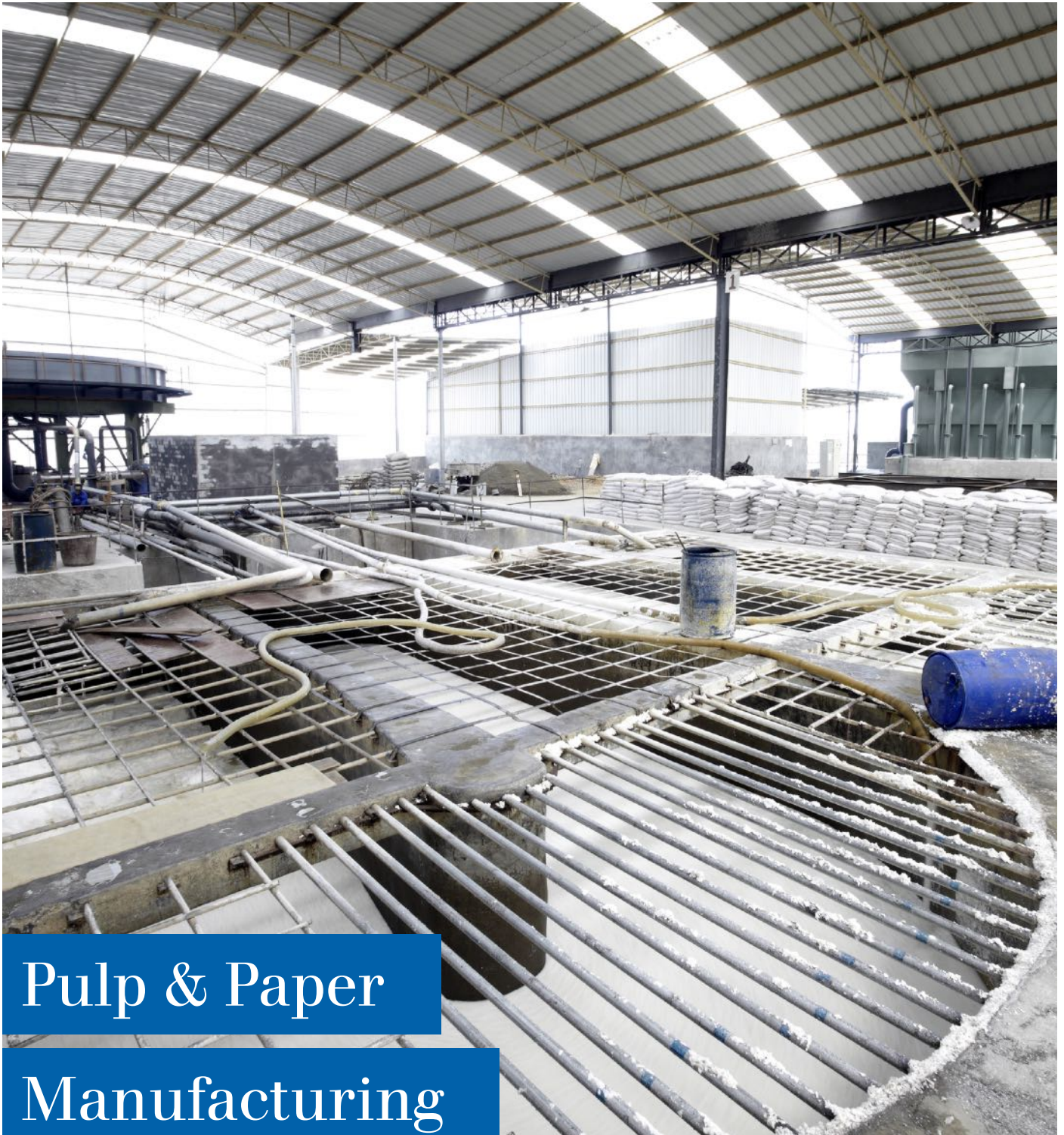




Pulp & Paper Manufacturing Application Note

Introduction

The processes involved in manufacturing paper and paperboard can generally be divided into three steps: pulp making, pulp processing, and paper/paperboard production. Pulp can be 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 such as cotton, flax or 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, this paper describes the processes at Kraft mills using wood, but also includes a general process overview for the other types of mills.

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, semi-chemical pulping combines chemical and mechanical methods. Secondary fiber mills mechanically separate pulp from wastepaper products. Non-wood fiber mills can use mechanical and chemical pulping processes.

Challenge

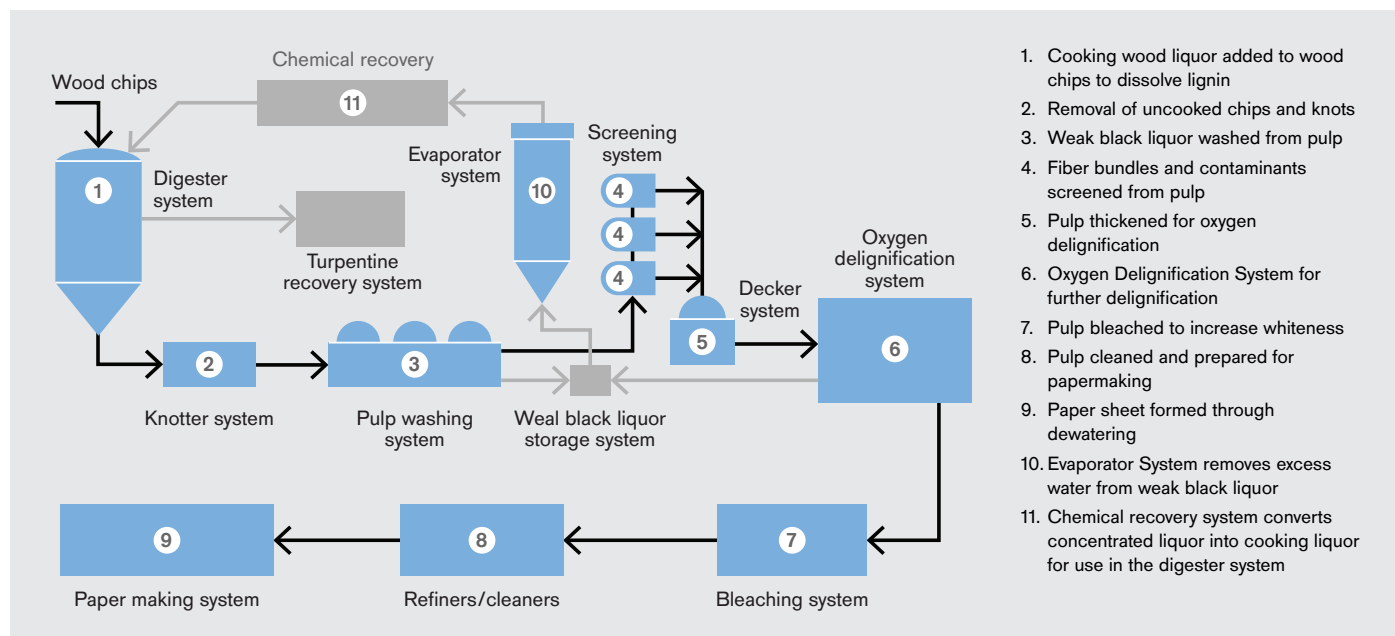
Gases that typically need to be monitored at a pulp and paper mill are bleaching chemicals like chlorine (Cl_2), chlorine dioxide (ClO_2), ozone (O_3) or hydrogen peroxide (H_2O_2); oxygen (O_2) from the delignification system; total reduced sulfur (TRS) such as hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide ($(\text{CH}_3)_2\text{S}$), and dimethyl disulfide ($(\text{CH}_3)_2\text{S}_2$), primarily released from wood chip digestion, black liquor evaporation, and chemical recovery boiler processes; volatile organic compounds (VOCs) such as terpenes, alcohols, methanol, acetone, and MEK from process chemicals that 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 wastewaters to a receiving waterway. Mills with indirect discharge may operate primary treatment systems designed for TSS reduction prior to discharge to a wastewater treatment facility .

The challenge with all these gases is to monitor them so they can be used safely – thus protecting workers and facilities.





The Process at Kraft Paper Mills

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 that 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 deknottting (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 used 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 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 what is called 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, the concentration of solids can range from 60 to 80 percent. The liquor then undergoes oxidation, which is necessary to reduce the 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. This is this a crucial step in the overall Kraft chemical recovery process, when 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 convert sodium carbonate (Na_2CO_3) into active sodium hydroxide (NaOH) and sodium sulfide (Na_2S)¹⁰.

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, 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 H₂S

In the Kraft process, sulfur oxides are a minor issue in comparison to the odor problems created by four reduced sulfur gases, together called total reduced sulfur (TRS): hydrogen sulfide (H_2S), methyl mercaptane (CH_3SH), dimethyl sulfide ($\text{CH}_3)_2\text{S}$ and dimethyl disulfide ($\text{CH}_3)_2\text{S}_2$. TRS emissions are primarily released from wood chip digestion, black liquor evaporation, and chemical recovery boiler processes.

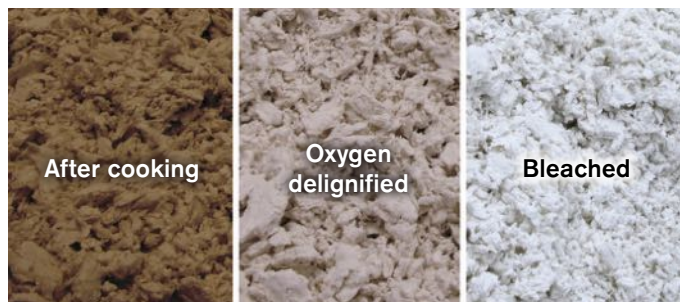
Gas detection with IR sensor or catalytic bead sensor for VOCs

VOCs include terpenes, alcohols, methanol, acetone and MEK from process chemicals, which are mostly solvent sprays and emissions from drying wet tissue and the water treatment process.

Gas detection with DrägerSensor O₂

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.

Bleaching brightens the pulp in a series of chemical operations that are together called a bleaching line, which 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.



Pulp bleaching

The dark color of the pulp is mainly due to residual lignin. This is removed gradually during bleaching.

Typically, the stages are sequenced as an alternating series of bleaching and extraction. 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.

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.

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

Gas detection

Depending on the chemicals used for bleaching, Dräger solutions include:

- **DrägerSensor Cl₂** (for Cl₂ or ClO₂)
- **DrägerSensor H₂O₂**
- **DrägerSensor O₂**
- **DrägerSensor O₃**

Final stages

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 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 conveyed through a series of presses to remove additional water and to continue the sheet forming process. The remaining water 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. Additional processes include calendaring (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

Gas collection systems or non-condensable 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

Some 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

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

The Process at Other Types of Paper Mills

Soda mills

The soda pulping process uses 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 manufacturing.

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), which 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.

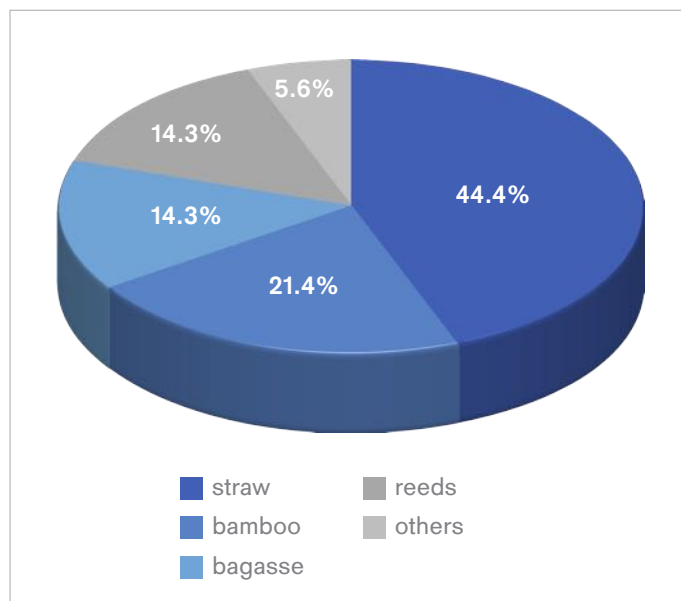
Secondary fiber pulping

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, which may be added directly into the pulper, include hypochlorite (HClO , NaOCl , $\text{Ca}(\text{OCl})_2$), hydrogen peroxide (H_2O_2), and sodium hydrosulphite ($\text{Na}_2\text{S}_2\text{O}_4$).

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.



Dräger Solutions

DrägerSensors for detecting VOCs

- OV Sensor 6810740 oder 6810745 0-20 / 0-200m, LDL 5 ppm (Polytron 7000 / Polytron 8100)
- PIR 7000 Typ 334 ab 0-1400 ppm / 0-100% UEG, MinRAT 350 ppm (Polytron 5700 / Polytron 8700)
- PIR 7000 Typ 340 ab 0-600 ppm / 0-100% UEG, MinRAT 120 ppm (Polytron 5700 / Polytron 8700)
- Cat Ex DQ Sensor 0-100% UEG, LDL 5% UEL (Polytron SE Ex / PEX 1000 / Polytron 5200 / 8200)
- Cat Ex LC Sensor 0-10% UEG, LDL 0,5% UEL (Polytron SE Ex / PEX 1000 / Polytron 5200 / 8200)

For cross-calibration details, please read the manual or contact your local product specialist.

Detecting toxic gases and oxygen (covering all gases found in a Kraft paper mill)

All Dräger toxic gas transmitters can effectively measuring toxic gases. Your local Dräger product specialist can recommend the best solution for your application.

Restrictions

Catalytic bead detectors: H₂S might poison the sensor

Splash guards: 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. 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 an increased response time.

Bleaching process: Ozone (O₃) is not usually used for the bleaching process because of its exceptional oxidative properties and high cost. Most paper mills are now using chlorine dioxide (ClO₂) where they used Cl₂ 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.

Gases included in Gas List

No.	Substance Chemical formula	Short S-formula	Further synonyms	Molw. g/mol	Dens. g/ml	Boil °C	P ₂₀ mbar	Flpt. °C	LEL PTB	LEL IEC	LEL NIOSH	LEL NFPA	LEL RUS	AIT °C
88	Chlorine CAS 7782-50-5 Cl ₂	Cl ₂		70.9 2.45 r	Gas	-34 -29 °F	Gas	NA	NA	NA	NA	NA	NA	NA
					1 ppm = 2.95 mg/m ³			1 mg/m ³ = 0.34 ppm						
No.	WEL Germany	TLV USA	MP	Detectable with		Suitable measuring ranges					Important remarks			
88	0.5 (1.5)	1c (3.0)	EC EC EC EC	Polytron 7000 and P 8100 Cl2 Polytron 5100 Cl2 Polytron 3000 Cl2 Polytron 2000 Cl2		Cl2: 1 / 10 / 100 ppm / LDL = 0.05 ppm 1 + 3 + 5 +10 + 20 + 30 + 50 ppm 1 or 10 or 25 ppm 10 ppm					S = 1.0			

No.	Substance Chemical formula	Short S-formula	Further synonyms	Molw. g/mol	Dens. g/ml	Boil °C	P ₂₀ mbar	Flpt. °C	LEL PTB	LEL IEC	LEL NIOSH	LEL NFPA	LEL RUS	AIT °C
89	Chlorine dioxide CAS 10049-04-4 ClO ₂	ClO ₂	Chlorine peroxide	67.5 2.33 r	Gas	11 52 °F	Gas	NA	NA	NA	NA	NA	NA	NA
					1 ppm = 2.81 mg/m ³			1 mg/m ³ = 0.36 ppm						
No.	WEL Germany	TLV USA	MP	Detectable with		Suitable measuring ranges					Important remarks			
89	0.1c (0.28)	0.1c (0.28)	EC	Polytron 7000 and P 8100 Cl2		ClO2: 1 / 10 / 100 ppm / LDL = 0.05 ppm					S = 0.45 (+/- 20%)			

No.	Substance Chemical formula	Short S-formula	Further synonyms	Molw. g/mol	Dens. g/ml	Boil °C	P ₂₀ mbar	Flpt. °C	LEL PTB	LEL IEC	LEL NIOSH	LEL NFPA	LEL RUS	AIT °C
162	Dimethyl disulfide CAS 624-92-0 (CH ₃) ₂ S ₂	DMDS C ₂ H ₆ S ₂	2.3 Dithiabutane	94.2 3.25 r	1.06	110 230 °F	28	10	1.1* (43)					370 11A T3
						1 ppm = 3.93 mg/m ³			1 mg/m ³ = 0.25 ppm					
No.	WEL Germany	TLV USA	MP	Detectable with				Suitable measuring ranges					Important remarks	
162			IR IR IR IR EC	PIR 7000 type 334, P 8700 type 334 Polytron 5700 type 334 PIR 7000 type 340, P 8700 type 340 Polytron 5700 type 340 Polytron 7000 and P 8100 H2S LC				85 / 100 %LEL (&) 100 %LEL (&) 40 / 100 %LEL 50 + 100 %LEL DMDS: 20 / 50 / 100 ppm / LDL = 1 ppm					S = 0.5	

No.	Substance Chemical formula	Short S-formula	Further synonyms	Molw. g/mol	Dens. g/ml	Boil °C	P ₂₀ mbar	Flpt. °C	LEL PTB	LEL IEC	LEL NIOSH	LEL NFPA	LEL RUS	AIT °C
256	Hydrogen peroxide CAS 7722-84-1 H ₂ O ₂	H ₂ O ₂	Hydrogen dioxide Hydroperoxide Dihydrogen dioxide	34.0 1.17 r	1.24	107 225 °F	1.9	NA	NA	NA	NA	NA	NA	NA
						1 ppm = 1.42 mg/m ³			1 mg/m ³ = 0.71 ppm					
No.	WEL Germany	TLV USA	MP	Detectable with				Suitable measuring ranges					Important remarks	
256		1 (1.4)	EC EC EC	Polytron 7000 and P 8100 H ₂ O ₂ HC Polytron 7000 and P 8100 H ₂ O ₂ LC Polytron 5100 H ₂ O ₂ LC				H ₂ O ₂ : 1000 / 4000 / 7000 ppm / LDL = 100 ppm H ₂ O ₂ : 1 / 5 / 300 ppm / LDL = 0.1 ppm 1 + 3 + 5 + 10 + 20 + 30 + 50 + 100 ppm					+ 100 + 300 ppm	

No.	Substance Chemical formula	Short S-formula	Further synonyms	Molw. g/mol	Dens. g/ml	Boil °C	P ₂₀ mbar	Flpt. °C	LEL PTB	LEL IEC	LEL NIOSH	LEL NFPA	LEL RUS	AIT °C
258	Hydrogen sulfide CAS 7783-06-4 H ₂ S	H ₂ S	Hydrosulfuric acid Sulfuretted hydrogen Sulfane	34.1 1.18 r	Gas	-60 -76 °F	Gas	Gas	3.9 (55)	4.0 (57)	4.0 (57)	4.0 (57)	4.0 (57)	270 11B T3
						1 ppm = 1.42 mg/m ³			1 mg/m ³ = 0.70 ppm					
No.	WEL Germany	TLV USA	MP	Detectable with				Suitable measuring ranges					Important remarks	
258	5 (7.1)	4 (5.7)	EC EC EC EC EC EC EC EC EC	Polytron 7000 and P 8100 H ₂ S Polytron 7000 and P 8100 H ₂ S HC Polytron 7000 and P 8100 H ₂ S LC Polytron 5100 H ₂ S Polytron 5100 H ₂ S HC Polytron 5100 H ₂ S LC Polytron 3000 H ₂ S Polytron 2000 H ₂ S				H ₂ S: 5 / 50 / 100 ppm / LDL = 0.5 ppm H ₂ S: 100 / 500 / 1000 ppm / LDL = 10 ppm H ₂ S: 10 / 50 / 100 ppm / LDL = 1 ppm 5 + 10 + 20 + 30 + 50 + 100 ppm 100 + 200 + 300 + 500 + 1000 ppm 10 + 20 + 50 + 100 ppm 20 or 50 or 100 ppm 20 or 100 ppm					P 8100 performance approved (FM)	

No.	Substance Chemical formula	Short S-formula	Further synonyms	Molw. g/mol	Dens. g/ml	Boil °C	P ₂₀ mbar	Flpt. °C	LEL PTB	LEL IEC	LEL NIOSH	LEL NFPA	LEL RUS	AIT °C
300	Methyl mercaptan CAS 74-93-1 CH ₃ SH	MeM CH ₄ S	Methanethiol Mercaptomethane Thiomethanol Methyl sulphydrate	48.1 1.66 r	Gas	6 43 °F	Gas	Gas	4.1 (82)	4.1 (82)	3.9 (78)	3.9 (78)	4.1 (82)	360 11A T2
						1 ppm = 2.00 mg/m ³			1 mg/m ³ = 0.71 ppm					
No.	WEL Germany	TLV USA	MP	Detectable with				Suitable measuring ranges					Important remarks	
300	0.5 (1.0)	10c (20)	EC	Polytron 7000 and P 8100 H ₂ S LC				MeM: 20 / 50 / 100 ppm / LDL = 1 ppm					S = 0.6	

No.	Substance Chemical formula		Short S-formula	Further synonyms	Molw. g/mol	Dens. g/ml	Boil °C	P ₂₀ mbar	Flpt. °C	LEL PTB	LEL IEC	LEL NIOSH	LEL NFPA	LEL RUS	AIT °C
335	Oxygen CAS 7782-44-7 O ₂		O ₂	R732	32.0 1.10 r	Gas	-183 -297 °F	NA	NA	NA	NA	NA	NA	NA	NA
						1 ppm = 1.33 mg/m³				1 mg/m³ = 0.50 ppm					
No.	WEL Germany	TLV USA	MP	Detectable with				Suitable measuring ranges				Important remarks			
335			EC EC EC EC EC EC EC	Polytron 7000 and P 8100 O2 Polytron 7000 and P 8100 O2 LS Polytron 5100 O2 Polytron 5100 O2 LS Polytron 3000 O2 Polytron 3000 O2 LS Polytron 2000 O2				5 / 25 / 100 vol% / LDL = 0.5 vol% 5 / 10 / 25 vol% / LDL = 0.5 vol% 5 + 10 + 20 + 25 + 50 + 100 vol% 5 + 10 + 20 + 25 vol% 25 vol% 25 vol%							

No.	Substance Chemical formula		Short S-formula	Further synonyms	Molw. g/mol	Dens. g/ml	Boil °C	P ₂₀ mbar	Flpt. °C	LEL PTB	LEL IEC	LEL NIOSH	LEL NFPA	LEL RUS	AIT °C
336	Ozone CAS 10028-15-6 O ₃		O ₃		48 1.55 r	Gas	-112 225 °F	Gas	NA	NA	NA	NA	NA	NA	NA
					1 ppm = 2.00 mg/m³				1 mg/m³ = 0.50 ppm						
No.	WEL Germany	TLV USA	MP	Detectable with			Suitable measuring ranges					Important remarks			
336		0.1 (0.20)	EC EC	Polytron 7000 and P 8100 Ozone Polytron 3000 Ozone			O3: 0.5 / 1 / 1.5 ppm / LDL = 0.02 ppm 0.5 ppm								

No.	Substance Chemical formula		Short S-formula	Further synonyms	Molw. g/mol	Dens. g/ml	Boil °C	P ₂₀ mbar	Flpt. °C	LEL PTB	LEL IEC	LEL NIOSH	LEL NFPA	LEL RUS	AIT °C
384	Sulfer dioxide CAS 7446-09-5 SO ₂		O ₂ S	Sulfurus oxide R764	64.1 2.21 r	Gas	-10 14 °F	Gas	NA	NA	NA	NA	NA	NA	NA
					1 ppm = 2.67 mg/m³				1 mg/m³ = 0.37 ppm						
No.	WEL Germany	TLV USA	MP	Detectable with			Suitable measuring ranges					Important remarks			
384	1 (2.7)	5 (13)	EC EC EC	Polytron 7000 and P 8100 SO2 Polytron 5100 SO2 Polytron 3000 SO2			SO2: 5 / 10 / 100 ppm / LDL = 0.5 ppm 5 + 10 + 20 + 30 + 50 + 100 ppm 10 ppm								

Drawings and 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 chemical 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 pare products, if necessary

Chemical Pulping Process Differences

Pulping process type	Typical pulp produced	Chemical used	Typical pulp yield %	Type of wood used	Typical pulp uses
Kraft	Kraft	– NaOH – Na ₂ S	40-50	– Softwood – Hardwood	Writing paper, paper bags, cardboard, specialty products such as rayon, acetate and cell phones
Soda	Soda	– NaOH	45-55	– Hardwood	Writing paper, specialty products such as rayon, acetate and cell phones
Sulfite	Acid Sulfite	– H ₂ SO ₃ – M(HSO ₃) (M=Ca, Mg, Na, NH ₄)	45-55	– Softwood – Hardwood	Writing paper, specialty products such as rayon, acetate and cell phones
Semi-chemical	Neutral Sulfite semi-chemical	– Na ₂ SO ₃ – Na ₂ CO ₃	65-80	– Softwood – Hardwood	Corrugated containers

Kraft Chemical Pulped-Chlorine Bleached Paper Production

Process steps	Material Inputs	Process Outputs	Major Pollutant Outputs*	Pollutant Media
Fiber furnish preparation	– Wood logs – Chips – Sawdust	– Furnish chips	– Dirt, grit, fiber, bark	Solid
			– BOD – TSS	Water
Chemical pulping Kraft process	– Furnish chips – Cooking chemicals – Sodium sulfide (Na₂S) – NaOH – White liquor (from chemical recovery)	– Black liquor (to chemical recovery system) – Pulp (to bleaching / processing)	– Resins, fatty acids	Solid
			– Color – BOD – COD – AOX – VOCs (terpenes, alcohols, phenols, methanols, acetone, chloroform, MEK)	Water
			– VOCs (terpenes, alcohols, phenols, methanols, acetone, chloroform, MEK) – Reduced sulfur compounds (TRS) – Organo-chlorine compounds (e.g. 3,4,5- trichloroguaiacol)	Air
Bleaching	– Chemical pulp – Elemental chlorine (Cl₂), chlorine containing compounds – Hypochlorite (HClO, NaOCl, Ca(Ocl)₂) Chlorine dioxide (ClO₂)	Bleached pulp	– Dissolved lignin and carbohydrates – Color – COD – AOX – Inorganic chlorine compounds (e.g. 1- chlorate (ClO₃)) – Organo-chlorine compounds (e.g. dioxins, furans, chlorophenols)	Water
			– VOCs (acetone, methylene chloride, chloroform, MEK, carbon disulfide, chloromethane, trichloroethane)	Air / Water

Kraft Chemical Pulped-Chlorine Bleached Paper Production (cont.)

Process steps	Material Inputs	Process Outputs	Major Pollutant Outputs*	Pollutant Media
Papermaking	– Additives – Bleached / Unbleached pulp	– Paper / paperboard product	– Particulate wastes – Organic compounds – Inorganic dyes – COD – Acetone	Water
Wastewater Treatment Facilities	– Process Water	– Treated effluent	– Sludge	Solid
			– VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)	Air
			– BOD – TSS – COD – Color – Chlorophenolics – Carbon disulfide – VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)	Water
Power Boiler	– Coal – Wood – Unused Furnish	– Energy	– Bottom ash: incombustible fibers	Solid
			– SO2 – NOx – 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 (BOS, suspended solids)	Water
Recovery Furnace	– Strong black liquor	– Smelt – Energy	– Fine particulates, TRS, sulfur dioxide	Air
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 mill 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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