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Abstract

The design of modern fibrelines today is driven by pressures to maximize energy efficiency, reduce the environmental impact, and optimise the capital and operating costs. Production of a premium quality product is essential.

Technologies such as modified cooking, two-stage oxygen delignification, ECF or ECF-light bleaching, and efficient washing and screening systems are implemented to allow maximum system closure and low water and chemical consumption. Dissolved organic material is increasingly recycled particularly the highly coloured filtrates produced in bleaching. End-of-pipe treatments are also used in combination with conventional biological treatment systems to control discharges to receiving waters.

This paper will review new and developing technologies and practices adopted by bleached kraft mills today, with reference to both continuous and SuperBatch-K® pulping. Key performance data for the fibrelines and effluent treatment systems of this new generation of kraft mills, will be discussed, particularly in relation to the issues facing the Indian industry – water use, low organic halide (AOX) discharge and effluent colour.

Introduction

Pressures to maximise energy efficiency, improve product quality, reduce environmental impact, and optimise capital and operating costs have significantly shaped the design of recent mills.

Producers have responded to these demands by adopting efficient, low impact designs on economies of scale that far surpass most existing mills. Modern mills have less equipment, but are of much larger capacity than 20th century mills. New fibrelines have been built mainly in Asia and South America where access to fast growing raw material, other production cost advantages, stable politics and economies, and surging demand from the East give favourable levels of cost and return. India's non wood and hardwood market pulp segment must compete in the longer term with these new fibrelines. This paper will allow mill operators to benchmark their mill performance against three of these new fibrelines.

Minimum Environmental Impact

Bleached kraft pulp (BKP) mills embodying the latest technologies and management practices aim to minimise pollutants released from the production processes. Rigid environmental standards are in place in most jurisdictions to ensure this is the case.

Technologies allowing maximum system closure, low water consumption and reduced environmental impact include:

- Modified cooking, 2-stage oxygen delignification,
- ECF or ECF-light bleaching,
- Efficient multistage drum washers or press washers in both the fibrelines and the bleach plant,
- Integrated warm and hot water systems,
- Integrated water supply and process cooling systems (cooling towers),
- Advanced evaporator condensate segregation and treatment systems, and
- Effective spill recovery systems and efficient biological treatment systems.
- High solids firing and efficient process vent gas collection systems to minimise TRS emissions

Dissolved organic material is increasingly recycled by highly efficient washers and in some unique circumstances via bleach plant filtrate recycle. Although these features are not new, they can be combined in new mills and take advantage of the improved equipment now available.

One essential criterion is that the technology should achieve the desired emissions in a cost-effective manner. There are various terms for this including Accepted Modern Technology (AMT) (1), Best Management Practice (BMP), or Best Available Technology (BAT), but the technology must be technically effective and economically viable on an industrial scale.

Key Parameters

To assess BKP mill environmental performance, the traditional effluent parameters monitored are Chemical Oxygen Demand (COD), five-day Biological Oxygen Demand (BOD5), Total Suspended Solids (TSS), Adsorbable Organic Halides (AOX), as well as water use and effluent discharge flow. There is increasing interest in reducing effluent colour, which will be discussed later.

Key air parameters include hydrogen sulphide and particulate emissions from the recovery boiler, lime kiln and power boiler, and chlorine dioxide from the bleach plant and chemical plant.

Veracel is considered to be one of the top performing bleached hardwood kraft mills in the world. Veracel Celulose is a Brazilian high brightness, eucalyptus mill using 2-vessel vapour-phase Lo-Solids® continuous cooking, and a hot chlorine dioxide ECF bleach sequence, with a design capacity of 900,000 air dried tonnes per annum (tpa) (2).

Veracel operates within the best environmental practices expected of a modern pulp mill. Key features are:

- The water intake is after effluent discharge to the river,
- Liquid effluents are treated in an activated sludge process,
- Atmospheric emissions are permanently monitored. There is one common stack for all air emissions,
- There is an odour perception network of 23 inhabitants of neighbouring communities, and
- Management and reuse of solid wastes (organic composting is used to produce fertilizers).

The 2007 environmental performance for the Veracel mill was well within the internal targets and the Best Available Technology (BAT) references (Table 1). Veracel is probably the only mill that discharges its effluent upstream of its intake, which is a requirement of the mill's operating licence.

Table 1. Veracel effluent performance compared with permit, BAT and internal targets

Parameters	Units	BAT	Internal Target	Actual YTD Dec 07 Average
AOX Effluent	kg/adt	<0.25	< 0.15	0.06
COD Effluent	kg/adt	8 – 23	12.0	6.7
BOD5 Effluent	kg/adt	-0.5-1.5	0.7	0.31
Suspended Solids	kg/adt	0.6-1.5	1.0	0.67
Water usage	m3/adt	-	30	27.7
Effluent discharge	m3/adt	30-50	27	24.7
TRS Recovery Boiler as H2S	ppm	-	0.20	0.05
TRS Lime Kiln as H2S	ppm	-	7.0	5.7
Odour complaints	No	-	0	11
Colour	mg/l	-	1000	520

Technologies that are implemented to allow maximum system closure and minimum water and chemical consumption in pulping and bleaching are discussed in the following section.

Kraft Fibreline Design

Pulping

State-of-the-art cooking includes both continuous and batch processes utilizing low cooking temperatures and optimised alkali profiles. Continuous cooking has predominated over the last decade, and typically consists of two-vessels for softwood and one- or two-vessels for hardwoods. With segregation of chips by species and quality the norm, the chip feed is of uniform quality and thus results in reduced processing upsets. Good impregnation is a key factor in achieving good yield. Lower cooking temperatures

(145-153°C) are typically used with kappa numbers in the range 26-35 for softwoods, 17-22 for birch and 15-18 for eucalypts.

Washing and screening

The washing equipment and configuration are different for most mills. Compared with the previous generation of mills, atmospheric diffusion washers and drum washers have been replaced in modern mills by presses, CB filters and multi-stage DD washers that achieve high Equivalent Displacement Ratios (EDRs).

Deknotting and primary screening can now be done in a single stage with knot separation and return to the digester chip bin via a blower system. Alternatively, recovered knots can be directly injected into the digesters.

Deknotting and screening can be carried out before or after oxygen delignification. Screening after oxygen delignification has advantages of:

- less foaming, making the pulp easier to screen,
- higher yields due to breakdown of shives,
- smaller and cleaner rejects, and
- heat balance advantages between the cooking and oxygen stages.

Deknotting and primary screening now occur in a single stage with knot separation and return to the digester chip bin via a blower system. Alternatively, knots can be directly injected into the digesters.

Screening can be either 3-stage or 4-stage. Rejects can be taken out of the system or recycled by washing and return to the oxygen delignification stage.

Oxygen delignification

Oxygen delignification is typically carried out at medium consistency and in two stages. This is a significant difference from mills of the previous decade where oxygen delignification was typically done in one stage.

The bulk of the delignification occurs in the first tower, which is typically run at lower temperature and higher pressure than the second reactor. The first reactor temperature is typically in the range 85 to 95°C, at a pressure of 6-8 bar, and with addition of around 60-70% of the alkali and oxygen charge.

Some mills add all chemicals to the first reactor. Typically, the retention time in the first tower is around half that of the second tower. The second reactor temperature is 95-100°C at a pressure of 3-5 bar. Temperatures and chemical charges are lower for hardwoods, reflecting the generally lower incoming kappa number compared with softwoods.

The degree of delignification varies between 50-60% for softwood, and 40-50% for hardwoods. A significant portion of the hardwood "kappa number" is hexeneuronic acid which lowers the overall degree of delignification compared with softwoods. Kappa targets are set to preserve pulp strength and pulp yield. Magnesium sulphate is often added to preserve strength, particularly for softwood pulps.

To conserve water, condensate from evaporation is sometimes used in the last stage of oxygen delignification for washing.

Bleaching

4-stage, Elemental Chlorine Free (ECF) bleaching sequences are the standard for bleaching in modern mills. The typical ECF sequence from mills of the 1990s was D (Eop) DD so little has changed in the modern bleach plants (3).

Modern bleach plants commonly operate with upflow towers in all stages, with interstage washing using DD washers or presses. The washing is typically counter current with white water from the pulp machine being used for washing on the final stage washer. Variations to true counter current washing have been developed to minimise pH transitions and to create alkaline and acid purge streams to manage metals, extractives and scaling.

The excess filtrates, both acid and alkaline, are often filtered to recover fibre before they are sewerred. To decrease emissions of COD, BOD5 and colour from the bleach plant, it is possible to recycle the alkaline filtrate from the Eop stage and use it for washing prior to the first bleaching stage.

All mills have on-line analysers and optimisation controls. The control of final brightness is very precise and quality downgrades are almost non-existent. To achieve this consistent quality and cost efficiency the bleach plants have a high level of on-line instrumentation that allows tracking, analysis and optimal control of the bleaching process. Standard deviation of the final brightness is typically less than +0.5% ISO.

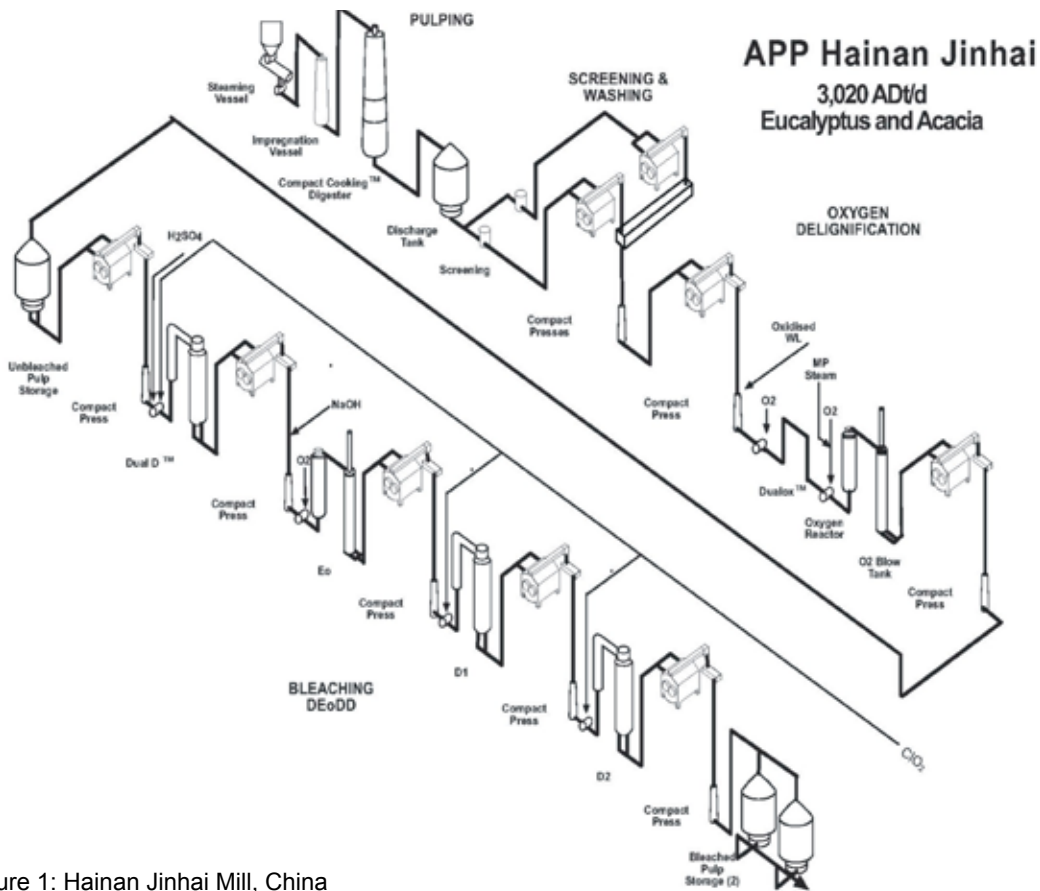


Figure 1: Hainan Jinhai Mill, China

Fibreline Examples

The Hainan Jinhai mill in China and the Valdivia mill in Chile are examples of modern bleached kraft mills employing the technologies discussed above.

Hainan Jinhai Pulp and Paper.

The world’s largest single-line pulp mill, Hainan Jinhai was designed to produce 1 million tpa of bleached hardwood kraft pulp. The mill is located on Hainan Island in southern China and covers 400 hectares.

Hainan Jinhai produced its first pulp in November 2004. The mill’s fibre supply is *Eucalyptus grandis* and *Acacia crassicarpa*, in approximately equal volume and is sourced internally from plantation forests. Environmental standards are strict and emissions are kept below the imposed standards. Hainan Jinhai utilises world-class technology – COMPACT Cooking™, two-stage Dualox™ oxygen delignification and DualD™ hot chlorine dioxide bleaching.

It has one of the world’s largest digesters with a bottom diameter of 12.5 metres and a recovery boiler with a design capacity of 5,000 tonnes per day of dry solids.

Mill capacity already exceeds the design capacity.

The mill’s production is used to supply pulp to several APP paper machines in China. Figure 1 illustrates the fibreline at the Hainan Jinhai mill.

Cellulosa Arauco Valdivia

The pulp mill in Valdivia, Chile started up in February 2004 and produces 550,000 tonnes of pulp annually. Valdivia is a ‘swing’ mill producing both radiata pine (60% of production) and eucalyptus pulp. The mill design and vendor equipment packages are based on a maximum capacity rate of 1,700 ad tpd for pine and 1,900 ad tpd for eucalyptus. *E. nitens* (70%) and *E. globulus* (30%) are the eucalyptus species pulped (2).

The mill is located in an environmentally sensitive area, especially with respect to air and water emissions. Very low loadings to the recipient waters are a key requirement, which are achieved by a combination of process selection and operational control. Concentrated and dilute non-condensable gases from the fibreline, evaporation and causticizing plants are collected, treated and incinerated in the recovery boiler. Effluent treatment consists of primary, secondary and tertiary treatment stages followed by disk filtration to minimise suspended solids prior to discharge.

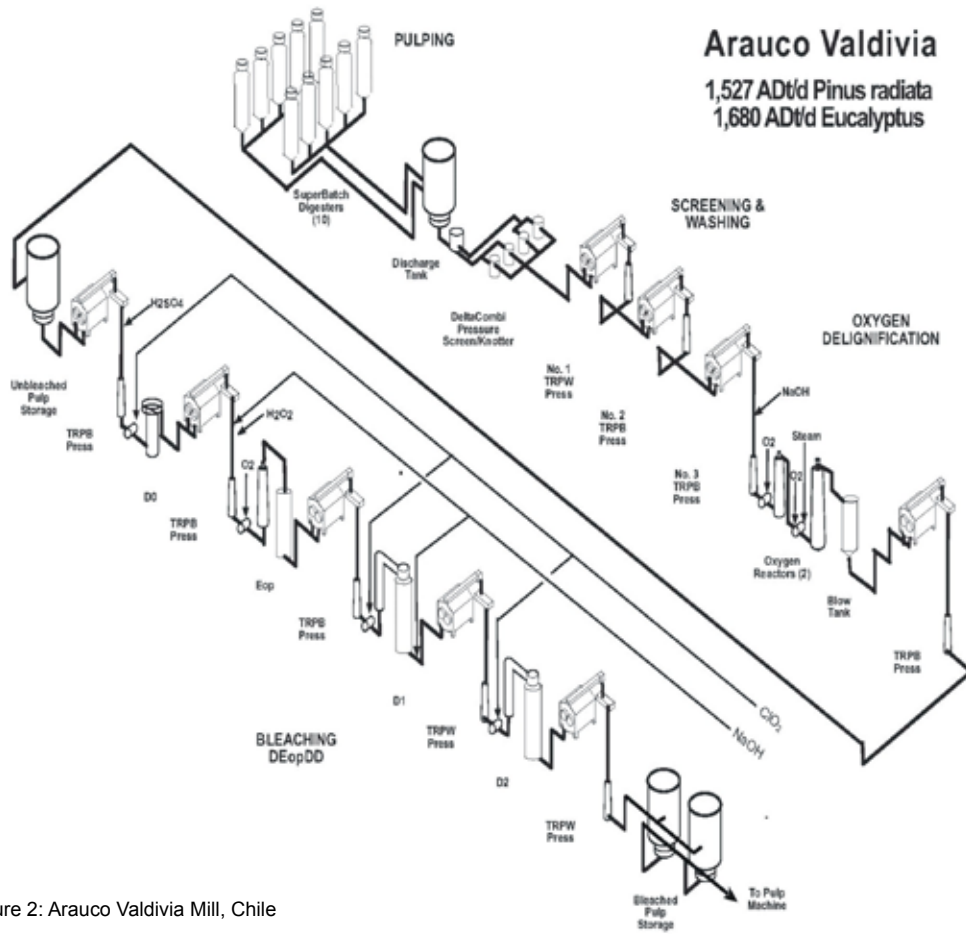


Figure 2: Arauco Valdivia Mill, Chile

The pulping line consists of ten SuperBatch-K digesters of 400 m³ capacity followed by 4 stages of washing and screening. Oxygen delignification is in two stages with 60% of delignification occurring in the first reactor. The ECF bleach sequence is D (Eop) D D. A perspective sketch of the fibrelines is shown in Figure 2.

Arauco Valdivia operates a 40 t/day methanol based SVP-SCW chlorine dioxide process, which includes washing and recycling of the neutralised sulphate by-product to the recovery system thereby reducing the need for make-up caustic is reduced. Oxygen is produced in a Vacuum Pressure Swing Adsorption (VPSA) process, which is based on nitrogen adsorption from air by a zeolite. Air is filtered, compressed and cooled before it enters the adsorber.

The average purity is 93% and the capacity at 100% is 50 t/d. There is also a system for externally supplied oxygen consisting of two liquid storage tanks. The Valdivia mill has two 70MW turbines. 51MW is consumed by the mill and 30 to 50MW are sent to the national grid. This amount depends on the wood species being processed.

Fibrelines Performance

The real measure of the success of the mills discussed is reflected in their overall performance - market, business and environmental performance.

For all three mills process control is excellent, product quality meets market standards and environmental performance is among the best in the world. It is not appropriate in this forum to discuss business and financial parameters except to say all three mills are low cost producers and as such their future is assured. Process performance is, however, very relevant. Table 2 shows key parameters that are commonly used to measure the control over each unit operation.

All mills have good process control tools and modern technologies which result in a very good overall performance that can be seen in the following results:

- Low variability of process and uniform quality parameters,
- High cooking yield,
- High prime quality (less than 1% of the annual production was not classified as prime quality), and
- Very low chemical consumption in the bleach plant.

Mills typically produce one prime grade of pulp only, which eliminates grade switching and maximises productivity.

Table 2. Fibreline Performance

Parameters	Veracel	Hainan Jinhai	Arauco Valdivia	
Wood Species	E. urograndis	Acacia E. grandis	P. radiata	E. nitens E. globulus
Digester				
Kappa Number	18	17-18	26	15
Kappa Std. Deviation	0.5		2.0	
Oxygen Delignification				
Delignification, %	38	30-44	61.5	37
Kappa Number	10.0	10-12	10.0	9.5
Kappa Std. Deviation	0.5		1.25	0.85
Washing Loss as kg COD/ADt	10.0	<3	6	6
Bleaching				
Brightness, %ISO	90.4	88-90	89.3	90.1
Viscosity In, dm ³ /kg	1100		844	943
Viscosity Out, dm ³ /kg	880	~700	737	833
Viscosity Loss, dm ³ /kg	220		107	110
Final Product				
Brightness, %ISO	90.4	88-90	90.3	90.6
Dirt, ppm	0.3	<5'	0.7	0.9

Note 1. Hainan dirt count units are mm²/m².

Effluent Treatment

Good environmental performance is also critical. This, of course, is influenced by the type of treatment system.

To illustrate the shape of future effluent treatment technologies, the Arauco Valdivia Mill is used. This mill is located in a very environmentally sensitive area, and based on some benchmarking of its permit, has some of the most stringent effluent limits for bleached kraft pulp mills anywhere. Valdivia has three permits that cover all parameters. The mill is in compliance with its permit targets.

There are three incoming sewers to the effluent treatment plant:

- The low solid system (bleach plant effluents, excess evaporator condensate),
- The general sewer for all other process streams from the mill, including effluent from landfill and the wood yard,
- The storm water system with an automatic divert to the effluent treatment system in case of contamination.

The Effluent Treatment area includes the following main systems:

- A Spill Pond with spill recovery pumps (130,000 m3),
- Primary treatment for the general sewer including an automatic screen and one primary clarifier with scraper and fibre sludge pump,
- Neutralization including a chemical mixing tank,
- Cooling Tower with two chambers,

- Secondary treatment comprising two parallel lines with aeration basin and secondary clarifiers including scrapers and fibre sludge pumps, and systems for aeration and nutrients,
- Tertiary treatment in two parallel lines, both including flocculation chambers with mixers and flotation basins, including scrapers and sludge pumps. The stage also includes systems for dispersion water and chemicals (alum, polymer and peroxide),
- Three disc filters in parallel to reduce suspended solids,
- Three final cooling towers to adjust the final effluent temperature, and
- Sludge handling, including two belt filter presses for sludge dewatering.

The effluent discharge to the river has on-line instrumentation to improve monitoring and control of the discharge. This information is sent to the Chilean authorities via web on-line.

Arauco Valdivia’s specific discharges of COD and colour are the lowest in the world (known to the authors) for a bleached kraft pulp mill. The AOX, BOD and TSS are also amongst the lowest in the world. In June 2007, Arauco announced that three changes to the mill are planned to further enhance environmental performance (4). These include the intake of mill water from downstream of the mill effluent discharge, the provision of reverse osmosis system ahead of the existing ion exchange plant for the treatment of boiler feedwater, and the installation of a membrane filtration system for treated effluent ahead of the tertiary treatment system. The use of these membrane systems will reduce effluent discharges.

Many studies have been done on the effluent toxicity using acute toxicity (CL50) and chronic toxicity testing.

The analyses do not show any impact on species in the recipient water (river). The effluent did not produce any lethal effect for the species *H. gracilicornis*, *D. obtusa*, *G. affinis* y and *O. mykiss* nor any chronic toxicity in *L. valdiviana*, *S. capricornotum*, *G. affinis* y and *O. mykiis*.

Arauco Valdivia uses tertiary effluent treatment, in addition to biological treatment. The tertiary treatment uses flocculation technology to remove additional organic material. The use of this technology contributes to the very low COD (and AOX) discharge numbers from the mill.

In terms of comparing technologies (or assessing the use of “best technologies”) tertiary treatment is usually only considered if the effluent receiving waters are of poor assimilative capacity or otherwise restricted, and as such, it is identified as a supplemental or optional technology in recent BKP best technology reviews (for example in the EU 2001, Australia 2004 and Uruguay 2006 reviews).

Use of tertiary treatment with precipitation technologies results in lower discharge of dissolved organic materials than mills with biological treatment alone. However, it incurs the expense of additional chemical use, and produces a tertiary treatment sludge, which is generally either land applied or burnt. The use of additional chemicals may also increase the discharge of salts (conductivity) from the mill. Salt discharge into receiving bodies may be a consideration for mills in India where there is agricultural use downstream.

For any mill, the selection of tertiary treatment is based on assessment of these alternate environmental factors, for the mill site considered.

Table 3. Effluent Treatment Performance.

Parameters	Veracel	Hainan Jinhai	Arauco Valdivia
Flow, m ³ /day	72,000	60,400	50,0 00
Primary Clarifier, # x m ³	1 x 25,080	Yes	1 x 5,000
Bio-Treat Type	Activated sludge	Anaerobic & aerobic	ASB
2 x 44,750			
Sec Clarifier, # x m ³	2 x 14.26	-	2 x 8,700
Tertiary, m ³		Yes	2 x 590
Spill Containment	By area		By area
Emergency Basin, m ³	60,000		130,000
Nutrients Applied	N2 as urea		
Cooling Towers	1		2
Final Effluent Parameters			
BOD, kg/adt	0.30		0.07
COD, kg/adt	6.7	< 3	1.5
TSS, kg/adt	0.67		0.23
AOX, kg/adt	0.06		0.03
Colour, kg/adt	520 mg/L		0.55
Temperature, °C	35		28.5

Note: 1. Hainan Jinhai from reference (5)
 2. Arauco Valdivia data corresponds to official data from 2007

Water Use

Water use is a global topic and particularly relevant in India. India’s Ministry of Water Resources is responsible for the development, conservation and management of water as a national resource. It has established parameters for treatment of effluent to acceptable levels before discharge. The “polluter” pays principle is applied in some cases.

Pulp and paper manufacture is typically a water intensive activity. Indian paper mills face the issues of sustained water supply and effluent limitations for colour and AOX. In some cases the small and medium mills have no effluent treatment.

Modern bleached kraft pulp mills consume 20 – 30 m³ per air dried tonne compared with the Indian industry average of 57 m³ per tonne for all grades (6). Therefore a driving force in the Indian industry is to reduce usage of fresh water and close water systems. This includes such measures as recycling bleach plant filtrates, recovering condensates, segregation of cooling water and reuse, increasing white water recycle and reuse of foul condensates.

Effluent Colour

Colour originates from the lignin and tannins in the incoming wood. Colour reduction of effluent is another significant issue in the Indian pulp and paper industry. In the pulping process approximately 90 – 95% of the lignin is removed from the wood in pulping and burnt in the recovery boiler. Oxygen delignification removes a further 2 – 3 % of the lignin, which is also collected as black liquor and sent to the recovery boiler for incineration. The remaining 2 – 3% of the lignin is removed in the bleach plant and does not enter the recovery cycle because of the high levels of inorganic compounds (mainly chlorides). It is discharged to the sewer. This accounts for a significant amount of the mill effluent colour load. A schematic of an approximate lignin profile through a bleached kraft fibre line is shown in Figure 3.

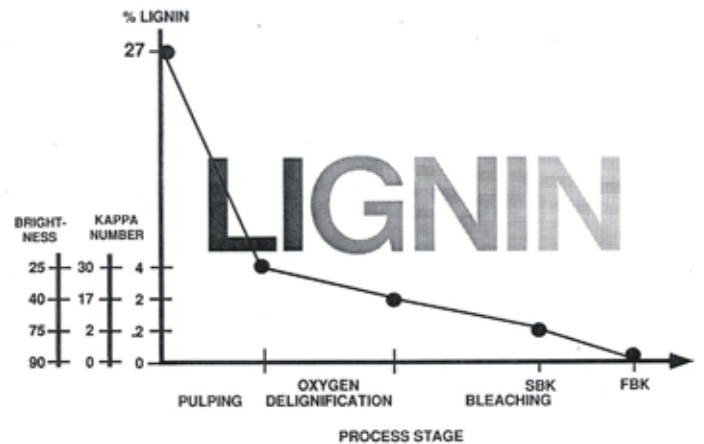


Figure 3: Lignin profile through a bleached softwood kraft fibre line (SBK semi-bleached kraft pulp, FBK fully-bleached kraft pulp)

Bleached kraft mills use a combination of in-process technologies to minimize colour generation and colour loss to wastewater. Additionally, effective wastewater treatment systems are used that typically include several treatment stages and modifications of conventional technologies, primarily for BOD₅, COD and toxicity reduction, but which can also impact colour. Technologies and practices to successfully reduce colour can be implemented either “In-process” or “End of pipe” and include:

In-process technologies:

Black liquor (BL) loss control – achieved with improved brown stock washing to minimise carryover of black liquor, effluent free knots and reject handling, and a closed screen room. The impact of intermittent BL losses (spills, overflows, etc) are minimised via a spill management system, including measurement and monitoring, spill prevention and a spill collection system.

Alkaline filtrate recycle – partial recovery of alkaline bleach plant filtrate is practiced by several mills. A chloride removal system is needed at high recycle levels. It is more easily implemented in TCF or ECF-light sequences.

Acid filtrate recycle – is less common. Removal of non-process elements is necessary to avoid scaling.

The acid filtrate is high in chlorides, but contains about 40% of the bleach plant colour, thus potential reductions in colour are significant.

End of pipe and wastewater treatment technologies:

Membranes – studies are on-going but success at the mill level has been limited. Membrane treatment is more suited to low volume, high concentration filtrates.

Chemical processes – precipitation is effective in reducing colour and is typically used to treat biologically treated effluent. Disadvantages include the generation of large amounts of sludge that can be difficult to dewater and dispose of. Aluminium salts are successfully used in tertiary treatment stages, with or without polymers. Use of polymers alone is also practised, to avoid large sludge volumes.

Oxidation processes – ozone, peroxide, or enhanced peroxide are effective in removing colour of whole mill effluent and bleach plant filtrates; this is an active area of research but there are no full-scale applications to date.

Evaporation and incineration – processes have been developed and demonstrated using EOP filtrates but there is no full scale implementation for ECF mills.

White rot fungi – effective in colour reduction but these have been demonstrated at lab-scale only.

Increases in effluent colour across treatment systems are common in mills using Aerated Stabilisation Basins (ASB) for effluent treatment. Colour increases of 20 – 40% are common. Increase in effluent colour is not seen in mills using activated sludge treatment. Colour reversion has typically been an issue for mills where oxygen delignification and ECF bleaching have been introduced.

Summary

Pressures to minimize the environmental impact of modern pulping lines have driven improvements in pulping and bleaching equipment and mill operating practices. Removal of the majority of lignin ahead of the bleach plant maximises the recycle of organic and chemical material to the recovery cycle. Filtrates are recycled and condensates are recovered and reused. Standard biological treatment of effluent can be supplemented with a tertiary treatment stage, particularly where receiving water discharges are restricted.

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