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ENVIRONMENTAL GUIDELINES FOR

Pulp and paper industry

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ENVIRONMENTAL ASPECTS OF THE PULP AND PAPER INDUSTRY

– a technical review –

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FOREWORD

In its first session held in June 1973, the UNEP Governing Council recognized the importance of environmental issues associated with industrial development, and in its decision noted the intention of the Executive Director to initiate work on environmental problems of specific industries.

The Pulp and Paper industry is one of the major industrial sectors agreed for examination. Consultations have been undertaken with experts nominated by Governments, industry and international governmental and nongovernmental Organizations, culminating in a Seminar, held in Paris on March 1975, where the state of the art of existing remedies, outstanding problems and possible avenues of research and development to resolve these environmental issues was assessed.

This report gives a synthesis of the evaluation that has taken place, and highlights the technical aspects that pertain to the environmental issues emanating from the Pulp and Paper industry.

The views expressed in this report do not necessarily represent the decisions or the stated policy of the United Nations Environment Programme, nor does mention of trade names or commercial processes constitute endorsement.

1. INTRODUCTION

The basic process for manufacturing paper has changed very little when compared to other industries. Although equipment efficiencies have been improved and production has increased in scale as well as becoming more automated, the fibrous raw material still has to be debarked and defibered in the presence of water, whether mechanically, chemically or semi-chemically, with strong inorganic chemicals (mainly alkali-sulphur compounds). Pulps then brought to the paper machine in an aqueous suspension, and dewatered in order to obtain paper, paperboard or similar products. Availability of abundant good water and fibrous raw material, as well as accessible courses for discharging mill effluents play an important role in siting a mill. The pulp and paper industry is one of the largest water-using industries, not only in terms of specific water use, but also in terms of the volume of output. Very few industries combine these two characteristics to the extent that the pulp and paper industry does.

It was estimated that the world production of paper and paperboard in 1973 was approximately 148 million metric tons. Pulpwood consumption, representing about 72 percent of the total quantity of fibrous raw material, was estimated to be 403 million m^3 (solid measure) during the same period (1). In OECD pulp and paper producing countries, which account for 85 percent of the world production, a typical sulphate mill producing 500 tonnes of pulp per day will use bout 100,000 m^3 water daily. This quantity is equivalent to the consumption of a city with a population of half a million.

Hence, water and water effluent are considered priority environmental issues, and major attempts are being successfully directed towards reducing and abating the quantities that are discharged. Air emissions and solid wastes from the pulp and paper industry are also environmental problems. With increasingly stringent environmental protection regulations, pollution abatement equipment are being added on to existing plants or incorporated in new installations.

The overall direction and thrust in pollution abatement are moving towards the development and implementation of processes that would produce low waste and any waste that is formed would be recycled and reused. The attainment of non-waste technological processes in production and manufacturing will serve the dual purpose of resource conservation and environmental enhancement.

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(1) Food and Agriculture Organization of the United Nations, FAO (1974) "Wood Fibre Resources and Pulpwood Requirements".
F.O. PAP/74/6 (Rev. 1).

2. ENVIRONMENTAL PROBLEMS

2.1. Water Pollution

Undesirable characteristics of pulp and paper effluents which may cause problems in receiving streams, municipal sewers or treatment plants are :

BOD_5 (Biological Oxygen Demand),	Heavy metals
COD (Chemical Oxygen Demand),	Toxic materials
TOC (Total Organic Carbon),	Turbidity
pH	Ammonia
Total suspended solids	Oil and Grease
Coliforms, total and fecal	Phenols
Colour	Sulphite

Additional characteristics are :

Nutrients (nitrogen and phosphorous) and
Total Dissolved Solids.

Analytical methods for these characteristics have been widely reported (1). Care must also be taken to ensure that samples taken for analyses are representative, properly handled and preserved.

Recommended storage procedures are :

Analysis	*Sample Storage*	
	Refrigeration @ 4° C	*Frozen*
BOD_5	up to one day in composite sampling systems	Lag Develops, must use fresh sewage seed
COD	up to several days	OK
suspended solids	up to several days	No
Volatile suspended solids	up to several days	No
Total solids	OK	OK

(1) *Standard Methods for the Examination of Water and Waste Water*, (1974) Prepared and published jointly by American Public Health Association, Americain Water Works Association, Water Pollution Control Federation. Thirteenth Edition, Fifth Printing.

For sample préservation, the recommendations are :

Characteristics	*Preservative*	*Maximum Holding Period*
Biochemical Oxygen Demand	Refrigeration at 4 °C	6 hours
Chemical Oxygen Demand	2 ml H_2SO_4 per liter	7 days
Solids	Non available	7 days
Colour	Refrigeration at 4 °C	24 hours
Metals, total	5 ml HNO_3 per liter	6 months
Metals, Dissolved	Filtrate, 3 ml, 1:1 HNO_3 per liter	6 months
Turbidity	Non available	7 days
Oil and Grease	2 ml H_2SO_4 per liter 4 °C	24 days
Phenolics	1.0 g $CuSO_4$/l + H_3PO_4 to pH 4 – 4 °C	24 hours
Sulphate	Refrigeration at 4 °C	7 days
Sulphide	2 ml Zn acetate per liter	7 days

The major characteristics of pulp and paper industry effluents causing environmental problems are suspended solids, representing undissolved substances in the waste water retained on a 0.45 micron filter. In some countries a 10 μm. filter is used instead. The residue retained on the filter is dried in an oven at 105 °C. Deposition of solids in quiescent stretches of a stream will impair the normal aquatic life of the stream. Sludge blankets containing organic solids will undergo progressive decomposition resulting in oxygen depletion and the production of noxious gases. Similar problems may result when excessive suspended solids are discharged into municipal sewer systems. Suspended solids are normally determined as an organic and an inorganic fraction. The organic fraction is generally defined as that portion which is volatilized or oxidized at 550 °C.

In 1970, the amount of suspended solids discharged to the receiving waters, have been estimated to approach 2.8 percent of the total combined production of pulp and paper.

Biochemical Oxygen Demand (BOD_5) is still the most widely used method for estimating the strength of biodegradable wastes. It must, however, be applied with great care, since the presence of certain compounds can inhibit the test. Although it is a useful method in characterizing industrial wastes, its use in monitoring is limited, because of the 5 days required to run the test. It is nevertheless expected that the BOD_5 parameter will continue to be a standard for regulatory agencies, yet a thorough understanding of this method is essential. The Chemical Oxygen Demand (COD) test can also be used to estimate the characteristics of an effluent. The results of the COD tests are usually higher than the corresponding BOD test because,

- many organic compounds which can be oxidized by potassium dichromate are not biochemically oxidizable,
- certain inorganic substances, such as sulphides, sulphites, thiosulphates, nitrites and ferrous iron are oxidized by dichromate, creating an inorganic COD, which is misleading when estimating the organic content of the waste water,
- the BOD results may be affected by lack of seed acclimation, giving erroneously low readings,
- COD results are independent of seed acclimation. The test may not include organics such as cellulose, that are not readily available to river bacteria.

Toxicity of pulp and paper mill effluents could be caused by sulphur compounds introduced into the pulping process, dissolved organic compounds of the raw materials, resin and fatty acids as well as heavy metals such as Mercury (if organic mercury compounds are used for wood preservation and slime growth control) and Zinc (if zinc compounds are used as brightening agents for mechanical pulp). With regards to toxicity that could be caused by mercury and zinc compounds, there are now alternative methods to eliminate their use which, therefore, should be discontinued.

Colour and turbidity of effluents present aesthetic problems. Colour of the pulp and paper industry's waste waters is caused mainly by the lignins of the wood as well as in some paper mills, by dyes. Low concentrations of compounds such as lignins will colour natural waters and this effect may be intensified when combined with other materials. Effluent colour problems give concern to both industry and regulatory agencies, because it is a visible indication of pollution.

This problem is even more acute in mixed industrial and recreational areas. Coliform (*Klebsiella pneumoniae*) has been identified in pulp and paper wastewater effluents (1). This bacterium was reported to represent as much as 80 percent of the total coliform present and to grow in sterilized wastewater samples. The report concluded that the question of pathogenicity has not been proven or disproven, but remains to be answered.

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(1) Knittel M.D. (1975) "Taxonomy of *Klebsiella Pneumoniae* isolated from Pulp. Paper Mill Wastewater". U.S.EPA - 600/2-75-024,June

2.2. Air Emissions

Of the air pollutants emitted by the pulp and paper industry, the following are considered as major pollutants giving rise to environmental problems.

Sulphur dioxide is a non-flammable, colourless gas found in air either as a gas or dissolved in water droplets. It can be detected by most people at concentrations of about 900 $\mu g/m^3$ or more. Sulphur dioxide partially oxidizes in air to form sulphur trioxide (SO_3), which readily combines with water vapour to form sulphuric acid (H_2SO_4). There are a large number of chemical methods currently used to measure SO_2 concentration in ambient air, amongst which the Pararosaniline and Acidimetric Methods are widely employed. In some countries, continuous recording instruments of coulometric or fuel cell types, for monitoring of SO_2 are also in general use. The principal advantages and limitations of these methods have been described in detail (1).

The emission of SO_2 in the pulp and paper industry is most acute in sulphite mills, but with sound operating practices and appropriate abatement methods, could be significantly controlled and reduced. However, difficulties arise with the waste liquor burning plants.

Particulates : – Non viable particulates can be subclassified as dusts, fumes and mists. In kraft paper mills for example, particulates occur primarily from the recovery furnace, the lime kiln and the smelt dissolving tank. They are caused mainly by the sublimation and condensation of inorganic chemicals. The sublimation and condensation produce a fume that initially is probably submicron in size but has a tendency to agglomerate. In addition, particulate emissions occur from power boilers and boilers fired with bark in combination with other fuels.

From the lime kiln, particulate emissions consist principally of sodium salts, calcium carbonate and calcium oxide, whilst from the smelt dissolving tanks, particulates are caused primarily by the entrainment of particles in the vent gases. Depending upon the physical, chemical and biological characteristics of particulates, the effects on human health, vegetation, materials and meteorology can be different. However, the effects of particulates in conjunction with oxides of sulphur have been confirmed to be more pronounced than when considered separately (2). Gravimetric and photometric principles are commonly used for the determination of particulates. The

(1) World Health Organization, WHO (1976) "Selected Methods of Measuring Air Pollutants". Published under the joint sponsorship of UNEP and WHO. WHO Offset Publication N°24.

(2) U.S. Environmental Protection Agency, EPA (1974) "Health Consequences of Sulphur Oxides" EPA 650/1-74-004, May.

advantages and limitations of the various methods based on these principles have been discussed and reviewed (1).

Odour : is an environmental problem, especially in the kraft industry, where problems arise from the use of sodium sulphide as one component of the digesting liquor. In the digesters hydrogen sulphide is evolved as a result of the equilibrium $S^{=} \rightleftharpoons HS^{-} \rightleftharpoons H_2S$ (aq) $\rightleftharpoons H_2$ (g). which is strongly pH dependent. Other organic sulphides such as methyl mercaptan, CH_3SH, dimethyl sulphide, $(CH_3)_2S$, and dimethyl disulphide $(CH_3)_2S_2$ are also formed. These sulphides are extremely malodourous and can be detected at concentrations as low as 1 part per billion. The odour detection thresholds (2), (3), for some of these compounds are.

H_2S, Hydrogen sulphide,	0.0047 ppm
SO_2, Sulphur dioxide,	0.4700 ppm
CH_3SH, Methyl mercaptan,	0.0021 ppm
$(CH_3)_2S$, Dimethyl sulphide,	0.0010 ppm
$(CH_3)_2S_2$, Dimethyl disulphide,	0.0056 ppm

2.3. Solid Waste

The industry generates a large amount of solid wastes comprising such components as bark, sludge, ash, mud, etc. The bark content of wood is estimated to represent between 8 and 13 percent by weight and in the pulping industry, about 70-80 percent of barking is carried out at the mill site. Normally, bark is burned to generate steam and hence air pollution abatement equipment would have to be installed to alleviate this form of environmental problem. A growing problem for the industry is to find acceptable means to dispose the large quantities of sludge that will result from its effort to reduce the suspended solids loads presently being discharged with the waste water effluents.

2.4. Soil Erosion.

This can be caused when the logging of wood for the pulp and paper industry is not carefully regulated and planned with reforestation programmes.

(1) World Health Organization, WHO (1976) *Op. Cit.*

(2) Leonardos G.D. Kendall and N. Barnard (1969) "Odor Threshold determinations of 53 Odorant Chemicals". *J. Air Poll. Control Assoc.* V 19, N° 2 p. 91.

(3) Hellman, T.M. and G.H. Small (1974) "Characterization of the Odors Properties of 101 Petrochemicals Using Sensory Methods". *J. Air Poll. Control Assoc.* V. 24, N° 10, p. 979.

Forests regulate surface run off and snow displacement, as well as transfer the surface run off into the soil, thereby replenishing and regulating groundwater levels. Forests also affect precipitation through the circulation of air masses above them causing changes in air temperature, humidity and pressure. In some regions, for example, total precipitation in summer in forest areas is 10 per cent higher than in sparsely wooded areas. When the percentage of the area covered by forest rises from 18 to 100 per cent, the amount of precipitation can increase by about 20 percent. It has been estimated that for each 10 per cent of forest cover, the average precipitation increases by about 2 per cent. In addition to having an impact on soil protection and water management, improper logging operations can also pose aesthetic problems, reducing the recreational amenities that a forest can provide.

3. WATER POLLUTION ABATEMENT

3.1. Reducing Effluents

One of the steps that can be taken to minimize the effects of effluent on receiving streams and treatment plants is to reduce the volume of such wastes. This may be accomplished by :

Water Conservation. A number of basic techniques could be used and these are :

- install water meters in each deparment/section to make operators cost and quantity conscious,
- install automatic valves to prevent loss through failure to close valves when water is no longer needed,
- install valves at the end of a hose, so that flow could be cut immediately, without the operator having to let water run while walking back to the supply point, to shut off flow,
- descale heat exchangers to prevent loss of heat transfer and subsequent inefficient and excessive use of cooling water,
- instigate leak surveys as a routine measure,
- use centralized control to prevent wastages from improper connections,
- recirculate/reuse cooling water,
- use high-pressure, low volume rinse sprays for more efficiency,
- high temperature washing in continuous digesters,
- change to air-cooling wherever feasible,
- in multi-grade paper mills, possible use of fine paper production effluent as process water for low grade board production.

Classification of waste waters, so that manufacturing process waters are separated from cooling waters and, therefore, the volume of water requiring intensive treatment is reduced. Furthermore, it is often possible to classify and separate the process waters, so only the most polluted are treated and relatively uncontaminated effluent is diluted and discharged without treatment.

Elimination of Batch or Slug Discharges of Process Waste waters, to minimize a surge of concentrated effluents being discharged into treatment plants or receiving streams. Two methods can be used to overcome slug discharges and these are, (a) alter production to increase the frequency and lessen the magnitude and (b) retain slug waste waters in holding basins from which they are allowed to flow continuously and uniformly over an extended period.

In the pulp and paper industry, a major endeavour to reduce the quantity of waste water is to "close" the white water system, so excess water from the paper making process is minimized or completely eliminated. According to a report (1) describing investigations made by the Swedish Environmental Care Project, specific water consumption for different paper products manufactured by Swedish mills could be significantly reduced by closing the system. The report states that water consumption in a closed type of system, could be reduced to about 20 m^3/tonne of paper, with the best technology presently available.

Suspended solids in the effluent can also be reduced to a level of about 50 mg/l, which is of the order of 1 kg/tonne or 0.1 per cent of production.

3.2. Treating Effluents

Pulp and paper mill wastes are generally treated by filtration, flotation and sedimentation for product recovery and removal of suspended particles.

Filtration devices are usually some variation of a revolving cylindrical, perforated screen or filter that removes the suspended solids in the form of a mat, which is subsequently scraped off the drum and could be returned to the paper making stock system.

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(1) Geiger C.G. (1975) "Environmental Aspects of the Pulp and Paper Industry", paper prepared under the joint UNIDO/UNEP Environment Programme and presented at the Sixth SIDA/UNIDO/SSIF In-plant Group Training Programme for Engineers in the field of Pulp and Paper Industries.

Sedimentation tanks or basins, normally constructed of concrete or steel are also used to remove by gravity particles in the effluent. The effectiveness of sedimentation depends on the settling characteristics of the suspended solids to be removed and on the hydraulic characteristics of the settling tank. For the settling of discrete particles in a continuous flow basin, the surface area A (m^2) and overflow rate, Q/A, (Q is the flow, m^3/h) are more important parameters than depth or detention time. In practice, however, the basins normally have a depth of about 2 to 4 m. and diameters from about 5 m. to 40 m. (some approaching 100 m.) with solids discharged at a maximum concentration of 6 to 8 per cent. The fillers present in the effluent make final clarification difficult and the effluents usually contain 30 ppm or more of suspended solids, unless up-flow type clarifiers are used. Effluents from fine paper mills generally have an overflow rate of 0.5 m^3/m^2h and from pulp and paper mill, the value is about 2 m^3/m^2h.

Flotation techniques are also used to recover fibre by introducing fine gas (usually air) bubbles into the liquid phase effluent. The bubbles attach to the particulate matter, and the buoyant force of the combined particle and gas bubbles is great enough to cause the particle to rise to the surface. The principal advantage of flotation over sedimentation is that very small or light particles that settle slowly can be removed more completely and in a shorter time. Once the particles have been floated to the surface they can be collected by a skimming operation. Chemicals are commonly used to aid the flotation process. The role of these chemicals is mostly to create a surface or a structure that car easily absorb or entrap air bubbles. Inorganic chemicals, such as aluminium and ferric salts and activated silica, can be used to bind the particulate matter together, and in so doing, create a structure that can easily entrap air bubbles. Various organic chemicals can also be used to change the nature of either the air-liquid interface or the solid-liquid interface, or both. These compounds usually collect on the interface to bring about the desired changes.

Chemical Treatment of pulp and paper mill effluents is carried out for a number of purposes, that is neutralization, precipitation and oxidation, either to render the effluent more amenable to subsequent treatment processes or to reduce the undesirable characteristics of the waste stream.

A three stage precipitation process with lime as a coagulant has been described (1). In the first stage, calcium sulphide settles out and is returned as a slurry to the cooking liquour make-up. In the second stage lignin is

(1) Nemerow, N.L. (1971) "*Liquid Waste of Industry, Theories, Practices and Treatment*". Addison-Wesley Publishing Co.

precipitated and converted to a cake on a rotary filter. In the third stage settling removes any colloidal material that is left when the pH is raised to 11. About 40 per cent BOD removal is reported to be obtained.

Massive lime treatment at a bleached kraft mill in America has also been reported (1). By treating the most highly coloured effluents only, the report states that approximately 70 per cent of the mill's total colour load and 20 to 40 per cent of BOD could be removed. However, the following problems were encountered : foaming and carry-over of solids from the clarifier are intensified ; the cooking liquour is more dilute ; lime kiln fuel requirements are increased ; and more foaming problems occur in the cooking liquor system. Because of the high lime requirements of this process, a second system using moderate quantities of lime has been developed in an unbleached kraft mill. In this stoichiometric lime system, pulp fibre serves as a precipitation and dewatering aid. Calcium hydroxide as a slurry is mixed with total mill effluent in direct proportion to flow. The mixture is retained in a flocculator and clarified in a centre-feed clarifier. The coloured substances are precipitated as calcium salts, together with the fibre and other settleable solids. The treated effluent is, therefore, saturated with calcium hydroxide. In one application, the effluent is aerated and then discharged to the receiving stream. The O.E.C.D. report states that this system is capable of operating successfully under widely varying conditions to give a relatively constant effluent colour in the range of 125 ppm APHA colour units. Performance is directly related to control of lime feed.

Biological Treatment

The process relies upon the capacity of microbial organisms to assimilate oxidizable organic substances in the influent. The systems, based on this process, that have evolved cover a wide range of reaction times and concentrations of biological solids. Each system has its own advantages and efficient performance can be obtained when a system is operating under optimum condition.

Generally, pulp and paper mill waste waters are deficient in nitrogen and phosphorous and these nutrients must be added to obtain effective biological oxidation of wastes. The ratio of BOD : N: P: is of the order of 100 : 5 : 1.

Oxydation ponds : – are usually designed for a loading of 10 to 300 lb.BOD/acre day (1.02 to 30.6 g/m^2 day). With loadings of less than 50

(1) Organization for Economic Cooperation and Development OECD (1972) "Advanced Pollution Abatement Technology in the Pulp and Paper Industry". OECD Paris.

lb BOD/acre day (5.10 g/m^2 day) efficiences of 90 per cent have been achieved. At the higher loadings, the efficiencies level off to about 60 to 70 per cent. Retention time is normally 10 to 30 days. Oxidation ponds are reliable, flexible, require no mechanical equipment, and have low operating costs. However, large land areas are required. The reported (1) effectiveness of oxidation ponds is :

Type of mill	*System*	*Pond Area $m^2 \times 10^5$ (Acres)*	*Maximum Retention time (days)*	*Influent (mg/1)*	*BOD Effluent (mg/1)*	*Removal (percent)*
Newsprint	Multiple	4.05 (100)	20	200	40	80
Newsprint	Single	5.66 (140)	15	180	110	39
Bleached kraft	Single	8.70 (215)	30	299	157	48
Bleached kraft	Single	7.08 (175)	35	108	36	67
Unbleached kraft	Multiple	15.16 (350)	82	200	30	90

Aerated lagoons : – this system has emerged as a common alternative where limited land area or location renders the oxidation pond unacceptable. However, greater capital and operating costs are involved and aerated lagoons have been observed to be sensitive to cold weather operation, especially with decreased detention times. Typically, land with aerated lagoons is about 2 acres per mdg (180 m^2 per l/sec) as compared to 40 acres per mgd (3660 m^2 per l/sec) for oxidation ponds. Optimal ratios of BOD : N is approximately 50 : 1 for 4 days aeration and could be increased to 100 : 1 for 15 days aeration. If aeration is extended beyond 15 days, nutrient addition is not normally required. With this system, about 0.1 to 0.2 lb (0.045 to 0.09 Kg) of sludge is produced for each pound (Kilogram) of BOD removed.

Activated sludge : – conventional, contact stabilization and completely mixed systems have been used for treating pulp and paper mill wastes. Conventional types have been found to be more suitable for sulphite mills. With retention time of 4 to 6 hours and mixed liquor suspended solids, MLSS of 2000 to 3500 mg/1,85 per cent BOD removal has been reported. With kraft mills, contact stabilization has been used. At 2 to 3 hr. contact time, 2 to 3 hours stabilization time, and MLSS of 2000 to 3500 mg/1 in the contact phase, 85 per cent BOD removal has also been similarly reported.

(1) Gehm. H.E. (1965), Chapter on "Pulp and Paper" *Industrial Waste Water Control*. Edited by C.F. Gurham, Academic Press Inc.

Both systems produce about 0.5 to 1 lb (0.23 to 0.45 kg) of excess sludge per lb. of BOD removed. Nutrients requirement are generally less than theoretical optimum of 1 mg/1 of nitrogen per 20 mg/1 of BOD and 1 mg/1 of phosphorous per 60 mg/1 of BOD, because of traces of these elements in the waste stream.

To achieve BOD removal of 85 per cent plus, loadings should not exceed 125 lbs per 1000 cu.ft. (2 Kg/1000 m^3) aeration volume. Optimum sludge settling generally occur in the final clarifier, over a loading range of 0.2 to 0.7 lb of BOD per (0.090 to 0.315 Kg of BOD per Kg) lb of MLSS. Activated sludge systems have very high capital and operating costs, as well as requirements for operation by highly trained personnel. Furthermore, they produce voluminous amounts of excess secondary sludges, characterized by their high resistance to dewatering. These systems give consistent performance, especially in severe climates and could be the most satisfactory system where available land area for treatment plants is very limited.

Rotating Biological Surface, consisting of discs or drums have also been investigated (1) on pilot plant scale for the treatment of insulating board, groundwood and sulfite effluents. The conclusions reached from the investigation are that this system is capable of high level treatment of pulp and mill wastes, but in most cases must be designed at hydraulic loading rates considerably lower than those normally specified for domestic sewage treatment. Resistance to shock loads was reported to be excellent and operation was found to be relatively simple. It was recommended that effluents of high initial BOD strength, (500 mg/1) be given special design considerations, possibly to include enlarged first stage. Secondary sludge generated by the rotating biological surface system was found to be basically comparable to sludge from activated sludge system in terms of settling, and dewatering properties, but most important, sludge generation rates were appreciably lower than those considered normal for the activated sludge process.

Although biological rotating surfaces are widely used in Europe, especially for treatment of domestic waste waters, in the United States this system with the help of the Environmental Protection Agency, has recently gained attention. There are at present no published applications of this system in actual pulp and paper mills, although Japan and a number of other countries have reported their use.

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(1) Gillespie W. (1974) "A Pilot Plant Investigation of rotating Biological Surface Treatment of Pulp and Paper Wastes". Stream Improvement Technical Bulletin N° 278, November, National Council of the Paper Industry for Air and Stream Improvement Inc. New York.

Other treatment methods to improve the quality, especially the colour, of the effluent include:

Activated carbon : – can remove dissolved organics, but cannot usually remove dissolved inorganics. Removal of suspended solids is possible in a carbon filter but it is not its primary function. In conjuction with other treatment techniques (sedimentation, lime colour removal, biological secondary treatment) a final effluent which will be acceptable as raw process water, could be provided.

A novel activated carbon treatment system, based on absorption that endeavours to avoid some of the problems associated with conventional granular and powdered carbon contacting systems, has been reported (1) for a pilot plant study. The system is a multistage countercurrent, agitated system with continuous counter-current transfer of both carbon and liquid from stage to stage as shown in Fig. 1.

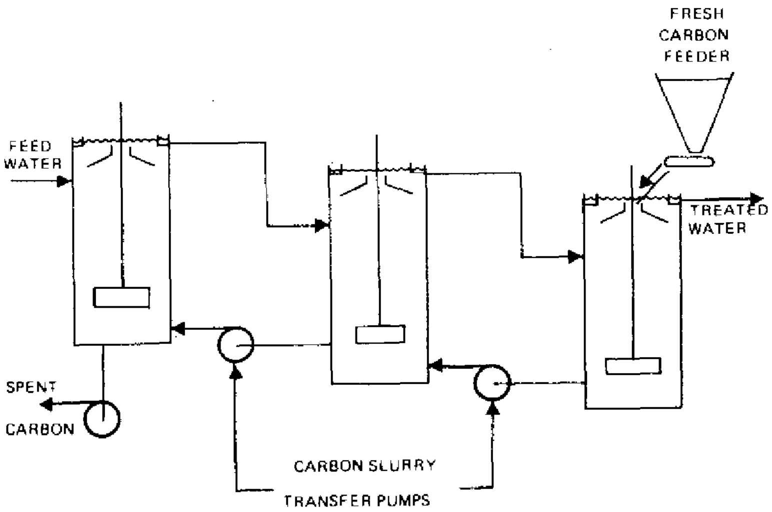

FIG. 1. FLOW SYSTEM FOR ACTIVATED CARBON ABSORPTION

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(1) Organization for Economic Cooperation and Development, OECD (1972) *Op. Cit.*

By using a size of carbon particles intermediate to the standard powdered and granular classifications, the system combines the advantages of both, due to the fact that

— the intermediate size carbon reaches its capacity much faster than the coarser granular carbon, because the absorption rate is inversely proportional to the square of the carbon particle diameter. A higher absorption rate by the intermediate size carbon results in a corresponding increase in carbon turn-over rate which means a decrease in carbon inventory. Hence, equipment size for the absorber decreases correspondingly.

— the new absorber system allows close control of the quality of the treated effluent by adjustments in carbon transfer rate and/or carbon slurry density. A closer tie between regenerator capacity and average carbon through put, eliminating costly off-stream inventory is possible, because of the continuous discharge of spent carbon. Primary clarifiers may be omitted in this system, as suspended solids in the effluent do not cause plugging problems as in the granular carbon column system.

— when compared with a powdered carbon system, intermediate size carbon has a higher settling rate, thereby precluding the need for flocculants and substantially reducing the clarification area needed. Use of the intermediate size carbon system allows a properly baffled and agitated tank to serve as both absorber and clarifier. Hence, equipment size as well as cost will be significantly lower.

Reverse Osmosis, Ion-Exchange, and Amine Treatment are other techniques currently being developed with potentials for commercial application in the near future.

A state of the art for treatment and reuse of kraft pulping effluent has been reportend (1).

Treatment Methods to eliminate the Discharge of Pollutants into Navigable Waters. The U.S. Federal Water Pollution Control Act Amendment, of 1972 (Public Law 92-500, October 18, 1972) Section 101, states that "It is the national goal that the discharge of pollutants into navigable waters be eliminated by 1985". This goal has been interpreted as "zero pollutant discharge" and technically has come to be accepted as meaning that discharged waters cannot contain any constituents or heat in concentrations greater than those of the waters into which the discharges occur. Hence,

(1) Timpe W.G., E. Lang and R.L. Miller (1973) "Kraft Pulping Treatment and Reuse – State of the Art" U.S. EPA Technology Series R2-73-164. February.

on this basis, no discharge would be made because the water quality of the discharge would be equal to that of the incoming water and consequently this water would be reused.

The pulp and paper industry, because of the inherent manufacturing process characteristics, ranks amongst the largest process-water using basic industries. To meet "zero pollutant discharge" requirement, advanced effluent treatment methods are required and a study (1) has been conducted to estimate what technology and cost would be involved. A schematic flow diagram of such a treatment system is shown in Fig. 2.

According to the NCASI report the capital and operating costs that might be incurred in meeting both the U.S. 1977 Best Practicable Control Technology Currently Available (BPCTCA) and the 1985 national goal of eliminating pollutant discharge into navigable waters, can be summarized as follows :

	"BPCTCA"	1985 National Goal	
	At Current Water Discharge	*1/2 Median* Water Discharge	*Median* Water Discharge
Capital Requirement (Billion Dollars)*			
. Reported expenditures prior to 1972 External	0.38		
In-plant	0.32		
. Additional for NSSC liquor disposal and sulfite liquor recovery	0.20		
. Additional for in plant revision to achieve water discharge reduction	–	0.9	–
. Additional for external treatment	1.00	2.5	4.3
Total	1.9	3.4	4.3
Cumulative Total	1.9	5.3	6.2
Cost per Daily Ton (1 000 US $/Ton)*	10	29	34
Operating Cost (US $/Ton)*			
Weighed Average Cost	4	19	32
Cumulative	4	23	36

* 1972 Dollars

(1) National Council of the Paper Industry for Air and Stream Improvement Inc. NCASI (1974)
"An Engineering Estimate of the Cost to the Paper Industry of Achieving Selected EPA National Effluent Limitation Levels".
NCASI Stream Improvement Technical Bulletin N° 270. January.

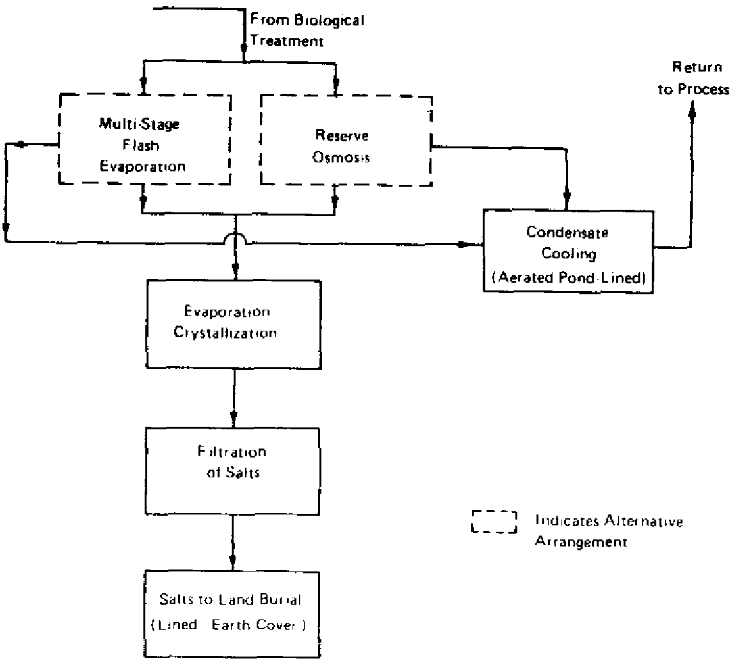

FIG. 2. SCHEMATIC FLOW DIAGRAM OF TREATMENT PROCESS TO MEET 1985 U.S. NATIONAL GOALS

4. AIR POLLUTION ABATEMENT

Air pollution abatement technology is directed at particulates, sulphur dioxide and odorous gases. Three general principles can be used to reduce air pollution in the pulp and paper industry. They are ; installing add-on equipment, process improvement and control, and process changes. Presently installing abatement equipment is the most widely used and effective method to control emissions. Although the effect of some operating variables on emission is known for some unit operations of the industry, the information is not definite enough to be used for emission control. Only in the kraft recovery furnace is data available to be able to minimize emissions by optimizing operating parameters. A schematic diagram of a typical kraft pulping process, indicating emission sources is shown in Fig. 3.

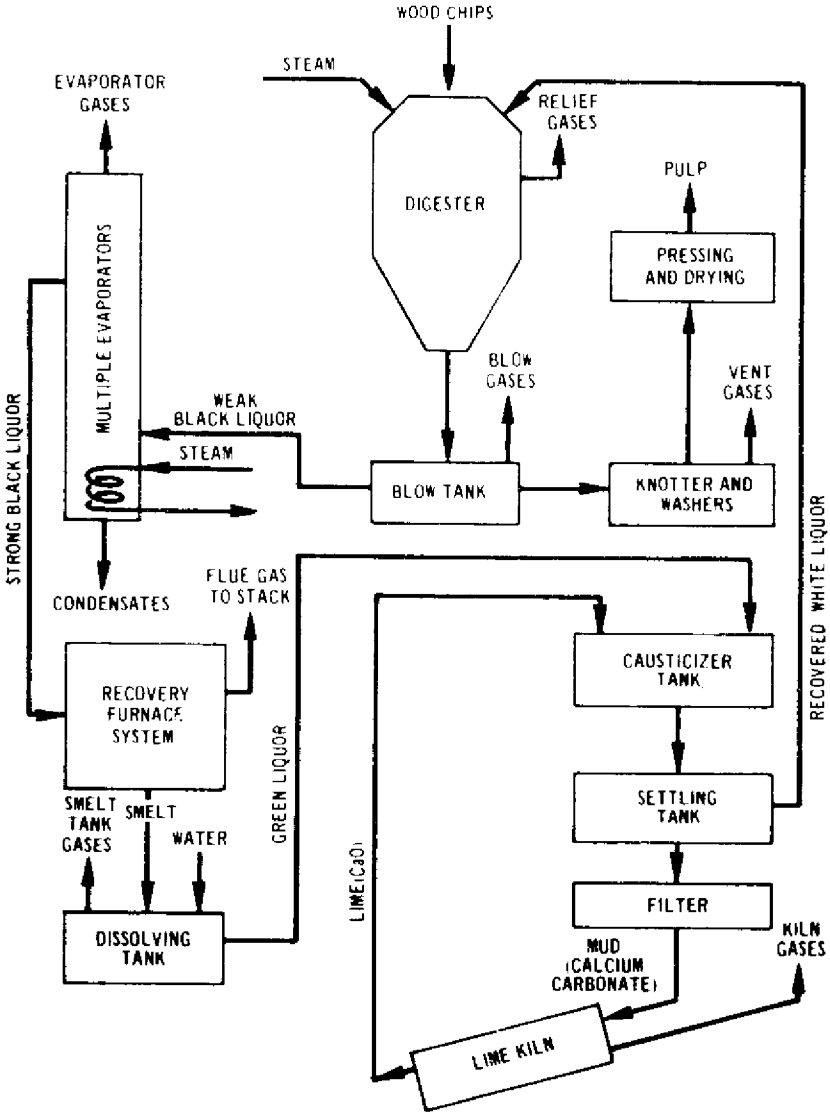

FIG. 3. KRAFT PULPING PROCESS INDICATING EMISSION SOURCES

4.1. Particulates Emissions, can be controlled by electrostatic precipitators, scrubbers, cyclone collectors and wire mesh demister pads.

Electrostatic precipitators are the main type of collectors used to control recovery furnace particulate emissions. The particulates consist primarily of sodium sulphate and sodium carbonate particles. The particulate concentration before reaching an abatement device normally ranges from 8 to 12 grains per standard cubic foot or 200 to 450 lb/T. ADP. The actual level of emission depends upon the abatement device efficiency, which is a function of the system design. In a conventional recovery furnace system, with flue gas direct contact evaporators, the particulate emission control consists of a contact evaporator followed by either a precipitator or a venturi recovery unit and possibly a secondary scrubber. If no contact evaporator is used, current designs for abatement are by precipitators alone, but not precluding the use of secondary scrubbers.

Scrubbers are used to remove particulates from lime kiln, smelt tank vents and other sources. A venturi recovery system using black liquor as a scrubbing medium serves as a primary particulate collection device as well as a flue gas direct contact evaporator.

Cyclone collectors and wire mesh demister pads are used to control particulate emissions from smelt tanks. Usually a liquid spray, and a lime mud weak wash is used, with these devices. For more efficient particle collection, packed towers and venturi scrubbers, incorporating a heat recovery system are being adopted for smelt tank particulate control.

4.2. Gaseous Emissions : can be controlled by a number of unit processes, and combustion, absorption and liquid phase oxidation are examples of abatement techniques using these principles.

Combustion involves the thermal oxidation of non-condensable reduced sulphur compounds to sulphur dioxide, which is considered less objectionable than the compounds from which it was formed, for example, non-condensable gases from multiple effect evaporators and digestors can be vented to the inlet of the combustion air fan of the lime kiln or a separate incinerator (1). In the lime kiln most of the sulphur dioxide reacts with lime in the kiln or is absorbed in the scrubber that controls particulate emissions from the kiln.

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(1) Blosser R.D. and B.H. Cooper (1967) "Current Practices in Thermal oxidation of Non-condensable gases in the Kraft Industry".
National Council of the Paper Industry for Air and Stream Improvement Inc. Atmospheric Pollution Technical Bulletin N° 34, November.

There are two major constraints with this method of gaseous emission control. First, the volume of the lime kiln combustion air limits the quantity of non-condensable compounds that can be handled and second, great care must be taken to avoid the occurence of explosive mixtures. In a batch digestion system, there can be a problem in preventing large surges of gas for combustion. This may be overcome by installing either large spherical tanks equipped with a movable non porous diaphragm or conventional gas holders (1). In Canada, lime kiln burning of digester and evaporator off-gases is almost standard but new installations are also required to have a stand-by system in case of lime kiln shut down.

Absorption usually involves scrubbing the gas stream with an alkaline process liquor, such as sodium hydroxide, lime mud, weak or white liquor. The types of equipment used are normally packed towers and sprayed mist pads for controlling emission of gases, such as hydrogen sulphide and methyl mercaptan, from the evaporator or digester.

Chlorination process can also be applied to sulphur containing gases from digester relief and blow condensers and multiple effect vents. If available, chlorine could be supplied from the chlorination stage washer effluent of the bleach plant. The dimethyl sulphide and disulphide are absorbed and oxidized to sulfone and methyl sulfonyl chloride respectively. This process is, however, of limited effectiveness.

Oxidation of sodium sulphide in the black liquor to sodium thiosulphate can be accomplished by the use of atmospheric oxygen or sometimes molecular oxygen. This is to prevent the formation of hydrogen sulphide by carbon dioxide and sulphur dioxide in the recovery furnace flue gases. The chemical reaction is represented by

$$2\,Na_2S + 2\,O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2\,NaOH$$

To be most effective, the black liquor oxidation must reduce sodium sulphide levels to 0.1 g/l or less in the black liquor entering the flue gas direct contact evaporator. Black liquor oxidation systems that use air are of three types (2), packed towers, bubble tray towers and air-sparged reactors, which may be equipped with mechanical mixing devices to enhance oxygen transfer.

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(1) Morrison J.H. (1969) "Collection and Combustion of Non-condensable Digester and Evaporator Gases".
Tech. Assoc. Pulp and Paper Industry, v. 52, N° 12, December.

(2) National Council of the Paper Industry for Air and Stream Improvement Inc., NCASI (1968) "Survey of Current Black Liquor Oxidation Practices in the Kraft Industry".
NCASI Technical Bulletin N° 39., December.

Air stripping has also been used to remove malodorous gases from condensate streams. The condensate is aerated in a closed, agitated tank and offgases are piped to the lime kiln. Tests on such an installation showed that 75 per cent and 85 per cent removal of dimethyl sulphide and methyl mercaptan, respectively were achieved (1).

Steam stripping is also being used for stripping of odorous gases from condensates. The method can be 98 per cent effective but high in energy consumption unless efficient heat recovery is part of the system. It has been estimated that 95 per cent plus steam stripping will require about 18 per cent steam on condensate.

The state for particulate matter collection generally is more advanced than for odour control. Limited published information is available on emissions control from semi-chemical pulping and sulphite pulping mills (2).

5. NEW PRODUCTION PROCESSES TO ABATE POLLUTION

With increasing requirement for environmental enhancement and resource conservation, the industry has been improving and developing manufacturing processes that produce low levels of wastes. A trend can also be observed that where residues are produced, they are increasingly recycled and reused. There are a number of such processes under development in the pulp and paper industry, mostly based on techniques which do not use sulphur or chlorine containing chemicals (3). Not only will this greatly reduce emission of odorous gases from sulphur compounds, but it will also permit the recycling of bleaching effluent to the chemical recovery system. These processes are thermochemical pulping, nitric acid pulping (4) based on rapid-cycle operation, alkaline oxygen and alkaline-sulphite.

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(1) Walter J.E. and H.R. Amberg (1970)."A Positive Air Quality Program at a New Kraft Mill". *J. Air Poll. Control Assoc.* v. 20 N° 1, p.9.

(2) National Council of the Paper Industry for Air and Stream Improvement Inc. NCASI (1974) "Atmospheric Emissions from the Pulp and Paper Manufacturing Industry – Report of NCASI – EPA Cooperative study Project". NCASI Technical Bulletin N° 69. February.

(3) Cox. L.A. and Worster H.E. (1971) "An Assessment of some Sulphur Free Chemical Pulping Processes". *Tech. Assoc. Pulp and Paper Industry.* v. 54, N° 11.

(4) Kalish, J.H. (1967) "Nitric Acid Pulping". *Tech. Assoc. Pulp and Paper Industry.* v. 50, N° 12.

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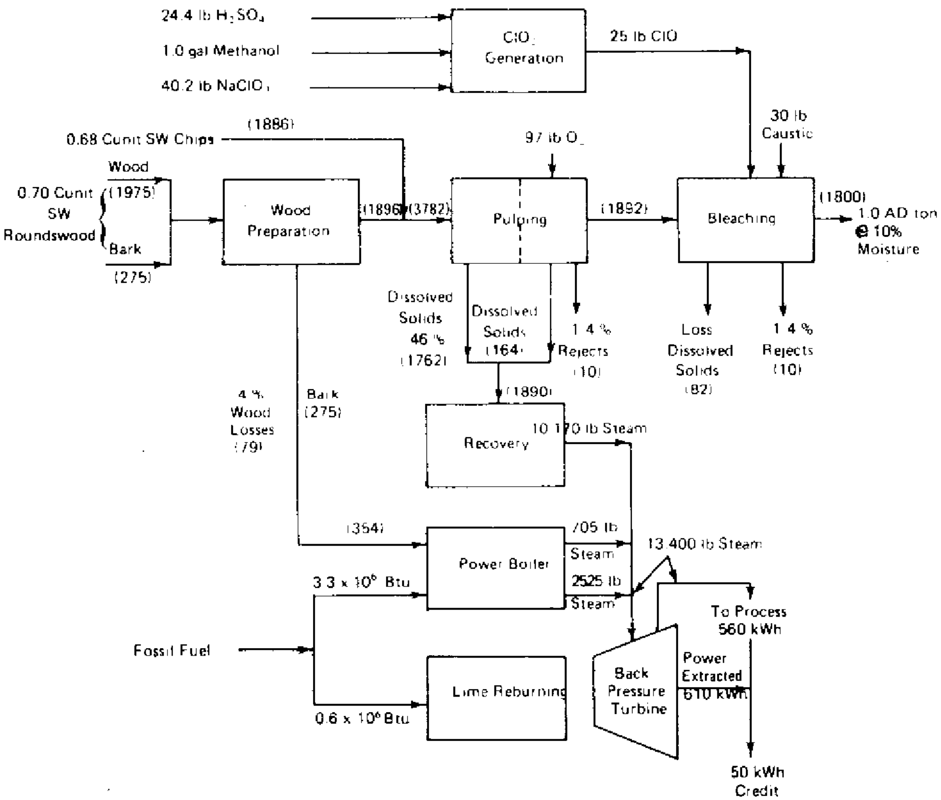
(2) National Council of the Paper Industry for Air and Stream Improvement Inc., NCASI (1968) "Survey of Current Black Liquor Oxidation Practices in the Kraft Industry".
NCASI Technical Bulletin N° 39., December.

same as the output from a proprietary process chlorine dioxide generator, and the caustic is sufficient to combine with all the chlorine going into the bleach plant to form sodium chloride.



Basis : 1.0 ADT slush pulp

( ) Indicates bone-dry (BD) lb . 1.0 air-dry (AD) ton = 1800 BD lb

1 cunit = 100 ft^3 of solid wood ; weight per BD cunit ranges from about 2200 lb to 3400 lb, depending on wood species

* Heat-to-power conservation in this type of turbine is typically about 4000 Btu/kWh.

FIG. 4. MATERIAL AND ENERGY BALANCE FOR ALKALINE–OXYGEN PROCESS (Ref. EPA 1976)

Countercurrent washing in the bleach plant, enabling the reduction of the total amount of fresh process water into the pulp mill, from 25,000 to 4,000 gallons per ton. Fresh water in the closed system is used primarily for make-up to the bleach plant counter-current washing process.

Reuse of all bleach-plant effluent in the pulp mill, in counter-current brown-stock washers. Hence all of the bleach plant chemicals and dissolved organics eventually go to the recovery furnace.

Removal of sodium chloride from the white liquor by evaporating the recovered white liquor and filtering off the crystallized sodium chloride. The latter can then be used as make-up for chlorine dioxide generation and could be used as make-up for chlorate production.

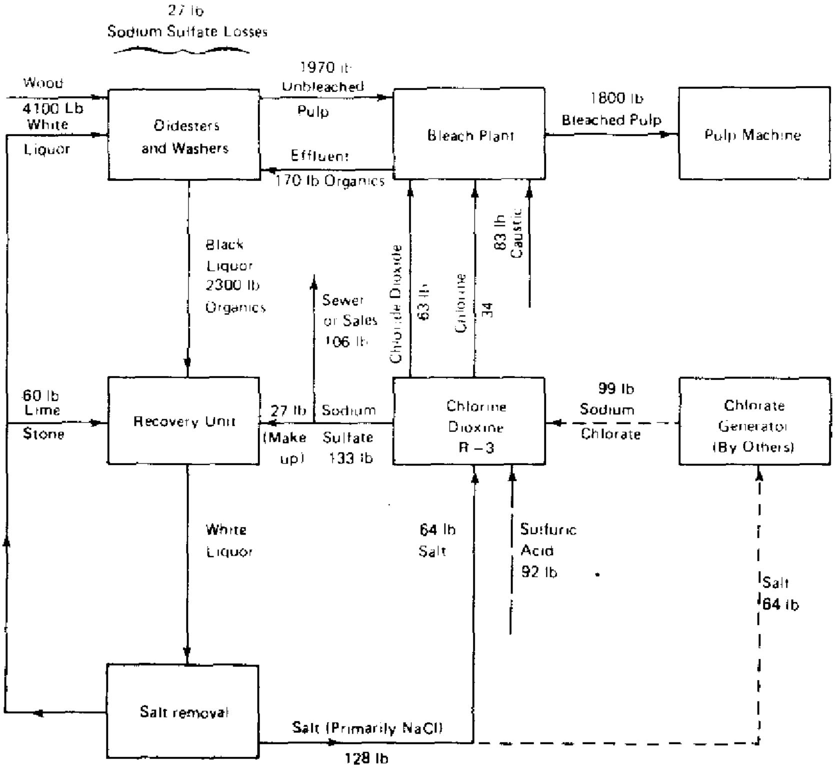


FIG. 5. MATERIAL BALANCE FOR RAPSON PROCESS
(Ref. EPA 1976)

Use of a proprietary process for chlorine dioxide generation. In this process, byproduct sodium sulfate is crystallized from the aqueous sulfuric acid used as a reaction medium, and the sulfuric acid is recycled to the chlorine dioxide generator. Thus, the only byproduct output from the chlorine dioxide generator is solid sodium sulfate (saltcake). A portion of this recovered saltcake can be used as make-up chemical in the kraft pulp mill, sold or discarded, since production will exceed make-up demand.

Change mill process to facilitate closing up the water system (condensate stripping to remove methanol, closing up the screen room, increased washing capacity, installation of spill tanks, etc). As a result of these modifications, a somewhat larger recovery furnace is required to accomodate the organics recycled from the bleach plant, and somewhat larger black liquor evaporation facilities are needed to handle the intermittent return of dilute effluent streams from the spill tanks.

In Fig. 5 a schematic diagram indicating process material balance in the Rapson process is shown.

A comparison of the Alkaline–Oxygen, and Rapson processes with a standard kraft slush pulp, based on a new mill basis, as reported in the EPA study, is shown below for annual production of 267,000 ADT.

Item	*Alkaline-Oxygen*	*Standard Kraft*	*Rapson Process*
Plant Investment, incl. pollution control (US \$ million)	146	154	140
Operating Cost, incl. pollution control (US \$ /ADT)	256	290	259
Purchased Energy 10^6 KCal/ADT (10^6 Btu/ADT)	1.08 (4.3)	1.86 (7.4)	0.53 (2.1)
Pollution Loads			
Water-Volume 10^3 l/ton (10^3 gal/ton)	117.5 (31)	117.5 (31)	75.8 (20)
BOD_5 Kg/ton (lb/ton)	14.9 (33)	29.7 (66)	None
TSS Kg/ton (lb/ton)	29.7 (66)	29.7 (66)	None
Color Kg/ton (lb/ton)	67.5 (150)	135.0 (300)	None
Air Emissions			
Particulates Kg/ton (lb/ton)	65.7 (146)	90 (200)	90 (200)
TRS Kg/ton (lb/ton)	(0)	10.8 (24)	10.8 (24)

5.3. Oxygen Bleaching

Another method which is expected to assume considerable importance in the near future is Oxygen Bleaching. This process consists of replacing, partly or entirely the first two stages of the conventional bleaching sequence (chlorination and caustic extraction) with oxygen under pressure (5 to 10 bar) in an alkaline medium (2 to 8 per cent NaOH on pulp). About 40 per cent of the BOD-load from sulphate pulp bleaching can be eliminated and the colour of the effluent is greatly improved. The conversion of a traditional 500 TPD hardwood kraft bleachery to oxygen bleaching, primarily for colour removal, incurred a net increase in total production costs (including capital charges) of about US $ 3 to 3.50 per tonne of product (1).

6. CONCLUSIONS

The major environmental problems facing the pulp and paper industry are waste water effluents and malodorous compounds.

Many techniques are available to abate and reduce oxygen consuming substances, colour, and suspended solids in the waste water. Unit operations consisting of screening, filtration, flotation and sedimentation are used to minimize the effluent's solid content. Unit processes involving chemical precipitation and biological oxidation are commonly applied to reduce the pollution effects of the waste water. More advanced treatment techniques such as the use of activated carbon, ion-exchange, and amine are also being developed. With the implementation of presently accepted in plant waste reduction techniques combined with an external effluent treatment system, the pollution characteristics of the waste can be significantly changed.

The magnitude of gaseous emission problems is considered to be more localized and not as serious as that of waste water discharge. Established and efficient collecting, precipitating and scrubbing techniques are available to control and reduce particulates and sulphur oxides in the waste gases. At present, there are, however, no satisfactory methods to overcome the malodorous problem caused by reduced sulphur compounds in old and conventional pulp and paper mills.

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(1) Organization for Economic Cooperation and Development, OECD (1973) "Pollution by the Pulp and Paper Industry". OECD Paris.

With increasing concern for environmental enhancement and resource conservation, major emphasis is been directed towards the development of low/non waste production processes. The Alkaline–Oxygen pulping, Rapson and Oxygen Bleaching processes show significant potential to alleviate many of the air, water and solid waste environmental problems of the pulp and paper industry.

Techniques and technological systems consisting of in-plant waste reduction, process modification external add-on abatement equipment and new production processes are available to reduce to acceptable levels the environmental impacts caused by the pulp and paper industry. The key issue concerns the criteria which will be considered acceptable, so that the optimum system could be designed and installed in a mill. Generalizations should be tempered with caution, because each individual siting of a pulp and paper mill needs specific evaluation based on the context of the relevant ecological, economic, social and political factors that prevail.

If the necessary additional cost can be expended, there are no compelling technical reasons why pulp and paper mills cannot be designed and operated with a minimum impact on the environment.

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