a sample drawn for quality analysis, and the right insert shows proper sample settling.

to trap further lime mud. A reverse, flushing cycle removes the embedded lime mud that is added to the bulk of the lime mud (from the white liquor clarifiers) before the lime mud washers.

Lime Mud Washer

The lime mud washer removes most of the 15%–20% entrained alkali (Na_2O basis) from the lime mud, usually by sedimentation washing. It is typically a settling tank (or two in series) where fresh (makeup) water is used to wash the lime mud. If it were not removed, the Na_2S would cause slagging in the kiln, and reduced sulfur compounds would be released as H_2S. About 1% alkali on lime mud remains after washing. The liquor (weak wash or weak white liquor) is then used to dissolve smelt from the recovery boiler. It is important to maintain a proper water balance during lime mud washing to avoid formation of excess weak wash. This must be sent to the sewer with loss of valuable chemical that creates a disposal problem.

Lime Mud Filter

Thick lime mud from storage is diluted to 25%–30% solids (as measured by an X-ray detector) before going to the lime mud filter. The lime mud filter is a rotary drum vacuum filter washer used for final lime washing and thickening to 60%–70% solids before the lime enters the kiln. Centrifuges have been installed instead of drum vacuum filter to thicken lime, but they have lower water removal, leading to increased energy costs and lower limekiln throughput.

Limekiln

The primary function of the limekiln is to convert calcium carbonate to calcium oxide for reuse in the causticizing process. The process involves heat and mass transfer between the kiln, fuel, primary and secondary air, drying of lime mud, and calcining of calcium carbonate. It is important to have a comprehensive understanding of the following processes for diagnosing operational problems; improving energy consumption; increasing production reducing emissions; increasing refractory life; reducing process instabilities; improving the product quality; and optimizing the kiln operations.

Rotary limekilns in the pulp and paper industry are large steel tubes that are lined on the inside with refractory bricks. These kilns range in size from 7 ft (2.1 m) in diameter by 175 ft (53 m) long to 13.5 ft (4 m) in diameter by 400 ft (122 m) long. The refractory lining is from 6 in. (15.2 cm) to 10 in. (25.4 cm) thick. Production capacities for these units range from 50 t/day (45 mt/day) to 450 t/day (400 mt/day) of CaO. Fig. 17.17 shows schematic of the exterior and interior of limekiln. Rotary limekilns are slightly inclined from the horizontal and are slowly rotated on a set of riding rings. Lime mud is introduced at the uphill, feed end and slowly makes its way to the discharge end because of the inclination and rotation. A burner is installed at the discharge end of the kiln where fuel is burned to form an approximately cylindrical flame. Heat transfer from this flame and the hot combustion gases that flow up the kiln dries, heats, and calcines the counterflowing lime solids.

The weight of the kiln is supported on riding rings that encircle the kiln. These riding rings contact carrying rolls supported by concrete piers. A large electric motor operating through a reducing gearbox and pinion drives the main gear attached to the kiln. Typically, the kiln is driven at speeds of 0.5–2 rpm, often with variable speed arrangements (Adams, 1996). Typical transit times for the lime through the kiln are from 1.5 to 4 h under normal operating conditions. This is set by the speed and by the slope of the kiln, which is between 1.5 and 3 degrees (5/16–5/8 in./ft). The rotation of the kiln requires the use of hoods and seals at each end for connection to stationary ancillary equipment. At the hot end, the firing hood provides support for the burner and the flame management equipment and also the openings and passages for the discharge of the reburned lime product. At the cold end, the hood provides openings for a lime mud feed screw or belt, a connection to

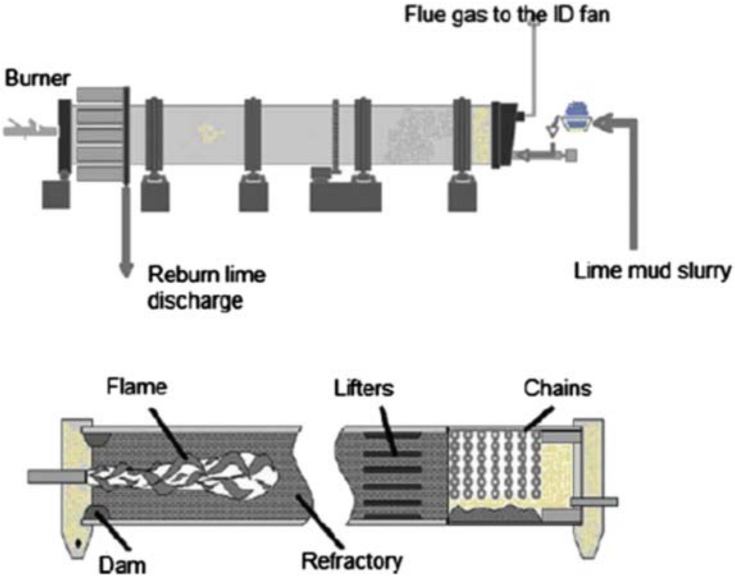

FIGURE 17.17 Schematic of the exterior and interior of a modern rotary lime reburning kiln. *ID*, induced draft. *Based on Adams, T.N., 1996. Lime kiln principles and operations. 1996 Kraft Recovery Short Course, Orlando, FL, 8–11 January.*

the induced draft fan and an important seal to limit the flow of tramp air. In older installations this hood is often an enlarged chamber in which dust and mud can be sluiced out of this area. Newer installations incorporate smaller hoods to improve the seal and reduce the length of the mud screw or belt. The burner and flame play an important role in product quality and refractory service life.

As with all combustion fired heat exchange equipment, higher flame temperatures mean higher production capacity and efficiency. However, excessive temperatures cause refractory damage and overburned, slow-reacting lime product. This trade-off in performance results in a compromise in flame length. Shorter flames are too hot and cause refractory damage and overburned lime, whereas longer flames cause some loss in production capacity and efficiency and loss of control of the product quality. A compact, medium-length flame approximately three times the kiln diameter in length is a good trade-off between efficiency and refractory service life. However, irrespective of the shape, the flame must not touch the refractory, or serious refractory washing will occur. At the cold end of the kiln, the relatively low gas temperature restricts heat transfer. To improve this, a section of chain is hung from the shell in this part of the kiln. This chain is made up of links that are typically 3/4 in. × 3 in. Hangers attach lengths of this chain directly to the kiln shell either from one end or both ends. When the chain is hung from one end it is referred to as curtain chain, and when hung from both ends it is most often called a garland system.

Wet lime mud is fed into the high end of the kiln, and the solid phase moves countercurrent to the flow of hot gases as the kiln rotates. The transfer of heat into the mud at the cold end is optimized by providing extended surface area, usually by means of steel chains attached to the kiln shell and hanging in the hot gases. In the hotter zones of the kiln, the metal shell is lined with refractory brick. As its temperature is increased, the lime mud material becomes plasticized and forms into pellets, aided by the rolling and lifting action of the kiln (Adams, 1996). Normally, the size of the aggregates ranges up to about 3 cm in diameter. Occasionally, the pellets keep on growing to form large balls or adhere to the brick to form rings. The soda content of the lime mud has a significant effect on its aggregating properties during the reburning operation and is typically controlled to less than 1% sodium oxide. The hot end of the kiln is typically maintained at 1150−1250°C by firing oil or gas. Without reclaiming heat from the kiln product, the reburned lime would be discharged at a temperature of about 950°C. Most modern kilns are equipped with integral tube coolers to recover the major portion of this heat in direct contact with part of the entering air. These coolers are attached to the discharge end of the kiln in such a way that the calcined lime falls into one of the coolers; it then reverses direction and flows countercurrent to the air to the opposite end of the cooler where it is discharged at a temperature of about 350°C. Air is supplied to the kiln by a forced draft fan, but the major work is done by the induced draft fan that pulls the combustion gases through the kiln. The gases leaving the kiln are laden with lime mud dust and should be cleaned up before discharge. In most cases, the dust is removed in a suitably designed scrubber, most commonly a venturi-type. The electrostatic precipitators have become the equipment of choice for this service, especially for the largest size kilns. Fig. 17.18 shows Abdritz's lime reburning kiln system.

Some mills with short limekilns or where the limekiln is bottleneck and higher throughput is required use *flash driers* to dry the lime mud to less than 1% moisture content before it enters the kiln. In flash drying, the exit gases of the kiln (much hotter than 200°C because dry mud is being fed into it) are used to dry the lime mud. The lime mud is combined with the gases in a mixer. The flue gases and water vapor are then separated from the lime mud in a cyclone.

FIGURE 17.18 Andritz's lime reburning kiln system ensures reliable and energy efficient production of high-quality lime for the recausticizing operation. *Courtesy: Andritz*

Heat is recovered from the flue gases and hot burned lime of the limekiln. A development of the early 1980s is the discharging of the hot, burned lime product through about 8–10 *integral tube coolers* forming a ring around the limekiln on the outer side of the discharge end. Secondary air flows through these tubes in the opposite direction as the lime so that it is preheated, thereby increasing the combustion temperature or lime throughput. However, the lime must remain above 320°C (600°F) so it will slake well. Sulfur oxides are not emitted to a large extent because the CaO is a good scavenger for the highly acidic forms of these compounds and $CaSO_3$ and $CaSO_4$ are formed. Emissions of nitrogen oxides are high because of the excess air and high combustion temperatures. See Chapter 15, Volume 2 for more information. Pure oxygen gas has been used as a partial substitute for air to decrease H_2S generation from the lime mud and increase lime mud throughput rates. Ring formation within the limekiln is part of the territory. If it becomes a severe problem, expensive shutdowns may result. Ring formation can result (Tran and Barham, 1991) when noncondensable gases are introduced to the limekiln, and the ring occurs from the formation of $CaSO_4$. The use of a Total Reduced Sulfur (TRS) scrubber column for the Non-Condensible Gases (NCG) before their introduction to the limekiln can drastically decrease ring formation. The exhaust gases must be treated to remove particulate matter. Usually a venture scrubber (Fig. 17.19) is used. The flue gases flow through a constriction on the order of 1 ft^2 with the introduction of a water spray to trap the particulates. In the mid-1970s, a few mills started using electrostatic precipitators (ESP, Fig. 17.11) to treat the limekiln exhaust gases. ESP have many advantages over the venturi scrubbers, including cleaner exhaust gases, easier control of the system, and low exhaust fan power requirements because the exhaust is not forced through a narrow

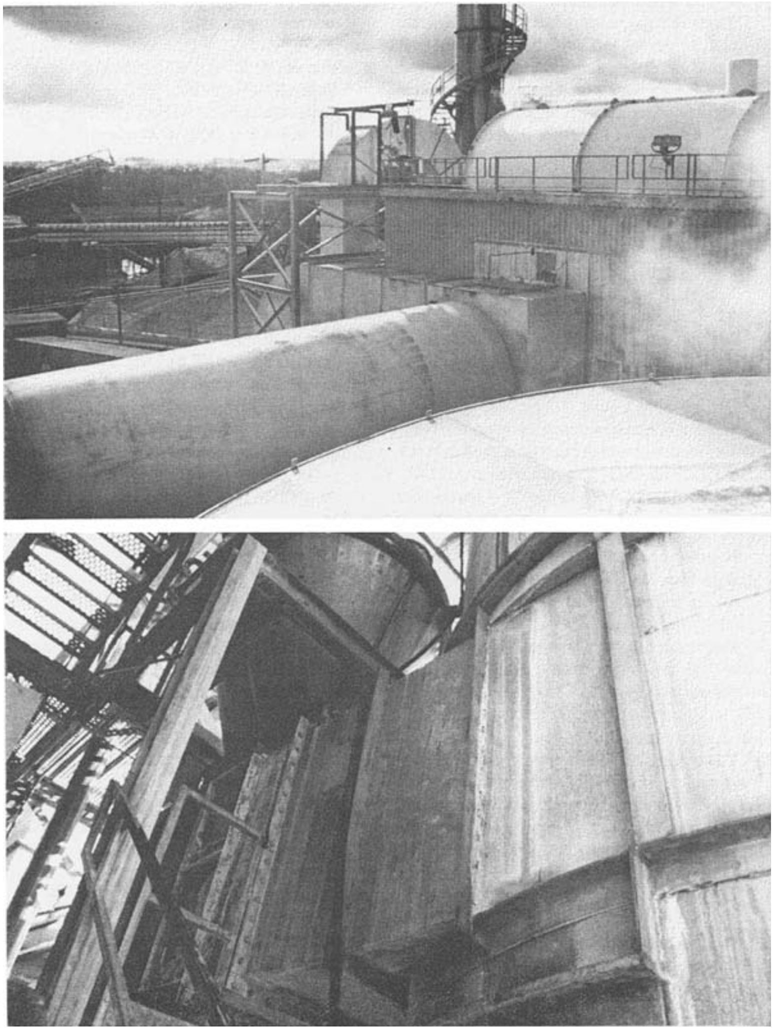

FIGURE 17.19 The top view shows the limekiln duct carrying the flue gases to the venturi scrubber (bottom) and from the scrubber to the chimney.

constriction. Now most new systems use electrostatic precipitators to capture the particulates.

Salt Cake (Na_2SO_4)

Salt cake is the makeup chemical for the kraft process that is used to replace chemicals lost (mostly through the pulp) in pulping. About 50—100 lb/ton pulp is normally dissolved in the concentrated black liquor just before spraying into the recovery furnace. The name “sulfate” process was derived from the use of this salt as a makeup chemical; however, sodium sulfate is *not* involved in the actual pulping process. The makeup chemical can be other chemicals as well.

Cross Recovery

Cross recovery is the collection of waste NSSC liquor and burning it in a nearby kraft mill. Kraft mills recover the sodium and sulfur as Na_2S and Na_2CO_3 after the recovery furnace. The kraft mill pays the Neutral sulfite semichemical (NSSC) mill for Na_2SO_4, which allows the NSSC mill to purchase fresh cooking chemicals (sulfur and either NaOH or Na_2CO_3).

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(Chap. 4); Smyth, Jr., J.A., The mathematics and variables of countercurrent brown stock washing, pp 21–26; Guillory, A.L., Sorbed soda and its determination, pp 27–31 (Chap. 6); Guillory, A.L., Brown stock washer efficiency and physical testing, pp 33–37 (Chap. 7); Perkins, J.K., Analyzing and troubleshooting a washing system, pp 39–45 (Chap. 8); and Perkins, J.K., Newly introduced methods of brown stock washing, pp 47–48 (Chap. 9).

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The specific heat of black liquor is fairly linear from 1 cal/g at 0% solids to 0.70 at 60% solids.

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EXERCISES

General

1. What are the three main objectives in the chemical recovery cycle?
2. Write the chemical equations as indicated.
   - **a.** Reaction of NaOH in the recovery boiler:
   - **b.** The formation of white liquor from green liquor:
   - **c.** The regeneration of calcium so it can be used in reaction (b):
   - **d.** Concentration of black liquor from 15% to 50% solids:
3. Where is turpentine recovered during kraft pulping? Where is tall oil collected?
4. What is cross recovery?

Pulp Washing

5. Indicate the effect of a high dilution factor in pulp washing on the following:

	Increase	Decrease
a. Sodium loss	—	—
b. Evaporation cost	—	—
c. Bleaching cost	—	—

6. The steam economy of the MEEs is 4.24; suppose the dilution factor in the brown stock washers goes from 3 tons water per ton pulp to 4 tons water per ton pulp. How much more steam is required to process a ton of pulp?

Liquor Concentration

7. What are the two types of bodies used in MEEs?
8. Black liquor is first concentrated to about 45% –50% solids using the MEEs. Final concentration is achieved by direct contact evaporators or by concentrators. Since the late 1960s, direct contact evaporators have not been installed in pulp and paper mills. Why is this the case?
9. Why is the concentration of black liquor usually limited to about 65%–75% solids before combustion in the recovery boiler? Why would a higher solids content be desirable?

Recovery Boiler

10. Describe the location of the oxidation and reduction zones in the recovery boiler. Give some examples of chemical reactions that occur in each of these zones.
11. What is the purpose of the electrostatic precipitator after the recovery boiler?
12. What would happen to the sodium sulfide if it was oxidized in the bottom of the recovery boiler? Is this beneficial?

Lime Cycle

13. What are the three zones in the limekiln in terms of what is happening to the lime?

14. What are the consequences of not removing the dregs from the green liquor?

Causticizing

15. Of what is the causticizing efficiency of white liquor a measure?

Miscellaneous

16. It has been a long practice at many mills to add some black liquor to the white liquor and chips before pulping. What are some possible advantages of adding black liquor to the digester as part of the digester charge?