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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

Pollution Prevention and Abatement Guidelines

for the

Pulp and Paper Industry

This document is one of the chapters prepared for a forthcoming set of pollution guidelines jointly prepared by the World Bank, UNIDO and UNEP. The purpose is to give a succinct overview of the main issues affecting the subject industry sector, and of the best technologies and techniques available to avoid undue environmental impact. The regulatory framework within which the industry operates is briefly described by examples, and target discharge limitations that are economically achievable with currently available technology are suggested. The intended readership includes project personnel in investment and development institutions as well as anyone who wish to familiarize themselves with the key aspects of the industry concerned. The information is not sufficient by itself for detailed project design. For this more elaborate advice can be obtained from the references quoted or from other specialized sources of information. Comments on the document should be submitted to Mr. Anil Somani, the World Bank, IFC/M.I.G.A., Headquarters, 1818 H Street, NW, Washington D.C. 20433, U.S.A., with copy to UNIDO, Att. Mr. Ralph Luken, P.O. Box 300, A-1400 Vienna, Austria.

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EXECUTIVE SUMMARY

Paper and board are made mainly from raw materials containing cellulose fibres. Worldwide, about 61% of cellulose fibres used for paper-making are produced from wood, 34% from recycled paper and 5% from non-wood cellulosic resources such as bagasse, cereal straws, bamboo, reeds, esparto grass, jute, kenaf, flax and sisal. In developing countries about 60% of cellulose fibres originate from non-wood raw materials.

All the main processes in the pulp and paper industry, from raw material preparation over pulp preparation and bleaching to papermaking, require measures to protect the environment from process discharges. The industry has also a long tradition of integrating environmental controls in the process design with extensive recycling and reuse of waste streams.

Toxic substances generated in the conventional bleaching process using chlorine have received much attention in recent years. These can be reduced and some substances eliminated completely by oxygen prebleaching and substitution of chlorine with chlorine dioxide as well as using peroxide or other process technology. In many countries consumers now accept or prefer unbleached or less bright paper products for environmental reasons. This has resulted in increased use of unbleached or chlorine-free bleached pulp and recycled fibres in the manufacture of paper and board.

The chemical pulp manufacturing process generates a large oxygen consuming liquid waste stream. This can be limited by efficient washing of pulp, collection of the black liquor displaced and extracted in the washing process and by incineration of the evaporated black liquor. In developing countries, producing about 15% of the world pulp often from non-wood raw material, most mills are small - below 100 adt/day. These mills are associated with a high pollution load since they often have no incineration of black liquor and recovery of chemicals as equipment for these processes is too expensive. It is therefore of utmost importance to develop a lowcost chemical recovery system for such small pulp mills.

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1. INTRODUCTION

Paper and board are made mainly from raw materials containing cellulose fibres. Worldwide, about 61% of cellulose fibres used for paper-making are produced from wood, 34% from recycled paper and 5% from non-wood cellulosic resources such as agricultural residues, natural plants and cultivated crops. In developing countries about 60% of cellulose fibres originate from non-wood raw materials, such as, bagasse, cereal straws, bamboo, reeds, esparto grass, jute, kenaf, flax and sisal.

Wood, as well as non-wood raw materials (other than cotton), consist of only 50-60% cellulose fibres. The remaining constituents (lignin and hemicellulose) extracted in the chemical pulping process must be incinerated or used as a byproduct and/or treated to avoid organic waste pollution.

Some processes in the pulp industry generate toxic substances, such as chlorinated organic compounds from chlorine bleaching of pulp. The concern over the environmental effect of these substances is resulting in tighter effluent standards and the development of cleaner pulp and paper technologies and techniques.

The properties of raw materials, such as fibre length and width decide strength properties of paper manufactured from these pulps. Short fibre length raw materials, e.g., bagasse and straw, result in low strength of paper. They are suitable for production of writing and printing papers but less suitable for production of packaging papers. Mechanical pulps have a low strength as the fibres are degraded to shorter particles in the mechanical treatment, and lignin is not extracted from the fibres. These pulps have, however, high opacity and are suitable for newsprint manufacture.

More intensive bleaching is required for high brightness pulps. The amount of bleaching chemicals depends on the pulping process and the lignin content of raw material. Sulphate (kraft) pulps require more bleaching chemicals than sulphite pulps resulting in generation of more toxic compounds. The trend in the past was to consume writing and printing papers of high brightness and use bleached or semi-bleached pulps for high grade packaging materials. Environmental awareness has reverted this trend to some extent. Chlorine-free bleached pulp is now used for some products even if the brightness is lower. Unbleached pulp is used for paper and board products such as envelopes, packaging materials, etc.. Writing papers for writing pads and note books are manufactured from recycled fibres (waste paper) even if the brightness is lower.

2. MANUFACTURING PROCESSES

The main processes in the pulp and paper industry are raw material preparation, pulp preparation, pulp bleaching and papermaking (Figures 1 and 2) and paper converting.

Mills that only produce pulp which they sell to paper mills in other locations are called market pulp mills. Integrated pulp and paper mills are producing pulp and paper at the same site. The pulp is usually pumped to the paper mills as a slurry. Non-integrated paper mills are producing paper only and are obtaining pulps from market pulp mills and/or use waste paper as fibre source. In converting plants, paper and board is converted to final products such as coated papers, bags, corrugated boxes and other products. Converting operations may be a part of a paper mill or separately situated.

Cellulosic Fibrous Raw Material Preparation

Wood may be received at the pulp mill as logs, chips, and sawmill residues. Agricultural residues such as bagasse or straw are received in bales. Bamboos are usually received in bundles.

The bark from wood logs is first removed by friction with other logs in barking drums by using mechanical tools or water jets (hydraulic debarking). Barking drums may be operated with or without water. Better debarking is achieved and wood losses are lower when water is used, but polluting substances are extracted from the bark. The cleaned wood logs or bamboo sticks are disintegrated by chipping into particles of suitable size (about 30 x 30 x 4 mm). The chips are screened to separate those which are too small or too large and transferred to storage bins or piles for later use. Bagasse is depithed in a dry or wet process.

Pulp Preparation

Cellulose pulp is produced from wood or non-wood cellulosic raw materials. The raw materials are processed with solutions of chemicals under controlled conditions of temperature and time or by separating fibres from the raw material by mechanical or combination of mechanical and chemical means.

Paper-making pulps are used for the manufacture of paper and board, while dissolving pulps are primarily used for conversion into chemical derivatives of cellulose and synthetic fibre manufacture.

Mechanical pulps are papermaking pulps made entirely by mechanical means from various raw materials, but usually softwood, in some cases at elevated pressure and temperature. Groundwood pulp is made by grinding wood logs against the abrasive surface of a large rotating stone. Pressure groundwood is made under elevated pressure and temperature. Mechanical processing of wood chips or saw dust through disc refiners produces refiner mechanical pulp. Thermomechanical pulp is made using treatment in disc refiners under elevated temperature and pressure.

Mechanical pulps from softwoods and some light coloured low density hardwoods can be made without chemical pretreatment. Non-wood raw

materials require usually chemical pretreatment to achieve desired mechanical and optical properties.

Mechanical pulps have good opacity and can therefore be used in low cost writing and printing papers. However, they do not have sufficient brightness and strength properties for better grade papers and soon discolour. Bleaching is therefore necessary to satisfy the demands of better paper products. Post treatment with chemicals may improve strength properties.

Chemi-mechanical pulps are papermaking pulps made by mechanical means after a chemical pretreatment. Chemi-mechanical pulps include chemi-thermo-mechanical pulps usually with sodium sulphite pretreatment of softwoods or hardwoods and in some cases of bagasse. Cold soda pulps are pretreated with caustic soda.

Semichemical pulps are papermaking pulps made by quick cooking and mechanical treatment of softwood and hardwood chips.

Chemical pulps are made by cooking fibrous raw materials in large pressure vessels (digesters) with solution of chemicals at elevated pressure and temperature. Digestion proceeds to the point at which most of the non-cellulosic components binding the fibres are dissolved and the fibres can be separated by mild mechanical action, e.g., by blowing the cooked chips from the digester.

The main chemical pulping processes are the kraft (sulphate) (about 70% of world production), soda and sulphite processes. Sulphate chemical pulps are obtained by cooking of raw materials with aqueous solutions of caustic soda and sodium sulphide. Soda chemical pulps are cooked with caustic soda only, while sulphite pulps are cooked with bisulphite liquor with or without free dissolved sulphur dioxide. While it is possible to cook all cellulosic raw materials by the kraft and soda process, some hardwoods cannot be cooked by the bisulphite process. Kraft pulps are a variety of sulphate pulps with high mechanical strength used mainly for manufacture of papers of high quality and durability.

Unbleached chemical pulps are used mainly for manufacture of packaging materials. For manufacture of writing and printing papers the brightness of pulp is increased by bleaching.

Waste paper is an important raw material in paper and board manufacture. An increasing amount is reclaimed after consumer use and/or from converting processes. Worldwide, waste paper recovery in 1989 was 35% and its utilization 34%. Some countries recover more than 50%. Waste paper is a very significant part of the municipal waste. Its recovery and utilization are ecologically desirable as it reduces landfill space requirements. In countries with shortage of wood, waste paper utilization is preventing over-cutting of forests. Replacement of virgin pulp by waste paper also decreases energy

demand as energy consumption in waste paper processing is considerably lower than in pulp manufacture.

Waste paper is treated mechanically (slushed, screened and refined) for utilization in paper and board manufacture. De-inking with alkalies and surfactants followed by washing and/or flotation of ink is used for better grades such as newsprint or writing papers. The BOD and COD discharge in mechanical waste paper processing is about 15 to 20 kg BOD₅ and 70 kg COD per tonne of waste paper processed. In de-inking, emissions are higher (BOD₅ 15 to 40 kg/t, COD 50 to 90 kg/t).

Losses in repulping and screening of waste paper vary between 1-35% depending on waste paper grade. However, the solid wastes would have been dumped in any event. Waste paper is used mainly in board packaging and tissue paper manufacture, but utilization in writing and printing paper, especially newsprint after de-inking is increasing.

Pulp Bleaching and Drying

The most common bleaching agents for all mechanical pulps are peroxides. Hydrosulphites and peroxides are used individually or in combination when bleaching groundwood. Sodium or hydrogen peroxide and sodium hydrosulphite are the specific chemicals frequently used. Zinc hydrosulphite is gradually abandoned due to the toxicity of zinc.

In chemical pulp bleaching elementary chlorine, sodium or calcium hypochlorite and chlorine dioxide are used. Alkalies, mainly caustic soda sometimes combined with oxygen and/or peroxide are used to extract chlorinated reaction products.

Oxygen prebleaching is increasingly used to reduce consumption of elementary chlorine, which forms partially toxic chlorinated compounds. Elementary chlorine can be avoided in hardwood kraft and sulphite pulp bleaching. This is achieved by substituting chlorine with chlorine dioxide in combination with oxygen prebleaching and, in some cases, use of peroxides.

The market pulp to be used in non-integrated paper mills is converted on a Fourdrinier or double wire machine or cylinder mould to a thick mat. The mat is subjected to mechanical pressure in a series of presses and then dried to air-dry condition (about 10% moisture content). The wet pulp can also be dried in a flash drying system and pressed in bales. Sometimes wet market pulp is used omitting the final drying step.

Papermaking

In an integrated paper mill the pulp is transferred as a slurry directly to the papermaking process. The non-integrated paper mill receives the pulp in

dry or semi-dry form. The paper stock¹ is prepared by repulping the dry or semi-dry pulp in water.

The stock is mechanically treated in beaters or refiners to produce paper with necessary characteristics. The level of cutting and surface brushing varies with the type of pulp used and the desired paper properties.

Paper is made by deposition of a suspension of fibres and fillers on to the moving forming device of a paper machine. Here the largest part of the water is removed. The water remaining in the wet web is removed by pressing and finally by drying on a series of heated hollow cylinders.

There are different paper machine designs:

- Fourdrinier former.
- Cylinder or vat paper machine.
- Twin-wire paper machine.

Chemical additives may be a part of the paper stock to improve the papermaking process and the properties of the paper. Rosin is used to reduce water absorption of paper and prevent blotting of ink. Fine pigments are added to increase opacity and brightness of writing and printing papers. These pigments, or fillers, are generally white and usually of mineral origin such as clay, calcium carbonate and titanium oxide. Many other additives such as wet strength resins, dyestuff, starches and other substances may be used depending on the end use requirements. Retention aids are used to reduce loss of solid particles such as fillers and short fibres during sheet making.

Paper and board are made stronger, smoother, glossier and water absorption may be reduced by surface sizing in the paper machine. The same results can be achieved by applying coating slips or other materials in liquid form on one or both surfaces of the product in or off the paper machine. Mechanical treatments as calendering with heat and pressure are also used to achieve desired physical properties.

A coating slip is a slip in which the pigment is generally a white mineral of very small particle size. It also contains an adhesive or binder such as casein, starch and synthetic polymers. Other additives such as colouring matter, dispersants or viscosity modifiers may also be present. The coating slip is applied, levelled and the excess removed by various applicators such as rolls, a blade, rods or a uniform stream of compressed air called air knife.

¹ Stock is an aqueous suspension of one or more papermaking pulps and other materials from the stage of disintegration of the pulp to individual fibres to the formation of the web or sheet of paper or board.

3. WASTE CHARACTERISATION AND ENVIRONMENTAL IMPACTS

Pulp and paper manufacture can have a considerable impact on the environment as solid, liquid and gaseous wastes are generated in various parts of the operations. The greatest environmental impact comes from pulping and bleaching of chemical pulp. Possible points of emission in chemical pulping and bleaching are presented in Figure 1. Mechanical pulping and papermaking, displayed in Figure 2, generate fewer pollutants.

Waste Quantities and Qualities

Air Emissions

Power plants in pulp and paper mills, producing steam and electricity, are a source of NO_x, CO, sulphur dioxide and fly ash emissions. When using low-grade coal or sulphur rich fuel oil sulphur dioxide and fly ash emissions may be high. If natural gas is used as fuel, sulphur dioxide and fly ash are not emitted.

The kraft (sulphate) cooking process generates highly malodorous hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl-disulphide. These compounds make up the total reduced sulphur (TRS) groups. In the sulphite cooking processes sulphur dioxide is generated. The bisulphite processes emit odorous compounds containing reduced sulphur in small amounts. Fly ash particles are generated if the chemicals from cooking are recovered by incineration of waste liquor in a recovery furnace. Some sulphur dioxide is also formed in the recovery furnace. Ash particles from a sulphate pulp mill consist mainly of sodium carbonate and sulphate, while from a magnesium-bisulphite mill the particles consist of magnesium oxide. No appreciable emissions are generated in the soda process except fly ash from soda recovery.

Elementary chlorine and chlorine dioxide are emitted in small amounts from various parts of a bleach plant such as washers, towers, tank vents, sewers. Generally, concentrations are not significant, but the emissions are odorous and irritating. The total chlorine and chlorine dioxide emission are about 0.2-0.4 kg/t of pulp. Hydrogen sulphide may be generated in poorly mixed parts of covered tanks.

Water Discharges

Water is used in large quantities in the manufacture of pulp and paper. In the various process steps it dissolves the chemicals used as well as the non-cellulosic materials generated in pulping of raw materials.

The quantity of waste water discharge from modern mills has decreased considerably in the last two decades due to increased in-plant recycling of water.

The main parameters for characterizing the degree of contamination of liquid-effluent include 5-day biological oxygen demand (BOD₅) and total suspended solids (TSS). Colour is important for characterization of chemical pulping effluent. Some countries use the 7-day biological oxygen demand (BOD₇) and chemical oxygen demand (COD) as parameters. COD expresses full oxidation of the organic substances in effluent. Effluent from biological treatment of wastewater may be characterized by nitrogen and phosphorous content. Typical values of water flows, BOD₇ and TSS emissions for untreated liquid effluent are shown in Table 1.

Type of production	Water flow	BOD ₇	TSS
	m ³ /t of product	kg/t of product	
Sulphate (kraft) pulp mill (bleached)	40	20	15
Groundwood	-	15* 30**	8
Thermomechanical pulp	-	22* 35**	8
Fine paper mill, sulphate new machine	20	1.6	1.4
Fine paper mill sulphate (old paper machine)	60	2.4	7
Tissue paper (from waste paper)	25	15.0	---
News print paper (mechanical pulps)	10-20	-	-
* unbleached - peroxide bleached --- depends on waste paper grade			
Source: The Finnish Pulp and Paper Research Institute (1992).			

Amount of TSS generated depends on raw material type. For tissue paper from waste paper TSS can be very low if the mill water system is almost closed.

In dry debarking the BOD₅ discharges are negligible (0 - 3 kg/t of wood), but are higher in wet debarking (4 - 12 kg/t). If bagasse is sprinkled with recycled water during storage, discharges may be 20 to 40 g BOD₅/t of bagasse pulp.

In chemical pulping about 50% of the raw material is dissolved in the cooking liquor generating 300 to 390 kg BOD₅ and a colour corresponding to 1100 - 1200 kg Platinum per ton of pulp. In kraft pulp mills and in most sulphite mills 95 to 99 per cent of the dissolved substances are extracted from the pulp by washing, evaporated and eliminated by incineration. The condensate from evaporation of kraft (sulphate) cooking waste liquor (black liquor) contains 12 - 20 kg BOD₅/t pulp and is treated internally. The BOD load of sulphite waste liquor condensate is higher and is sometimes treated externally by anaerobic digestion.

Generation of pollutants from mechanical pulping is 15 to 25 kg BOD₅/t of pulp and in chemi-mechanical pulping three to four times higher.

Bleaching of chemical pulps generates additional BOD load, highly coloured material and chlorinated organic substances, especially in the chlorination and alkaline extraction stages. The amount of AOX (absorbable organic chlorine) in these effluents is 3 to 8 kg/t of pulp. This can be reduced by oxygen prebleaching and by extended delignification resulting in a lower lignin content of pulp and consequently in a reduced need for elementary chlorine in bleaching.

Generation of pollutants from peroxide or hydrosulphite bleaching of mechanical pulps are not as high as in chlorine bleaching of chemical pulps.

Waste water from pulping also contains suspended solids, mainly short fibres and rejects from screening (cleaning) of pulp. The discharges are usually about 10 to 50 kg/t of pulp. The amounts depend on the raw material used and may be higher if agricultural residues are processed or dissolving pulp produced.

In non-integrated paper mills the BOD₅ discharges are low (usually 2 kg/t of paper) as only a negligible part of the pulp is dissolved. Some chemical additives are not completely absorbed by fibres and contribute to BOD₅ discharges, such as rosin size or unmodified starches. Other substances as retention aids may contribute to nitrogen content in waste water.

When waste paper is used for papermaking the BOD₅ emissions are 15 to 20 kg/t and in de-inking 15 to 40 kg/t of processed waste paper.

The suspended solids in papermaking waste waters are short fibres and fillers such as clay or calcium carbonate. Amounts vary widely, typically between 2 to 20 kg/t of paper, depending on the pulp used, amount of fillers and grade of paper produced.

Solid Wastes and Sludges

The characteristics and amounts of solid wastes and sludge will vary considerably from one mill to another. The main source of solid wastes is

wastewater sludge from sedimentation and biological treatment of effluent. Bark and wood waste represent a considerable amount, but is usually burned. Ash from power plant and bark burning, is also significant. Other wastes are paper trash and miscellaneous materials (Table 2).

TABLE 2. SOLID WASTES IN PULP AND PAPER MILLS (Scandinavian Common Practice)					
Type of waste	Kraft pulp mill integr. *	Woodfree papers **	Coated papers	Wood containing papers	Paper and board waste paper ***
	Kg/t	kg/t	kg/t	kg/t	kg/t
Bark, wood residues	300 ⁽¹⁾	-	-	150	19
Screening rejects	(2)	5	(2)	(2)	62
Sludge, dregs **	45	25	35	35	92
Incineration residues ***	10	20	25	15	6
Others	5	5	5	5	4
(1) Incinerated					
(2) Included in sludge					
* as dry matter					
** non-integrated					
*** depends on fuel used					
Source: The Finnish Pulp and Paper Research Institute (1992).					

Fugitive Emissions

See under air emissions above!

Upset and Emergency Conditions

See under occupational health and safety below!

Impact on Receptors

Discharges

Waste waters from pulping have a biological oxygen demand (BOD₅) which at higher levels has a negative influence on the biological balance of the

recipient waters (rivers, lakes). Carbohydrates and their degradation products are mainly responsible for high BOD₅. Lignin is biodegradable in the long term only and is responsible for the brownish colour of effluent.

Chlorinated organic compounds in bleaching effluent (AOX) are toxic and have sub-lethal effects on fish even at a dilution ratio of 1 to 5000 and may bioaccumulate in fish. The amount of toxic materials can be reduced to some extent by biological treatment of waste waters. Level of toxicity depends upon specific chemical identity of AOX which consists of many chlorinated compounds, e.g., dioxins and furans.

There are indications that in the pulping process some yet unidentified non-chlorinated compounds may be generated that have adverse environmental effects.

Chlorine and especially chlorine dioxide air emissions can be detected by odour in adjacent populated areas if emitted gases are not collected and neutralized.

Malodorous TRS compounds influence negatively the atmosphere and are irritating to population. The odour threshold is extremely low as shown in Table 3. Toxic effects are at many times higher concentration.

Compound	Type of odour	Approximative Odour Threshold	Formula
Hydrogen Sulphide	Rotten eggs	1 ppb	H ₂ S
Methyl Mercaptan	Rotten cabbage	1 ppb	CH ₃ SH
Dimethyl Sulphide	Vegetable sulphide	10 ppb	CH ₃ SCH ₃
Dimethyl Disulphide	Vegetable sulphide	10 ppb	CH ₃ SSCH ₃

Source: Bibliography 12

The product

Cellulose fibres are separated from non-toxic vegetable raw materials. However, dioxins are generated in traces in chlorination bleaching of chemical pulps. The content of dioxins in pulp is extremely low and only products with direct contact with food or frequent contact with skin may require pulp without dioxin content. This can be achieved by reducing or excluding chlorine in bleaching.

Occupational Health and Safety

The products of pulp and paper manufacture are not harmful to health, but some chemicals used in the process are dangerous.

Caustic soda

Caustic soda is usually transported to pulp mills as 50% solution. It will cause damage by skin contact and should be washed away immediately with water. Caustic soda is particularly damaging for the eyes. Persons handling caustic soda should wear protective clothing and safety goggles.

Chlorine

Chlorine gas in the air has a penetrating odour and a yellow-green colour. It is a respiratory irritant. The factory threshold of chlorine gas is 0.2 to 3.5 ml/m³. Concentrations of 3 to 5 ml/m³ can be tolerated for 30 minutes without any subjective feeling of malaise. Running of eyes and coughing occurs at concentrations of 15 ml/m³ and higher. Exposure to concentrations of 40 to 60 ml/m³ leads to the development of toxic tracheobronchitis.

Employees in the chlorination area should have escape-type respirators. Personnel entering an area with high chlorine concentrations should be equipped with self-contained breathing apparatus and full protective clothing suitable for dealing with liquid chlorine.

Chlorine dioxide

Chlorine dioxide is highly irritant on inhalation routes. The effect is similar to chlorine. Chlorine dioxide is inflammable with organic substances.

Hydrogen sulphide and organic reduced sulphur compounds (TRS)

Hydrogen sulphide is irritating and injurious already at low concentrations. Acute poisoning is quick but detoxification is also fast. Exposure to concentrations of 100 - 140 mg/m³ for several hours may result in light poisoning, while poisoning may occur at 280 mg/m³ after one hour. Concentrations over 1400 mg/m³ may be poisonous after a few minutes only. These concentrations are highly unlikely in a mill atmosphere, but may occur in covered tanks and chests.

Methylmercaptan and dimethylsulphide are similar to hydrogen sulphide, but are less irritating and less poisonous, but more malodorous even at lower concentrations. Chemicals for improving paper properties have to be handled with care.

Noise

Noise in a paper mill is an important occupational hazard. Fast moving machines, such as vacuum pumps, refiners, etc. generates intensive noise. Aids for ear protection are required to avoid health damage.

A paper machine has fast moving cylinders, roll presses and similar mechanically dangerous parts. Entering of limbs should be avoided by protective railing, nets etc.

4. POLLUTION PREVENTION AND CONTROL

Management Implications

Effective pollution prevention and control requires a strong commitment from management. A corporate environmental policy that gives clear goals and targets related to health, safety and the environment should be established and communicated to all employees. Adequate resources and an implementation plan is required to ensure that targets can be met and the results reported.

Pollution prevention and control measures can be divided into three general categories: eliminating as much waste as possible at the point of generation; recycling wastes back into the production process or into saleable products; and treatment of wastes to reduce their volume or toxicity. Source reduction and recycling provide in general better solutions in both economic and environmental terms. It should therefore be established practice that all opportunities for reducing or recycling wastes have been exhausted before any investment in end-of-pipe treatment is made.

Source Reduction

Good housekeeping and proper management minimize spills and other accidental discharges. Specific measures for source reduction include:

- Application of dry instead of wet debarking eliminates BOD discharges from wood debarking.
- Application of retention aids, which increase retention of fibres and especially fillers in the paper sheet, reduces the concentration of suspended solids in papermaking waste water.
- Appropriate screening system, e.g., increasing hydrocyclone stages reduces screening rejects.

Chlorinated compounds from bleaching are reduced by:

- **Uniform delignification by improved control of chip size and cooking conditions such as temperature and chemical concentrations.**
- **Good washing of pulp before bleaching.**
- **Reducing lignin content in pulp before bleaching by extended delignification in cooking or by pre-bleaching with oxygen under elevated pressure or by combination of both methods.**
- **Low chlorine multiple (low chlorine charge on lignin), pH control and split addition of chlorine in the chlorination stage.**
- **Partial or complete substitution of chlorine by chlorine dioxide in the chlorination stage. This is further enhanced by use of high intensity mixers at critical bleach chemical addition points.**
- **Application of oxygen and/or peroxide at hydrostatic pressure in the alkali extraction stage.**
- **Application of peroxide bleaching especially in bleaching of sulphite pulps.**

Air emissions may be reduced by:

- **Displacement cooking, i.e., injecting cold black liquor before blowing the pulp from the digester, reduces TRS emissions. The TRS generated in cooking is dissolved in the black liquor and can be stripped in a distillation column and incinerated in the lime kiln or other incinerator.**
- **Black liquor oxidation reduces TRS emissions in the recovery furnace.**
- **Incineration of highly concentrated black liquor (about 75% concentration) instead of a black liquor of 60 - 65% solids, nearly eliminates sulphur dioxide emissions from the recovery boiler.**

Recycling and/or By-product Recovery

The pulp and paper industry has a long tradition of recycling and reuse of water, process chemicals and raw materials. Examples of this include:

- Recovery of pulping chemicals by collection, evaporation and incineration of pulping waste liquor (black liquor) eliminates at least 90 - 98 % of dissolved substances contributing to BOD and colour emissions.
- Hot stock screening of pulp before washing, instead of screening washed pulp, improves collection of liquid waste (black liquor) from pulp. Rejects (coarse fibres) from washed pulp still contain appreciable amounts of dissolved solids contributing to BOD. The rejects from hot stock screening are refined and recycled to the pulp.
- Improved control of the pulp washing process and application of high-efficiency washers such as belt washers increase collection of dissolved solids in black liquor to 97 - 99% with a corresponding decrease of BOD emissions.
- Anaerobic biological processing of condensate from black liquor evaporation may reduce BOD₅ in condensates by 90%.
- Suspended solids discharged in waste water can be reduced by recycling of process water especially after improved primary recycled water treatment.

Add-on Treatment Technologies

Air emissions

Sulphur dioxide emissions are not a problem in the pulp mill itself, as these can be reduced by proper operation of the chemical recovery boiler. Use of auxiliary fuel with high sulphur content in the boiler plant may require desulphurization and flue gas scrubbing.

The TRS gases in the sulphate mill should be carefully collected in various parts of the mill by headers, hoods and venting equipment. Condensate from evaporation of black liquor should be stripped of TRS in a column and incinerated to sulphur dioxide with the other TRS gases. This is usually achieved in a lime kiln. In mills with an unfavourable location, standby incineration equipment should be installed to prevent heavy emissions in case the lime kiln is not in operation.

Electrostatic precipitators and scrubbers should be used to remove particulate emissions from the recovery furnace, boiler plant and lime kiln.

Liquid wastes

Liquid wastes should be reduced in both volume and concentration preferably by in-plant waste minimization measures. Spills and accidental discharges should be continuously monitored. Storage basins before treatment will serve to absorb these discharges and provide for a constant loading on the effluent treatment facilities. Volume of liquid waste can be reduced by increased water recirculation. For some raw materials and products, e.g., box board from waste paper, completely closed mills exist.

External effluent treatment includes neutralization, primary treatment to remove settleable solids and biological (secondary) treatment to reduce BOD₅ and toxicity. Screens placed ahead of these treatments remove large pieces discharged to the sewers from process operations or by accident.

Effluents from individual bleaching stages may be either highly acidic or highly alkaline. Effluent from mechanical pulp mills and most paper mills is mildly acidic. Where the pH in the effluent requires only a small adjustment, a liquid alkali such as caustic soda, or an acid, such as sulphuric acid can be used for neutralization. Where wastes are highly acidic lime is used for neutralization.

Settleable solids are removed in a clarifier, usually a circular tank in which the particles are allowed to settle to the bottom. In some cases slow stirring is used to cause an agglomeration of particles. Flocculators are sometimes added to enhance flocculation. Some mills use settling basins either following or in place of clarifiers. They function entirely by gravity, and have a retention time of up to 8 hours. The sludge collected at the bottom of these units are withdrawn at regular intervals and handled by various disposal methods.

Biological treatment is now required for effluent from new mills in most industrialized countries. Such treatment facilities are also being installed at many older mills. This type of treatment reduces the oxygen demand and the acute toxicity of the effluent and usually renders it non-toxic to fish, thus making it suitable for discharge to most surface waters.

Where sufficient land is available, aerated lagoons are most often used to provide extended detention of pulp and paper mill effluent. This system will consist of one or more lagoons equipped with aerating devices and providing a retention period of several days. As a rough guide, one cubic metre of lagoon capacity will be required per 30 grams of BOD₅ in the influent. As an average, the system will provide a 90% reduction in BOD₅, with a total retention period of about 10 days.

The activated sludge process is even more effective but because of the higher capital and operating costs, its use is limited to situations where sufficient land is not available. The activated sludge process also requires a high

degree of operator attention and skills. Other methods, such as oxidation ditches and trickling filters, have also been effective.

The most important waste water technologies (aerated lagoons and activated sludge) are effective but require high investment and operation costs. In activated sludge treatment large amounts of sludge has to be disposed of (about 5 tons of 15% concentration sludge per ton of decreased BOD₅). The use of anaerobic treatment technology is rapidly increasing as a cost-effective way of meeting more stringent effluent limitations. Anaerobic treatment produces biogas which can be used as fuel in the mill.

Capital, Operating and Maintenance costs

In 1991, 10% of the total investment costs in the pulp and paper industry were for environmental protection. The operating costs have been 1.6-1.9 % of the total operating costs. Waste water treatment costs depend on the process applied.

A cost comparison between activated sludge and aerated stabilization basin for a 270,000 ADT/a greenfield mill shows the following data (prices USA, I-Quarter 1983):

<u>Treatment</u>	<u>Activated sludge</u>	<u>Aerated stabilization basin</u>
<u>Type of cost</u>		
Total capital costs (million US\$)	39.7	27.2
Capital costs per ton of pulp (US\$/adt)	147	100
Capital costs assuming 10% interest and 20 years of pay back (US\$/adt)	17	12
Operating cost per ton of pulp (US\$/adt)	11	6
Total (US\$/adt)	28	18

The increase in the total pulp operation costs is expected to be between 7 to 9 per cent and 4 to 6 per cent for activated sludge treatment and aerated stabilization basin, respectively. This percentage however will depend very much on the mill characteristics.

Ultimate Disposal Options

Biological treatment produces large volumes of sludge. Land disposal, by lagooning or dumping, has been used to handle sludge. This method is being used less and less because of odours from decomposition of the materials, potential pollution of surface and ground waters, and land use considerations. However, with the application of proper sanitary landfill measures this method should create few or no environmental problems.

Dewatering followed by incineration of sludge is now receiving wider usage. Vacuum double wire press filtration produces a filter cake containing 20 to 30 percent solids. Chemical conditioning with ferric chloride, alum, or polyelectrolytes will greatly aid poorly filterable sludges. Although costs are high three types of incineration are used: burning in a specially designed incinerator (e.g. fluidized bed); burning in the bark boiler; and burning in a power boiler for fossil fuels.

An alternative disposal option is application of waste water after primary treatment for irrigation, which is now used in several mills in tropical developing countries especially in rice fields. Soil conditions and waste water quality are limiting factors.

5. GLOBAL OVERVIEW OF DISCHARGE GUIDELINES

Water pollution is of primary interest in most countries. Typical waste water discharge limits are shown in Table 4.

Type of production	BOD ₅	TSS	AOX
	Pollutants kg/t of air dry product		
Bleached kraft (sulphate) pulp	3-8	4-10	1-2
Mechanical pulp	2-5	4-6	-
Paper production (uncoated)	1-6	2-6	0.01-0.04

Source: Bibliography 6 and 15

In the USA the Environmental Protection Agency (EPA) has established technology-based regulations at various levels. These regulations do not consider the absorbing capacity of receiving waters on grounds that most

advanced regulations can be introduced only gradually. The main levels are as follows:

Best practicable control technology currently available (BPT):
Based on the average of the best existing performance of direct discharges in the industry. BPT is generally the first stage or baseline regulation for an industry and it covers conventional pollutants only.

Best available technology economically achievable (BAT):
Represents the best existing performance in the industry controlling the direct discharge of toxic and non-conventional pollutants. BAT is the second stage of regulation.

New source performance standards (NSPS): Based on best available demonstrated technology and apply to new direct discharging facilities. NSPS are at least as stringent as BPT and BAT.

The current EPA (1988), BPT and NSPS standards for BOD and TSS for bleached sulphate (kraft) wood pulp are given in Table 5. While BPT standards are guidelines for existing mills, NSPS standards are guidelines for major modifications of existing mills or for new mills.

TABLE 5. BPT AND NSPS STANDARDS FOR BOD AND TSS IN USA (1988)								
Type of production	Max 30 day average				Max per day			
	(in kg/t air-dry pulp)							
	BOD ₅		TSS		BOD ₅		TSS	
	BPT	NSPS	BPT	NSPS	BPT	NSPS	BPT	NSPS
Bleached kraft market pulp	8.05	5.5	16.4	9.5	15.4	10.3	30.4	18.2
Bleached kraft fine papers	5.5	3.1	11.9	4.8	10.6	5.7	22.2	9.1
Source: Bibliography 6								

In China there are different limits for old and new pulp mills as shown in Table 6.

Type of production	Maximum volume of waste water (m ³ /t of pulp)	BOD ₅ (mg/l)	TSS (mg/l)
New mill			
- unbleached pulp	150	150	200
- bleached pulp	240	150	200
Old mill			
- unbleached pulp	190-220	150-180	200-250
- bleached pulp	280-320	150-180	200-250

Source: Bibliography 8

Step-wise decreases in chlorinated compound discharges from bleaching of pulp are anticipated in Sweden and other countries as shown in Table 7. Dioxins (TCDD and TCDF) are in very low quantities in bleach effluent, and the amount is only a small fraction compared to other industries. Dioxins can be eliminated by oxygen bleaching and good washing of pulp. In Australia, the limit for new eucalyptus mills is 5 ppt of Dioxin 2,3,7,8, TCDD per tonne of pulp.

Level	Raw material	AOX (kg/adt)	Expected implementation
Basic level	softwood	2	1992
	hardwood	1	
Level I	softwood	1	1995 - 1998
	hardwood	0.5	
Level II	softwood	0.5	2000 - 2005
	hardwood	0.3	
Level III	softwood	0.1	2010
	hardwood		

Source: Bibliography 9

TABLE 8. PROPOSAL FOR NEW EMISSION STANDARDS FOR GERMAN PAPER MILLS (1989)

Type of production	TSS	COD	BOD ₅		NH ₃ N ^a	Tot-P ^b	AOX ^c
	mg/l	mg/l	kg/t	mg/l	mg/l	mg/l	kg/t
Uncoated fine paper	50	3	1	-	10	3	0.04
Coated fine paper	50	6	2	-	10	3	0.04
Tissue	50	9	3	-	10	3	0.04
True pergament	50	12	6	-	-	3	0.025
White board	-	2	-	25	10	3	0.02
Integrated groundwood if >50% TMP is used	-	3	-	25	10	3	0.01
	-	5	-	25	10	3	0.01
Wastepaper	-	5	-	25 ^d	10	3	0.012

^aFor effluent exceeding 500 m³/d
^bFor effluent exceeding 1000 m³/d
^cIn special cases this value enlarges to 0.12 and 0.2 kg/t adt
^dIf water used is lower than 103 m³/t the limit is 0.25 kg/t up to a maximum of 50 mg/l

Source: Bibliography 6

The proposed/target guidelines for paper mills in Germany are rather stringent as shown in Table 8.

Air emissions limits are more difficult to specify. Current emission limitations are shown in Table 9.

TABLE 9. CURRENT EMISSION LIMITATIONS (monthly averages)

Process	Particulate mg/m ³	SO ₂ mg/m ³	H ₂ S mg/m ³	Total sulphur kgS/adt
Recovery boilers	100-50	800-1,000	8-10	-
Power boilers	100-200	500-800	-	-
Lime kilns	150-300	-	10-50	-
Kraft mills	-	-	-	1.5-2.5
Sulphite mills	-	-	-	2.5-5.0

Source: Bibliography 15

In Sweden regulations for discharges are individually stipulated for each mill. Some examples for kraft pulp mills are given below:

- H₂S** Lime kiln: 50 mg/m³ normal dry gas which can be exceeded during 10 (5) % of the running time per month; recovery boiler: 10 mg/m³ normal dry gas which can be exceeded during 10 (5) % of the running time per month.
- Sulphur** Total emission of sulphur (yearly average) from: kraft pulp process: 1-1,5 kg/ton of pulp (as S); sulphite pulp: 2-3 kg/ton of pulp (as S)
- Cl₂/ClO₂** 0,2-0,3 kg/ton of pulp monthly average.
- Particulates** Monthly averages from: recovery boiler in new mill: 150 mg/m³ normal dry gas; lime kiln in new mill: 150 mg/m³ normal dry gas; power boiler: 250 mg/m³ normal dry gas.

6. TARGET/PREFERRED GUIDELINES

In some countries like Germany or Sweden, there are already proposed limits which can be considered as target guidelines. (Table 7, 8). The USA NSPS standards can also be considered as target guidelines. However, there are at present time no European or global target guidelines. For small non-wood based pulp and paper mills these guidelines are, in practice, very difficult to achieve mainly for economic reasons.

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FIGURE 1: Possible points of emissions in chemical pulp production

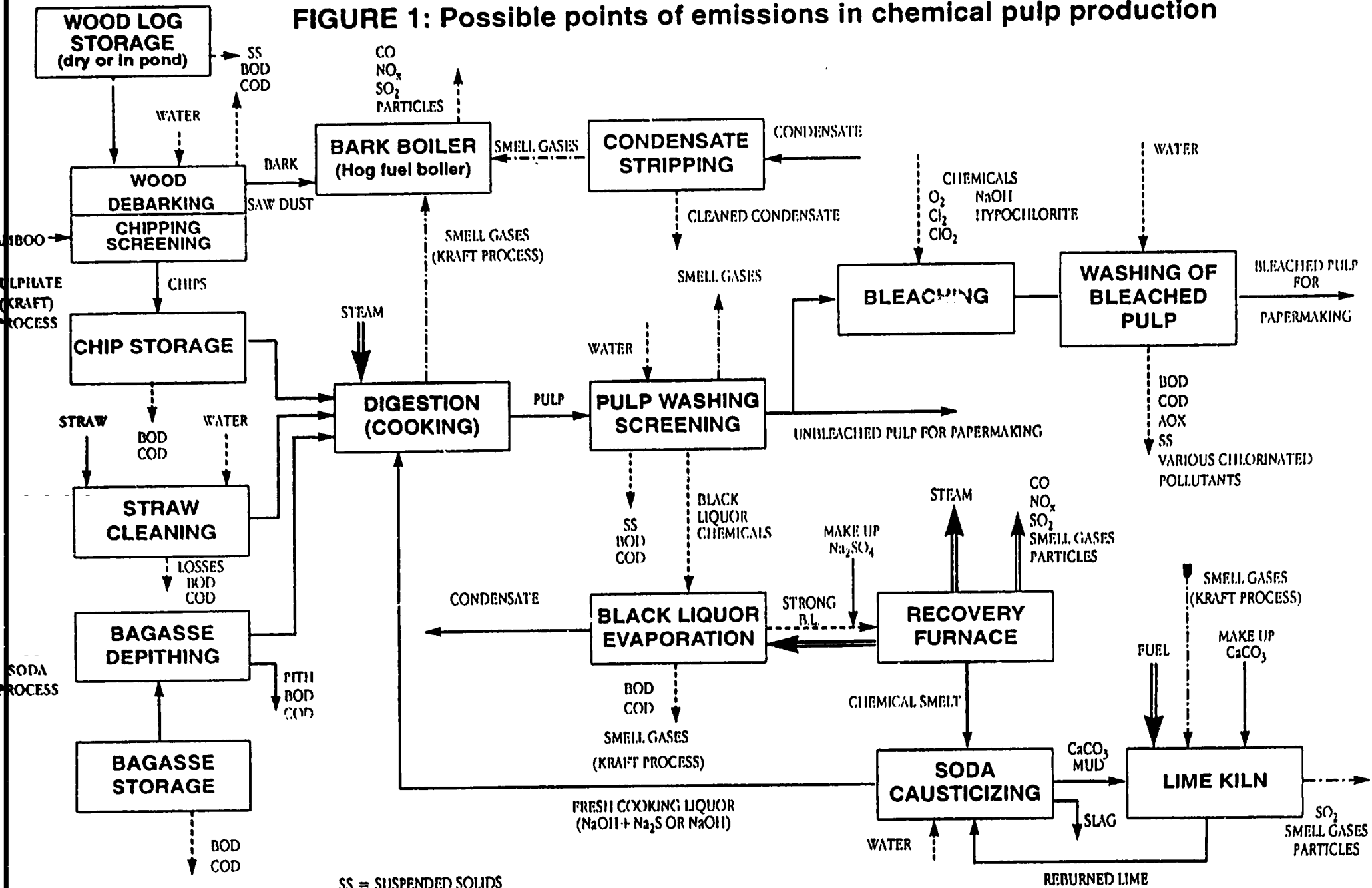
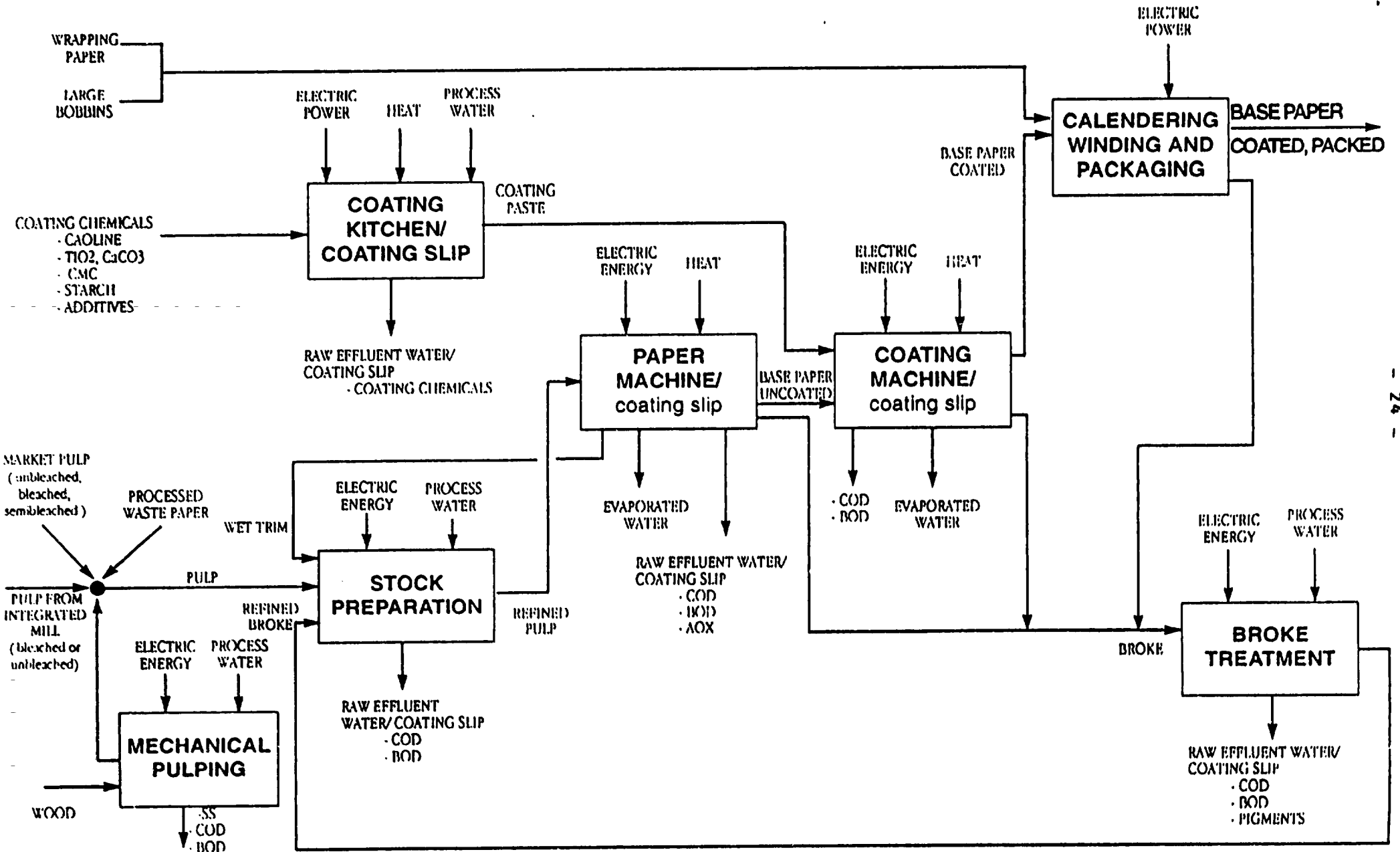


FIGURE 2: Paper board production (possible points of emissions)



APPENDIX A

**PRINCIPAL GRADES OF PULP AND PAPER PRODUCTION
FROM WOOD CELLULOSE FIBRES**

1. **BLEACHED KRAFT: DISSOLVING PULP** means the production of a highly bleached pulp by a process utilizing a highly alkaline sodium hydroxide and sodium sulphide cooking liquor. Included in the manufacturing process is a "pre-cook" operation termed prehydrolysis. The highly bleached and purified dissolving pulp is used principally for the manufacture of rayon or its ester and other products requiring the virtual absence of lignin and a very high alpha cellulose content.
2. **BLEACHED KRAFT: MARKET PULP** means the production of bleached pulp by a "full-cook" process utilizing a highly alkaline sodium hydroxide and sodium sulphide cooking liquor. Included in this subcategory are mills producing papergrade market pulp as the only product.
3. **BLEACHED KRAFT: FINE PAPERS** means the production of bleached pulp by a "full-cook" process utilizing a highly alkaline sodium hydroxide and sodium sulfide cooking liquor. This pulp is used to manufacture fine papers.
4. **BLEACHED KRAFT: B.C.T. PAPERS** means the production of bleached pulp by a "full-cook" process utilizing a highly alkaline sodium hydroxide and sodium sulfide cooking liquor. This pulp is used to manufacture a variety of papers with clays and fillers contents less than eight per cent. Included in this subcategory are mills producing paperboard (B), coarse (C) papers, and tissue (T) papers.
5. **PAPERGRADE SULPHITE** means the production of highly bleached and purified pulp by a "full-cook" process using very strong solutions of bisulfites of calcium, magnesium, ammonia, or sodium containing an excess of free sulphur dioxide. This pulp is used principally for the manufacture of rayon and other products requiring the virtual absence of lignin and a very high alpha cellulose content.
6. **DISSOLVING SULPHITE** means the production of highly bleached and purified pulp by a "full-cook" process using very strong solutions of bisulfites of calcium, magnesium, ammonia, or sodium containing an excess of free sulphur dioxide. This pulp is used principally for the manufacture of rayon or its ester and other products requiring the virtual absence of lignin and a very high alpha cellulose content.
7. **SODA** means the production of bleached pulp by a "full-cook" process utilizing a highly alkaline sodium hydroxide cooking liquor. This pulp is used principally to manufacture a wide variety of papers such as printing and writing papers.

8. **GROUNDWOOD: CHEMI-MECHANICAL** means the production of pulp, with or without brightening, utilizing a chemical cooking liquor to partially cook the wood followed by mechanical defibration by refining at atmospheric pressure. This pulp is used to produce a variety of products including fine papers, newsprint, and molded fiber products.
9. **GROUNDWOOD: THERMO-MECHANICAL** means the production of pulp, with or without brightening, by a brief cook utilizing steam, with or without the addition of cooking chemicals such as sodium sulfite, followed by mechanical defibration by refiners which are under pressure. This pulp is used in a variety of products such as newsprint and tissue products.
10. **GROUNDWOOD: FINE PAPERS** means the production of pulp, with or without brightening, utilizing only mechanical defibration by either stone grinders or refiners. This pulp is used to manufacture coarse (C) papers, molded (M) fiber products, and newsprint (N).
11. **GROUNDWOOD: C.M.N. PAPERS** means the production of pulp, with or without brightening, utilizing only mechanical defibration by either stone grinders or refiners. This pulp is used to manufacture coarse (C) papers, molded (M) fiber products, and newsprint (N).
12. **DE-INKED PULP** means the production of secondary pulp, sometimes brightened or bleached from recycled waste papers in which an alkaline treatment and/or surfactant washing may be utilized to remove contaminants such as ink and coating pigments. The pulp is used, frequently in combination with chemical pulp, to manufacture a wide variety of papers such as printing, tissue, and newsprint.
13. **NON-INTEGRATED FINE PAPER** means the manufacture of fine papers from wood pulp or de-inked pulp prepared at another site. Fine papers are relatively high in price, and include grades such as printing, writing, and technical.
14. **NON-INTEGRATED TISSUE PAPER** means the manufacture of tissue papers from wood pulp or de-inked pulp prepared at another site. Tissue papers include grades such as facial and toilet papers, paper diapers, and paper towels.
15. **NON-INTEGRATED TISSUE PAPERS (FROM WASTE PAPER)** means the manufacture of tissue papers from recycled waste papers. Tissue papers include grades such as facial and toilet papers, paper diapers, and paper towels.
16. **UNBLEACHED KRAFT** means the production of pulp without bleaching by a "full-cook" process, utilizing a highly alkaline sodium hydroxide and sodium sulphite cooking liquor. This pulp is used principally to manufacture linerboard, the smooth facing of "corrugated boxes", but it is also utilized for other products such as grocery bags and cement sacks.

17. **SODIUM BASE NEUTRAL SULPHITE SEMI-CHEMICAL** means the production of pulp without bleaching utilizing a neutral sulfite cooking liquor having sodium base. Mechanical fibrizing a neutral sulphite cooking liquor having a sodium base. Mechanical fibrizing follows the cooking stage, and the principal product made from this pulp is the corrugating medium or inner layer in the corrugated box "sandwich".

18. **AMMONIA BASE NEUTRAL SULFITE SEMI-CHEMICAL** means the production of pulp without bleaching, using a neutral sulfite cooking liquor having an ammonia base. Mechanical fibrizing follows the cooking stage, and the pulp is used to manufacture essentially the same products as in sodium base NSSC.

19. **UNBLEACHED KRAFT-NSSC (CROSS RECOVERY)** means the production of unbleached kraft and sodium base NSSC pulp in the same mill where in the spent NSSC liquor is recovered within the unbleached kraft and NSSC subcategories.