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DEVELOPMENT OF STANDARDS OF AOX

FOR

SMALL SCALE PULP AND PAPER MILLS

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FOREWORD

Generation of toxic organo-chloro-compounds is a serious issue in small pulp & paper industries due to use of molecular chlorine and chlorine based bleaching chemicals. These small pulp & paper mills are unable to go for cleaner technologies basically due to its higher cost. At present, there is no legislative control for AOX generation for this category of pulp & paper industries. In view of these facts ,therefore, Central Pollution Control Board (CPCB) has taken-up the project to develop standards for Adsorbable Organic Halides(AOX) and entrusted the project to Central Pulp & Paper Research Institute (CPPRI), Saharanpur. The in-depth studies in selected small pulp & paper industries and preparation of basic document in development of standards in pulp & paper industries were accordingly carried-out by CPPRI.

Shri H.K.Karforma, SEE, Sh. S.K. Gupta, EE and Mrs. Hima Jwala, SRF have co-ordinated project activites and prepared the present Report under the guidance of Sh. P.M. Ansari, Additional Director and Dr. B. Sengupta, Member Secretary of Central Pollution Control Board.

I trust the document will be useful to all those interested in pollution control in the pulp & paper industry.

(J.M. MAUSKAR)

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PREFACE

Increased environmental awareness, customer preferences for eco - friendly products, recognition of adverse impact of chlorinated phenolic compounds formed during bleaching of pulp with chlorine have resulted in adoption of cleaner technologies by the pulp and paper mills abroad and in India to reduce the level of AOX (Adsorb- able Organic Halides) at source and efforts are continued to achieve zero discharge through the system closure. However small scale pulp and paper mills in India are still continuing with conventional bleaching process and are using high dosage of chlorine to bleach the pulp of high kappa number resulting in the generation of high level of AOX in the effluents. These mills have limitations to adopt the modified technologies to reduce the kappa number of the pulp (which governs the consumption of bleaching chemicals) due to use of mixed fibrous raw material rich in silica and low scale of operation which also restricts the setting up of conventional chemical recovery system.

Looking into the problems and limitations of these mills in adoption or up-gradation of technologies , Central Pollution Control Board (CPCB) has taken–up a project on “Development of Standards of AOX for Small Scale Pulp & Paper Mills” with an objective to assess the status of technology and permissible level of AOX in effluents for this category of pulp & paper mills.

Five mills were selected for the study and two visits were undertaken to produce reliable information about level of AOX in existing mills.

The studies conducted has given useful information on the status of the technology and the level of AOX in the small scale pulp and paper mills .

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1.0 Introduction

Today with increasing environmental pressure, changing customer preference, there is a urgent need to critically evaluate the bleaching techniques adopted by the Indian pulp & paper industries. It has been well established that the discharge of chlorinated organic compounds in the effluent and also in the end product have adverse effect on fauna and flora. The environmental hazards of the bleach plant effluent are considered related to the use of chlorine containing bleach chemicals especially molecular chlorine. The developed countries recognized the consequences of toxic chemicals generated during bleaching by employing molecular chlorine and over a period of time, the mills in Scandinavian countries; Canada and USA have slowly eliminated the use of molecular chlorine in last two decades and now are slowly moving towards total chlorine free bleaching (TCF) techniques. The ECF & TCF techniques have proved beyond doubt, the advantages in terms of cleaner environment and product quality but the economics are still not very clear.

The bleaching of pulp with elemental chlorine and chlorine based chemicals has become a major global environmental concern. The discharge of chlorinated phenolics (formed during bleaching with chlorine) in mill effluents became an issue in early 1970's when measurement techniques became available and high concentration of chlorinated phenolics was detected in fish stock receiving bleach plant effluent . Consequently environmental regulatory authority became active and finalised norms and guidelines to reduce the discharge of chloro-organics in mill effluents. After recognizing the adverse/ toxic effect of chlorinated phenolics generated during bleaching of pulp with chlorine based chemicals, the efforts were made to develop the technologies to reduce the kappa number of pulp and to improve pulp washing to minimize the carryover of organic matter alongwith pulp going to bleach plant as both the factors govern the consumption of bleach chemicals . Subsequently most of the pulp mills in developed countries have adopted new pulping and bleaching techniques to reduce the discharge of chlorinated phenolics in mill effluents. Some of the new process technologies are listed below:

- Extended delignification
- Improved pulp washing
- Oxygen delignification
- Elemental chlorine free bleaching
- Oxidative alkali extraction bleaching

The use of elemental chlorine in the developed countries has gradually phased out and some of the pulp mills have even adopted total chlorine free bleaching techniques. However the majority of pulp mills still continue to use chlorine dioxide for bleaching of pulp to achieve high and stable brightness . Indian paper mills continued to use elemental chlorine since the measurement of these chlorinated organic compounds was not felt necessary .

In early seventies, due to increased demand of paper and acute shortage of forest based raw materials, the Indian Government encouraged the setting of small paper mills based on non-conventional agro residues fibrous raw materials. As a result , a number of small paper mills having capacity from 5 to 30 t/day were set up in order to meet the increased demand of paper and paper boards. Second hand equipments and paper machines were imported which were originally designed to process forest-based raw materials. As a result the level of technology was not up to the optimum level to process the agro residues. These pulp and paper mills are operating without chemical recovery system because of size constraint and therefore produce pulp normally with high kappa number ranging from 30 to 32 due to economic reasons and the major part of lignin is removed in subsequent bleaching stage. Other important aspect is the poor efficiency of existing pulp washing system. Due to their inherent nature, the pulps produced from these agro residues are difficult to wash with existing brown stock washers .The low efficiency of pulp washing system results in high carryover of organic matter alongwith pulp going to bleach plant, which ultimately increases the demand of bleaching chemicals.

The small scale paper mills and most of them utilize non-conventional agro residue and waste paper, are operating without chemical recovery system because of their size constraint and they are discharging black liquor as effluent which is major source of pollution. In 1980's, the consequences of black liquor discharge were realized and industries were forced to treat their waste waters to the level of discharge norms. The water consumption in this category of mills varied from 125 to 175 m^3/t of paper which leads to the problems related to handling and treatment of large volume of effluent. The pulp produced from these mills normally have high kappa number in absence of chemical recovery system and major part of lignin present in pulp is removed in subsequent conventional bleaching stage by using elemental chlorine and hypochlorite resulting in generation of high level of AOX in effluents.

Most of the pulp and paper mills , have expanded their production capacity and are now producing paper 50 -100 t/day. Few mills producing chemical pulp above 60 t/day have even installed the chemical recovery system for recovery of chemicals by incineration of black liquor. Due to increased environmental awareness and imposition of stringent discharge norms,, these mills are looking for an economically viable chemical recovery system or cost effective methods for treatment of their black liquor to become environmentally compatible.

The Indian paper industry which primarily utilizes about 25% wood, 45% nonwood and about 30% waste paper invariably bleach the pulp by chemicals like molecular chlorine, calcium hypochlorite which are responsible for the formation of chloro compounds. The quantity of chlorine applied show a wide variation from 50-200 kg since it is generally observed that the nonwood fibers are rather difficult to bleach compared to wood fibers. The total available chlorine requirement for different raw materials is given below in Table-I.

Table-I

Chlorine Requirements

Raw material	Kappa No.	Cl_2 in C-stage %	Total available chlorine required, %
- Wood (Eucalyptus)	25	Kappa x 0.18 = 4.5	6 – 8 %
- Bamboo	25	Kappa x 0.25 = 6.3	8 – 10 %
- Bagasse	25	Kappa x 0.22 = 5.5	8 – 10 %

2.0 Bleaching chemical and Bleaching sequences

The pulp is normally bleached with elemental chlorine and hypochlorite, which leads to the formation of variety of chlorinated phenolic compounds. With increasing environmental awareness and recognition of the adverse and toxic effects of these chlorinated phenolic compounds, most of the pulp mills in developed countries have adopted modified pulping & bleaching processes to reduce the discharge of chlorinated phenolic compounds. The elemental chlorine which contributes 70-80% of total AOX has been partially or fully substituted with chlorine dioxide by the pulp mills in the developed countries.Some of the pulp mills have adopted even Total Chlorine Free (TCF) bleaching process to get rid of AOX related problems.

In India, due to economic considerations molecular chlorine & its compounds are used for producing bleached grade paper. The most common bleaching sequences adopted by the Indian Pulp & paper mills is CEH or CEHH. Use of chlorine di-oxide, hydrogen peroxide & oxygen reinforced alkali extraction is also limited to very few mills which are producing rayon grade pulp & high brightness quality papers. Approximately 2.5 millions tones of chemical pulp is produced in India, 60% of this is high brightness bleached pulp (mostly bleached by chlorine & chlorine based chemicals).

The small scale pulp and paper mills based on agricultural residues uses elemental chlorine and hypochlorite for bleaching of pulp having kappa no 30-32. The consumption of chlorine in this category of mills is comparatively higher and varies from 150 to 260 kg/t of pulp. The reasons for higher consumption of chlorine in these mills are

- High kappa number of unbleached pulp.
- High carryover of black liquor alongwith pulp going to bleach plant.
- Poor bleaching response of agro residues.
- Low efficiency of processing equipments.

The small scale pulp mills are normally using CEHH sequence for bleaching of the pulp to the required brightness level and a few mills use only hypochlorite.

The bleaching chemicals are applied in multistage sequences wherein chemicals are mixed with pulp and over a period of retention time provided, the spent chemicals and dissolved impurities are removed by washing. The bleaching sequences can conveniently be broken into two segments as given in Table-II. The delignification partial sequence has the principle function of lignin removal and the brightening partial sequence has action of increasing brightness.

Table –II

BLEACHING SEQUENCES

Delignification partial Sequences	**Brightening partial Sequences**
CE	H
CDE	D
D-CE	HD
CEO	HED
OCE	HDED
	DED
	DEPD
Examples of Bleaching Sequences	
CEH	
CDEODED	
ODCEOD	
ODCEOPDEPD	

C - Chlorine, E - Extraction with sodium hydroxide
D - Chlorine dioxide, O - Oxygen,
P - Hydrogen peroxide H - Hypochlorite.

The traditional mode of delignification uses chlorine followed by extraction and hypochlorite treatment. Oxygen is another effective delignifying agent, which is widely used to enhance the extraction stage, and it is being used in advance of chlorine in order to reduce the carryover of organic matter to bleach plant. The hypochlorite and ClO_2 are mainly used for brightening of pulp. CEH is the traditional sequence used by the mills to produce bleach pulp. But with increasing environmental pressure to reduce or eliminate organochlorine, the use of chlorine is decreasing rapidly with oxygen, peroxide and ClO_2 providing more environmentally compatible bleaching.

3.0 Formation Of Chlorinated Compounds

The conventional kraft wood pulp bleaching which includes chlorination typically produces 5.4-7.0 kg of chlorinated organic materials per ton of bleached pulp while agro-based pulp bleaching produces organic chloro-compounds to the tune of the 5-9 Kg per tonne of pulp. Approximately 300 different compounds in bleached pulp mills effluents have been identified and about 200 of these are chlorinated organic compounds. The main general types of chlorinated compounds in bleach pulp mill effluents are listed below in Table-III:

Table-III

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

It has been well established that a series of chloro-phenols are formed during bleaching process. The nature and extent of formation of chloro-organics is determined primarily by the residual lignin content in the pulp and the type of bleaching chemicals employed. The discharges of chlorinated organic compounds in mill effluents have long been known to exhibit acute, chronic and some mutagenic toxicity to aquatic life. Studies conducted in developed countries reveal that the low molecular weight chlorinated compounds are major contributor to toxicity and mutagenicity. The most of chlorine is bonded with high molecular weight organic compounds, which are stable against biodegradation, and contributes little to toxicity and mutagenicity. However, the past studies conducted indicate that these high molecular weight chloro compounds might be broken down to smaller more biologically active compounds and can cause long-term toxic effect to the recipients.

Toxic Properties Of Some Of Chloro Phenolic Compounds

Chlorophenolics

Laboratory and field studies conducted elsewhere reveal that the chlorinated compounds present in alkali extraction bleach effluent are found more toxic and contributes more than 90% of acute toxicity. The chloro-compounds like trichlorophenol, tri and tetra chloroguaiacols in particular may accumulate in fish and are responsible for acute toxicity.

Polychlorinated Dioxins & Furans

Among the chlorinated phenolics, the dioxins & dibenzofurans are a group of chlorophenoles which have been found to have toxic effects. The prominent among the dioxins are 2,3,7,8 tetra chloro dibenzo dioxin (TCDD) & 2,3,7,8 tetra chloro dibenzo furan (TCDF).

It is clear that out of 100% AOX, the percentage of dioxins is less than 0.1%, which is supposed to be highly lypophyllic and bioaccumalble compounds. Such compounds are formed when unchlorinated dibenzo dioxin (DBD) & dibenzo furan (DBF) present in unbleached pulp are chlorinated in chlorination stage. The oil based pulp mill additives particularly brown stock deformers have been identified as potential sources of such compounds. Laboratory studies indicate a sharp increase in quantity of PCDD and PCDF when elemental chlorine consumption is increased beyond 10-15 kg Cl2/t pulp. The dioxins are quite resistant to degradation and have an elevated potential for bioaccumulation. The toxic effect and toxic levels of dioxins fixed by different countries and agencies are given below in Table-IV:

Table - IV

Agency / Country	Risk dose	Toxic / health effect
EPA	6.4×10^{-3}*	Cancer
Germany	1.0 *	Cancer/reproductive
Netherland	4.0 *	Cancer
Switzerland	A **	
FDA	5.7×10^{-2}	Cancer

* - Picograms of 2,3,7,8 TCDD/kg of body weight/day

**** -** The studies have not established the safety levels**.**

TCDD has been reported to cause cancer in rats but its effect on humans has been the center of much debate and its still yet to establish. As per Centre for disease control, Atlanta ,low level exposure to dioxins may not be dangerous but higher concentrations of dioxins can be quite harmful.

Carcinogenic & mutagenic compounds

Bleach plant effluents contains chloroform and carbon tetra chloride, which have been classified as carcinogens. The hypochlorite stage is the major producer of chloroform. The various chlorinated benzenes, phenols, epoxystearic acid and dichloromethane present have also been classified as suspected carcinogens. Some of the chlorinated compounds formed in C-stage have been identified as strong mutagens. However a very limited information regarding tendency of mutagens to bioaccumulation is available.

Biological effect of bleach plant effluents

It is well known that bleach plant effluent mainly due to chlorocompounds are toxic to fish and other organisms. The stability and tendency of bioaccumulation of toxic compounds are important from environmental point of view, some of the biological effect of chloro compounds characterized in laboratory studies are summarized below:

- <u>Effects on fish:</u>

  - *Acute toxicity:*
    - Egg mortality
    - Percentage of fertilised egg.
    - Acute toxicity to newly hatched fry.

  - *Late effects*: Surival and stress tolerance of fry from exposed parents.

  - *Effects on behaviour*: Response to rotary flow.

  - *Physiological and Histological sublethal effect*:
    - Growth rate
    - Histological changes in lever.
    - Occurrence of parasitic in gills of flounder

  - *Bioaccumulation*:
    - Effect on primary production in natural mixed phytoplankton populations.

  - *Genotoxic effects*:
    - Mutagenic effects
    - Carcinogenic effects.

4.0 Legislation To Control AOX Discharge

Due to increased public awareness, the environmental regulatory authorities in developed countries planned the strategies and formulated the guidelines to reduce the discharge of chlorinated organic compounds from pulp and paper industry. Most of the pulp mills in developed countries have adopted new pulping and bleaching technologies in order to reduce the generation of chloro organics. Currently the level of AOX ranges from 1.50 to 3.00 kg./t in kraft and sulphite pulp mills and mills are further planning to reduce or eliminate the generation of AOX.

Recently in U.S.A., Environmental Protection Agency (EPA) has issued the guidelines for discharge of AOX, Dioxins and 12 numbers of other chlorinated organic compounds in the effluents. In India in the year 1992, CPCB, proposed the maximum discharge limit for chloro-organic compounds as Total Organic Chlorine (TOCl –2kg/t product) for large pulp and paper mills. Therefore it has now become necessary to monitor and regulate the discharge of chlorinated compounds in effluents. The discharge limits for organo chlorine in some of the developed countries is given below in Table-V.

Table – V
DISCHARGE LIMITS OF AOX IN DIFFERENT COUNTRIES

COUNTRY	**DISCHARGE LIMITS, Kg/tp**	MODE
Sweden	<1.0	TOCl
Canada	<1.5	AOX
Germany	<1.0	AOX
India	2.0	TOCl

5.0 Background Of The Project

Energy & Environment are the major challenging issues before the Indian pulp and paper industry. The increased environmental awareness, global competitiveness, change in customer preferences for eco-friendly products have resulted in the imposition of stringent environmental discharge norms by environmental protection agencies.

Small scale pulp and paper mills , a major segment in Indian paper sector are now facing major environmental problems primarily because of processing non-conventional agro residues fibrous raw materials with technologies and equipments which were initially designed to process wood based raw materials and also having limitations in adopting conventional chemical recovery process because of size constraints.

Looking into the problems & limitations relating to processing of agro based mixed fibrous raw materials, obsolete technology, production of pulp with high kappa number in absence of chemical recovery process, high magnitude of pollution loads (SS,COD&BOD) in small paper mills, CPCB has taken-up a study on assessment of AOX level in the effluents discharged by small scale pulp and paper industry and status of technology available for its control.

6.0 Objective & Scope of the Work

The main objective of the study was to assess/evaluate the status of technology and to generate data based information on existing level of AOX in small scale pulp and paper mills producing writing & printing and speciality paper from agro residues , waste paper and market pulp. The study included collection of effluent samples from identified sampling points from selected mills for analysis of AOX to assess the generation and final discharge (after secondary treatment) of AOX level in this category of mills. The report includes the evaluation of efficiency of the existing pulp washing system in terms of carry over of black liquor alongwith unbleached pulp going to the bleach plant.

The study is important from environmental point of view and generated the data base on level of AOX in effluents of agro based pulp and paper mill using conventional bleaching process for producing writing and printing paper . The findings of the study will increase an awareness in the pulp & paper industry on the status of technology and the level of AOX in their mill effluents so that the mills may implement the measures to reduce the level of AOX in the mill effluents.

Criteria for selection of paper mills

The paper mills were selected broadly on the basis of raw materials used, bleaching practice employed, size of the mill and the end products. Following criteria was adopted for selection of paper mills:

- Mills based on straw, bagasse and grasses (Sarkanda) using conventional bleaching process
- Mills based on bagasse using conventional bleaching process producing speciality paper
- Mills with chemical recovery system based on agro residues using conventional bleaching process
- Mill based on agro residues using only hypochlorite bleaching
- Effluent treatment facilities.

Methodology

In each of the selected paper mill, two visits were performed to conduct the in-depth studies in order to generate a representative and realistic data based information on AOX level in these category of pulp and paper mills.

Preliminary Survey of the Selected Mills

The preliminary survey of selected pulp and paper mills was conducted through questionnaire requesting the mills to furnish the detailed information related to size of mills, usage of raw materials, process employed, end product, existing effluent treatment facilities, disposal of treated effluent etc which were also confirmed during the visit to selected pulp and paper mills.

Identification of Sampling Points

- Combined bleach plant effluents
- Influent to ETP / Primary Clarifier
- Overflow of primary clarifier
- Final treated effluent

Laboratory Studies on Bleaching of Pulp

The laboratory studies on bleaching of the unbleached pulps collected from respective paper mills were also conducted using mills bleaching conditions in order to confirm the level of AOX. The studies included:

- Collection of washed unbleached pulp (before bleach plant).
- Estimation of carryover of black liquor alongwith unbleached pulp.
- Determination of kappa number of unbleached pulp.
- Bleaching of pulp using mill conditions.
- Analysis of bleach effluents generated.

Analysis of samples

The selected pulp and paper mills were visited for indepth study. The sampling and flow measurement were done from identified points for a period of 24 hours in order to collect the composite samples. The composite effluent samples collected were preserved for further analysis of required pollution parameters.

The unbleached pulp samples collected from selected paper mills were also bleached in laboratory using bleaching conditions followed in respective mills and thus bleach effluents generated were analysed for pollution parameters especially for AOX in order to confirm the level of AOX generated in respective paper mills.

- pH
- Suspended Solids
- Chemical Oxygen Demand
- Biological Oxygen Demand
- Adsorbable Organic Halides

Evaluation of Efficiency of Pulp Washing System

The efficiency of existing pulp washing system in selected paper mills was also evaluated by estimation of carryover of black liquor COD alongwith pulp going to the bleach plant.

Measurement of AOX

The preserved effluent samples (composite) collected from the mills and those generated in laboratory bleaching were analysed for AOX as per DIN method – 38409H (Flask Procedure) by using DX-20 DOHRMANN AOX analyzer.

Measurement of flow rate of effluent in paper mills

The measurement of flow rate of effluent discharged in paper mills is a critical and sensitive issue. Deviation in the flow rate is always expected because most of these paper mills do not have systematic and uniform channels carrying effluents. However all precautions & efforts have been taken in measuring the quantity of effluent discharged. The flow rate of effluent generated was measured at different time interval during sampling period by using measuring devices provided in channels i.e V notch, rectangular notch and also by using float velocity method.

7.0 Results Of Mill Studies On AOX Level In Pulp & Paper Mills

The details of each selected paper mills related to location, mills size, usage of raw materials, process employed, end product, pollution load, AOX level, effluent treatment facilities and disposal of treated effluent etc. are given below:

Mill A:

The paper mill is producing 65 - 70 ton of chemical pulp per day to produce writing and printing paper. The main fibrous raw materials used are wheat straw, sarkanda, bagasse and waste paper. The chemical pulp of kappa number about 25-30 is bleached by using conventional bleaching process to a brightness level of 75-80%. The mill has recently commissioned the third paper machine based mainly on waste paper.

The mill has recently installed a full-scale biomethanation plant for treatment of black liquor **(Fig-8)**. The biomethanation plant is working successfully for treatment of black liquor with an average reduction in COD & BOD of about 45 % & 75% respectively. The biogas produced about 10000 - 11000 m^3/d is used in the boiler. The other streams i.e. bleach plant effluent, paper machine back water along with anaerobically treated black liquor are being taken to conventional effluent treatment plant consisting of primary clarifier, primary aeration based on diffused aeration, secondary aeration system provided with fixed mechanical aerators and secondary clarifiers **(Fig-9)**. The treated effluent is finally discharged into a canal, which is used down stream by farmers for irrigation of their land.

The composite effluent samples collected from different points were analysed for various pollution parameters including AOX. The results of analysis are given in Table-1 & Fig 4. The results indicate that the generation of AOX varied from 7.85 to 7.90 kg/t of finished paper, which was reduced by about 12% after primary clarifier, and about 40% after secondary biological treatment.

The overall removal of AOX found was about 51% (Table-6 & Fig-3 **).** The level of AOX in finally treated effluent was about 4.0 kg/t of finished paper (Table-6 &

Fig-4). The laboratory studies conducted on bleaching of pulp using mill conditions confirms the maximum generation of AOX of about 9.0 kg/t of pulp (Table–7 & Fig –2) which is lowered by about 12- 15 % when expressed on finished paper product.

The reduction in AOX, COD & BOD after secondary treatment was about 51, 20 & 40 % respectively (Fig - 5**)**. The high level of AOX may also be due to the high carryover of COD alongwith pulp i.e. 33 kg/t of pulp which increases the consumption of bleach chemical (Table – 8 & Fig –7). The waste water discharge measured during sampling period was 130-140 m^3/t of finished paper (Fig - 6). The performance of secondary effluent treatment plant with respect to removal of SS, COD & BOD was not found satisfactory. During the sampling, the values of SS, COD & BOD in final discharge were found much higher than the stipulated discharged norms.

Mill B:

The mill is producing about 19800 ton per annum of writing and printing paper from bagasse, wheat straw, rice straw, grasses and waste paper. The unbleached pulp of kappa number 26-30 is bleached with about 14% chlorine by using CEPH bleaching sequence to a brightness level of 78-80%. The mill is using oxidative alkali extraction bleaching with peroxide to improve the quality of pulp & bleach plant effluent.

The mill has an effluent treatment plant consisting of anaerobic lagoon for treatment of black liquor , primary clarifier, aeration system & secondary clarifier for treatment of mill effluents including black liquor after anaerobic lagoon **(Fig - 10).**

The mill has facility for pretreatment of black liquor known as "lignin removal process" where acidified fibre is mixed with black liquor to reduce the pH and thus precipitated lignin adsorbed on to the surface of acidified fibre is separated by clarifier. The pretreated black liquor alongwith other effluents is treated through conventional ETP. The finally treated effluent is discharged into a local canal where part of which is used for irrigation by farmers.

The composite effluent samples collected from different points were analysed for pollution parameters including AOX and the results are given in Table-2 and also depicted in Fig-4**.**The level of AOX generated in mill effluent varied from 5.5 to 6.8 kg/t of paper which reduced by 6-7 % after primary clarifier and about 35% after biological treatment (Table–6 & Fig-3). The level of AOX in final discharge measured was about 4.0 kg/t of paper (Fig–4). The level of AOX was also confirmed in laboratory bleaching studies and it was found about 9.0kg/t of pulp (Table–7 & Fig-2).

The performance of biological effluent treatment plant evaluated during sampling period has been found to be below the optimum level as the reduction in COD, BOD & AOX was found to be about 24,34 &36 % respectively (Fig–5). The waste water discharge measured was about 160-170 m^3/t of paper. (Fig- 6) The high carryover of COD alongwith pulp was about 30 Kg/t of pulp (Fig-7) which indicates low efficiency of existing pulp washing system. The levels of suspended solids, COD & BOD measured in final discharge during sampling period were also higher than the stipulated discharge norms.

Mill C:

The mill has installed capacity of about 38600 ton per annum and produces fine quality of speciality papers including newsprint from bagasse, market pulp (soft & hard wood) and waste paper. The mill is using chemi-mechanical process for pulping of depithed bagasse in order to preserve or to retain hemicelluloses in pulp which is one of the specific requirement for these type of speciality papers. The bagasse pulp of kappa number 55-58 is bleached by using CE_HH bleaching sequence and 23-26 % of total chlorine is used to bleach the bagasse pulp to the brightness level of 72-74 %. The market pulp and waste paper are blended with bleached bagasse pulp depending on the quality of end product to be produced.

The mill is the first mill which has installed full scale biomethanation plant based on CSTR process for treatment of semi chemical black liquor . The plant is working satisfactorily with an average saving of 15-20 % of total energy requirement of paper mill in addition to the substantial reduction in COD & BOD .The anaerobically treated black liquor alongwith bleach plant effluent is treated in the existing effluent treatment plant consisting of high rate thickener (clarifier), aeration tank and secondary clarifier while paper machine back water after treatment separately through high rate thickener & pressure filter is recycled (60-70%)for reuse in internal process and the rest is discharged after mixing with secondary treated pulp mill effluent **(**Fig-11)

The composite effluent samples collected from different points were analysed for various pollution parameters including AOX. The results of analysis are given in Table – 3 .The level of AOX generated in mill effluent ranged from 11-12 kg/t of paper which reduced by about 10% after primary clarification and further by about 41% after secondary effluent treatment process while the overall removal of AOX was found to be about 51% (Table –6 & Fig-3). The level of AOX in final discharge varied from 5.50 to 6.0 kg/t of paper (Table – 3 & Fig-4).

The laboratory studies were also under taken by bleaching of pulp using mill conditions to estimate the level of AOX on pulp basis. The results given in Table-**7** indicate that the generation of AOX in mill is very high and it is about 18.0 kg/t of pulp (Fig-2). Since the mill is producing more than 100 ton of paper by blending of high proportion of waste paper & market pulp alongwith bleached bagasse pulp of about 40 ton, therefore the level of AOX measured in mill effluent was about 11-12 kg/t of paper produced. The high level of AOX is due high kappa number of unbleached pulp which requires high dosage of chlorine to bleach the pulp to a level of 72-74 %. The carryover of black liquor alongwith pulp in terms of COD was also estimated to assess the efficiency of existing pulp washing system & the carryover of COD measured was about 35 kg/t of pulp (Fig-7), which further increases the consumption of bleaching chemicals resulting in additional generation of AOX.

The removal efficiency of SS, COD & BOD after biological effluent treatment plant evaluated during the studies was about 63, 45 & 71 % respectively (Fig-5).The high level of SS, COD & BOD in final discharge indicate that the existing effluent treatment plant is over loaded and values of these parameters are still higher than the discharge norms even after diluting the treated pulp mill effluent by 20-25% with clear paper machine water. The discharge of waste water varied from 100-110 m^3/t of paper which is below the norms (Fig –6).

Mill D:

The paper mill is producing about 25-30 tons of writing & printing paper including 20-25 % of kraft paper from rice straw, gunny bags & waste paper. The chemical pulps produced from rice straw (kappa no. 15-18) & gunny bags (kappa no. 30-35) are bleached separately with hypochlorite using about 16% & 22 % of total chlorine respectively.

The mill has effluent treatment plant consisting of anaerobic lagoon for treatment of black liquor, primary clarifier, aeration tank & secondary clarifier for treatment of other waste water including part of anaerobically treated black liquor (Fig -12)

The composite effluent samples collected from identified points were analysed for various pollution parameters and the results are given in Table - 4 **.**The level of AOX generated in mill effluent varied from 4.5 to 5.0 kg/t of paper including 20-25 % of kraft paper (Fig –2) which reduced by about 19% after primary clarifier and by about 52% after biological treatment (Table- 6 & Fig –3). The overall removal of AOX after secondary treatment was found about 62% and the level of AOX in finally treated effluent was found below 2.0kg/t of paper (Fig –4). The level of AOX in mill effluent was also confirmed by bleaching of pulp in laboratory using mill conditions (Table- 7& Fig –2**)**.

The removal efficiency of COD, BOD, AOX was found to be about 74, 90 & 62 % respectively (Fig –5). The performance of effluent treatment plant was found higher compared to the performance of effluent treatment plant evaluated in other agro based paper mills. The level of COD, BOD in final discharge measured was about 440 mg/l & 50 mg/l respectively while the level of SS was quite high in final discharge i.e 300 mg/l. The higher removal of COD, BOD & AOX may be because the mill is treating only 25-30% black liquor along with other waste water through existing effluent treatment plant while rest of the black liquor is discharged after mixing with treated effluent into a local canal leading to sea. The waste water discharged varies from 120–130 m^3/t of paper (Fig –6). The carryover of COD along with unbleached pulp was 40 kg/ t of pulp which is comparatively higher **(**Table-8 & Fig–7).

Mill E:

The paper mill is producing about 100t/d of writing and printing paper from wheat straw bagasse, sarkanda and cotton linters. The chemical pulp of kappa number 20-22 is bleached with about 10.5% total chlorine by using CEHH bleaching sequence to a brightness level of 81- 83 %.

The black liquor generated is incinerated in chemical recovery boiler and the bleach plant effluent alongwith other waste water is treat ed by existing biological effluent treatment plant consisting of primary clarifier, aeration tank and secondary clarifier **(**Fig- 13).

The composite effluent samples collected from identified points were analysed for required pollution parameters and the results are given in Table – 5. The results of analysis indicate that the generation of AOX varied from 2.5 to 2.6 kg/t of paper, which is reduced by 25-28 % after primary clarifier, & about 35% after biological treatment (Table-6 & Fig-3). The overall reduction in AOX through secondary treatment was about 54 % and the level of AOX in final discharge was about 1.20 kg/t of paper (Table – 6 & Fig-4). The maximum generation of AOX was about 4.80 kg/t of pulp in effluents generated during laboratory bleaching of pulp (Table – 7 & Fig –2).

The average reduction in SS,COD & BOD through biological treatment process observed was 54,61 & 86 % respectively(Fig –5) and the level of these parameters in final treated effluent was found close to discharge standards. The waste water discharge measured during sampling period varied between 60-72 m^3/t of paper (Fig –6) which is well below the discharge norms and also even less compared to waste water discharged in wood based large pulp mills. The carryover of black liquor COD i.e 33 kg/t pulp (Table- 8 & Fig –7 **)**alongwith pulp indicate that the efficiency of existing pulp washing system is more or less similar to the mills producing writing and printing paper from agro residues.

8.0 General Observations & Conclusion

Based on studies conducted on the status of technology and level of AOX in selected agro based pulp and paper mills producing writing and printing & specialty papers, the following general observations & conclusion are made with respect to discharge of AOX in these category of mills.

- Most of pulp and paper mills are using wheat straw , rice straw, bagasse, sarkanda, grass, cotton linter, waste paper and to some extent market pulp (soft wood and hard wood).
- Almost all the mills are employing soda pulping process for producing the chemical pulp of high kappa number due to economic reasons & the kappa number of pulp varies normally between 30-32 except in case of mill C where kappa number normally varies between 50-55 and major part of lignin is removed in subsequent conventional bleaching stage .

- The mills having chemical recovery system are normally producing pulps having kappa number 20-22 for production of writing and printing paper.
- Most of the mills have brown stock washers for washing of pulp but the washing efficiency of these washers has not been found satisfactory as there are 50-70% of higher carry over of black liquor alongwith pulp as compared to wood based mills.
- Most of the mills are using conventional CEHH bleaching sequence to bleach the pulp to a brightness level of 75-80% and only a few mills use hypochlorite bleaching.
- The consumption of chlorine for bleaching of pulp normally varies from 140 to 160 kg/t of pulp except Mill C where chlorine consumption varies between 230-260 kg/t of pulp due to bleaching of chemi-mechanical pulp while in mill having chemical recovery system the consumption of chlorine is about 100 kg/ t of pulp.
- The level of AOX generated in these mills normally varies from 5.0 to 8.0 kg/t of paper except Mill C where level of AOX was found to be more than 11 kg/t of paper.
- In the mill having chemical recovery system, the level of AOX generated was below 3.0 kg/t of paper primarily due to low consumption of chlorine .
- The level of AOX in the finally treated effluent normally varies from 3.75-4.0 kg/t of paper in mills using CEHH bleaching process except Mill C where level of AOX was found to be about 6.0 kg/t of paper
- In mills having chemical recovery system , the level of AOX in finally treated effluent was found to be about 1.20 kg/t of paper and is very much comparable to level of AOX found in large paper mills using bagasse as main fibrous raw materials.
- The removal of the AOX after primary clarifier observed varies from 6-28% depending upon the performance of the clarifier. The removal of AOX may be due to adsorption of chloro-lignin compounds on to the surface of the suspended fibers settled during primary clarification of mill effluents.
- The reduction in AOX after biological secondary treatment varies from 30 -52% depending on performance of ETP, while overall removal of AOX varies from 35-60% after secondary treatment including primary clarification.
- A wide variation in removal of pollution loads through biological effluent treatment was observed and the efficiency of COD removal varies from 20-45% and BOD from 50-70% . The low reduction in COD and BOD may be due to overloading of existing effluent treatment plant and also low biodegradability of black liquor discharged as effluent.
- In the mills equipped with chemical recovery system, the performance of effluent treatment plant was found comparatively satisfactory and the removal of COD & BOD was about 61&87 % respectively.
- The level of AOX was also confirmed in laboratory by using mill conditions for bleaching of pulp collected from respective paper mills. The level of AOX varied from 5.0 to 9.0 kg/t of pulp while in case of Mill C , the level of AOX was about 18.0 kg/t of pulp.

- Since most of paper mills are using recycled fibre along with chemical pulp, therefore the level of AOX measured in mill effluent was on lower side depending on the fibre furnish and also extent of mixing of other steams with bleach plant effluent.
- The waste water discharge in these category of mills normally varies from 100 to 170 m^3/t of paper while in mills having chemical recovery system, the discharge of waste water was found exceptionally low i.e 60-70 m^3/t of paper. It appears that small and medium size paper mills are also aware about water conservation and the discharge of waste water has been reduced drastically to achieve the discharge norms.
- The finally treated effluent discharged by most of these mills is used by local farmers for irrigation of their crops and the excess waste water is discharged into nearby river or sea .
- The high level of AOX observed in these pulp and paper mills may be due to following reasons:

  - High kappa number of unbleached pulp.
  - High carryover of black liquor alongwith pulp going to bleaching plant.
  - Use of high dosages of chlorine.
  - Obsolescence in technology & equipments.
  - Low efficiency of existing effluent treatment plant.

9.0 Technological Developments To Reduce The Discharge Of AOX

Pulp & paper mills have incorporated various measures in pulp mills to reduce the kappa number and also to minimize the carry over of organic matter alongwith pulp as it governs the bleach chemical demand during the bleaching process. Some of these measures include oxygen delignification ,extended delignification , improved pulp washing, substitution of elemental chlorine with chlorine dioxide , oxidative alkali extraction stage bleaching etc. However these technological developments have been limited to the developed countries particularly due to the advantages like uniform fibrous raw material (wood) and large scale of operation of the pulp mills.

Most of the pulp mills in developed countries have adopted modified pulping and bleaching technologies. Use of elemental chlorine which contributes a major portion of AOX has almost been substituted with chlorine dioxide.. However in India also, the trend has been set-up among the large scale pulp & paper mills to adopt cleaner technologies like RDH pulping , ODL, chlorine di-oxide bleaching etc which has favourable impact on environment Some of the cleaner technologies adopted by pulp mills to reduce the level of chlorinated phenolic compounds are given below:

Extended Delignification

The pulp mills normally use kraft process in batch or continuous digesters to remove the lignin as much as possible during pulping of wood based fibrous raw material but the process has limitation that the wood based fibrous raw material can not be delignified to a low kappa number .Since the kappa number is the main factor which governs the demand of chemicals for bleaching of the pulp the process was modified to achieve maximum possible delignification during cooking of raw materials and now most of the mills in developed countries are employing RDH, modified continuous cooking, super batch process etc to reduce the kappa number of the unbleached pulp. Modified pulping processes are energy efficient , require less chemicals for cooking of raw materials and produce the pulp of low kappa number with better strength properties as compared to conventional pulping processes but the high capital investment and high level of operation restrict the adoption of these technologies in Indian pulp & paper mills.

Small scale pulp and paper mills normally use soda pulping process due to absence of chemical recovery system. Additive pulping, where anthraquinone is used with cooking chemicals to increase the selectivity of the lignin removal during pulping process may be tried in agro based mills to reduce the kappa number of unbleached pulp.

Improved Pulp Washing

The pulp mills normally use brown stock washers for extraction of black liquor and for washing of pulp The washing efficiency of these washers depend on nature and quality of fibrous raw materials. Most of the small mills use brown stock washers for washing of pulp produced from agro residues but the efficiency of these washers are not satisfactory as high carry over of black liquor along with pulp was observed in agro based mills. Since the pulp from agro residues is difficult to dewater so the mills can use the modified washing system like belt filter press, double wire washer etc to minimize the carry over of the black liquor alongwith pulp entering the bleaching section .

Oxygen Delignification

Oxygen delignification is a well established technology and most of the pulp mills abroad are using the process to reduce the kappa number of pulp before bleaching stage. Single stage oxygen pre bleaching of the pulp reduces the pulp kappa number by 50-60 % and two stage oxygen pre-bleaching reduces the pulp kappa number by 80%.

The process is limited to large pulp & paper mills abroad and Indian paper mills have limitation in adopting the process due to high capital investment involved and low scale of operation . The process needs to develop an economically viable oxygen pressure vessel for low scale of operation as the capacity of our small scale pulp mills varies from 5–100 ton /day.

Chlorine Dioxide Substitution

The elemental chlorine is the major source of toxic chlorinated phenolics and dioxins compounds and contribute more than 70% of total AOX . The chlorine dioxide because of its high oxidation potential decreases the formation of chlorinated phenolics, colour, AOX, dioxins etc in addition to improved quality of pulp. Most of the pulp mills in developed countries have substituted or replaced elemental chlorine with chlorine dioxide while in India large pulp mills have now started the use of chlorine dioxide. At present none of the small scale paper mill in India is using chlorine dioxide because of the involvement of high cost of installation of chlorine dioxide plant and high cost of chlorine dioxide produced. However understanding the need of the hour, these mills should consider the use of chlorine dioxide for bleaching of pulp to reduce the toxic chloro organics in the effluent .

Oxidative 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 in India have already started the use of oxygen or hydrogen peroxide in alkali extraction stage. Small scale pulp and paper mills producing bleached variety of paper must use oxygen or hydrogen peroxide in oxidative alkali extraction stage of bleaching as the process can be used without any major changes in existing bleaching system.

The adoption of modified pulping and bleaching processes in pulp mills abroad has resulted in an increased recycling or reuse of the waste water to the internal process and efforts are being continued to achieve zero discharge. However the small scale pulp and paper mills in India are looking for cost effective measures to reduce the pollution loads as the adoption of the developed technologies (discussed above) in these mills may not be viable due to low scale of operation and use of mixed agro based fibrous raw materials . These mills are however required to operate the pulp mill under controlled conditions to reduce the kappa number and also to modify their pulp washing system to minimize the carry over of black liquor along with pulp in order to reduce the discharge of chlorinated phenolics compounds.

10.0 Recommendations

Detailed studies were conducted in small scale pulp and paper mills operating with and without chemical recovery system and producing writing & printing and specialty papers from agro residues, waste paper and market pulp. On the basis of the studies conducted on status of technology and level of AOX, the following recommendations are made:

(i) Majority of the mills are using low dosages of caustic for cooking of mixed fibrous raw materials resulting in high kappa number of unbleached pulp produced. The mill should operate the pulp mills under optimum conditions to achieve kappa number below 20 for bleachable grade pulp.

(ii) Efficiency of the existing pulp washing systems are not found to be satisfactory as high carryover of black liquor alongwith pulp was observed. The pulp mills should minimise the carryover of black liquor alongwith pulp through modified pulp washing system to reduce the consumption of chlorine.

(iii) The mills should use appropriate equipments & optimum conditions for bleaching of pulp. The mills using only hypochlorite for bleaching should use conventional bleaching process.

(iv) The mill producing speciality paper from chemi-mechanical pulp, should produce high yield chemical pulp & the pulp should be bleached by oxidative bleaching process to reduce the discharge of AOX.

(v) The mills should expand the capacity of the existing pulp mill appropriately for installing chemical recovery system. If it is not possible, these mills should either produce unbleached variety of paper or should restrict production of bleachable chemical pulp and rest of fiber furnish must be met out by blending with secondary fiber or purchased pulp.

(vi) The mills should adopt the following measures to reduce the level of AOX:
   - Controlled pulp mill operation to reduce pulp kappa number to about 20.
   - Improved pulp washing to minimise carryover of black liquor.
   - Introduce oxidative alkali extraction stage bleaching.
   - Regular & proper monitoring of ETP to achieve desired removal efficiency of pollution loads.

(vii) (Based on the study, following standards for AOX in treated effluentof small scale pulp & paper mills were prepared;
AOX- 3.0 Kg/tonne of paper produced from January 2005;

(vii) The above proposed standards were agreed in Peer & Core Committee and Central Board with effective dates as December 2002 and December 2004 respectively

(viii) Ministry of Environment & Forests (GOI) has notified following standards of AOX in case of small scale pulp & paper industries vide notification G.S.R.546(E), dated 30.08.2005:

- AOX – 3.00 Kg/ton of paper produced with effect from the date of notification i.e 30.8.2005 :
- AOX – 2.00 Kg/ton of paper produced with effect from the 1st day of March, 2006.

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TABLE – 1
Mill A

Details	EXERCISE I	EXERCISE I I	Average
1. Installed capacity, t/ year	47450	47450	47450
2. Raw materials	Wheat straw, sarkanda, bagasse, indegenous/ imported waste paper		
3. Paper production, t /day	124.0	137	130.50
a. W & P Grade	124.0	137	130.50
b. Kraft	--	--	--
4. Pulping process	Soda	Soda	Soda
5. Kappa no. of unbleached pulp	30–31	30 – 31	30– 31
Bleaching sequence	C_{10}-E $_{3.5}$-H $_{4.0}$-H $_{2.0}$		
6. Bleached pulp brightness, % ISO	74 -75	74-75	74-75
7. Characteristics of waste water (Influent to ETP)			
a. Flow, m^3/ day	14618	14763	14691
b. pH	6.7	6.7	6.7
c. Suspended solids, mg/l	1600	2800	2200
d. COD, mg/l	7725	5339	6532
e. BOD, mg/l	2255	1525	1890
f. AOX, mg/l	67.3	73.0	64.6
g. AOX, kg/day	979.0	1078.0	1028.0
h. AOX , kg/ t of paper	7.9	7.9	7.9
8. Characteristics of waste water (Primary clarifier overflow)			
a. pH	7.0	7.6	7.3
b. Suspended solids, mg/l	1120	1000	1060
c. COD, mg/l	5076	5011	5043
d. BOD, mg/l	2203	1492	1847.5
e. AOX, mg/l	52.2	61.9	57.0
9. Characteristics of treated waste water			
a. pH	7.0	7.3	7.15
b. Suspended solids, mg/l	750	920	864
c. COD, mg/l	6437	4277	5357
d. BOD, mg/l	1052	671	864
e. AOX, mg/l	32.9	35.6	34.2
f. AOX, kg/day	481	525	503
g. AOX , kg/ t of paper	3.87	3.84	3.85
10. Efficiency of ETP			
a. Reduction in SS, %	53.12	67.14	60.13
b. Reduction in COD, %	17.0	19.9	18.4
c. Reduction in BOD, %	53.0	56.0	54.5
d. Reduction in AOX, %	51	51	51

TABLE – 2
Mill B

	Details	EXERCISE I	EXERCISE II	Average
1.	Installed capacity, t / year	19800	19800	19800
2.	Raw materials	Bagasse, wheat straw, rice straw, wild grass Waste paper (NDLKC)		
3.	Paper production, t / day	49.5	51.1	50.3
	a. W & P Grade	49.5	51.1	50.3
	b. Kraft	--	--	--
4.	Pulping process	Soda	Soda	Soda
5.	Kappa. no. of unbleached pulp	30-31	30-31	30-31
6.	Bleaching sequence	$C_{8.0}$-$E_{2.5}$ $p_{0.5}$-$H_{6.0}$		
7.	Bleached pulp brightness, % ISO	78 – 80	78 – 80	78 - 80
8.	**Characteristics of waste water** (Influent to ETP)			
	a. Flow, m^3/ day	8105	8766	8435.5
	b. pH	7.2	6.7	6.95
	c. Suspended solids, mg/l	700.0	600.0	650.0
	d. COD, mg/l	1822.0	1445.0	1633.5
	e. BOD, mg/l	616.0	378.0	497.0
	f. AOX, mg/l	41.68	32.50	37.09
	g. AOX, kg/day	337.0	284.6	310.8
	h. AOX , kg/ t of paper	6.8	5.57	6.185
9.	**Characteristics of waste water (Primary clarifier overflow)**			
	a. pH	7.2	6.6	6.9
	b. Suspended solids, mg/l	300.0	180.0	240.0
	c. COD, mg/l	1640	1156	1398.0
	d. BOD, mg/l	610.0	250.0	430.0
	e. AOX, mg/l	40.36	29.40	34.83
10.	**Characteristics of treated waste water**			
	a. pH	6.6	6.7	6.65
	b. Suspended solids, mg/l	220.0	140.0	180.0
	c. COD, mg/l	1366.5	867.0	1116.7
	d. BOD, mg/l	369.6	154.0	261.8
	e. AOX, mg/l	23.63	24.0	23.8
	f. AOX, kg/day	191.07	210.5	200.8
	g. AOX , kg/ t of paper	3.86	4.12	3.99
11.	**Efficiency of ETP**			
	a. Reduction in SS, %	68.57	76.66	72.6
	b. Reduction in COD, %	25.0	40.0	32.5
	c. Reduction in BOD, %	40.0	59.26	49.63
	d. Reduction in AOX, %	43.2	26.0	34.6

TABLE – 3
Mill C

Details	EXERCISE I	EXERCISE II	Average
1. Installed capacity, t / year	38500	38500	38500
2. Raw materials	Bagasse, market pulp (shoft + hard wood) and waste paper		
3. Paper production, t / day	112.5	103.2	107.8
a. W & P Grade	112.5	103.2	107.8
b. Kraft	--	--	--
4. Pulping process	Mechano - Chemical		
5. Kappa no. of unbleached pulp	55-58	55-58	55-58
6. Bleaching sequence	C_{12}-$E_{3.0}$-$H_{5.5}$-$H_{6.5}$		
7. Bleached pulp brightness, % ISO	72-73	72-73	72-73
8. Characteristics of waste water (Influent to ETP)			
a. Flow, m^3/ day	11250	10320	10785
b. pH	6.9	6.1	6.5
c. Suspended solids, mg/l	2100	1800	1900
d. COD, mg/l	2840	2943	2892
e. BOD, mg/l	980	1202	1091
f. AOX, mg/l	121.5	112.0	117.0
g. AOX, kg/day	1367	1156	1261
h. AOX , kg/ t of paper	12.15	11.20	11.68
9. Characteristics of waste water (Primary clarifier overflow)			
a. pH	6.9	6.6	6.75
b. Suspended solids, mg/l	1050	800	925
c. COD, mg/l	2155	2908	2532
d. BOD, mgl/l	800	1042	961
e. AOX, mg/l	86.2	109.0	97.6
10. Characteristics of treated waste water			
a. pH	6.9	6.6	6.75
b. Suspended solids, mg/l	800	650	725
c. COD, mg/l	1500	1659	1579
d. BOD , mg/l	260	380	320
e. AOX, mg/l	55.2	60.2	57.7
f. AOX, kg/day	621.0	621.3	621.15
g. AOX , kg/ t of paper	5.56	6.02	5.79
11. Efficiency of ETP			
a. Reduction in SS, %	62.0	63.90	62.95
b. Reduction in COD, %	47.0	43.63	45.32
c. Reduction in BOD %	73.47	68.39	70.93
d. Reduction in AOX, %	54.5	46.25	50.38

TABLE – 4
Mill D

Details	EXERCISE I	EXERCISE I I	Average
1. Installed capacity, t/ year	**6000**	**6000**	**6000**
2. Raw materials	Rice straw, gunny, cotton linter and waste paper (kraft)		
3. Paper production, t / day	25.9	27.3	26.6
a. W & P Grade	20.55	21.1	20.8
b. Kraft	5.35	6.2	5.77
4. Pulping process	Soda	Soda	Soda
5. Kappa. no. of unbleached pulp	29-30	29-30	29-30
6. Bleaching sequence	H_8-H_4-H_4(Rice straw)		H_{12}-H_6-H_4(Gunny)
7. Bleached pulp brightness, % ISO	Rice straw (75-78), Gunny (65-68)		
8. Characteristics of waste water (Influent to ETP)			
a. Flow, m^3/ day	3238	3549	3394
b. pH	6.8	7.0	6.9
c. Suspended solids, mg/l	1520	2140	1830
d. COD, mg/l	1505	1949	1727
e. BOD, mg/l	511	706	608.5
f. AOX, mg/l	38.2	34.0	36.0
g. AOX, kg / day	124.0	121.0	122.5
h. AOX , kg / t of paper	4.79	4.43	4.61
9. Characteristics of waste water (Primary clarifier overflow)			
a. pH	7.3	6.7	7.0
b. Suspended solids, mg/l	320	300	310
c. COD, mg/l	616	765	690
d. BOD, mg/l	207	256	231
e. AOX, mg/l	27.3	31.2	29.3
10. Characteristics of treated waste water			
a. pH	7.5	7.35	7.4
b. Suspended solids, mg/l	260	340	300
c. COD, mg/l	405	478	441.5
d. BOD, mg/l	35.0	65.0	50.0
e. AOX, mg/l	12.3	15.7	14.0
f. AOX, kg/day	40.0	56.0	48.0
g. AOX , kg/ t of paper	1.54	2.05	1.8
11. Efficiency of ETP			
a. Reduction in SS, %	83.0	84.0	83.5
b. Reduction in COD, %	73.0	75.0	74.0
c. Reduction in BOD, %	93.15	90.79	91.97
d. Reduction in AOX, %	67.80	53.80	60.80

TABLE – 5
Mill E

Details	**EXERCIS I**	**EXERCISE II**	**AVERAGE**
1. Installed capacity, t / year	33,000	33,0000	33,000
2. Raw materials	Wheat straw, bagasse, sarkanda, and Cotton linter		
3. Paper production, t / day	106.3	94.8	100.5
a. W. &. P. Grade	106.3	94.8	100.5
b. Kraft	--	--	--
4. Pulping process	Soda	Soda	Soda
5. Kappa. no. of unbleached pulp	22-23	22-23	22-23
6. Bleaching sequence	$C_{6.5}$ – $E_{3.2}$- $H_{3.5}$-$H_{0.5}$		
7. Bleached pulp brightness, % ISO	81-83	81-83	81-83
8. Characteristics of waste water (Influent to ETP)			
a. Flow, m^3/ day	6554	6858	6706
b. pH	6.5	6.5	6.5
c. Suspended solids, mg/l	150	160	155
d. COD, mg/l	391	1018	704.5
e. BOD, mg/l	178	366	272
f. AOX, mg/l	41.4	33.8	37.6
g. AOX, kg/day	271.3	232.0	251.6
h. AOX , kg/T of paper	2.56	2.45	2.51
9. Characteristics of waste water (Primary clarifier overflow)			
a. pH	6.7	6.8	6.75
b. Suspended solids, mg/l	100	127	113.5
c. COD, mg/l	354	937	645.5
d. BOD, mg/l	160	350	255
e. AOX, mg/l	33.95	26.9	26.9
10. Characteristics of treated waste water			
a. pH	7.1	7.7	7.4
b. Suspended solids, mg/l	70	88	79.0
c. COD, mg/l	166	352	259
d. BOD, mg/l	34.4	24.0	29.2
e. AOX, mg/l	19.87	15.22	17.54
f. AOX, kg/day	130.23	104.4	117.3
g. AOX , kg/ t of paper	1.23	1.10	1.17
11. Efficiency of ETP			
a. Reduction in SS, %	53	45.0	49.0
b. Reduction in COD, %	57.5	65.4	61.45
c. Reduction in BOD, %	80.65	93.40	87.00
d. Reduction in AOX, %	52.0	54.97	53.50

Table – 6

SUMMARY OF AOX LEVELS IN EFFLUENTS OF DIFFERENT PULP& PAPER MILLS

Details	Mills				
	A	B	C	D	E
Pulping process	Soda	Soda	Chemi-mechenical	soda	Soda
Kappa No.	30-31	30-31	55-58	29-30	22-23
Bleaching Process	C-E-H-H	C-E_P-H	C-E_H-H	H-H-H	C-E-H-H
Total Cl2 %	16	14	24	16	10.5
Elemental Cl2	10	8	12	--	6.5
Pulp production	69	41	41.5	22.2	72.8
Brightness %	74-75	78-80	72-73	75-78	81-83
AOX, kg/t Paper					
➢ **Influent**	7.9	6.2	11.68	4.60	2.51
➢ **P/C over flow**	6.4	5.8	9.75	3.7	1.79
➢ **Treated Effluent**	3.85	3.99	5.79	1.80	1.17
AOX removal, %					
➢ **Primary Clarifier overflow**	18.98	6.5	16.50	19.57	28.69
➢ **ETP**	39.85	31.2	40.60	51.35	34.64
➢ **Overall removal**	51.00	35.6	50.40	60.87	53.39

Table - 7

RESULTS OF AOX IN EFFLUENTS GENERATED IN LABORATORY BLEACHING OF PULPS

S.No.	SAMPLE SOURCE	Kappa No.	Cl_2, %	Total Cl_2, %	Brigh. %	AOX, mg/l	AOX kg/t pulp
1.	**Mill A**	30.2	10.0	16.0	75.3	69.2	8.823
2.	**Mill B**	30.6	8.0	14.0	78.0	87.35	9.145
3.	**Mill C**	57.7	12.0	23.5	80.9	145.0	18.357
4.	**Mill D**	29.59	--	19.0	78.0	178.76	4.79
5.	**Mill E**	22.2	6.5	10.5	82.6	36.9	4.73

Table – 8

PERFORMANCE OF EXISTING PULP WASHING SYSTEM
(Carryover of black liquor alongwith unbleached pulp)

S.No.	SAMPLE SOURCE	Raw material	No. of BSW_s	Carry over COD kg/t pulp
1.	**Mill A**	Wheat straw, Bagasse, Sarkanda & indigenous/imported waste paper	4	33
2.	**Mill B**	Wheat straw, Bagasse, Rice straw, Wild grass & waste paper (NDLKC)	3	30
3.	**Mill C**	Bagasse, market pulp (soft + hard wood) & waste paper	2	35
4.	**Mill D**	Rice straw, Gunny, Cotton linter & Waste paper (Kraft)	1	40
5.	**Mill E**	Wheat straw, Bagasse, Sarkanda & cotton linter	3	33

Table – 9
RESULTS OF ANALYSIS OF EFFLUENT GENERATED IN LABORATORY BLEACHING OF PULPS

S.No.	SAMPLE SOURCE	pH	TSS, mg/l	COD, mg/l	BOD, mg/l	AOX, mg/l
1.	**Mill A**	4.9	1100	1193	327	69.2
2.	**Mill B**	2.6	510	1044	250	87.35
3.	**Mill C**	2.0	1620	2123	649	145.0
4.	**Mill D**	6.5	710	3332	1010	178.76
5.	**Mill E**	6.7	520	920	360	36.9

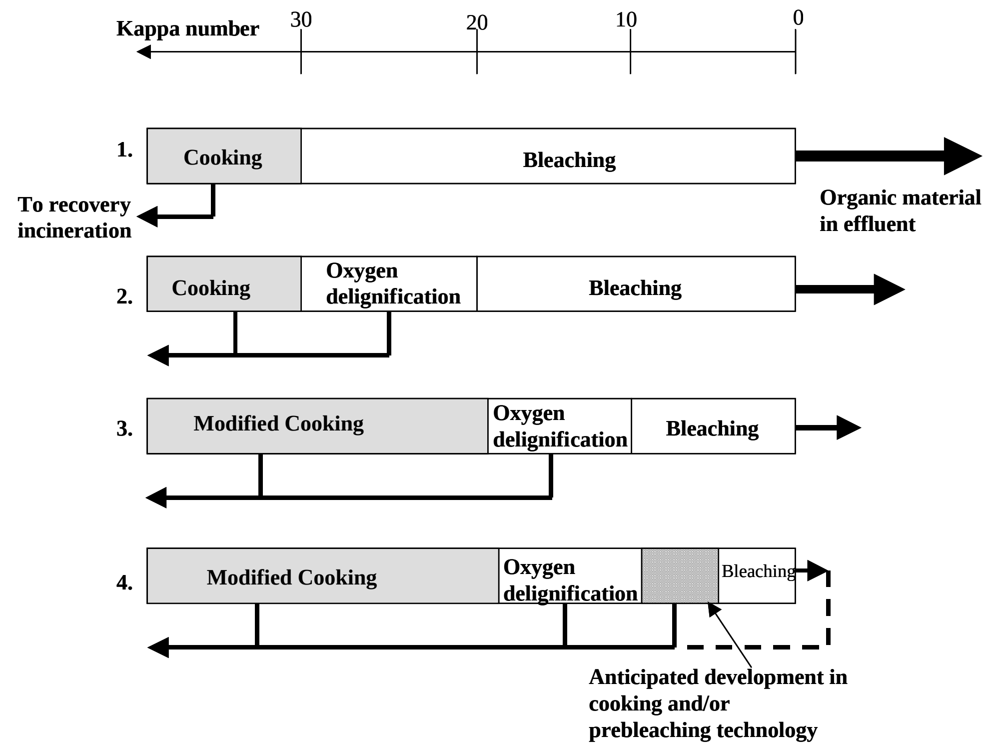

Fig-1. DEVELOPMENT OF ALTERNATE PULPING PROCESS

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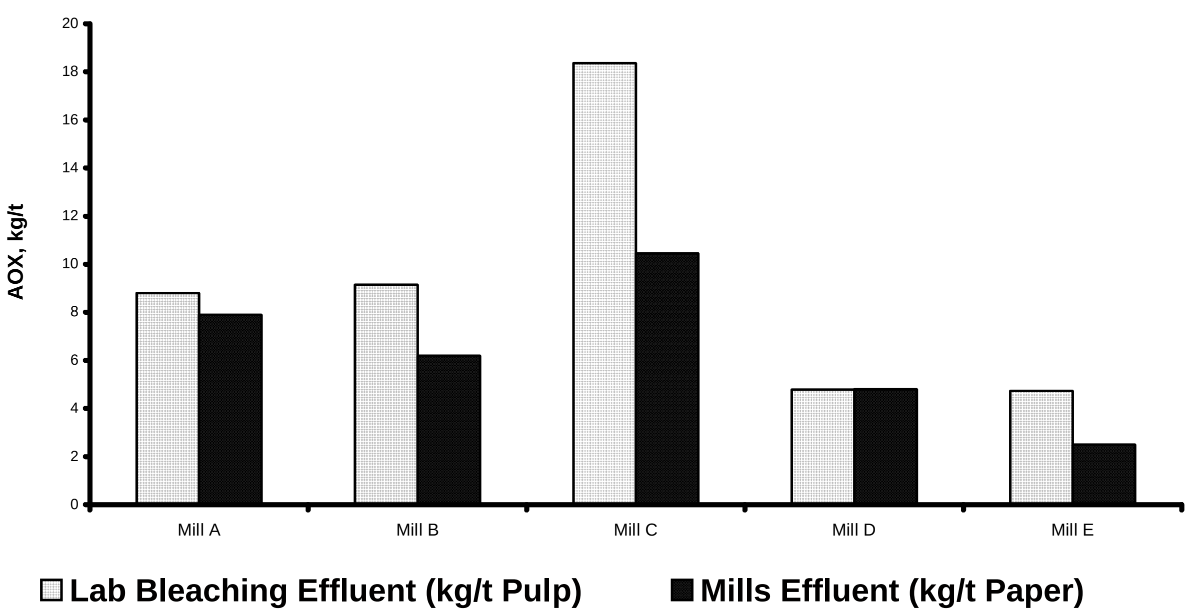
Fig-2. RESULTS OF AOX IN EFFLUENTS GENERATED IN LABORATORY BLEACHING AND MILL EFFLUENTS



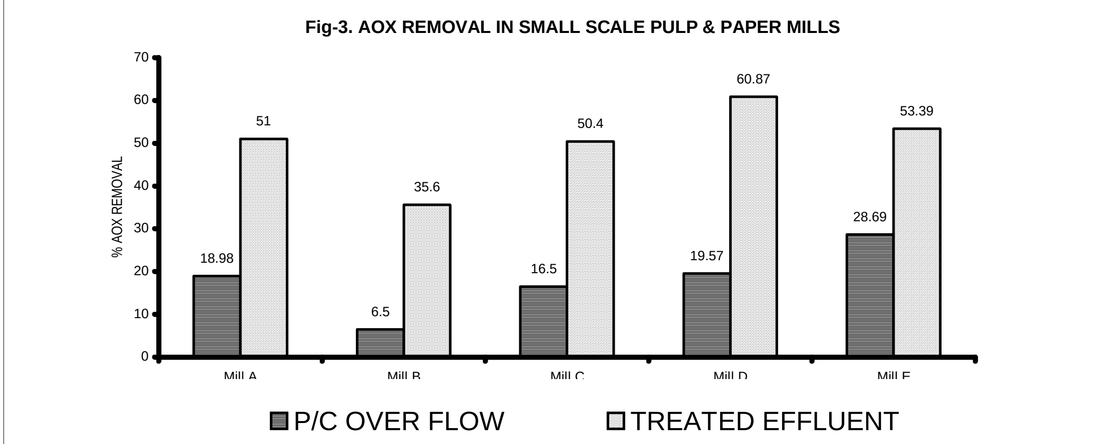


Fig-3. AOX REMOVAL IN SMALL SCALE PULP & PAPER MILLS
% AOX REMOVAL
0
10
20
30
40
50
60
70
18.98
51
6.5
35.6
16.5
50.4
19.57
60.87
28.69
53.39
P/C OVER FLOW
TREATED EFFLUENT

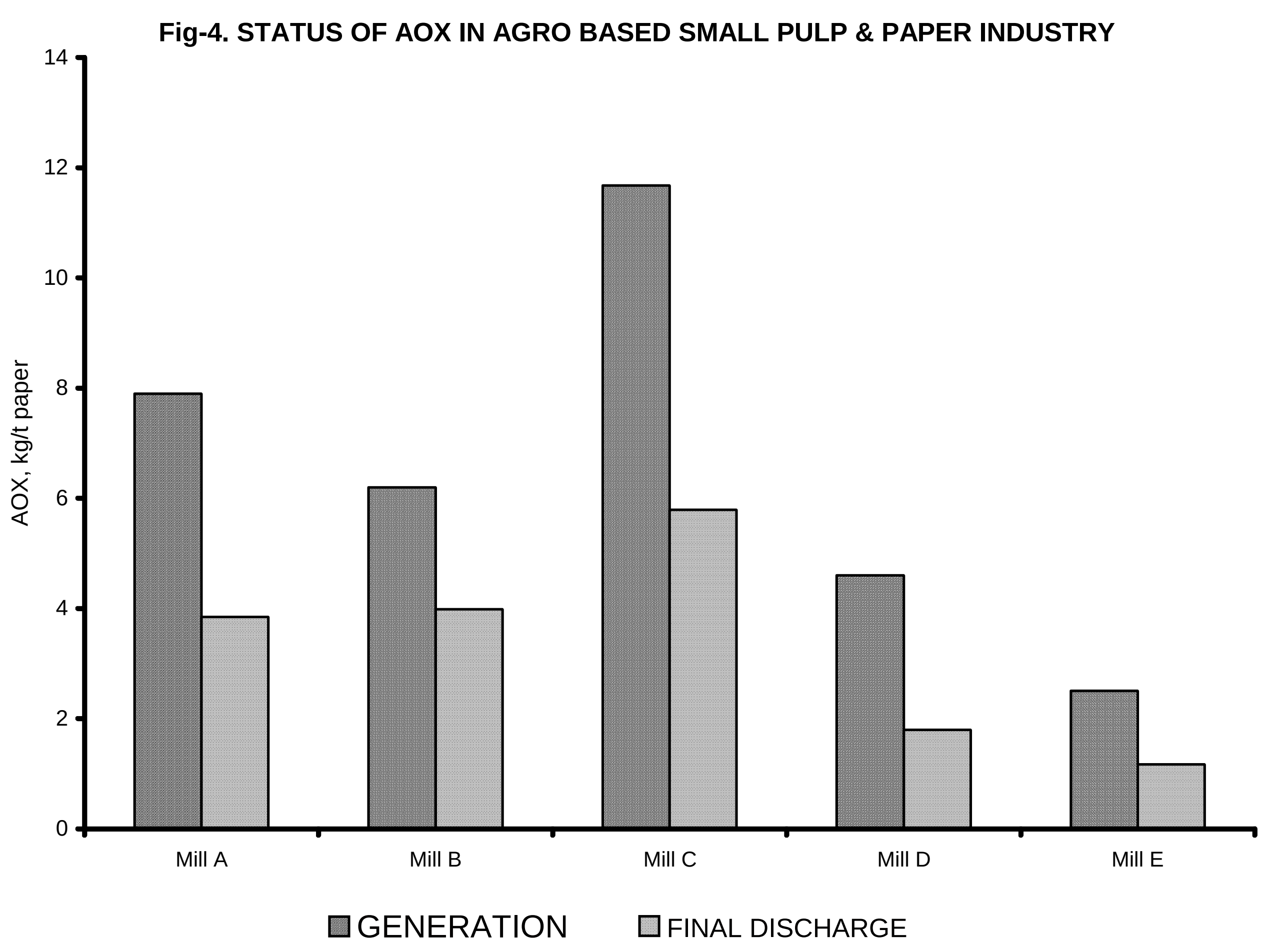


Fig-4. STATUS OF AOX IN AGRO BASED SMALL PULP & PAPER INDUSTRY
AOX, kg/t paper
0
2
4
6
8
10
12
14
Mill A
Mill B
Mill C
Mill D
Mill E
GENERATION
FINAL DISCHARGE

Fig-5. PERFORMANCE OF ETP IN SELECTED AGRO BASED PULP & PAPER MILLS

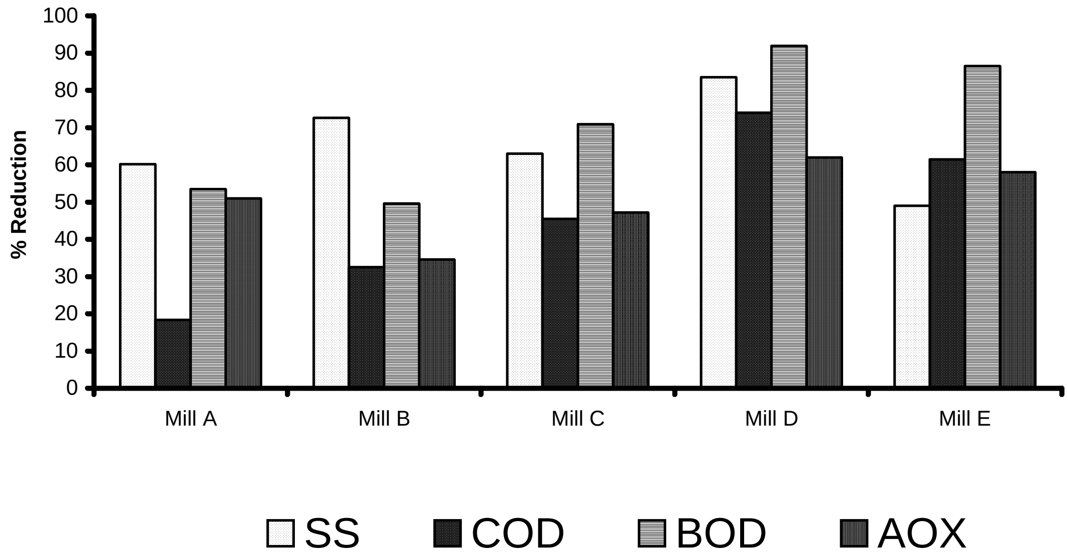


Fig-6. WASTE WATER GENERATION IN AGRO BASED PULP & PAPER MILLS

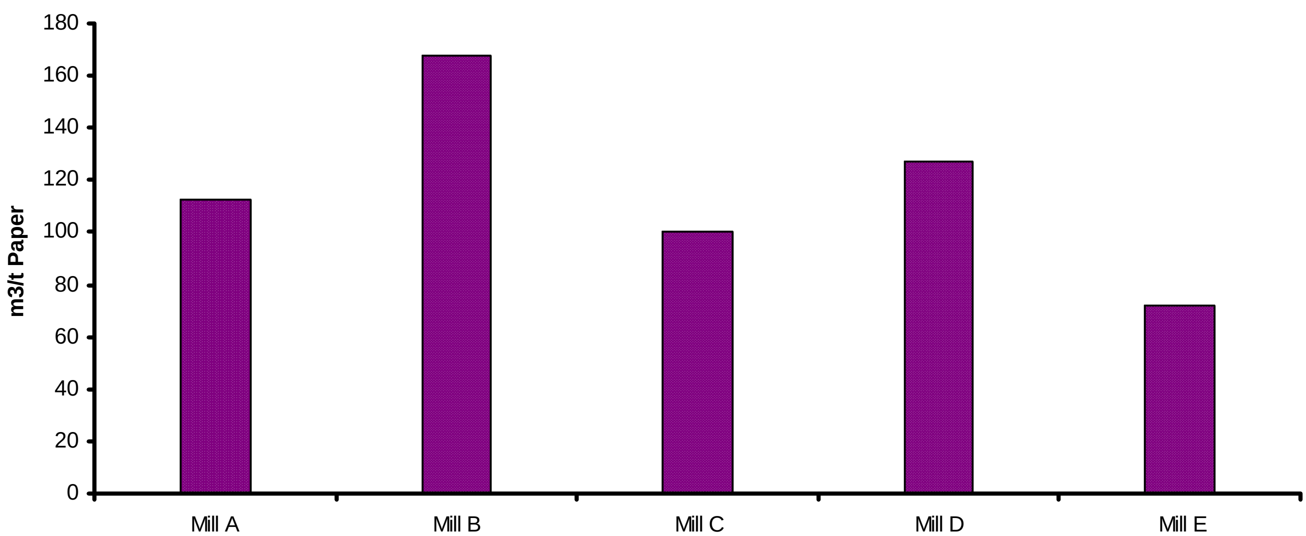


Fig-7. CARRYOVER OF BLACK LIQUOR ALONG WITH UNBLEACHED PULP IN AGRO BASED PULP AND PAPER MILLS

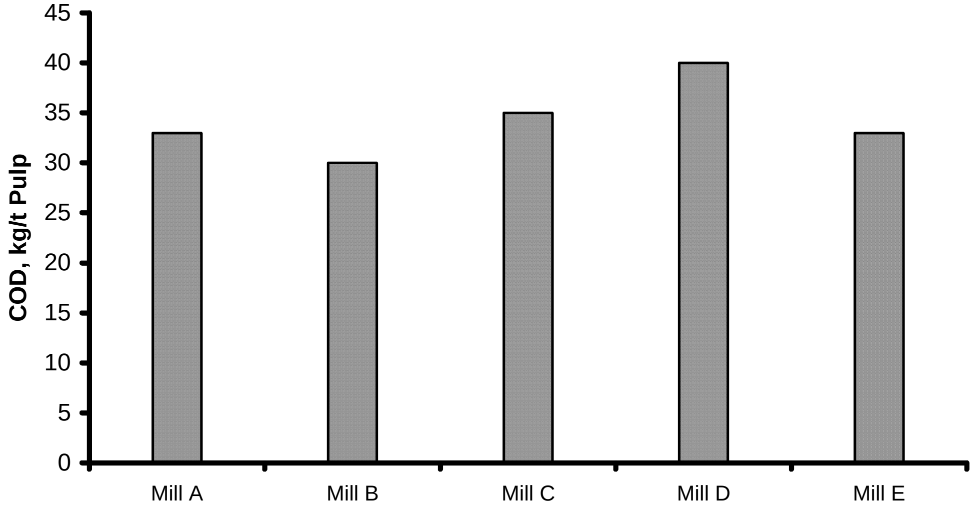


Fig. 8: Process flow diagram of Bio-methanation plant at Mill A

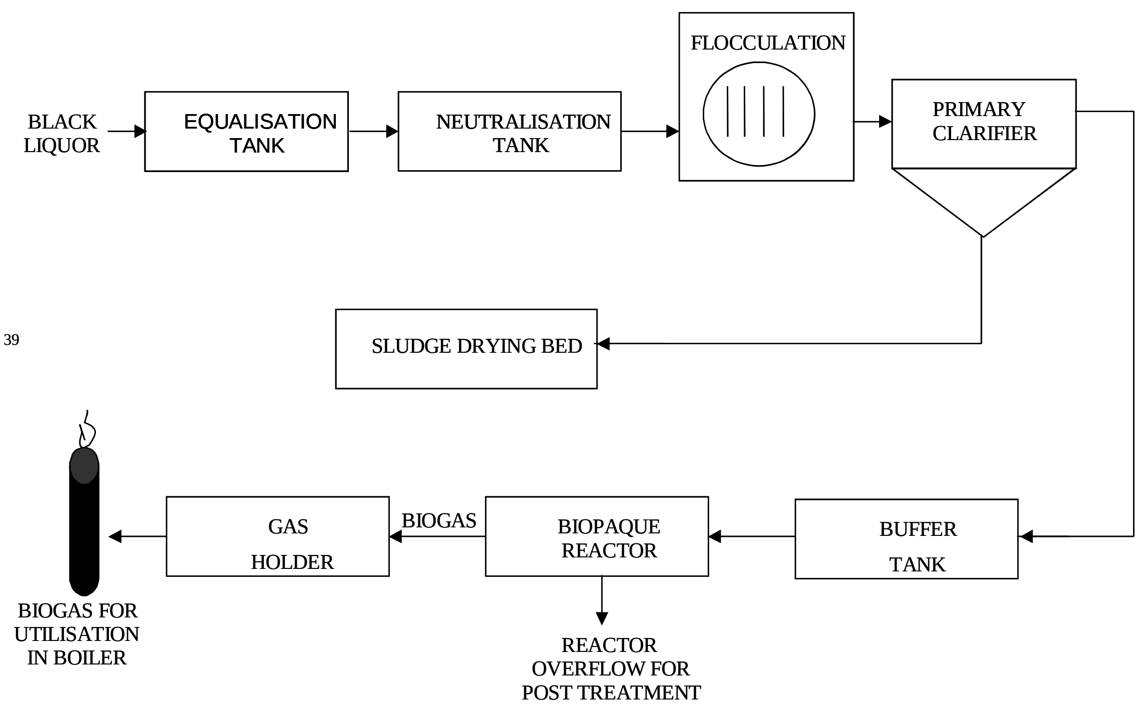


Fig 9: Process flow diagram of Effluent Treatment Plant at Mill A

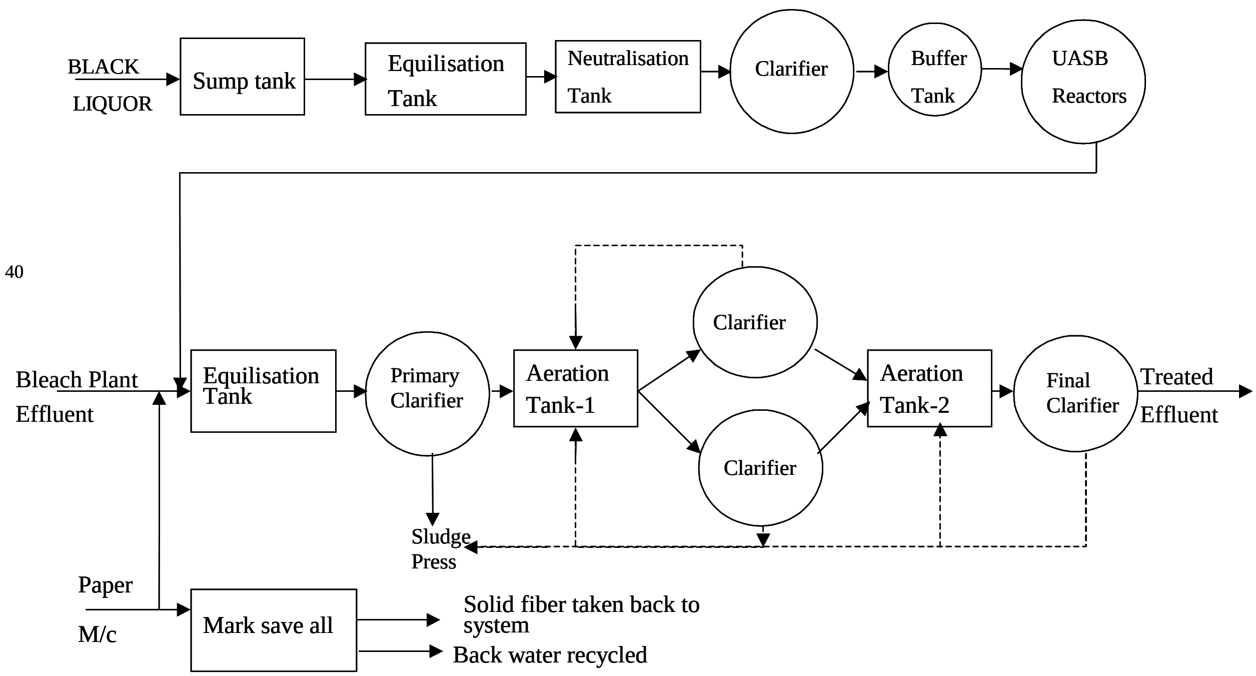


Fig.10: Flow Diagram of Effluent Treatment Plant at Mill B

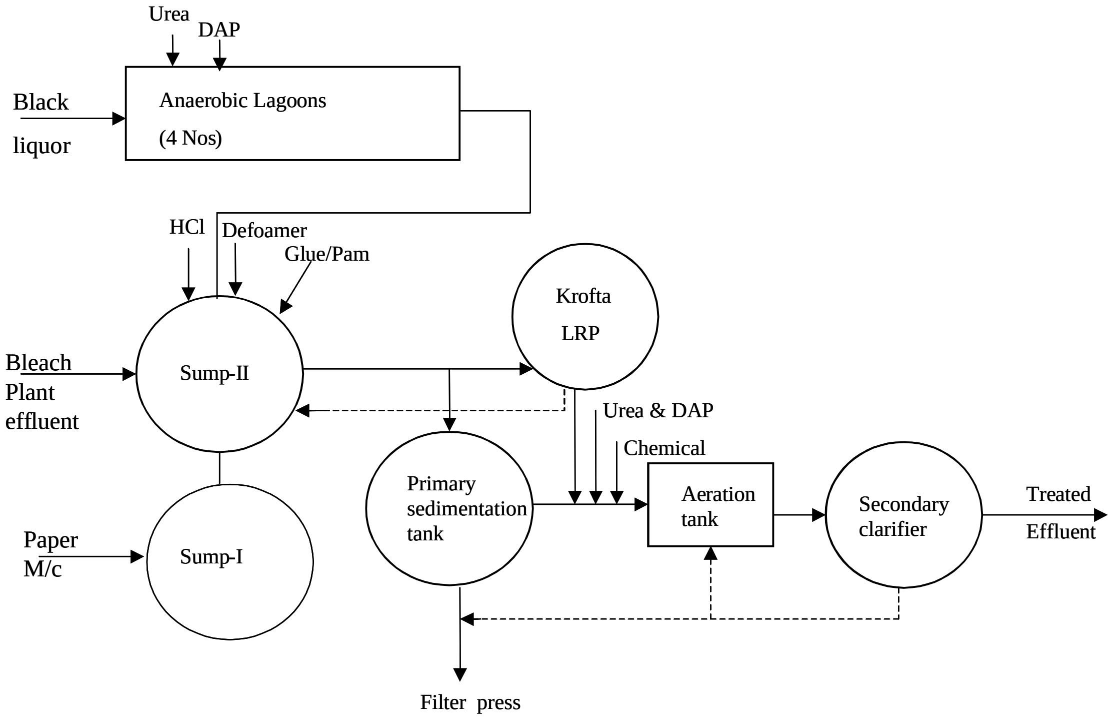


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Fig.11: Flow Diagram of Effluent Treatment Plant at Mill C

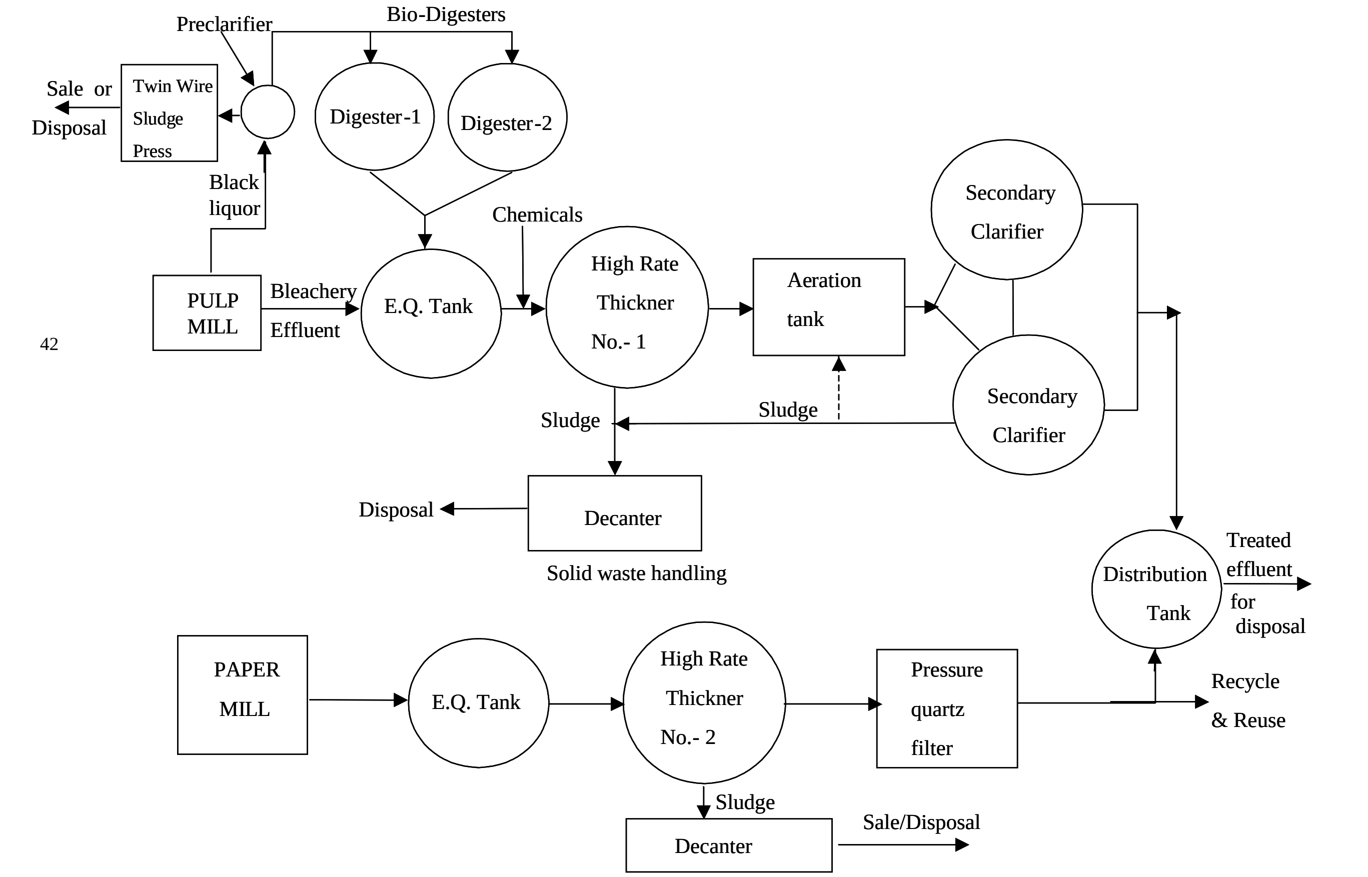


Fig.12: Flow Diagram of Effluent Treatment Plant at Mill D

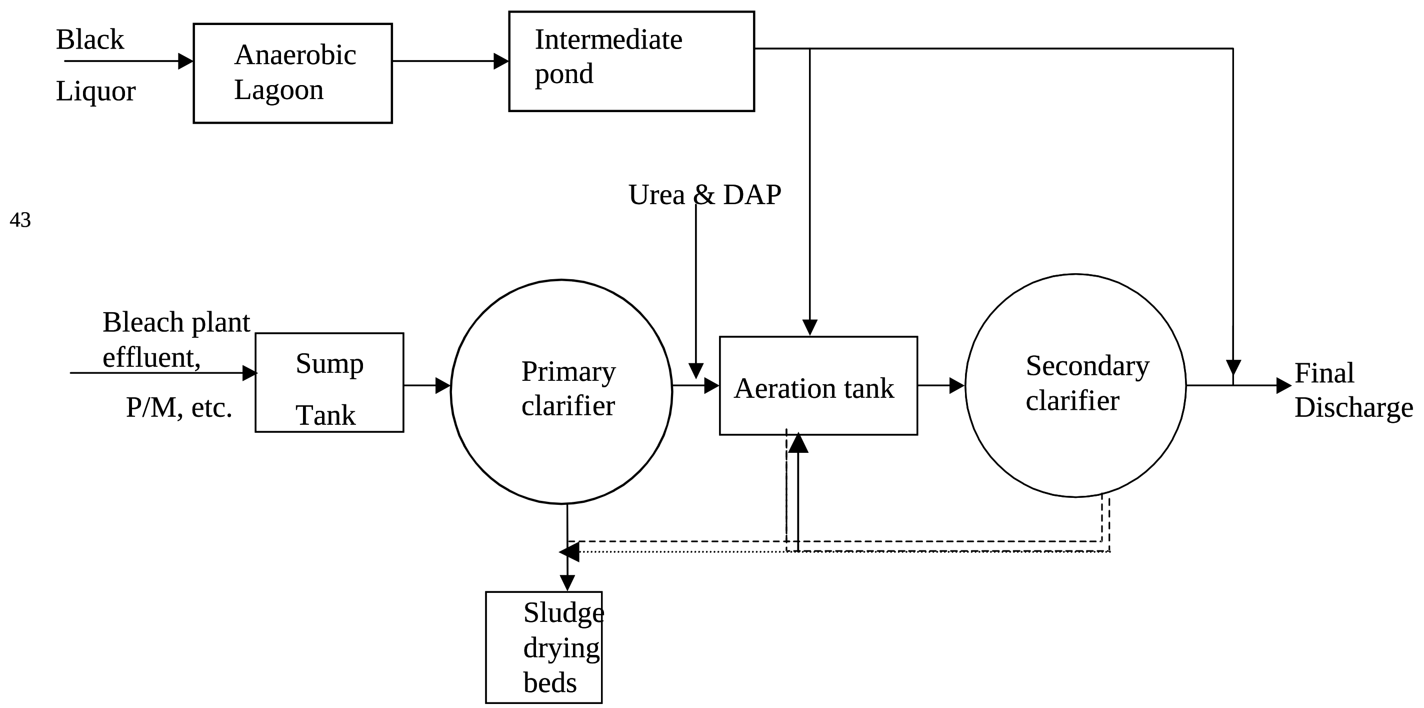
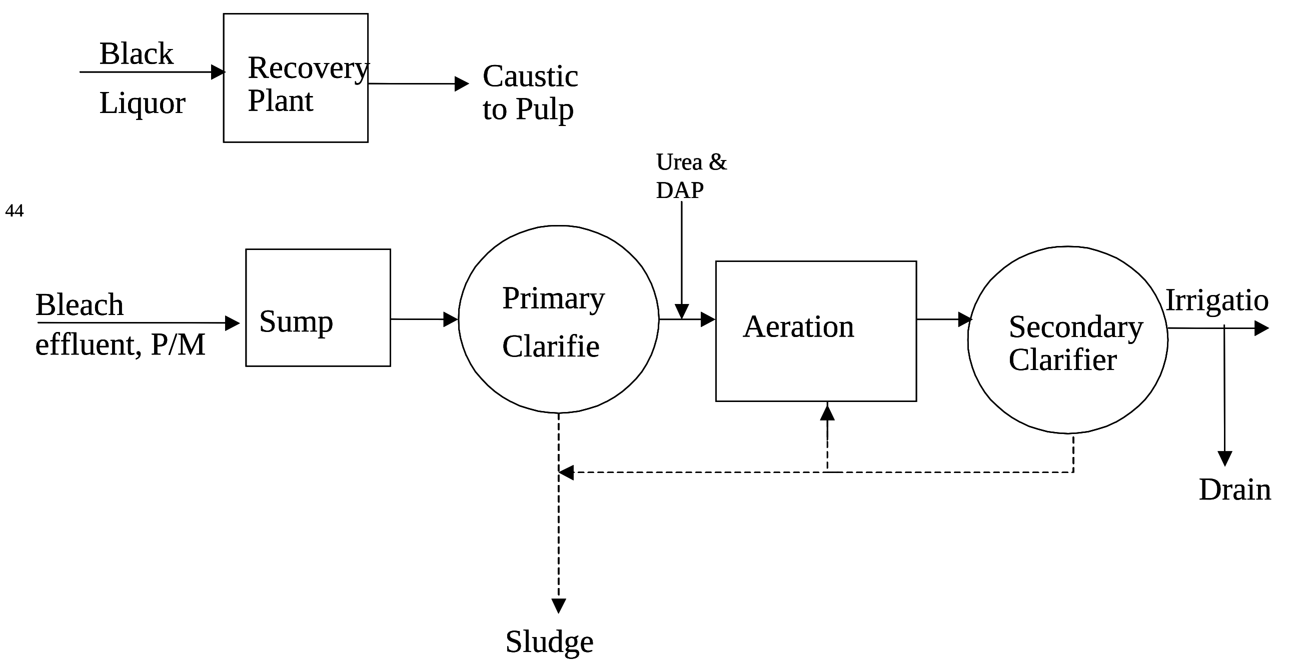


Fig.13: Flow Diagram of Effluent Treatment Plant at Mill E



ABBREVIATIONS

AOX	-	ADSORBABLE ORGANIC HALIDES
BOD	-	BIOLOGICAL OXYGEN DEMAND
C	-	CHLORINATION
COD	-	CHEMICAL OXYGEN DEMAND
CPCB	-	CENTRAL POLLUTION CONTROL BOARD
CSTR	-	CONTINUOUS STIRRED TANK REACTOR
E	-	EXTRACTION
ETP	-	EFFLUENT TREATMENT PLANT
H	-	HYPOCHLOTRITE
P	-	PEROXIDE
SS	-	SUSPENDED SOLIDS
TOCl	-	TOTAL ORGANIC CHLORINE