72 3. PULPING FUNDAMENTALS

Kraft green liquor semi-chemical process

The green liquor semi-chemical pulping process for corrugating medium uses green liquor as the pulping liquor. The green liquor can be obtained from an associated kraft mill or from a recovery boiler specifically for the green liquor mill. In either case, the lime cycle is not required for liquor regeneration.

De-fiberator or hot stock refiner

The de-fiberator, also called the hot stock refiner, is an attrition mill designed to break apart the hard semi-chemical chips into pulp.

Cross recovery

Cross recovery is the use of the waste liquor of a semi-chemical mill as the make-up chemical in the kraft recovery plant. For example, the Na_2SO_3 in the waste liquor of an NSSC mill, when added to the kraft recovery boiler, is converted to Na_2S during burning of the liquor and furnishes the kraft mill with its make-up sulfur and sodium. Fresh make-up chemicals are used to generate the pulping liquor for the NSSC mill. Obviously, the size of the NSSC mill is limited by the make-up chemical requirements of the kraft mill. In a green liquor semi-chemical mill, fresh chemical is taken from the kraft green liquor storage while the spent pulping liquor is simply returned to the kraft recovery cycle.

3.6 GENERAL CHEMICAL PULPING

Delignification

Delignification is the process of breaking down the chemical structure of lignin and rendering it soluble in a liquid; the liquid is water, except for organosolv pulping.

Kappa number, permanganate number

The kappa number is a measure of the lignin content of pulp; higher kappa numbers indicate higher lignin content. A similar test is the permanganate number (or K number). The kappa number is used to monitor the amount of delignification of chemical pulps after pulping and between bleaching stages. For more detail on pulp tests, how they are carried out, and their significance, see Chapter 6.

Pulp viscosity

The pulp viscosity (see Section 6.3) is a measure of the average chain length (*degree of polymerization, DP*) of cellulose. It is determined after dissolving the pulp in a suitable solvent such as cupriethylenediamine solution. Higher viscosity indicates a higher average cellulose DP that, in turn, usually indicates stronger pulp and paper. Decreases in viscosity result from chemical pulping and bleaching operations and to a certain extent are unavoidable, but must be minimized by proper attention to important process parameters. Cellulose viscosity has little importance in mechanical pulping since the cellulose chains are not appreciably degraded by this operation.

Fiber liberation point

The fiber liberation point occurs when sufficient lignin has been removed during pulping that wood chips will be soft enough to break apart into fibers with little or no mechanical action.

Full chemical pulps, unbleached, bleached

A pulp produced by chemical methods only is known as a full chemical pulp. Most chips are at the fiber liberation point after cooking at 130-180°C (265-355°F) with appropriate pulping liquors. The total pulp yield is about 50 percent, and the pulp contains about 3-5% lignin. These pulps have high strength and high cost. The common methods are the kraft process (also called alkaline or sulfate process with a cooking pH above 12) and the various sulfite processes with a wide range of pH cooking conditions. An older method, enjoying only limited use these days on hardwoods and nonwood fiber such as straw, is the soda process that uses sodium hydroxide as the only active pulping ingredient. Unbleached pulp is a full chemical pulp as it comes from the pulping process. It is light to dark brown in color. Bleached pulp is a white pulp produced by bleaching full chemical pulps.

Dissolving pulp

Dissolving pulp is a low yield (30-35%) bleached chemical pulp that has a high cellulose content (95% or higher) suitable for use in cellulose derivatives such as rayon, cellulose acetate, and cellophane (see the end of Section 2.6 for a description of these materials.) Dissolving pulp is



Fig. 3-10. The top of a batch digester where digester loading occurs. In the background several additional digester tops are visible.

manufactured by the kraft process using an acid prehydrolysis step to remove hemicelluloses or by an acid sulfite process. Improved cellulose purity is achieved by a cold alkali extraction of the pulp.

Digester

The digester is a pressure vessel used for cooking chips into pulp. Digesters are designed to operate in either a continuous mode, if in a long, narrow tube-shape, or in a batch mode.

Batch digester

Batch digesters are large digesters, typically 70-350 m³ (2,500 to 12,500 ft³), that are filled with wood chips and cooking liquor. The top of a batch digester is shown in Fig. 3-10. A diagram of a batch digester is shown in Fig. 3-11. A laboratory batch digester is shown in Fig. 3-12.

Typically a mill has a bank of six to eight digesters so that while several are cooking, one is filling, one is blowing, one might be under repair, etc. Heating with steam may be *direct*, where steam is added directly to the digester which dilutes the cooking liquor, or *indirect*, where steam is passed through the inside of tubes within the digester which allows reuse of expensive steam condensate and gives more uniform heating. The *cooking time* is the length of time from initial steaming of chips to the start of digester blowing; the *time to temperature* is the length of time from initial steaming to the point where the desired cooking temperature is reached; and the *time at temperature* is the length of time from when the cooking temperature is reached until the digester blow starts.

A typical sequence of events for an entire cook is as follows: 1) The digester is first opened and filled with chips, white liquor, and black liquor. 2) After initial circulation of the liquor additional chips are added as the contents settle. 3) The digester is then sealed and heating with steam begins. The temperature rises for about 90 minutes until the cooking temperature is achieved. 4) The cooking temperature is maintained for about 20-45 minutes for the kraft pro-



Fig. 3-11. A stationary batch digester with indirect heating of the liquor. Reprinted from *Making Pulp and Paper*, ©1967 Crown Zellerbach Corp., with permission.



Fig. 3-12. A laboratory batch digester with product (below).

cess. During the heating time, air and other noncondensable gases from the digester are vented. 5) When the cook is completed, as determined by the kappa of pulp from the digester, the contents of the digester are discharged to the blow tank. 6) The digester is opened and the sequence is repeated.

Continuous digester

A continuous digester is a tube-shaped digester where chips are moved through a course that may contain elements of presteaming, liquor impregnation, heating, cooking, and washing. Chips enter and exit the digester continuously. Continuous digesters tend to be more space efficient, easier to control giving increased yields and reduced chemical demand, labor-saving, and more energy efficient than batch digesters. Since continuous digesters are always pressurized, special feeders must be used to allow chips at atmospheric pressure to enter the pressurized digester without allowing the contents of the digester to be lost. *Screw feeders* are used for materials like sawdust and straw. A moving plug of fiber is used to make the seal. *Rotary valves* (Fig. 3-16) work like revolving doors. A pocket is filled with wood chips or other fiber source at atmospheric pressure. When the valve is rotated it is sealed from the atmosphere and then opened into the digester where the contents are deposited.

Kamyr digesters (Figs. 3-13 to 3-15) are large, vertical digesters, where chips enter the top and exit the bottom continuously in a plug flow. In 1992, 390 Kamyr digesters were operational worldwide with a rated capacity of 77 million tons per year. The chips are exposed to various areas



Fig. 3-13. The Kamyr continuous digester. Reprinted from *Making Pulp and Paper*, ©1967 Crown Zellerbach Corp., with permission.



Fig. 3-14. Two vessel hydraulic digester with extended MCC[™] and two stage diffuser washer. Courtesy of Kamyr, Inc.



Fig. 3-15. A two-vessel Kamyr digester.

of the digester where they are impregnated with liquor, heated to the cooking temperature, held at the cooking temperature to effect pulping, and partially washed. The pulp is then sent to the blow tank.

In the typical process chips from the bin are introduced to a low pressure pre-steaming chamber where the chips are transported by a screw feed. Here flash steam at atmospheric pressure preheats the chips and drives off air so that liquor penetration will be enhanced. The chips pass through the high pressure feeder where cooking liquor carries them to the digester. Most of the liquor is returned to the high pressure feeder. Impregnation occurs for about 45 minutes at 130°C so cooking will be much more uniform. Liquor heating occurs in the zone formed by two external liquor heaters. The cooking zone merely supplies the appropriate retention time for cooking to take place. The pulping reaction is terminated with the addition of cold, wash liquor from the brown stock washers that displaces the hot, cooking liquor.

The M & D digester (Messing and Durkee) is a long digester inclined at a 45° angle. A diagram of this is shown in Fig. 3-16, and an actual digester is shown in Fig. 3-17. This digester is often used for kraft pulping of sawdust or semi-chemical pulping methods. It has some use for kraft pulping of wood chips. The chips or sawdust enter the top, go down one side of the digester, return back up the other side being propelled by a conveyer belt, and exit out the top. The cooking time is about 30 minutes. A midfeather plate separates the two sides of the digester. Since the size of these shop-fabricated digesters are limited to about 2.4 m (8 ft) diameter, they are used for relatively small production levels.

Another continuous digester is the *Pandia* digester (Figs. 3-18 and 3-19), which is horizontal, uses a screw feed, and is often used in kraft pulping of sawdust, semi-chemical pulping of chips with short cooking times, and pulping of nonwood fiber such as straw.

Digester charge, relief, and blowing

The *digester charge* includes the wood chips and cooking liquor in a digester. *Digester relief* occurs while the chips are heated to temperature and during the cooking process to relieve the pressure caused by the formation of volatile gases. These gases are released and condensed to improve the pulping process. This removes air from within and around the chips; increasing the liquor circulation and evenness of cooking; reduces the digester pressure, which reduces fiber damage during the blow; and allows collection of turpentine, if desired.

Digester blowing occurs at the end of a cook when the contents of a digester are cooled to about 100°C (212°F) and allowed to escape to atmospheric pressure. There is usually sufficient force in a full chemical pulp to cause fiber separation. If the contents are blown from temperatures near that of cooking, 170°C (340°F) for kraft cooking,



Fig. 3-16. The M&D continuous digester. The inserts show various aspects of the rotary valve. Courtesy of Andritz Sprout-Bauer, Inc.



Fig. 3-17. The M & D continuous digester. To the right is the blow tank. The top insert shows a hydraulically driven exit valve and the bottom insert shows an electric-motor driven exit valve.

the pulp often loses a significant (10-15%) amount of its strength.

Blow tank

Blow tanks are large, cylindrical vessels that receive the hot pulp from the digesters (Fig. 3-20). Agitators mix the pulp from the digester with dilute black liquor so the pulp slurry can be pumped and metered for the correct consistency. The heat of the hot gases from the blow tank are recovered by the *blow heat accumulator*, a large heat exchanger. Up to 1000 kg (2000 lb) of steam per ton of pulp is generated by batch digesters and some continuous digesters and must be condensed. Continuous digesters like the Kamyr are able to recover the heat more efficiently by liquor displacement methods, although this technology is being applied to batch digesters in the rapid displacement heating method.

Condensation of the blow gases also decreases pollution by recovering most of the volatile reduced sulfur compounds, organic compounds such



Fig. 3-18. A Pandia continuous digester with two tubes. The insert shows the feed valve.

as methanol, and related materials known together as *foul condensate*. The condensate is sometimes used for dilution water in applications such as lime mud dilution or brown stock washing where the foul compounds will be trapped prior to a combustion process. Non condensable gases are often



Blow Line

Vent

Fig. 3-19. Pandia digester. Reprinted from *Making Pulp and Paper*, ©1967 Crown Zellerbach Corp., with permission.

Fig. 3-20. Blow tank. Reprinted from *Making Pulp and Paper*, ©1967 Crown Zellerbach Corp., with permission.

diverted to the lime kiln for combustion. The pulp is then sent to be screened and cleaned in the brown stock washers.

Liquor

Cooking or pulping liquors are aqueous solutions of chemicals used for delignification of wood by pulping.

Chemical concentration

The chemical concentration is measure of the concentration of the pulping chemical in the liquor. For example, in sulfite pulping the liquor may be 6% SO₂, indicating 6 grams of sulfite chemical (SO₂ basis) per 100 ml of liquor. In this case if the liquor:wood ratio is 4:1, the percent chemical on wood is 24% as SO₂. The following is an important relationship, not the definition of chemical concentration.

chemical concentration in liquor =

percent chemical on wood liquor to wood ratio

Chemical charge (to a process), percent chemical on wood (or pulp for bleaching)

The chemical charge or chemical on wood is another fundamental parameter of chemical pulping processes. It is the measure of the weight of chemical used to process a material relative to the weight of the material itself. This applies to any chemical process, such as pulping and bleaching. For example, typically, kraft pulping is carried out with 25% total alkali on wood. This would indicate 500 lb of alkali as sodium oxide (in the U.S. sodium-based chemicals are reported in terms of sodium oxide) for 2000 lb of dry wood. Chemicals in sulfite pulping are expressed on an SO₂ basis. Also, when bleaching mechanical pulp, one might use "0.5% sodium peroxide on pulp". This means that for every one ton of oven-dry pulp, 10 lb of sodium peroxide are used.

chemical charge =
$$\frac{\text{mass dry chemical used}}{\text{mass dry material treated}} \times 100\%$$

Liquor to wood ratio

The liquor to wood ratio, liquor:wood, is normally expressed as a ratio; typically, it has a LIVE GRAPH Click here to view



Fig. 3-21. Pulping selectivity curve.

value of 3:1 to 4:1 in full chemical pulping. Rarely it is expressed as a percent. The numerator may or may not include the weight of water coming in with the chips, but either way it must be specified to avoid ambiguity. The liquor to wood ratio is kept as small as possible while maintaining good digester operation, including good liquor circulation for even cooking.

$$\frac{\text{liquor}}{\text{wood}} = \frac{\text{total pulping liquor mass}}{\text{dry wood mass}}$$

Delignification selectivity

Delignification selectivity is an important concept during pulping and bleaching operations where it is desired to remove lignin while retaining as much holocellulose as possible. Delignification selectivity is the ratio of lignin removal to carbohydrate removal during the delignification process. While this ratio is seldom measured directly, it is measured in a relative manner by yield versus kappa plots as shown in Fig. 3-21. Here condition "A" is more selective than condition "B" since for a given kappa number the yield is higher for "A" than for "B".

A high selectivity alone does not mean that pulp "A" is better than "B" since the plot does indicate the condition, such as the viscosity, of the pulp. For example, acid sulfite pulping is more selective than kraft pulping; however, acid sulfite



Fig. 3-22. Screening terminology in TIS 0605-04, Screening symbols, terminology, and equations.

pulp is weaker than kraft pulp because the cellulose has a lower degree of polymerization due to acid hydrolysis.

Hot stock refining, defiberating

Chemical pulps and, especially semi-chemical pulps, must be refined after the cooking process to liberate the individual fibers. For chemical pulps, this is relatively easily accomplished in the presence of hot liquor, which is the basis of hot stock refining. Defiberating only separates the fibers for thorough pulp washing; the fibers must be further refined for papermaking.

Rejects, knotter or screener and pulp screener

Rejects are portions of wood, such as knots, that do not sufficiently delignified to fiberate. The hard, poorly cooked lumps of wood are separated





Fig. 3-23. Hypothetical relationship of total and screened yields to cooking time or H-factor.

from pulp by coarse screening equipment (3/8 in. holes) prior to pulp washing. Coarse sreenings from sulfite pulping are not reused in bleached grades of pulp. Coarse screening from kraft pulping are repulped. Suggested screen terminology is shown in Fig. 3-22. If pulps are undercooked, the screened yield may actually decrease because much of the (potential) pulp is removed in the screens, as shown in Fig. 3-23.

After washing, pulps are screened to remove shives, dirt, and other contaminants to protect processing equipment and the product's integrity. Shorter fibers screen more easily, thus hardwoods are easier to screen than softwoods. Redwood pulps (long fibers) require about twice the screen capacity as spruce pulps. Similarly, mechanical pulps screen more easily than chemical pulps. Recently, pulp is screened prior to washing for improved washing efficiency. See Section 8.2 for information on pressure screens.

Brown stock washers

Chemical pulps require more washing than mechanical pulps in order to recover process chemicals, but mechanical pulps require more screening to remove shives, knots, and so forth. If chemical pulps are not properly washed, foaming will be a problem, additional make-up chemicals will be needed, more bleaching chemicals will be required, and additional pollutants will result. There are several types of brown stock washers available: 1. Diffuser washing systems, which are slow, lead to high liquor dilution, and are therefore being phased out. 2. Press type washers. 3. Countercurrent flow stock washers. 4. Rotary vacuum drum washer with a drop length of pipe to supply a vacuum with two to four stages (Plate 12). 5. Double wire press washers (Plates 14-16). 6. Diffusion washers.

Rotary vacuum washers

Rotary vacuum drum washers are, by far, the most common type used. These consist of a wiremesh covered cylinder that rotates in a tub of the pulp slurry with valve arrangements to apply vacuum as is suitable. As the drum contacts the slurry, a vacuum is applied to thicken the stock. The drum rotates past wash showers where the pulp layer is washed with relatively clean water to (more or less) displace black liquor. The vacuum is cut off beyond the wash showers and the pulp mat is dislodged into a pulper. Most of the washing actually occurs at the pulpers between washing stages. Daily loadings for brown stock washers are about 8 t/m² (0.8 dry tons/ft²) for softwood, 6 t/m² (0.6 dry tons/ft²) for hardwood, and 1-2 t/m² (0.1-0.2 dry tons/ft²) for straw pulps. Hardwoods are more difficult to wash than softwoods and have higher chemical losses, partly due to the higher ion-exchange capacity of hardwoods from the carboxylic groups of their hemielluloses.

Typically, about 80% of the contaminants are removed at each stage, so at least three stages are required to thoroughly wash the pulp. Use of additional stages results in lower water consumption, higher recovery of chemicals, and lower pulp dilution. Fig. 3-24 shows a typical configuration of vacuum drum washers for pulp washing. Fig. 3-25 shows an individual vacuum drum washer.

Air is constantly sucked into the pulp sheet and must be separated from the spent cooking liquor to prevent foaming as it is further processed. This causes much foam to form in the seal tanks. Chemical and mechanical defoamers are often used here. The method of applying the wash water influences foam formation.

Diffusion washing

Diffusion washing (Fig. 3-26) was first used by Kamyr for washing chips at the bottom of their digesters. The technique was extended for brown stock washing and washing of pulp between bleaching stages.

Double-wire press

Plate 14 shows a double-wire press suitable for market pulp production, brown stock washing, pulp washing between bleaching stages, or stock thickening. Plate 15 shows a double-wire press designed for brown stock washing. Notice this configuration incorporates the counter-current washing technique.

Brown stock

The washed, screened pulp is called *brown* stock. See Section 4.2 for more information on pulp washing from a chemical recovery point of view where dilution is considered.

Anthraquinone (AQ), soluble anthraquinone (SAQ)

Anthraquinone (whose structure is shown in Fig. 3-27) is a pulping additive used in kraft, soda alkaline sulfite processes to increase or delignification and decrease carbohydrate degradation. It works by going through a cycle which leads to the reduction of lignin and the oxidation of the reducing endgroup of cellulose from an aldehyde to a carboxylic acid as shown in Fig. 3-28. In the latter case the carbohydrates are stabilized against the alkaline peeling reaction, leading to an increase in pulp yield. Because anthraquinone goes through a cyclic process, it is typically used at about 0.1% on wood and results in a 1-3% increase in pulp yield. The use of anthraquinone was first reported in 1977. Modifications of anthraquinone, such as soluble anthraquinone (SAQ, Fig. 3-27), properly called 1,4-dihydro-9,10--dihydroxyanthracene (DDA), have been



Fig. 3-24. Brown stock washers showing countercurrent flow.



Fig. 3-25. Vacuum drum washer suitable for brown stock washing, bleaching, or pulp thickening. Courtesy of Sunds Defibrator.





Fig. 3-27. Structures of AQ and SAQ.

oxidation of reducing end of cellulose (minimization of alkaline peeling reaction)



lignin reduction and cleavage

Fig. 3-28. Cyclic action of anthraquinone.

shown to be even more effective. While not used extensively in North America, anthraquinone and SAQ are widely used in Japan and other countries where fiber supplies are quite limited and expensive.

Prehydrolysis

Prehydrolysis is a dilute acid hydrolysis with 0.5% sulfuric acid for 30 min at 100°C and is used to partially depolymerize the hemicelluloses of wood with little effect on the cellulose. Chips pretreated in this fashion followed by kraft pulping give a pulp with very high cellulose content, but low yield, suitable for dissolving pulp.

3.7 SODA PULPING

Soda pulping, invented in England by Burgess and Watts in 1851, uses sodium hydroxide as the cooking chemical. Finding little enthusiasm in England for this new process, Burgess brought the method to the U.S. in 1854 and the first mill was started in 1866. Many of the early soda mills converted to the kraft process once it was discovered. The soda process still has limited use for easily pulped materials like straws and some hardwoods, but is not a major process. Anthraquinone may be used as a pulping additive to decrease carbohydrate degradation.

A recent development is the use of oxygen in soda pulping. While oxygen bleaching is not very specific to delignification compared to other bleaching methods, it is fairly specific to delignification relative to other pulping methods.

3.8 KRAFT PULPING

Kraft pulping

In 1879, Dahl, a German chemist, used sodium sulfate as a makeup chemical for soda pulping to regenerate NaOH; actually Na₂S was formed and, unexpectedly, gave much faster delignification and stronger pulps, since shorter cooking times are used resulting in less carbohydrate degradation. This led to the kraft (or sulfate) process, which is now the dominant process. Although related work on the process had been done earlier, Dahl discovered the kraft chemical recovery process, which is perhaps more important than the kraft cooking process. The first kraft mill went into operation in 1890 in Sweden because the German papermaking industry did not accept this new process. The process developed and grew quickly from 1915 to 1930, especially in the southern U.S. where the resinous pine species did not pulp well by the sulfite process with calcium base.

Kraft pulping is a full chemical pulping method using sodium hydroxide and sodium sulfide at pH above 12, at 160-180°C (320-356°F), corresponding to about 800 kPa (120 psi) steam pressure, for 0.5-3 hours to dissolve much of the lignin of wood fibers. It is useful for any wood species, gives a high strength pulp (kraft means strong in German and Swedish), is tolerant to bark, and has an efficient energy and chemical recovery cycle. The disadvantages are the difficulty with which the pulps are bleached compared to sulfite pulps, low yields due to carbohydrate losses, and sulfur in its reduced form provides emissions that are extremely odiferous (they can be detected by the olfactory sense at 10 parts per billion). Another consideration is that a green field (starting in an empty field) mill of 1000 tons per day production including bleaching and paper machines costs about \$1 billion. About 75-80% of U.S. virgin pulp is produced by this process. Important variables during kraft cooking are:

- 1. Wood species (though all species can be pulped) and chip geometry.
- 2. Ratio of effective alkali to wood weight.
- Concentration of effective alkali and liquor:wood.
- 4. Sulfidity.
- 5. H-factor. (Which, in turn, is a function of cooking time and temperature.)

For example, all other factors being equal in kraft pulping, a higher concentration of cooking chemical shifts the cooking selectivity (Fig. 3-21) from "A" towards "B" (unfavorable), but decreasing the liquor to wood ratio shifts the curve from "B" to "A" (useful, but more evaporation costs).

The importance of uniform wood chips in regards to species, chip thickness, and chip geometry cannot be over stressed. Even with careful screening of wood chips, variability in wood means that some of the pulp will be over-cooked and some of it will be undercooked. Fig. 3-29 and Plate 13 of the same material demonstrates this point. Electron microscopy shows that overthick chips have incomplete fiber liberation (kappa number of 94.7). Fine chips overcook (kappa number of 36.9), leading to lignin condensation and dark, rigid fiber clusters. The pulp from the accept chips has a kappa number of 42.4.

The penetration of liquors at pH above 13 in wood is about the same in all three directions (Fig. 3-30). This is why chips for kraft cooking are separated on the basis of their thickness.

The degree of a kraft cook is often indicated as *soft*, *medium*, or *hard* based on the pulp texture. Soft cooks, for bleachable grades of pulp, have a lignin content of 3.0-5.2% (20-35 kappa number) for softwoods or 1.8-2.4% (12-18 kappa) for hardwoods. Medium softwood cooks for bag and saturating papers have a lignin content of 5.2-7.5% (35-50 kappa). Hard softwood cooks are 9-11% lignin (60-75 kappa) for top linerboards and 12-16.5% lignin (80-110 kappa) for bottom liners.



Fig. 3-29. Over-thick (top), accept (middle), and fine chips (bottom) cooked under identical conditions by kraft pulping.

H-factor

The H-factor is a pulping variable that combines cooking temperature and time into a single variable that indicates the extent of reaction. Although different temperatures might be used, the degree of cook can be accurately estimated by this method provided that other variables such as active alkali, sulfidity, and the liquor to wood ratio remain constant. There is no analogous variable for sulfite or soda pulping.

The rate of delignification approximately doubles for an increase in reaction temperature of 8° C. To obtain a bleachable kraft softwood pulp of about 5% lignin, one typically cooks for about 1.5 hours at 170°C. This corresponds to 0.75 hour at 178°C or 3 hours at 162°C. The integral of the reaction rate with respect to time combines these two parameters into the single parameter, the H factor. By using the H factor, cooks of varying reaction times and temperatures can be compared in a meaningful manner. This important process control variable is discussed in Section 16.6.

White liquor

White liquor is fresh pulping liquor for the kraft process, consisting of the active pulping species NaOH and Na₂S, small amounts of Na₂CO₃ left over from the recovery process, and oxidized sulfur compounds and other chemical impurities from wood, salt water, corrosion, etc.

Black liquor

Black liquor is the waste liquor from the kraft pulping process after pulping is completed. It contains most of the original cooking inorganic elements and the degraded, dissolved wood substance. The latter include acetic acid, formic acid, saccharinic acids, numerous other carboxylic acids (all as the sodium salts), dissolved hemicelluloses (especially xylans), methanol, and hundreds of other components. It is an extremely complex mixture.

About 7 tons of black liquor at 15% solids [about 10% organic chemicals and 5% inorganic chemicals with a total heat content of 13.5-14.5 MJ/kg solid (5500-6500 Btu/lb solid)] are produced per ton of pulp. The black liquor must be concentrated to as high a solids content as possible before being burned in the recovery boiler to maximize the heat recovery. The viscosity rises rapidly with concentration above 50%, with softwood black liquors being more viscous than hardwood black liquors. Black liquor is usually fired at 65-70% solids content. More information on black liquor is in Section 4.3.

Green liquor, chemical recovery

Green liquor is the partially recovered form of kraft liquor. It is obtained after combustion of the black liquor in the recovery boiler. Green liquor is produced by dissolving the smelt from the recovery boiler (Na_2S , Na_2CO_3 , and any impurities) in water. Further processing of the green liquor converts it to white liquor. The kraft chemical recovery cycle is fairly complex and detailed. It is considered in detail in Chapter 4.

Pulping chemicals

The active chemicals in the kraft liquor are Na_2S and NaOH. Other chemicals in kraft liquors are important because they are involved in the recovery process; these include Na_2CO_3 and Na_2SO_4 . Still other chemicals such as NaCl are important as contaminants that may build up in the system. The amounts of chemicals are reported on an Na_2O basis in North America. Various combinations of these chemicals are given special names because these combinations can predict how the liquor will behave better than considering the amount of chemicals themselves. Pulping chemicals are reported as concentrations in liquor or as a charge on dry wood.



Fig. 3-30. The effect of pH on wood permeability. ©1957 TAPPI. Reprinted from Stone, J.E., *Tappi J.* 40(7):539-541(1957) with permission.



The chemical analysis, method of reporting the cooking chemicals, and calculations of the liquor properties described in the paragraphs below is reported in detail in Chapter 16.

Total chemical or total alkali (TA)

Total alkali is the sum of all sodium salts in the liquors (as Na_2O) that contribute to AA (i.e., NaOH or Na_2S) or are capable of being converted to AA in the kraft cycle. Specifically NaOH, Na_2S , Na_2CO_3 , and $Na_2S_xO_y$ (as Na_2O) are included. All chemical amounts may be reported as concentrations of g/L or lb/gal or as a percent relative to oven-dry wood.

$$TA = NaOH + Na_2S + Na_2CO_3 + Na_2S_rO_y$$

Total titratable alkali (TTA)

TTA is the sum of all of the bases in the white liquor that can be titrated with strong acid. Generally this includes NaOH, Na₂S, and Na₂CO₃ (as Na₂O), although small amounts of Na₂SO₃ and other acids might be present. A typical value for TTA is 120 g/L (7.5 lb/ft³).

$$TTA = NaOH + Na_2S + Na_2CO_3 \quad (as Na_2O)$$

Active Alkali (AA)

AA includes the active ingredients in the pulping process, i.e., NaOH + Na₂S (both as Na₂O). A typical value for AA is 100 g/L (6.4 lb/ft³). Research clearly demonstrates that the active alkali should be kept constant during cooking by adding alkali during the cooking process as it is consumed, but this is difficult to carry out commercially and not practiced.

$$AA = NaOH + Na_2S$$
 (as Na_2O)

Effective alkali (EA)

EA is the ingredients that will actually produce alkali under pulping conditions. The effective alkali is about 12-18% on wood for the production of unbleached kraft and 18-24% on wood for the production of bleached grades, with hardwoods using the lower amounts due to their lower lignin contents. Above 55 g/L EA, cellulose decomposition relative to lignin removal increases dramatically; consequently a liquor:wood ratio above 3:1 should be used.

$$EA = NaOH + \frac{1}{2} Na_2S \quad (as Na_2O).$$

Sulfidity

Sulfidity (of white liquor) is the ratio of Na₂S to the active alkali, expressed as percent. Typically a mill runs in the vicinity of 24-28% sulfidity, depending largely on the wood species pulped. Sulfidity increases the rate of delignification which occurs by nucleophilic action of the hydrosulfide anion (HS⁻). The net effect is cleavage of β -arylether linkages of lignin as well as the methoxy groups, the latter leading to the production of mercaptans. Sulfidity may protect against carbohydrate degradation directly, but the decreased cooking times also result in less carbohydrate degradation. All chemicals are as Na₂O.

sulfidity =
$$\frac{Na_2S}{NaOH + Na_2S} \times 100\%$$

If the sulfidity is too low, the lignin content of the pulp may be relatively high and carbohydrate degradation may be severe, leading to low pulp strength. If the sulfidity is too high, emissions of reduced sulfur compounds may increase and corrosion rates in the recovery process may be high.

Causticity

Causticity is the ratio of NaOH to active alkali (as always both chemicals are on an Na_2O basis), expressed as a percentage. Obviously,

causticity + sulfidity =
$$100\%$$

the term sulfidity is used much more commonly than causticity. All chemicals are as Na_2O .

causticity =
$$\frac{\text{NaOH}}{\text{NaOH} + \text{Na}_2\text{S}} \times 100\%$$

Causticizing efficiency

The causticizing efficiency is the ratio of NaOH to NaOH and Na₂CO₃ (as Na₂O). This is a measure of how efficient causticizing is; it represents the percentage of the Na₂CO₃ from the recovery boiler that is converted back into useful NaOH cooking chemical. A value of 78-80% is typical commercially.

causticizing eff. =
$$\frac{\text{NaOH}}{\text{NaOH} + \text{Na}_2\text{CO}_3} \times 100\%$$

Reduction efficiency

The ratio of Na_2S to Na_2S and Na_2SO_4 in green liquor is known as the reduction efficiency. This is a measure of reduction efficiency of sulfur in the recovery boiler; preferably, this value is high. Typically it is 95% and not routinely measured in the mill. In addition to sodium sulfate, other oxidized forms of sulfur are present such as sodium sulfite and sodium thiosulfate.

reduction eff. =
$$\frac{\text{Na}_2\text{S}}{\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4} \times 100\%$$

Dead load

Inorganic materials, principally NaCl, present in kraft liquor, but cannot be regenerated in the recovery process to AA, contribute to the dead load. Dead load merely circulates through the system thereby decreasing energy recovery and throughput during chemical recovery, increases corrosion, and may interfere with pulping.

Residual Alkali

The effective alkali remaining in a cook at its completion is termed residual alkali. The level of residual alkali determines the final pH of the liquor. At a pH of about 12, some hemicelluloses in the liquor may be deposited on the fibers with a slight increase in yield. If the pH drops much below 12, lignin may deposit on the pulp, increasing the kappa number and bleaching requirements or decreasing the bonding of unbleached pulps. Scaling and lignin precipitation will occur during black liquor concentration if the pH is low.

Polysulfide cooking

One important modification of the kraft process is the use of polysulfide in the cooking liquor, i.e. $NaS(S)_nSNa$ where *n* is about 4-6, to mitigate the alkaline peeling reaction. The concept of polysulfide kraft cooking dates back to the 1940s. Small amounts of polysulfide apparently increase corrosion, whereas large amounts decrease corrosion by passivation of the digester surface. Few mills use this method because it has several problems. For example, sulfur addition to white liquor generates polysulfide, but subsequent liquor recovery leads to large increases in TRS and SO₂ emissions. The *MOXY* process is a method whereby some of the sodium sulfide is converted to sodium polysulfide and sodium hydroxide. It is an oxidation with compressed air in a reactor containing a specially treated activated carbon catalyst.

Modifications/developments of kraft pulping

Rapid displacement heating (RDH) for batch digesters and modified continuous cookingTM (MCC) for continuous digesters such as the Kamyr (for which it was developed) improve kraft pulping by increasing uniformity, although by slightly different mechanisms. One aspect of the improvements is that alkali is of more constant concentration during cooking. Furthermore, it is important to have adequate sulfide present at the beginning of the cook to improve the selectivity of delignification.

Rapid displacement heating, RDH, is a recent modification of kraft cooking in batch digester that promises high strength pulps and decreased steam consumption. The first installation was at the Nekoosa Packaging mill in Valdosta, Georgia. The process was developed by the Rader Division of Beloit and involves pre-impregnation of steam packed chips with weak black liquors (usually three) of increasing temperatures. The final hot black liquor is then displaced with a mixture of hot white and black liquors at the cooking temperature. Since the liquor is preheated the heating time is minimal and production is increased. The original purpose of this method was to recover the energy of the warm black liquor and decrease digester heating time; however, many other benefits have been obtained.

Cooking is achieved using direct steaming until the desired H factor is achieved. Wash water then displaces the hot, black liquor which passes through a heat exchanger to warm incoming white liquor. Since blowing is at a lower temperature, pulp strength is increased. Good process control is important with RDH.

It is known that the NaOH is depleted to a high extent in black liquor, but large amounts of the sulfide remain. Wood is able to absorb sulfide from black liquor (Tormund and Teder, 1989). This means (hypothetically) the RDH process allows one to cook at high effective sulfidities without the problems of recovering liquor containing high sulfidities. In short, the RDH process allows some direct recovery of sulfide, allowing substantially lower concentrations of sulfide in the prepared cooking liquor. It is also known that the effective concentration of sulfide is low at the initial stage of conventional kraft cooks. Thus, sulfide depletion is less likely to occur during cooking with the RDH process (where extra sulfide is obtained from the black liquor) so that pulping selectivity is improved. Decreased sulfide in black liquor has numerous advantages including decreased foaming, corrosion, and TRS emissions.

Residual alkali in the black liquor is able to cleave acetyl groups from the hemicelluloses and form salts of the phenolic groups of lignin, thereby decreasing the alkali consumption in white liquor that is later introduced. This has a leveling effect on the concentration of alkali during the cook. Better diffusion of cooking chemicals, especially sulfide, before cooking would lead to more selective delignification so that lower kappa numbers may be achieved. Holding black liquor at elevated temperature before concentration also lowers its viscosity so that it can be fired at slightly higher Another advantage is that the solids content. washing action inside the digester from the wash water before blowing the digesters helps keep dilution minimal and improves the washing efficiency. If excess recovery boiler capacity is available, this technique could be modified by using some green liquor to wash the chips. This lowers chemical demand during pulping, and the green liquor goes back to the recovery boiler.

Modified continuous cooking, MCC (Fig. 3-14) is a countercurrent process where the concentration of alkali is lower than normal at the beginning of the cook and higher towards the end of the cook. The addition of alkali throughout the cook is an old concept that has been attempted in many ways in the past, but has been difficult to implement. The concentration of dissolved lignin towards the end of the cook is decreased by the countercurrent operation. (One wonders what happens to hemicelluloses that are sometimes redeposited on the fibers towards the end of the cook due to the decreased pH as much of the alkali has been consumed.) Proponents of the process claim higher pulp viscosity, brighter pulps, lower kappa numbers, easier bleaching, etc. The pulp is said to be suitable for oxygen delignification down to a kappa number of 12. The first commercial demonstration of the process was carried out in Varkaus, Finland.

Another modification of the kraft process is to replace about 20% of the sodium sulfide with sodium sulfite in the *sulfide-sulfite process*. The sulfite presumably is able to effectively cleave some lignin linkages to improve the pulping process, to give higher yields, increased brightness and strength, and increased fiber flexibility.

3.9 SULFITE PULPING

Introduction

The first known patent on work related to sulfite pulping was granted to Julius Roth in 1857 for treatment of wood with sulfurous acid. Benjamin Tilghman is credited with the development of the sulfite pulping process and was granted a U.S. patent in 1867. Numerous difficulties (mainly from sulfuric acid impurities that led to loss of wood strength and darkening of the pulp) prevented commercialization of the sulfite process initially. The first mill using the process was in Sweden in 1874 and used magnesium based on the work of the Swedish chemist C. D. Eckman, although calcium became the dominant metal base in the sulfite pulping industry until 1950.

The sulfite pulping process is a full chemical pulping process, using mixtures of sulfurous acid and/or its alkali salts (Na⁺, NH₃⁺, Mg²⁺, K⁺ or Ca²⁺) to solubilize lignin through the formation of sulfonate functionalities and cleavage of lignin bonds. By 1900 it had become the most important pulping process, but was surpassed by kraft pulping in the 1940s. It now accounts for less than 10% of pulp production. Woods with high pitch contents or certain extractives (such as the flavone dihydroquercitin in Douglas-fir) are not easily pulped at the lower pH's. Once the dominant pulping process, now less than 10% of pulp is produced by the sulfite method in this country, partly due to environmental considerations. Some advantages of sulfite pulping are bright, easily bleached pulps, relatively easily refined pulps, pulp that forms a less porous sheet that holds more water than kraft pulps (for use in grease-resistant papers), and pulps with higher yield than kraft.

Disadvantages include a pulp that is weaker than kraft, not all species of wood can be pulped easily, cooking cycles are long, and chemical recovery is fairly complicated or, in the case of calcium, impractical. (In the case of ammonia, the sulfur is recovered, but the ammonia must be replaced as it is burned in the recovery process.) The process involves treating wood chips with the cooking liquor at 120-150°C (250-300°F) from 500-700 kPa (75-100 psig).

Liquor preparation

The liquor is ordinarily made at the mill by burning sulfur to form SO₂ and dissolving this in water to produce sulfurous acid (H_2SO_3) . Before sulfur is oxidized to form SO_2 , it is handled above 160°C (320°F) since it is then a liquid and easy to convey. During combustion of sulfur at 1000°C (1830°F), the amount of oxygen must be carefully regulated to insure complete oxidation, but not over oxidation that would result in the formation of sulfur trioxide (which forms sulfuric acid when added to water.) The SO₂ gas is cooled fairly rapidly (if cooled too slowly an undesired equilibrium reaction is favored with sulfur trioxide) prior to reaction with water. The sulfurous acid is then treated with alkaline earth element (as the hydroxide or carbonate salt) in an acid-base reaction. The reactions are summarized as follows (where $M = Na, K, NH_4, \frac{1}{2}Ca \text{ or } \frac{1}{2}Mg$ and are in solution as their ions):

> $S + O_2 \rightarrow SO_2$ $SO_2 + H_2O \rightleftharpoons H_2SO_3$ $H_2SO_3 + MOH \rightleftharpoons MHSO_3 + H_2O$ $MHSO_3 + MOH \rightleftharpoons M_2SO_3 + H_2O$

For example:

 $2H_2SO_3 + CaCO_3 \rightleftharpoons Ca(HSO_3)_2 + H_2O + CO_2$

The highly deleterious reactions that produce sulfuric acid that quickly degrades the cellulose and delayed the first commercial use of sulfite pulping are as follows:

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

One can easily check for sulfuric acid in cooking liquor using TAPPI UM 600 to see if this is a problem at one's mill. It is accomplished by filtering the liquor, adding formaldehyde, adding BaCl₂ to precipitate sulfate as $BaSO_4$, settling overnight, filtering the precipitate, igniting the precipitate, and weighing the precipitate. UM 657 is analysis of sulfur burner gases for SO₂ and SO₃ by the Orsat apparatus.

Sulfite pulping

The sulfite cooking liquor is heated only part way to the desired temperature and held with the wood chips until uniform liquor penetration is achieved, particularly in acid sulfite processes. This is very important, even more important than uniform liquor penetration in the kraft process. Without uniform liquor penetration, the chips will char since there may not be enough base to supply the necessary buffering action. In short, the sulfurous acid is able to penetrate the wood chip very quickly in the vapor form of SO₂, leading to high concentrations of sulfurous acid in the center of the chip. Long impregnation times allow the metal bases to "catch up" and buffer the system. The temperature is then raised quickly to the desired cooking temperature. After the proper cooking time, the digester pressure is reduced from 90 to 40 psig prior to blowing the chips. Sudden decompression during blowing effectively separates the wood fibers. Pressure is reduced before blowing to prevent damage to the fibers. Important variables are wood species, base ion, maximum cooking temperature, cooking time (8-14 hours), acid concentration, and liquor to wood ratio (3.25-4:1) (The magnefite process uses a pH of about 3.5 and cooking time of about 4 ¹/₂ hours at 130-135°C. This method has a higher retention of hemicellulose.) In general, the sulfite process produces a medium strength pulp with soft, flexible fibers. The lignin content is low and the pulps are easily bleached using about one-half the amount of bleaching chemicals that kraft pulps require. Yields are from 40-52%. Spruce, balsam fir, and hemlock are the preferred species. Resinous species such as southern pine and Douglas-fir (which contains a compound which inhibits pulping) are not suitable to acid sulfite cooking. Aspen, poplar, birch, beach, maple, and red alder are hardwoods suited to sulfite pulping due to uniformity of structure and low extractive contents. These pulps impart softness and bulk in the final sheet.

Sulfite pulping base metals

Calcium is the traditional base used in sulfite pulping. Limestone (CaCO₃) reacts with H_2SO_3 in pressurized towers to produce the pulping liquor. The liquor is used at a pH of 1-2 (maintained with excess SO₂); at higher pH values, calcium sulfite precipitates. The cooking temperature is 140°C. Pulping is characterized relative to the other bases by intermediate pulping rate, moderate amount of screenings, high scaling tendencies, and no chemical recovery. Developments in sulfite pulping since 1950, including the use of the bases mentioned below, which are soluble in much wider pH ranges and have chemical recovery cycles, have greatly increased the versatility of the sulfite process.

Magnesium based sulfite pulping is carried out at a pH below 5 and is characterized relative to the other bases by intermediate pulping rate, moderate scaling and screenings, and relatively simple chemical recovery. There are two major processes: acid sulfite at pH below 2 and bisulfite pulping at pH 4.5 (the magnefite process). Due to limited solubility of magnesium sulfite, magnesium based sulfite pulping must be carried out below pH 5. See the *magnefite process* below for more information. The magnesium based sulfite pulping system has a relatively simple recovery process, for example, as shown in Fig. 3-31.

Sodium based sulfite pulping can be carried out at any pH. NaOH or Na_2CO_3 may be used to form the cooking liquor from H_2SO_3 . The process is characterized by a slow pulping rate, low amounts of screenings and low scaling and complex chemical recovery.

Ammonium based sulfite pulping is very similar to sodium based pulping (since the ammonium ion is very similar to the sodium ion) except for two important differences. The cooking rate is faster than the other three bases mentioned and the ammonium ion is lost in chemical recovery by combustion; however, the use of fresh ammonia (which reacts as ammonium hydroxide) allows the sulfur to be recovered in a relatively simple process. The upper practical pH limit is about 9; above this pH free ammonia begins to be significant. At pH 9.24 at 25° C half of the ammonium appears as free NH₃.

$$NH_4^+ = H^+ + NH_3$$
 $pK_a = 9.24$ at 25°C

Potassium based sulfite pulping has been studied in the laboratory and gives pulping results similar to those of sodium. It has the advantage that the spent liquor makes a good fertilizer if liquor recovery is not to be practiced as in the case of small mills that may be used for nonwood fibers (Wong and Derdall, 1991).

Cooking liquor

The cooking liquor is the fresh pulping liquor for the sulfite process, consisting of a mixture of SO_2 together with one of the bases (alkali ions).

Brown (or red) liquor

Brown or red liquor is the waste liquor from the sulfite pulping process.

Actual forms of sulfite-based cooking chemicals

The cooking chemicals all start out with SO₂. This is in turn dissolved in water to give H_2SO_3 or alkali solution to give HSO_3^{-1} or SO_3^{-2} .

Sulfur dioxide is SO_2 , a gas formed by burning sulfur; it has an acrid, suffocating odor and limited solubility in water.

Sulfurous acid is H_2SO_3 , the reaction product of SO_2 and water.

Monosulfite salt or sulfite is the completely "neutralized" form (salt) of H_2SO_3 : M_2SO_3 , where M = monovalent cation (Na⁺, K⁺, NH₄⁺ or $\frac{1}{2}Ca^{2+}$, $\frac{1}{2}Mg^{2+}$). For example Na₂SO₃ is sodium monosulfite or, simply, sodium sulfite.

Bisulfite salt is the "half-neutralized" salt of H_2SO_3 : MHSO₃. Though not used by the industry, the preferred term is hydrogen sulfite. For example NaHSO₃ is sodium bisulfite or, preferably, sodium hydrogen sulfite.

Cooking chemical terminology

All sulfite-based cooking chemicals are expressed on a molar-equivalent-to- SO_2 basis, but expressed as a weight percent SO_2 . (This is rather confusing and explained in detail in Chapter 16 with examples.) For example, the formula



Fig. 3-31. Babcock and Wilcox process for magnesium-based sulfite chemical recovery. Reprinted from EPA-625/7-76-001.

weights for Na₂SO₃ and SO₂ are 126 and 64 g/mol, respectively. Therefore, a solution containing 126 g/L of Na₂SO₃ is equal to 64 g/L on a SO₂ and would be expressed as 6.4% SO₂. The cooking chemicals are expressed as *total*, *free*, or *combined* SO₂. The term *true free* SO₂ is also used.

Total SO_2 is, for sulfite cooking liquors, the ratio of the total weight of SO_2 to the total weight of the solution containing the SO_2 , usually expressed as a percent. Total SO_2 is determined by the Palmrose method, titration with potassium iodate (TAPPI Standard T 604).

total SO_2 = free SO_2 + combined SO_2 .

Free SO_2 is the amount of sulfite chemical, based on SO_2 , present in the form of the free acid, H_2SO_3 , plus that which can be converted to free acid (i.e., $\frac{1}{2}$ of the HSO₃, see reaction below the next definition), as a percent of total liquor weight. It is determined by titration with NaOH.

Combined SO_2 is the difference between the total and free SO_2 , expressed as percent of total liquor weight; it is the SO_2 existing in the form of the monosulfite salt, plus that which can be converted to the monosulfite salt ($\frac{1}{2}$ of the HSO₃⁻). Two moles of bisulfite form one mole of sulfurous acid and one mole of monosulfite by the reaction below; the equilibrium is very, very far to the left.

$$2 \operatorname{HSO}_3^- \rightleftharpoons \operatorname{H}_2 \operatorname{SO}_3 + \operatorname{SO}_3^2$$

True free SO_2 : In liquors where the free SO_2 exceeds the combined SO_2 , the difference is equal to the true free SO_2 and represents the actual amount of sulfurous acid in the pulping liquor.

Square liquor

A square sulfite cooking liquor has equal amounts of *free* SO_2 and *combined* SO_2 . Since the actual species is all HSO₃, there is very little buffering capacity unless a buffer such as sodium carbonate is added.

Acid sulfite process

The acid sulfite process, uses a cooking liquor that is strongly acidic (pH 1.5-2, and, therefore, has a preponderance of free SO₂ in solution), with a pulping temperature of 125-145 °C (260-290 °F), and a cooking time up to 7 hours. A long heating time (3 hours) is necessary to prevent diffusion of SO_2 ahead of the base that causes lignin to condense at high temperature in the center of the chip causing a "black cook". The base is usually calcium. Due to acid hydrolysis, the result is a weak pulp, with low hemicellulose content suitable for dissolving pulp, tissue paper, and glassine.

Bisulfite process

A full chemical pulping process with higher liquor pH (3-4), and nearly equal amounts of free and combined SO₂ in the liquor ("square" liquor) is known as the bisulfite process. The temperature is 160-180°C with a cooking time of 0.25-3 hours giving yields of 55-75%. The Arbisco process uses sodium as the base; the magnefite process uses magnesium. Ammonia is also a suitable base, and, more recently, potassium is being used as the base. This pulp is suited for medium grades of paper such as newsprint and writing papers.

Alkaline sulfite

The alkaline sulfite, full chemical pulping process uses a chemical charge containing approximately equal amounts of NaOH and Na₂SO₃ at temperatures of 160-180 °C (320-356 °F) and 3-5 hours at the maximum temperature. This process produces pulps fairly similar in quality to kraft pulps in terms of yield, brightness, bleachability, and strength.

Magnefite process

The magnefite process is used at pH 4.5 and 160°C (320°F) with Mg^{2+} as the base. The process is often used to produce reinforcing pulps for newsprint. Chemical recovery is necessary due to the high cost of the base. One recovery process is summarized in Fig. 3-31. Spent sulfite liquor is concentrated to 55% solids and burned at 1350°C (2460°F). MgO and SO₂ are recovered. The MgO is slurried in water to give a slurry containing 50-60% Mg(OH)₂ which is used to scrub SO₂ from the flue gases using a bubble cap tower or venturi scrubber.

$$MgO + HOH \rightarrow Mg(OH)_{2}$$
$$Mg(OH)_{2} + 2 SO_{2} \rightarrow Mg (HSO_{2})_{2} + H_{2}O$$

Stora process

The Stora process is a two stage sulfite process with a mild neutral sulfite stage followed by an acid sulfite stage to give a pulp with high yield and low kappa compared to kraft cooking.

Sivola process

The Sivola process is a three stage sulfite process for producing dissolving pulps. The neutral sulfite stage provides sulfonation of lignin for easy removal, the second stage of acid sulfite is then used to lower the molecular weight of cellulose for viscosity control and hemicelluloses for their subsequent removal, and the final stage of basic sulfite removes the hemicelluloses.

Chemical recovery

Chemical recovery in the sulfite process involves 6 steps:

- 1. Washing of the spent sulfite liquor from the pulp.
- 2. Concentration of the spent sulfite liquor.
- 3. Burning of the concentrated liquor.
- 4. Heat recovery during liquor combustion.
- 5. Pulping chemical regeneration.
- By-product recovery (mostly in Ca²⁺ based system).

If ammonia is used as the base, it cannot be recovered in the burning process since it is converted to H₂O and N₂; consequently, fresh ammonia must be used for each batch of pulp. Mg^{2+} and Na⁺ bases must be recovered due to their high costs. Magnesium has a well developed, proven recovery system whereby it and sulfur are recovered in their original forms, MgO and SO₂. In this process, the spent sulfite liquor is concentrated to 55% solids, prior to burning at 1370°C (2500°F) in special furnaces. The magnesium is recovered from the gases as MgO which is slurried in water to form Mg(OH)₂. The Mg(OH)₂ is then used in the scrubbers to trap SO₂, generating Mg(HSO₃)₂. The reactions are summarized as follows:

 $MgCO_3 + 2H_2SO_3 \rightarrow Mg(HSO_3)_2 + CO_2 + H_2O$ $MgO + HOH \rightarrow Mg(OH)_2$ $Mg(OH)_2 + 2SO_2 \rightarrow Mg(HSO_3)_2 + HOH$

Sulfite byproducts

There are several important byproducts to sulfite cooking. The hexoses, produced by acid hydrolysis of hemicellulose and cellulose, are sometimes fermented to ethanol leaving lignosulfonates (salts of sulfonated lignin) which are water soluble at useful pH's. The lignosulfonates are used in leather tanning, drilling mud dispersants, ore flotation, and resins. Alkaline oxidation of lignosulfonates leads to the production of vanillin, that is, artificial vanilla. It takes only a few mills to meet the world's demand for artificial vanilla.

3.10 OTHER PULPING METHODS

Extended delignification

Chemical pulping and bleaching of chemical pulps are both delignification reactions. Of course, bleaching reactions are much more specific for lignin removal than pulping, but are much more expensive. Improvements in pulping that allow cooking to lower lignin contents and new processes before conventional bleaching are referred to as extended delignification.

A variety of pretreatment processes (many of which are experimental) applied to pulp lower the amount of bleaching chemicals required, leading to lower levels of chlorinated organic materials.

Organosolv pulping

Organosolv pulping is largely an experimental pulping procedure using organic solvents such as methanol, ethanol, acetic acid, acetone, etc. to remove lignin. It has the advantages of having no sulfur emissions and a simple chemical recovery process which would allow relatively small mills to be constructed.

Klason was the first to try to remove lignin from wood by dissolving it in acidified alcohol solutions in solutions of 5% HCl in ethanol in 1893. Cooking dry spruce chips for 6-10 hours led to dissolution of 28-32% of the wood.

The AlCell (alcohol cellulose) process of Repap enterprises using 50% ethanol and 50% water at 195°C for approximately 1 hour has been demonstrated at 15 t/d. The company plans to build a 300 t/d mill in Newcastle, N.B. to pulp hardwoods. One advantage of the system is a relatively simple recovery system (evaporation of the liquor to recover the alcohol) that allows small mills to be economically feasible. The pulp has tensile and burst strengths and brightness equal to kraft pulp and a higher tear strength by 6-7% (at 400 CSF). For an unknown reason, the pulp appears to be particularly amenable to oxygen delignification without significant strength loss. Also DED bleaching gives a brightness of 90 ISO. Lignin, furfural, and hemicelluloses are obtained as byproducts.

Young (1992) describes a 450 ton per day mill in Germany using the organocell solvent pulping process. The mill uses a single-stage process with 25-30% methanol as the solvent to pulp spruce. The alkali charge is 125 g/L with a liquor to wood ratio of 4.2:1. Anthraquinone, 0.1% on wood, is also used. The cooking temperature is about 160°C (320°F). Bleaching is carried out with an $O_{E/P}PP$ process.

The use of oxygen with methanol, ethanol and propanol has also been investigated as a pulping technique (Deinko et al., 1992).

Biological pulping

Biological pulping is an experimental process whereby chips are pretreated with white rot fungi or lignin degradation enzymes. While researchers (promoting additional research funding) sometimes paint a very favorable picture for this process, the high costs of growth media, biological reactors, and other factors are not mentioned. It appears that this is modestly effective as a treatment before mechanical pulping. When reading publications in this area, see if cellulose viscosities are measured as an indicator of selectivity of lignin attack. Many of the strength improvements and yields observed with these methods do not consider the effect of fungal hyphae.

Other, novel pulping methods

Fengel and Wegener in *Wood* list other, unconventional pulping processes (p. 464) with references. They include nitric acid pulping, organosolv pulping, pulping with a variety of organic solvents, and formaldehyde pulping.

3.11 MARKET PULP

Many mills sell their pulp on the open market. The pulp must be prepared in thick sheets of 50% moisture content if shipping costs are not high (for example, for short distances) or dry lap of 80-86% solids. Plate 14 shows a double wire press suitable for making wet lap, washing pulps, or thickening stock. Plate 16 shows a double wire press used for making wet lap. The machine acts like a slow paper machine, having a notable similarity in purpose. Some mills make wet lap for their own use to keep paper machines running when the pulp mill is shut down.

3.12 ANNOTATED BIBLIOGRAPHY

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Pollution aspects

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100 3. PULPING FUNDAMENTALS

EXERCISES

General aspects of pulping

- 1. What are the two principal mechanisms whereby fibers are separated from the woody substrate?
- 2. What are the four broad categories of pulping processes?
- 3. Check the appropriate column for the pulp-type exhibiting the <u>higher</u> value for each of the following properties:

	Chemical	Mechanical
a)	Yield	
b)	Tensile strength of paper	
c)	Unbleached brightness	
		<u> </u>
d)	Sheet density	
e)	Opacity of paper	

Mechanical pulping

- 4. What happens if steaming temperatures of 145°C or higher are used during the production of TMP pulp?
- 5. Chemical pulp has been traditionally used to strengthen newsprint made with stone groundwood pulp. More recently lower amounts of chemical pulp or no chemical pulp has been used with newsprint made from thermomechanical pulp or CTMP. Why is this the case?

Chemi-mechanical pulping

6. Describe the pretreatment processes of wood in the chemi-mechanical pulping methods?

Chemical pulping

- 7. What are the two major categories of pulping digesters?
- 8. The yield versus kappa number is the most fundamental relationship for chemical pulping methods. What does this information tell us about the selectivity of a process for lignin removal relative to carbohydrate removal?
- 9. If an inexpensive pulping process is highly selective for lignin removal, is it necessarily good for making paper?
- 10. Explain how anthraquinone (a pulping additive) stabilizes cellulose and hemicelluloses during alkaline pulping. (From what does it stabilize the carbohydrates?)

Kraft pulping

- 11. What are the two active chemicals in the kraft pulping process? Is sulfate an active pulping chemical? Why is the kraft process also called the sulfate process?
- 12. The H-factor combines what two kraft pulping variables? Does the H-factor alone tell you the degree of cook?

Sulfite pulping

- 13. Why has calcium-based sulfite pulping, once the dominant pulping process, been replaced by other pulping processes?
- 14. What are the two forms of SO_2 in sulfite cooking liquors? Give these by their common names and the corresponding chemical forms.
- 15. Briefly describe how chemical recovery occurs in magnesium based sulfite pulping.

Market Pulp

16. What is market pulp?