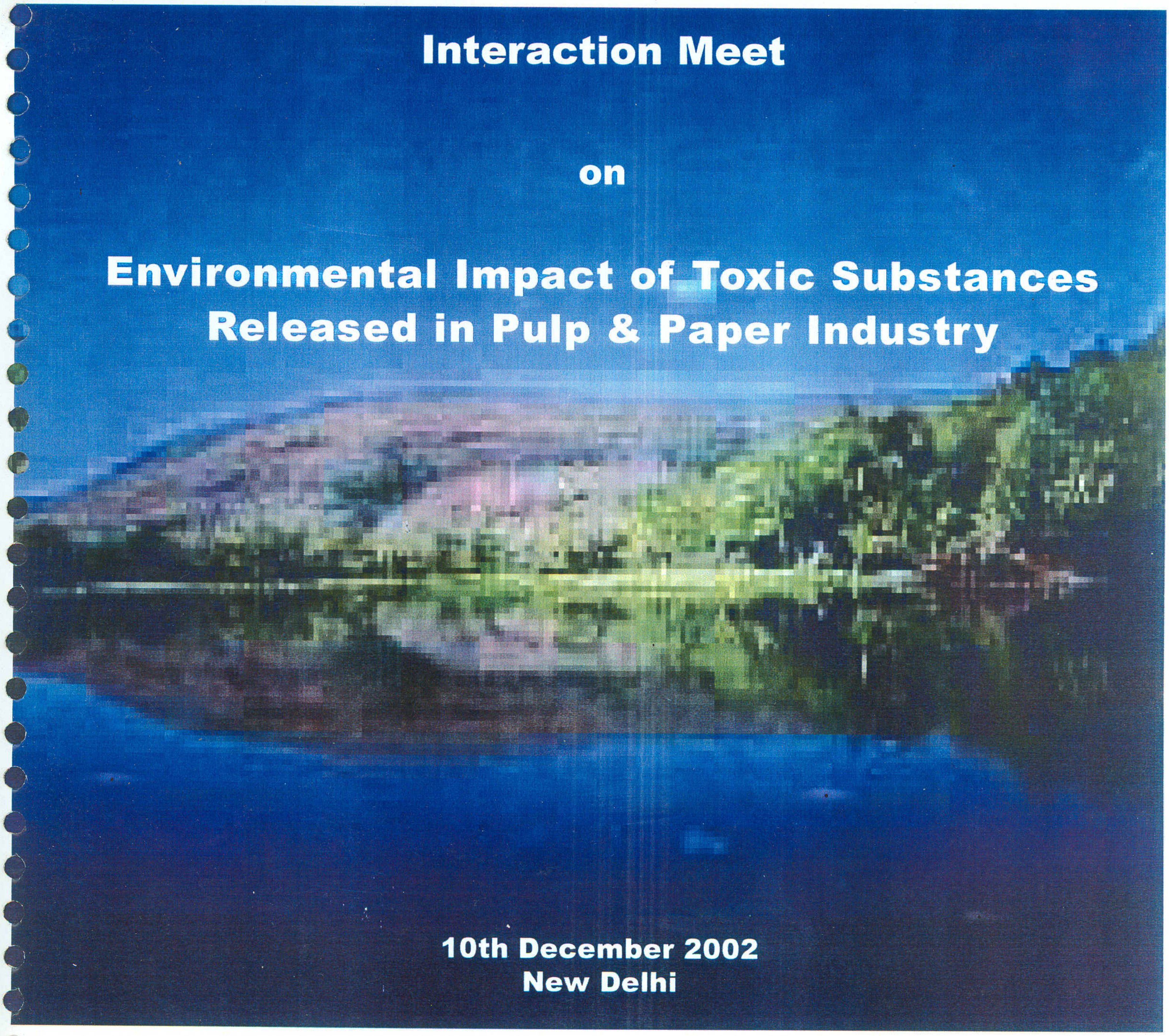

Interaction Meet

on

Environmental Impact of Toxic Substances Released in Pulp & Paper Industry

10th December 2002
New Delhi

Organised by

CENTRAL PULP AND PAPER RESEARCH INSTITUTE
SAHARANPUR / NEW DELHI

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CENTRAL PULP AND PAPER RESEARCH INSTITUTE
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Dr. A. G. KULKARNI
Director

PREFACE

In a liberalized economy, the sustainable industrial development and compliance with environmental regulations has become top priority. Pulp and Paper Industry is one of the polluting industries, and discharge of persistent organic pollutants (POP) is one of the major concerns of the Industry. The pulp and paper industry uses wide range of chlorine and chlorine based bleaching chemicals for bleaching of pulps. During the bleaching process chlorinated organic compounds are generated. The control and reduction of these chlorinated compounds is one of the major issues and challenges before the industry.

Significant proportions of paper production is accomplished by using sulfide based cooking chemicals and malodorous methyl mercaptans generated during pulping operations are emitted into open atmosphere. It has become important for the Industry and R&D Institutions like CPPRI to make concerted efforts for control and reduction of these gaseous organic pollutants.

CPPRI has carried out extensive work in these areas and is now organizing this One day Interaction Meet on "Environmental Impact of Toxic Substances Released in Pulp and Paper Industry" with an objective to focus on various issues like magnitude of discharge of these wastes such as; AOX, gaseous emission and solid wastes in pulp and paper industry and their control strategies.

I am sure that the Interaction Meet will provide an excellent opportunity to Scientists & Engineers to discuss the status of technological developments in the respective areas and how to control and manage these wastes, and also to discuss as to how CPPRI can help & assist the Paper Industry in addressing these challenging environmental issues.

(Dr. A. G. Kulkarni)

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INVITED TECHNICAL PAPERS FOR PRESENTATION

POLLUTION ABATEMENT IN SHREYANS PAPERS - A CASE STUDY

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1. Introduction

Shreyans papers is a unit of Shreyans group of industries. It is an agro based integrated pulp and paper mill using non-conventional raw materials mainly wheat straw, bagasse, sarkanda, jute waste and very small quantity of imported waste paper for making writing and printing grade papers.

The mill commenced the commercial production in the year 1982 with installed capacity of 10,000 MT per annum and simultaneously installed effluent treatment plant based on activated sludge system designed and supplied by M/s Hindustan Dorr-Oliver Ltd comprising of primary clarifier, aeration tank, secondary clarifier and sludge drying beds.

To keep up with changing technology, the plant process and technology were continuously upgraded. Mills undertook ambitious modernisation-cum-modification project in the year 1991 and is now producing 30,000 MT per annum writing and printing grade papers.

The industrial atmosphere is changing very fast and this has affected the society with improved economic conditions on one hand but adverse impact on environment on the other. Pulp and paper industry which provides basic necessity or the nation has become synonymous with degradation of environment through pollution and deforestation.

Problem of pollution abatement is intimately associated with utilisation of wastes, while going through various operations and processes. Waste generated may be solid waste such as dust generated in raw material preparation section, reject of screening system, reject of centricleaning system, sludge generated at effluent treatment plant, boilers fuel ash or it may be in the form of spent pulping liquor, effluent from bleaching section, stock preparation department, paper machine, chemical recovery section etc.

Disposal of spent pulping liquor in small and medium size agro residues based paper units has always been the object of study. Direct disposal of spent liquor not only creates problem of polluting ground water but it is wasteful also.

Growing awareness about pollution free environment in society and government makes it obligatory on the part of management of pulp and paper industries to treat these wastes and recycle it as far as possible. Pulp and paper industry can continue to provide paper, the basic necessity without ill effects through an environment protection programme suitably balanced between reduction of influent load and treatments of effluent.

Shreyans has adopted this approach and steps taken not only made environment protection effective but has yielded good results and even added to the revenues. This paper deals with these aspects of environmental protection.

2. Manufacturing process

The mill is based on non-conventional raw materials like wheat straw, bagasse, sarkanda, jute waste etc. Wheat straw, bagasse, sarkanda and kahi grass which are available in plenty in nearby areas as agricultural residues or waste, however jute waste is obtained from West Bengal. Raw materials are received from nearby areas by trucks or tractor trollies during the harvesting season. Material is stored in mill yard and supplied to the cutter house either manually or by tractor trollies. Mill yard has a storage capacity of 6000 MT raw materials. Wheat straw and cut sarkanda are passed through two stage wet cleaning system followed by screw press to get raw material with 0.2 to 0.25% Chloride content, 40 to 50% silica reduction and 30-35% dryness. The water is partially recycled to minimise polluting discharge but remaining water contains considerable quantity of suspended soilds and hence passed through sand trap and decker to reduce suspended solids. Bagasse depithing is carried out in moist depither. Two bailing presses are installed in yard area to convert loose bagasse in bale form. Jute waste sorting is carried out manually before digestion.

The mill uses soda process for digestion of wheat straw, sarkanda and bagasse in Pandia type Continuous Digester using about 14-15% alkali. However, jute caddies digestion is carried out in batch rotary spherical digesters using 10-11% alkali and 0.05% Anthraquinone.

Washing of mixed cooked pulp is carried out in 4 stage Brown stock washing system with closed screening and centricleaning. Wash water flow in brown stock washing system is counter current.

Bleaching of unbleached pulp is carried out in multi stage bleaching plant by adopting CEHH bleaching sequence to raise the brightness of pulp to 80-81% but whenever brightness is raised to 82-83% CEpHH bleaching sequence is followed. The total chlorine consumption is around 14-14.5% out of which 60% is used in the form of elemental chlorine.

3. Upgradation of ETP system

Shreyans Industries Ltd started its paper division in the year 1982 with effluent treatment plant designed and supplied by M/s Hindustan Dorr-Oliver Ltd based on activated sludge system comprising of one primary clarifier, one aeration tank having three numbers of fixed surface aerators of 50 HP each and one secondary clarifier.

Effluent treatment plant gave good COD and BOD reduction initially but as soon as the waste paper based pulp consumption reduced in furnish due to increased agro residues pulp production the quality of treatment effluent was not as per specifications prescribed by Punjab Pollution Control Board. Shreyans appointed National Environmental Engineering Research Institute (NEERI), Nagpur as consultant to have the quality of treated effluent as per specifications prescribed by PPCB. One equilisation tank,one reaction tank, one clarifier of 40 M dia and one aeration tank with 4 surface floating aerators of 50 Hp each were added in ETP system as per advice of NEERI , to convert ETP system from single stage activated sludge system to double stage activated sludge system and system was started under guidance and supervision of NEERI but desired reduction of BOD and COD values as prescribed by PPCB could not be achieved.

4. Installation of Chemical Recovery system

The shortage of forest based wood raw materials has led to increasing use of non wood agricultrual residues as raw materials for pulping. The conventional sulphur based kraft process has been replaced in such cases by non sulphur soda process. Conventional alkali recovery system comprises of plant and equipments for converting the inorganic chemicals to suitable form for reuse after causticisation. Conventional Recovery system is complex and capital intensive.

The small and medium size mills using agricultural residues with soda cooking have been letting black liquor into the drain as installation of conventional recovery system is found to be uneconomical and as a consequence pulp and paper mills were looking forward for alternate chemical recovery system.

Shreyans took initiative in installing 75 TPD black liquor solids FBR in 1995 after studying various alternate options available. Fluidised Bed Reactor (FBR) technology based on modified copeland process as developed by M/s Enders Process Equipment Corp.,USA became a major break through for technological development after successful commissioning and operation of FBR at Shreyans for last eight years and total black liquor generated in the mill is being burnt and converted into soda ash pellets and disposed off to various manufacturers using soda ash as raw material for sodium silicate manufacturing. Removal of black liquor from effluents makes it possible to meet environmental standards in outgoing effluent.

5. Improvement and modifications done in the effluent treatment process.

5.1 Sludge handling

There were sludge drying beds for handling primary and excess secondary sludges. These sludge drying beds were periodically excavated and were disposed off as land fill, which was very costly affairs. Saltec press (twin wire belt press) was installed for dewatering of primary and excess secondary sludge to 20-26% consistency and sold to board mills.

5.2 Colour reduction

Colour to a certain extent was removed in the primary and two stage secondary treatment but from aesthetic point of view this was not enough so treatment with coaugallants and flocculating agents was started after treatment with coaugallants and flocculating agents was started after biological treatment and tremendous reduction in colour, BOD and COD was observed. Seven numbers of plate and frame filter presses were installed to handle tertiary sludge and sludge obtained is used as land fill.

5.3 Reduction in volume of chemical sludge

Sedimentation saveall is installed to reduce volume of tertiary sludge as handling capacity of plate and frame filter presses is very limited.

6. Inplant treatment measure

By closing the inplant water usage cycles, the fresh water requirement has been kept as low as 100 Meter Cubic per ton of finished paper. The recycling of waste water in various sections is explained as below.

6.1 Back water discharged from paper machine is taken to a sedimentation saveall to recover fibre which is recycled back to the system. The overflow of saveall is collected in reservoir alongwith other paper machine water such as wire pit water, couch pit decker water , Vacuum pumps sealing water, press rolls cooling water, pope reel cooling water, compressor cooling water etc and used in

- Slushing of purchased pulp and waste paper.
- Stock dilution in paper machine
- Vat and tower dilution in pulp mill
- Bleached centricleaner pit dilution
- Washing of pulp at alkali, hypo I and II washer.

6.2 Bleach washer filtrates in pulp mill at the stages CEHH are recycled for vat and tower dilution in counter current

6.3 Brown stock washers are running in counter current with closed screening. Tertiary centricleaner reject is passed through a decker for thickening and filtrate is recycled to black liquor system and thickened reject is sold to board mills.

6.4 Condensate from paper machine and chemical recovery are recycled back to the boiler house.

6.5 Combined condensate of recovery plant is used for washing on final brown stock washer and in raw material wet cleaning system.

6.6 Back water is used in pulper no.1 of wet cleaning system. Fresh water is used in only pulper no.2 as per requirement otherwise combined condensate is used.

6.7 Black liquor spills are collected in tank and recycled back to the system.

6.8 Pandia type continuous digester was installed for digestion of agro residues to get more uniform pulp in respect to Kappa no. and reject with 1.0 -1.5% less Caustic addition.

6.9 CFS reject and pre riffler vib.screen rejects are sold to board mills.

6.10 Paper machine centricleaner reject is passed through a riffler to settle down fibres and ash content. Clear water is discharged in main drain however settled fibre and ash are excavated periodically and sold to board mills.

6.11 Wet cleaning system backwater is passed through sand trap and decker to take out sand and raw material fines. Sand traps are periodically cleaned and excavated. Sand is used as land fill however fibres taken out by decker are used in system alongwith wet cleaned material., approx. 3-4 tonnes raw materials is recovered per day.

6.12 Treated effluent is used exclusively for horticulture purpose inside the mill.

6.13 The Chemical recovery plant generates large quantity of lime sludge during recausticisation. Mill is surrounded by agricultural land and hence its disposal was very difficult. Recausticisation plant was made shut and soda pellets being sold directly to the sodium silicate manufacturers.

6.14 Thoroughly washed hypo mud is discharged in effluent drain and ultimately settles in primary clalrifier alongwith other suspended solids.

6.15 Pith generated from bagasse depithing plant is used in medium pressure boilers as fuel.

6.16 High pressure and medium pressure boilers are using rice husk as fuel. Boilers are privided with fluidised bed and autocontrol system for better combustion efficiency. Boiler ash is at present disposed off as a land fill in area surrounding the mill premises.

6.17 Blowers for rice husk feeding to boilers have been replaced by belt conveyor to reduce air pollution.

6.18 High pressurer boiler is equipped with Trema cyclone and wet scrubber however medium pressure boilers are equipped with Multicyclone and wet scrubber to keep suspended particulate matter well within the limit.

6.19 Flue gases of FBR are passed through Venturi scrubber to concentrate black liquor from 20-25% solids to 40-45% solids. Secondary scrubber is installed in outlet passage of flue gases where weak black liquor/water is sprayed to remove suspended particulate matters.

6.20 The mill has taken a project under guidance of CSSRI, Karnal to divert its treated effluent through forestry and aprox. 100 acres land with Eucalyptus plantation has already been covered under this project.

7. Future plans.

7.1 In view of encouraging results of Eucalyptus plantation for diversion of its treated effluent the mill plant to further cover more land under this project.

7.2 In an endeavour to further reduce effluent pollution arising from the bleaching section of the mill, the mill is introducing the use of Oxygen in the bleaching system by incorporating Oxygenerated extraction (Eo) which would enhance the removal of lignin present in the pulp thus reducing use of Chlorine in hypochlorite stage and ultimately reducing the colour and toxicity of effluent.

This project after the introduction of Eo stage system in the bleach plant is expected to provide the mill with a platform from which it can in future pursue further process enhancement and better environmental performance.

7.3 From an environmental point of view pulp washing after the cooking is one of the most important operation in pulp mill. An efficient washing operation is essential for the process economy and necessary for the further treatment of the pulp.

Carryover of organic substances to bleaching results in increased discharges of chlorinated organic compounds which are to some extent toxic and slowly degradable. Mill is planning to upgrade its brown stock washing system.

7.4 Chemical sludge and waste activated sludge generated at ETP are difficult to handle through double wire filter press and plate and frame filter presses. Mill is going to install mud washer which was taken out from Chemical Recovery for this purpose and the work is under progress.

AOX LEVEL AND CONTROL STRATEGIES IN TNPL

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ABSTRACT

Economic liberalization and growing environmental awareness among the public, politicians and consumers become the serious concern to all the manufacturing industry including pulp and paper. Chlorinated organic compounds is one of the main regulating parameter in the pulp and paper mill wastewater set by the various regulating authorities in both state and central government, due to the persistence in natural habitat and bioaccumulating nature of these compounds in higher level organisms in the food chain. In this paper we have discussed AOX (Adsorbable Organic Halogen) generation and concentration in the various process inter mediate in the TNPL one of the bagasse based pulp and paper industry in India and also the AOX removal efficiency in the activated sludge process in the first part. In the second part we have discussed about various R & D and plant efforts made in our mill to reduce and degrade the AOX in the pulp mill as well as in the secondary sludge.

INTRODUCTION

The pulp and paper industry continues to expand its production capacity and most of the new plants are being built in the newly industrialized countries. The majority of the mills are using kraft or sulphate and soda process to manufacture chemical pulp. In both the process fibrous raw materials (wood or non wood) are cooked in order to dissolve lignin which binds the fibers together. Kraft process is dominant among chemical pulping process and uses sodium sulfide as an additional component in the pulping liquor along with sodium hydroxide. In the kraft pulping process, recovery cycle is a well defined integrated part which is designed to recover pulping chemicals and to reduce water pollution by combusting organic mater in the spend liquor and to generate process steam. The unbleached pulps produced by cooking process are generally darker due to the presence of chromophoric (light absorbing) compounds which are the functional groups of degraded and altered residual lignin, more tightly bound to the fibres than the original lignin component. This can be either removed or converted by bleaching to produce high brightness pulp used to manufacture fine paper. This done by the multi stage bleaching process using oxidizing chemicals, such as chlorine, chlorine - di - oxide, hypochlorite, hydrogen per oxide, ozone and oxygen. Traditionally chlorine and chlorine compounds are used to bleach the pulps in most of the developing countries like India and other countries due to the economical reasons.

CHLORINATED ORGANIC COMPOUNDS IN THE BLEACH PLANT.

Among the chlorinating agents used for the bleaching process molecular chlorine is the most reactive and undergo complex and series of reactions involving chlorination, oxidation and demethylation and results in the formation of wide range of structurally diverse organic compounds fig. 1. Some of these compounds are chlorinated at various level and few of these components are considered to be harmful to environment due to the following reasons. 1. Highly resistant to biotic and abiotic degradation. 2. Toxic to biota. 3. Bioaccumulating at higher level (Neilson *et al.*, 1991, 1994). One of the key impacts of the discharge of bleach plant efficient to near by ecosystem is the presence of persistent bio-accumulating substance such as polychlorinated dibenzodioxin (PCDD) and dibenzofuran (PCDF) in higher level organism such as crabs clams, mussels and fish. The bioaccumulation of the chlorinated dibenzodioxin and dibenzofurans in commercially important aquatic species lead to the closure of several fisheries. In addition to the chlorophenolic compounds derived form fibrous raw materials, oil based defomers have also been identified as precursor materials for PCDD and PCDF. Among the congener 2,3,7,8 Tetrachlorodibenzo-p-dioxin (TCDD) is the most toxic (Johnston *et al.* 1996) and has toxicity equivalent factor-1. As a result, and complexity of bleaching effluents in relation to their organochlorine content, the regulating agencies imposed guidelines to monitor the discharge of organochlorine as absorbable organic halogens (AOX) and related components (See Appendix).

Studies conducted on organochlorine discharge form Sweden in the early 1980, before process change from conventional chlorine based bleaching to ECF(Elemental chlorine free bleaching and TCF (Total chlorine free bleaching), indicates that the quantities of organiochlorine discharge were extremely high and it is estimated that nearly 5kg of organically bound chlorine was product per tone of pulp. However, at present the discharge level has come down to around 0.2 kg/t for the bleached kraft industry. This is mainly because of the conversion of bleaching to ECF and TCF process. But it is a matter of concern that most of the mills in developing countries still uses conventional chlorine based bleaching sequence (Johnston *et al.*, 1996).

AOX CONTROL MEASURES

Growing environmental awareness among the public, politicians and consumer become serious concerns to pulp and paper industry and it began to research and implement ways of reducing formation and discharge of AOX form mill effluent, in addition to BOD and COD. These can be broadly classified as process external and process internal. Process internal measure are generally done by various process modification to reduce are stop spillage arising form pulping, bleaching and chemical recovery operations and these measure also leads to economic benefits by reducing the chemical loss. Next one to reduce the organochlorine is by increased removal of lignin before the pulp is sent to the bleach plant. Enhanced lignin removal reduce the consumption of bleach chemicals used and intern positively effects bleach plant effluent quality including AOX. This can be carried out by improved brown stock washing, reducing the kappa number during cooking process by anthraquinone pulping, rapid displacement heating, oxygen delignification. The next major area in process internal measures to reduce the organochlorine generation is the modification of bleaching sequence by replacing the chlorine with chlorine dioxide (ECF bleaching) or by non chlorine bleaching chemicals such as ozone, oxygen and peroxide (TCF bleaching).

Process external measures mainly refers to various effluent treatment plants such as activated sludge process, aerated lagoons and anaerobic plants which are used to reduce the pollutants including AOX . The treatment efficiently to reduce AOX compounds varies according to raw materials used and process conditions. Almost all wastewater system operate in pulp and paper industry contains AOX in the treated effluent and ETP sludge when chlorine based chemicals are used for bleaching process (Saunamaki *et al.*, 1991, Johnston *et al.*, 1996).

AOX LEVEL IN TNPL

TNPL uses bagasse as main source of fibrous raw materiel to produce the pulp. By nature bagasse contains less lignin and its fibers are open and easily assessable for delignification during cooking when compared to other raw material such as hardwood and softwood. Because of the above said fact, bagasse require less cooking chemicals and at the same time the unbleached pulp kappa number is also less when compound to wood pulp. This leads to the less bleaching chemical consumption and AOX generation. At present, our AOX generation in the bleach plant is around 1560 kgs per day and account for about 3.12 kg per tone pulp even with conventional bleaching sequence such as CEPH (Fig-2). The bleach plant effluent is being sent to waste water treatment plant to reduce the pollution load along with other wastewater.

In TNPL, wastewater generated during various stages process is mainly divided into two major stream. The first one, having high BOD and low volume is treated by anaerobic system followed by activated sludge process. This stream contains wastewater from bagasse washing and bagasse yard and there is no chance that this stream will contain AOX. The second stream, having low BOD and high volume is treated directly through activated sludge process and it contains wastewater from bleach plant, paper machine, SRP and power boiler. The daily AOX levels (for about a month) at various stages of the ETP is as follows and it varies form 22.38 to 33.55 ppm at primary clarifier inlet, 18.56 to 28.97 ppm at primary clarifier outlet, 16.34 to 23.34 ppm at activated sludge lagoon inlet, 7.57 to 17.2 ppm at secondary clarifier outlet and 6.43 to 10.07 ppm at final outlet (Fig. 3). The average values of these are also present in to Fig-3. The AOX discharged kgs per day and kgs per tonne of production in presented in the Fig.4. It various from 0.6 kg/t to 0.8 kg/tonne of production as against the 2.6 kg AOX prescribed by Central Pollution Control Board (CPCB 2kg as TOCl).

The total AOX reduced across the wastewater treatment in TNPL is around 70% of which 3-4% is removed along with primary sludge and 9-11 % is carried along with waste activated sludge and remaining is removed by the microbial oxidation in the activated sludge process. The percentage reduction slightly varies when compared to earlier reported values and confirms that the concentration AOX is getting reduced in the activated sludge process (Baneerjee *et al.*, 1996, Wilson and Holloram 1991). .In continuation to the above, average results of monthly analysis of the AOX in final effluent for the year 2000, 2001 and 2002 are presented in the Fig. 5, along with quantity of effluent discharge. AOX discharge kgs per day and AOX discharge kgs per tonne of production during the past three years (Fig. 6) clearly indicates that the values are well below the limit set by the CPCB.

AOX CONTROL IN TNPL

As stated earlier, TNPL uses bagasse as principal source of fibrous and requires less chemical for cooking. The unbleached kappa number ranges form 9-12 as against 20-22 for hardwood and 28-30 for softwood and consume less bleach chemical and produce less AOX during the bleaching process (Fig. 2). The alkali increased bleach chemical consumption and higher generation of AOX during bleaching. Therefore, to reduce the alkali loss and reduce AOX generation, screw press was installed in the hardwood street and we have made arrangement to install for the chemical bagasse street. Further to improve at washing efficiency and to reduce the alkali loss we are also using wash-aid chemicals.

As mentioned earlier the secondary sludge form activated sludge carry considerable amount of AOX and it is understood that the microorganism play important role in the mineralisation/degradation of AOX (Neilson *et al.*, 1990, Mohn and Tiedje 1992). To understand their AOX degradation potentials, microbial AOX degradation experiments were carried out in R&D using white rot fungi isolated from wood yard. It is found that these fungi are able to reduce the AOX level in the bleach plant effluent and also in the sludge (Fig- 7 & 8). After getting the positive result in the laboratory AOX degradation, studies were carried out in the field by microbial composting process to reduce AOX in the secondary sludge. The sludge along with bagasse pith (30:70 ratio) was used as raw material to make composting pile and over that, waste activated sludge was sprayed frequently to maintain the moisture, to improve the C/N ratio and also to reduce the AOX level in the sludge. The initial results shows that nearly 39.1% AOX is getting degraded during the windrow microbial composting process and further studies are being carried out to confirm results.

The AOX level during the bleaching process can be reduced by the following three methods: 1. Substitution of D for C in the C stage. 2. More delignification after C stage (EOPstage). 3. More delignification before the C stage without sacrificing final brightness of the pulp. Keeping the above facts in our mind and to have preliminary knowledge to modify our bleach plant to become more environmentally friendly, we have carried out various R&D studies in the laboratory to identify the impact of various bleach sequence on AOX generation and compared with existing impact of various bleach sequence on AOX generation and compared with existing bleaching sequence. The results are presented in the Table-1. This indicates that oxygen delignification stage in the bagasse street substantially reduce the AOX generation up to 81% when compared to existing CEH bleaching sequence or replacing the E stage with OP will reduce the AOX level around 72.85% (Fig. 4). For the hardwood street, we are planing to adopt the second strategy i.e. introduction of EOP stage to have more delignification after C stage.

REFERENCE

Banerjee S., Kemeny T.E., R Sackellare and M.D. Juszynski (1996). AOX and COD Removal in the activated sludge basin. *Proceeding of Tappi International Environmental Conference. pp 159-162.*

John Caray, Eric Hall and Neil Mccubbin (2002). Review of the scientific basis for AOX effluent standard in the British Columbia. *Technical Report prepared for the minister of water, Land and Air protection in British Columbia.*

Mohn W.W. and J.M. Tiedje (1992). Microbial reductive dehalogenation. *Microbial Review* **56(3)** 482 -507.

Neilson A.H., Allard A., Hynninger and M Remberger (1997). Distribution, fate and persistence of organochlorine compounds formed during production of bleached pulp. *Toxicological and Environmental Chemistry* **30**: 3-41.

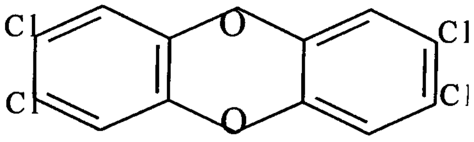
Neilson A.H., Allard A., Hynninger M. Remberger and J. Viktor (1990). The environmental fate of chlorophenolic constitutes of bleachery effluents. *Tappi Journal* 73 (8): 239-247.

Saunamaki R., Tokinan k., Jarvinen R. and M. Salvolanian (1991). Factors affecting the removal and discharge of organaochlorine compounds of activated sludge treatment plant. *Proceedings of Tappi International Environmental Conference.* pp 813-819.

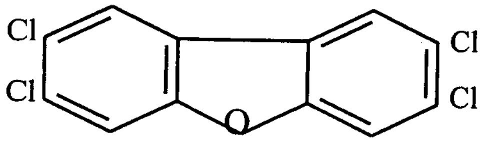
Wilson D.G. and M.F. Holloran (1991). Degrease of AOX with various external effluent treatment. *Proceedings of Canadian Pulp and paper Technical Association. 77th annual meeting.* Quebec, Canada 281 -283.

Table: 1. AOX generation in various bleaching sequence of Bagasse pulp.

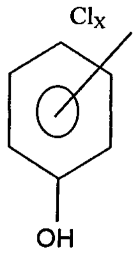
S.No	Bleaching Sequence	AOX kg/T
1	CEH	2.21
2	OCEH	0.42
3	OH	1.03
4	OD	0.17
5	(OP) H	0.6
6	(OP) P	0.00
7	(OP) D	0.16



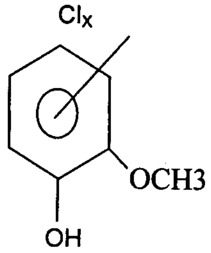
2,3,7,8 - TCDD



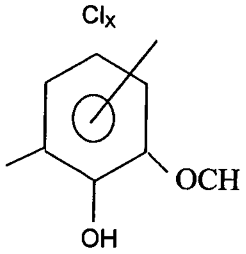
2,3,7,8 - TCDF



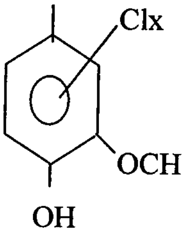
CHLOROPHENOL



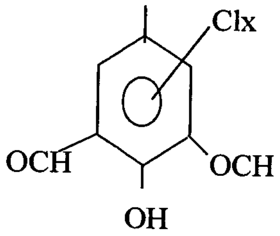
CHOROGUAIACOL



CHLOROSYRINGOL



CHLOROVANILIN



CHLOROSYRINEALDEHYDE

Figure: 1. Stucture of some important chlorinated organic compounds present in the bleach plant effluent

Appendix - I

US EPA New effluent limitations guidelines and pretreatment standards for existing, non-TCF bleached kraft or soda paper grade pulp mills.

COMPOUND	MONTHLY AVE.	DAILY MAX	POINT/FREQUENCY
TCDD	Not Specified	ML**	Bleach Plant/Monthly
TCDF	Not Specified	31.9 ppq	Bleach Plant/Monthly
2,4,6-Trichlorophenol	Not Specified	<ML**	Bleach Plant/Monthly
2,4,5-Trichlorophenol	Not Specified	<ML**	Bleach Plant/Monthly
2,3,4,6-Tetrachlorohenol	Not Specified	<ML**	Bleach Plant/Monthly
Pentachlorophenol	Not Specified	<ML**	Bleach Plant/Monthly
3,4,6-Trichloroguaiacol	Not Specified	<ML**	Bleach Plant/Monthly
3,4,5-Trichloroguaiacol	Not Specified	<ML**	Bleach Plant/Monthly
4,5,6-Trichloroguaiacol	Not Specified	<ML**	Bleach Plant/Monthly
Tetrachloroguaiacol	Not Specified	<ML**	Bleach Plant/Monthly
3,4,6-Trichlorocatechol	Not Specified	<ML**	Bleach Plant/Monthly
3,4,5-Trichlorocatechol	Not Specified	<ML**	Bleach Plant/Monthly
Tetrachlorocatechol	Not Specified	<ML**	Bleach Plant/Monthly
Trichlorosyringol	Not Specified	<ML**	Bleach Plant/Monthly
Chloninated phenolic chloroform	4.14 gm/ton	6.92 gm/ton	Bleach Plant/Weekly
AOX	0.623 kg/ton	0.951 kg/ton	Final Effluent/Daily

**ML= Minimum Level for the Analytical Method

US EPA New effluent limitations guidelines and pretreatment standards for existing, non-TCF bleached kraft or soda paper grade pulp mills that discharge to POTWs

COMPOUND	MONTHLY AVE.	DAILY MAX	POINT/FREQUENCY
TCDD	Not Specified	<ML**	Bleach Plant/Monthly
TCDF	Not Specified	31.9 ppq	Bleach Plant/Monthly
2,4,6-Trichlorophenol	Not Specified	<ML**	Bleach Plant/Monthly
2,4,5-Trichlorophenol	Not Specified	<ML**	Bleach Plant/Monthly
2,3,4,6-Tetrachlorohenol	Not Specified	<ML**	Bleach Plant/Monthly
Pentachlorophenol	Not Specified	<ML**	Bleach Plant/Monthly
3,4,6-Trichloroguaiacol	Not Specified	<ML**	Bleach Plant/Monthly
3,4,5-Trichloroguaiacol	Not Specified	<ML**	Bleach Plant/Monthly
4,5,6-Trichloroguaiacol	Not Specified	<ML**	Bleach Plant/Monthly
Tetrachloroguaiacol	Not Specified	<ML**	Bleach Plant/Monthly
3,4,6-Trichlorocatechol	Not Specified	<ML**	Bleach Plant/Monthly
3,4,5-Trichlorocatechol	Not Specified	<ML**	Bleach Plant/Monthly
Tetrachlorocatechol	Not Specified	<ML**	Bleach Plant/Monthly
Trichlorosyringol	Not Specified	<ML**	Bleach Plant/Monthly
Chloninated phenolics chloroform	4.14 gm/ton	6.92 gm/ton	Bleach Plant/Weekly
AOX	1.41 kg/ton	2.64 kg/ton	Bleach Plant/Daily

**ML= Minimum Level for the Analytical Method

Appendix - II

US EPA guidelines for minimum analytical level for the chlorinated organic compounds

COMPOUND	MINIMUM LEVEL	EPA TEST METHOD
2,3,7,8-TCDD	10 ppq (pg/L)	1613
2,3,7,8-TCDF	10 ppq (pg/L)	1613
2,4,6-Trichlorophenol	2.5 ppb (μg/L)	1653
2,4,5-Trichlorophenol	2.5 ppb (μg/L)	1653
2,3,4,6-Tetrachlorohenol	2.5 ppb (μg/L)	1653
Pentachlorophenol	5.0 ppb (μg/L)	1653
3,4,6-Trichloroguaiacol	2.5 ppb (μg/L)	1653
3,4,5-Trichloroguaiacol	2.5 ppb (μg/L)	1653
4,5,6-Trichloroguaiacol	2.5 ppb (μg/L)	1653
Tetrachloroguaiacol	5.0 ppb (μg/L)	1653
3,4,6-Trichlorocatechol	5.0 ppb (μg/L)	1653
3,4,5-Trichlorocatechol	5.0 ppb (μg/L)	1653
Tetrachlorocatechol	5.0 ppb (μg/L)	1653
Trichlorosyringol	2.5 ppb (μg/L)	1653
AOX	20 ppb (μg/L)	1650

Federal requirements in Canada for effluent discharge limits for chlorinated organic compounds

COMPOUND	UNITS	MAX. DAY
TCDD	Nano g/ T	1500
TCDF	Nano g /T	5000

Effluent discharge limits (AOX) for chlorinated organic compounds

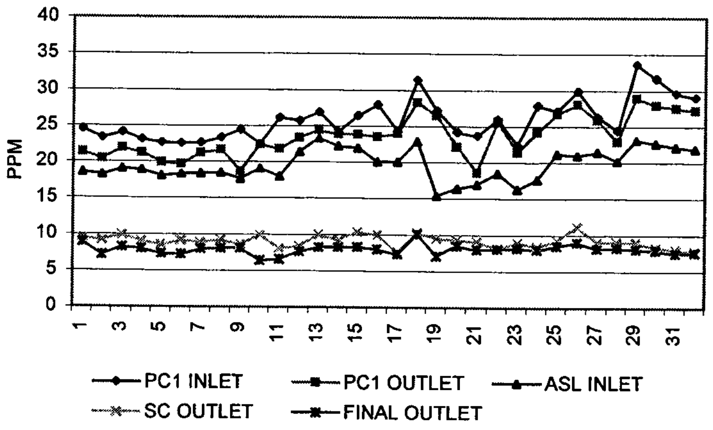
Country/ Agency	UNITS	LIMIT
World Bank	Kg/ T	0.4
European Union	Kg /T	0.25
Germany	Kg/T	0.35
Austria	Kg/T	0.50
France	Kg/T	1.0
Sweden and Finland	Kg/T	<1.5*
Japan	Kg/T	<1.5#
India	KG/T	2.0†

*Current level 0.2 kg/t
Current level 0.8 kg/t
† As TOCL

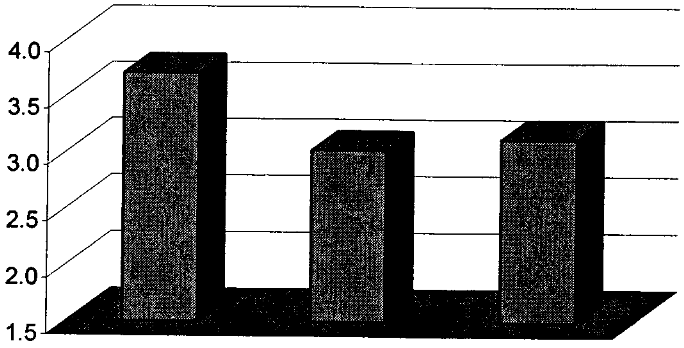
APPENDIX - III

COGENERS		TOXICITY EQUIVALENT FACTORS
2,3,7,8	TCDD	1.0
Other	TCDD	0.0
1,2,3,7,8	PeCDD	0.5
Other	PeCDD	0.0
1,2,3,4,7,8	HxCDD	0.1
1,2,3,6,7,8	HxCDD	0.1
1,2,3,7,8,9	HxCDD	0.1
Other	HxCDD	0.0
1,2,3,4,6,7,8	HpCDD	0.01
1,2,3,4,7,8,9	HpCDD	0.01
Other	HpCDD	0.0
2,3,7,8	TCDF	0.1
Other	TCDF	0.0
1,2,3,7,8	PeCDF	0.05
Other	PeCDF	0.0
1,2,3,4,7,8	HxCDF	0.1
1,2,3,6,7,8	HxCDF	0.1
1,2,3,7,8,9	HxCDF	0.1
Other	HxCDF	0.0
1,2,3,4,6,7,8	HpCDF	0.01
1,2,3,4,7,8,9	HpCDF	0.01
Other	HpCDF	0.0

AOX VALUES AT VARIOUS STAGES OF ETP



AOX GENERATION KGS/T OF PULP



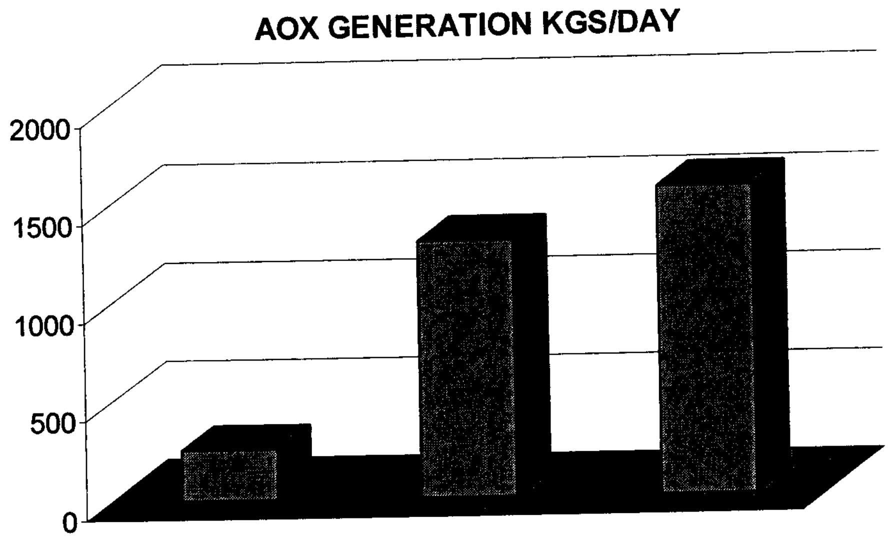


FIGURE : 3 AOX values at various stages of ETP

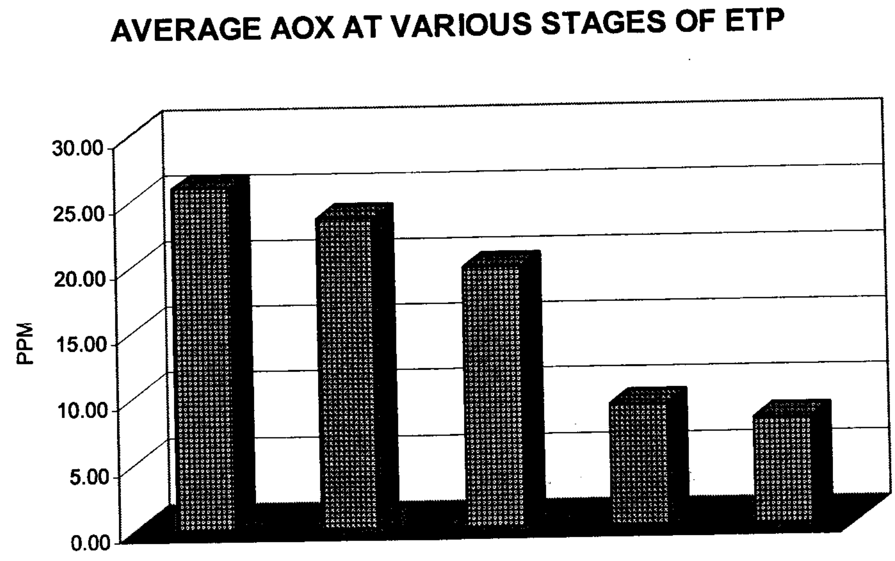
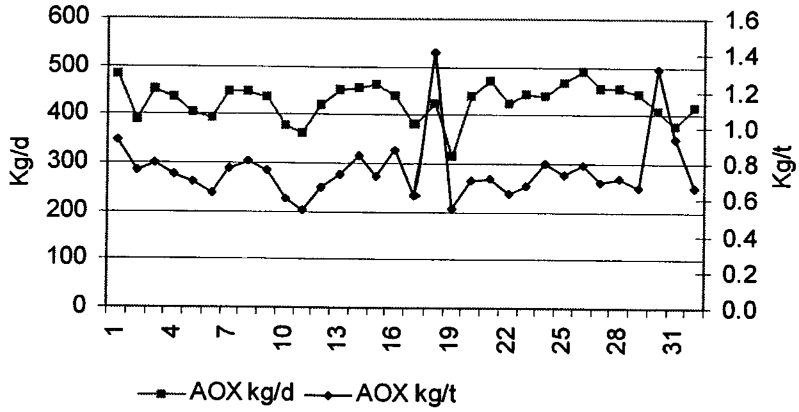
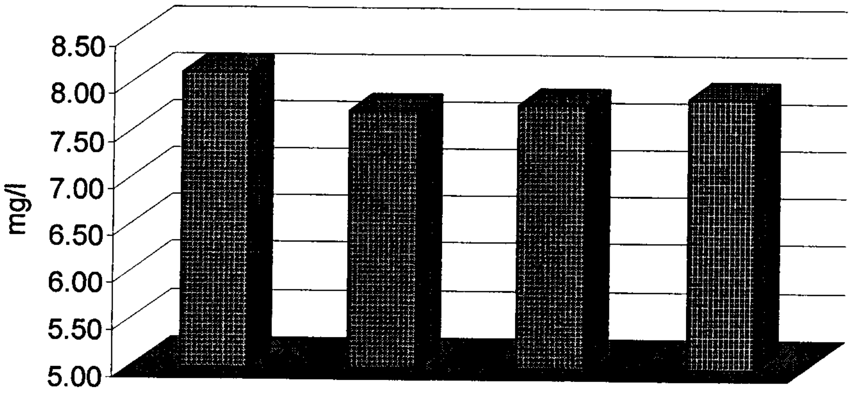


FIGURE: 2 Aox generation in the pulp mill

AOX DISCHARGE IN FINAL TREATED EFFLUENT



AOX CONCENTRATION IN TREATED EFFLUENT



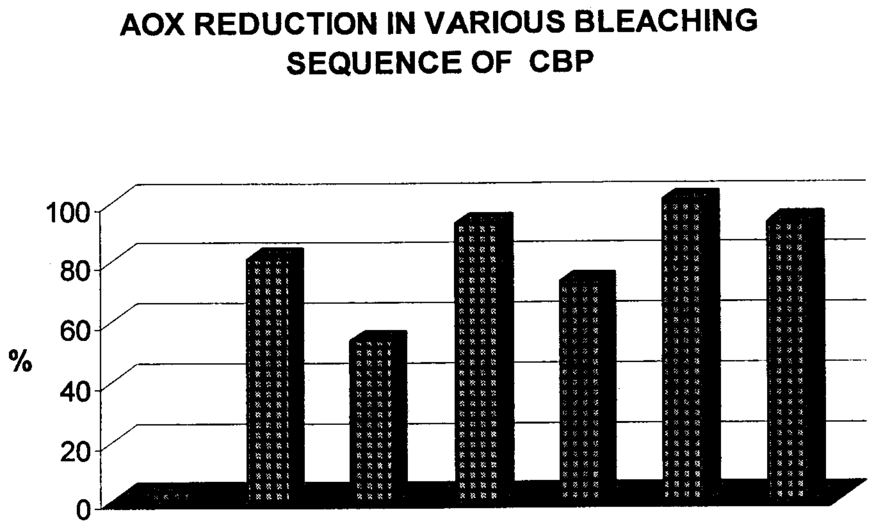


FIGURE: 4 Daily AOX discharge and AOX generation during various bleaching sequence

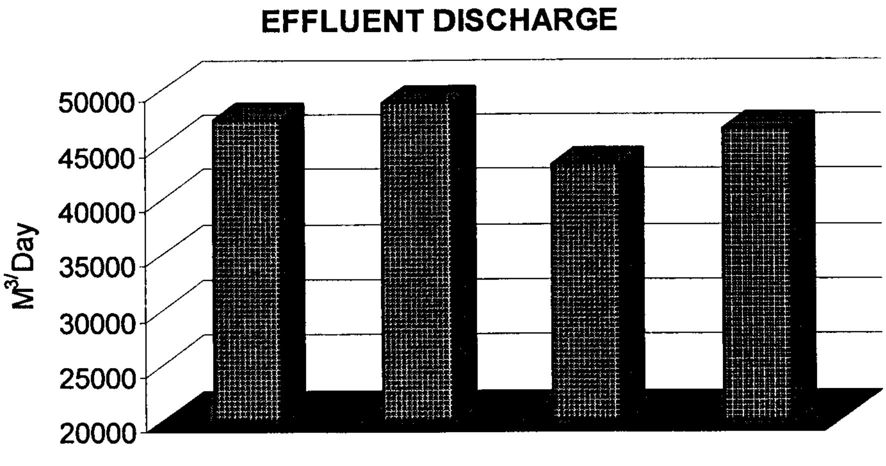
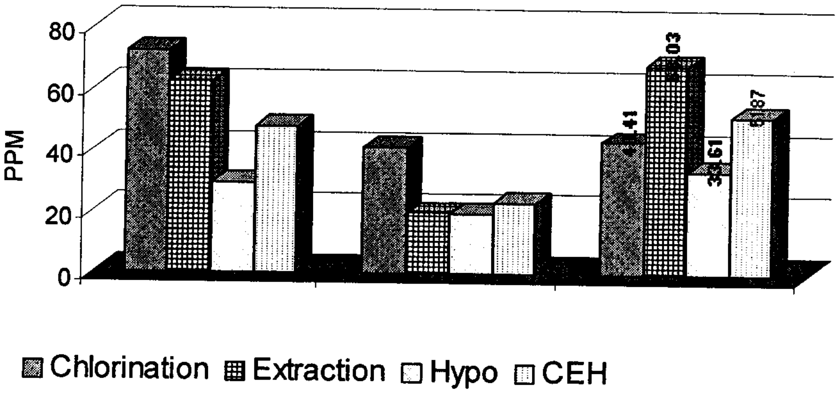
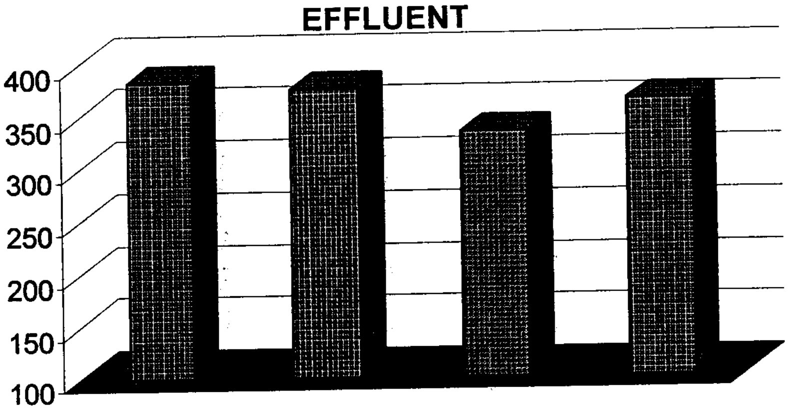


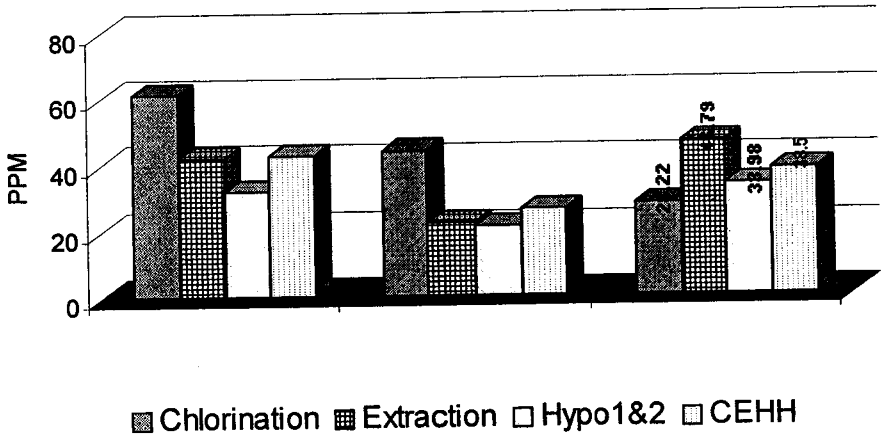
FIGURE: 5 Average Aox concentration and effluent discharge

CHEMICAL BAGASSE PULP EFFLUENT AOX DEGRADATION BY WHITE ROT FUNGI





AOX DISCHARGED KGS/DAY IN TREATED EFFLUENT



HARDWOOD PULP EFFLUENT AOX DEGRADATION BY WHITE ROT FUNGI

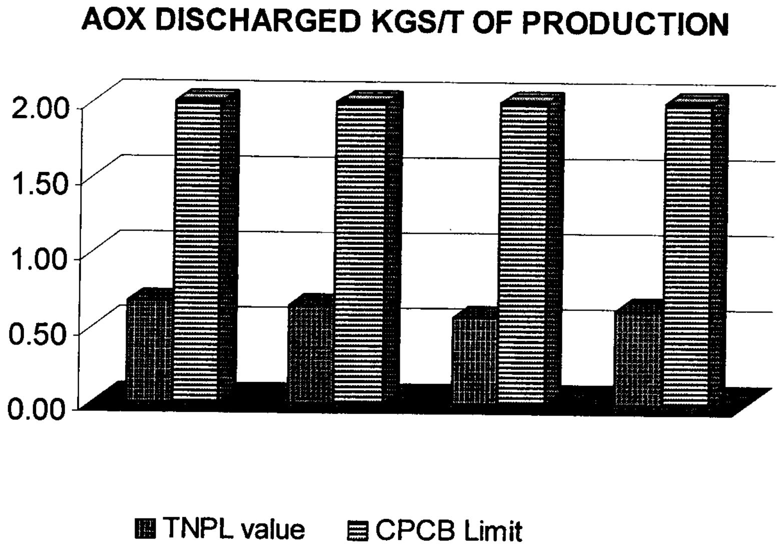
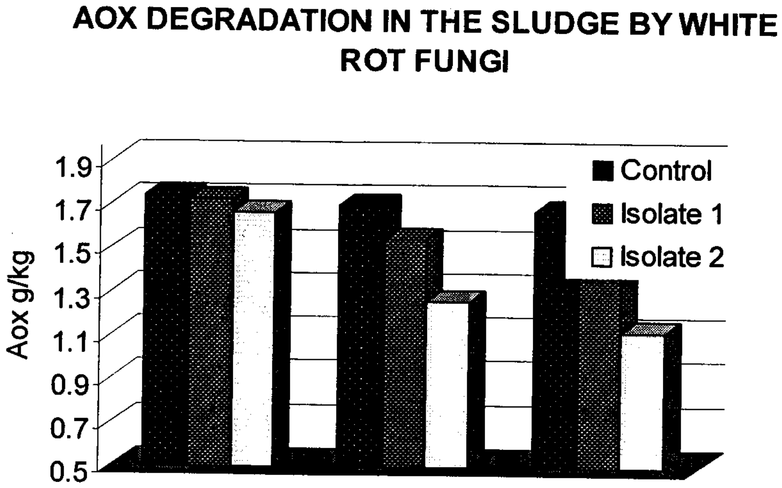


FIGURE :6 AOX discharge in final treated effluent



AOX DEGRADATION DURING COMPOSTING

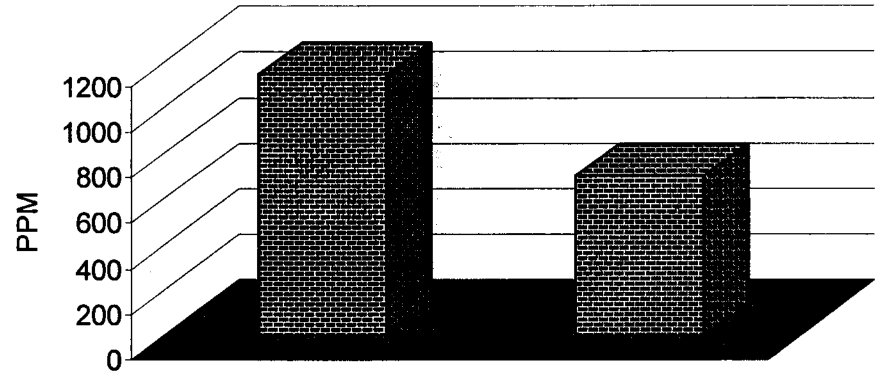


FIGURE: 8 AOX Degradation in the sludge and during composting

MODERN TECHNOLOGY OF PULP WASHING THROUGH CHEMI WASHER

PAVAN KUMAR SURI
VICE PRESIDENT (OPERATIONS)
THE ANDHRA PRADESH PAPER MILLS LTD.
RAJAHMUNDRY - 533 105

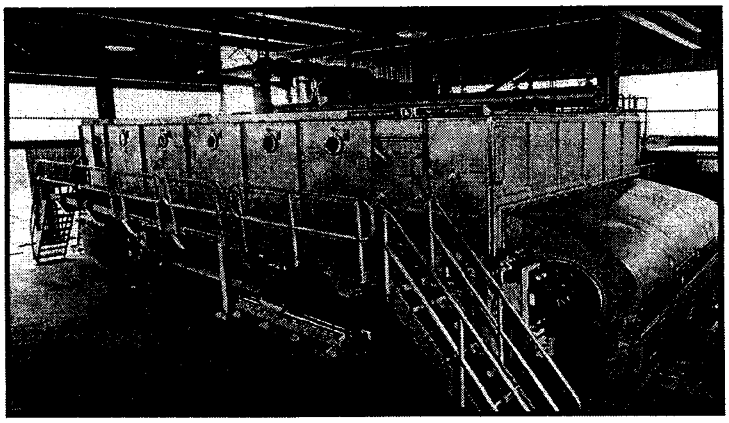
TECHNOLOGY OPTIONS FOR PULP WASHING

- ➢DD WASHER
- ➢BELT WASHER (CHEMI WASHER)
- ➢PRESSES
- ➢DRUM WASHER
- ➢DD WASHER
- ➢BELT WASHER (CHEMI WASHER)
- ➢PRESSES
- ➢DRUM WASHER

CRITERIA FOR SELECTION

- SPACE REQUIREMENT
- WASHING EFFICIENCY
- SAFETY OF PERSONNEL & EQUIPMENT
- POWER CONSUMPTION
- ENVIRONMENT FRIENDLINESS
- EASE OF MAINTENANCE
- INVESTMENT
- RUNNING COST
- MAINTENANCE COST

✓LESS SPACE REQUIREMENT AND LOWER HEIGHT



CHEMI WASHER

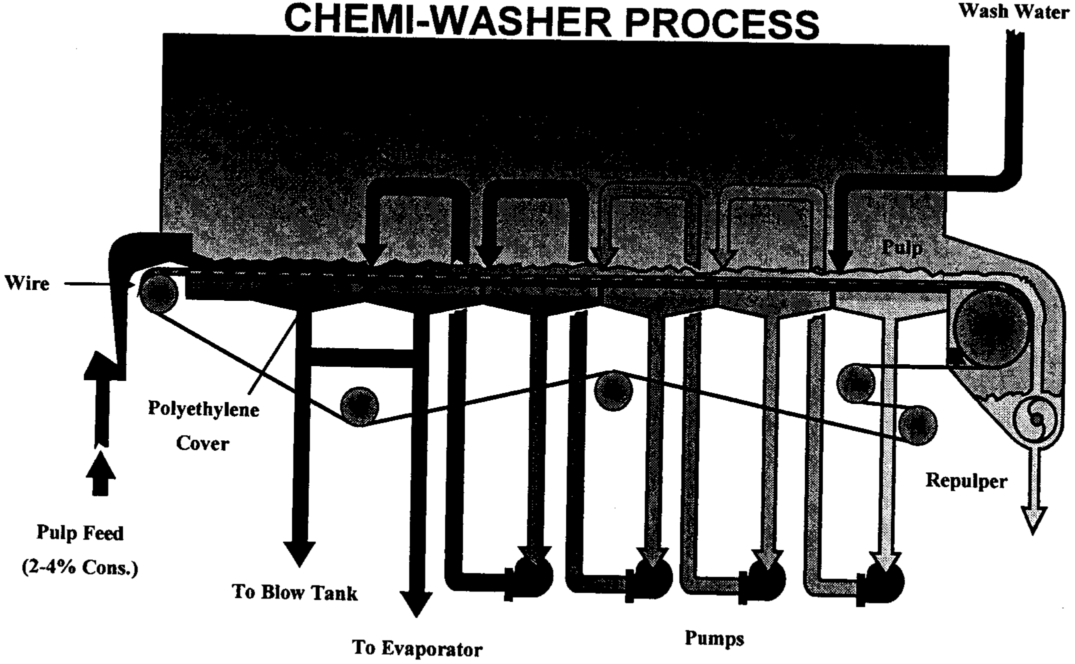
✓BETTER WASHING EFFICIENCY WITH LOW DILUTION FACTOR

DILUTION FACTOR

CHEMI WASHER
DD WASHER
PRESS
DRUM WASHER

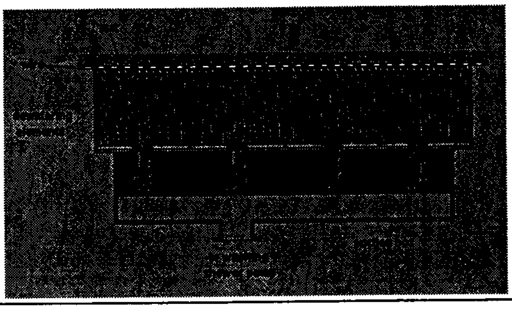
✓BETTER WASHING EFFICIENCY WITH LOW DILUTION FACTOR

CHEMI-WASHER PROCESS



BETTER WASHING EFFICIENCY WITH HIGHER WBL SOLIDS AND MINIMUM CHEMICAL LOSS

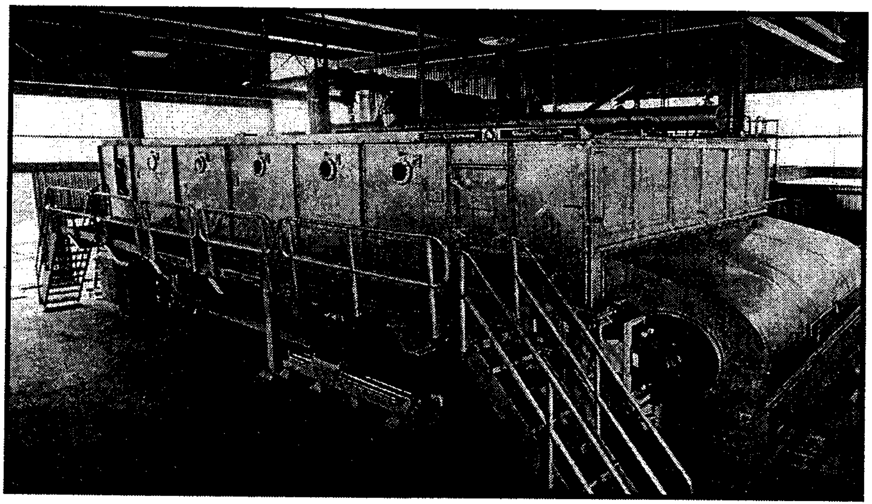
	CHEMICAL LOSS(KGS/T)	TOTAL SOLIDS (%)
DD WASHER	13.0	17.5
CHEMI WASHER	12.5	19.0
PRESS	13.0	15.0
DRUM WASHER	15.0	15.0



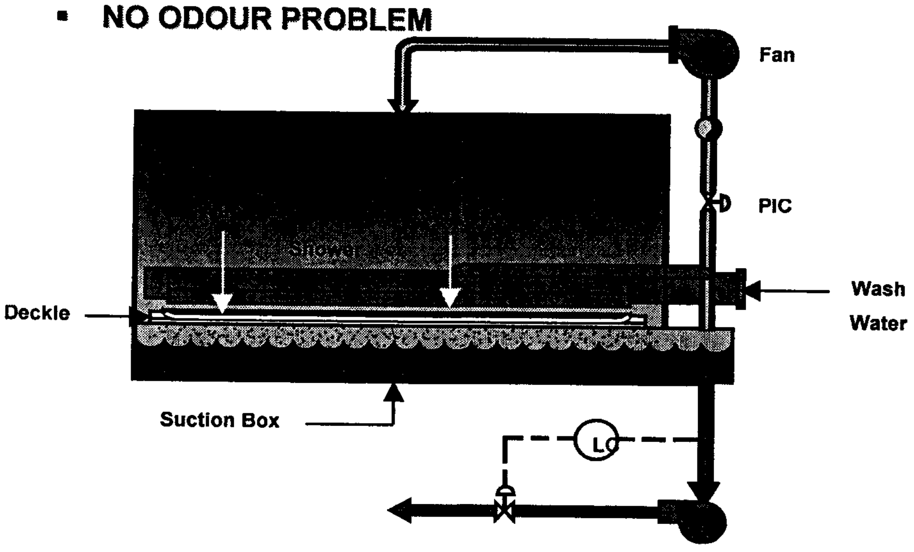
LOWER POWER CONSUMPTION

	(KWH / TON)
CHEMI WASHER	40 - 45
DD WASHER	65 - 70
DRUM WASHER	80 - 85
PRESS	95 - 100

SAFETY OF PERSONNEL & EQUIPMENT TOGETHER WITH EASE OF MAINTENANCE



- **LESS FRESH WATER CONSUMPTION**
- **NO ODOUR PROBLEM**



Closed design for environmental friendliness

ECONOMICS

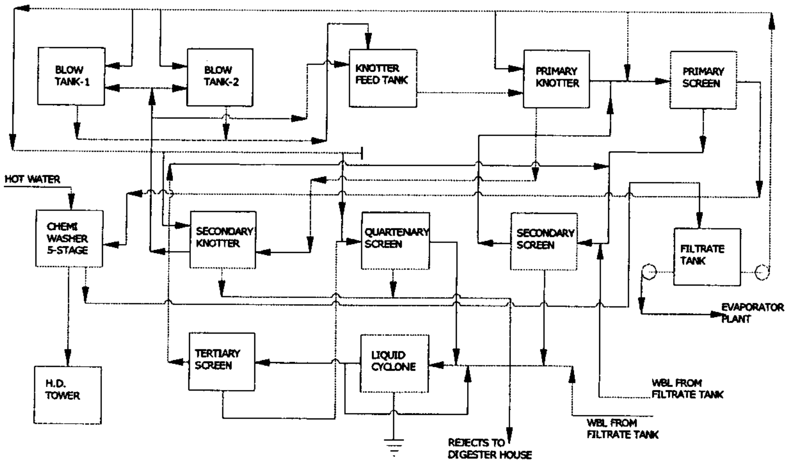
INVESTMENT : Rs. 2,460 Lakhs

POWER, STEAM AND CHEMICAL SAVING : Rs. 615 Lakhs p.a.

SALIENT FEATURES OF CHEMI WASHER

- **HORIZONTAL BELT TYPE**
  - **COMPACTNESS**
  - **EASE OF OPERATION**
- **5 STAGE COUNTER-CURRENT WASHING SYSTEM**
  - **NO INTERMEDIATE SEAL TANKS**
  - **LOW DILUTION FACTORS**
  - **HIGHER BLACK LIQUOR CONCENTRATION**
- **ENERGY EFFICIENT**
  - **LOW POWER CONSUMPTION**
  - **HOT STOCK SCREENING AT MEDIUM CONSISTENCY**
  - **NO INTERMEDIATE SEAL TANKS**
  - **STEAM SAVING IN BLACK LIQUOR EVAPORATION**
- **ENVIRONMENT FRIENDLY**
  - **NO ODOUR PROBLEM DUE TO CLOSED SYSTEM**
  - **LESS FRESH WATER CONSUMPTION DUE TO LOW DF**

BLOCK DIAGRAM OF CHEMI WASHER HOT STOCK SCREENING & WASHING



BIODEGRADATION OF AOX FROM PAPER AND PULP INDUSTRY WASTEWATER

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Agharkar Research Institute, Pune-411004

ABSTRACT

Chlorinated organic compounds are generated during the bleaching of pulp in pulp and paper industry. These compounds are formed as a result of reaction between residual lignin of wood fibres and chlorine. They belong to the class of recalcitrant chemicals as they endure for long periods in natural ecosystems. Some of the compounds have half life periods upto 20-30 years. Most of the chlorinated organic compounds are toxic and show tendency to bioaccumulate. Many of them are proven carcinogens and mutagens.

Physical and chemical methods are not feasible for degradation and detoxification of AOX compounds from pulp and paper industry effluent. In addition, these methods prove very expensive. Advanced treatment processes have also been developed and applied for treatment pulp and paper mill effluent. However, these processes are mainly designed to reduce BOD and COD load of wastewater and do not necessarily remove AOX compounds. Certain fungi, aerobic and anaerobic bacteria possess ability to degrade AOX compounds. Basic studies on isolation and metabolic pathways of these microbes have been carried out extensively. Development of biological processes for specific treatment of the AOX compounds are thus essential to solve pollution problems arising due to chlorinated organics in pulp and paper industry wastewater.

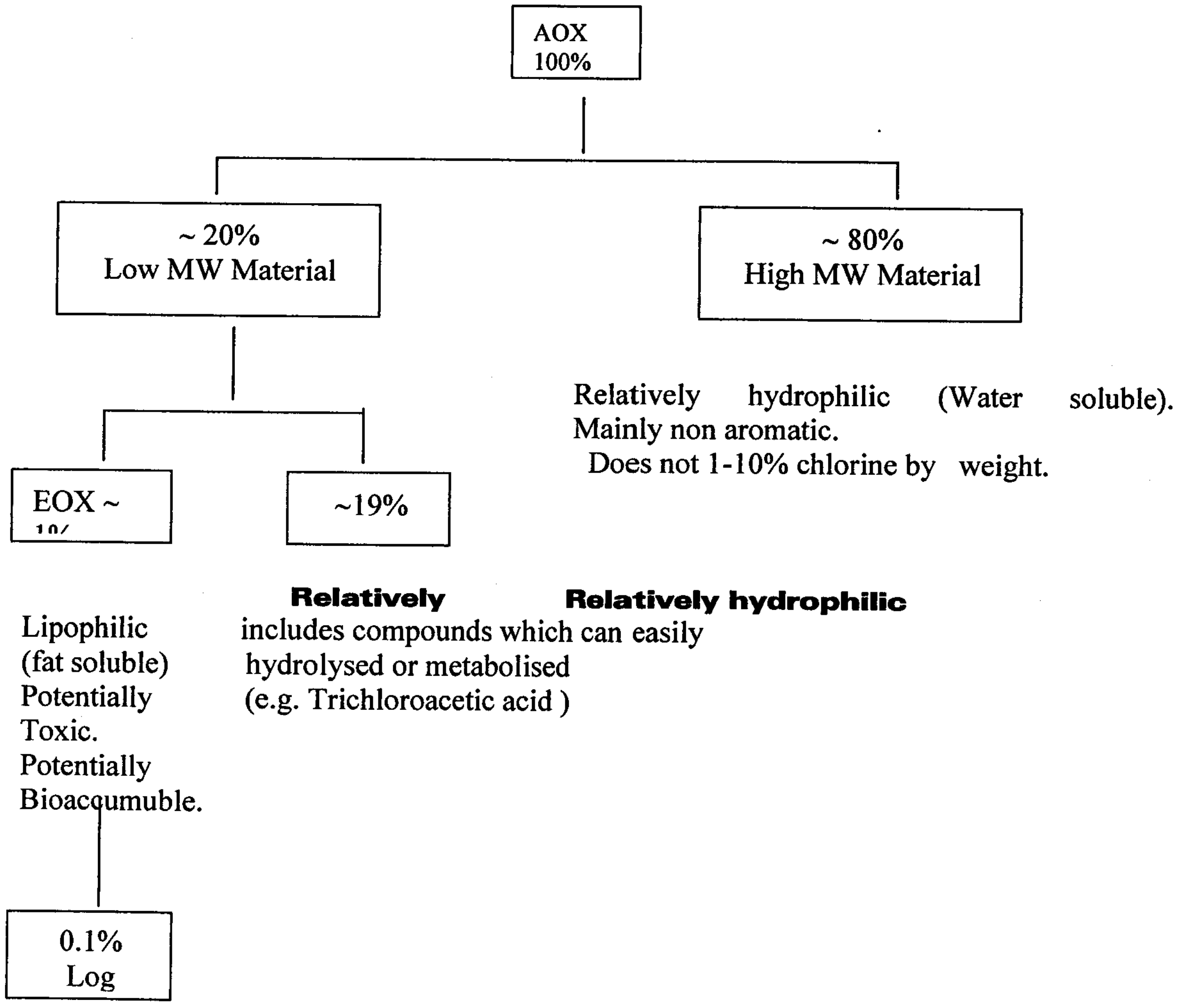
INTRODUCTION:

The pulp and paper mill sector is one of the oldest industries in India. The first paper mill was commissioned in 1812 in the Eastern State of Wast Bengal. Today, there are about 406 pulp and paper mills in the country with an annual installed capacity of 6.2 million tons.

The industry generates large volumes of wastewater. Of the different waste streams, bleach plant effluents are considered to be the most polluting. The toxicity is mainly due to the various chlorinated organic compounds generated during the bleaching of pulp with chlorine and other chlorine substituents. These compounds are formed from the reaction between residual lignin of wood fibres and chlorine. About 330 different chlorinated organic compounds have been identified in the pulp and paper wastewater.

TYPES OF CHLORINATED ORGANIC COMPOUNDS GENERATED DURING BLEACHING:

Of the total chlorine used in the bleach plant, about 90 % form common salt (NaCl) and 10% or less gets bound to the organic material removed from the pulp. The organically bound chlorine is also termed as AOX. This is further classified as follows:



Relatively hydrophilic (Water soluble). Mainly non aromatic.
Does not 1-10% chlorine by weight.

Relatively **Relatively hydrophilic**
includes compounds which can easily hydrolysed or metabolised (e.g. Trichloroacetic acid)

Lipophilic
(fat soluble)
Potentially
Toxic.
Potentially
Bioaccumuble.

Highly lipophilic bioaccumulable (e.g. Dioxins - 44% chlorine by wt.)

Fig. 1: Characteristics of AOX in the effluent from conventionally bleached kraft pulp.

The high molecular weight chlorolignins are non-toxic whereas the low molecular weight chlorolignins have the capacity to penetrate the cell membranes and are potentially toxic. This fraction is also bioaccumulable. Hence, it is environmentally important.

The various chlorinated organic compounds generated in bleach plant are shown below:

Table1: Chlorinated organic compounds in bleached pulp mill effluents

Type	Number of varieties	Amounts (g/t pulp)
Chlorinated phenolics	40	Up to 100
Chlorinated aldehydes, ketones and lactones	45	500
Chlorinated acids	40	Up to 500
Chlorinated hydrocarbons	45	-
Chlorinated ethers	20	-
High molecular mass	-	Up to 4 kg Cl

TOXICITY OF AOX COMPOUNDS :

The toxic effects of chlorinated organic compounds range from, carcingenecity, mutagenecity to very acute and chronic toxicity.

2,4 dichlorophenol; 2,4,5,trichlorophenol; pentachlorophenol, chlorinated dioxins, dibenzofurans and chloroform are carcinogenic. Many other compounds such as epoxy stearic acid, dichloromethane are suspected carcinogens. Carcinogenecity is generally determined by Ames test. However, there are certain discrepancies where the compound may be positive in Ames test but animal tests show no effect.

Chlorocatechols are strong mutagens.

The LD 50 values for rats (oral administration) for chlorinated organic compounds range from a few micrograms per kg body weight to about 13000 mg/kg body weight. Following table gives LD 50 values for some of the chlorinated organic compounds.

Table 2: Toxicity of different Chloro-organic compounds

Compound	System	LD$_{50}$ values (mg/ Kg body wt.)
Chloroform	Rat (oral)	300
Carbon tetrachloride	Mouse (oral)	4620
2,3,7,8 TCCD	Rat	22 μg/Kg
	Mouse	284 μg/Kg
1,2,3,7,8 pentachloro dibenzodioxin	Guinea pig	3 μg/Kg
	Mouse	338
1,2,3,4,7,8	Guinea pig	73
	Mouse	85
Monochlorobenzene	Rat (oral)	2910
Dichlorobenzene	Rat (oral)	500
Trichlorobenzene	Rat (oral)	750
Tetrachlorobenzene	Rat (oral)	934-2328
Hexachlorobenzene	Rat (oral)	3500
4 chlorophenol	Rat (oral)	500
2,4 dichlorophenol	Rat (oral)	3600
2,4,5 trichlorophenol	Rat (oral)	850
2,4,6 trichlorophenol	Rat (oral)	820
2,3,4,5 tetrachlorophenol	Rat (oral)	140
Pentachlorophenol	Albino rats	175μg/Kg
"	Rat oral	27-78
Tetrachloroethane	Rat (oral)	200
Trichloroethane	Rat (oral)	10000
Dichloroethane	Rat (oral)	680
Tetrachloroethylene	Rat (oral)	13,000
PCB (Arochlor 1221) (1224) (1243)	Rat (oral)	4000 8700 10000
Chlorinated dibenzodioxins	Rat (oral)	120 μg/Kg
"	Guinea pig	0.6-2.2 μg/Kg

Tetrachlorodibenzodioxins (TCDD) are known to produce typical skin rash called 'chloracne'. They also cause changes in skin colour , hyperpigmentation, excessive hair growth , liver damage and polyneuropathies in arms and legs. Short exposures to chlorinated benzenes are known to cause drowsiness, headache, eye-irritation, sore throat, etc.

Chronic exposures to chlorophenols result in kidney and liver damage, loss in weight , general fatigue and low appetite. Dioxins cause many reproductive and immune system disorders, abnormal fetal development. In fish they decrease growth rate and produce histological changes in liver.Chlorinated benzenes cause immunological disorders. They may also show porphyria, renal degeneration and adverse effects on lungs.

Some of the compounds are known to cause anti-hormonal effects. Dioxins in humans cause disruption of regulatory hormones. Poly chlorinated biphenyls have anti-estrogen properties that can inhibit calcium deposition during egg shell development, leading to insufficiently strong shells and premature loss. Anti-androgen effects may lead to adverse effects on male reproductive capabilities of bird and animal species.

LEGISLATION:

Due to the severety of the toxic effects of these compounds governments in many countries have imposed limits on the amount of AOX discharged from pulp mills .

Table 3: Regulations for discharge of chlorinated organic compounds measured as AOX (kg/t pulp) from bleaching of chemical pulps

Country	1994	1995-2000	2000-2005
Australia	1.0[a]		
Austria	0.75 - 1.5	0.5 - 1.0	
Belgium	1.5		
Canada			
Alberta	0.29[a] / 1.5		
British Columbia	1.5		0
Ontario		1.5	0.8

Quebec[b]	1.5 (HW)	1.0 - 2.0	
Finland[b]		1.0 - 2.0	
Germany[b]	1.0		
India[e]		2.0	
Norway[b]	1.0 - 2.0		
Japan[c]	1.5		
USA[d]		0.156	
Sweden	1.2 - 1.5	0.3 - 1.0	0.3 - 0.5

[a] Limits for new mills

[b] Lower limits for hardwood pulps

[c] Guidelines of Japan Pulp, Paper and Paperboard Association

[d] Proposed regulation on "Cluster Rules" by EPA

[e] Proposed by Ministry of Environment and Forest, Government of India

Table 4: Polychlorinated phenolic compounds proposed for regulation by the US EPA

Polychlorinated phenols	**Minimum level, ppb (µg/l)[a]**
Pentachlorophenol	5.0
2,3,4,6-Tetrachlorophenol	2.5
2,4,5-Trichlorophenol	2.5
2,4,6-Trichlorophenol	2.5
3,4,5-Trichloroguaiacol	2.5
3,4,6-Trichloroguaiacol	2.5
4,5,6-Trichloroguaiacol	2.5
3,4,5-Trichlorosyringol	2.5
3,4,5,6-Tetrachlorocatechol	5.0
3,4,6-Trichlorocatechol	5.0
3,4,5-Trichlorocatechol	5.0
3,4,5,6-Tetrachloroguaiacol	5.0

[a] The minimum level is defined as the concentration at which the analytical system gives recognizable mass spectra (corrected for background) and acceptable calibration points, using EPA method 1653

PHYSICAL AND CHEMICAL METHODS OF AOX DESTRUCTION:

Incineration, coagulation, flocculation, adsorption and membrane techniques and chemical oxidation methods have been used to treat bleach plant effluents. However, these methods are costly and sometimes unreliable.

MICROORGANISMS ABLE TO DEGRADE AOX COMPOUNDS:

MICROORGANISMS ABLE TO DEGRADE AOX COMPOUNDS:

Biodegradation is defined as the molecular degradation of an organic substance resulting from the complex action of different enzymes present in living organisms. A substance is said to be biodegraded when environmentally undesirable properties are lost. Microorganisms are said to be versatile with respect to their nutrition and metabolism. Many of the organic compounds which are not metabolised by higher plants & animal are easily catabolised or degraded or decomposed by microorganisms. Many aerobic and anaerobic bacteria, fungi, algae, protozoa, actinomycetes have be shown to degrade chlorinated organic compounds.

Actinomycetes:

Actinomycetes are known to degrade chlorinated aromatic compounds alongwith many other complex organic compounds. The actinomycetes produce less biomass. They can grow over a wide range of pH and temperature and are resistant to dessication. They produce less sludge as compared to bacteria and fungi. Hence, they are advantageous in treatment of waste water having low nutrient conditions. However, degradation by actinomycetes requires presence of other organisms for complete mineralization. Examples of actinomycete exhibiting chloro-organic degradation include *Streptomyces, Nocardia* and *Actinomyces.* (Kobayashi & Rittmann, 1982)

Phototrophic microorganisms:

These include algae, cyanobacteria and photosynthetic bacteria. These organisms are of potential importance in situations involving low concentrations of nutrients, because they are able to obtain energy from sunlight and carbon by CO_2 fixation. Low substrate concentration is not a problem with these microorganisms. Some cyanobacteria & photosynthetic bacteria are able to fix N_2, hence they can survive in bacterial growth. Some algae & cyanobacteria transform certain compounds to the same extent as bacteria do e.g. *Oscillatoria, Dunaliella.* However, in majority of cases only partial degradation is carried out i. e. transformation of the substrate is brought about. Examples of phototrophic microorganisms degrading chlorinated organic compounds include *Agnenellum, Anabaena Nostoc, Chlorella,* etc. Application of phototrophic microorganisms for removal of AOX demands large space area. This is the major obstacle in application of these micro-organisms. (Kobayashi & Tchan, 1978; Cerniglia *et al,* 1980; Kobayashi & Rittmann, 1982)

Fungi:

Fungi reduce the COD, BOD, color-compounds and also remove chloro-compounds. The chlorocompounds are degraded during the secondary metabolism stage when one of the nutrients nirogen, phosporus and carbon is depleted. Fungi also, like actinomycetes, generally cause incomplete metabolism of chlorinated organic compounds. Hence, they require subsequent bacterial association for complete mineralization. Enzyme which catalyse the degradation reaction are laccases, lignin peroxidases and Mn peroxidases. The action of both lignin peroxidases and Mn peroxidases need Mn2+, which is oxidised to Mn3+. Mn3+ is the actual oxidising agent attacking the lignin molecule. Laccases use molecular oxygen as co-substrate. Fungi have been shown to dechlorinate PCB, DDT, lindane, chlorinated anilines, polychlorinated phenolics (PCP), chlorolignin etc. Dechlorination is accompanied by extensive polymerization of the substrate. *T. versicolor and P. chrysosporium* (peroxidase) enzymes are most widely studied. (Especially for degradation of the chlorophenolics). Immobilized lignin peroxidases have been shown to decolourize and dechlorinate kraft effluent. Two commercial processes have been developed using fungal enzymes for decolorisation and decontamination of pulp and paper mill effluent; - one using laccase from *C. versicolor* and other using lignin peroxidases of *P. chrysosporium* strain.

mill effluent; - one using laccase from *C. versicolor* and other using lignin peroxidases of *P. chrysosporium* strain.

Fungi have better potential for biodegradation as compared to bacteria as they excrete the operating system i.e. extracellular enzymes. Hence, they can degrade / breakdown large molecules. Therefore, they are especially useful in degradation high molecular weight chlorolignin compounds. The best studied fungus is *Phanerochaete chrysosporium* . Many other fungi have been reported for biodegradation of chloro-organic compounds. e.g. *Phanerochaete chrysosporium, Coriolus versicolor, Schizophylum commune, Tinctoporia borbonica, Aspergillus niger, Penicillium sp., Trichoderma sp.* (Bajpai & Bajpai,1997; Bajpai, 2000).

Bacteria :

Different bacteria have been shown to bring about dechlorination of organic compounds. Here, presence or absence of oxygen plays a pivotal role. Aerobic bacteria use oxidative reactions while degradation by anaerobic bacteria takes place via reductive type of reactions

Aerobic bacteria: A number of aerobic bacteria are reported to use chlorinated organic compounds as the substrate for growth (Neilson, 1990, Mohn & Tiedjei, 1992).

Table 5: Chlorinated organics as growth substrates for aerobic bacteria

Microorganism	**Compound**
Pseudomonas sp.	Polychlorinated biphenyls; 1,2 dichlorobenzene; 2,5 dichlorobenzene; 1,4 dichlorobenzene;Chlorobenzoate; 3,4 dichlorobenzoate; 3,5 dichlorobenzoate; 3 methyl benzoate; 4 chlorophenol
Flavobacterium	Polychlorinated biphenyls
Vibrio	Polychlorinated biphenyls
Spirillum	Polychlorinated biphenyls

Rhodococcus chlorophenolicus	Pentachlorophenol
Mycobacterium fortuitum	Pentachlorophenol
Spingomonas chlorophenolica	Pentachlorophenol
Alcaligenes eutrophus	3,4 dichlorobenzoate, Polychlorinated biphenyls, 3 chlorobenzoate
Arthrobacter	Pentachlorophenol, Polychlorinated biphenyls, 4 chlorobenzoate
Burkholderia cepacia	2,4,5 trichlorophenol
Corynebacterium	2,4 dichlorobenzoate
Micrococcus	4 chlorobenzoate, Polychlorinated biphenyls

Advantages:

Aerobic treatments are usually complete converting organic fraction to CO_2. Aerobic bacteria have fast growth rate and hence these treatments are possible within few days to weeks.

Disadvantages :

- Applicable only to those conditions where sufficient molecular oxygen is available. The rate of degradation is proportional to dissolved oxygen and therefore aeration always improve the efficiency. This demands large input of energy thereby making the process costly.
- High specificity of substrates utilisation.

Anaerobic bacteria: Many anaerobic bacteria in pure as well as in consortia are known to dechlorinate chloroorganic compounds in absence of molecular oxygen / under anoxic conditions (Fantroussi *et al*, 1998; Holliger *et al*, 1999). Table 6 & 7 list the majority of anaerobic bacteria studied and the compounds they degrade.

Table 6: Anaerobic bacteria which can dechlorinate chlorinated organic compounds as substrate or by cometabolism:

Micro-organism	**Compound**
Acetobacterium woodii	Chloroform, Carbon tetrachloride, tetrachloroethene
Clostridium formicoaceticum	Tetrachloroethene
Clostridium rectum	Hexachlorocyclohexane Tetrachlorocyclohexene
Clostridium thermoaceticum	Carbon tetrachloride

Table 6: Anaerobic bacteria which can dechlorinate chlorinated organic compounds as substrate or by cometabolism:

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Clostridium rectum	Hexachlorocyclohexane Tetrachlorocyclohexene
Clostridium thermoaceticum	Carbon tetrachloride
Dehalobacterium formicoaceticum	Dichloromethane
Desulfobacterium autotrophicum	Trichloroethane, Carbon tetrachloride
Methanosarcina barkeri	Carbon tetrachloride, 1,2-Dichloroethane, Chloroform
Methanosarcina mazei	Carbon tetrachloride, 1,2-Dichloroethane, Chloroform
Methanothrix soehngenii	1,2-Dichloroethane
Methanosarcina thermoautotrophicum	Carbon tetrachloride, 1,2-Dichloroethane
Methanosarcina thermophila	Trichloroethene
Methanolobus tindarius	Tetrachloroethene
Shewanella putrifaciens 200	Carbon tetrachloride
Sporomusa ovata	Tetrachloroethene
Staphylococcus epidermidis	1,2,4-Trichlorobenzene

Table 7: Anaerobic bacteria which can dechlorinate chlorinated organic compounds via dehalorespiration:

Micro-organism	**Compound**	**E donor**
Desulfomonile tiedjei	Tetrachloroethene, Trichloroethene, 3-Chlorobenzoate, Pentachlorophenol	H_2, pyruvate, formate
Isolate 2CP1	2-Chlorophenol, 2,6- Dichlorophenol	Acetate
Desulfitobacterium chlororespirans	2,4,6-Trichlorophenol, 3Cl-4OH-phenylacetate	H_2, pyruvate, formate
Desulfitobacterium hafniense	Pentachlorophenol, 3Cl-4OH-phenylacetate	Pyruvate, tryptophan
Desulfitobacterium frappieri	2,4,6-Trichlorophenol, 3Cl-4OH-phenylacetate	Pyruvate
Desulfitobacterium dehalogenans	Tetrachloroethene, 3Cl-4OH-phenylacetate, 2,4,6-Trichlorophenol	H_2, pyruvate, formate
Desulfitobacterium PCE- 1	Tetrachloroethene, 2-Chlorophenol, 3Cl-4OH-phenylacetate, 2,4,6-Trichlorophenol	Pyruvate, formate
Desulfitobacterium PCE- S	Tetrachloroethene, Trichloroethene, 2,4,5-Trichlorophenol, Pentachlorophenol	Pyruvate
Dehalobacter restrictus	Tetrachloroethene, Trichloroethene	H_2
Isolate TEA	Tetrachloroethene, Trichloroethene	H_2

Advantages:

- Reductive dehalogenation is the only known biodegradation mechanism for certain significant pollutants including polychlorinated biphenyls, pentachlorophenol, hexachlorobenzene, perchloroethane.
- Dechlorination of highly substituted chloro org. e.g. Pentachlorophenol degradation takes place only under anaerobic conditions.

Disadvantages:

- The process is slow as compared to aerobic treatment and demands large surface area. It can not bring about complete mineralization of the chlorocompounds and usually has to be coupled to aerobic process.
- Less effective on less substituted chlorinated organic compounds such as monochlorobenzene.

MECHANISM OF DEGRADATION

Different bacteria possess different enzymes and exhibit different mechanisms od degradation. These pathways have been extensively discussed by Reineke (Reineke 2001). Following are the major types of reactions/ pathways of dechlorinations.

A) By aerobic bacteria:

Degradation of Chloroaromatic Compounds: Biodegradation of chloro-substituted aryl compounds can be considered complete only when its carbon skeleton is converted to intermediary metabolites & organic chlorine is returned to mineral state. The removal of chlorine may take place before aromatic ring cleavage or after ring cleavage. The initial dechlorination of higher chlorinated aromatics leads to chloro-catechols, chloroprotocatechuates or chlorodrydroquinones.

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- **Elimination of Chlorine Substituent Prior To Ring Cleavage:** There are three mechanisms of dechlorination prior to ring cleavage namely Hydrolytic, Oxygenolytic, and Reductive.

(i) Hydrolytic dechlorination : Replacement of chlorine by hydroxyl radical is observed in chlorobenzoates and chlorophenols. Dechlorination reaction utilizes water as the hydroxyl donor & not the molecular oxygen. This type of mechanism is observed in degradation of 4 chlorobenzoate by *Micrococcus* spp. *Pseudomonas* spp., *Nocardia* sp., *Alcaligenes* sp. & *Arthrobacter* spp.

(ii) Oxygenolytic dechlorination : Chlorine carbon bond is cleaved by mono and di oxygenase reactions. The oxygen of the hydroxyl groups originates from molecular oxygen

Monooxygenase : Initial dechlorination of pentachlorophenol occurs by this mechanism producing tetrachloro-p-hydroquinone. Bacteria showing this kind of mechanism are *Arthrobacter sp, Flavobacterium sp* & *Mycobacterium fortuitum.*

Dioxygenase :. This type of mechanism is observed for chlorobenzoates like 2-chloro, 3-chloro, 2,4, Dichloro, 2,5 dichloro & 3,4 dichlorobenzoate, 1,2,4,5 tetrachlorobenzene & 4 chlorophenyl acetate. Initial dioxygenases which are responsible for ring activation, produce cis-dihydrodiols which are further transformed by dehydrogenases to give catechols.

Fig. 2: Schematic presentation of dechlorination prior to ring cleavage 1. Hydrolytic 2. Oxygenolytic 3. Reductive Dechlorination

- **Dechlorination After Ring Cleavage:** Chlorocatechols are subject to degradation through modified ortho pathway. Degradation of chlorohydrogquinones proceeds through hydroquinone pathway. The degradation pathways of chlorocatechols or chlorohydeoquinones converge at the stage of chloro-maleylacetate. In the next step, 3-oxoadipate is the common metabolite formed in the degradation pathway used for aromatics and chloroaromatics. Besides these funneling pathways, some divergence is seen for chlorocatechols and chloroprotocatechuates leading into the meta pathway.

Peripheral pathways: In these pathways, an aromatic compound without a hydroxyl group is activated through a multicomponent dioxygenase such as benzene dioxygenase or biphenyl 2,3 dioxygenase using molecular oxygen. Subsequently, the resulting dis-dihydrodiol is converted by a dehydrogenase to give a 1,2 diphenolic structure, regaining the aromatic stage. The resulting diphenol is substrate for ring cleavage, often metal cleavage which requires another mole of molecular oxygen.

During aniline degradation, the stage of diphenol is reached by the action of an aniline dioxygenase eliminating NH3 at the same time. In this case, no dehydrogenase is needed. Phenol will be converted by a monooxygenase reaction to produce catechol.

During the degradation of binuclear aromatics, the formation and cleavage of the 1,2 diphenol take place twice. The first cis-dihydrodiols, which result during degradation of dibenzo-p-dioxin and dibenzofuran, are unstable hemacetals. Therefore, the ether bond is cleaved spontaneously, and a dehydrogenase is not

During the degradation of binuclear aromatics, the formation and cleavage of the 1,2 diphenol take place twice. The first cis-dihydrodiols, which result during degradation of dibenzo-p-dioxin and dibenzofuran, are unstable hemacetals. Therefore, the ether bond is cleaved spontaneously, and a dehydrogenase is not necessary to reach the 1,2-di-phenolic structure. Meta cleavage by a dioxygenase yields yellow product that is subject to hydrolytic shortening of the side chain.

The peripheral degradation of a multitude of aromatics converges at the stage of catechol. Chlorocatechols are formed via the mentioned sequences from chlorinated compounds.

Central Degradative Sequences: Modified ortho pathway - Ring cleavage by chlorocatechol 1,2 dioxygenase with consumption of molecular oxygen results in the formation of the corresponding chloro-us-cis-muconate. Further degradation by a chloromuconate cycloisomerase leads to a lactone, which eliminates chlorine as HCl from position 4 or 5 bringing about the formation of an exocyclic double bond. In this way, a chloro dienelactone is formed. It is transformed to the corresponding chloro maleylacetate via hydrolytic cleavage by chloro dienelactone hydrolase.

3-oxoadipate pathway: The use of chlorocatechols as a source of carbon and energy by bacterial cells requires the synthesis of the last two enzymes of the well-known 3-oxoadipate (β-ketoadipate) pathway - 3-oxoadipate: succinyl-CoA transferase and 3-oxoadipyl-CoA thiolase - to reach the Krebs cycle). Thus modified ortho pathways depend on the presence of the 3-oxoadipate pathway in a host strain in order to operate. Various benzoate or p-hydroxybenzoate-degrading bacteria fulfill this requirement. In a classic study on the taxonomy of pseudomonads, only 65% of the 175 strains of the fluorescent group (*Pseudomonas* degradation takes place via 3-oxoadipate. Two species of the acidovorans group, *Pseudomonas acidovorans* and *Pseudomonas testosteroni* (today *Comamonas testosteroni*) were characterized by meta cleavage of protocatechuate, the intermediate in the degradation of p-hydroxybenzoate.

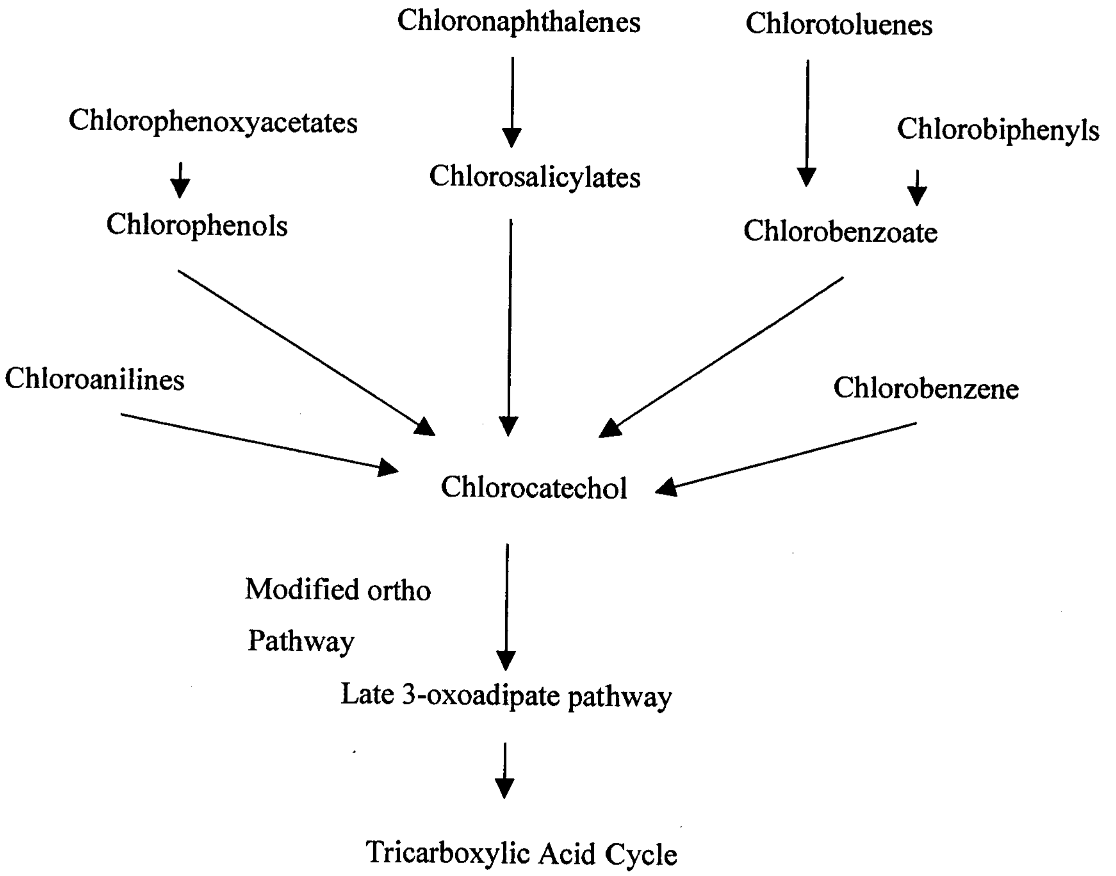

Fig 3: Schematic presentation of the mineralization of chloroaromatics .

Degradation of Chlorinated Aliphatic Compounds:

As Growth Substrate: Chloroaliphatic compounds as growth substrate by aerobic bacteria. Cultures have been shown to grow on hydroxylated or carboxylated chloroaliphatics also. The degree of recalcitrance of chlorinated aliphatic compounds to aerobic degradation generally increases with an increasing degree of chlorine substitution. Different types of mechanisms have been found in different organisms. These include:

1. Hydrolytic dehalogenation.
2. Glutathione S-transferase dependent dehalogenation
1. Lyase catalysed dehalogenation
2. Hydratase catalysed dehalogenation
3. Dehalogenation by oxygenases
4. Dehalogenation during beta oxidation
5. Dehydrohalogenation
6. Dehalogenation by methyl transferase/dehydrogenase
7. Oxidative dehalogenation - chlorinated alkanes.

As Cometablism: Chloroaliphatic compounds can also be degraded via cometabolic processes. Example - Dechlorination of trichlorethene by *Methylosinus trichosporium.*

(B) By anaerobic bacteria:

- The chlorinated compound may serve as the sole source of carbon and energy for the bacterium e.g. *Dehalobacterium formicoaceticum.*

- The compound may act as a cometabolite : Cometabolism is a process in which the enzymes and co-factors which have been evolved to degrade other substrates fortutiously convert chlorinated compounds. Example : *Shewanella putrifaciens & Acetobacterium woodii.* Carbon monoride dehydrogenase is involved in CCl_4

metabolism of *Acetobacterium woodii.* Experiments with *Shewanella putrefaciens* 200, suggested that cytochromes are involved in CCl_4 reduction.

- Some bacteria are capable of utilizing the energy generated in the dechlorination process for the synthesis of ATP. The process is referred to as dehalorespiration. In this process, the chlorinated compound acts as the electron acceptor and H_2 or formate, tryptophan, pyruvate, acetate, act as electron donor. The compounds degraded in this way are PCE, TCE, chlorobenzoate, chlorophenols. Dichloroethane, Chloroethene e.g. *Dehalobacter restrictus, Dehalospirillum multivorans, Desulfuromonas chloroethenica, Dehalococcoides ethenogenes, Desulfitobacterium sp. Desulfomonile tiedje.*

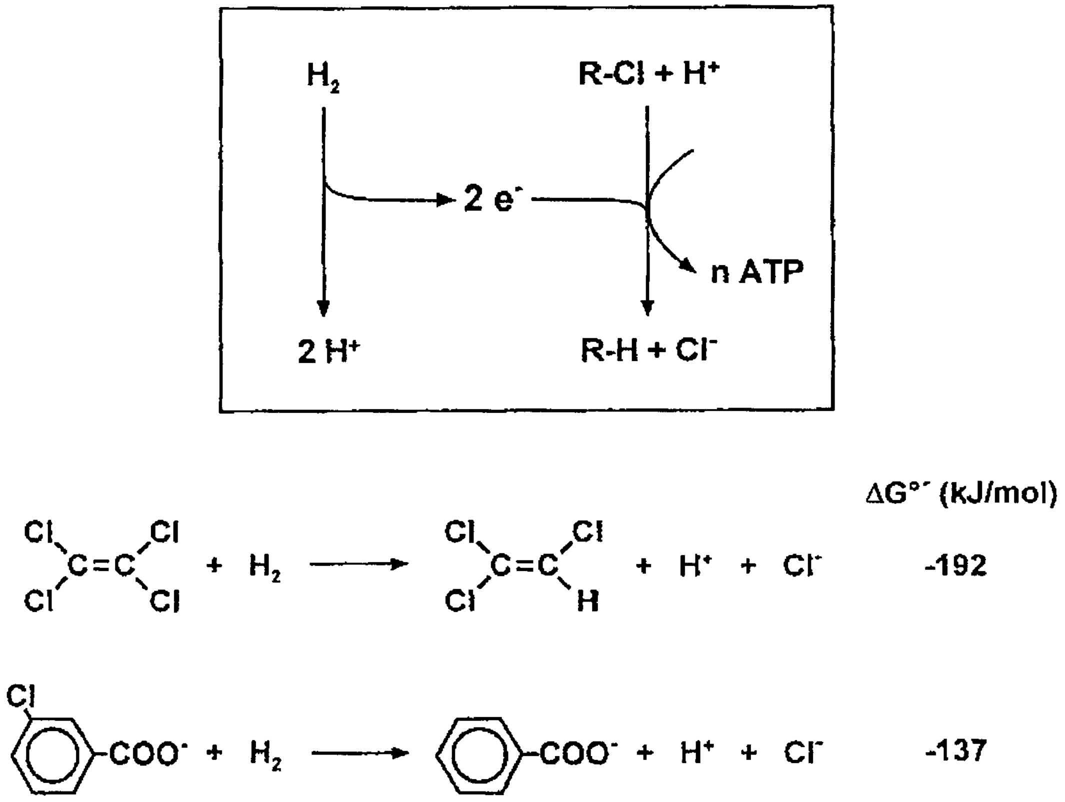

Fig.4 : Schematic representation of dehalorespiration with H_2 as electron donor and tetrachloroethene or 3-chlorobenzoate as electron acceptor.

BIOLOGICAL TREATMENT TECHNOLOGIES:

Numerous biological treatment technologies for variety of waste waters and wastes are reported in the literature. These include aerobic as well as anaerobic ones. The effectiveness of biodegradation depends on several factors: structure of the compound, the presence of exotic substituents and their position in the molecule, solubility of the compound and concentration of the pollutant. For aromatic halogenated compounds, a high degree of halogenation requires high energy by the microorganisms to break the stable carbon-halogen bonds Chlorine as the substituent alters the resonant properties of the aromatic substance as well as the electron density of specific sites. This may result in the deactivation of the primary oxidation of the compound by microorganisms. Additionally, the positions occupied by substituted chlorines have stereochemical effects on the affinity between enzymes and their substrate molecule.

The water solubility of the compound has a vital role in its degradation. Microorganisms than those with low solubility easily access compounds with high aqueous solubility. For PCBs, highly chlorinated congeners are very insoluble in water. This could account for the resistance of highly chlorinated PCB congeners to biodegradation.

Pollutant concentration is also a major factor affecting biodegradation. In general, a low pollutant concentration may be insufficient for the induction of degradative enzymes or to sustain growth of competent organisms. On the other hand, a very high concentration may render the compound toxic to the organisms. At low concentration range, degradation increases linearly with increase in concentration until such time that the rate essentially becomes constant regardless of further increase in pollutant concentration.

Other environmental factors affecting degradation are temperature, pH, presence of toxic or inhibitory substance and competing substrates, availability of suitable electron acceptors, and interactions among microorganisms. All these factors interplay and make the rates of biodegradation unpredictable.

Biological treatment of AOX wastewater

Aerobic Processes: Biological oxidation is the most widely used technique to remove BOD and chlorinated organics because of its effectiveness. Leach *et al* (1978) reported the biodegradation of seven compounds representing the major categories of toxicants in a laboratory batch aerated lagoon. Gergov *et al* (1988) reported that biological treatment, especially the activated sludge process, removed 75-95% of chlorophenolics.

While the Swedish researchers found that the biological treatment is ineffective in removing TOCl, American mills reported, an average of 50-90% TOCl removal by an aerated lagoon or activated sludge process. Gergov et al (1988) investigated pollutant removal efficiencies in mill scale biological treatment system. They found that 48-65% of AOX was removed in the activated sludge process. The aerated lagoon was found to be less efficient than the activated sludge. Recently, Deardorff *et al* (1994) reported that the efficiency of AOX removal through biotreatment of combined bleach plant effluent increases with increasing chlorine dioxide substitution. Jokela *et al* (1993) reported that aerobic lagoon system removed 58-60% of the organochlorine compounds from the water phase, and the full scale activated sludge plants removed 19-55%. Both biotreatments removed all sizes and classes of organochlorine molecules and slightly shifted the relative size distribution of the compounds remaining in the water phase towards the higher molecular masses.

Anaerobic Processes: Anaerobic biological treatment can also efficiently destroy chlorophenolic compounds, mutagenicity and acute toxicity. The Enso-Fenox Process was capable of removing 64-94% of the chlorophenol load and toxicity, mutagenicity and chloroform in the bleaching effluent. Raizer-Neto *et al* (1991) studied the efficiency of anaerobic treatment in reducing chlorinated organic compounds in a fixed bed reactor. AOX removal efficiency was primarily affected by increasing AOX concentration and was only about 50% for 50 mg/l COD. BOD5 removal efficiencies were affected at higher AOX concentrations of 100 mg/l. AOX loading rate or hydraulic residence time were found to be more important limiting factors than bleaching for AOX concentration. For AOX loading rates under 40 mg/l and an AOX concentration as high as 130 mg/l in the effluent feed, COD and BOD5 removal were about 80%. Fitzsimons *et al* (1990) reported 35-40% COD and 42-45% AOX reductions in a 1.5-day anaerobic treatment.

EK and Erikson (1987) proposed a process based on UF and anaerobic and aerobic biological treatments. The UF was used to separate the high molecular mass material, which is relatively resistant to biological degradation. Anaerobic microorganisms were believed to be able to remove highly chlorinated substances more efficiently than aerobic microorganisms. The last remaining chlorine atom was removed by aerobic microorganisms. The combined treatments typically removed 80% of the AOX, COD and chlorinated phenolics and completely eliminated chlorate. Lafond and Ferguson (1991) reported that anaerobic treatment in an upflow hybrid reactor removed 17-40% of AOX.

Guo *et al* (1990) investigated degradation of model compounds - chlorophenols (pentachlorophenols, 2,4,6-trichlorophenol, and 2,4-dichlorophenol) and chloroguaiacols (4,5-dichloroguaiacol and 4,5,6-trichloroguaiacol) in pure water solution by fungal treatment using an RBC. They found that at concentration of 30 mg/l, 80-85% of chlorophenols and chloroguaiacols could be degraded after 3-4 h of treatment. Meanwhile, some of these compounds were methylated to chloroanisoles and chloroveratrols.

Enzymatic Treatment : Some enzymes also seem to have the potential to remove color and AOX from pulp and paper mill effluents. Peroxidase, laccase etc. are the most important of these. The use of microbial or enzyme-based treatment offers some distinct advantages over physical and chemical AOX precipitation methods, in that only catalytic and not stoichiometric amounts of the reagents are needed, and the low organic concentrations and large volumes typical of bleaching effluents are, therefore, less of a problem. Also, both complete microbial systems and isolated enzymes such as peroxidases and laccases have been shown to reduce the acute toxicity by polymerizing and thereby rendering less soluble many of the low molecular mass nonchlorinated and polychlorinated phenolics.

Arcand and Archibald (1991) carried ot a systematic study on direct dechlorination of chlorophenolic compounds in pulp and paper mill effluents by laccase from *T.versicolor.* It was found that most of the laccase secreted by *T. versicolor* could partially dechlorinate a variety of chlorophenolics. The rate and extent of Cl- release were found tobe substantially affected by substrate and enzyme concentration and the presence of multiple laccase substrates. The dechlorination as found to be accompanied by extensive polymerization of the substrate.

BIOFILM REACTORS

Microorganisms can grow in suspended culture and or attached to a surface forming a microbial biofilm. Suspended growth reactors are the most commonly used in the treatment of wastewater since the microorganisms can attack the pollutant where they are, that is, in solution. Where aeration is needed, addition of oxygen is easy. However, when continuous process is used, treated waste stream is continuously removed from the reactor and the suspended biomass is partially removed from the reactor. When the influent rate (dilution rate) is high there is a possibility of cell washout. Only the cells that are attached remain in the reactor. In this case, immobilization of cells is an advantage.

Immobilization is easy to achieve since microorganisms have the ability to attach on almost any surface exposed to an aqueous environment (Henze, 1995). An initially clean surface binds dissolved chemicals (both organic and inorganic) found in the bulk fluid, followed by the attachment of microorganisms. Microorganisms accumulate on the surface matrix and produces extracellular polymers to form a gel-like material called biofilm.

In practice the development of a functional biofilm usually take about 14 days under aerobic conditions(Henze, 1995). Growth is faster on surfaces with earlier growth than on clean surfaces. Building-up is selective and bacteria that are not attached are washed out. The use of wild type microorganisms performs better in a biofilm reactor than do pure strains of specialized laboratory microorganisms. The depth and composition of the biofilm are influenced by many factors. These are nature and concentration of the organic substrate, nature of the microorganism, superficial velocity, water characteristics such as pH and electrolyte concentration, and the nature of the support media.

One of the more important advantages of biofilm reactors is the presence of microbial diversity due to concentration gradients of electron donors, acceptors, and other environmental parameters, including biological products. Both aerobic and anaerobic conditions can be maintained within the reactor. When diffusion of oxygen is limited, the inner portion of the biofilm becomes anaerobic while the outer portion is aerobic. If on the other hand, diffusion of nutrients is limited, the bacteria at the bottom of the biofilm are starved resulting in a weakening of the adhesion.

This causes the biofilm to slough off the medium by hydraulic erosion. A naked area in the solid medium is produced and new microorganisms are attached. In effect there is a cyclic growth and sloughing off of biofilm within the reactor.

The support media commonly utilized in biofilms are rock, sand, charcoal, diatomaceous earth, activated carbon, gelatin, and wood. Properties of the media such as surface area, surface roughness, pore volume, pore size, adsorption properties, density and specific gravity affect the depth and composition of the biofilm. Solid supports with diameters of 150 to 300 μm provide the best adhesion for microorganisms. For mixed population, the sand support favors the faster-growth organisms over methanogenic organisms (Kindzierski,1992). For low substrate levels, sand media yield inconsistent quality with anaerobic systems due to lack of attached biomass.

Biofilm reactors offer several advantages compared to suspended reactors. Biofilm reactors are able to mimic the environment in which microorganisms have existed and competed. The growth for some microbial species is very poor in suspended reactors while biofilms have the ability to maintain large microbial diversity in a relatively stable form. Other advantages are high mean cell residence times, lack of sludge handling to maintain the biomass, and better response to toxicity. Microorganisms are also buffered against toxic materials and shock loads. Another important advantage is the potential combined anaerobic-aerobic metabolism resulting in higher degradation rates than in suspended cells.

One drawback of the biofilm reactor is when the pollutant to be degraded is either heavier or lighter than water. In both cases, the pollutant is not readily available to the microorganisms thus, limiting the biodegradability of the compound. To address this problem, the biofilm may be fluidized. In the fluidized bed reactor, the microorganisms are immobilized on the surface of particles suspended in the reactor. The reactor is operated in an up flow condition and the particles are kept in suspension by the drag forces caused by the fluid flow against the support. The top portion of the vessel is expanded to provide a calming zone that allows the particles to settle back to the fluidized portion of the vessel.

Fluidized reactors can contain biomass in higher concentration (up to 40,000 g/L) than those typically found in suspended growth reactors. The fluidized reactor had been used in the treatment of methylene chloride, BTEX compounds, and TCE.

Application of bioflim processes for Pulp and Paper Industry Wastewater

Fixed bed biofilm reactors such, as the BIOFOR process, are proven for the biological primary and secondary effluent treatment in the pulp and paper industry since over 15 years in many plants (Helble *et al*, 1999). An advanced treatment process was developed during the last five years to improve the treated effluent quality in view of stronger environmental regulations and the possibility for reuse of treated effluent in the pulp and paper industry. The combination of ozone with fixed bed biofilm reactor is one of the most efficient tertiary effluent treatment processes to give maximum elimination of COD, colour and adsorbable organohalides (AOX) with minimum of ozone dosage. It is an optimisation of a chemical and biochemical oxidation process. This method provides an effective elimination of polluting and disturbing substances and transfers the oxidative part into a small amount of biological excess sludge.

CONCLUSION AND RECOMMENDATIONS:

Over the years, extensive research is being done on various aspects of chlorinated organic compounds. This has led to adapt certain norms on throwing out these compounds in environment. The norms are very stringent in developed countries compared to other countries. This is mainly due to difference in industrial technologies used in the developed countries and other countries. It is also related to socioeconomic problems in developing countries. Many of the developed countries are well equipped with ultramodern instrumentation needed to measure the levels of chlorinated organic compounds either individually or collectively as AOX or PCB. This problem has to be solved. The required instruments should be cost effective and easily available, easy to operate and repairs, etc. Reliable portable instruments to measure AOX or PCB should be developed and used.

Amongst the existing treatment technologies none is cent percent effective. More research by environmental engineers and microbiologists is needed to develop treatment technologies which would safe guard our environment from pollution due to AOX and PCB.

References:

Arcand, L. R. & Archibald, F. S. (1991). *Enz. Microbiol.Technol.* 13:194

Bajpai, P. & Bajpai, P. K. (1997) . Reduction of organochlorine compounds in bleach plant effluent. *Adv Biochem. Technol. Biotechnol.* 57: 213-259.

Bajpai, P. (2000). Microbial degradation of pollutants in pulp mill effluents. *Adv. Appl. Microbiol.* 48: 79- 134.

Cerniglia, C. E., Gibson, D. T. & van Baalen, C. (1980). *J. Gen. Microbiol.* 116: 495-500.

Deardorff, T. L., Willhelm, R. R., Nonni, A. J., Renard, J. J. & Phillips, R. B. (1994). *Tappi J.* 77(8): 163-173.

Ek, M. & Eriksson, K. E. (1987). 4th Int. Symp. Wood Pulping Chem., Paris, France.

Fantroussi, S. El., Naveall, H. & Agathos, S. N. (1998). Anaerobic dechlorinating bacteria. *Biotech. Prog.* 14: 167-188.

Fitzsimons, R., Ek, M., & Eriksson, K. E. L. (1990). Anaerobic dechlorination / degradation of chlorinated organic compounds of different molecular masses in bleach plant effluent. *Env. Sci. Technol.* 24: 1744-1748.

Gergov, M., Priha, M., Talka, E., Valtilla, O., Kanges, A. & Kukkonen, K. (1988) (1988). Tappi J. 71(12): 175-184.

Guo, H. Y. , Chang, H. M., Joyce, T. W. & Glasser, J. H. (1990). In: Biotechnology in Pulp and Paper Manufacture. Eds. T. K. Kirk & H. M. Chang. pp 223-230. Butterworth-Heinemman Stoneham.

Helble, A., Schlayer, W. , Liechti, P. Jenny, R. & Mobius, C. H. (1999). Advanced effluent treatment in the pulp and paper industry with a combined process for ozonation and fixed bed biofilm reactors. Wat. Sci. Technol. 40(11-12): 343-350.

Henze, M. (1995). Wastewater Treatment: biological and Chemical Process. Germany: Springer-Verlaag.

Holliger, C., Wolfarth, G. & Diekert, G. (1999). Reductive dehalogenation in the energy metabolism of anaerobic bacteria. *FEMS Microbiol. Rev.* 22: 383-398.

Jokela, J. K. , Lauie, M., Ek, M. & Salkinoja-Salonen, M. (1993). *Env. Sci. Technol.* 27(3): 547-552.

Kindzierski, W. B., Gray, M. R., Fednak, P. M., Hrudy, S. E. (1992). Activated carbon and synthtic resins as support material for methanogenic phenol degrading consortia: Comparison of surface characteristics and initial colonization. *Water Environmental Resources* 65: 766-775.

Kobayashi, M., Tchan, Y. T. (1978). *Wat. Res.* **12: 199-201.**

Kobayashi, H. & Rittmann, B. (1982). Microbial removal of hazardous organic compounds. *Environ. Sci. Technol.* 16: 171A-183A.

Lafond, R. A. & Fergusson, J. F. (1991). In: Proc. Tappi Environ. Conf. 797-812. Tappi Press. Atlanta, Georgia.

Leach, J. M. Mueller, J. C. & Walden, C. C. (1978). *Process Biochem.* 13(1), 18-26.

Mohn, W. W. & Tiedje, J. M. (1992). Microbial reductive dehalogenation. *Microbiol. Rev.* 56: 482-507.

Neilson, A. H. (1990). The biodegradation of halogenated organic compounds. *J. Appl. Bacteriol.* 69: 445-470.

Raizer- Neto, E., Pichon, M., Rouger, J. (1989). In: Proc. 4th Int. Biotechnol. Conf. In Pulp & Paper industry.,. Raleigh, North Carolina. pp. 71

Reineke, W. (2001). Aerobic and anaerobic biodegradation potential of micro-organisms. In: The handbook of Environmental Chemistry Vol. 2. Part K. Biodegradation and persistence: B. Beek. Germany: Springer-Verlag.

ENVIRONMENTAL IMPACT OF TOXIC CHLORINATED PHENOLICS RELEASED IN PULP & PAPER INDUSTRY & ITS CONTROL MEASURES

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INTRODUCTION

The release of toxic chlorinated phenolic compounds during bleaching of pulp with chlorine became an environmental issue in seventies when high level of these toxic compounds were detected in fish, (particularly of streams which received bleach plant effluent). Moreover the cause of acute and chronic toxicity in these aquatic organisms was also attributed to the chlorinated phenolic compounds. It has been reported that the use of chlorine based bleaching chemicals generate number of phenolic compounds which contain varying number of chlorine atoms attached to benzene ring. The toxicity of chlorinated phenolic compounds increases with the increase of chlorine atoms in the ring. For e.g. 2,3,7,8 tetrachloro bibenzo dioxin is reported to be extremely toxic and has tendency to persist in environment for long time. The major part of chlorine is associated with high molar mass which constitute about 70% of total organic chlorine associated with organic fractions. Later on the detection of dioxins and furans in product, sediments, ETP sludge have received extensive media attention.

The imposition of strict environmental regulations, public awareness to the adverse effect of chlorinated phenolic compounds have initiated R&D organisations, pulp mills to develop the technologies to control the release of these toxic compounds in mill effluents. In the same perspective, efforts were made to develop the technologies to reduce the residual lignin content to the lowest possible extent in the unbleached pulp before bleaching process and find alternatives of elemental chlorine and hypochlorite to minimise the formation of these toxic, mutagenic and carcinogenic chlorinated compounds. This resulted in adoption of new fibre line (including modified pulping and bleaching technologies) by almost all the pulp mills in developed countries.

With growing environmental awareness & public perception & availability of eco friendly high brightness imported paper , stricter environmental legislations and judicial activism, the Indian pulp & paper mills are facing serious environmental challenges for their sustainability as well as ability to compete even in domestic market. In Indian scenario almost all mills are employing conventional pulping processes and are still persisting with high dosages of chlorine based bleaching chemicals to attain high brightness paper due to economic reasons which results in release of high level of toxic chlorinated phenolic compounds. Moreover, the scale of operation and use of mixed fibrous raw materials are among the major limitations of the Indian pulp & paper mills to adopt the new ecofriendly technologies.

The present paper highlights the technological level, status of adsorbable organic halides (AOX), their environmental impact and the integrated approach to control the release of the toxic chlorinated phenolic compounds in Indian pulp & paper mills.

PULPING & BLEACHING TECHNOLOGIES PRACTISED IN INDIA & ABROAD

With the increase in awareness about the adverse environmental impact of AOX & dioxin, most of the pulp mills in developed countries have adopted new pulping and bleaching techniques to reduce the discharge of chlorinated phenolic compounds in mill effluents, some of these are :

- Extended delignification
- Improved pulp washing
- Oxygen delignification

- Elemental chlorine free (ECF) & Total Chlorine Free(TCF) bleaching
- Oxidative alkali extraction bleaching

The use of elemental chlorine (which contributes 70- 80% of total AOX) has gradually phased out in most of the developed countries. Some of the pulp mills have adopted even Total Chlorine Free (TCF) bleaching process. However the majority of pulp mills still continue to use chlorine dioxide for bleaching of pulp to achieve high and stable brightness . In contrast Indian paper mills have continued with the use of elemental chlorine for production of bleached grades of papers due to economic reasons and moreover the measurement of the chlorinated organic compounds was not felt necessary till recent past . Till now techno- economic consideration have restricted the adoption of modern methods of pulping like extended pulping & oxygen delignification by the large integrated mills and major part of lignin is still removed in bleaching stage. The conventional CEH or CEHH bleaching sequences are commonly used by Indian mills to bleach the pulp to the desired brightness level. The consumption of chlorine in large mills varies from 35-60 kg/t of pulp. The small scale agro based mills in the absence of chemical recovery produce normally pulp of high kappa number and major part of lignin is still removed in subsequent bleaching process.

Use of chlorine dioxide, hydrogen peroxide & oxygen reinforced alkali extraction is limited to very few large mills which are producing rayon grade pulp & high brightness quality papers. An estimate indicates that approximately 2.5 million tonnes of chemical pulp is produced in India, 60% of this is high brightness bleached pulp mostly bleached by chlorine & chlorine based chemicals.

FORMATION OF CHLOROPHENOLIC COMPOUNDS

The nature & extent of formation of chlorophenolic compounds is determined primarily by the residual lignin content in the pulp and type of bleaching chemicals employed. The bleaching of pulp with chlorine based chemicals generates various chlorinated phenolics **(Table- 1 & Fig- 1)** which include chlorinated resin acids, fatty acids , chlorinated phenolics, dioxins & furans. The identification and characterisation of bleach plant effluents for individual chlorinated compounds are exceedingly complex, so a generic measurement is used normally to indicate the level of these compounds in environmental samples like **Adsorbable Organic Halides (AOX), Extractable Organic Halides (EOX) & Purgable Organic Halides (POX)**. The distribution of various AOX related compounds released during bleaching of pulp in general is illustrated in **Fig-2**. As indicated about 80% of chlorine is associated with high molecular weight lignin material (MW>1000D) commonly referred as chloro-lignin. The main environmental concern is the generation of the low molecular weight chlorinated organic material (MW<1000D) as this fraction is considered to contain compounds which are toxic due to their ability to penetrate the bacterial cell membranes and has tendency to bioaccumulate in the fats of higher organism. The nature of chlorophenolic compounds depend on type of raw material used and bleaching sequence employed .

Among the chlorinated phenolics, the dioxins and dibenzofurnas are a group of chlorophenolics which have been found to have toxic effects. The prominent among the dioxins are 2,3,7,8 tetra chloro dibenzodioxin (TCDD) and 2,3,7,8 tetra chloro dibenzofuran (TCDF) **(Fig-3)**. The major source of chlorinated dioxins has been found to be the Chlorination Stage and its formation is mainly dependent upon :

- Kappa number of brown stock
- Active chlorine multiple
- Mixing conditions during chlorination
- Carryover of COD alongwith washed unbleached pulp and
- Wash water quality.

ENVIRONMENTAL IMPACT OF CHLORINATED PHENOLICS

As discussed earlier, the discharge of chlorinated phenolic compounds formed during bleaching of pulp with elemental chlorine using conventional bleaching became an environmental concern when high level of these compounds were detected in fish of streams receiving bleach plant effluent. Earlier the high molar chlorinated, compounds was thought to contribute little or no toxicity to the aquatic organisms due to its large size of molecule. But later on, the studies conducted revealed that high molecular weight chlorolignin accumulated in sediments & over a period of time, these compounds further break down into more biologically active lower molar mass which can cause toxicity to the aquatic life .

Chorinated Phenolic Compounds :

Low molecular weight chlorinated phenolic are reported to cause acute toxicity and mutagenicity due to their ability to penetrate living cell membrane. The chlorinated organic compounds present in alkali extraction stage (E) effluent are found more toxic and contributes more than 90% of acute toxicity. The major examples of such compounds are trichlorophenol, tri & tetra chloroguaicol which have tendency to accumulate in fish and are responsible for acute toxicity. The formation of these compounds is directly proportional to the consumption of chlorine and a sharp increase in the formation of tri & tetra chloroguaiacols has been observed when active chlorine multiple was increased from 0.15 to 0.20 **(Fig - 4)**.

Carcinogenic & Mutagenic Compounds :

Some of the chlorinated phenolic compounds like chloro catechols formed in chlorination stage have been identified as strong mutagens.Chloroform & carbon tetra chloride produced during bleaching of pulp have also been classified as carcinogenic. The use of hypochlorite in bleaching has been reported to be the major source of these compounds.Studies conducted in developed countries revealed that the fish exposed to chlorinated phenolics discharged by bleached pulp mills demonstrated impaired function of lever, enzyme system, metabolic cycle as well as increase in the incidence of spinal deformities and reduced gonad development in both laboratory and field studies.

Polychlorinated Dioxins & Furans

Dioxins have received extensive media attention after Stockholm declaration of dirty dozen persistent toxic pollutants (POP) where in dioxins and furans have been put under the category of unintended industrial by products as these chlorinated dioxins have not any known use. The list PoP (commonly called as dirty dozen is given in **Table -2.** Some other interesting facts about dioxins are summarised below:

- There is no known use for dioxins
- Dioxin is slow to break down and can last for long period.
- Animals consume dioxin contaminated water and plants and then it accumulates in their fat.
- People are exposed to dioxin through eating food high in fat, like dairy products and beef.
- Dioxin can be transmitted from mother to child during pregnancy and nursing.

The preliminary studies conducted on toxicity of dioxins on humans yielded contradictory findings. However, recently it has been accepted that dioxins even in trace amounts may cause a wide range of other adverse effects on human health. Some of them are listed below

- **Low-exposure effects:**
    1. Altered immune function.
    2. Increased susceptibility to infections, and
    3. Thyroid and liver function abnormalities.
- **Higher levels of dioxin exposure :**
    1. Birth defects,.
    2. Child growth retardation,
    3. Reduced levels of male reproductive hormones,
    4. Diabetes, and cancer
- **Human carcinogen**

  Dioxins are classified by the International Agency for Research on Cancer as a known human carcinogen.

Though the level of dioxins is less than 0.1% (of total AOX) but these compounds are reported to be highly lypophyllic and bioaccumulable compunds. As such there is no safe level of dioxins. Such compounds are formed when unchlorinated dibenzodioxin (DBD) and dibenzofuran (DBF) present in unbleached pulp are chlorinated with elemental in chlorination stage. The oil based pulp mill additives particularly brown stock defoamer have been identified as potential sources of such compounds. Laboratory studies indicate a sharp increase in quantity of PCDD & PCDF when elemental chlorine consumption increased beyond 10-15 kg /t pulp.

LEGISLATION TO CONTROL AOX DISCHARGE

In the 1960's,when environmental consciousness was made related to the discharge of pollutants in mill effluents, the biological treatment plants were introduced in many of pulp & paper industry to reduce the pollution loads especially from bleach plant effluents which is the major source of pollution in large integrated pulp and paper mills.

The main emphasis was given for characterization & identification of hazardous chloro-organics present in bleach effluents when analytical methods & instruments became available. The new analytical methods and studies conducted created a basis for development of legislation for regulation of the level of chlorophenolics in discharge of pulp mills.

In the convention held in Paris for the prevention of pollution from land based sources & rivers, the AOX limit in general was set at 1.0 kg/t effective from 1995 for all types of bleached chemical pulp mills. The proposed AOX limit in general has been accepted by Belgium, Denmark, France, Germany, Ireland, Luxemburg, The Netherlands, Norway, Portugal, Spain, Sweden and U.K. Government agencies around the world have responded by imposing standard for emissions of Total Organic Chlorides (TOCl), AOX or dioxins in mill effluents and in some cases, limiting the levels of these compounds found in paper products. Most countries have specified the maximum discharge limit for AOX or TOCl in mill effluent. A typical example is the Swedish TOCl standard of 0.10 kg/t by the year 2010.

The U.S. Environmental Protection Agency (EPA) on the other hand has issued a guideline to regulate the discharge of AOX & chlorinated compounds under so called **cluster rules** for several categories of pulp mills **(Table-3)**.

Based on studies conducted by CPPRI on Assessment of AOX level in Indian Pulp and Paper Industry, Central Pollution Control Board (CPCB) has finalised to impose the limit for discharge of AOX in mill effluents. The regulation for discharge of AOX in various countries are given in **Table-4**.

STATUS OF AOX LEVEL IN INDIAN PULP & PAPER MILLS

In contrast to Internatioanl scenario, the Indian pulp and paper industry is characterised by low operational capacity, obsolescence in technology, high use of chlorine based bleaching chemicals , high water consumption and poor environmental performance. A comparative picture of technological status and level of AOX in Indian mills and those of developed countries is given in Table-5 Due to economic reasons the general trend in our country is to make pulp with high kappa no. using mild chemicals. Further delignification is achieved in bleaching stage which is mostly chlorine based resulting in high consumption of chlorine and leading to high level of AOX generation.

Large Paper Mills:

The generation of AOX in general is higher in mill producing writing and printing paper and vary from 4.0 to 5.0 kg. AOX/t paper (due to use of chlorine based chemicals for bleaching) while in newsprint and rayon grade mills it is less than 1.0kg.AOX/t paper. The recent trend inmost of the large mills is to use oxidative alkali extraction employing peroxide. Only a few writing and printing paper mills which have switched over to chlorine dioxide bleaching or employed oxygen delignification have low level of AOX in their mill effluents.

Small Paper Mills:

Further the problem of AOX is more severe in small agro based mills producing writing and printing paper. Since most of these mills are not having chemical recovery, they produce pulp of higher kappa no. and subsequently use higher chlorine dosage in bleaching stage to achieve desired brightness level. Moreover due to inherent poor drainage properties of agro residues coupled with poor washing efficiency of the washers (which leads to higher COD carry over along with the pulp to bleaching process) and low bleaching response of agro residues, the consumption of chlorine in these varies from 150 to 260 kg/t of pulp. This results in a high level of AOX generation between 6- 10 kg/t pulp. A comparative picture of status of AOX in Indian mills is indicated in **Table -6.**

MEASURES FOR REDUCTION /CONTROL OF AOX

In response to environmental concerns, governmental regulations on emission of chlorinated organic matter and to also market demand, the pulp and paper industry has acted worldwide since the mid-1970's by developing & introducing a number of new processes & process modification in order to minimize the discharge of chlorinated phenolics. The main strategy behind the development of internal process changes has been to remove as much lignin as possible before the pulp enters to bleach plant and also to replace elemental chlorine in bleaching process by other bleaching agents. As a result most of paper industry in developed countries have adopted modified processes & techniques to reduce kappa number , improved pulp washing system and bleaching techniques etc. and some of paper mills have achieved even lower value of AOX below 0.5kg/t pulp.

However, as discussed earlier, Indian paper mills still uses elemental chlorine which is considered major contributor of AOX. However some of paper mills in India have already started the use of chlorine dioxide, oxidative alkali extraction. J.K. Paper Mill is the only mill to introduce successfully RDH pulping, oxygen delignification, chlorine dioxide bleaching in order to improve the quality of product & bleach plant effluent. In last two decades the major efforts world wide have been to adopt & modify the inplant measures rather than at the end of pipe treatment in order to reduce the formation of chlorinated phenolic compounds. The inplant measures include extended delignification, efficient pulp washing, oxygen delignification enzyme pretreatment ECF,TCF bleaching, oxidative alkali, extraction etc. Some of these measures as well as those which can be implemented without any major modification in existing processes to control the discharge of AOX in Indian mills are discussed below:

(A) Adoption of New Technologies :

(i) Oxygen Delignification

The process is used to treat the washed unbleached pulp to reduce the kappa number before bleaching stage. One of the requirements of the process is a special pressure vessel to maintain the desired treatment conditions. Almost all the pulp mills in developed countries are now using oxygen delignification process due to its inherent advantages . Some mills in these countries are even going / planning for two stage delignification process to further reduce the kappa number below 10. The main limitations for adoption of the process by Indian pulp and paper mills is again the low scale of operation and high capital investment. The scale of operation in most of Indian pulp mills varies from 100 to 275 t / day which restricts the adoption of oxygen delignification by these mills . Though J.K Paper Mill which is producing 300 tpd pulp is employing oxygen delignification process but the kappa number reduction efficiency is lower and varies between 30-35% one reason of which is use of mixed fibrous raw materials.

(ii) ClO_2 Substitution

The use of chlorine dioxide in bleaching not only reduces the formation of toxic and harmful, chlorinated dioxins but also improves the quality of pulp. Most of the pulp mills abroad have switched over to the use of chlorine dioxide bleaching in view of its advantages related to substantial reduction in formation of dioxins, furans and AOX related compounds. Few Indian mills have started the use of chlorine dioxide in chlorination stage along with elemental chlorine and also in the final stage of bleaching, to get a stable and high brightness level. One of the main requirement for induction of chlorine dioxide stage is to completely changeover to special grades of alloyed stainless steel (SS) system to prevent corrosion. This calls for heavy investments and scrapping the entire existing system in bleaching for induction of chlorine dioxide to substitute the elemental chlorine.

(B) Upgradation/ Regtrofication in Existing Process / Technologies:

(i) Controlled Pulp Mill Operation

The kappa no. of unbleached pulp is the main factor which governs the bleach chemical demand and ultimately responsible for AOX generation. Under the controlled and uniform cooking process, the kappa no. of pulp produced from wood may be attained between 18-20 without having any degradation in fibre quality. The mills must operate their pulp mill under controlled & optimum conditions to reduce the kappa number of pulp below 20.

(ii) Improved Pulp Washing

The carryover of organic matter alongwith pulp due to inefficient washing increases the consumption of bleach chemicals resulting in higher generation of AOX. Washing of pulp is an important step and can help in minimizing the carryover of organic matter to bleach plant. The existing washing system needs to be modified / upgraded to minimize the carryover of COD alongwith pulp between 15-20 kg/t. pulp.

(iii) Oxidation Alkali Extraction Bleaching

The addition of small amount of oxygen or peroxide in alkali extraction stage improves the quality of bleach plant effluent by reducing colour & AOX . Most of the large paper mills have already started the use of hydrogen peroxide in alkali extraction stage. However the mills should also increase the use of oxygen in the alkali extraction stage due to the advantage of higher delignification and consequently less AOX generation .

(iv) Improved Chemical Mixing.

Improved mixing of chemicals in bleach plant is an important step. If the bleaching chemicals are not rapidly & uniformly distributed through the pulp, there is chance of a portion of pulp being over bleached.

(C) External Measures:

(i) Recycling of Bleach Plant Effluent (C & E Stage)

In Indian mills C & E stage are the major contributors in generation of AOX. Reduction in their discharge by reuse/ recycle in the process can help to reduce the level of AOX to a greater extent. C stage effluent is acidic in nature while E stage effluent is the most polluted stream which limits possibility for their reuse in the process as it leads to adverse impact on product quality and as well as corrosion problem in system infrastructure. However, in mills employing oxidative extraction (E-stage) bleaching, the major part of E- stage filtrate is being reused in bleach plant. Detoxification of the bleach plant effluent by physico- chemical treatment methods can help in addressing to the above limitations to a greater extent. This requires removal of inorganic / recalcitrant and toxic compounds by physical / chemical treatment methods like membrane filtration, electroflocculation, chemical precipitation etc. CPPRI has been actively working in this area and the preliminary results obtained are encouraging and are summarised in **Table- 7, 8 and 9.** Further work on assessing the techno-economics of the treatment methods & disposal of chemically precipitated sludge is under progress.

(ii) Effective Operation of ETP

In the study conducted by CPPRI it has been found that AOX reduction by 45-70% is achievable by conventional effluent treatment practices. However the extent of reduction depends upon the operating conditions of ETP. Over the years most of the Indian paper mills have increased their pulp mill capacity without simultaneous expansion of their ETP's effluent handling capacity. This has resulted in poor performance efficiency of these ETP. The mills are required to operate their ETP under optimum conditions to achieve the maximum efficiency to reduce AOX & other oxygen consuming pollutants.

(D) Other Measures :

(i) Increased Use of Recycled Fibre

The mills particularly small agro base mills must reduce/limit the production of chemical pulp and should use maximum proportion of recycled fiber to supplement the fiber furnish for production of bleached variety of paper grades. Such supplementary recycled fiber must be bleached with hydrogen peroxide.

(ii) Environmental Auditing

The regular environmental auditing is necessary which help to assess and also to improve the performance of process & the ETP. Due to increased environmental pressure and market competitiveness, the most of the mills are now going for ISO. Some mills are even accredited with ISO 14000, where regular environment auditing of the mill is mandatory.

CONCLUSIONS

Today the environmental issues particularly control of AOX is the major environmental challenge before the Indian pulp and paper industry for its sustainability and environment compatibility. The environmental challenges related to AOX generation have already been over come by pulp and paper mills in developed countries by adoption of new fiber line incorporating modern pulping and bleaching technologies. However Indian pulp & paper industry is still at cross roads due to its inability to adopt these modern technologies due to low scale of operation , use of mixed raw materials, and high capital investment . With the concept of eco- labeling and life cycle assessment of the product already introduced in international market , Indian pulp and paper industry should timely gear up to become cost competitive and environmental compatible to compete/ survive in this era of open market economy . Though the ultimate solution to this is adoption of modern fiber line to start with , the Indian pulp and paper industry must face the challenge in a phased manner by adopting short term & long term strategies to develop and employ new technologies in order to make pulp and paper industry more cost competitive and environmentally compatible.

The ultimate solution to control the release of these toxic compounds is the adoption of new technologies. As most of new technologies are of imported origin and highly capital intensive and some time these technologies need modification to make suitable to our context. So there is an urgent need to develop the indigenous capability to develop the technologies suited to process the fibrous raw material available to Indian pulp and paper industry.

CPPRI has been in forefront in helping the paper industry & equipment manufacturer to build up the indigenous capability to make the Indian pulp & paper industry cost competitive & environmental compatible related to control the discharge of these toxic compounds in mill effluents.

TABLE-1

CHLORINATED PHENOLIC COMPOUNDS GENERATED DURING BLEACHING OF PULP WITH CHLORINE BASED CHEMICALS

Type	No. of Species,	Amounts
Chlorinated acids	40	Upto 500g/t pulp
Chlorinated phenolics	40	Upto 100g/t pulp
Chlorinated aldehydes, Ketone and lactones	45	----
Chlorinated hydrocarbons	45	----
Chlorinated others	20	----
High molecular weight Materials	--	Upto 4kg.Cl/t pulp

TABLE – 2

LIST OF DIRTY DOZEN PERSISTENT TOXIC POLLUTANTS (POP) (Stockholm convention)

S. No.	Compounds	Source
1.	Aldrin	Pesticide
2.	Chlordane	Pesticide
3.	DDT	Pesticide
4.	Dieldrin	Pesticide
5.	Endrin	Pesticide
6.	Heptachlor	Pesticide
7.	HCB	Pesticide
8.	Mirex	Pesticide
9.	Toxaphene	Pesticide
10.	PCBs	Industrial
11.	**Dioxins**	**By-product**
12.	**Furans**	**By-Product**

TABLE – 3

POLYCHLORINATED PHENOLIC COMPOUNDS PROPOSED FOR REGULATION BY THE U.S.E.P.A.

Polychlorinated phenols	**Minimum level, ppb (µg/L)***
Pentachlorophenol	5.0
2,3,4,6 - Tetrachlorophenol	2.5
2,4,5 - Trichlorophenol	2.5
2,4,6 - Trichlorophenol	2.5
3,4,5 - Trichloroguaiacol	2.5
3,4,6 - Trichloroguaiacol	2.5
4,5,6 - Trichloroguaiacol	2.5
3,4,5 - Trichlosyringal	2.5
3,4,5,6 - Tetrachlorocatechol	5.0
3,4,6 - Trichlorocatechol	5.0
3,4,5 - Tetrachlorocatechol	5.0
3,4,5, 6 - Tetrachloroguaiacol	5.0

The minimum level is defined as the concentration at which the analytical system gives recognizable mass spectra (corrected for background) and acceptable calibration points, using EPA method 1653

TABLE –4
REGULATIONS FOR DISCHARGE OF AOX (KG/T)

Country	**1994**	**1995-2000**	**2000-2005**
Australia	1.0	-	-
Austria	0.76- 1.5	0.5-1.0	-
Canada	1.5	-	1.0
Germany	1.0	-	-
India	2.0	2.0	1.0*
Japan	1.5	-	-
Norway	1.0-2.0	-	-
Sweden	1.2 – 1.5	0.3 – 1.0	0.3- 0.50
USA	-	0.62	-

- Proposed limit

TABLE- 5

STATUS OF AOX IN INDIAN PULP AND PAPER MILLS

Type of product	Kappa No.	COD Carry over during washing Kg.COD/t. pulp	Consumption of Cl_2 Kg./t. pulp	AOX Level Kg./t. Paper GEN- FINAL Discharge
Rayon grade Pulp	12 - 16	--	25 - 28	0.7-1.0 < 0.50
News print chemical pulp	20 - 22	--	20 - 25	0.50-0.60 <0.50
Writing & Printing Paper:				
Large Mills	15 - 26	20 – 25	35 - 110	2.0 – 4.5 1.0 - 2.5
Small Mills (Agro-based)	30 - 32	30 – 40	140 - 160	6.0-10.0 4.0 - 6.5

TABLE -6
TECHNOLOGICAL STATUS IN LARGE INTEGRATED PULP & PAPER MILLS

S. No.	Particulars	India	International
1.	Installed capacity, t/d*	250	1500
2.	Capacity utilisation, %*	70	100
3.	Raw materials used	Bamboo, eucalyptus , mixed hardwoods, bagasse	Soft wood & hard wood
4.	Pulping process	Sulphate	Sulphate
5.	Modified Pulping Process (RDH)	Not Employed**	Employed
6.	Oxygen Delignification	Not Employed**	Employed
7.	Bleaching Process	Conventional**	ECF & TCF
8.	AOX in final discharge, kg/t paper	2.0-2.5	0.5-1.0

* Average capacity under which most of the mills fall.

**Except J.K. Paper Mills Ltd., Orissa

TABLE-7

CHEMICAL TREATMENT OF BLEACH PLANT EFFLUENT

(AGRO BASED MILL)

Parameters	C-stage effluent	E-stage effluent	Combined bleach plant effluent
(A) Effluent Characteristics			
pH	1.8	7.1	6.6
COD mg/l	3528	2307	2883
AOX mg/l	48.2	125.3	50.02
colour, PCU	3372	6778	3689
(B) Chemical Dosages			
Alum : COD	1:1	0.5:1	1:1
Lime : COD	1.0 : 1	0.5:1	1:1
PAA, ml/l (1% solution)	1:1	2.0	2.0
(C) Treated Effluent Characteristics			
pH	5.5	5.6	5.0
COD mg/l	1033	438	542
AOX mg/l	23.82	62.2	21.06
colour, PCU	145	246	156
(D) Removal Efficiency, %			
COD	71	81	81
AOX	51	50	57
Colour	95	96	96

TABLE-8

CHEMICAL TREATMENT OF BLEACH PLANT EFFLUENT (WOOD BASED MILL)

Parameters	C-stage effluent	E-stage effluent	Combined bleach plant effluent
(A) Effluent Characteristics			
pH	2.0	9.0	6.4
COD mg/l	851	3048	612
AOX mg/l	46.16	134.0	37.8
colour, PCU	392	11320	1048
(B) Chemical Dosages			
Alum : COD	1:1	0.5:1	1:1
Lime : COD	0.75 : 1	0.5:1	1:1
PAA, ml/l (1% solution)	1.0	10.0	2.0
(C) Treated Effluent Characteristics			
pH	5.5	5.5	5.5
COD mg/l	240	596	306
AOX mg/l	18.14	25.43	13.23
colour, PCU	67.0	363	61.0
(D) Removal Efficiency, %			
COD	72	80	50
AOX	61	81	65
Colour	83	97	94

TABLE-9

TREATMENT OF BLEACH PLANT EFFLUENT THROUGH ELECTROFLOCULATION (WOOD BASED MILLS)

Particulars	**Untreated Eop effluent**	**Treated Eop effluent 2 Lit. volume**	**% Reduction**	**Treated Eop effluent 5 Lit. volume**	**% Reduction**
pH	11.7	9.3	-	8.5	-
COD, mg/l	1159	395	66	458	61
BOD, mg/l	178	69	61	105	41
AOX, mg/l	42.8	10.5	76	14	67
Colour, PCU	1133	60	95	135	88
Power consumption Watt h. / l	-	21	-	11.6	-

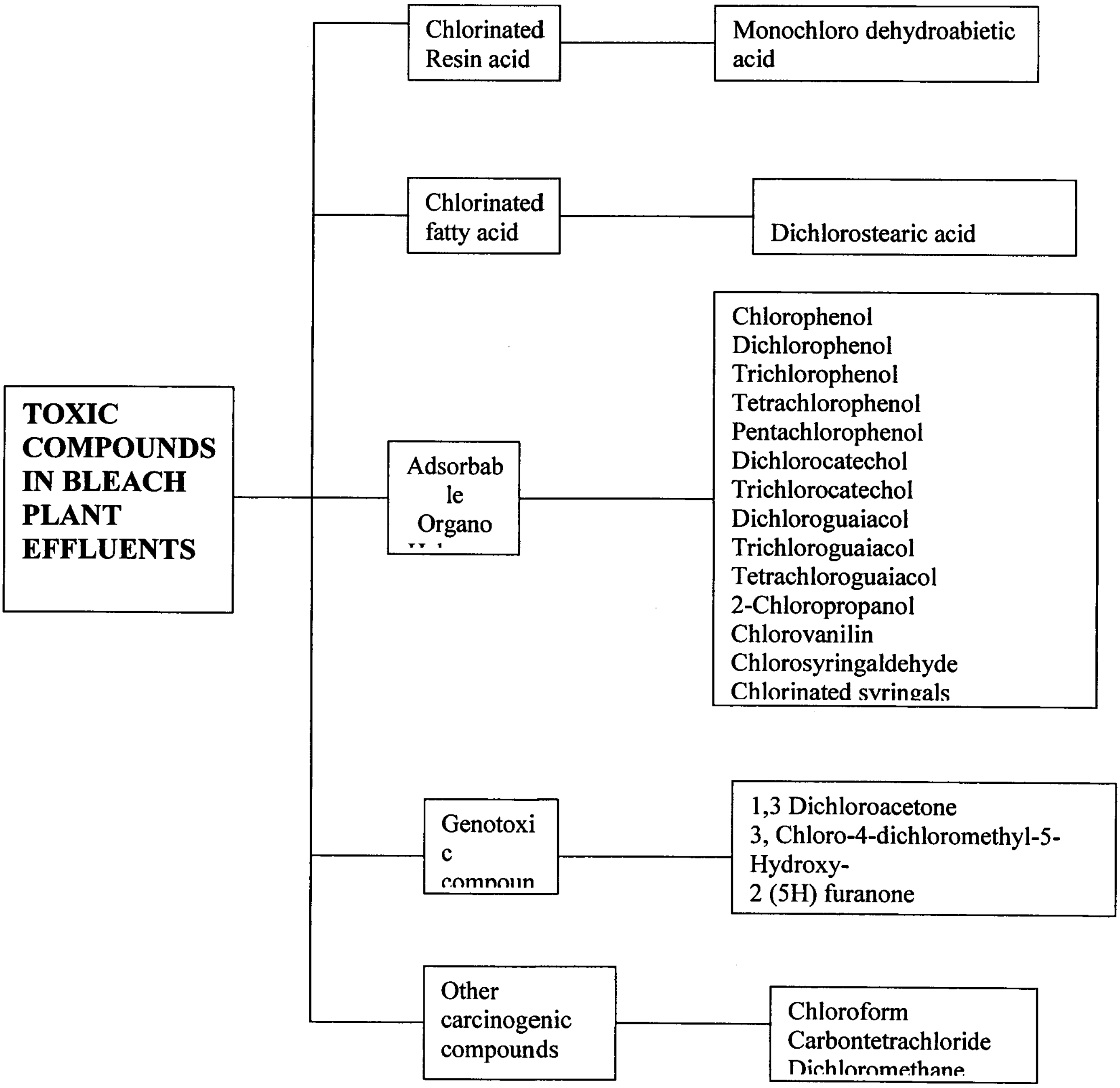


FIG.-1 TOXIC COMPOUNDS IN BLEACH PLANT EFFLUENTS

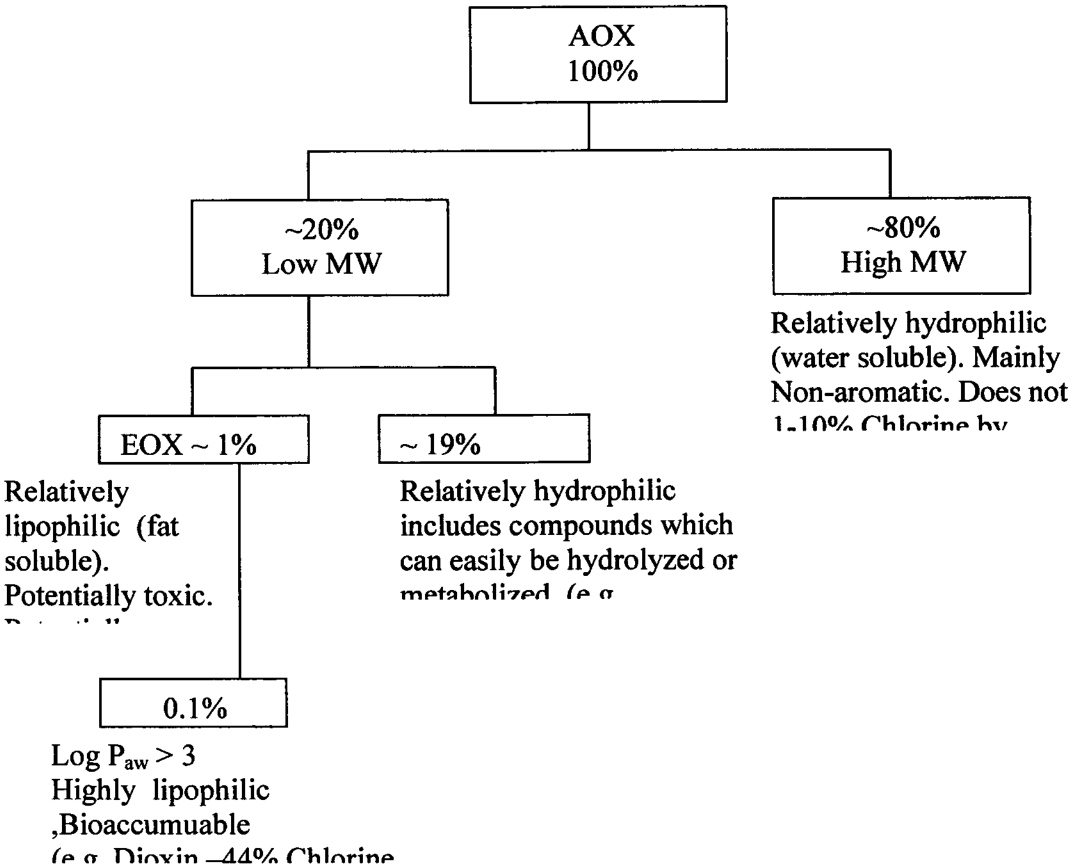
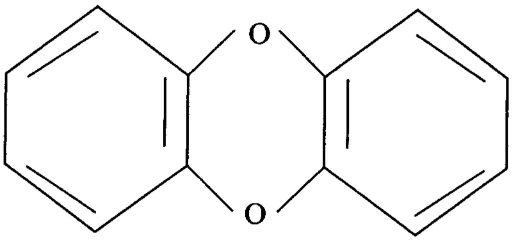
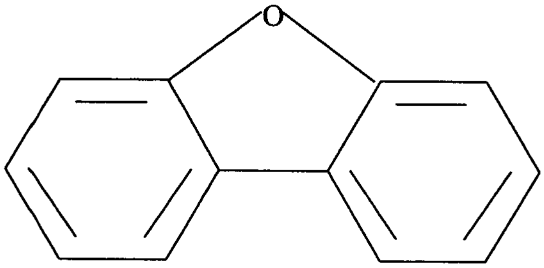


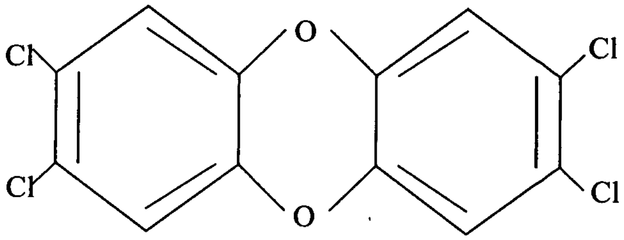
FIG- 2: DISTRIBUTION OF CHLORO PHENOLIC



DIBENZO-P-DIOXIN(DPD)

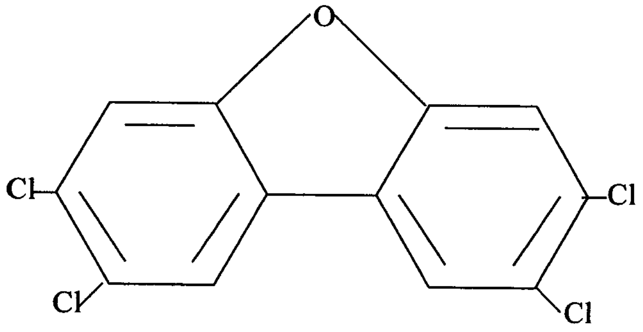


DIBENZOFURAN(DPF)



2,3,7,8-TETRACHLORO-DIBENZO-P-DIOXIN

(2,3,7,8-TCDD)



2,3,7,8-TETRACHLORO-DIBENZOFURAN

(2,3,7,8-TCDF)

FIG.- 3 STRUCTURES OF CHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS

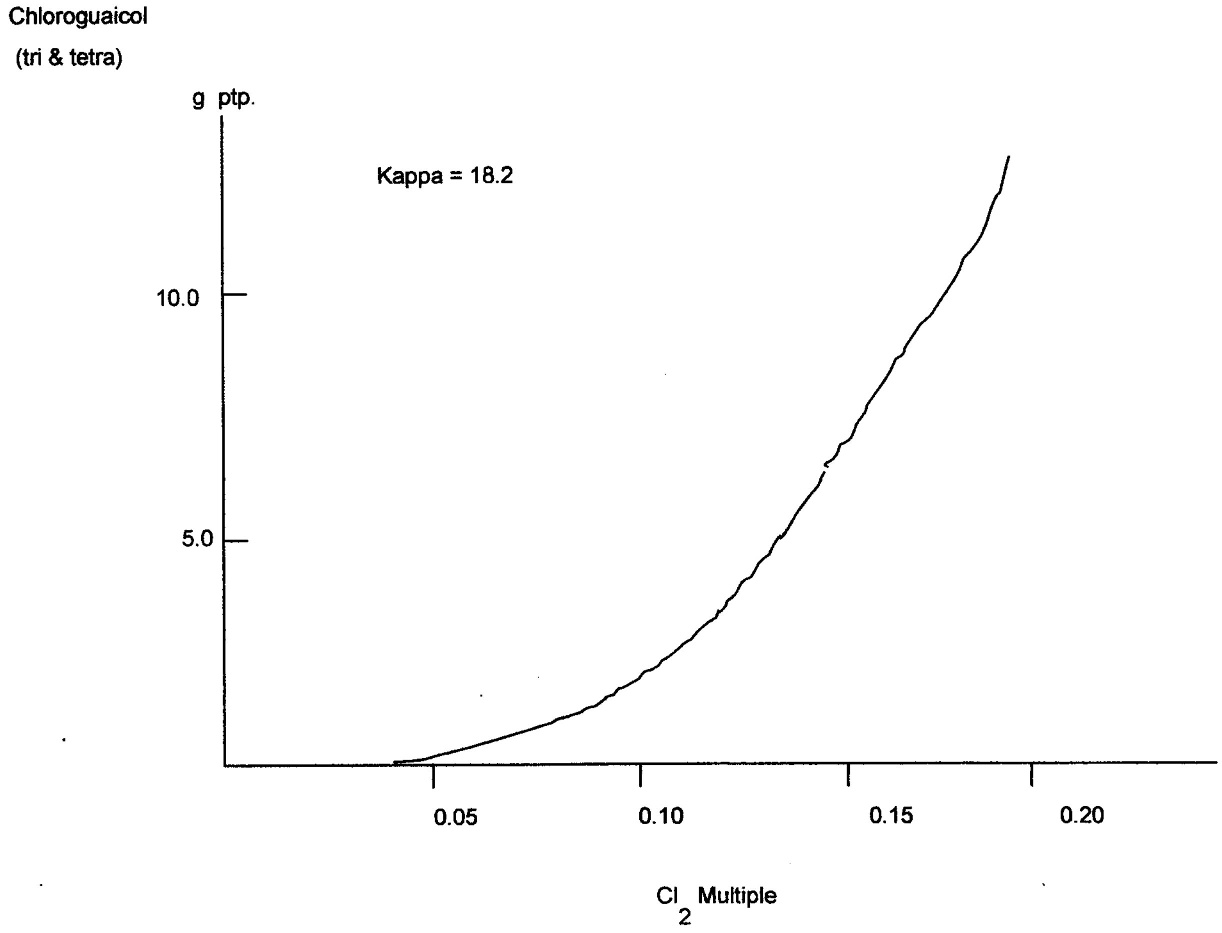


FIG.-4 THE FORMATION OF TRI & TETRACHLOROGUAIACOLS VS CHLORINE MULTIPLE IN CHLORINATION STAGE

ENZYMATIC PREBLEACHING OF PULPS TO CONTROL AOX RELEASE IN PULP MILL EFFLUENTS

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Abstract

Environmental concern and the strict legislation regarding imposition of the discharged norms/for adsorbable organic hallides (AOX) in Indian paper industry has prompted the mills to develop and look for alternative technologies with low AOX levels in the effluents discharged. In response to these pressures alternative bleaching techniques have been developed to reduce or eliminate the use of chlorine or chlorine based chemicals in the bleaching sequence. Enzymatic prebleaching, however has been developed as one of the promising alternative & the technology has received considerable attention in the last decade. Number of pulp and paper mills world-wide have commercially adopted the process, but the technology is still in nascent stage, though it shows promising future in Indian paper industry.

Central Pulp and Paper Research Institute as a part of promotion of clean and green technology in Indian paper industry could identify biotechnology as one of the promising and up-coming cleaner production option.

The present paper discusses the results based on the work carried out at CPPRI in the area of enzymatic bleaching of pulps.

1. INTRODUCTION

The environmental concern regarding imposition of the effluent discharges norms for AOX is forcing the industry to reduce or eliminate the use of chlorine or chlorine based chemicals in bleach sequence. Many of the alternate technologies have not yet proved feasible especially because of higher investment and operating cost and also the negative effect on the pulp quality. Under the prevalent conditions enzymatic prebleaching of pulps employing xylanases enzymes could prove to be a promising option as an environmental friendly technology & is early adaptable by the pulp and paper industry.

The primary goal of chemical pulp bleaching is to reduce the residual lignin of pulp without effecting the carbohydrate and! or the physical properties of the pulps. Two different enzyme approaches have been generally in use for achieving the goal, which include.

1. Use of helnicellulases (specifically xylanases) enzymes as prebleaching agents (bleach booster) for enhancing the chemical removal of lignin in multistage bleaching sequence.

2. Another alternative approach is direct delignification of the unbleached pulps using enzymes called ligninases or laccases, which acts directly on the residual lignin in the pulp (1).

The first approach, which is the use of xylanase enzyme as prebleaching agents for chemcial pulps has been successfully, applied in pulp and paper mills worldwide using various xylanases preparations of different origins. But the technology still is in nascent stage as far as Indian Paper Industry is concerned.

Xylanase enzymes used in bleaching of chemical pulps are being developed by Companies which claim their products suitable as prebleaching agents for the pulps produced in the paper industries. However, these enzymes, which are marketed by several suppliers are found to be highly sensitive to the conditions like temperature, pH & doses of the enzymes (2,3). Therefore it becomes difficult for the pulp and paper mills to decide which particular enzyme should suit to the specific requirement of their industry in order to achieve desired effect.

In view of the above, Central Pulp & Paper Research Institute (CPPRI) has been engaged for the last many years in conducting studies on evaluation of various xylanase enzyme preparations which are available globally and also being developed indigenously by several reputed biotechnological laboratories to study their response on the type of pulps produced in Indian paper mills(4).

The present paper highlights the studies carried out at the Institute in which several xylanase enzymes have been evaluated for their bleach response on Kraft wood and Kraft bagasse pulps, in order to explore potential for commercial application of the enzyme prebleaching technology in Indian paper industry.

2. MATERIALS & METHODS

2.1 Sources of Xylanase enzymes:

Several xylanase enzyme preparations used in the present investigations were procured from National &

International enzyme manufacturing companies! laboratories which are denoted as A,B,C,D & E The details about the xylanase preparation is given in Table-I.

TABLE-1 SOURCES OF XYLANASE ENZYMES

Xylanase enzyme	Source
A	Produced indigenously from an indigenous microbial strain
B	Indigenously manufactured
C	Imported
D	Imported
E	Indigenously manufactured

2.2 Pulp Samples:

Wood Kraft Pulp samples were procured from a nearby large integrated Pulp & Paper Mill employing - Eucalyptus as major raw material where as Kraft bagasse Pulp was obtained from an agro based mill in Maharasthra equipped with chemical recovery system.

2.3 Enzyme assay Techniques:

All the enzymes were tested for filter paper activity for cellulase contamination by the method of Mandals . & Weber and xylanase activity was measured by the method of Bailey et. al (5).

2.4 Xylanase Pretreatment of Pulps:

Enzymatic Pretreatment of the pulps was canied out under the optimised conditions as mentioned in Table- 2.

TABLE-2 ENZYME PRETREATMENT CONDITIONS

	Pulp treated with Enzymes				
Parameters	A	B	C	D	E
Dose of enzyme, IU/g	7.0	10	5.0	5.0	10
Consistency of pulp, %	10	10	10	10	10
Retention time, min	120	120	120	120	120
PH at 25 deg. C	6.2	8.2	8.5	8.5	8.5
Temperature , deg. C	45-50	45-50	45-50	45-50	45-50

2.5 Process conditions used during bleaching of Pulps:

Process conditions employed for bleaching of Pulps both with & with out enzyme preparation is shown in table-3.

TABLE-3. PROCESS CONDITIONS USED DURING BLEACHING OF PULPS

Particulars	**Chlorination stage**	**Alkali Extraction Stage**	**Hypo Stage**
Temperature, deg. C	Ambient	60	40
Pulp consistency, %	3.0	8.0	
Retention Time, min	30	60	120
Final pH	1.8-2,0	>10.5	>9.-0

3. RESULTS AND DISCUSSION:

While optimising the dosages of enzymes during enzyme treatment of woof Kraft and bagasse Kraft pulps, it was observed that excess dosages of xylanase enzymes for a longer time has resulted in decreased pulp yield and strength properties of the pulps. This could probably be due to loss of hemicelluloses by the action of enzyme. However under optimised dosages of enzymes i.e. 5-7 IU/gm of pulps and optimised treatment conditions (Table-2), no significant loss in pulp yield could be observed except with enzyme preparation E wherein even the treatment of the pulp at optimised conditions of time and temperature could result in 1.5% pulp yield loss along with drop in viscosity which was reduced from 560 to 510 cm3/g of the pulp leading to loss in strength properties (Table-4). Reasons for the same could be attributed to contamination of xylanase with cellulase activity, which could be ascertained by determination of the cellulase activity in the xylanase enzyme by filter paper activity. Therefore this enzyme named as E was found to be unsuitable for its application in bleaching of pulps.

TABLE-4
CHARACTERIZATION OF UNBLEACHED PULP FOR YIELD & OTHER PARAMETERS OF WOOD KRAFT PULP BEFORE & AFTER ENZYME TREATMENT

		Pulp treated with enzymes				
Parameters	Control	A	B	C	D	E
Pulp Yield, ,%	99.89	99.82	99.62	99.80	99.74	98.10
Kappa number of pulp	18.0	16.5	16.7	16.6	17.0	16.0
Brightness, %ISO	27.5	28.5	29.0	28.4	28.0	29.0
CED Viscosity, cm^3/g	560	620	590	557	604	510

3.1 Effect of xylanase treatment on bleach chemical requirement

Bleaching of the xylanase enzyme treated Kraft pulps, both wood and bagasse have been found to respond in 11 different manner than untreated pulps while bleaching with conventional CEH bleach sequence. Based on optimisation studies of the chlorine dosages during chlorination stage, it was observed that significantly less chlorine is required to bleach Kraft wood and Kraft bagasse pulps while bleaching to similar targeted brightness level.

Table - 5 shows the effect of various xylanase preparations on the bleach chemical requirement during conventional CEH bleach sequence of wood Kraft pulps with a targeted brightness level of 80% ISO. From the results shown it is clearly seen that there is a reduction of nearly 14 - 15% of chlorine demand with all the enzymes preparations in case of wood Kraft pulps except enzyme preparation D, where chlorine saving of only 9.3% could be noticed. Further the enzyme treated pulps could be bleached to higher brightness with a gain in brightness level of 2-3% ISO in all the cases while using similar chlorine dosages as in case of control pulp sample.

TABLE- 5

EFFECT OF ENZYME PRETREATMENT ON BLEACH CHEMICAL REQUIREMENT USING VARIOUS XYLANASE PREPARATIONS ON KRAFT WOOD PULP

		A		B		C		D		E	
Parameters	Control	ET1	ET2	ET1	ET2	ET1	ET2	ET1	ET2	ET1	ET2
Savings in elemental chlorine	-	-	15	-	15	-	14	-	9.3	-	-
% Reduction in Kappa No. after X stage	-	8.0		7.2		7.3		5.5		11.1	
% reduction in Kappa No. After XCE stage	-	28.0	-	25.9	14.5	26.0	16.0	27.0	23.0	-	-
Final brightness of the pulp, % ISO	80.0	82.5	80.0	82.5	81.3	83.0	80.2	82.0	80.0	83.0	80.0

X - Enzyme treatment

XCE - Enzyme, Chlorination & Extraction

ETI - Enzyme treated Pulp treated with similar chlorine dose

ET2 - Enzyme treated Pulp treated with optimised less chlorine dose

Reduction in chlorine requirement or improved pulp brightness in case of enzyme treated pulps was reflected from the reduction in Kappa number of the unbleached pulps after enzyme treatment and further after the alkali extraction stage. The reduction in kappa number by 7-8% after enzyme treatment and further reduction of kappa number by more than 25% after alkali extraction was achieved in enzyme treated pulps.

Similar observation were made in case of Kraft bagasse pulps where nearly 18% reduction in chlorine demand could be observed in enzyme treated pulps with targeted brightness level of 83.0% wherein brightness gain of 2.0% ISO could be achieved when the enzyme treated pulp was bleached with similar chlorine dose of 5.1% as in case of control pulp. Results are shown in Table-8. This reduction in chlorine demand and gain in pulp brightness is also reflected from reduction in kappa number of the enzyme treated pulp where 20% reduction in kappa number after alkali extraction stage could be noticed.

3.2 Effect of enzyme treatment on unbleached pulp yield and physical properties of wood Kraft and bagasse Kraft pulps.

Table -6 shows the bleach chemical demand, Strength & Optical properties of Kraft wood pulp treated with identified xylanase enzyme preparations B & D against control. From the results shown in Table-6, it is clearly evident that with a savings of nearly 15% chlorine demand employing enzyme preparation B, no loss in strength properties like burst, tensile & tear could be noticed, however the tear index was improved significantly from 5.3 Mn m^2/g to 6.0 Mn m^2/g whereas in case of enzyme D treated pulps, the strength properties, though were at par with control pulp but the chlorine savings were lower i.e 9.3% only. With regards to the optical properties of the enzyme treated pulps, there is an improvement in the yellowness of the pulp both with enzyme preparations B & D, since the yellowness of the enzyme treated pulps were decreased from 14.94 %to 9.79% & 10.65% respectively.

TABLE-6

ENZYMATIC PREBLEACHING OF KRAFT WOOD PULP USING XYLANASE

Bleaching of Pulp using Conventional CEH Sequence Before & After Enzyme Treatment

Particulars	Control	Enzyme B	Enzyme D
Chlorination			
% Chlorine Applied	3.9	3.3	3.54
% Chlorine Consumed	94	99	96
%, chlorine savings	-	15	9.23
Alkali Extraction			
% NaOH Applied	1.30	1.30	1.5
% NaOH Consumed	61.1	63.2	58.3
Final Ph	10.88	10.76	11.21
Kappa no.	3.51	2.99	3.2
Hypo Stage			
% Hypo Applied	1.8	1.8	1.8
% Hypo Consumed	71.0	75.0	68.0
Brightness, % ISO	80.0	82.05	82.0
Brightness Gain, %	-	2.5	2.0

Strength and optical properties of the wood Kraft pulps before & after enzyme treatment using two identified xylanase enzymes B & D

Parameters	Control	Enzyme B	Enzyme D
Revolution PFI	4000	4000	4000
Freeness CSF	220	250	250
Apparent density, .g/m^3	0.79	0.76	0.75
Burst index Kpa.m2/g	4.43	4.49	4.51
Tensile Index , Kpa.m^2/g	64.4	64.3	64.4
Tear Index, Mn m^2/g	5.3	6.0	5.3
	Optical properties		
Opacity, %	92.2	91.2	91.0
Yellowness, %	14.94	9.79	10.65

Similar observations could be made in case of Kraft bagasse pulps. Treatment of the Kraft bagasse pulp with xylanase enzyme B preparation showed no loss in pulp yield or pulp viscosity (Table- 7). Bleach chemical demand of both enzyme treated and untreated pulps & the results of strength properties were shown in table-8. From the results it is clearly evident that strength properties of the enzyme treated pulps like Burst, Tear and Tensile could be maintained at par with control pulps with improvement in optical properties particularly in respect of yellowness which was dropped from 13.5 to 9.2 - 9.6% (Table-8).

TABLE -7

YIELD & OTHER CHARACTERISTICS OF UNBLEACHED KRAFT BAGASSE PULP BEFORE & AFTER ENZYME TREATMENT USING mENTIFIED XYLANASE (B) ENZYME

Parameters	Pulp treated with enzymes	
	control	Enzyme treated
Pulp yield, %	99.20	99.02
Kappa number of unbleached Pulp	26.2	25.5
Kappa No. of CE Stage	5.07	4.04
Brightness, % ISO	30.3	3.08
CED Viscosity	535	520

TABLE-8

XYLANASE PRETREATMENT OF KRAFT BAGASSE PULPS & STRENGTH & OPTICAL PROPERTIES

Bleaching of Pulp using Conventional CEH Sequence Before & After Enzyme Treatment			
Particulars	Control	ET-1	ET-2
	Chlorination		
% Chlorine Applied	5.1	5.1	4.2
% Chlorine Consumed			
%, chlorine savings	-	-	17.6
	Alkali Extraction		
% NaOH Applied	2.0	2.0	2.0
% NaOH Consumed	74.2	61.2	73.8
Final Ph	10.24	11.55	10.25
Kappa no.	5.07	4.04	4.30
	Hypo Stage		
% Hypo Applied	2.0	2.0	2.0
% Hypo Consumed	80.0	80.0	74.0
Final Brightness of pulp % ISO	83.0	85.0	84.0
	Strength and optical properties		
Parameters	Control	Enzyme B	Enzyme D
Revolution PFI	500	500	500
Freeness CSF	335	350	355
Apparent density, .g/m^3	0.66	0.74	0.72
Burst index Kpa.m2/g	2.60	3.05	2.55
Tensile Index , Kpa.m^2/g	45.5	56.0	45.0
Tear Index, Mn m^2/g	4.05	4.40	4.20
	Optical properties		
Brightness of pupls, % ISO	83.0	85.0	84.0
Yellowness, %	13.5	9.2	9.6

. ET1 -- Pulp treated with similar chlorine dose

. ET2 -- Pulp treated with less optimized Chlorine dose

3.3 Impact of enzyme treatment on environment

Characterization of the resultant bleach effluent from wood Kraft pulps and Kraft bagasse pulps before and after enzyme treatment indicated that effluent properties namely AOX (Adosorbable Organic Halides) & COD are improved indirectly through the use of xylanase treatment which helps in release of lignin and other chromophore bearing compounds and allowing the use of lesser quantities of elemental chlorine or other chlorine based compounds in subsequent bleach sequence. Results of characterization of enzyme treated wood Kraft pulp and Kraft bagasse pulps against control pulps are shown in Table-9. From the table it is clearly indicated that AOX level was reduced to 0.69 kg/tp in case of hard wood Kraft & 1.0 kg/tP in Kraft bagasse pulps compared with control pulps where AOX was reduced from 2.29 kg/tp to 1.6 kg/tp and from 4.13 kg/tp to 3.13 kg/tp respectively. Further decreased ratio of COD to BOD from 7.7 to 3.9 and from 4.12 to 3.33 in bleach effluent from Kraft wood and Kraft bagasse after enzyme treatment is an indication of improved biological treatability of the bleach effluent.

TABLE-9

CHARACTERISTICS OF BLEACH EFFLUENTS OF KRAFT WOOD & KRAFT BAGASSE PULPS BEFORE & AFTER ENZYME TREATMENT USING XYLANASE ENZYME B

	Wood Kraft Pulp		Bagasse Kraft Pulp	
Parameters	**Control**	**Enzyme treated**	**Control**	**Enzyme Treated**
AOX, Kg/tp	2.29	1.60	4.13	3.13
COD, Kg/tp	23.3	28.5	34.6	50.7
BOD, Kg/tp	3.02	7.31	8.5	15.0
COD: BOD ratio	7.7:1	3.9:1	4.1:1	3.3:1

4. CONCLUSION

1. Enzymatic prebleaching of chemical pulps using xylanase enzyme could prove to be an effective technology in reducing the chlorine demand to the tune of 15% & 18%

with gain in bleached pulp brightness of 2-3 % ISO while reducing the AOX level in bleach effluent to more than 25% in case of wood Kraft and Kraft bagasse pulps.

2. Xylanase enzyme respond better on wood Kraft pulps than non-woody raw materials due to the nature of the hemicelluloses wherein it has been observed that hard wood hemicelluloses are more responsive to xylanase enzyme action than those in Pulps from Kraft bagasse mills, due to the nature of the hemicelluloses. It has been observed that hard wood hemicelluloses are more responsive to xylanase enzyme action than those in pulps from agro residue raw materials.

3. Studies indicated that before selection of a particular xylanase enzyme preparation it is important to evaluate the enzymes for their activity and cellulase contamination, since excess dose of xylanase enzyme and cellulase contamination results in loss of pulp yield and strength properties of the pulp as in case of enzyme preparation E

4. Before introducing enzyme-prebleaching technology in any mill it is important to evaluate particular enzyme preparation for its response towards pulp being produced in the mill for various parameters as discussed in the paper.

5. Enzyme being sensitive and specific in nature, it is very important to optimise the temperature, pH, dosages and proper dispersion or mixing of the enzyme with the pulp in order to achieve the targeted response.

6. The technology is relatively new as far as Indian paper industry is concerned. Efforts are required by researchers, technologists and enzyme manufacturers to isolate new xylanase enzymes suitable for pulps being produced in Indian paper industry from wood and non wood based raw materials and also to investigate the effect of other hemicellulases and lignolytic enzymes like laccase and lignin peroxidases on pulp bleaching to further reduce requirement of chlorine based chemicals.

5. LITERATURE CITED:

I. Wong. K.K.Y; Martin. L.A; Garna F.M; Saddler. J.N & De Jong. E; "*Bleaching boosting and direct brightness by multiple xylanase treatments during peroxide leaching of Kraft pulps*"; Biotechnology Bioengineering; 54; 312-318,1997.

2. Kantelinen. A; et.a1. " "*Proposed mechanism of the enzymatic bleaching of Kraft pulp with xylanases*"; Holzforschung; 47; 318-324; 1993

3. Wong. K.K.Y, De Jong. E, Saddler. J.N & Allison. R.W; "Mechanism ofxylanase aided bleaching of Kraft pulp. Part-II Target substrates"; APPITA J. 50: 509- 518; 1997

4. Jain R. K,. M, Mathur. R.M & Kulkmi. A.G; "*Enzymatic prebleaching of pulps: challenges & opportunities in Indian pulp & paper industry*"; accepted for presentation in forthcoming 8Th International Conference on Biotechnology in the Pulp & Paper Industry 8th (ICBPPI), to be held at Helsinki, Finland; June 4 -8, 2001.

5. Bailey. M.J, Bailey. P & Poutanen. K; "*Interlaboratory testing methods for assay of xylanase activity*", J. Biotechnology; 23; 257

TOXIC EFFECTS OF ODOROUS EMISSION ON HUMAN HEALTH

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Abstract

Increasing awareness through the media has spread the awareness about pollutants and their toxic effects amongst the public. The data available, even to the general public is sufficient to link the level of pollutants and its effect on the human health. The problem of odour from the paper mills, which was experienced by the local populace in known to have health hazards. As a consequence, the Indian Paper Industry now grapples with the problems associated with the monitoring of these odorous compounds and their reduction/elimination.

In this paper an attempt has been made to discuss the toxic and odorous emission from pulp and paper mills , their effect, current status of these pollutants, and future policies that may need to me adopted by the industry for the reduction/mitigation of emission of these odorous pollutants.

INTRODUCTION

Kraft mill odor has long been a problem for large mills in India. With the increasingly restrictive environmental regulation posed by the federal agencies and growing environmental competitiveness in pulp and paper mill operation, the control of these emissions has gained strategic importance for the Industry. The Industry is now looking into technologies and processes that could achieve a mill operation with minimum environmental impact.

The emission of non condensable odorous gases (NCG'S) has always been a source of problem to the local habitat around the paper mills. These NCG's are released from many operations of the pulp and paper industry such as digester relief and blow , recovery boiler, lime kiln, black liquor storage tanks, evaporator vents etc.

NON CONDENSABLE GASES

The major source of these odors are due to the presence of hydrogen sulphide, methyl mercaptan and dimethyl disulphide - which are sometimes refered to as Total Reduced Sulfur (TRS) compounds. (1)

METHYL MERCAPTAN

The molecular formula for the methyl mercaptan is CH_3SH . It is a gas at normal temperature (B.P.5.8°C) and is extremely foul smelling even at very low concentration. It is formed during the kraft cooking by the reaction of hydrosulfide ions and the methoxy lignin compounds of the wood.(2)

Methyl Mercaptan dissociates in an aqueous solution to methyl mercaptide ions and this dissociation is completed above a pH of 12.0.

CH_3SH is also present in low concentration as a dissolved gas in the black liquor. As the pH decreases, methyl mercaptan gas is evolved from the black liquor.

DIMETHYL SULPHIDE

The molecular formula of dimethyl-sulphide is $(CH_3)_2S$ .This is a non-acidic liquid with B.P. 38°C. Dimethyl disulphide is primarily formed through the reaction of methyl mercaptan ion with the lignin component of the wood . It does not dissociate as H_2S and methyl mercaptide do. Dimethyl sulphide may also be formed by the disproportion of methyl mercaptan. At normal liquor temperature, it is highly volatile.

DIMETHYL DISULPHIDE

The molecular formula for the dimethyl-disulphide is $(CH_3)_2S_2$. It is also non-acidic liquid at B.P.-112°C. It is formed by the addition of methyl mercaptan throughout the recovery furnace especially in the oxidation towers.

HYDROGEN SULPHIDE

It is feebly acidic gas which partially ionizes in aqueous solution. The ionization proceeds in two stages with the formation of hydrosulphide and with increasing pH, Sulphide ions. Hydrogen sulphide along with methyl mercaptan is responsible for the characteristic odour of pulp and paper mill.

Hydrogen sulphide generally represents the largest gaseous emissions from the kraft process. Two of the most effective means for reducing the hydrogen sulphide emission from kraft mill are black liquor oxidation and maintaining tight control of critical process operating variables (3).

MONITORING AND ANALYSIS OF NCG

Monitoring and analysis of NCG's is a difficult task till date in India because there is no methods prescribed by the BIS for NCG's except H_2S in ambient air. However there is only one method available for the Methyl Mercaptan in ASTM (4) which is based on colorimetery . This method requires a standard compound i.e. Lead methyl mercaptide which is not available even with the top chemicals manufacturers companies of India as well as of world because of low shelf life and very high chemical cost. Except CH_3SH other NCG's can only be analyzed through GC method which is complicated mainly due to the requirement of standard gases which are again not available easily in India.

The monitoring part of these gases requires special type of sampling kit by which only the Non Condensable gases are collected in a sampling bag. The gases have to pass through a series of impingers and then from a condenser to cool the gases so that only the non-condensable portion of the flue gas is collected as a sample. The collection of these gasses requires special type of transparent bags which have to be imported.

TOXIC EFFECTS OF NCG'S ON HEALTH

Pollution of atmosphere affects the life of millions of peoples in all parts of the world specially those living in a large industrialized cities with unpleasant odor, fume, dust and corrosive gases which are injurious to human health and damage crops and property.

In all communities, there is a wide variation in the susceptibility of individuals to the effects of air pollution. Healthy adults can tolerate relatively high concentration of harmful substances without suffering harm while the very old, the very young and the sick are relatively much more sensitive. To handle this variation a statistical concept must be used. The aim is to protect the great majority of the even the susceptible subgroups from significant harm. Growing recognition of the cyclical nature of human development and resulting impacts has stimulated the evaluation of a new study approach referred to as human health risk assessment.

The main problem associated with the NCG's gases are their nauseous odor which are detectable by human beings at very low concentrations. The lower detectable limits for Hydrogen sulfide, methyl mercaptan and dimethyl sulfide and dimethyl disulfide are presented in table-1

TOXIC EFFECT OF CH_3SH

It has been reported that CH_3SH exhibits a toxicity similar to, but less than that of H_2S . Others have reported the toxicity of both compounds being the same . Methyl mercaptan affects the central nervous system and can cause convulsions and narcosis at high concentration. It causes paralysis of the respiratory center . At lower levels it produce pulmonary edema.(5)

The toxic effect of CH_3SH can be easily understood by case highlighted by Sults et al. where a man emptying gas cylinders of CH_3SH was over-exposed. He was found comatose at the worksite and hospitalized . He developed acute hemolytic anemia and methano-globlineamia and remained in a deep coma until dying , 28 days after the accident.

TOXIC EFFECT OF H_2S

H_2S is a toxic gas and it is widely generated in nature from geothermal sources. This gas is used in large quantity in research laboratory for growing sulfide crystals . H_2S reacts vigorously with living tissues and causes several effects on health , depending on the gas concentration. Also H_2S paralysis the olfactory system and therefore it is considered more dangerous than Carbon monoxide.(6)

As reported in some literature hydrogen sulphide causes headache, nausea, eye-nose-throat irritation etc. It can cause respiratory and eye injury. Hydrogen sulphide is also corrosive to metals like iron, steel, copper and cement.

TOXIC EFFECTS OF METHANOL

Methanol is released from recovery boiler . Methanol is reported to cause suspected developmental toxicants, neuro-toxicants , gastrointestinal or liver toxicants (7).

STATUS OF NON-CONDENSABLE GASES

At present, there are no standard limits prescribed for the emission of NCG'S in India. However, this position is not likely to remain as such for long as studies are already underway for fixing the norms for the emission of these gases in India.

When the work on NCG was started at CPPRI, there was a problem for the correct sampling procedure for these gases. Due to limitations of instrumentation, online sampling of the emission was not possible. The best option available was to develop a procedure for the representative sampling of NCG'S from the flue streams and then analyze the same by using detector tubes. For this purpose, extensive studies were carried out at CPPRI and after many trails, a procedure has been developed that results in the collection of only the non condensable gases from flue streams. This gas sample is collected in a sampling bag to which a tube is attached for carrying out the quantification.

CPPRI has developed technique to monitor the emission of NCG's and is capable of doing analysis by the tube method. Recently, a portable gas chromatograph has also been procured for carrying out direct on line analysis of these gases.

In the past we have monitored NCG on two different mills. One mill was based on hardwood while the other one was based on bagasse using continuous digester and less sulfidity. The comparative results of these gases are shown in table-2.

The results of this study clearly shows that very less amount of NCG's are released in mill which is based on the hard wood and uses high sulfidity.

In mill where wet scrubber is used to control these Non-condensable gases during our study we found that it is quite effective and about 90% reduction can be achieved using some alkali for wet scrubbing. The result of these comparative study are enclosed as table-3.

CONTROL TECHNOLOGIES OF NON-CONDENSABLE GASES

There are various technologies available for the control of non-condensable gases in the developed countries, but they are not feasible India because of the size of paper mill and type of raw materials.

In the developed countries all the concentrated along with diluted NCG's containing reduced sulfur compounds are treated by collecting the gases into sealed systems and eliminating these malodorous compounds by converting them into non – odorous forms (8).

As per the literature the most efficient way for the treatment of these NCG's is thermal oxidation and lime kiln is the suitable choice for the thermal oxidation of concentrated NCG's (9).

In some literature use of recovery boilers for the burning of these malodorous gases are also reported (10).

Wet scrubber with alkaline medium are also frequently used for the reduction of non-condensable gases at different NCG's emissions sources like lime kilns, evaporator vents, digester degassing etc. (11).

CONCLUSION

The past concept of acceptance of kraft mill malodorous emission has been replaced by most of the mills as active community concern for mills to clean up their emissions. Although some times these change of attitude is because of stringent environmental regulations but sometime it is due to the positive thinking of mill owner.

The rotten egg like odor emitting from the kraft pulp and paper mill is objectionable and is a nuisance and a safety hazard . These gases are highly toxic, very corrosive and potentially explosive . Careful consideration must be given to the design of an NCG's disposal system.

Recently, there have been efforts in the direction of reduction/ elimination of these NCG's by some of the major players in the Indian pulp and paper industry. However, with the impending limit on emission of these gases, more and more mill have to think in this direction.

EPA has already submitted a plan for the purpose of controlling total reduced sulfur emissions from existing Kraft pulp mills. The plan was submitted to fulfill the requirement of the clean air act. EPA has already given emission standard for five source points. i.e. recovery furnace, lime kilns, digesters, evaporators and smelt dissolving tanks tabulated in table-2 (12).

REFERRENCES:

1. Barynin,J.A.,Berg,L.,Lee,B., 1993, Recent Trends in NCG's Disposal System Design., pulp and paper Canada, p.p. T-409-413.
2. Jarvensivu, Mika, Maenappa Tom, Jounela Jamsa, Liisa, 200, field survey of reduced-sulfur emissions from a modern finish pulp mill, environmental progress, vol. 19. no-3, pp 147-155
3. Jones, H.R., 1973, Quantity and nature of gases emissions, Pollution control and chemical recovery in the pulp and paper industry, pp-57-99.
4. Standard test method for Mercaptan content of the atmosphere, Annual book of ASTM standards, 2001, section eleven, water and environmental technology vol-11.03, pp-47-50.
5. Threshold limit values for chemical substaces and physical agents in the workroom environment, American conference of Govermental Industrial Hygientists. Cincinati OH, 1978, p.p-21.

6. Godkari,S.C., Debnath, A.K., Katti, V.R.,Gupta, S.K., Sahni, V.C., development of Hydrogen Sulfide monitor, downloaded through internet site, http://www.barc.ernet.in/webpages/letter/news letter year 2000/ feb. 2000 html.
7. Health effects of pulp and paper mill effects, Downloaded through internet site, http:// www.rfu.org/health.htm.
8. Burgers, T., 1996, Collecting and burning non-condensable gases, Tappi course notes, craft recovery, pp-42-1-51.
9. Cannery, P., 1978, thermal oxidation of Kraft pulping., Tappi, 61 (3) .pp-31-35.
10. Weng, J., 1995, Simultaneous firing of a concentrated non-condensable gas stream in the power boiler and kiln, Pulp and paper Canada , 96 (1), pp-65-68.
11. Allan, M., Springer, 1986, Emission from Kraft pulping, Industrial Environmental Control,
12. Downloaded through internet from the federal register online via GPO access (wais.access.gpo.gov) vol. 64, number 207, rules and regulations. 1999.

TABLE-1

ODOR THRESH HOLD CONCENTRATIONS OF NCG'S

Sl. No.	**Name of the NCG's**	**Odor Thershold** (ppb)
1.	**H_2S** (Hydrogen Sulfide)	8 – 20
2.	**CH_3-SH** (Methyl Mercaptan)	2.4
3.	**CH_3-S-CH_3** (Dimethyl Sulfide)	1.2
4.	**CH_3-S-S-CH_3** (Dimethyl Disulfide)	15.5

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TABLE-2

STATUS OF NON-CONDENSABLE GASES AT TWO DIFFERENT MILLS

S.No.	**LOCATIONS**	**PARAMETERS (all are in ppm)**							
		H_2S		**CH_3SH**		**$(CH_3)_2S$ & $(CH_3)_2S_2$**		**CH_3OH**	
		Mill-A	**Mill-B**	**Mill-A**	**Mill-B**	**Mill-A**	**Mill-B**	**Mill-A**	**Mill-B**
1.	**Evaporator Vent**	900	22000	7300	48000	10000	48000	N.D.	22000
2.	**Digester Relief**	25	4400	190	2900	45	7500	N.D.	27
3.	**Digester Blow**	220	1100	1400	9000	18000	35000	N.D.	N.D.

TABLE-3
EFFECT OF WET SCRUBBER ON NCG'S

S.NO.	LOCATIONS	PARAMETERS			
		H_2S	CH_3SH	$(CH_3)_2S$ & $(CH_3)_2S_2$	CH_3OH
1	Evaporator vent from surface condenser without scrubber	22,000	43,000	48,000	N.D.
2	Evaporator vent from surface condenser with scrubber	1800	4000	2500	N.D.
3	Digester degassing without scrubber	4400	2900	7500	N.D.
4	Digester degassing with scrubber	250	N.D.	1000	N.D.

NOTE: all values are in ppm

N.D.: Not detected

TABLE-4
EPA STANDARD FOR NON-CONDENSABLE GASES

S.No.	Source Point	PPM (Volume) dry
1	Recovery furnace-old construction design	20
2	Recovery furnace-new design	5
3	Lime kiln	20
4	Digester systems	5
5	Multiple effect evaporator system	5
6	Smelt dissolving tank	20

SOURCE: Downloaded through internet from the federal register online via GPO access (wais.access.gpo.gov) vol. 64, number 207, rules and regulations. 1999.

WASTE DISCHARGES FROM RECYCLED PAPER BASED MILLS - THEIR NATURE, COMPOSITION & DISPOSAL TECHNIQUES

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Abstract

During the recycling operation of the recovered papers, the amounts of rejects produced and their composition depend largely on the recycled paper grades used in paper production. The present paper reviews the approximate quantities of rejects and sludges generated from different varieties of recovered paper, their nature and also the characteristics of the wastes. Some of these waste sludges are hazardous and toxic in nature containing traces of heavy metals and also halogenated toxic compounds like PCDD and PCDF. Land filling of these waste, which till recently was quite a normal practice today faces an environmental challenge due to the limited availability of land and nature of wastes generated, which makes its disposal rather difficult. The present article highlights the various other options, including the one of incineration incorporating fluidized bed combustion of waste for safe handling and discharge & simultaneous recovery of energy and new alternate developments in the area of sludge utilization.

INTRODUCTION

The aim of recycling recovered paper in the paper industry is to produce recycled fiber pulp suitable for use in the manufacture of different paper and board grades. Wastepaper use and processing have a sound environmental basis.

The use of secondary fibre is in harmony with the general principle of minimizing the amount of waste by recycling part of it. Still, the use of recycled fibre (RCF), especially when deinking is practiced, requires extensive and costly measures to avoid detrimental environmental impact. The reasons for this are the discharges of heavily polluted effluents and the large amounts of harmful solid rejects. Harmful substances in this context include heavy metals, chlorine compounds and formaldehyde.

Dinking of waste paper & the use of recycled fibre may have numerous environmental and operating benefits like forest resource preservation, decrease in chemical & energy use, decrease in odour emissions etc, but the handling & disposal of waste sludge is still a matter of great concern. Recyclers are known to produce much more sludge as compared to virgin mills, which is partly attributed to the fillers in the paper, and which for the most part, are not recovered. Sludge generation for Deinked (D.I) mills is even more pronounced as the sludge contains ink along with fibre large amounts of fillers & coating material.

Different process systems for different end product also give different amounts of effluents and rejects.

The total amount of solid rejects leaving the recycled fibre plant as sludge can vary from 10% to 60% depending on the process for the wastepaper treatment. The highest amounts are obtained in deinking for the production of tissue pulps. The effluents from recycled fibre plants are generally treated together with other effluents from the mill.

The treatment normally is started with a primary stage for SS removal by sedimentation or flotation. This stage will often remove also a part of the COD and BOD, and this effect can be enhanced by chemical flocculation. If higher removal rates are required, further treatment by biological methods must be applied. Activated sludge as well as anaerobic methods is widely in use today, with good results.

Effluent treatment produces sludge as the end product. This sludge, together with the sludge from deinking, is dewatered and then disposed of through landfill or incineration. Other possibilities, with a future potential, are land spreading on farmland and disposal in cement manufacturing plants.

The type and volume of waste that occurs in recovered paper processing depend on the recovered paper grades and the amount of effort invested in separation at the processing stages to guarantee the desired products quality and paper machine run ability. The waste from recovered paper processing can be heavy and coarse rejects, light and fines rejects, and sludges . A further distinction is type and origin between sludges from deinking floatation and sludges from the micro floatation of process water or washer filtrates. Table 1 shows the percentages of waste amounts related to the recovered paper used depends on the paper and board grades produced.

TABLE 1

AMOUNTS OF REJECTS AND SLUDGES FROM VARIOUS RECOVERED PAPER GRADES

Produced paper	**Recovered paper variety**	**Waste quantity, % w/w**	**Waste,% w/w**			
			Rejects		**Sludges**	
			Heavy weight & coarse	**Light weight & fine**	**Flotation deinking**	**White water clarification**
Graphic paper	News, magazine	15-20	1-2	3-5	8-13	2-5
	Superior grades	10-25	<1	<3	7-16	1-5
Hygienic paper	Files, office paper, ordinary, medium grades	28-40	1-2	3-5	8-13	15-25
Market DIP	fice paper	32-40	<1	4-5	12-15	15-25
Liner, fluting Board	Sorted mixed recov. Paper, supermarket waste	4-9	1-2	3-6	-	0-1

Solid waste composition and characteristics

Table 2 depicts the composition of waste that occur at different stages of recovered paper processing .The waste from disintegration, cleaning and screening is reject material or rejects. The waste material that occurs during floatation deinking and the cleaning of process water from wash deinking are sludges. Because today's processing methods are selective only to a limited degree, both rejects and deinking sludges continue to contain a certain proportion of fibers and fines. Sludges also results from clarification and biological treatment of wastewater.

TABLE 2

REJECTS FROM DIFFERENT STAGES IN A PLANT FOR DEINKED PULP

Sl. No	Source of rejects	Kind of rejects	Reject thickening equipment. Consistency out	Further handling of rejects
1	Pulper	Bigger contaminations, such as plastic bags, bookbinders, bottles, shoes, strings, tools, toys, wires, wood pieces	Coarse screen. High dryness	Landfill
2	High density cleaning	Glasses, nails, paper clips, pins, staples	Inclined screen + reject compactor. High dryness	Landfill
3	Prescreening	Long, thin and wide contaminants, plastic, polystyrene, stickies...	Inclined screen + reject compactor. High dryness	Landfill
4	Flotation deinking	Mostly printing ink but also stickies, filler and clay	Centrifuge or wire press. 30-50% dry solids content.	Incineration or landfill, cf. Section3.3
5	Forward cleaning	Small compact particles with high specific surface are such as sand, shives, hard particles from UV-colors, coating colors, lacquers...	Bar screen. Relatively high dryness	Landfill
6	Fine screening	Plastic fragments, hotmelts, stickies	Inclined screen + reject compactor. High dryness	Landfill
7	Light weight reject removal	Light weight contaminants, hotmelts, stickies	Bar screen. Relatively high dryness	Landfill
8	White water Clarification	Colloidal material, so called secondary stickies, clay, fillers, fines, very small ink particles	Dissolved air flotation + centrifuge or wire press. 30-50% dry solids content.	Incineration or landfill, cf. Section3.3
9	Handling of reject filtrates	(From the inclined screen, coarse screen, sludge dewatering, reject compactor, cleaning (after the bar screen) and from bleeding off of white eater)	-	Effluent treatment

Rejects:

The amounts of rejects produced and their composition depend largely on the recovered paper grades used in paper production. **Fig.-1** shows the proportion of reject sample from production of newsprint & packaging paper from recycled fibres.

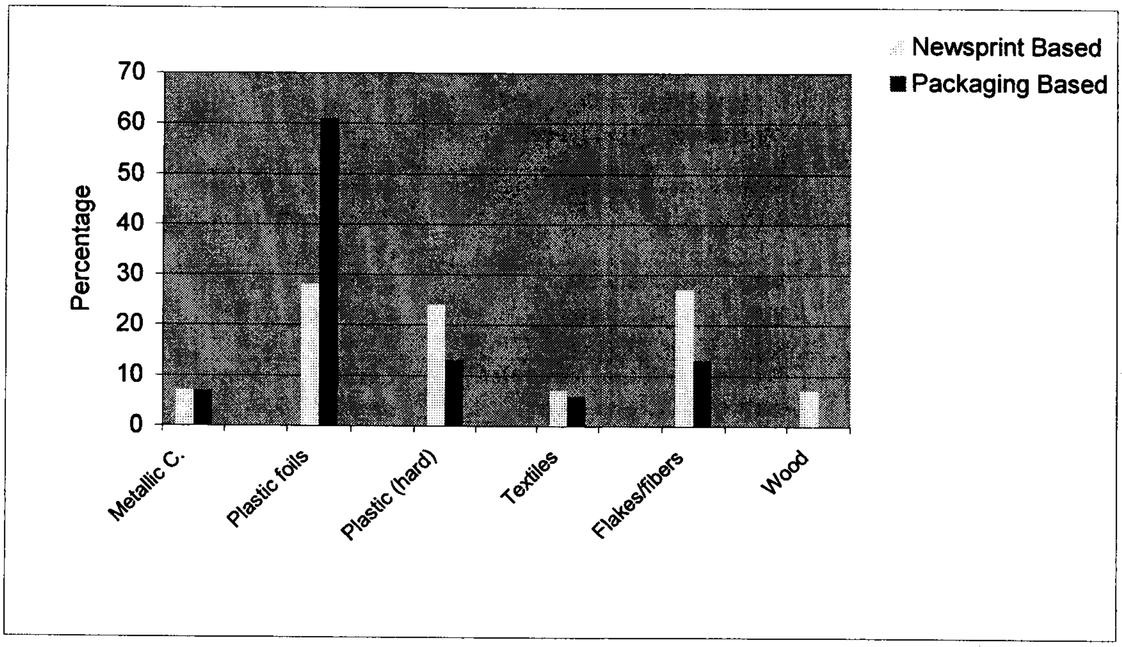

FIG. 1 COMPOSITION OF REJECT SAMPLE

In the chemical composition of rejects, the high total chlorine content is the sum of organic and inorganic chlorine which amount to 55% by weight of rejects on a dry basis. PVC containing materials such as the following are the main sources of this chlorine content:

- Self adhesive tapes.
- Carrier handles from solid boards and corrugated board containers.
- PVC foil laminates from the packaging sector.

- PVC products thrown in error in to recovered paper containers.

The high chlorine content limits their use as an energy source.

Deinking Sludges: An Overseas Experience.

Deinking sludges consist of fillers and coating pigments, fibres, fibre fines and printing inks and adhesive components. Detailed characterization of the sludges from nearly 10-14 numbers of mills in developed countries indicate average dry content value in the range of 51.2, ash content as 54.8, heating value averaging around 6940 kJ/kg. The levels of heavy metals for sludges of recovered paper processing is generally low. The deinking plants have less contamination than those of municipal wastewater treatment.

Traces of halogenated organic compounds such as polychlorinated biphenyls (PCB), polychlorinated dibenzodioxins and poly-chlorinated dibenzofurans (PCDF) also require consideration. PCB compounds are used in carbon less paper, however their use is declining. PCDD & PCDF concentrations of deinking sludges show a similar decline. Due to the continuing change from elemental chlorine bleaching of chemical pulp to chlorine dioxide and to oxygen bleaching, the level of toxic waste discharge is on continual decline.

Sludge Composition – An Indian Survey:

Characterization of sludges is an important prerequisite to evaluate the suitability of waste sludge for final disposal - landfilling / combustion. Results in **Table-3** indicate that the sludge sampleas are characterized by high moisture content compared to those in developed countries, as the sludge dewatering is not practiced in Indian mills. In general, the sludge samples are characterized by high moisture content, modest heating values and can therefore be termed as difficult to burn fuels.

TABLE-3
WASTE SLUDGE SAMPLES CHARACTERIZATION

Particulars	**Mill-I**	**Mill-II**	Mill-III	
	Clarifier sludge	**Clarifier sludge**	**Deinked sludge**	**Clarifier sludge**
Production, t/d	70	80	54	-
End product	Liner boards	Duplex Boards	Newsprint	
Type of waste paper	Pre-consumer	Post consumer	Post consumer	
Sludge production, t/d	3.6	5.0-6.0	5.0	-
Ash in incoming raw material, % w/w	0.35-11.4	0.14-24.5	1.0-17.0	
Dewatering equipment	Not present	Not present	Not present	
Moisture, % w/w	89.0	96.7	-	89.2
Volatiles, % w/w	63.1	66.0	50.7	47.0
Ash, % w/w	32.0	31.8	60.0	64.2
Higher heating Value, kJ/kg	13400	11400	7500	6600

The ash content is low for clarifier sludge compared to the deinked sludge. The reason is attributed to the quality of incoming waste paper and the system configuration for contaminant removal, which is different for both end varieties.

Handling of Sludges - Heavy Metal Discharges:

Heavy Metals: The main effects of heavy metals are their toxicity when the products are in use, their environmental impact in manufacturing processes and the final disposal of products, and their intensification of yellowing or flavour and odour impairment.

The origins of the metals are the metal-containing printing inks in recycled, deinked printed matter. There is at present a tendency to use non-metal-containing inks, resulting in decreasing metal discharges from deinking plants. These discharges are, however, still significant. The total metal content in the recycled paper will be distributed between the finished paper, the effluents, the sludges and the other streams.

The concentration of lead, arsenic and copper are much higher in recycled pulps compared to other pulps. Printing ink is the main source of copper.

The large variation in the lead content of wastepaper is due to the large difference between

the mineral sources from which the coating and filler materials derive. Lead enters the product with filler and coating materials.

The Concentration of cadmium is markedly higher in recycled pulps than in chemical pulps. The concentration is higher in ground wood pulp than in the other primary pulps.

Chromium level is also higher in recycled pulp, although the concentration occasionally may reach several mg per kg in the primary pulps, too. The main source of chromium is filler and coating materials.

Nickel, barium and zinc were more abundant in recycled than in primary pulps.

Mercury concentration is below the detection limit in all the pulp except in ground wood pulp.

TABLE 4

METAL DISTRIBUTION BETWEEN PRODUCT AND WASTE STREAMS FOR DEINKING PLANTS

Stream	Metal %				
	Cr	Cu	Ni	Pb	Cd
Paper	70	20	84	83	41
Deinking Sludge	18	68	6	11	7
Effluent Sludge	8	9	3	4	23
Effluent	2	2	5	1	24
Others	2	1	2	1	5

Dioxines and furans: The Importance of chlorinated compounds lies chiefly in their potential toxicity when the products are being used or disposed of. Contents of PCDDs and PCDFs (Poly Chlorinated dibenzo-p-dioxines and –furanes) in tissue products have been found around 0.7-1.0 pg/g measured as Nordic equivalent. Contents on collected wastepaper have been found to be of the order of 0.4-2pg/f. Papers being used as furnish in deinking/newsprint operations, do have PCDD and PCDF distribution between product/effluent/sludge have been estimated to be 30/20/50%.

Chloroform: It is formed in the bleaching of recycled fibre pulp with hypochlorite. It has been found in effluents from such operations. However hypo bleaching of this type of pulp is practically abandoned by now, so the chloroform problem should have been eliminated.

Formaldehyde: Formaldehyde is both allergenic and toxic. It can be harmful if released from the packing used for photographic supplies. The formaldehyde concentrations in virgin pulps were negligible. In chemical pulps the formaldehyde concentration is below the detection limits. Amount of formaldehyde in recycled pulps are very low and somewhat lower than the values measured in mechanical pulps.

Current Disposal Techniques:

Currently the following disposal practices are prevalent in developed countries.

Disposal Technique	**Mills using methods,%**
Land filling	69
Incineration	27
Land spreading	8
Others	8

Of all these, land filling is the most commonly used disposal method and land filling dewatered sludge is often the least expensive disposal methods in terms of capital costs, although large land areas are required particularly in case of deinked sludge. Another problem with land filling is the possibility of leakage of hazardous components from deinked sludges particularly heavy metals. It is now becoming a less viable option as environmental problems and restrictive legislation are making landfills a burning issue.

Land spreading technique is more appealing, however in case of paper mill sludges, the concern is for temporary nitrogen immobilization, which begins about one month after plowing of the organic matter, therefore addition of supplementary nitrogen fertilizer is essential for enhanced microbial activities.

Sludge incineration therefore in future holds significant potential as it allows to recover heat from the wastes simultaneously reducing the landfills volumes. The energy recovery may go up to the tune of 10,000 kJ/kg based on organic content.

The dewatering and drying of sludges & rejects are the important waste handling practices. Dewatering is an essential stage of waste handling regardless of the recycling and disposal methods. All conventional or non-conventional methods for material and energy recovery benefit from a high dry solids content of rejects and sludges.

Dewatering: Nearly all wastes from recovered paper processing with the exception of the dewiring units, ragger and drum pulper rejects has an original dry content of only 1-6%. For this reason, the first step in waste treatment is dewatering. **Table-5** summarizes the most common dewatering systems. The differences in the dry solids contents are due to different pressure levels and times.

TABLE -5

COMPOSITION AND DEWATERING OF REJECTS AND DEINKING SLUDGES

Particulars	**Heavy weight & Coarse Rejects**	**Light weight & fine rejects**	**Deinking Sludges**
Composition	Glass nails, sand, stones, paper clips, pins, staples, textiles, wood pieces, wet strength papers	Sand, textiles, fibres, coating colors, plastic fragments, hot melts, stickies	Fillers, pigments, fibres, fines, printing inks, stickies.
Dewatering facilities	Screens Vibrating screens Screw classifiers Rake classifiers	Screens Disk thickeners Dewatering drums Gravity tables Screw presses	Dewatering drums Gravity tables Belt filter presses Screw presses
Achievable dry solids, %	60-80	50-65	One stage operation<15 Two stage operation>65

Sludge Incineration:

Recent years have seen growing interest in use of other types of wastes including sludges & rejects for energy production due to:

- Increased costs of fossil fuels and purchased power.
- Reduced landfill capacities & increased landfill costs.
- More stringent environmental regulations governing this waste use.
- Development of new combustion technologies with highly effective flue gas cleaning technologies.

In recovered paper processing mills, the following combustion technologies are primarily used for reject and sludge combustion.

- **Grate combustion** -The fuel is fed mechanically on to the grate. Travelling grates are most common types.
- **Fluidized & circulating fluidized bed combustion:** In fluidized bed combustion, the fuel is fired in a bed of inert solids fluidized by air.
- **Multiple hearth combustion:** This technique is especially suitable for the combustion of moist and paste like waste and is decade old technology.

Selection of Combustion Technology: The choice of combustion technology depends on the operating conditions and nature of waste. Fluidized combustion is the most suitable for treatment of sludges and rejects. Combustion in this occurs quickly and completely. Fluctuations of heating value of the fuel or changing proportions of noncombustible components such as sand, metals or fillers do not have a negative influence on the combustion efficiency. **For low GCV fuels stationary and for high GCV fuels the circulating fluidized bed technologies are more suitable.** However, FB combustion technology involves higher investments when compared with grate and multiple hearth furnaces.

Emissions from Incineration Plants: The most important atmospheric pollutants are solid particles/dust, SO_2, NO_X, HF, HCl various heavy metals and trace organic components such as dioxins and furans.

However, if sludge incineration occurs properly with sufficient retention time, uniform and complete combustion and efficient solid particle removal, flue gases with very low dioxin and furan concentration will result.

REFERENCES

1. Miner,R., Berger,H, etal: *"Environmental considerations and information needs associated with an increasing reliance on recycled fibre"*. TAPPI Symposium Notes Focus 95+ Landmark Paper Recycling Symposium (1991)
2. Rappe, C., Glas,B. and Wiberg, K.: *"Solved and remaining PCDD and PCDF problems in the pulp industry"*. Conference paper: DIOXIN'90, Bayreuth FRG, 1990.
3. Paasschens, C., Habets, L. and de Vegt, A.: *"Anaerobic effluent treatment of recycled paper mill effluent in the Netherlands"*, TAPPI J 74 (1991): 11, 109.
4. Louhimo, J.T. and Mullen, J.F., *"Sludge burning in fluidized bed boilers"*. Environmental Issues TAPPI PRESS Anthology of published papers (1990), 416
5. Sixour, VK,: *"Environmental considerations in the design and sitting of a secondary fibre mill"*. TAPPI Proceedings, 1991 Environmental Conference, p. 1121
6. Diehn, K.: *"Recycling a deinking mills waste through landspreading"*, TAPPI Proceedings, 1991 Environmental conference p. 739
7. Strobel, C.L.: *" Development of residuals management at Inland containers recycle mill"*, TAPPI Proceedings, 1991 Environmental Conference, p. 747.

PUBLISHED RESEARCH PAPERS IN THE AREA OF ENVIRONMENT

THE FATE OF ADSORBABLE ORGANIC HALOGENS (AOX) IN ACTIVATED SLUDGE PROCESS OF AGRO BASED PULP AND PAPER INDUSTRY

The Fate of Adsorbable Organic Halogens (AOX) in Activated Sludge Process of Agro-based Pulp and Paper Industry

Chinnaraj S., Malathi R., Reddy K.P. and Venkoba Rao G.

ABSTRACT

The performance of wastewater treatment plant based on Activated sludge process treating effluent from bagasse based integrated pulp and paper mill has been investigated to find out the extend of AOX (Adsorbable Organic Halogens) reduction during vaqrious stages of treatment along with other conventional pollutants like Suspended Solids, Chemical Oxygen Demand and Biochemical Oxygen Demand. The overall reductions were 93, 77 and 98 percent for Suspended solids, Chemical oxygen demand and Biochemical oxygen demand respectively. It was found that AOX reduction across the wastewater treatment plant was 69.3%, out of which 53.8% was removed in the activated sludge biological treatment, out that 43.7% was found to be removed by microbial metabolism while remaining was getting carried away along with waste activated sludge.

INTRODUCTION

In any manufacturing process, it is possible to identify several sources of discharges having potential adverse effect on the environment. In paper manufacturing process pulp mill plays an important role where un-bleached pulp is made by chemically degrading and dissolving lignin content of the raw materials like wood, bagasse, bamboo etc. Since, complete lignin removal at this cooking stagte result in deterioration of the pulp strength, a small portion is allowed to remain in the pulp . This residual lignin which makes the pulp brown color and has to be removed by bleaching before the pulp is used for making writing and printing paper.

Bleaching is the multistage process involving various bleaching chemicals, such as, chlorine, hypochlorite, chlorine dioxide, oxygen, hydrogen peroxide and ozone. Among the above bleaching agents, chlorine and chlorine compounds have been used predominantly. This is because, they are highly efficient and economical. An alkaline extraction stage using NaOH usually follows each bleaching stage to extract the products formed by the bleaching reaction. They are mainly fragments of lignin macromolecules that have been modified during the bleaching process, for example, chlorinated lignin or oxidized lignin.

The presence of chlorinated lignin or chlorinated organic compounds in the bleach plant effluent found to have some detrimental effect on the environment[1]. Therefore, various government agencies have proposed stringent dischare regulation on discharge of these compounds to surrounding environment. These compounds are collectively called Total organically bound chlorine (TOCI). They include, polychlorinated

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organic compounds, such as Chlorophenol, Chloroguaiacols, Chlorocatechols, 2,3,7,8- terachlorodibenzodioxin and 2,3,7,8- tetrachlrodibenzofuran. Estimation of TOCl gave low value because of incomplete recovery from resin column. An alternate method was soon evolved and being known as Adsorbale Organic Halogen (AOX) Analysis. Major pulp and paper producing countries around the world enforced regulations for AOX discharge in the final treated effluent[2,3,4]. including India[5].

Several studies have been carried out on AOX degradation and removal, for example, by aerobic bacteria[6,7], anaerobic bacteria[8], ultrafilteration followed by anaerobic and aerobic system[9], activated sludge process and aerated stabilization basin[10]. Extensive studies were carried out in Europe, North America and Scandinavian countries on AOX toxicity, degradation and removal efficiency where they use wood as raw materials mainly Softwood[11]. The nature of organic chlorine synthesis during bleaching, degradation and removal efficiency by microbial system differs considerably according to raw materials and process used to manufacture pulp[12,13].

Most of our mills in India use agrobased raw materials and practically no information is available on AOX degradation and removal by microbial system. Therefore, the present study was carried out to understand the microbial degradation efficiency of AOX along with other parameters such as pH, Suspended Solids, Chemical Oxygen Demand and Biochemical Oxygen Demand in the activated sludge process of largest agro based pulp and paper industry.

EXPERIMENTAL

The effluent treatment plant receive effluent from two streams, one with high BOD which contains mostly bagasse washing and bagasse-yard effluent and other one contains bleach plant and paper machine effluents. The second stream (Figure: 1) was selected for present study, because, chlorinated organics are produced during bleaching process. Composite samples were

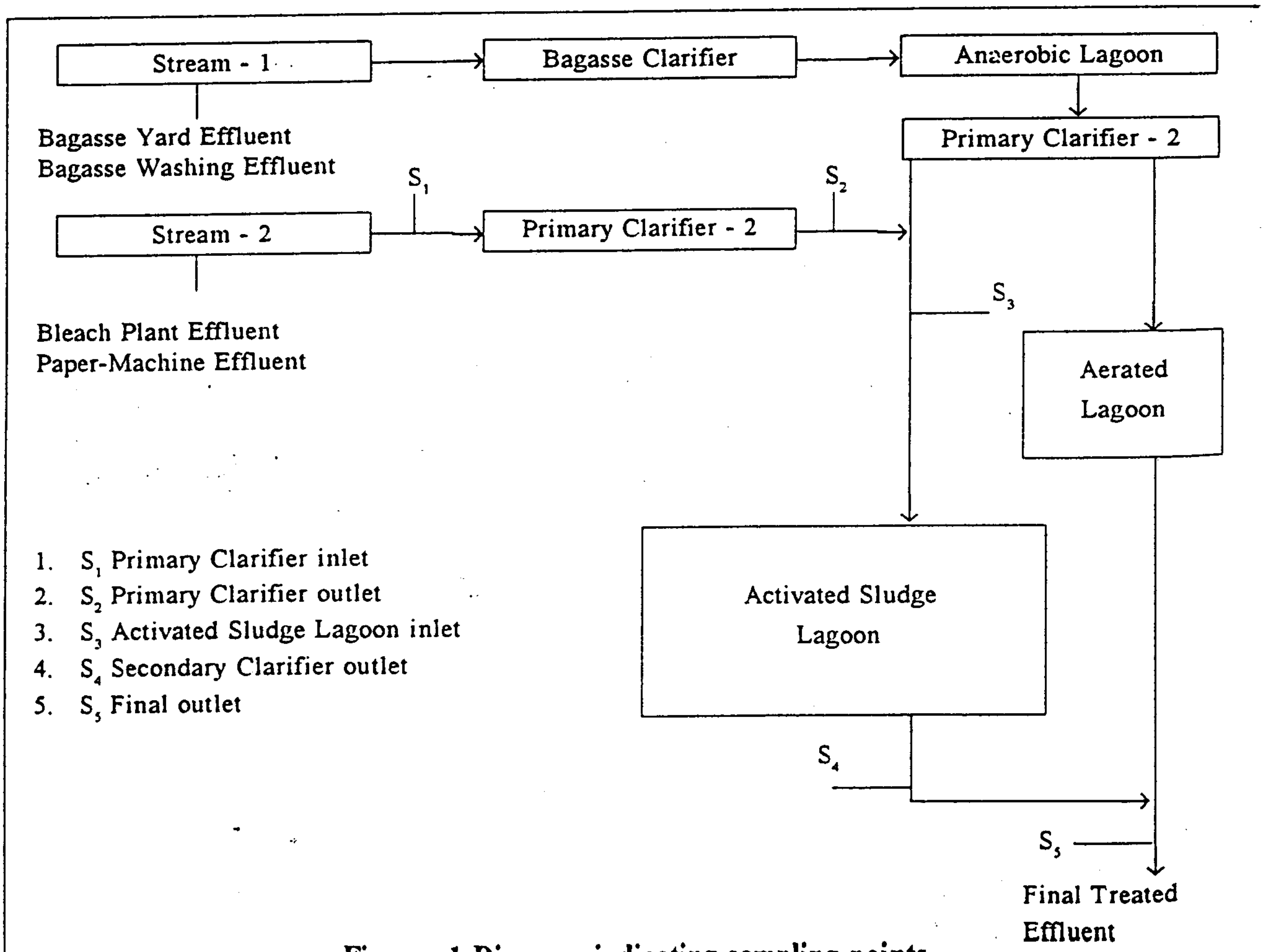


Figure: 1 Diagram indicating sampling points

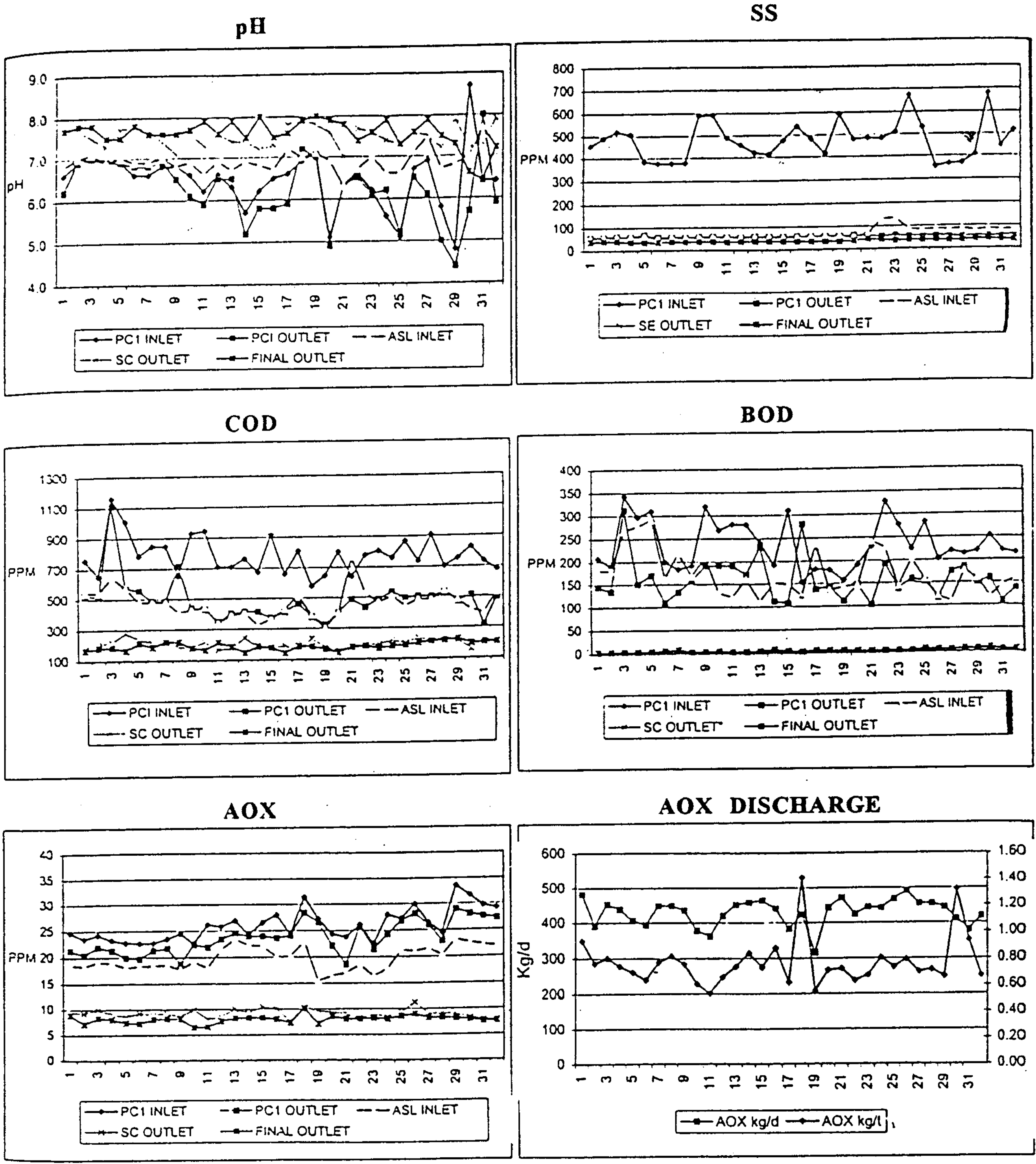


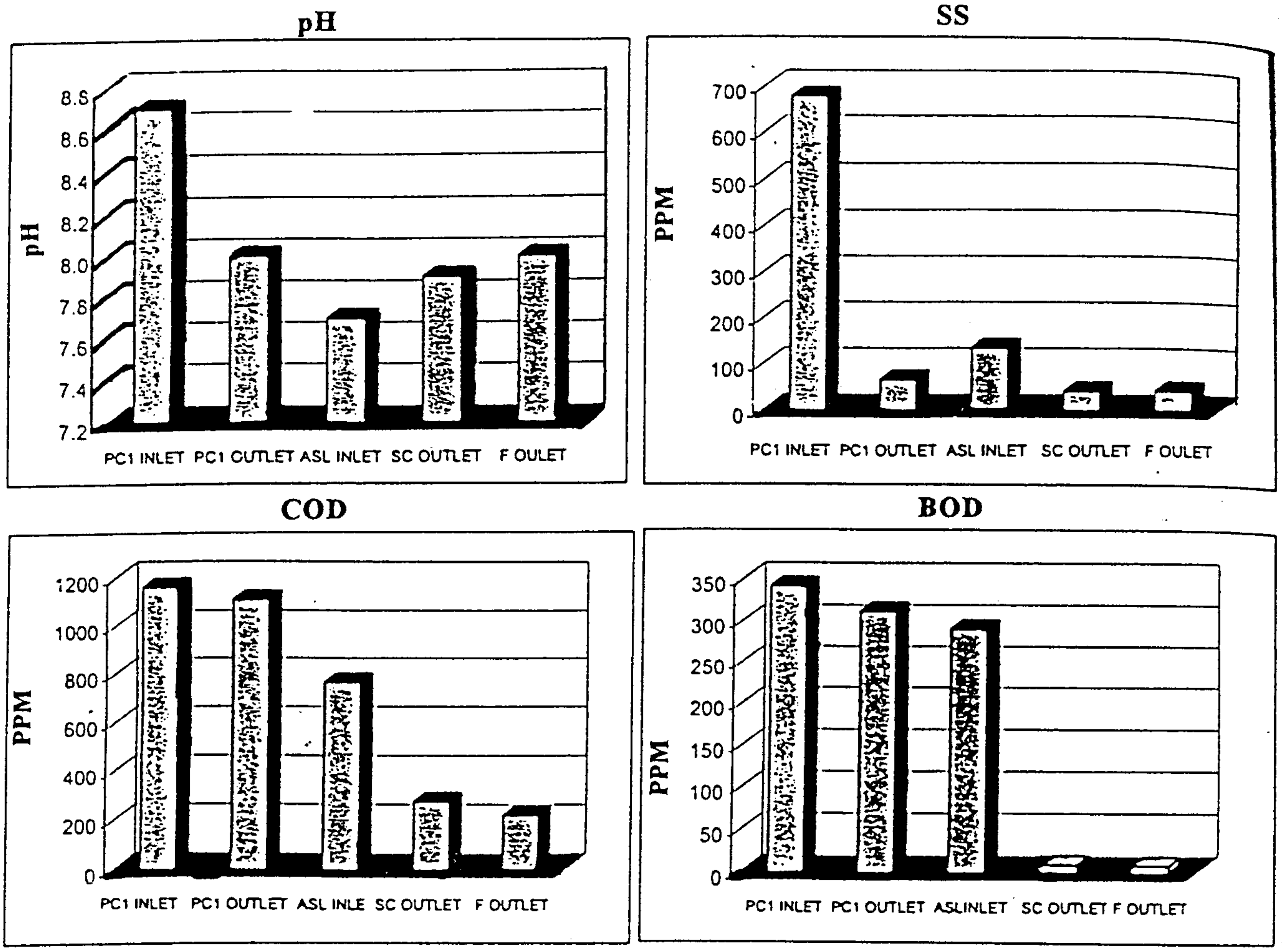
Figure: 2 Daily pH, SS COD, BOD, AOX values and AOX discharge during study period

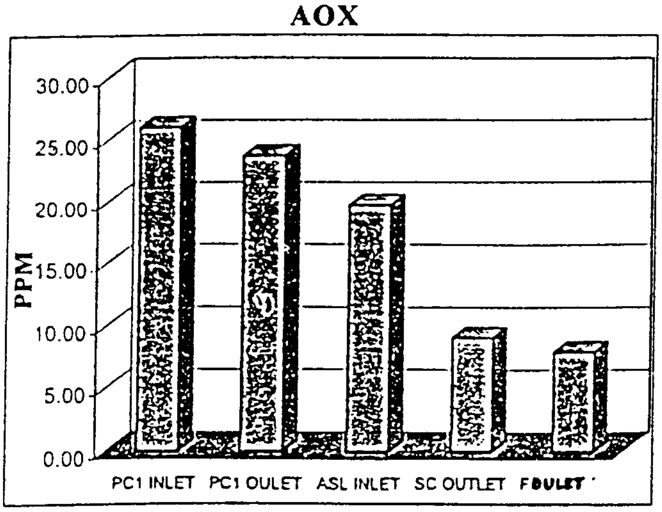
collected and analyzed every day for about one month. pH, Suspended Solids, Chemical Oxygen Demand and Biochemical Oxygen Demand were analyzed as per the standard methods (SS:2540D, BOD : 521 0B & COD :22 B). AOX was analyzed using AOX analyzer (ECS 1200 AOX Analyzer, Euroglas Analytical Instruments, The Netherlands) as per the ISO column method (ISO 9562:1989-E)[15].

RESULTS

Daily values of pH, Suspended Solids, Chemical

Figure: 3 Average values of pH, SS COD, BOD, AOX in various stages of ETP





Oxygen Demand and Biochemical Oxygen Demand across ETP plant are presented in Figure 2 and average values are presented in Figure3. The overall reductions were 93, 77 and 98 percent for Suspended solids, Chemical oxygen demand and Biochemical oxygen demand respectively.

AOX values at various stages of ETP are presented in Figure 2 and varies from 22.38 to 33.55 ppm at primary clarifier inlet, 18.56 to 28.97 ppm at primary clarifier outlet 16.34 to 23.34 ppm at activated sludge lagoon inlet, 7.57 to 11.2 ppm at secondary clarifier outlet and 6.43 to 10.07 ppm at final outlet. Average values of AOX are presented in Figure 3. Overall average AOX inlet to Activated sludge lagoon is about 985 kgs/day (50,000 m^3 X 19.69 ppm) of which nearly 455 kgs is let out in the treated effluent. This account about 53.8% removal in Activated sludge lagoon alone. To find out AOX discharged in the waste activated sludge, secondary clarifier underflow was analyzed and result are presented in Table 1. The average value was about 40 ppm and this accounts for nearly 10.2% of total AOX, is further diluted to 8.0 ppm by mixing with aerated lagoon outlet and discharged as treated effluent. Total AOX discharged per day and per tone of production is given in the Figure 3 and average was about 429 kg/day and 0.77 kg/tonne.

Table-1 AOX Concentration at Secondary clarifier under flow sludge

S. No.		AOX ppm
1.		44.30
2.		45.03
3.		38.38
4.		35.38
5.		30.55
6.		44.26
7.		39.68
8.		39.75
9.		38.92
10.		40.15
	Avg.	**39.68**

DISCUSSION

Wastewater treatment plant in pulp and paper industry are primarily designed to reduce the conventional pollutants like Total solids, Total dissolved solids, Suspended solids, Chemical oxygen demand and Biochemical oxygen demand. However, it has been found that wastewater treatment like aerated stabilization basin and activated sludge process, primarily designed to treat conventional pollutants also found to remove or reduce AOX produced during bleaching process. The percentage reduction of AOX was reported to vary 14 to 65%[16,17] and in the present study i.e. wastewater treatment process using agrobased pulp and paper mill effluent accounts for about 69.3% reduction in AOX along with other conventional pollutants like Suspended solids (93%), Chemical oxygen demand (77%) and Biochemical oxygen demand (98%). Among the overall 69.3% AOX reduction in ETP, actual reduction in the activated sludge lagoon is only 53.7%. There are two principal mechanism by which AOX is removed in the biological treatment system.. They are 1. Microbial degradation, 2. Adsorption on to the sludge.

MICROBIAL DEGRADATION

In microbial degradation, AOX compounds having molecular weight below 1000 are ingested by bacterial cells and metabolized and in the fungal system, the AOX reduction is by dechlorination of Chlorinated phenolic compounds which result in release of Chlorine and phenoxy radicals. Phenoxy radicals undergo further non enzymatic reactions with other compounds present in the systems resulting polymerization[2].

These repolymerized compounds are considered to be resistant to microbial degradation and adsorbed on sludge or send out along with treated effluent. Earlier studies indicates that biodegradation of AOX by microorganism reduce the concentrations of these compounds in the bleach plant effluent, but not completely[18]. This is in accordance with present study where actual microbial degradation accounts for about 43.7 percent as evidenced by other studies[17,19]. Most of non degraded compounds are found to accumulate in the sediments of water body and degraded slowly by anaerobic biota widely distributed in the sediments. But it is premature to conclude that complete dechlorination could take place under anaerobic condition.[18,20] The deficient dechlorination capability of aerobic and anaerobic biological system is due to the selection of readily available degradable compounds during bleaching and other process by microbial flora in the treatment system.[21]

ADSORPTION ON TO THE SLUDGE

Most of the hydrophobic chlorinated organic compounds adsorb to on the solid surface like fiber fines, clay and bacterial flocs present in sludge. Generally AOX compounds resistant to microbial degradation are carried away by the treated effluent or sludge. This is evidenced by the presence of AOX content in the sludge (39.68ppm) and secondary clarifier outlet. Nearly 100 kg was removed by sludge by adsorption which accounts for about 10.2% of total AOX entering to activated sludge lagoon.

Fears have been expressed that groundwater would be contaminated by the AOX present in sludge, however we have found that during the composting of sludge along with waste pith and bagasse, the AOX compounds are getting mineralized and the leachate from composting contains little or no AOX. Therefore, the role of terrestrial micro and higher organisms and their metabolic capabilities will differ from aquatic or wastewater treatment environment and it is found that higher terrestrial organisms are mainly capable of accumulating chlorophenolic compounds.[19,21]

Other studies indicate that degradation of AOX varied according to raw materials used to manufacture pulp and kappa number. For example, for pine pulp with 30.2 and 25.7 kappa number the AOX reduction was 48% and 57% and for birch pulps with kappa number 17.6 and 16.4 the reduction was 59% and 65%

respectively.[22] This indicates that low kappa number of the pulp favors, high reductions of AOX in the activated sludge proces probably due to the higher degradation of lignin during pulping. In our case, the total reduction was 69.3% which is quite high due to the low kappa number of bagasse pulp and may be due to structure difference of lignin present in the bagasse and AOX produced during bleaching process when compared to other raw materials.

To conclude, it is a fact that major fraction of organochlorine compounds of bleach plant effluents occurs in the form of high molecular weight materials and their structure is not fully elucidated. Unless the structure of these compounds are fully characterized, their biodegradation or biotransformation potentials cannot be assessed completely. At the same time it is important to note that all the chlorinated organic compouds are not the exclusive products of chemicals and paper industry. Many hundredds of chlorinated organic compounds are natural metabolites of bacteria, fungi, algae, lichens and higher plants.[23] To what extent these natural and industrial process contribute to global balance of organochlorine is unknown factor. Studies need to be focused in this area. Till then, the total estimation techniques like AOX will give fare idea about their persistence, biodegradation and biotransformation in industrial and natural habitat.

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REFERENCE:

1. Corner, O.B.I., T.G. Kovacs, R.H. Voss and P.H. Martel, 1993. A study of the relationship between laboratory bioassay response and AOX content for pulp mill effluents. Journal of Pulp and Paper Science, 19 (1) : 33-39
2. Shrinath, A. and I. Jerry Bowen, 1995. An overview of AOX regulation and reductions strategies. Anthology of published paper, TAPPI Press, 1991-94, 31-45.
3. Berry, R.,M., C.E. Luthe, R.H. Voss, P.E. Wrist, P. Axegard, G. Gllerstedt, P.O. Lindblad and I. Popke, 1991. The efects of recent changes in bleached softwood kraft mill technology on organochlorine emission. An International Prospective, Pulp and Paper Canada, 92 (6) : 43:53.
4. Folke, J., H. Edde and Karl-Johan Lehtinen, 1991. The scientific foundation of adsorbable organohalogens (AOX) as a regulatory parameter for control of organochlorine compounds. Proceedings of TAPPI, Environmental Conference, 517-527.
5. The Gazette of India, Part II Section 3, Subsection 1.
6. Neilson, A.H., A. Allard, P.A. Hynning, M. Remberger, L. Lander, 1983. Bacterial methylation of chlorinated phenolsand guaicols: Formation of veratrols from guaiacols and high molecular weight chlorinated lignin Applied and Environmental Microbiology, 45(3): 774-783.
7. Allard, A.S., M. Remberger, and A.H. Neilson 1987. Bacterial O Methylation of halogen substituted phenols. Applied and Environmental Microbiology, 53 (4) : 839-845.
8. Allard, A.S., P.A. Hynning, C. Lindgren, M. Remberger, and A.H. Neilson 1991. Dechlorination of Chlorocatechcols by stable enrichment cultures of anaerobic bacteria. Applied and Environmental Microbiology, 57 (1) :77-84.
9. Ek, M. and MC. Kolar, 1990. Reduction of AOX in bleach plant effluent by a combination of ultrafilteration and biological methods. Biotechnology in Pulp and Paper Industry. (eds. T.K. Krik and Hoo -Min Chang) Butterworth Heinemann, MA, USA, 271-287.
10. Lafleur, L.E., T.M. Busquet and D.L. Cook, 1998. Effect of biological treatment on pulp mill effluent chemical characteristics. Chlorine and Chlorine Compounds in the Paper Industry. (ed. V. Turoski) Ann Arbor Press, Chelsea, Michigan, USA, 119-142.
11. Turoski, V., 1998. Chlorine and chlorine compounds in the paper industry Ann Arbor Press, Chelsea, Michigan, USA, pp 359.
12. Gergov, M., M. Priha, E. Talka, O. Valttila, A. Kangas and K. Kukkonen, 1988. Chlorinated organic compounds in effluent treatment at kraft mill. TAPPI Journal, 71 (12) : 175-184.
13. Stromberg, L., R. Morck, F. De Sousa and O. Dahlman, 1995. Effects of internal process changes and external treatment of effluent chemistry. Environmental fate and effects of pulp

and paper mill effluents (eds. Mark R. Servos et al.,) St. Lucie press, Delray Beach, FL, USA, 3-19.

14. Standard methods for the estimation of water and wastewater. (20th Edition, eds. L.S. Clesceri, A.E. Greenberg and A.D. Eaton) American Public Health Association, 1014, Fifteenth Street, NW, Washington DC, 2005-2605, USA.,

15. International Standard, Water Quality : Determination of adsorbable organic halogens (AOX). ISO 9562-1989-09-01.

16. Banerjee, S., T.E. Kemeny, R. Sackellares and M.D. Juszynski, 1996. AOX/COD removal in Activated Sludge Basin. Proceedings of TAPPI International Environmental Conference, 159-162.

17. Wilson, D.G. and M.F. Holloran, 1991. Decrease of AOX with various external effluent treatments. Proceedings of Canadian Pulp and Paper Technical Association 77th Annual Meeting, Quebec, Canada, 281-283.

18. Neilson, H., A.S. Allard, P.A. Hynning M. Remberger and T. Viktor, 1990. The environmental fate of chlorophenolic constituents of bleaching effluents. TAPPI Journal, 73 (3) : 239-247.

19. Taylor, J. and B.C. Squamish, 1995. Activated sludge treatment of kraft pulp mill effluent. Proceedings of Canadian Pulp and Paper Technical Association 81th Annual meeting, Montreal, Quebec, 49-55.

20. Allard, A.S., M. Remberger, T. Viktor and A.H. Neilson, 1998. Environmental fate of chloroguaiacols and chlorocatechols. Water Science and Technology, 20 (2) : 131 -141.

21. Neilson, H., A.S. Allard, P.A. Hynning and M. Remberger, 1994. Chlorine hazard assesment. A strategy for evaluating organic chmpounds in the aquatic environment. *Environmental Science and Technology*, 28: 278-288.

22. Gergov, M., A. Kangas and K. Kukonen, 1988. Chlorinated organic compounds in effluents treatment at kraft mills. *Proceedings of TAPPI Environmental Conference, 443-455.*

23. Gribble, G.W., 1998. The natural production of organochlorine compouns. *Chlorine and chlorine compounds in the Paper Industry.* (ed. V. Turoski). Ann Arbor Press, Chelsea, Michigan, USA, 89-108.

CONTROL OF AOX DISCHARGES IN PULP AND PAPER INDUSTRY – ROLE OF NEW FIBER LINE

Control of AOX Discharges in Pulp & Paper Industry- The Role of New Fibreline

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ABSTRACT

The increased environmental awareness, cost competitiveness and quality consciousness particularly about high brightness chlorine free paper have forced the pulp and paper industries switch over to new fibre line with cleaner production options like ECF & TCF bleaching process to control the discharge of AOX below the toxicity level. However, the Indian pulp and paper industry is still persisting with the use of conventional pulping and high dosage of chlorine to produce high brightness product due to technological and economic constraints. With the emergence of regulation of discharge of AOX as an environmental issue in recent times, Indian pulp & paper industry is at cross road as it is faced with the challenge of becoming both cost competitive as well as environment friendly to survive in the international market. The present paper highlights the status of AOX level, level of technology, integrated approach and constraints to adopt the new fibre line to reduce the discharge of AOX to make Indian pulp & paper Industry more eco-friendly and internationally competitive.

INTRODUCTION

The bleaching of pulp with chlorine based chemicals produces toxic chlorinated phenolic compounds some of which are bioaccumlable and persist in environment for a long time. The increased environmental awareness, customer preferences for ecofriendly (chlorine free) products and imposition of stringent discharge norms have forced the pulp mills to adopt cleaner production options to reduce the kappa number of unbleached pulp so as to minimize /eliminate the use of chlorine based bleaching chemicals. The development process to reduce the kappa number of unbleached pulp is depicted in Fig. 1. With the development of technologies like extended delignification, oxygen delignification, improved pulp washing, chlorine dioxide bleaching etc., most of the pulp mills in developed countries have introduced new fiber line to produce paper products of high brightness ranging from 85-90% with AOX generation below toxicity level. The advantages of consistent supply of uniform wood based fibrous raw materials and high scale of operation have facilitated the switchover in these mills. Indian pulp and paper industry is still employing conventional pulping and bleaching process and have limitations to adopt the new modified fibre line to produce quality paper of international standards primarily because of low scale of operation and use of mixed fibrous raw materials. However inspite of all these limitations the Indian paper mills are managing to produce paper of brightness above 80% ISO which obviously is at the cost of increased chlorine consumption resulting in high level of AOX generation.

Technological status of Indian pulp & Paper Mills

The pulp and paper industries in India are scattered, old and vary in terms of size, use of fibrous raw material, process employed, machinery used and end products. These mills use a wide range of fibrous raw materials to produce variety of paper. In view of AOX discharge the paper mills are categorised broadly into :

Large Scale Mills	(with chemical recovery process)
Small Scale Mills	(without chemical recovery process)

The technological status of these mills is discussed below:

Scale of Operation

The scale of operation in large scale pulp and paper mills ranges from 100- 275 tonnes of pulp per day which in small mills is in range from 20-70 tonnes pulp per day. The low scale of operation of Indian paper mills is primarily due to scarcity of wood and inconsistent supply of other forest based raw materials. Further, the resource constraint is another reason for low scale of operation. Almost all the small scale mills are operating without chemical recovery system because of size constraint and are discharging their black liquor along with other streams.

Level of Technology

Pulping process

The kappa number of the unbleached pulp produced varies between 18-26. The reason for maintaining high kappa are the mixed raw material pulping and capacity limitation of chemical recovery boiler . By the same process the integrated agro residue based mills are producing pulp of kappa number between 14-16. J.K. Paper Mills, Orissa is the only mill employing modified RDH pulping process and oxygen delignification process i.e. advanced pulping technologies to produce pulp of better quality and low kappa number between 12-14 by using bamboo and eucalyptus.

Almost all the small scale agro based mills are employing soda pulping for producing pulp of high kappa number i.e 30-32 due to economic reasons as conventional chemical recovery system is not practiced and major part of lignin is removed in subsequent conventional bleaching process using elemental chlorine and hypochlorite .

Pulp washing system

The large integrated mills normally use conventional brown stock washers (BSW) with counter current washing for extraction of black liquor and washing of pulp. The efficiency of BSW's is defined in terms of soda losses and carry over of organic matter along with pulp entering the bleaching section. Due to inherent quality of fibers in the pulp from these raw materials and washing technology employed, the carryover of the organic matter, in terms of COD is generally on higher side. The washing efficiency of existing BSW's operating in small mills are even more lower as 50-70% higher carry over of COD alongwith pulp compared to large wood based mills has been observed which results in increase of demand of bleaching chemicals.

Bleaching process

Most of the large integrated mills are using conventional CEHH sequence for bleaching of pulps to a brightness level of 80-85% ISO, primarily to produce quality products of international standards. Some mills have started the use of chlorine dioxide alongwith elemental chlorine during chlorination and in final stages of bleaching only to get higher and stable brightness of pulp. The consumption of total chlorine in these mills varies from 60-100 kg/ tpulp . Most of these pulp mills are now using oxidative alkali extraction bleaching to increase pulp brightness and improve the quality of pulp and bleach plant effluent. The small scale mills based on agro residues also use conventional CEHH/ HH sequence to bleach the pulp to a brightness level of 75-80%. The consumption of chlorine in these mills is comparatively high and vary around 140-160 kg/t pulp primarily because of high kappa number of unbleached pulp and also high carry over COD along with pulp .

The pulp mills in developed countries have incorporated various measures to changeover to new fibre line in pulp mills which includes extended delignification, improved pulp washing, oxygen delignification , chlorine dioxide bleaching etc. However , the application of these technological development is mostly limited to developed countries primarily due to advantages of consistent supply of wood based fibrous raw materials and high capacity of pulp mills. The use of mixed fibrous raw materials, low scale of operation , high capital investment are the major constraints which restrict Indian pulp and paper mills to switch over to new cleaner production fibre line. The techno-economics of the modern pulping and bleaching technologies in Indian perspective is indicated in Table-1.

Status of AOX level in Pulp and Paper Mills Indian perspective

In the last decade, extensive R&D studies were conducted by CPPRI related to formation of AOX during bleaching of pulp produced from various fibrous raw materials commonly used by Indian pulp and paper mills , assessment of status of technology and level of AOX in both large and small scale mills producing bleached variety of paper and also the measures to control the discharge of AOX.

Table 1 Techno-economics of New Pulping & Bleaching Process in Indian Perspective

Technologies	Minimum Investment Rs. Crore	Level of Operation t/d	Limitations
Extended Delignification raw materials	55-60	>350	Low level of operation Use of mixed fibrous
Oxygen Delignification	20-25	>300	High capital investment
Chlorine dioxide bleaching (2.0-2.5 t/d)	32-35	~ 300	Age of mills Require new infrastructure

Source : Information available in literature and from association of mills

Table 2 Status of AOX in Indian Pulp and Paper Mills

Type of product	Kappa No.	COD Carry over during washing kg COD/T pulp	Consumption of Chlorine kg/t pulp	AOX level kg/t Paper	
				Gen.	Final Discharge
Rayon grade Pulp	12 - 16	Kappa No. Differ 1.5 units	25 - 28	0.7-1.0	<0.50
Newsprint chemical pulp	20 - 22	—	20 - 25	0.50-0.60	<0.50
Writing & Printing Paper:					
Large Mills	15 - 26	20 - 25	35 - 110	2.0-4.50	1.0-2.50
Small Mills (Agro-based)	30-32	30 - 40	140 - 160	6.0-10.0	4.0-6.50

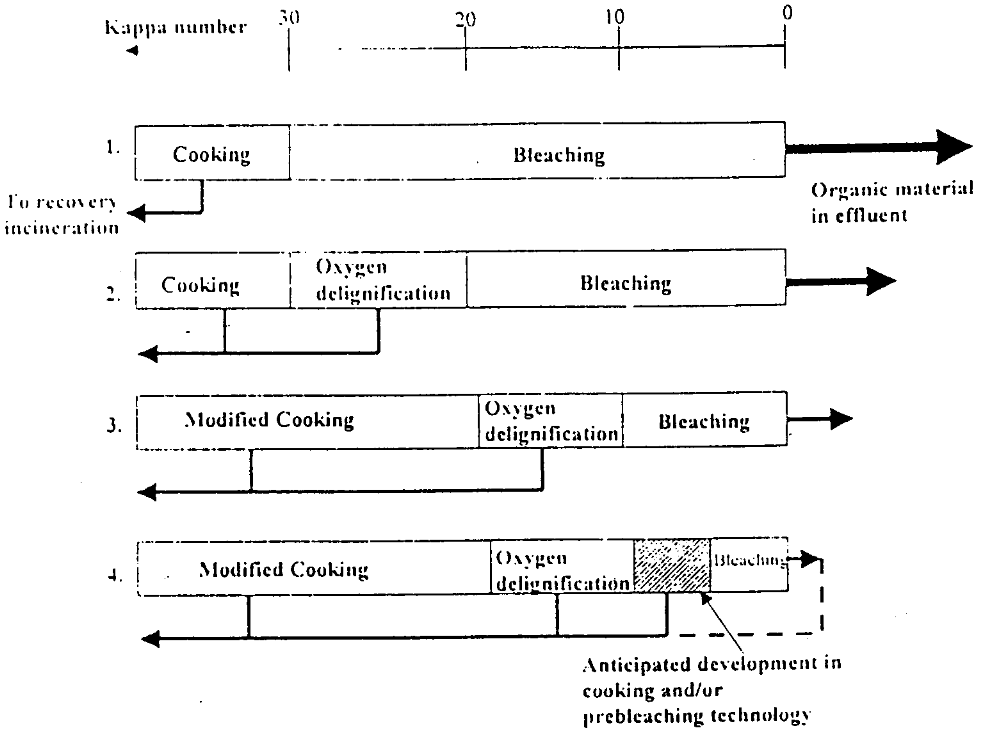

Fig. 1 Development of alternate pulping process

The level of AOX in large scale integrated mills varies between 2.0 -4.5 kg/t paper . Low level of AOX was observed in the mills using RDH , oxygen delignification and chlorine dioxide bleaching as compared to mills using conventional CEHH bleaching process. In small scale mills the scenario of AOX discharge is more alarming as these mills are using high dosage of chlorine to bleach pulp of high kappa number due to economical reasons . The generation of AOX in these mills varies from 6-10 kg /t paper . The high level of AOX is primarily due to following reasons :

- High kappa number of pulp due to absence of chemical recovery.
- High carryover of black liquor alongwith pulp going to bleaching plant.
- Use of high dosage of elemental chlorine.
- Obsolescence in technology & equipments.

The level of AOX generated and finally discharged in Indian pulp and paper mills is given in Table 2.

Integrated approach to reduce AOX level

In view of increased global competitiveness, preference for eco-friendly paper products, imposition of stringent environmental regulations, Indian pulp and paper mills particularly large mills are required to adopt energy efficient and environmentally friendly new fibre line to efficient and environmentally friendly new fibre line to become at par with the international status. This appear to be a difficult task primarily due to low scale of operation and use of mixed fibrous raw materials. However the level of AOX and other pollutants may be reduced to maximum extent in Indian paper mills by adoption of integrated approach involving better house keeping, process optimisation and other measures. These measures as given below, may be implemented with minor process modification and some capital investment to reduce the level of AOX :

Controlled Pulp Mill Operation

The large integrated as well as small scale mills are producing unbleached pulp of high kappa number with a fear of drop in pulp strength if kappa number reduces below 20. Laboratory studies conducted at CPPRI reveals that kappa number can be reduced to around 18 without any degradation in pulp properties. However to obtain pulp around kappa number 18 the mills will be required to operate the pulp mills under controlled and uniform cooking conditions to avoid any degradation in pulp properties. Small mills are also required to produce bleachable grade pulp below kappa number 25.

Imporved Pulp Washing

Usually the soda loss and carry over of organic matter along with pulp during washing observed was comparatively higher in Indian mills. The high carry over of organic matter along with pulp increases the bleaching chemical demand and ultimately contributes significant quantity of AOX in bleached plant effluents. It is desirable that the pulp mills should minimise the carryover of black liquor along with pulp i.e. below 15 kg COD/t pulp through modified pulp washing system to reduce the bleach chemical demand.

Substitution of Elemental Chlorine with Chlorine dioxdide

Most of the pulp mills in developed countries have eliminated the use of elemental chlorine as it is the major contributor of AOX. However the chlorine dioxide generation system is little bit expensive and use of chlorine dioxide requires new anti corrosive infrastructure in bleach plants including washing sysytem. However mills particularly large mills should use the chlorine dioxide to the maximum possible extent along with elemental chlorine as its use minimize the AOX formation substantially as well as improves the quality and pulp brightness.

Oxidative Alkali Extraction Bleaching

The studies conducted at CPPRI indicates 12-15% AOX can be reduced by using oxygen or peroxide in alkali extraction bleaching stage. The pulp and paper mills producing bleached variety of paper must use oxygen or hydrogen peroxide in oxidative alkali extraction stage of bleaching since the process can be used without any major changes in existing bleaching system.

Improved Chemical mixing in the bleach plant

Improved mixing of chemicals in bleach plant is an important step. If the bleaching chemicals are not rapidly & uniformly distributed through the pulp, there is chance of a portion of pulp being over bleached.

Increased Use of Recycled Fibre

The utilization of waste paper (recycled fiber) for paper production has now been on high priority all over the globe as an approach towards resource conservation and becoming environmentally compatible. The paper mills particularly the small scale agro based mills, where achieving kappa number of unbleached pulp below 20 is not economically viable in absence of chemical recovery system should restrict their bleachable grade pulp production and supplement the rest fibre furnish by blending with secondary fiber or purchased pulp. Similarly large paper mills should also explore the possibility of using maximum proportion of recycled fiber to supplement the fiber furnish for production of bleached variety of paper grades. Such supplementary recycled fibre must be bleached with hydrogen peroxide to reduce the overall level of AOX in the effluents.

Post Digester leaching of pulp

The conventional pulping process has limitations to avoid degradation of cellulose during cooking of fibrous raw material to produce the unbleached pulp of kappa number below 20. In order to preserve the strength properties of pulp, CPPRI developed a process known as alkali leaching or post digester leaching primarily for leaching out the lignin and its degraded products adsorbed onto the fiber surface of pulp produced from agro residues. The process has been found effective to reduce the kappa number of pulp having kappa number more than 25. The process coupled with efficient pulp washing system can be used in agro based mills producing the pulp of high kappa number in absence of chemical recovery and also in large mills which are forced to produce pulp of high kappa number due to capacity limitations of chemical recovery boiler.

Enzymatic prebleaching

An extensive R& D studies were conducted by CPPRI on potential and application of enzymatic biobleaching to reduce the consumption of chlorine in order to reduce the formation of AOX in bleach plant effluent. The results achieved in laboratory and mill scale trials reveal that the enzymatic treatment of unbleached pulp reduces the total chlorine requirement by about 10-15% and about 2-3 units gain in brightness level depending on the pulp quality and enzyme used. Some of the large mills have started the use enzymatic pre bleaching to achieve high brightness of pulp.

Elimination of Chlorination Stage Filtrate Recycle.

Recycling of chlorination filtrate (without treatment) for wet dilution is usually practiced in mlls which results in build up of AOX level. Hence it is desired that in absence of any suitable treatment system like ultrafiltration, reverse osmosis , chemical treatment etc. the chlorination stage filtrate recycling should be avoided.

Biological Treatment process

Biological methods i.e. activated sludge process, aerated lagoon etc have been found effective in removal of organo chlorine compounds. Biological effluent treatment plants can remove of COD,BOD & AOX to the tune of 70-80%,90-95% & 45-70 % respectively. The reduction in AOX level in different categories of mill by conventional biological effluent treatment plants is indicated in Figure-4. Anaerobic treatment can efficiently destroy chlorophenolics compounds, mutagenicity & acute toxicity. Anaerobic reactors have been reported to reduce the AOX by 40-45 %. However the anaerobic microbes are very sensitive and many chlorinated phenolics including H_2O_2 have been reported to cause severe inhibition & toxic effect to anaerobic microbes when exceed beyond tolerance limit. Thus regular & proper monitoring of ETP is necessary to avoid overloading so as to achieve desired removal efficiency of pollution loads .

CONCLUSION

In the changed scenario , the need to switch over to new fiber line involving the technologies such as extended delignification , oxygen delignification, chlorine dioxide bleaching has become a necessity of pulp and paper industry to address the environmental issues particularly control of discharge of AOX related compounds below toxicity level. Most of the pulp mills indeveloped countries have switched over to new fiber line with cleaner production techniques because of consistent supply of wood based fibrous raw materials and high capacity of pulp mills . The low scale of operation, use of mixed fibrous raw materials and high capital investment are the major bottlenecks which restrict the Indian pulp and paper mills to adopt these new technological developments by. As such these mils continue to rely on conventional pulping and bleaching technologies to produce high brightness paper of international standard. However inspite of these constraints, the mills will have to adopt the appropriate measures / strategies to address the above environmental issues for its survival. Thus an integrated approach involving better house keeping, optimisation of process variables ,restricting the chemical pulp production , increasing the recycled fiber proportion in the fiber furnish , operation of effluent treatment plants under optimum conditions etc. is required to be adopted by the Indian pulp and paper industry to become internationally competitive and environmentally compatible.

CONVERSION OF ORGANIC SOLID WASTE IN TO ENERGY – OPTIONS IN THE PULP AND PAPER INDUSTRY

CONVERSION OF ORGANIC SOLID WASTES TO ENERGY – OPTIONS IN THE PULP AND PAPER INDUSTRY

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Abstract

Generation of solid waste is increasing day by day per person in the current scenario of the changing lifestyle in India. Although there are several guidelines given by MOEF for the collection and disposal of solid wastes, but their follow-up part is lacking. General awareness about the harmful effects of solid waste is also not satisfactory inspite of the efforts made by Government through Television and Newspapers.

Solid waste generated from industrial activity is increasingly being regarded as a potential source of energy. The industries are now looking for available technologies to recover the energy from these wastes.

Pulp and paper industry generates a lot of solid waste from various stages of manufacture right from raw material preparation to paper making. They generate waste in both the form i.e. inorganic and organic solid waste. In this context an attempt has been made to form binderless briquettes from organic solid waste of pulp and paper industry. Briquettes can be made by densification of solid waste like rice straw, wheat straw dust, chipper dust , ETP sludge and pith.

Briquettes are a good example of 'Waste to Energy' and can replace coal or cow dung as fuel in villages. In industries these briquettes can be used as energy source for partial replacement of conventional fossil fuels.

The present paper describes the process for the briquetting of organic solid waste from pulp and paper industry. The machinery used for the briquetting is described and characterization details are presented on the final product. The potential energy savings are also described.

Introduction

Generation of solid waste is a general phenomenon in process industry. This is a matter of concern because of its huge quantity as well as the nature of the waste . Pulp and Paper Industry is not an exception and generates a significant quantity of waste at various stages of production during large scale as well as small/mini scale mill operation. The nature and quantity of waste materials produced are determined mainly by the scale of mill operation, grades of paper or board, the cellulosic raw material used and the effluent treatment methods. Small mills using agro residues, generate more organic solid waste compared to big mills based on wood and bamboo. Central Pulp and Paper Research Institute identified and characterized the main sources of organic solid waste generation in the mills and proposed remedies, for their utilization. Out of the proposed remedies, one is the use of these organic wastes as a source of heat energy.

Various raw materials commonly available and used for paper making in this country have specific waste generation implications and can be traced to certain associated characteristics of each fibrous species. The organic waste generated comprises 57% of the total waste generated for small mills.

Selection of Suitable Equipment

There is rapid increase in the general awareness regarding pollution and its harmful effect .People are more concerned about their surroundings than ever before(Disposal of solid waste at any place is no more a safe business). In the recent years with substantial hike in fuel prices and more stringent environmental regulations, the emphasis has shifted to disposal of biomass waste material for efficient recovery of energy. Significant efforts have been made in developing countries, for generating steam from briquettes made from industrial wastes with studies focused on minimizing auxiliary fuel requirement and emissions to produce steam at conditions suitable to meet process demands.

Dewatering of Waste ETP Sludge

The solid wastes generated from raw material storage yard and raw material preparation section with a moisture content in the range of 5-15% depending on the climatic condition can be converted to briquettes or pallets without any major problem.

The effluent treatment plant in a large paper mill produces a sludge that is approximately 80% primary sludge and 20% secondary sludge on a weight basis. The sludge varies in solid content from 2 to 4% depending upon the specific process. So it has to be dewatered before use as a fuel

To increase the solid content to maximum 50 - 60 % various types of dewatering equipments such as

1. Belt Press.
2. Screw press.
3. Vari-NIP twin roll press.
4. Somat dewatering system.

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can be adopted depending upon the conditions and the requirement.

The desired dryness in sludge can be achieved either by the sun drying or with the waste process steam or flue gases to increase the solid contents for burning.

These waste either can be converted to energy by mass burning or after densification in the form of briquettes. The associated problems in mass burning pith and dust of raw material are that they have a low bulk density, therefore specially designed combustion chambers are required. Handling and storage problems are more and due to its low calorific value, these can only be burnt with other fuels, since actual calorific value is low. To get equivalent results in steam production for one tonne of coal 2 tons of rice husk has to be burnt.

In case of effluent sludge, mass burning either alone or together with other fuels is possible. The actual calorific values are reduced by ash content (25 to 30%) and moisture content (40 to 50%) to 1650 kcal/kg(table-1).The associated problems are that it has to be shredded before use in FB boiler , high moisture content and low calorific value.

The solid wastes, that are accumulated in the treatment of pulp and paper mill wastes, whether dewatered or under watered, require either reuse or disposal, the latter being the more common practice. Incineration has at least initially, become an attractive disposal alternatives on sludges.

However, even if incineration becomes common on a wider array of sludges, the disposal of high ash sludges and the residues from incineration will generate an on going need for land filling operations. Table-2 shows the elemental composition including heavy metals of different mills effluent sludge.

Evaluation of Sludge Burnability

The combustion characteristics of dewatered sludge as such or in the form of briquettes do not differ much from that of bark or other biomass fuel. The bulk of the sludge is made up of pulp fibers.

Table -3 shows the fiber analysis of dewatered sludge. The major differences between the sludge and bark are the moisture content and heating value as shown in table –4.

The heating value of dewatered sludge is also very inconsistent, the average heating value of sludges from mill to mill also varies. Table-4 shows the heating value of sludges and other solid wastes. The heating value - sludge moisture - thermal efficiency relationship is a balance that must be maintained when burning sludges.

Operating Problems

The operating problems of mass burning of sludge are listed hereunder:

1. Stack gas opacity increases with increased amount of sludge.
2. Combustion of high content fuel will lower steam production . Therefore an alternative fuel source has to be installed or the amount of sludge in the fuel is to be minimized.
3. The ash produced tends to stick to equipments in recirculation system.
4. Burning high sludge containing fuel (50-100% by weight) requires more monitoring and control on the part of the operators.
5. The thermal efficiency is low due to increasing moisture content of the sludge . An external fuel system has to be provided in such cases.
6. It has to be shredded for efficient burning in case of mass incineration.

These problems can be overcome if it is briquetted

Briquetting of Solid Waste

The process involves the compaction of loose material under pressure usually carried out by addition of a binder to obtain a stable product. In case of lignocellulosic wastes, the lignin in the substrate acts as binding agent due to its thermoplastic property. Therefore, no external binder is needed in the process.

The experimental briquitting unit consists of a hammer mill, dosing machine and a briquetting press. The hammer mill is used to convert sugarcane top, straws and grasses into dust, which is then blown into the dosing machine. ETP sludge is added in required amount. This mixture is then fed into the briquetting machine through a screw conveyor.The briquetting mechine consists of a piston which moves the raw material inside a tapered die with pressure resulting in formation of briquttes.

Heating Value of Different Dust Mixtures

To assess the heating values of different combinations of dust i.e. straw, pith and sarkanda calorific values were determined with the help of bomb calorimeter. Table-5 gives the heating values of dust mixtures of straw, pith and sarkanda in different proportions determined in a bomb calorimeter. A comparison between calorific value of dust mixtures as determined in bomb calorimeter and the calculated arithmetic mean heating values show that they are not the same.

Air Dried Weight of Final Briquettes

Table-6 shows the weight of the briquettes after air drying for a constant length of time. The weight indicates that they can very easily fall to the bottom of the hogged fuel boiler.

Briquetting trials

Briquettes were made using straw dust and effluent sludge, straw and effluent sludge, pith and effluent sludge and also with raw sludge by varying the moisture content of the raw material and also the ratio of sludge and dust, pith or straw. At higher moisture content of about 20 to 30% of sludge, the briquettes require further drying to increase the compactness for handling. It was also observed that by addition of effluent sludge with straw dust and pith the sludge is working as a binder of the dust and also as a lubricant for the die. At low moisture content (5-10%) of the feeding material, the briquettes are not as compact in formation and are breaking on dropping. At a moisture content of around 30% of the feeding material the briquettes were quite compact and upon drying on storage are quite durable for rough handling. The drying after briquetting is very quick and within two days the moisture content is 10-12% even by air drying . Table-7 shows the moisture content in final briquettes with different composition of waste material and also at different moisture in sludge.

To determine this optimum point, the briquettes were formed at 60% solid content. These briquettes were dried in an oven for various lengths of time. Figure -1 illustrates the drying rate. However, they can be sun dried also with the same results.

The compactness and resistance to abrasion is also very important to measure usefulness of the briquettes to withstand the forces normally experienced during material handling. Because of the need of increased strength and the need to curtail microbial growth, the briquettes should be dried to 80% solid content if they are to be stored for any length of time.

Once the briquettes are dried, they do not absorb moisture to a great extent. They retain their shape, though they become soft after several weeks of storage under humid condition. An appropriate flow sheet has been shown in figure-2 for briquetting the solid waste, drying, storage, incineration and possibilities of making it as a fuel.

The proposed solid waste burning process consists of briquetting of organic waste material for use as fuel. The materials which can be used to form briquettes are the fiber dust from raw material section, screen and centricleaner rejects and the sludge from the effluent treatment plant and finally coal dust from boiler house waste.

A number of advantages were postulated for the briquetting approach.

1. Compared to fire wood or loose biomass, briquettes give much higher boiler efficiency because of low moisture and higher density.
2. Briquettes have high specific density (1200 kg/m^3) and bulk density (800 kg/m ^{3}) compared to (60-180 kg/m ^{3}) of loose biomass.
3. Loading unloading and transportation cost are much less.
4. Storage requirement is drastically reduced.
5. Sustained burning as compared to mass burning .
6. Can be used in coal fired boilers & without much modification.
7. Shall not make stack gas opaque as in case of sludge in loose form.
8. The ash will not stick to the equipment as in the case of mass burning.
9. Can be used as domestic fuel also.

It is the cheapest fuel as compared to other fuels as shown in table-8.

Commercial Evaluation

A commercial evaluation of the briquette burning plant is summarized as under

Equipment Cost:

There are three major pieces of equipment to be purchased for this process for conditioning the sludge and then briquetting.

1. Equipment to increase the solid content from 30% to 40% prior to briquetting.
2. A briquetting machine.
3. Equipment to dry the green briquettes.

Because of slow heat drying rate, it is much easier and more economical to initially increase the solid content of the raw sludge by some mechanical means. It exists in the waste treatment after first stage dewatering at 40-50% solids but is too moist for efficient briquetting. Therefore a second stage of water extraction by means of screw press to 60-70% is essential. In Indian context, however, sun drying will be the most economical option.

Briquetting machine of piston and dye type is suitable for Indian raw material provided the moisture content is maintained at around 30%. For higher solid content the briquettes required further drying which is automatic man drying by storage for 2 to 3 days . An economic analysis is performed based on setting up if a briquetting machine is given in table-9.

Conclusion

In comparison to other waste disposal methods adopted in paper industry based on agro-residue raw materials though options such as land spreading or composting for silviculture of agricultural purposes are possible, however, their uses get restricted due to economical or environmental reason depending on nature of paper mill process.

Combustion, therefore, offers the only potential large scale use at this time. Briquetting of these solid wastes suitable for burning in a hog fuel boiler would minimize other methods of disposal costs and would simultaneously satisfy some of the current and future fuel requirements. No Technical difficulties are foreseen with the sludge and other organic solid wastes briquetting process. There should be no difficulty in drying the briquettes appropriately for burning. The burning characteristics of each particular sludge and other organic solid wastes must be evaluated before incineration process begins, however, potential technical difficulties might be the slagging of ash and fouling of surface.

Finally the likelihood of tightening of regulation governing land disposal also support the installation of the process.

ACKNOWLEDGEMENT:

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References

1. Sell, N.J. and McIntosh, T.H., TAPPI, 71(3), 117 (1989).
2. Sell, N.J., Mcintosh, T.H. Jayne, T., Rchfeldt, T. and Doshi, M., TAPPI, 72(11), 181 (1990).
3. Morris, K.W. and Santyr, G.M., Pulp and Paper Canada, 1988,50.
4. Larry Roteinson, 1985 Engineering Conference, TAPPI press.

TABLE - 1
NET HEAT VALUE DERIVED FROM ORGANIC WASTE CONCEPT

The calorific value, Ash % and moisture % of different wastes from a particular mill are found to be as follows

Raw Material	Moisture, %	Ash, %	Calorific value
Straw dust	15	22	3600
Pith	50	10	3588
Effluent sludge	40	27	1660

TABLE-2
ELEMENTAL COMPOSITION OF SLUDGE SAMPLES

Parameter	Paper Mill			
	A	B	C	D
Nitrogen	0.70	0.85	0.6	0.52
Phosphorus	0.13	-	-	-
Potassium	1.74	0.09	0.28	0.17
Calcium	1.74	2.98	5.06	8.17
Magnesium	0.06	1.11	1.2	2.74
Sulfur	-	-	0.27	-
Iron	0.27	0.20	1.30	0.11
Manganese	0.012	0.014	0.011	0.039
Aluminum	-	-	7.08	-
Sodium	0.45	0.66	0.05	0.55
Tin	0.02	-	-	-
Chromium	0.004	-	0.0027	-
Copper	0.0099	0.0004	0.0028	0.0006
Lead	0.001	-	0.0019	-
Nickel	0.0013	0.0004	0.0009	0.0002
Mercury	-	-	0.000016	-
Zinc	0.006	0.009	0.0044	0.0031

(Values are in %)

TABLE -3
FIBER CLASSIFICATION OF EFFLUENT SLUDGES

Mesh specification	PAPER MILL			
	A	B	C	D
	% Fraction (w/w)			
+30	04.10	03.90	10.00	06.30
+50	03.00	05.20	17.60	05.70
+100	05.60	11.00	13.60	19.80
+200	03.70	07.50	02.30	17.90
-200	83.60	72.40	56.50	50.30

TABLE -4
MOISTURE, ASH AND GROSS CALORIFIC VALUE (AVERAGE VALUE) OF DIFFERENT SOLID WASTES

Type of waste	Moisture Content (%)	Ash (%)	Gross calorific value (Kcal/kg OD material)
Straw Dust	15	22	3500
Sarkanda Dust	15	24	3560
Pith	40	10	3590
WWT sludge	60	27	2500
Bark	25	-	4500

TABLE-5
WASTE COMPOSITION AND HEAT VALUE

Waste material Composition	composition percentage		
	25:75	50:50	75.25
	(Calorific Value, kcal/ OD kg of material)		
A:B	3500	3400	3260
C:D	3460	3400	3320
A:C	3200	3340	3385
B:D	3410	3475	3530
A:D	3380	3360	3360
B:C	3422	3070	3520

A -Wheat Straw Dust
B - Pith
C - Rice Straw Dust
D - Sarkanda Dust

TABLE -6
LENGTH AND WEIGHT OF FINAL BRIQUETTES AFTER AIR DRYING (DIAMETER OF BRIQUETTE IS 60 mm)

Briquette Sample	Length (cm)	Weight of Briquette (gm)	O.D. weight (gm)	Moisture (%)
Effluent sludge & straw dust	2.75	59.10	56.20	4.91
Effluent sludge	2.75	70.78	66.18	6.50
Sludge & bagasse pith	2.75	54.45	50.98	6.37

TABLE -7
CONDITIONS OF BRIQUETTING TRIALS IN THE BRIQUETTING ASSEMBLY

Effluent sludge, % Moisture	Fibrous waste ,% Moisture	Weight ratio , sludge : other waste	% Moisture in feed mixture	% Moisture in out coming briquettes
Sludge(40%)	Pith(20%)	3:1	35.80	31.50
Sludge(40%)	Pith(20%)	1:1	30.25	27.00
Sludge(40%)	Pith(20%)	2:1	34.00	30.00
Sludge(40%)	Straw dust (15%)	3:1	34.00	29.80
Sludge(40%)	Straw(17%)	3:1	34.50	29.50
Sludge(35%)	Pith(20%)	3:1	31.00	27.20
Sludge(35%)	Pith(20%)	1:1	27.80	24.50
Sludge(35%)	Pith(20%)	2:1	29.80	25.40
Sludge(35%)	Straw dust (14 %)	3:1	30.20	26.00
Sludge(35%)	Straw(17%)	3:1	30.20	26.50

TABLE- 8
BRIQUETTES – THE CHEAPEST FUEL

Fuel	Calorific value K cal/kg	Cost Per Kg/ltr	Efficiency (%)	Cost Per 1000 k cal. (Rs.)
Heavy Furnace Oil	9900	11.00	85	1.30
Kerosene	8900	10.00	85	1.32
Diesel	9400	15.00	85	1.87
LPG	9500	20.00	90	2.34
Coal Grade "B"	5000	2.50	75	0.66
Coal Grade "B"	4000	2.00	75	0.66
Briqutte	2400	0.51	70	0.30

TABLE-9
ECONOMICS OF BRIQUETTING OF WASTES

Capacity of Paper Mill	50 TPD
Organic Solid Waste Generation @ 0.65 T/T of Paper produced	32 TPD
Capacity of Briquetting plant	2 T/H
Cost of Press	15.0 Lakhs
Land and site development	2.0 Lakhs
Building	3.0 Lakhs
Inventory (spares)	3.5 Lakhs
Total (inventory + capital investment)	23.5 Lakhs
Machine + Spares	18.5 Lakhs
Yearly Interest on Capital @ 16 %	3.2 Lakhs
Yearly depreciation(Assume plant Life 8 years)	1.88Lakhs
Interest + depreciation	5.08 Lakhs
OPERATING COST PER DAY	
Waste raw material @ Rs. 250/T X 32 T/D	Rs. 8000/-
Electrical Power ,70 kWh ,16 Hr /Day , @ Rs. 4.5	Rs. 5000/-
Maintenance + Spares	Rs. 680/-
Labor(12 Persons @ Rs.100/-)	Rs. 1200/-
Interest per day	Rs. 970/-
Depreciation per day	Rs. 570/-
Total Operating Cost Per Day	Rs. 16,420/-
Energy Per Day 32X10^3X2400 (Kcal/ kg)	76.8 X 10^6
Equivalent Coal (76.8 X 10^6) / 4500	17 MT
Price of Coal (B-Grade)	Rs. 2000/T
Cost of Product	Rs. 34,000/ Day
Savings : 34,000 –16,420 or 17,580 X 330	=Rs.17,580/ Day=58 Lakhs/ Year
Coal Equivalent 17 X 330	5610 T/ Year
Pay Back period	5 Months
Cost of Disposal	
Transportation + Loading + Unloading	= Rs. 1600/-
Rs. 50 X 32 X 330	=Rs.5,28,000/Year
TOTAL SAVING : (58+5)	= 63 Lakhs

PAY BACK WITH DISPOSAL COST = 4.5 MONTHS

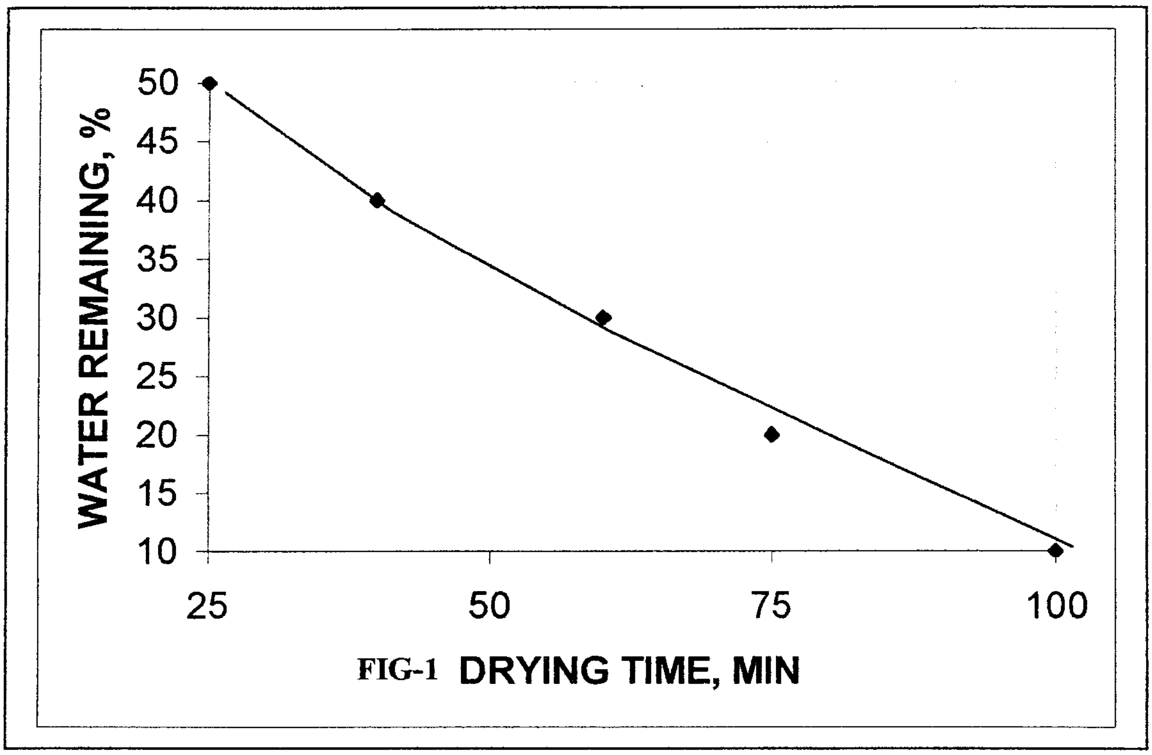

FIG-1 DRYING TIME, MIN

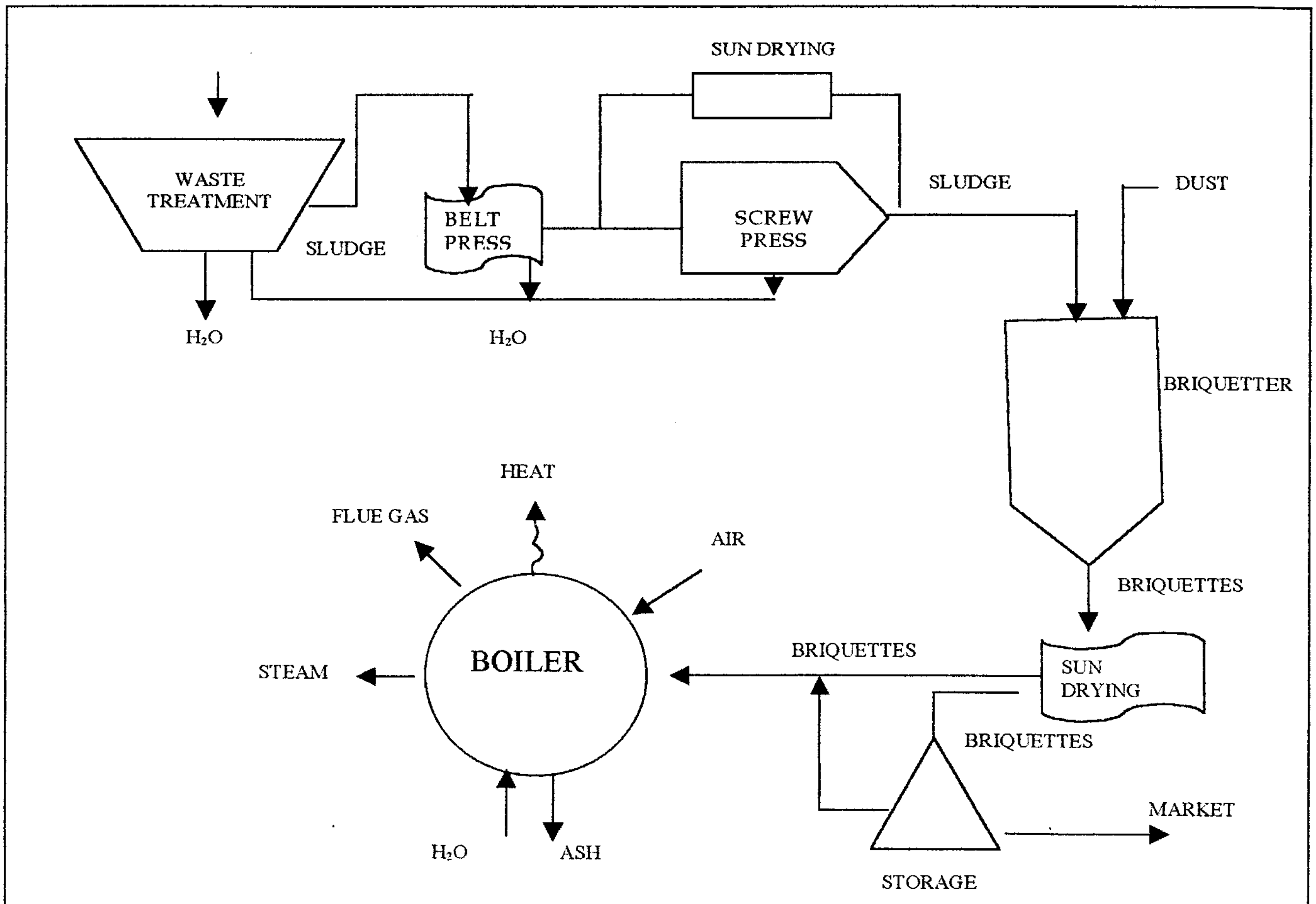

FIG-2 **FLOW SHEET FOR BRIQUETTING AND BURNING SYSTEM**

ENZYMATIC PREBLEACHING OF KRAFT PULPS : AN OPTION FOR CLEANER PRODUCTION TECHNOLOGY IN INDIAN PAPER INDUSTRY

Enzymatic prebleaching of kraft pulps : An option for cleaner production technology in Indian paper industry

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ABSTRACT:

Strict legislation and the environmental concerns regarding imposition of the effluent discharge norms in respect of Absorbable Organic Halides (AOX) in Indian paper industry is forcing the mills to look for alternate techniques to reduce or eliminate the use of elemental chlorine in bleach sequence. Among various technological options available, xylanase enzyme prebleaching could prove to be one of the promising options before the mills to reduce the generation of chlorinated organic compounds while improving the final brightness of bleached pulps. Although the technology has commercially been adopted in number of paper mills world-wide, but as far as Indian paper industry is concerned, it is still in the developing stage.

Central Pulp & Paper Research Institute carried out extensive studies in the area of xylanase prebleaching of pulps procured from wood and non-wood based mills. The present paper discusses the response of five identified xylanase enzyme preparations on the pulps procured from wood based (eucalyptus + bamboo) and bagasse based mills. Out of five enzyme preparations, four are available globally and one produced from an indigenous microbial strain. The response of three xylanase enzymes was found to be encouraging. The savings in terms of elemental chlorine is found to be to the tune of 15-20% during conventional CEH bleach sequence with simultaneous reduction of AOX level to 20-30% in both Kraft wood and Kraft bagasse pulps. Brightness gain to a level of 2.5-3.5 % ISO could be attained, while maintaining similar or slightly improved strength properties. Based on these findings, efforts are continued to commercialise the process in Indian paper mills employing identified xylanase enzymes.

INTRODUCTION

In the rapidly changing field of pulp bleaching, efforts have been made to adjust the process to meet the current challenges, which are driven by the environmental and economic forces. The environmental concern regarding imposition of the effluent discharges norms for AOX is forcing the industry to reduce or eliminate the use of chlorine or chlorine based chemicals in bleach sequence. Many of the alternate technologies have not yet proved feasible especially because of higher investment and operating cost and also the negative effect on the pulp quality. Under the prevalent conditions enzymatic prebleaching of pulps employing xylanases enzymes could prove to be a promising option as an environmental friendly technology & is early adaptable by the pulp and paper industry.

The primary goal of chemical pulp bleaching is to reduce the residual lignin of pulp without effecting the carbohydrate and/ or the physical properties of the pulps. Two different enzyme approaches have been generally in use for achieving the goal, which include.

1. Use of hemicellulases (specifically xylanases) enzymes as prebleaching agents (bleach booster) for enhancing the chemical removal of lignin in multistage bleaching sequence.

2. Another alternative approach is direct delignification of the unbleached pulps using enzymes called ligninases or laccases, which acts directly on the residual lignin in the pulp (2).

The first approach, which is the use of xylanase enzyme as prebleaching agents for chemical pulps has been successfully, applied in pulp and paper mills worldwide using various xylanases preparations of different origins. But the technology still is in nascent stage as far as Indian Paper Industry is concerned.

Xylanase enzymes used in bleaching of chemical pulps are being developed by Companies which claim their products suitable as prebleaching agents for the pulps produced in the paper industries. However, these enzymes, which are marketed by several suppliers are found to be highly sensitive to the conditions like temperature, pH & doses of the enzymes (3,4). Therefore it becomes difficult for the pulp and paper mills to decide which particular enzyme should suit to the specific requirement of their industry in order to achieve desired effect.

In view of the above, Central Pulp & Paper Research Institute (CPPRI) has been engaged for the last many years in conducting studies on evaluation of various xylanase enzyme preparations which are available globally and also being developed indigenously by several reputed biotechnological laboratories to study their response on the type of pulps produced in Indian paper mills(5).

The present paper highlights the studies carried out at the Institute in which several xylanase enzymes have been evaluated for their bleach response on Kraft wood and Kraft bagasse pulps, in order to explore potential for commercial application of the enzyme prebleaching technology in Indian paper industry.

MATERIALS & METHODS

2.1 Sources of Xylanase enzymes :

Several xylanase enzyme preparations used in the present investigations were procured from National & International enzyme manufacturing companies/ laboratories which are denoted as A,B,C,D & E The details about the xylanase preparation is given in Table-1.

2.2 Pulp Samples :

Wood Kraft Pulp samples were procured from a nearby large integrated Pulp & Paper Mill employing Eucalyptus as major raw material where as Kraft bagasse Pulp was obtained from an agrobased mill in Maharasthra equipped with chemical recovery system.

2.3 Enzyme assay Techniques :

All the enzymes were tested for filter paper activity for cellulase contamination by the method of Mandals & Weber and xylanase activity was measured by the method of Bailey et. al (1).

2.4 Xylanase Pretreatment of Pulps :

Enzymatic Pretreatment of the pulps was carried out under the optimised conditions as mentioned in Table-2.

2.5 Process conditions used during bleaching of Pulps :

Process conditions employed for bleaching of Pulps both with & with out enzyme preparation is shown in table-3.

RESULTS AND DISCUSSION:

While optimising the dosages of enzymes during enzyme treatment of woof Kraft and bagasse Kraft pulps, it was observed that excess dosages of xylanase enzymes for a longer time has resulted in decreased pulp yield and strength properties of the pulps. This could probably be due to loss of hemicelluloses by the action of enzyme. However under optimised dosages of enzymes i.e. 5-7 IU/gm of pulps and optimised treatment conditions (Table-2), no significant loss in pulp yield could be observed except with enzyme preparation E wherein even the treatment of the pulp at optimised conditions of time and temperature could result in 1.5% pulp yield loss along with drop in viscosity which was reduced from 560 to 510 cm^3/g of the pulp leading to loss in strength properties (Table-4). Reasons for the same could be attributed to contamination of xylanase with cellulase activity, which could be ascertained by determination of the cellulase activity in the xylanase enzyme by filter paper activity. Therefore this enzyme named as E was found to be unsuitable for its application in bleaching of pulps.

Effect of xylanase treatment on bleach chemical requirement

Bleaching of the xylanase enzyme treated Kraft pulps, both wood and bagasse have been found to respond in a different manner than untreated pulps while bleaching with conventional CEH bleach sequence. Based on optimisation studies of the chlorine dosages during chlorination stage, it was observed that significantly less chlorine is required to bleach Kraft wood and Kraft bagasse pulps while bleaching to similar targeted brightness level.

Table - 5 shows the effect of various xylanase preparations on the bleach chemical requirement during conventional CEH bleach sequence of wood Kraft pulps with a targeted brightness level of 80% ISO. From the results shown it is clearly seen that there is a reduction of nearly 14 - 15% of chlorine demand with all the enzymes preparations in case of wood Kraft pulps except enzyme preparation D, where chlorine saving of only 9.3% could be noticed. Further the enzyme treated pulps could be bleached to higher brightness with a gain in brightness level of 2-3% ISO in all the cases while using similar chlorine dosages as in case of control pulp sample.

Reduction in chlorine requirement or improved pulp brightness in case of enzyme treated pulps was reflected from the reduction in Kappa number of the unbleached pulps after enzyme treatment and further after the alkali extraction stage. The reduction in kappa number by 7-8% after enzyme treatment and further reduction of kappa number by more than 25% after alkali extraction was achieved in enzyme treated pulps.

Similar observation were made in case of Kraft bagasse pulps where nearly 18% reduction in chlorine demand could be observed in enzyme treated pulps with targeted brightness level of 83.0% wherein brightness gain of 2.0% ISO could be achieved when the enzyme treated pulp was bleached with similar chlorine dose of 5.1% as in case of control pulp. Results are shown in Table-8. This reduction in chlorine demand and gain in pulp brightness is also reflected from reduction in kappa number of the enzyme treated pulp where 20% reduction in kappa number after alkali extraction stage could be noticed.

Effect of enzyme treatment on unbleached pulp yield and physical properties of wood Kraft and bagasse Kraft pulps.

Table -6 shows the bleach chemical demand strength & optical properties of Kraft wood pulp treated with identified xylanase enzyme preparations B & D against control. From the results shown in Table-6, it is clearly evident that with a savings of nearly 15% chlorine demand employing enzyme preparation B, no loss in strength properties like burst, tensile & tear could be noticed, however the tear index was improved significantly from 5.3 Mn m^2/g to 6.0 Mn m^2/g whereas in case of enzyme D treated pulps, the strength properties, though were at par with control pulp but the chlorine savings were lower i.e 9.3% only. With regards to the optical properties of the enzyme treated pulps, there is an improvement in the yellowness of the pulp both with enzyme preparations B & D, since the yellowness of the enzyme treated pulps were decreased from 14.94 % to 9.79% & 10.65% respectively.

Similar observations could be made in case of Kraft bagasse pulps. Treatment of the Kraft bagasse pulp with xylanase enzyme B preparation showed no loss in pulp yield or pulp viscosity (Table-7).Bleach chemical demand of both enzyme treated and untreated pulps & the results of strength properties were shown in table-8. From the results it is clearly evident that strength properties of the enzyme treated pulps like Burst, Tear and Tensile could be maintained at par with control pulps with improvement in optical properties particularly in respect of yellowness which was dropped from 13.5 to 9.2 - 9.6% (Table-8).

Impact of enzyme treatment on environment

Characterisation of the resultant bleach effluent from wood Kraft pulps and Kraft bagasse pulps before and after enzyme treatment indicated that effluent properties namely AOX (Adosorbable Organic Halides) & COD are improved indirectly through the use of xylanase treatment which helps in release of lignin and other chromophore bearing compounds and allowing the use of lesser quantities of elemental chlorine or other chlorine based compounds in subsequent bleach sequence. Results of characterisation of enzyme treated wood Kraft pulp and Kraft bagasse pulps against control pulps are shown in Table-9. From the table it is clearly indicated that AOX level was reduced to 0.69 kg/tp in case of hard wood Kraft & 1.0 kg/tp in Kraft bagasse pulps compared with control pulps where AOX was reduced from 2.29 kg/tp to 1.6 kg/tp and from 4.13 kg/tp to 3.13 kg/tp respectively. Further decreased ratio of COD to BOD from 7.7 to 3.9 and from 4.12 to 3.33 in bleach effluent from Kraft wood and Kraft bagasse after enzyme treatment is an indication of improved biological treatability of the bleach effluent.

CONCLUSION

1. Enzymatic prebleaching of chemical pulps using xylanase enzyme could prove to be an effective technology in reducing the chlorine demand to the tune of 15% & 18% with gain in bleached pulp brightness of 2-3 % ISO while reducing the AOX level in bleach effluent to more than 25% in case of wood Kraft and Kraft bagasse pulps.

2. Xylanase enzyme respond better on wood Kraft pulps than non-woody raw materials due to the nature of the hemicelluloses wherein it has been observed that hard wood hemicelluloses are more responsive to xylanase enzyme action than those in Pulps from Kraft bagasse mills, due to the nature of the hemicelluloses. It has been observed that hard wood hemicelluloses are more responsive to xylanase enzyme action than those in pulps from agro residue raw materials.

3. Studies indicated that before selection of a particular xylanase enzyme preparation it is important to evaluate the enzymes for their activity and cellulase contamination, since excess dose of xylanase enzyme and cellulase contamination results in loss of pulp yield and strength properties of the pulp as in case of enzyme preparation E.

4. Before introducing enzyme-prebleaching technology in any mill it is important to evaluate particular enzyme preparation for its response towards pulp being produced in the mill for various parameters as discussed in the paper.

5. Enzyme being sensitive and specific in nature, it is very important to optimise the temperature, pH, dosages and proper dispersion or mixing of the enzyme with the pulp in order to achieve the targeted response.

6. The technology is relatively new as far as Indian paper industry is concerned. Efforts are required by researchers, technologists and enzyme manufacturers to isolate new xylanase enzymes suitable for pulps being produced in Indian paper industry from wood and non wood based raw materials and also to investigate the effect of other hemicellulases and lignolytic enzymes like laccase and lignin peroxidases on pulp bleaching to further reduce requirement of chlorine based chemicals.

TABLE-1 SOURCES OF XYLANASE ENZYMES

Xylanase enzyme	**Source**
A	Produced indigenously from an indigenous microbial strain
B	Indigenously manufactured
C	Imported
D	Imported
E	Indigenously manufactured

TABLE- 2 ENZYME PRETREATMENT CONDITIONS

Parameters	**Pulp treated with Enzymes**				
	A	**B**	**C**	**D**	**E**
Dose of enzyme, IU/g	7.0	10	5.0	5.0	10
Consistency of pulp ,%	10	10	10	10	10
Retention time, min	120	120	120	120	120
PH at 25° C	6.2	8.2	8.5	8.5	8.5
Temperature, ° C	45-50	45-50	45-50	45-50	45-50

TABLE-3. PROCESS CONDITIONS USED DURING BLEACHING OF PULPS

Particulars	**Chlorination stage**	**Alkali Extraction Stage**	**Hypo stage**
Temperature, ^{0}C	Ambient	60	40
Pulp Consistency, %	3.0	8.0	8.0
Retention Time, min	30	60	120
Final pH	1.8-2,0	>10.5	>9.0

TABLE-4 CHARACTERIZATION OF UNBLEACHED PULP FOR YIELD & OTHER PARAMETERS OF WOOD KRAFT PULP BEFORE & AFTER ENZYME TREATMENT

Parameters	Control	Pulp treated with enzymes				
		A	B	C	D	E
Pulp yield , %	99.89	99.82	99.62	99.80	99.74	98.10
Kappa number of Pulp,	18.0	16.5	16.7	16.6	17.0	16.0
Brightness, % ISO	27.5	28.5	29.0	28.4	28.0	29.0
CED Viscosity, cm^3/g	560	620	590	557	604	510

TABLE- 5 EFFECT OF ENZYME PRETREATMENT ON BLEACH CHEMICAL REQUIREMENT USING VARIOUS XYLANASE PREPARATIONS ON KRAFT WOOD PULP

Parameters	Control	Pulp treated with Enzymes									
		A		B		C		D		E	
		ET1	ET2	ET1	ET2	ET1	ET2	ET1	ET2	ET1	ET2
Savings in elemental chlorine	--	--	15	--	15	--	14	--	9.3	--	
% Reduction in Kappa No. after X stage	---	8.0		7.2		7.3		5.5		11.1	
% Reduction in Kappa No. XCE Stage	---	28.0	--	25.9	14.5	26.0	16.0	27.0	23.0	--	--
Final brightness of the pulp, % ISO	80.0	82.5	80.0	82.5	81.3	83.0	80.2	82.0	80.0	83.0	80.0

X - Enzyme treatment

XCE - Enzyme, Chlorination & Extraction

ETI - Enzyme treated Pulp treated with similar chlorine dose

ET2 - Enzyme treated Pulp treated with optimised less chlorine dose

TABLE-6 ENZYMATIC PREBLEACHING OF KRAFT WOOD PULP USING XYLANASE

Bleaching of Pulp using Conventional CEH Sequence Before & After Enzyme Treatment

Particulars	Control	Enzyme B	Enzyme D
Chlorination			
% Chlorine Applied	3.9	3.3	3.54
%, Chlorine Consumed	94	99	96
% , chlorine savings	--	15	9.23
Alkali Extraction			
% NaOH Applied	1.30	1.30	1.5
% NaOH Consumed	61.1	63.2	58.3
Final pH	10.88	10.76	11.21
Kappa no.	3.51	2.99	3.2
Hypo Stage			
% Hypo Applied	1.8	1.8	1.8
% Hypo Consumed	71.0	75.0	68
Brightness, % ISO	80.0	82.5	82.0
Brightness Gain, %	--	2.5	2.0

Strength and optical properties of the wood kraft pulps before & after enzyme treatment using two identified xylanase enzymes B & D

Parameters	Control	Enzyme B	Enzyme D
Revolution PFI	4000	4000	4000
Freeness, CSF	220	250	250
Apparent density, g/m^3	0.79	0.76	0.75
Burst index. Kpa.m^2/g	4.43	4.49	4.51
Tensile Index , Kpa.m2/g	64.4	64.3	64.4
Tear Index, Mn m2/g	5.3	6.0	5.3
Optical properties			
Opacity , %	92.2	91.2	91.0
Yellowness , %	14.94	9.79	10.65

TABLE -7 YIELD & OTHER CHARACTERISTICS OF UNBLEACHED KRAFT BAGASSE PULP BEFORE & AFTER ENZYME TREATMENT USING IDENTIFIED XYLANASE (B) ENZYME'

Parameters	Pulp treated with Enzyme	
	control	Enzyme treated
Pulp yield , %	99.20	99.02
Kappa number of unbleached Pulp	26.2	25.5
Kappa No. of CE Stage	5.07	4.04
Brightness ,% ISO	30.3	30.8
CED Viscosity	535	520

TABLE-8 XYLANASE PRETREATMENT OF KRAFT BAGASSE PULPS & STRENGTH & OPTICAL PROPERTIES

Parameters	Control	ET1	ET2
Chlorination			
% Applied Chlorine	5.1	5.1	4.2
% Chlorine Consumed			
% Chlorine savings	--	--	17.6
Alkali Extraction			
% NaOH Applied	2.0	2.0	2.0
% NaOH Consumed	74.2	61.2	73.8
Final pH	10.24	11.55	10.25
Kappa no. of Pulp	5.07	4.04	4.30
Hypo stage			
% Hypo Applied	2.0	2.0	2.0
% Hypo Consumed	80.0	80.0	74.0
Final brightness of the pulp ,% ISO	83.0	85.0	84.0
Strength and Optical properties			
Parameters	**Control**	**ET1**	**ET2**
Revolution PFI	500	500	500
Freeness, CSF	335	350	355
Apparent density, g/m^3	0.66	0.74	0.72
Burst index. Kpa.m^2/g	2.60	3.05	2.55
Tensile Index , Kpa.m2/g	45.5	56.0	45.0
Tear Index, Mn m2/g	4.05	4.40	4.20
Optical Properties			
Brightness of pulps, % ISO	83.0	85.0	84.0
Yellowness	13.5	9.2	9.6

- ET1 -- Pulp treated with similar chlorine dose
- ET2 -- Pulp treated with less optimised Chlorine dose

TABLE-9 CHARACTERISTICS OF BLEACH EFFLUENTS OF KRAFT WOOD & KRAFT BAGASSE PULPS BEFORE & AFTER ENZYME TREATMENT USING XYLANASE ENZYME B

	Wood Kraft Pulp		Bagasse Kraft Pulp	
Parameters	**Control**	**Enzyme treated**	**Control**	**Enzyme treated**
AOX, Kg/tp	2.29	1.60	4.13	3.13
COD , Kg/tp	23.3	28.5	34.6	50.7
BOD, Kg/tp	3.02	7.31	8.5	15.0
COD: BOD ratio	7.7:1	3.9:1	4.1:1	3.3:1

LITERATURE CITED:

1. Bailey. M.J, Bailey. P & Poutanen. K; "Interlaboratory testing methods for assay of xylanase activity", J. Biotechnology; 23; 257 (1992)
2. Wong. K.K.Y; Martin. L.A; Gama F.M; Saddler. J.N & De Jong. E; "Bleaching boosting and direct brightness by multiple xylanase treatments during peroxide leaching of Kraft pulps"; Biotechnology Bioengineering; 54; 312-318, 1997.
3. Kantelinen. A; et.al. ; "Proposed mechanism of the enzymatic bleaching of Kraft pulp with xylanases"; Holzforschung; 47; 318-324; 1993
4. Wong. K.K.Y, De Jong. E, Saddler. J.N & Allison. R.W; "Mechanism of xylanase aided bleaching of Kraft pulp. Part-II Target substrates"; APPITA J. 50: 509- 518; 1997
5. Jain R. K,. M, Mathur. R.M & Kulkrni. A.G; "Enzymatic prebleaching of pulps: challenges & opportunities in Indian pulp & paper industry"; accepted for presentation in forthcoming 8Th International Conference on Biotechnology in the Pulp & Paper Industry 8th (ICBPPI), to be held at Helsinki, Finland; June 4 -8, 2001.