Application Note

Pulp & Paper

Introduction

The processes in the manufacture of paper and paperboard can, in general terms, be split into three steps: pulp making, pulp processing, and paper/paperboard production. Pulp is defined as watery fibrous substrate formed into paper sheets

Three major types of fibers are used to make pulp and paper products: wood; secondary fibers (recycled fibers); and non-wood fibers (e.g., cotton, flax, hemp). However, the majority of pulp and paper products are made from wood, and most wood mills use the Kraft pulping process *).

Because Kraft mills represent the majority of the industry, the processes at Kraft mills using wood will be described. A general process overview for each of the other types of mills is also provided.

Kraft, soda, and sulfite mills all use chemicals in their pulping processes. These processes differ primarily in the chemicals used for digesting wood chips. Mechanical pulping involves shredding or grinding wood chips without the use of chemicals and semi-chemical pulping combines chemical and mechanical methods. Secondary fiber mills mechanically separate pulp from waste paper products. Non-wood fiber mills can use mechanical and chemical pulping processes.

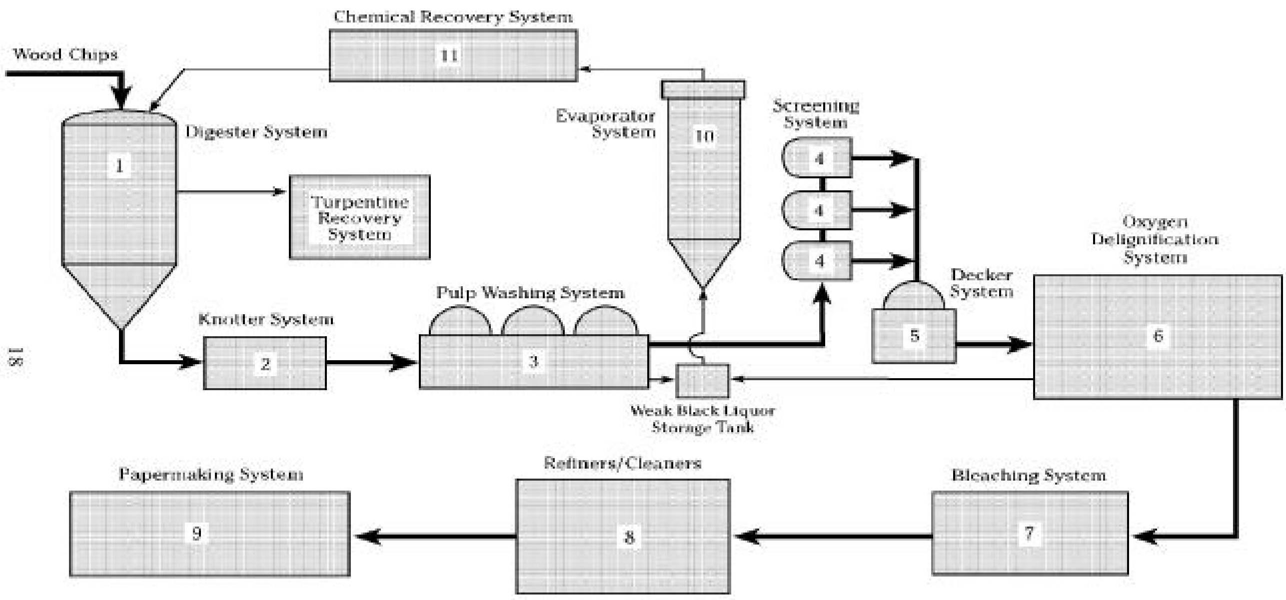
Market Segment

Pulp and paper industry

*) The German chemist C.F. Dahl developed the Kraft (from the German word meaning 'strong') pulping process in 1879.

Description of the Challenge

Typical gases to be monitored at a pulp and paper mill are: bleaching chemicals like Chlorine (Cl_2), Chlorine Dioxide (ClO_2), Ozone (O_3) or Hydrogen Peroxide (H_2O_2); Oxygen (O_2) from the delignification system; total reduced sulfur (TRS) like Hydrogen Sulfide (H_2S), Methyl Mercaptan (CH_3SH), Dimethyl Sulfide $(CH_3)_2S$, and Dimethyl Disulfide $(CH_3)_2S_2$ primarily released from wood chip digestion, black liquor evaporation, and chemical recovery boiler processes; VOCs (Terpenes, Alcohols, Methanol, Acetone, MEK) from process chemicals which are mostly solvent sprays and emissions from drying wet tissue and the water treatment process.
In addition, some plants also require gas detection for Sulfur Dioxide (SO_2) which is emitted in small amounts from the use of Sodium Hydrosulfite.
Pulp and paper mills usually operate wastewater treatment plants to remove biological oxygen demand (BOD), total suspended solids (TSS), and other pollutants before discharging waste waters to a receiving waterway. Mills with indirect discharge may operate primary treatment systems designed for TSS reduction prior to discharge to a Waste Water Treatments Plants (WWTP, see also application note APN0002).



1–Cooking liquor added to wood chips to dissolve lignin.
2–Removal of uncooked chips and knots.
3–Weak black liquor washed from pulp.
4–Fiber bundles and contaminants screened from pulp.
5–Pulp thickened for oxygen delignification.
6–Oxygen Delignification System for further delignification.
7–Pulp bleached to increase whiteness.
8–Pulp is cleaned and prepared for papermaking.
9–Paper sheet formed through dewatering.
10–Evaporator System removes excess water from the weak black liquor.
11–Chemical recovery system converts the concentrated liquor into cooking liquor for use in the digester system.

Figure 6.

Example Overview of a Kraft Pulping Mill with a Papermaking System

Kraft pulp processing steps
Wood consists of two primary components: cellulose and lignin. Cellulose, which is the fibrous component of wood, is used to make pulp and paper. Lignin is the "glue" that holds wood fibers together. Pulping is the process which reduces wood to a fibrous mat by separating the cellulose from the lignin. Kraft mills remove impurities from the raw pulp prior to bleaching or papermaking. The primary pulp cleaning operations include deknotting (in the knotter), brown stock washing (in the pulp washing system), and pulp screening (in the screening system).

Deknotting removes knots and other portions of uncooked wood from the pulp slurry.

Brown stock washing recovers spent cooking liquor (weak black liquor) for reuse in the pulping process. Efficient washing is critical to maximize the return of cooking liquor to chemical recovery and to minimize carryover of cooking liquor (known as brown stock washing loss) into the bleach plant.

Pulp screening removes the remaining oversized particles (fiber bundles and contaminants) from washed pulp.

Evaporator system: Weak black liquor collected from the pulp washers goes into a weak black liquor storage tank. The weak black liquor is sent to the multiple effect evaporator (MEE) to evaporate water and concentrate the weak black liquor in order to increase solids content.
Residual weak black liquor from the pulping process is concentrated by evaporation to form "strong black liquor." After brown stock washing in the pulping process the concentration of solids in the weak black liquor is approximately 15 percent; after the evaporation process, solids concentration can range from 60 to 80 percent. The liquor then undergoes oxidation for odor reduction. The oxidation step is necessary to reduce odor created when hydrogen sulfide is stripped from the liquor during the subsequent recovery boiler burning process.

The strong black liquor from the evaporators is burned in a recovery boiler. In this crucial step in the overall Kraft chemical recovery process, organic solids are burned for energy and the process chemicals are removed from the mixture in molten form. Molten inorganic process chemicals (smelt) flow through the perforated floor of the boiler to water-cooled spouts and dissolving tanks for recovery in the recausticizing step.

Smelt is recausticized to remove impurities left over from the furnace and to convert Sodium Carbonate (Na_2CO_3) into active Sodium Hydroxide (NaOH) and Sodium Sulfide (Na_2S). The recausticization procedure begins with the mixing of smelt with "weak" liquor to form green liquor, named for its characteristic color. Contaminant solids, called dregs, are removed from the green liquor, which is mixed with Lime (CaO). After the lime mixing step, the mixture, now called white liquor due to its new coloring, is processed to remove a layer of lime mud ($CaCO_3$) that has precipitated. The primary chemicals recovered are Caustic (NaOH) and Sodium Sulfide (Na_2S). The remaining white liquor is then used in the pulp cooking process. The lime mud is treated to regenerate lime in the calcining process.

In the calcining process, the lime mud removed from the white liquor is burned to regenerate lime for use in the lime mixing step. The vast majority of mills use lime kilns for this process.

> Gas detection with **DrägerSensor H_2S**: In the Kraft process, Sulfur Oxides are a minor issue in comparison to the odor problems created by four reduced sulfur gases, called together Total Reduced Sulfur (TRS): Hydrogen Sulfide (H_2S), Methyl Mercaptan (CH_3SH), Dimethyl Sulfide $(CH_3)_2S$, and Dimethyl Disulfide $(CH_3)_2S_2$. The TRS emissions are primarily released from <u>wood chip digestion</u>, <u>black liquor evaporation</u>, and <u>chemical recovery boiler</u> processes.
> Gas Detection with IR sensor or catalytic bead sensor for **VOCs** (Terpenes, Alcohols, Methanol, Acetone, MEK) from <u>process chemicals</u> which are mostly solvent sprays and emissions from <u>drying wet tissue</u> and the <u>water treatment</u> process.

Oxygen delignification: Some mills that produce bleached pulp may also have an oxygen delignification stage either in the pulping area or as a pre-bleaching stage. High efficiency oxygen delignification minimizes the amount of bleaching chemicals needed

> Gas detection with **DrägerSensor O_2**

Bleaching brightens the pulp in a series of chemical operations that are together called a bleaching line. A bleaching line typically consists of a sequence of three to six bleaching stages. The number of stages varies depending on the brightness requirements of the pulp and the specific design of the mill. Typically, the stages are sequenced as an alternating series of bleaching and extraction stages. In a bleaching stage, the pulp is treated with chemical bleaching agents. In an extraction stage, chemicals (usually sodium hydroxide) are added to neutralize the chemical reactions and the acidity of the pulp prior to the next bleaching stage. An extraction stage is not required in all cases.
Each bleaching stage consists of three steps: mixing of pulp and bleaching chemical (and in some cases steam); reaction of the chemical with the pulp in a retention tower; and washing the chemical out of the pulp.

Chemicals	Abbreviation
Chlorinated Bleach Chemicals	
Elemental chlorine	C
Hypochlorite	H
Chlorine dioxide	D
Chlorine with chlorine dioxide substitution	(CD), (C+D)
Non-chlorinated Bleach Chemicals	
Oxygen	O
Peroxide	P
Ozone	Z

Oxygen-reinforced extraction (or oxidative extraction) and peroxide-reinforced extraction processes used separately or together have been shown to reduce the amount of elemental chlorine and chlorine dioxide needed in the bleaching process while increasing the pulp brightness. Gaseous elemental oxygen (in the case of oxygen-reinforced extraction) and aqueous hydrogen peroxide (in the case of peroxide extraction) are used as a part of the first alkaline extraction stage to facilitate the solubilization and removal of chlorinated and oxidized lignin molecules.

Gas detection: depending on the chemicals used for bleaching, **DrägerSensor Cl_2,** for Cl_2 or ClO_2; **DrägerSensor H_2O_2; DrägerSensor O_2; DrägerSensor O_3**

The final stages at a pulp and paper mill include the preparation of pulp for papermaking and the actual papermaking process. In the pulp preparation area, the pulp fibers are cleaned to remove unwanted particles (such as dirt and sand) from the pulp stock. The cleaned fibers will then undergo some level of refining. In the refining process, the pulp fibers are subjected to mechanical action to develop their optimal papermaking properties with respect to the product being made. Wet additives are used to create paper products with special properties or to facilitate the papermaking process. Wet additives include resins and waxes for water repellency, fillers such as clays, silicas, talc, inorganic/organic dyes for coloring, and certain inorganic chemicals (calcium sulfate, zinc sulfide, and titanium dioxide) for improved texture, print quality, opacity, and brightness.
In the papermaking process, the pulp stock is converted into paper. This process begins when the pulp stock is distributed across the forming table. On the forming table, the paper sheet formation starts as the excess water contained in the pulp stock drains from the pulp fibers. The newly formed paper sheet is removed from the forming table and is conveyed through a series of presses to remove additional water and to continue the sheet forming process. The remaining water contained in the paper sheet is removed as the sheet travels around a series of steam-heated cylinders.
After the paper sheet leaves the dryers, it may undergo several other processes, depending on the final paper product. These additional processes include; calendering (where the sheet is pressed to reduce thickness and smooth the surface), winding (where the sheet is wound onto a reel), and coating (where various chemical or dyes are applied to the paper sheet).

Gas collection systems or noncondensible gas (NCG) systems, are used to collect gases from the various pulping processes and transport them to an appropriate air pollution control device. There are two basic categories of NCGs: low volume, high concentration (LVHC); and high volume, low concentration (HVLC).

Low volume, high concentration (LVHC) systems typically collect gases from the following systems:

- digester system
- turpentine recovery system
- evaporator system
- steam stripper system
- any other system serving one of these functions

High volume, low concentration (HVLC) systems typically collect gases from the following systems:

- knotter system
- pulp washing system
- screen system
- oxygen delignification system
- weak liquor storage tanks
- any other equipment serving one of these functions

A number of mills use a dedicated incinerator to control NCG emissions, but most mills use process combustion sources such as the lime kiln, power boilers, or a recovery boiler.

Condensate stripping

The pulping process equipment may include a steam stripper system to remove organics and total reduced sulfur (TRS) compounds from various liquid process condensate streams. Steam stripping is a multistage distillation separation process that uses direct steam as the heat source. The pulping process condensate streams most often stripped are the turpentine decanter underflow, blow steam condensates, and certain evaporator condensates. The stripped condensates may then be used as hot process water.

Kraft pulping process condensates originate from the following systems:

- digester system
- turpentine recovery system
- evaporator system

Other types of paper mills

Soda mills
The soda pulping process utilizes an alkaline liquor with sodium hydroxide as the only active chemical. Except for the difference in chemicals used, this process is the same as that described for the kraft mill.

Sulfite mills
The sulfite pulping process uses an acid solution of sulfurous acid (H_2SO_3) and bisulfite ion (HSO_3^-) to break the lignin bonds between wood fibers, while Kraft mills use an alkaline solution. Because the sulfite cooking process is an oxidizing reaction, Sulfur Dioxide (SO_2) is generated instead of the reduced sulfur compounds generated by the Kraft process (a reducing reaction). Thus, the chemical recovery processes at sulfite mills are different than at Kraft mills. Otherwise, the process is similar to the Kraft process.

Semi-chemical mills
Semi-chemical pulping involves partial digestion of wood chips in a weak chemical solution such as sodium sulfite (Na_2SO_3) and sodium carbonate (Na_2CO_3) followed by mechanical refining for fiber separation. Semi-chemical pulps are typically bleached with hydrogen peroxide (H_2O_2) in a bleach tower. Semi-chemical pulp is very stiff, making this process common in corrugated container manufacture.

Mechanical pulping
Mechanical pulping uses physical pressure instead of chemicals to separate wood fibers. Mechanical pulping processes have the advantage of converting up to 95 percent of the dry weight of the fiber source into pulp, but require an enormous amount of energy relative to chemical pulping. Mechanically produced pulp is of lower strength than chemically produced pulp and is used principally for newsprint and other non-permanent paper goods.

Mechanical pulps are brightened with hydrogen peroxide (H_2O_2) and/or sodium sulfite (Na_2SO_3). The brightening chemicals are applied during the pulp processing stage (e.g., in-line brightening), or in chemical application towers. These chemicals only brighten the pulp and do not permanently bleach the pulp. Typically, bleaching of mechanical pulps using chlorine or chlorine dioxide is not practiced because of the high cost of bleaching chemicals and negative impact on pulp yield.

Secondary fiber pulping
Secondary fibers include any fibrous material that has undergone a manufacturing process and is being recycled as the raw material for another manufactured product. Secondary fibers have less strength and bonding potential than virgin fibers. The fibrous material is dropped into a large tank, or pulper, and mixed by a rotor. The pulper may contain either hot water or pulping chemicals to promote dissolution of the paper matrix. Debris and impurities are removed by “raggers” (wires that are circulated in the secondary fiber slurry so that debris accumulates on the wire) and “junkers” (bucket elevators that collect heavy debris pulled to the side of the pulper by centrifugal force).

Deinked secondary fibers are usually bleached in a bleach tower, but may be bleached during the repulping process. Bleach chemicals may be added directly into the pulper. The following are examples of chemicals used to bleach deinked secondary fibers: hypochlorite ($HClO$, $NaOCl$, $Ca(OCl)_2$), hydrogen peroxide (H_2O_2), and sodium hydrosulphite ($Na_2S_2O_4$).

Non-wood fiber pulping
Non-wood pulping is the production of pulp from fiber sources other than trees. Non-wood fibers used for papermaking include straws and grasses (e.g., flax, rice), bagasse (sugar cane), hemp, linen, ramie, kenaf, cotton, and leaf fibers. Pulping of these fibers may be performed by mechanical means at high temperatures or using a modified Kraft or soda process.

Solution from Dräger

Example:

1. Detection of VOC's (from solvents in process chemicals):

Polytron SE Ex and cross-calibration for solvent monitoring using 40 %LEL Propane. Adjust channel card to 92 %LEL as the applied span gas concentration (this implies the factor 2.3).

Polytron XP Ex and cross-calibration for solvent monitoring using 40 %LEL n-Butane. Select C_9H_20 (n-Nonane) in the gas configuration menu and chose 80 %LEL instead of 40 %LEL as the applied span gas concentration (this implies the factor 2.0).

Polytron IR Ex is suitable to detect a great number of flammable liquids when calibrated for Methane or Acetone. Since the linearity is of lesser interest, a typical „sensitivity adjustment to be on the safe side" for Polytron IR Ex would be:

- Category: Propane
- Measuring range: 0 to 50 %LEL
- Apply 2.0 % by Vol. Methane
- Adjust to 30 %LEL
- Reduce measuring range down to min. 20 %LEL, if required.

Polytron IR robust gas detector with SS 316 stainless steel housing, sophisticated double compensated optics which ensures less than 2 %LEL signal drift over 24 month, wide temperature range covering all climates (- 40 to + 65°C) and beam block warning before failure to schedule maintenance because of build-up of deposits on the optics.

Recommendation:
Other than **Polytron IR**, none of the detectors should be submersed in water because of possible damage. Only Polytron IR has IP 66 & IP 67 ingress protection, can be hosed off and is fully operational again.

2. Detection toxic gases and oxygen (covering all gases found in a Kraft paper mill)

Polytron 2, Polytron 2 XP Tox a universal transmitter which accepts any DrägerSensor, downloads sensor-specific information from the embedded sensor EEPROM. The sensor has an embedded temperature element which allows to compensates the sensor signal in the range of - 40 to + 65 °C.

Advantages of the Dräger Solution

Catalytic bead detectors:	- economical solution
IR detectors:	- lower measuring ranges along with higher sensitivities result in larger monitoring areas - constant sensitivity over lifetime of the instrument - can be submersed without damage (IP 66 & IP 67)
Open Path:	- monitoring of large areas - low cost of ownership - fast response time
DrägerSensor:	- bigger sensor means bigger electrodes and more electrolyte, hence faster response, higher accuracy, more stability and longer life - embedded micro-chip and temperature element - sensor recognition, numerous self-test functions, remote calibration and signal compensation over the whole temperature range of typically - 40 to + 65 oC

Restrictions

Catalytic bead detectors: - H_2S might be poisoning the sensor

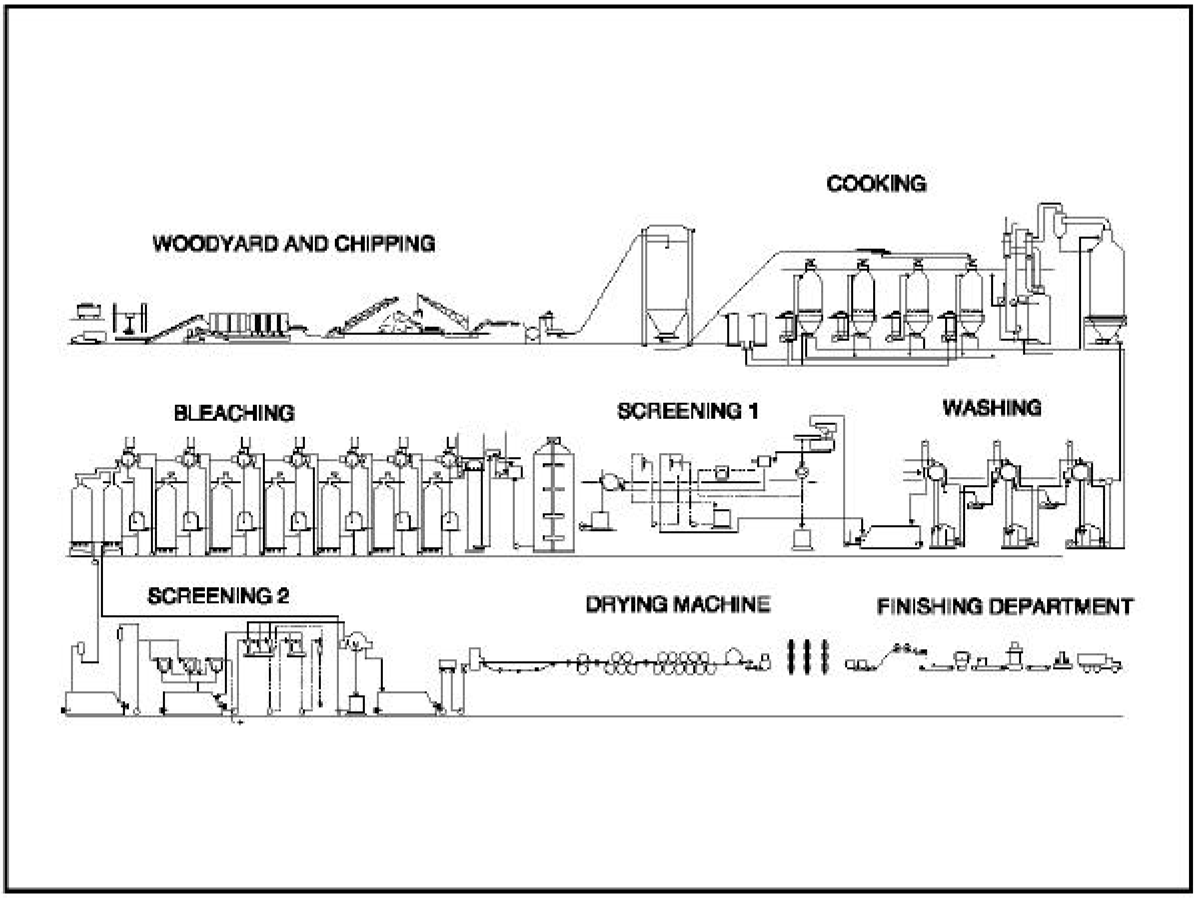
Due to the nature of the pulping process, the transmitters are exposed to excessive moisture and fibers. If possible a splash guard should be used. Dust filters need to be checked on a more frequent basis. Only for Chlorine and Chlorine Dioxide monitoring a dust filter or splash guard should not be mounted. These gases might get trapped on moist surfaces which could result in a increased response time.

References (internal, external)

Information from Sweden:

Usually Ozone O_3 is not used for the bleaching process because of it's high cost. Most paper mills are now using Chlorine Dioxide ClO_2, where they used Cl_2 in the past. A typical installation has 5 to 10 points right around the bleaching process, with a measuring range of 0 to 1 ppm.

Drawings & Pictures



Appendix

Pulp Manufacturing Process Sequence	
Process Sequence	**Description**
Fiber Furnish Preparation and Handling	Debarking, slashing, chipping of wood logs and then screening of wood chips/secondary fibers (some pulp mills purchase chips and skip this step)
Pulping	Chemical, semi-chemical, or mechanical breakdown of pulping material into fibers
Pulp Processing	Removal of pulp impurities, cleaning and thickening of pulp fiber mixture
Bleaching	Addition of chemicals in a staged process of reaction and washing increases whiteness and brightness of pulp, if necessary
Stock Preparation	Mixing, refining, and addition of wet additives to add strength, gloss, texture to paper product, if necessary

Chemical Pulping Process Differences

Pulping Process Type	Typical Pulp Produced	Chemicals Used	Typical Pulp Yield Percent	Type of Wood Used	Typical Pulp Uses
Kraft	Kraft	NaOH, Na_2S	40-50	Softwood and hardwood	Writing paper; paper bags; cardboard; specialty products such as rayon, acetate, and cellophane
Soda	Soda	NaOH	45-55	Hardwood	Writing paper; specialty products such as rayon, acetate, and cellophane
Sulfite	Acid sulfite	H_2SO_3, $M(HSO_3)$ (M=Ca, Mg, Na, NH_4)	45-55	Softwood and hardwood	Writing paper; specialty products such as rayon, acetate, and cellophane
Semi-chemical	Neutral Sulfite Semi-chemical	Na_2SO_3 Na_2CO_3	65-80	Hardwood	Corrugated containers

Exhibit 19: Kraft Chemical Pulped-Chlorine Bleached Paper Production

Process Step	Material Inputs	Process Outputs	Major Pollutant Outputs*	Pollutant Media
Fiber Furnish Preparation	Wood logs Chips Sawdust	Furnish chips	dirt, grit, fiber, bark	Solid
			BOD	Water
			TSS	
Chemical Pulping Kraft process	Furnish chips	Black liquor (to chemical recovery system), pulp (to bleaching/processing)	resins, fatty acids	Solid
			color	Water
			BOD	
			COD	
			AOX	
			VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)	
			VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)	Air
	Cooking chemicals: sodium sulfide (Na_2S), NaOH, white liquor (from chemical recovery)		reduced sulfur compounds (TRS)	
			organo-chlorine compounds (e.g., 3,4,5- trichloroguaiacol)	

Exhibit 19: Kraft Chemical Pulped-Chlorine Bleached Paper Production				
Process Step	**Material Inputs**	**Process Outputs**	**Major Pollutant Outputs***	**Pollutant Media**
Bleaching	Chemical pulp	Bleached pulp	dissolved lignin and carbohydrates	Water
			color	
			COD	
			AOX	
			inorganic chlorine compounds (e.g., chlorate (ClO_3^-))[1]	
	Elemental chlorine (Cl_2), chlorine containing compounds		organo-chlorine compounds (e.g., dioxins, furans, chlorophenols)	
	Hypochlorite ($HClO$, $NaOCl$, $Ca(OCl)_2$) Chlorine dioxide (ClO_2)		VOCs (acetone, methylene chloride, chloroform, MEK, carbon disulfide, chloromethane, trichloroethane)	Air / Water
Papermaking	Additives, Bleached/ Unbleached pulp	Paper/paperboard product	particulate wastes	Water
			organic compounds	
			inorganic dyes	
			COD	
			acetone	
Wastewater Treatment Facilities	Process wastewaters	Treated effluent	sludge	Solid
			VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)	Air
			BOD	Water
			TSS	
			COD	
			color	
			chlorophenolics	
			carbon disulfide	
			VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)	

Exhibit 19: Kraft Chemical Pulped-Chlorine Bleached Paper Production

Process Step	Material Inputs	Process Outputs	Major Pollutant Outputs*	Pollutant Media
Power Boiler	Coal, Wood, Unused furnish	Energy	bottom ash: incombustible fibers	Solid
			SO_2, NO_x, fly ash, coarse particulates	Air
Chemical Recovery System				
Evaporators	Black liquor	Strong black liquor	evaporator noncondensibles (TRS, volatile organic compounds: alcohols, terpenes, phenols)	Air
			evaporator condensates (BOD, suspended solids)	Water
Recovery Furnace	Strong black liquor	Smelt	fine particulates, TRS, sulfur dioxide	Air
		Energy		
Recausticizing	Smelt	Regenerated white liquor	dregs	Solids
		Lime mud	waste mud solids	Water
Calcining (Lime Kiln)	Lime mud	Lime	fine and coarse particulates	Air

* Pollutant outputs may differ significantly based on mill processes and material inputs (e.g., wood chip resin content).
[1] Chlorate only significantly produced in mills with high rates of chlorine dioxide substitution to reduce dioxin and furan production.

Sources: *Pollution Prevention Technologies for the Bleached Kraft Segment of the U.S. Pulp and Paper Industry* (EPA-600-R-93-110), *Development Document for Proposed Effluent Limitations Guidelines and standards for the Pulp, Paper, and Paperboard Point Source Category (1993)* and air release data from *Pulp, Paper and Paperboard Industry - Background Information for Proposed Air Emission Standards: Manufacturing Processes at Kraft, Sulfite, Soda, and Semi-Chemical Mills (NESHAP; 1993).*

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