

THE PULP AND PAPER INDUSTRY

In New Zealand, paper is made from wood using the "Kraft" process. This is a part mechanical, part chemical process that produces a strong pulp. It has several disadvantages, in terms of complexity and set up costs as well as having a low pulp yield and producing unpleasant-smelling sulfur compounds, but it is still internationally the most widely used pulp and paper process. The manufacturing process is outlined below.

Step 1 - Wood preparation

The bark is removed from in-coming logs, and these are then chipped. Sometimes, the wood arrives at the plant already chipped, meaning that this step is unnecessary.

Step 2 - Cooking

The wood chips are heated in a solution of NaOH and Na₂S in a pressure cooker, during which time a lot of the lignin (the reinforcing substance that make tree cells wood hard and 'woody' rather than soft like those of other plants) is removed from the wood. The pressure is then released suddenly, causing the chips to fly apart into fibres.

Step 3 - Pulp washing

The pulp is washed with water to wash out the cooking chemicals and lignin from the fibre so that they will not interfere with later process steps.

Step 4 - Pulp screening

A sieve is used to remove knots and clumped-together uncooked fibres from the pulp.

Step 5 - Bleaching

This is done in two stages. Firstly the pulp is treated with NaOH in the presence of O₂. The NaOH removes hydrogen ions from the lignin and then the O₂ breaks down the polymer. Then, the pulp is treated with ClO₂ then a mixture of NaOH, O₂ and peroxide and finally with ClO₂ again to remove the remaining lignin.

Step 6 - Paper making

The fibres are mechanically treated to make them bond better to each other (strengthening the paper), chemicals added to provide special properties such as colour or water resistance, and then the water is squeezed out and the pulp is rolled smooth and dried.

Various ancilliary processes result in the recovery of CaO, NaOH and Na₂S, the major chemicals used in the process. Various utilities ensure that such conditions as sufficient reaction times and adequate mixing are met.

On site processing removes the lignin from the liquid wastes, and solid wastes are generally taken to a landfill. Efforts continue to be made to reduce water consumption by recycling, as smaller volumes are easier to process. The most obvious environmental problem continues to be the sulfurous emissions that give Kraft pulping plants their characteristic smell. These are decreased by gas incineration, but are not able to be wholly eliminated.

INTRODUCTION

Paper is a major product of the forestry industry, and is used widely in our society. Paper products are used not only in their obvious applications in the publishing industry and for writing on, but also in a variety of specialty papers, cardboards, brown papers etc. In addition, various chemicals are produced as a byproduct of the pulp and paper industry (see articles).

Paper is made by pulping wood, bleaching this pulp and then spreading it out into sheets to make it into paper. At various stages of the process, chemicals are used to give the paper particular properties, such as the bleaching chemicals that make paper white (and which also enable it to subsequently be coloured). The pulping process that is used in New Zealand is known as "kraft pulping" which relies on a combination of heat, chemicals and mechanical pulping to convert the wood into a smooth, soft pulp suitable for use in paper making.

Kraft pulping is the main pulping process (together with mechanical pulping) used today, and is the only one discussed below. The kraft process has several advantages:

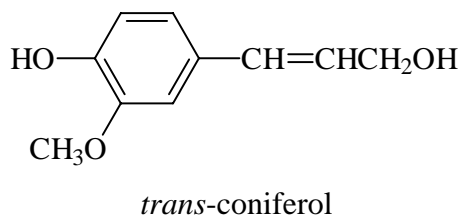
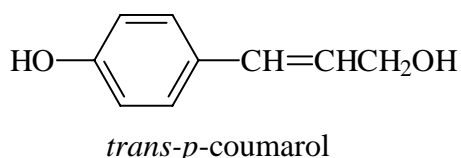
- It can be used with virtually all wood species
- It can easily handle the extractives in most coniferous wood
- The pulp has very good strength (the word 'kraft' means 'strong' in Swedish)
- The recovery process for the chemicals is well established

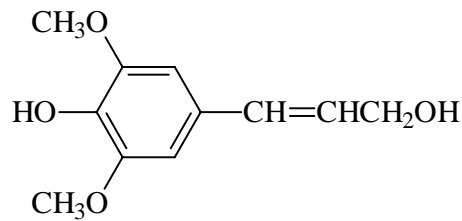
However, there are also disadvantages:

- The pulp yield is quite low at about 45 - 50%
- The equipment used for the chemical recovery is extensive and costly to install
- Sulphurous compounds, which are odorous in the parts per billion range, are formed in the process
- Fairly complicated processes are required for bleaching the pulp

Lignin

The main component of wood that needs to be removed to turn it into paper is a compound known as lignin. This name refers to a group of chemicals that are essentially three dimensional polymers of *trans*-coniferol, *trans*-sinapyl and *trans*-*p*-coumarol (see below), along with hemicelluloses and aromatic carboxylic acids. Lignin is the reinforcing compound that is deposited on tree cell walls to make the wood strong enough to carry the weight of the tree crown. However, it is also the compound that makes wood pulp brown, so it is removed from all wood pulp except that used to make brown paper and some cardboards.





trans-sinapol

THE MANUFACTURING PROCESS

The process whereby timber is converted into paper involves six steps. The first four convert the logs into a mass of cellulose fibres with some residual lignin using a mixture of physical and chemical processes. This pulp is then bleached to remove the remaining lignin and finally spread out into smooth, pressed sheets (often with chemicals added to provide particular properties such as colour or water resistance). For some papers (e.g. cardboards and 'brown paper') the bleaching step is unnecessary, but all white and coloured papers require bleaching.

Step 1 - Wood preparation

Wood is delivered to the kraft mill in one of two ways: whole logs and sawmill chips (residuals from sawmills). The logs have their bark removed, either by passing through a drum debarker or by being treated in a hydraulic debarker. The drum debarker, which consists of a slightly inclined, rotating drum is best suited to small diameter logs. The hydraulic debarker, which uses high pressure water jets, can handle large diameter logs. The removed bark is a good fuel, and is normally burnt in a boiler for generating steam.

After debarking, the logs are chipped by multi knife chippers into suitable sized pieces, and are then screened to remove overlarge chips. The *thickness* of the chips is the most important parameter, as this determines the speed and the thoroughness of the impregnation of the cooking chemicals into the wood chip. Neither debarking nor chipping are usually necessary for sawmill chips.

Step 2 - Cooking

The "cooking process" is where the main part of the delignification takes place. Here the chips are mixed with "white liquor" (a solution of sodium hydroxide and sodium sulphide), heated to increase the reaction rate and then disintegrated into fibres by 'blowing' - subjecting them to a sudden decrease in pressure. Typically some 150 kg of NaOH and 50 kg of Na₂S are required per tonne of dry wood. This process is, like any chemical reaction, affected by time, temperature and concentration of chemical reactants. Time and temperature can be traded off against each other to a certain extent, but to achieve reasonable cooking times it is necessary to have temperatures of about 150 - 165°C, so pressure cookers are used. However, if the temperature is too high then the chips are delignified unevenly, so a balance must be achieved.

The kinetics of the kraft pulping is quite well understood, but the reaction is heterogenous and therefore difficult to examine. To determine when to interrupt the cooking, a model relating time, temperature and cooking chemical charge is used. The degree of delignification is the most important parameter for determining pulp quality, and is normally

expressed in what is called a "Kappa number". This number is directly related to the amount of lignin still remaining in the cooked pulp.

There are two different cooking systems; batch and continuous. In batch cooking, chips and white liquor are charged to a pressure vessel and are then heated with steam to a set temperature for a set time. When the correct delignification has been achieved, the cook is "blown" (the pressure is suddenly released so that the cooked chips disintegrate into fibres). In the continuous process, chips and white liquor are fed continuously to the top of a tall pressure vessel. The chips move down the 'digester' by gravity (as a plug) to be finally blown from the bottom of the vessel. The cooking time cannot be varied in this case (it is set by the production rate) and only the temperature and the chemical charge can be controlled.

Many developments have taken place during the last decade to improve the 'science' of kraft pulping. The challenge has been to remove as much of the lignin as possible without degrading the cellulose and without losing too much yield. It is now well known that the concentrations of NaOH, Na₂S and dissolved lignin during the various phases of the delignification are of crucial importance for the pulp strength. Generally speaking, it is desirable to have a high sulphide concentration in the beginning of the cook, a low lignin concentration in the liquid phase towards the end of the cook, and an even alkali concentration during most parts of the cook. How to achieve this in practice under conditions of high temperature and high pressures has been a challenge, and much development is still going on.

Step 3 - Pulp washing

Because of the high amounts of chemicals used in the cooking wood in kraft pulping, the recovery of the chemicals is of crucial importance. The process where the chemicals are separated from the cooked pulp is called pulp washing. A good removal of chemicals (inorganic and organic) is necessary for several reasons:

- The dissolved chemicals interfere with the downstream processing of the pulp
- The chemicals are expensive to replace
- The chemicals (especially the dissolved lignin) are detrimental to the environment

There are many types of machinery used for pulp washing. Most of them rely on displacing the dissolved solids (inorganic and organic) in a pulp mat by hot water, but some use pressing to squeeze out the chemicals with the liquid. An old, but still common method is to use a drum, covered by a wire mesh, which rotates in a diluted suspension of the fibres. The fibres form a mat on the drum, and showers of hot water are then sprayed onto the fibre mat.

Step 4 - Pulp screening

Apart from fibres, the cooked pulp also contains partially uncooked fibre bundles and knots. Modern cooking processes (together with good chip screening to achieve consistent chip thickness) have good control over the delignification and produce less "rejects". Knots and shives are removed by passing the pulp over pulp screens equipped with fine holes or slots.

Step 5 - Bleaching

Pulp produced by the kraft process is brown. This presents no problem for certain uses, e.g. for sack paper, most corrugated boxes, some bag paper etc. However, a major proportion of the kraft pulp that is made is used for white or coloured papers such as writing and printing papers, and then the pulp needs to be bleached.

Bleaching involves removing virtually all of the lignin that still remains after cooking, as the lignin contains the chromophoric groups which make the pulp dark. Strictly speaking, bleaching and cooking are both delignification processes, and modern developments have tended to blur the difference between the two processes. However, traditionally the name 'bleaching' is reserved for delignification that is taking place downstream of the cooking process. In practice, there are two separate "bleaching" process steps: oxygen delignification and final bleaching.

To measure the lignin content in pulp, a number called the "Kappa number" is used. The Kappa number is directly proportional to the lignin content of the pulp. Pulp from the digester has a Kappa number of 20-35 for softwood and 15-20 for hardwood (hardwood contains less lignin and can therefore be cooked to a lower Kappa number). Oxygen delignification removes about half of the lignin remaining after the cooking process, so that the Kappa number of the oxygen delignified pulp is typically 12-18 for softwood. The final bleaching removes all remaining lignin and decreases the Kappa number to zero.

Oxygen delignification

In oxygen delignification, washed pulp is treated with a highly alkaline solution of sodium hydroxide. The high pH ionizes phenolic groups in the lignin, which are then attacked by molecular oxygen. The aromatic part of the lignin is partly destroyed and it is then depolymerised to lower molecular weight compounds. These are more soluble in water and can be removed from the fibres. It is important that the pulp has been at least partly washed beforehand because the black liquor solids in unwashed pulp consume oxygen. After the oxygen delignification stage, the pulp has to be washed very well, as otherwise the organics carry over to the final bleaching process, consuming chemicals there and also decreasing the environmental benefits.

The highly alkaline conditions of oxygen delignification also make carbohydrate fractions in the fibres react with oxygen to a certain extent. As these reactions break down the polymer chains of cellulose, and thus decrease the pulp strength, these reactions must be kept to a minimum. It has been found that it is the radical species of oxygen which are particularly harmful to the carbohydrates. The formation of radicals is promoted by the presence of certain metal ions. However, it has been found that magnesium salts inhibit metal ion activity, and magnesium sulphate is therefore normally added as a protector in oxygen delignification.

Oxygen is only sparingly soluble in water, and the controlling factor on the reaction rate is therefore normally the concentration of dissolved oxygen around the fibre. Originally a high pulp consistency (30-40%) was used to overcome this restriction. However, modern high intensity mixers can distribute the oxygen in very small bubbles on the fibres, and these mixers have made it possible to operate at "medium consistency" (10-12%). Medium consistency has several advantages: the equipment is simpler and the risk of fire (because of the use of oxygen) is virtually eliminated.

Oxygen delignification can significantly decrease the water pollution from the final (normally chlorine or chlorine dioxide based) bleaching. In addition, it is an effluent free process. All dissolved lignin and other organics (as well as the inorganic chemicals) are recovered in the black liquor and returned to the chemical recovery system, rather than being discharged as effluent as they are in chlorine-based bleaching. Finally, oxygen is a fairly cheap bleaching chemical, although the capital costs are high for an efficient system. On the

negative side, the process has the potential to degrade the pulp strength if it is not controlled properly.

Final bleaching

The final bleaching is always carried out in several stages to improve the efficiency of the chemicals used, and to decrease the strength loss of the pulp. There are quite a number of bleaching chemicals used commercially, and many more have been tried in the laboratory. The chemicals used are:

- Chlorine
- Chlorine dioxide
- Sodium hypochlorite
- Oxygen
- Peroxide
- Ozone

Of these chemicals, the first three contain chlorine atoms, whilst the last three use non-chlorine oxidizing compounds. Elemental chlorine (Cl_2) was for many years the work horse of the bleaching process. It is efficient in bleaching the pulp and (if properly used) does not degrade the pulp strength. However, it produces a large amount of chlorinated organic compounds in the effluent, and strenuous efforts have therefore been made to decrease its usage. For the same reason, the use of sodium hypochlorite (which also tended to affect the pulp strength) is now virtually eliminated.

Modern bleach plants therefore use no *elemental* chlorine. They are what is called ECF plants: elemental chlorine free bleach plants. Chlorine dioxide, which is used instead (in addition to non-chlorine compounds), is environmentally much more benign than Cl_2 . However, while chlorine dioxide is good at preserving pulp strength, it is not as effective as elemental chlorine in delignification/bleaching. ECF plants therefore have to have a rather low incoming Kappa number, and this is normally achieved by using oxygen delignification ahead of the final bleaching.

Most ECF plants use a three step bleaching process of chlorine dioxide followed by a mixture of NaOH, O_2 and peroxide (the 'extraction' stage) and then finally chlorine dioxide again. At Kinleith, because of the efficiency of the oxygen delignification, the peroxide is no longer necessary and a sequence of chlorine dioxide then NaOH and O_2 followed by more chlorine dioxide is used. The chlorine dioxide stages normally run at a pH of 3-4.5, and the 'extraction' stages at a pH of 10-11. The temperature is kept at 70-80 °C to achieve sufficiently fast rate of reaction.

The amount of chlorinated toxic compounds in the effluent from a correctly operated ECF plant is small (especially after secondary treatment) and the effects on the environment appear rather insignificant. However, especially in Europe, there is a perception that using "chlorine" in any form when bleaching is undesirable, and bleaching without using any form of chlorine compounds, so-called total chlorine free bleaching (TCF bleaching) has been developed. In TCF bleaching only oxygen, peroxide and ozone (in addition to caustic and certain chelating agents) are used. TCF bleached pulp can nowadays reach virtually the same brightness as ECF bleached pulp, but the strength is somewhat lower. Such plants require inevitably oxygen delignification and also, usually, cooking to a lower Kappa number. Chemical costs are also normally higher. TCF pulp is not made in New Zealand.

Step 6 - Paper making

Paper making is the process whereby pulp fibres are mechanically and chemically treated, formed into a dilute suspension, spread over a mesh surface, the water removed by suction, and the resulting pad of cellulose fibres pressed and dried to form paper.

The mechanical treatment of the fibre normally takes place by passing it between moving steel bars which are attached to revolving metal discs - the so-called refiners. This treatment has two effects: it shortens the fibre (fibre cutting) and it fibrillates the fibre. The latter action increases the surface area, and as the fibres bond together in the paper sheet by hydrogen bonding, the increased surface area greatly increases the bonding and strength of the paper. Paper strength is dependent on the individual fibre strength and the strength of the bonds between the fibres. It is usually the latter, which is the limiting factor. Refining increases the interfibre bonding at the expense of the individual fibre strength, but the net result will be an increase in paper strength. Pressing and calendering (feeding through rollers) increase density and promote smoothness.

Various chemicals are added, e.g. to give water resistance, to give increased strength (see Industrial Resins article), to produce coloured paper, or to serve as inorganic fillers.

Henry and Sealy Fourdrinier have given their name to the Fourdrinier paper machine, the first of which was first used in 1804. The stock is diluted to 0.5-1.0% consistency, and then flows as a flat stream onto an endless travelling wire screen. Water (containing a considerable amount of filter and fine material) is extracted through the wire screen, and this is then circulated back to dilute the oncoming stock. The wire and the web pass over suction boxes, and the web is finally removed from the wire at about 20% solids. After being pressed to some 35-40% solids, the web passes round a large number of steam heated cylinders to be dried until it finally contains some 95% solids and 5% water.

Modern developments have tended towards so-called twin-wire machines, which overcome the difference in two-sidedness caused by water draining through the bottom side of the web only. The twin wires are nowadays usually synthetic fibre fabrics, between which the stock is introduced.

ANCILLIARY PROCESSES

A variety of ancilliary processes are used to recover the chemicals used at various stages of the process. The dilute liquor from the pulp washing (containing the dissolved inorganic and organic solids) is called "black liquor". The dissolved organics have to be removed for environmental reasons, and their burning also generates most of the heat energy required by the kraft mill. The dissolved sodium hydroxide and sodium sulphide are regenerated so that they can be reused in the white liquor, and thus the escape of an environmental pollutant is prevented.

The four steps involved in chemical recovery are outlined below.

Step 1 - Evaporation

The black liquor from the pulp washing contains 15-17% solids, and this needs to be concentrated to about 60-70% solids before it can be burnt in the recovery furnace. "Spill liquors" may also be recovered from various places in the mill, and these dilute liquors supply further amounts of water, which needs to be evaporated.

Evaporation is carried out using multiple effects, normally 5 to 7 effects in series. In systems of this type, the vapour obtained in one evaporator effect becomes the heating steam for the next effect. Process steam enters the system at effect no. 1, while the vapour from the last effect is condensed, producing a vacuum in the latter effects.

Black liquor evaporation consumes a substantial part of the heat energy required in the kraft process. However, it is much more efficient to carry out this evaporation in multiple effect evaporators than in the subsequent recovery boiler. Because of this, there has been a constant effort to try to reach higher liquor solids from the evaporators. The limit is set by the increase in viscosity and boiling point that takes place when the solids increase.

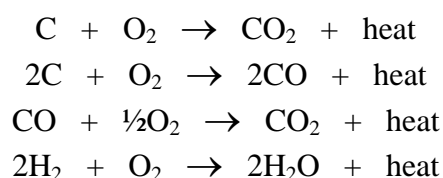
Step 2 - Combustion of the black liquor in the recovery boiler

The recovery boiler burns the organic material in the concentrated black liquor, at the same time reducing the oxidised sulphur compounds to sulphide. The burning of the organics generates high pressure steam in the boiler, which is normally passed through a turbine, generating electricity. The low pressure steam, which is exhausted from the turbine, is then used for process heat in the pulpmill and papermill.

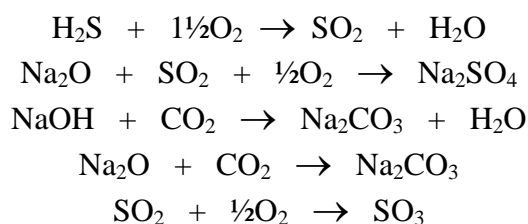
A modern recovery boiler is a complex and expensive chemical reactor, and the chemical reactions taking place inside it are many and complicated. The inorganic material is recovered as molten salts (a 'smelt'), which is then dissolved in dilute alkali. The resulting liquor is called 'green liquor' and consists mainly of sodium carbonate and sodium sulphide.

To compensate for chemicals that are being lost in the pulp mill cycle, sodium and sulphur chemicals are added to the black liquor before combustion. Traditionally, sodium sulphate has been the normal 'make-up' chemical, supplying both sodium and sulphur. However, modern mills only lose small amounts of sulphur, and it has become necessary to partially use 'sulphur free' make-up chemicals in form of caustic (NaOH) or soda ash (Na₂CO₃).

The following reactions very simply explain the combustion of the combustible organic compounds:



In conjunction with the above combustion the following chemical reactions are also occurring:



The chemical transformation that takes place in the recovery boiler is not just due to combustion, but also involves the reduction of sodium sulfate to sodium sulfide. The main reaction is:



This reaction consumes heat, i.e. it is endothermic.

Since sodium sulfate does not help in the cooking process, it is important to obtain maximum reduction of sulfate into sulfide within the recovery boiler. A measure of the quality of this reduction (in the smelt or green liquor) is called reduction efficiency. It is expressed as follows:

$$\text{Reduction efficiency}(\%) = \frac{\text{Na}_2\text{S} \times 100}{\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4}$$

Poor or low reduction efficiency results in extra energy consumption in the digester and recausticizing areas. Modern recovery boilers firing high dry solids content black liquor typically have very high reduction efficiencies, up to 99% - 100% when measured from the smelt. Reduction efficiency measured from the green liquor is typically somewhat lower, since some Na₂S gets oxidized by the oxygen in air.

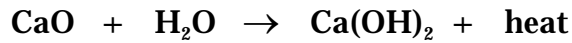
The 'green liquor' (a solution of the Na₂CO₃ and Na₂S - the non-volatile combustion components) is then causticised as the first step to Na₂CO₃ removal.

Step 3 - Causticising

As well as dissolved sodium based chemicals (Na₂CO₃, Na₂S and smaller amounts of NaOH, Na₂SO₄ and NaCl), the green liquor also contains small amounts of suspended solids, called "dregs". This material mostly consists of unburned carbon and insoluble metal hydroxides. To avoid problems in the causticising and lime burning processes, these dregs must be removed as much as possible. This can be done either using a gravity clarifier (as described below) or using the more recently developed green liquor filter.

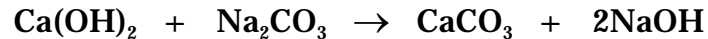
In essence, clarifiers are large circular tanks so sized that the liquid rise rate is slower than the terminal velocity of the settling particles. A typical rise rate is 0.5 m/h. The dregs particles collect in the bottom of the clarifier and are then raked by a very slowly rotating scraper to a central removal point. The thickened dregs are washed to remove dissolved chemicals and are then discharged, normally to the sewer or to landfill. The dilute alkali solution resulting from the wash is recycled.

Clarified green liquor and burned lime (calcium oxide) are fed continuously in metered amounts into a reaction vessel, called a slaker. The calcium oxide reacts with the water in an exothermic reaction to form calcium hydroxide or milk-of-lime:



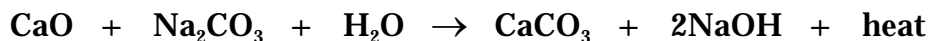
The slaker also contains a “classifier” section which removes unreacted particles (grit). These are taken to landfill.

After slaking, the slurry is carried through a series of agitated tanks, which provide the retention time for the causticising reaction as shown below:



As with all chemical reactions, an equilibrium exists between the reactants and the products. The causticising reaction is also relatively slow (while the slaking reaction is fast), so in order to achieve close to equilibrium in a reasonable time, a high temperature (about 100°C) is maintained.

The overall reaction for the slaking and causticizing reactions are:



Step 4 - Conversion of CaCO₃ to CaO

The slurry from the causticisers is pumped to a clarifier which, as for the green liquor clarifier mentioned previously, is a gravity settling device. Generally the white liquor clarifier also serves as a white liquor storage tank.

The thickened “lime mud” underflow from the clarifier contains about 40 % suspended solids. This slurry is washed by diluting it with water or dilute alkali and then allowing the suspended solids to settle in another clarifier (similar to the white liquor clarifier) called “mud washer”. The resulting dilute alkali solution (“weak wash”) is used for dissolving the smelt coming from the recovery boiler to make new green liquor. The thickened washed mud is stored before a final washing and dewatering stage on a rotary drum washer.

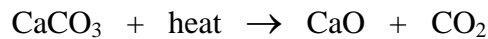
Just as for green liquor clarification, filters are nowadays becoming more common both in white liquor clarification and in mud washing.

The Ca₂CO₃ sludge (“mud”) coming from storage is washed and dewatered on a filter, which increases the solids content to 70 - 80 %. Washing out the sodium compounds as much as possible is important for several reasons:

- The sodium sulphide can contribute to the emission of H₂S from kiln stack
- Sodium salts melt and function as a glue for the lime particles, producing rings and balls inside the kiln

After washing and dewatering, the mud is then dried and reburnt (calcined). Usually both operations are carried out in a slowly rotating lime kiln. In such a kiln, wet mud is fed into one end of the inclined kiln, and is slowly transported towards the other end. A burner, fed with natural gas or fuel oil, supplies hot gases which travel countercurrently to the mud. The

mud dries and is then calcined at a temperature of about 1,000 - 1,200 deg. C in a heat absorbing reaction as follows:



To increase the heat transfer in the cooler end of the kiln, an extended area is provided by using steel chains attached to the kiln shell and hanging in the hot gases. The hotter part of the kiln is lined with refractory bricks.

Modern kilns are equipped with tube coolers to cool the outgoing lime and to recover the heat. This is done by heating the incoming combustion air.

The gases leaving the kiln are laden with lime dust, which must be removed. This is done either in venturi-type scrubber or, in more modern plants, by electrostatic precipitators.

UTILITIES

Reaction towers

For each stage in the bleaching sequence a “tower” is used to achieve sufficient retention time. Typical retention times required are 1 - 4 hours, depending on type of reaction. The towers have to be able to withstand the required temperature and chemical environment. Chlorine dioxide especially is a very aggressive chemical and such towers usually have a ceramic tile lining on a steel base, or they can be made from more exotic materials such as titanium.

Chemical mixers

Good mixing of the bleaching chemicals into the pulp is absolutely critical for efficient bleaching, and over the last decade there has been a major breakthrough in this area. In the early 1980's the art of mixing was revolutionized with the arrival of the Medium Consistency (MC) mixer. These mixers are based on the principle of fluidisation of the pulp with a consistency of about 10 %. The fluidisation of the pulp is achieved by subjecting the pulp to heavy shear forces to destroy its network strength while it “flows” through narrow slots. The normally rather thick, almost solid pulp slurry behaves like water under these conditions, and it is comparatively easy to disperse liquids and also gases efficiently into the pulp.

Washers

The solubilized lignin is removed by washing the pulp, normally after each stage in the bleaching sequence. Such washing is particularly important when there is a change in pH.

The same washing equipment as in the washing of cooked pulp can be used, e.g. drum filters, presses or so called “diffuser washers”. However, it is important that the corrosive nature of the chemicals is taken account when choosing the material for these washers. Highly alloyed stainless steel or titanium are common, but reinforced plastic can also be used for certain components.

Pumps

Pumps are used for transporting pulp, chemicals, water and wash liquors. For liquids and pulp up to a consistency of 4-5 % (low consistency), centrifugal pumps can be used. For pulp with a consistency of 10-12 % (medium consistency), positive displacement pumps were used in the past. However, since the discovery of fluidisation mentioned above, these

pumps have mostly been replaced with specialized so called MC-pumps, which fluidize the pulp and then use conventional centrifugal forces for imparting the pressure increase that is required.

ENVIRONMENTAL CONSIDERATIONS

Liquid effluent

Traditionally, the pulp and paper industry have been large users of water. Nowadays, strenuous efforts are being made to decrease the water usage, as any treatment of the effluent is made easier if the volume is decreased. Also, by intensive recirculation and reuse of liquid waste streams within the mill, the amounts of contaminants can be reduced in the effluent.

The major categories of water pollution of concern to the pulp and paper industry are: suspended solids (mainly fibre), biological oxygen demand, toxicity and colour. Each of these effects can be minimized by internal or external means, external meaning treatment of the final effluent outside the mill.

The suspended solids can be decreased internally by recirculating fibre containing process streams within the mill. Externally, suspended matter can be removed from the effluent in a conventional clarifier by settling. Removal efficiencies in the order of 80-90% of the suspended solids are generally achieved. The recovered sludge can be taken to landfill or further dewatered and burnt.

Oxygen demand (usually measured as BOD - biological oxygen demand - or COD - chemical oxygen demand) in the effluent can be decreased by in-mill measures, like good washing, recovery of black liquor spills, treatment of methanol containing condensates, and especially by the oxygen delignification process, described in the section on bleaching. However, biological treatment of the effluent is usually required to decrease the BOD sufficiently. This can be done in large stabilisation basins with oxygen supplied by surface diffusion, or in aerated basins in which the oxygen transfer rates are increased by the use of mechanical aerators. Nutrients are often added to enhance bacterial activity and thus promote the biological breakdown of wastes. When space is limited, more intensive processing of effluent is possible by using the activated sludge process.

Effluents from pulp and paper mills are only weakly toxic by conventional measurements, especially if they have been through biological treatment. However, the effluent from the bleaching process contains a variety of substances, some of which are known or suspected of being toxic, genotoxic or mutagenic. Chlorinated organics that are produced in the chlorine bleaching processes are of particular concern. There has therefore been a trend to change from chlorine to the much more benign chlorine dioxide as a bleaching agent as described above. If oxygen delignification is used, it will substantially decrease the amount of chlorinated compounds in the effluent.

Colour can be a problem, especially when the effluent is discharged into receiving waters with a high transparency. Most of the colour derives from the bleaching process, and oxygen delignification will help substantially against this pollutant as well. External removal of colour can be carried out, but it is difficult and expensive.

The wastewater that finally leaves the plant is discharged into the Waikato River. It is routinely monitored and the results reported to the Regulatory Authority, Environmental Waikato.

Atmospheric emissions

Chemicals are emitted to the atmosphere as gaseous and particulate emissions (dust).

Gaseous emissions consist of sulphur dioxide, nitrogen oxides, chlorine dioxide and reduced sulphur gases. The first two are not generally a problem, and chlorine dioxide emissions can be virtually eliminated by scrubbing with suitable liquids. However, reduced sulphur gases are a major problem because of their intensive odour. The typical kraft mill odour is due to small discharges of hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide. Recovery boilers used to be the major source of emissions of reduced sulphur, but improved technology has mainly eliminated this problem. Collection of sulphurous gas streams from various vents in the pulp mill, and incinerating these gases in the lime kiln or in a dedicated incinerator has also decrease the odour problem, but not wholly eliminated it.

Dust (particulate) emissions are in the form of 'saltcake' (sodium sulphate) from the recovery boiler, lime dust from the lime kiln and fly ash from the bark boiler. All these emissions can be decreased to low levels by using efficient scrubbers, and especially by using electric precipitators, which is now the method of choice for removing particulates from all these sources.

As for water all discharges into the air are routinely monitored and reported.

PULP AND PAPER MILLS IN NEW ZEALAND

Below brief facts about all the pulp and paper mills in New Zealand are given.

Carter Holt Harvey

Kinleith

2 Paper Machines - 235 000 tonnes per annum
1 Pulp Dryer - 420 000 tonnes per annum
2 Kraft Pulp Mills

Penrose

1 Paper Machines - 67 000 tonnes per annum
(uses paper given for recycling, not wood chips or logs)

Whakatane

1 Paperboard machine - 80 000 tonnes per annum
Pulp mill

Kawerau

3 Paper Machines - 55 000 tonnes per annum
Pulp Mill

Mataura

2 Paper Machines - 25 000 tonnes per annum

Tasman Pulp and Paper Company Limited

Kawerau

- 3 Paper Machines - 400 000 tonnes per annum
- 2 Mechanical Pulp Mills - 315 000 tonnes per annum
- 2 Kraft Pulp Mills - 290 000 tonnes per annum

Pan Pacific Forests Industries (NZ) Ltd.

Karioi

- 1 Pulp Mill - 125 000 tonnes per annum

Originally three articles written by Sven Johnsson (Carter Holt Harvey) as revisions of articles in the first edition. Combined and edited by Heather Wansbrough with assistance from Mikael Lindstrom and with reference to <http://swsmail.atlanta.com/~japi/kraft.htm> (information on the Kraft Recovery Process provided by the Tampella Power Corporation).

Editorial addition: The introduction to the forestry section of the first edition included a comprehensive flow diagram of the whole Kinleith site. We reproduce this as **Figure 1** on the next page. Although probably no longer accurate, it does illustrate what is involved in the engineering design of a large complex, and could still be relevant to this current article.

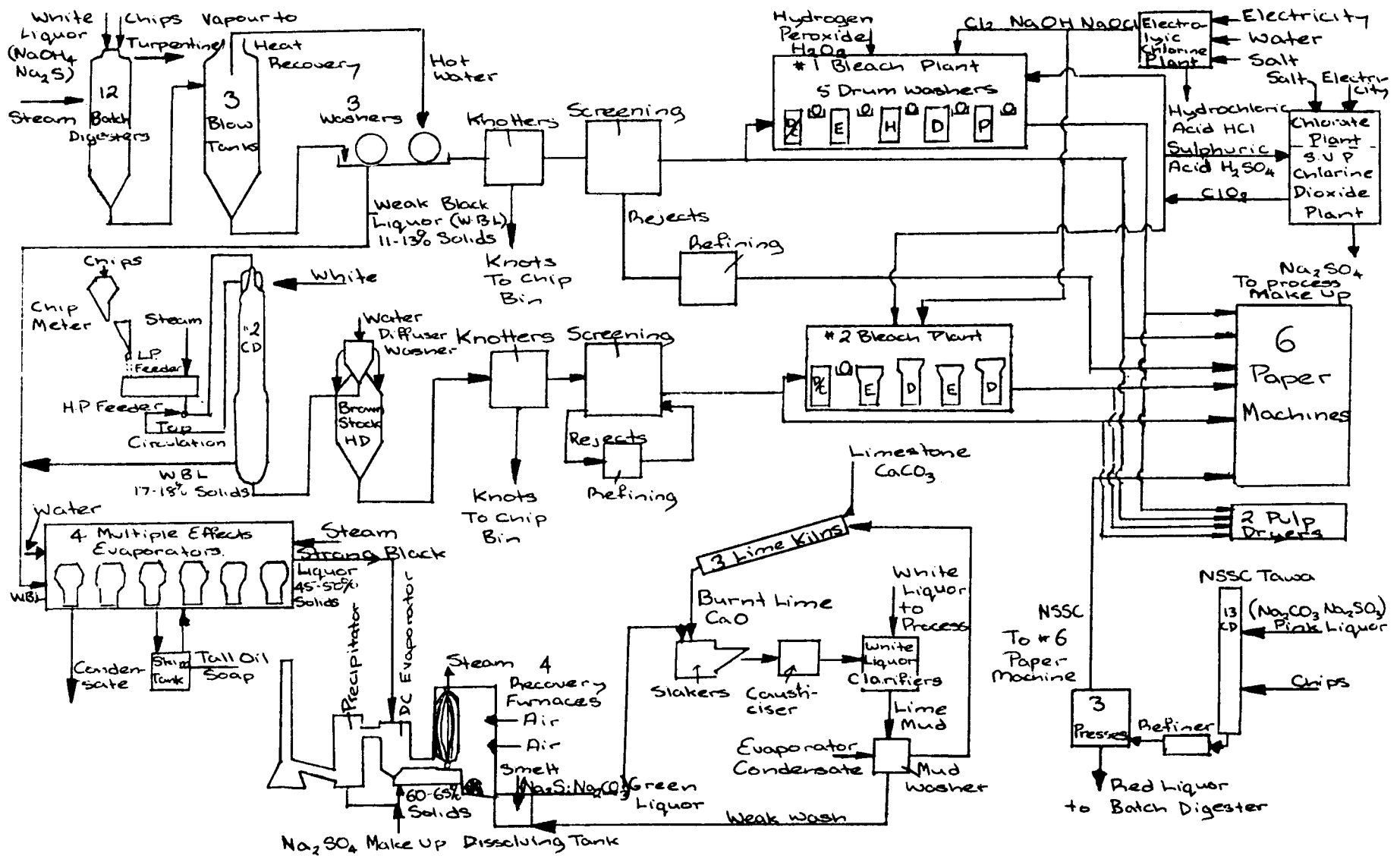


Figure 1 - Flow sheet of Kinleith site in 1976