Integrated Approach to Reduce Adsorbable Organic Halides (AOX) in Pulp Manufacture

Mittal S.K. and Maheshwari Subhash

INTRODUCTION:

The pulp and paper industry due to its higher consumption of resources including woody raw material, water and energy, always remains under scrutiny by all the concerned who have eco-efficient thinking. This environmental emphasis gradually further deepended and shifted from comparatively short term effects to effects by the persistent and bio accumulable compounds formed in the manufacture of bleached chemical pulp using chlorine compounds. Adsorbable organic halides have gained more attention in this regard in recent past.

Present paper discusses, the basis of AOX formation and its environmental impacts. The various developments taken in the direction to reduce formation of organically bound halides including AOX are summarized in this article. The issues related to reduction of organically bound halides in existing mills are presented in this paper. The efforts made at PHOENIX and in progress are also briefly described.

The various logical experiences and studies clearly indicate that reduction of AOX depends on efficient operation of the mills and incorporation of a number of modifications in the present mills, which in turn involved investments. In view of these facts it is concluded that very positive and concerted efforts are required by the pulp and paper industry and regulatory authorities to address this issue, so that the required improvements are achieved without jeopardizing the performance, competitiveness and all economics of the industry.

The industrial activities and developments are the inseparable part of material civilization. By supplying the various products and services, the industrial activities provided to humanity the most basic needs, which have become now the essential part of our life. These are also helping to meet the continually unfolding desires and aspirations of human being. In general the industries have contributed and continue to contribute considerable economic benefits to the people world over. But the activities of the many industries also proved to have potential for adverse impacts both short term and long term on the quality of life.

The pulp and paper industry world over has major contributions in the industrial structure of many countries. The pulp, paper, paperboard and the products derived from them have become essential needs of the time. But the activities associated with this industry due to its higher consumptions of resources including woody raw material, water and energy alsways remain under critical scrutiny by all the concerned who have eco-efficient thinking.

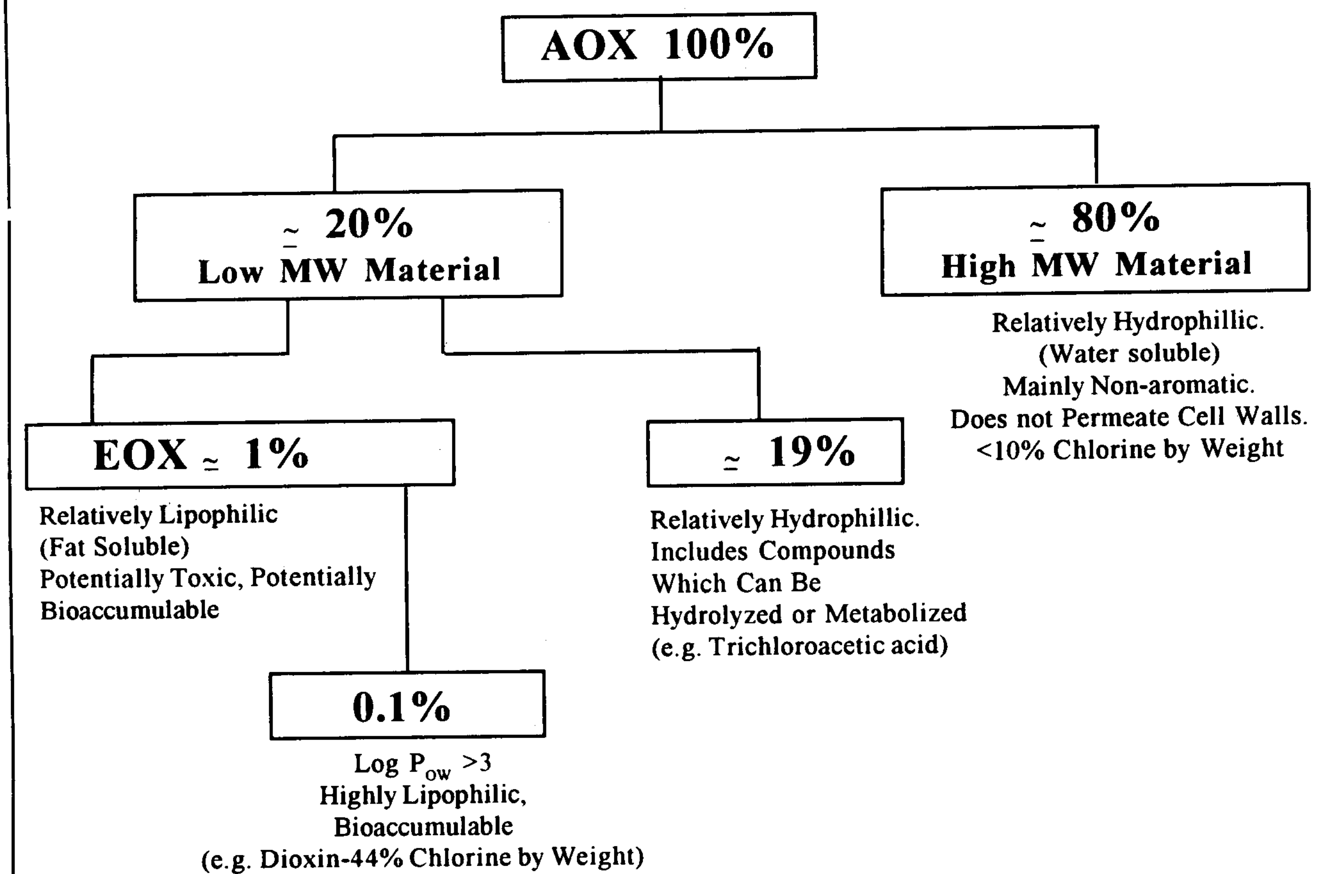
The chlorinated organic compounds have acquired bad reputation for the environmental concerns and first in series were DDT, then PCBs and subsequently chlorinated in the environment for decades and get accumulate inside the tissues of living organisms and where they interfere with the bio chemical process. These worrisome observations and facts attracted the attention of environmentalists and public. The bleached kraft pulp mills using chlorine and chlorine compounds have come under critical observations in this regard. The level of understanding of various toxic compounds in bleached kraft mill effluent has been increasing considerably in recent years. Adsorbable Organic Halides (AOX) has become one main environmental indicator for the industry. The present paper discusses the integrated approach for the pulp and paper industry for consideration to reduce the AOX concerns.

ADSORBABLE ORGANIC HALIDES (AOX)

Absorbable Organic Halides, mainly chlorides with reference to pulp bleaching, is not a single pure material. It is multitude of compounds of varying molecular weights and degrees of fat solubility with the latter

Phoenix Pulp & Paper Public Co., Ltd.
183/2, Maliwan Road, P.B. No. 102
Khon Kaen - 40, 000 Thailand

FIG. -1 CHARACTERISTICS OF AOX IN EFFLUENT



being measure of the tendency to accumulate in living organism. A typical physical as well as chemical classification of AOX presented in the effluent from conventionally cooked and bleached pulp is given in Fig-1.

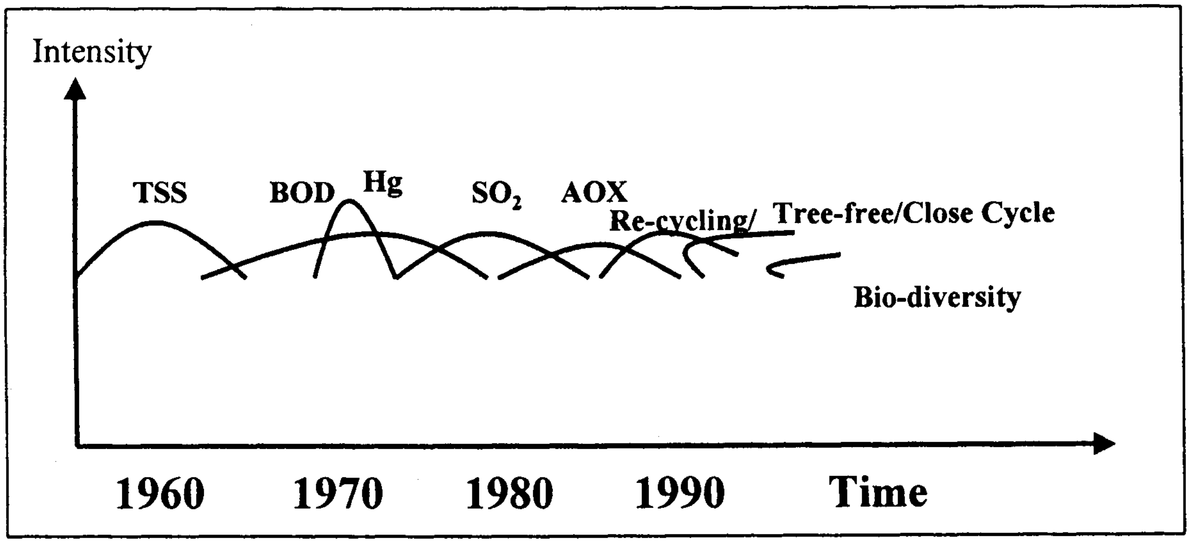
It can be seen from the figure that as such 80% or more organically bound chlorine corresponds to high molecular weight (MW >1000) chlorinated lignin material. These fragments as reported are not amenable to compound - specific analysis because of their relating high molecular mass and heterogeneous nature. As these are relatively higher water soluble or so to say hydrophilic in nature. It may be also mentioned that these compounds contain comparatively lower content of chlorine approximately 10% by weight. In bleaching process due to oxidation of the aromatic structure of lignin gets destroyed and has very low possibility of their conversion to problematic poly chlorinated aromatic compounds in nature.

The remaining 20% of organically bound chlorides found in bleaching effluent correspond to relatively lower molecular weight (MW < 1000) material. The information based on various research findings indicate that this part of AOX contains those compounds which thas potential environmental impacts due to their ability to penetrate in cell membrane or their natural tendency to bio accumulate in tissues of organism. Out of 20% for nineteen percent of these low molecular weight AOX are relatively hydrophilic and can be hydrolyzed or metabolized. The remaining 1% fraction, which is extractable only by non-polar solvents, is referred as Extractable Organic Halides (EOX) This fraction contains compounds which are reported as potentially toxic and bio accumulable.

Keeping these facts in view and constant progress in research activities to get better information and understanding will help to judiciously conclude the environmental impact of these compounds. However, at present, the AOX has been considered as environmental parameter and hence requires greater attention how to over come or reduce its generation and

Environmental Issues Affecting the Industry

EMISSION STANSDARD



Waves of Environmental Hot Topics

discharge from bleached pulp and paper mills.

LIGNIN AND AOX- BASIC ISSUES

The main target for manufacture of bleached chemical pulp from woody raw material is to remove or modify lignin to maximum possible extent. Lignin, which is a random, three-dimensional macromolecule of phenyl propane building blocks and due to its color and odor lignin, requires removal to get purer cellulose fibers. The generation of AOX has been directly correlated to the lignin compounds, generally measured as Kappa No., which enters to bleach plant.

The reduction of AOX generation and disposal can be achieved by three main possible ways.

- Reduction of lignin before pulp enters to bleach plant

- Use of such chemicals which generate minimum AOX.

- Destruction of AOX at end of the pipe treatment.

REDUCTION BEFORE BLEACH PLANT

The effective removal of lignin before bleach plant is considered as first and most appropriate approach to resolve the problem of AOX. The practice presently followed and efforts made and in use are summarized below.

CONVENTIONAL COOKING

The convention kraft cooking is one most commonly used step to remove the lignin from raw material and to make the content ready for bleaching. However, it has certain limitations to bring down lignin i.e. pulp kappa number below certain level, without adversely affecting the process and quality of pulp.

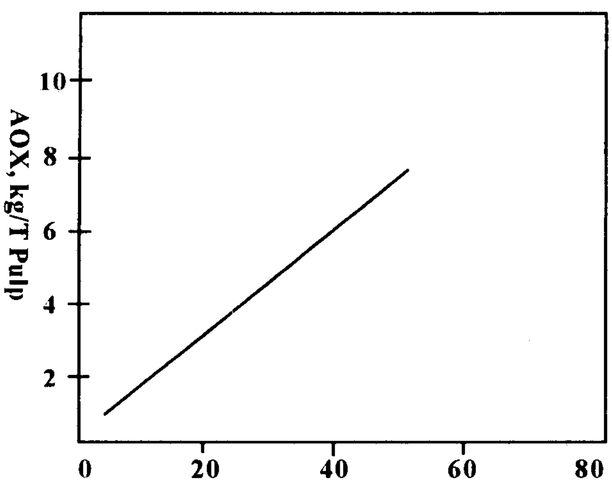
OPERATING PARAMETERS

The operating parameters including cooking chemicals, temperature and time are very important for efficient removal of lignin these should be adjusted in such a manner that maximum delignification is achieved without pulp degradation. The efforts should be made to avoid lignin precipitation during the cooking or at storage stages both for pulp and liquor. The lignin precipitation results in higher bleaching chemical consumptions and higher AOX generation.

USE OF ADDITIVES

The use of pulping additives can be also considered to get reduction in kappa number and subsequently reducing the AOX generation, with other advantages like higher pulp yield, cooking chemical reduction, lower odor etc depending on the present operating conditions and requirements of the mills and at the same time overall economics.

Fig. -2 Active Chlorine - AOX generation



REMOVAL OF BARK

While using wood it is very important to remove the bark which constitutes average 12-18% on as such basis of wood depending on the wood type, age etc.

As such the lignin contant in bark is higher then debarked wood and requires higher alkali during cooking and at the same time gives very low pulp yield and poor pulp quality. In spite of using higher alkali this portion of wood gives high kappa number meaning more lignin entering to bleach plant from this fraction and ultimately resulting in higher bleaching chemical requirement and AOX generation. It has been experienced by many mills that removal of bark improves over all productivity of the mill. It may be mentioned that bark can be utilized as fuel or can be converted to bio-fertilizer that is in great demand nowadays. Keeping these facts in view, mills using woods with bark should consider using debarked wood to reduce the AOX generation.

EXTENDED COOKING SYSTEM

The limitation in removal of lignin below certain level by conventional cooking process paved the way for modification of cooking process by increasing the selectivity of delignification and without adversely affecting the pulp quality and yield. This is achieved by using higher hydroxide and hydrogen sulfide ions concentrations in bulk delignification phase and there by decrease the amount of slowly reacting residual lignin. This also results in increase in rate of delignification in bulk phase, which helps to further reduce the cooking temperature. The decrease in cooking temperature minimizes carbohydrate degradation and pulp strength loss and improves pulp bleachability. The lowering of pulp kappa number and improving bleachability of the pulp result in lower bleach chemicals requirement and ultimately lower AOX generation.

OXYGEN DELIGNIFICATION

The use of oxygen as extension of delignification has become the integral part of new pulp mills. The main advantage of use of this stage is environmental performance and to some extent operating cost advantage as it is in close cycle with brown stock washing. However, it is capital intensive and requires additional capacity in recovery system. Due to these reasons it becomes quite difficult to incorporate the system in existing mills until and unless the mill is going ahead with major expansion activity of recovery cycle system. However, this system can be incorporated if recovery system is operating under lower capacity utilization.

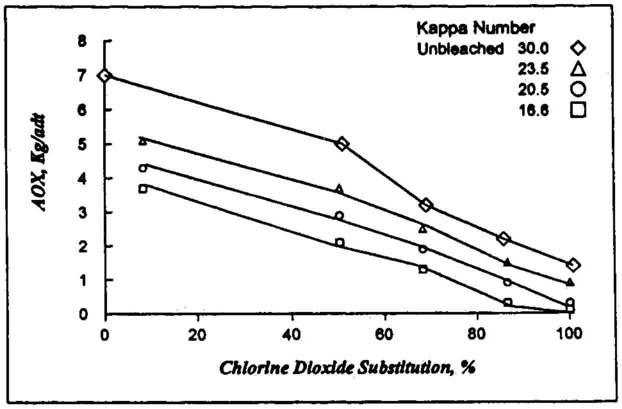
The most obvious benefit of incorporation of oxygen delignification is to reduce of 35-40% bleaching chemicals requirement and which ultimately results in lowering of chlorinated organic compounds generation from in bleach plant. The exact advantage of AOX reduction is dependent on the type of chlorine compounds are in use. If elemental chlorine is in use the advantage is most significant. Apart from AOX reduction equivalent reduction of other pollution loads like COD, BOD, color, dissolved solids both organic and inorganic is achieved. The use of single stage oxygen was common till few years back, however now most of new mills are opting for two stages.

PULP BLEACHING

The extension of delignification or removal of residual lignin from unbleached pulp to make the pulp brighter is the main function during pulp belaching. The common bleaching chemicals used in bleach plant are given below.

Symbol	Chemical	Symbol	Chemical
C	Chlorine	Z	Ozone
D	Chlorine dioxide	E	Sodium hydroxide
H	Hypochlorite	X	Enzymes
O	Oxygen	Q	Chelating agent
P	Hydrogen peroxide	A	Acid

Fig. -3 ClO_2 Substitution and AOX Formation



Three chlorine compounds i.e. chlorine, hypochlorite and chlorine dioxide are commonly used for bleaching and these are also associated for generation of AOX. The use of chlorine came after hypochlorite as preferred chemical because of its lower cost, improved selectively to remove lignin and also the metal ions from the pulp. The active chlorine equivalents for these chemicals are given below.

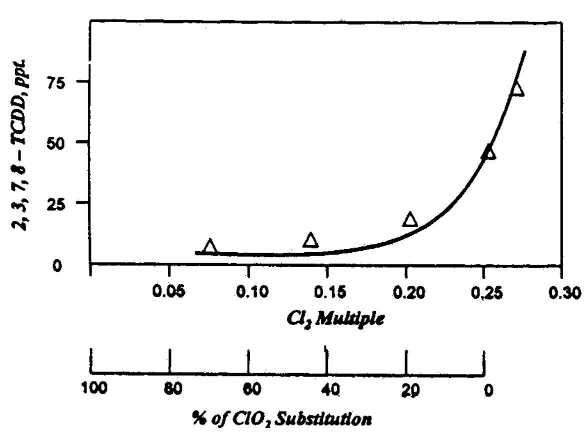
i Chlorine - 1.0 kg Active chlorine/kg Cl_2

ii Hypochlorite - 0.95 kg Active chlorine/kg NaOCl

iii Chlorine dioxide - 2.63 kg Active chlorine/kg ClO_2

The use of hypochlorite has come under question mainly due to formation of chloroform during removal of lignin and adverse affect on pulp properties. Hence, its use is avoided in any modern bleach plant and gradually being removed from existing bleach plants. The chemicals/stages in bleach plant, which requires special attention for reduction of AOX, are briefly considered below.

Fig. -4 Effect of ClO_2 substitution and Chlorine multiple on Dioxin Formation



USE OF CHLORINE

The chlorination stage traditionally has been the first and main stage for major removal of lignin and purification of the pulp during bleaching. The chlorination followed by alkali extraction selectively removes about 75-80% lignin from the unbleached pulp. However, use of chlorine has come under strict scrutiny due to formation of organically bound halides. AOX formation has been shown to be directly proportional to the amount of active chlorine consumed in bleaching (Fig. 2).

USE OF CHLORINE DIOXIDE

Chlorine dioxide has emerged as one of the most important chemicals used for pulp bleaching due to its selectivity towards removal of lignin and as very good particle bleaching chemical. At the same time chlorine dioxide is most common and widely recognized solution both for reduction of AOX and dioxin emission problem. The substitution of chlorine by chlorine dioxide and its impact on AOX/Dioxin are presented in Fig-2 & 4. It may be noted that unlikely to chlorine it has to be manufactured at the plant site used.

It may be noted that there is also direct relation between chlorine multiple i.e. the ratio of percent active chlorine.and pulp kappa number on Dioxin formation (Fig.-4).

OXIDATIVE EXTRACTION

The use of oxygen reinforced caustic extraction, as designated as Eo stage, has rapidly spread throughout the bleached kraft pulp mills. The actual process changes required for this stage are installation of reactor before extraction and addition of 5 kg oxygen with little extra alkali. The cost of additional chemicals normally justified in all cases by reduction of bleaching chemicals in early stage or subsequent stages. the use of peroxide in this stage along with oxygen has also gradually becoming popular. However; the economics of use of peroxide depends on individual mills operations and performance.

The increase in the oxidative potential by reinforcement of oxygen and/or peroxide in extraction stage is an effective way to also break the chemical bonds between halogen and carbon of AOX molecules.

TABLE-1 LIGNIN BALANCE-SUMMARY

PARTICULAR	Conventional Cooking			Conventional Cooking with ODL			EDL +OD			Light - ECF		
	Kappa	Lignin	Percent	Kappa	Lignin	Percent	Kappa	Lignin	Percent	Kappa	Lignin	Percent
1. Raw Material	-	27.0	100	-	27.0	100	-	27.0	100	-	27.0	100
2. Unbleached Pulp	25	3.75	13.9	25	3.75	13.9	17.0	2.55	9.4	17.0	2.55	9.4
3. Oxy. Delig.	-	-	-	18	2.7	10.0	11.0	1.65	6.1	9.5	1.42	5.3
4. Pre Bleached pulp	-	-	-	-	-	-	-	-	-	3.0	0.45	1.7
5. Final Pulp	-	0.13	0.5	-	0.13	0.5	-	0.13	0.5	-	0.11	0.4
6 Effluent	-	3.62	13.4	-	2.56	9.5	-	1.51	5.6	-	0.35	1.3

Basic Data = Avg. Lignin in RM = 27%. Lignin in Pulp % = Kappa No. x 0.15

This ultimately results in reduction of AOX. The overall oxidative extraction stage is most operation and cost friendly stage in bleach plant to reduce the organically bound halides.

USE OF ENZYME

The use of enzymes - Xylanases has extensively being researched at laboratory stage to reduce the lignin in the pulp entering to bleach plant and consequently reduce bleaching chemicals. Many plant scale trials are also performed and some of them met the targets set. In general it can be confirmed that use of enzyme offers reduction in bleaching chemicals and consequently AOX reduction. The efforts are continuing to isolate more selective xylanses enzyme, which will be operation friendly, cost effective and cause minimum adverse affect on pulp quality and yield.

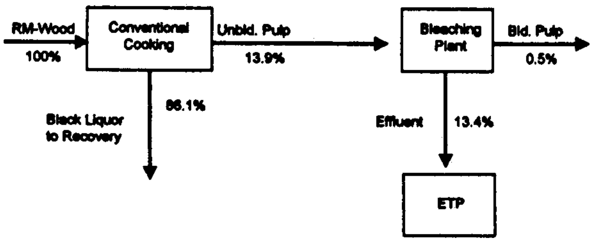
INTER-STAGE WASHING

The inter stage washing both at the brown stock and bleach plant has significant effect on reduction of AOX. The efficient inter stage brown stock washing with the use of minimum dilution water and results in minimum carry over of both inorganic and organic load and at the same time lower volume to bleach liquor recovery cycle. The increase organic load results in increase bleaching chemical demand and intern additional pollution load on effluent, in terms of COD, BOD dissolved solids, color and organically bound chlorides, the inter stage washing in bleach plant stages also has similar effect as of brown stock washing. It is recommended to use suitable and efficient equipment, optimum processing parameters and efficient recycling of backwater.

TOTAL CHLORINE FREE BLEACHING

The total chlorine free (TCF) bleaching took good position in Scandinavian countries to accommodate the customers' requirement and regulatory demand to eliminate organically bound chlorides discharge. However, many research findings and mill experiences showed that no signification environmental benefits could be achieved comparatively while using the TCF bleaching sequence. This is mainly due to most of the mills are unable to close fully their bleach plants. EDTA/DTPA or similar chelating agents, used in TCF bleaching sequence where ozone and peroxide are the main bleaching chemicals, are carried to effluent. These chemicals have comparatively lower rate of biodegradability and ultimately adverse environmental acceptance.

Fig. -5 Lignin Balance - Conventional Process



END-OF-PIPE TREATMENT

As mentioned above effluent from bleaching pulp mills contains wide variety of high and molecular weight organically bound chlorides. The removal of chlorinated organics from bleach plant effluent both by aerobic and anaerobic treatments is reported. It has been also experienced that activated sludge system for effluent treatment has been found more effective to remove more than 50% AOX from the effluent. It has been also reported that sequential anaerobic/aerobic treatment has been found more effective to remove the chlorinated organic compounds. It may be mentioned that implementation and adoption of effluent treatment technology will depend on individual mills requirement.

The removal of AOX can also be accomplished by chemical treatment methods i.e. using Ozone, Peroxide or advance Oxidation Process, lime/alum treatment etc. The implementation of end-of-pipe treatment requires very careful assessment with respect to both capital investment and operating cost.

LIGNIN BALANCE IN PULP MAKING PROCESS

As mentioned above the lignin entry in bleach plant is the main criteria of use of bleaching chemicals and ultimately the formation of organically bound halides. Hence lignin removal both at cooking stage and bleach plant is very important. The following four approaches for bleached pulp manufacture, except TCF bleaching, are mainly in practice world over with marginal variations and which involves for generation of organically bound chlorides. The typical lignin balance in fiber lines of these four approaches is presented below :-

CONVENTIONAL COOKING & BLEACHING

The conventional kraft cooking for bleached chemical pulp is quite common where we get pulp kappa number around 25. The pulp passes through the bleach plant of 3-4 stages with use of combination of different bleaching chemicals. The lignin balance of such plant is presented in Fig-5. The discharge of lignin as shown in the figure indicates the expected generation of AOX from the bleach plant.

CONVENTIONAL COOKING WITH OXYGEN DELIGNIFICATION

The introduction of oxygen delignification as extension of delignification for conventional cooking has shown appreciable advantage to reduce lignin entering to bleach plant and use of bleaching chemicals. A reduction of 35-40% pollution load including AOX, COD, BOD, Color, dissolved solids are obtained. The figure-6 shows that only about 9.5% of total lignin in wood goes to effluent from the bleach plant.

EXTENDED COOKING SYSTEM WITH OXYGEN DELIGNIFICATION

The most commonly acceptable system at present is use of extended cooking system to further reduce the

Fig. -6 Lignin Balance
Conventional Cooking with ODL

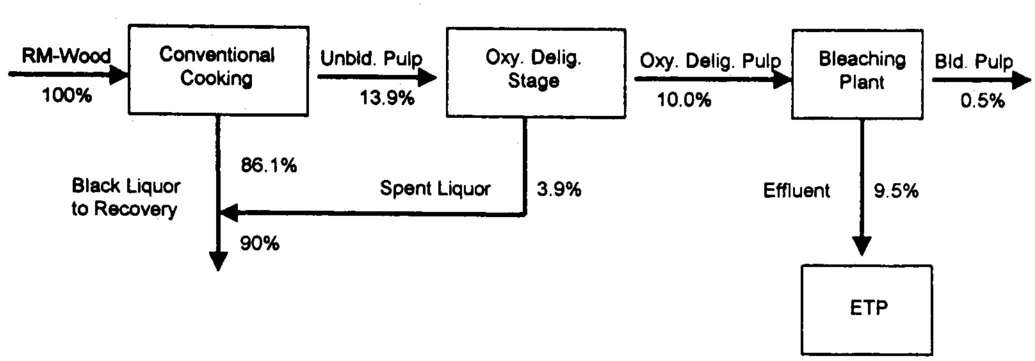


Fig. -7 Lignin Balance EDL with ODL

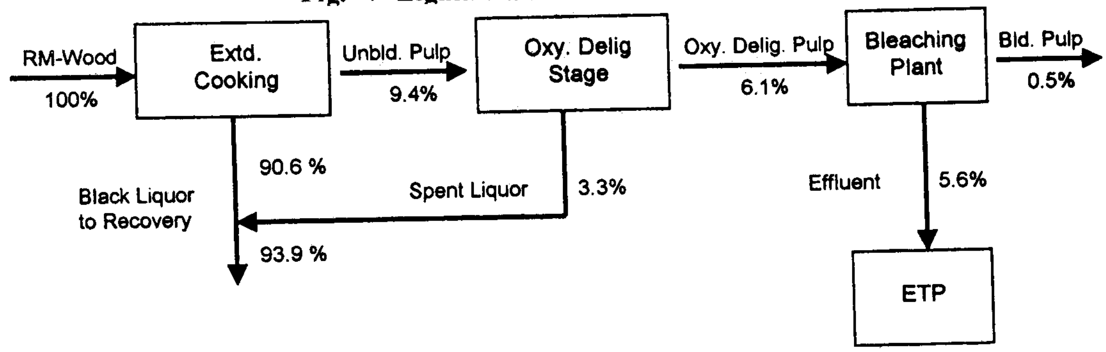


Fig. -8 Lignin Balance Light-ECF Bleaching

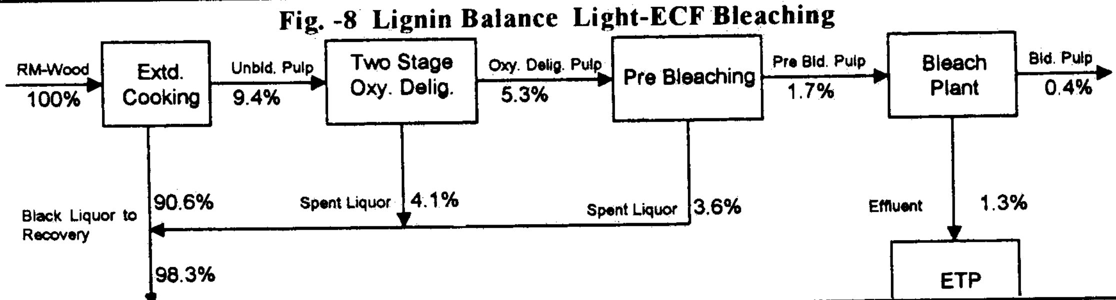
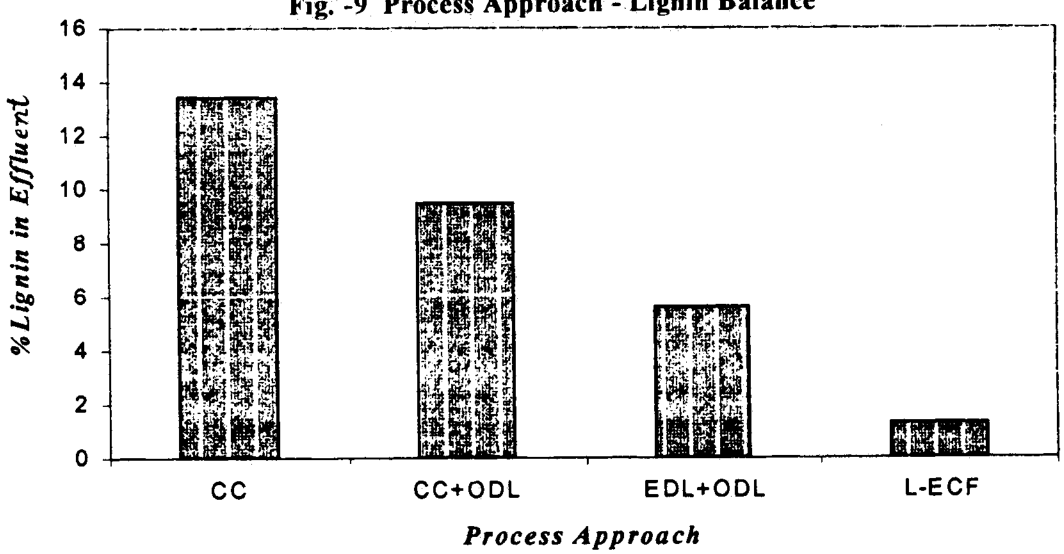


Fig. -9 Process Approach - Lignin Balance



lignin and subsequently carry out oxygen delignification. In this system pulp of at 10-11 kappa number enters in bleach plant and about 5.6% lignin goes to the effluent from bleach plant (Fig. 7). The AOX compound will be formed in bleaching and go with the effluent. It is quite common that for the system chlorine in normally not considered as bleaching chemical and bleaching sequence is normal as elemental chlorine free.

LIGHT- ELEMENTAL CHLORINE FREE BLEACHING

In order to further improve the system as described above or rather close the system this approach is adopted. In this approach after extended delignification, which commonly uses two-stage oxygen delignification. The pulp obtained is passed through chelating stage to remove the metal ion and ozone in used in first stage of bleaching which is followed by oxidative extraction stage may or may not be use peroxide. The Eo stage becomes the part of brown stock washing and recovery operation. This system significantly reduces AOX formation and discharges to effluent. The lignin balance is shown in Fig-8.

A summary of lignin balance of above approaches

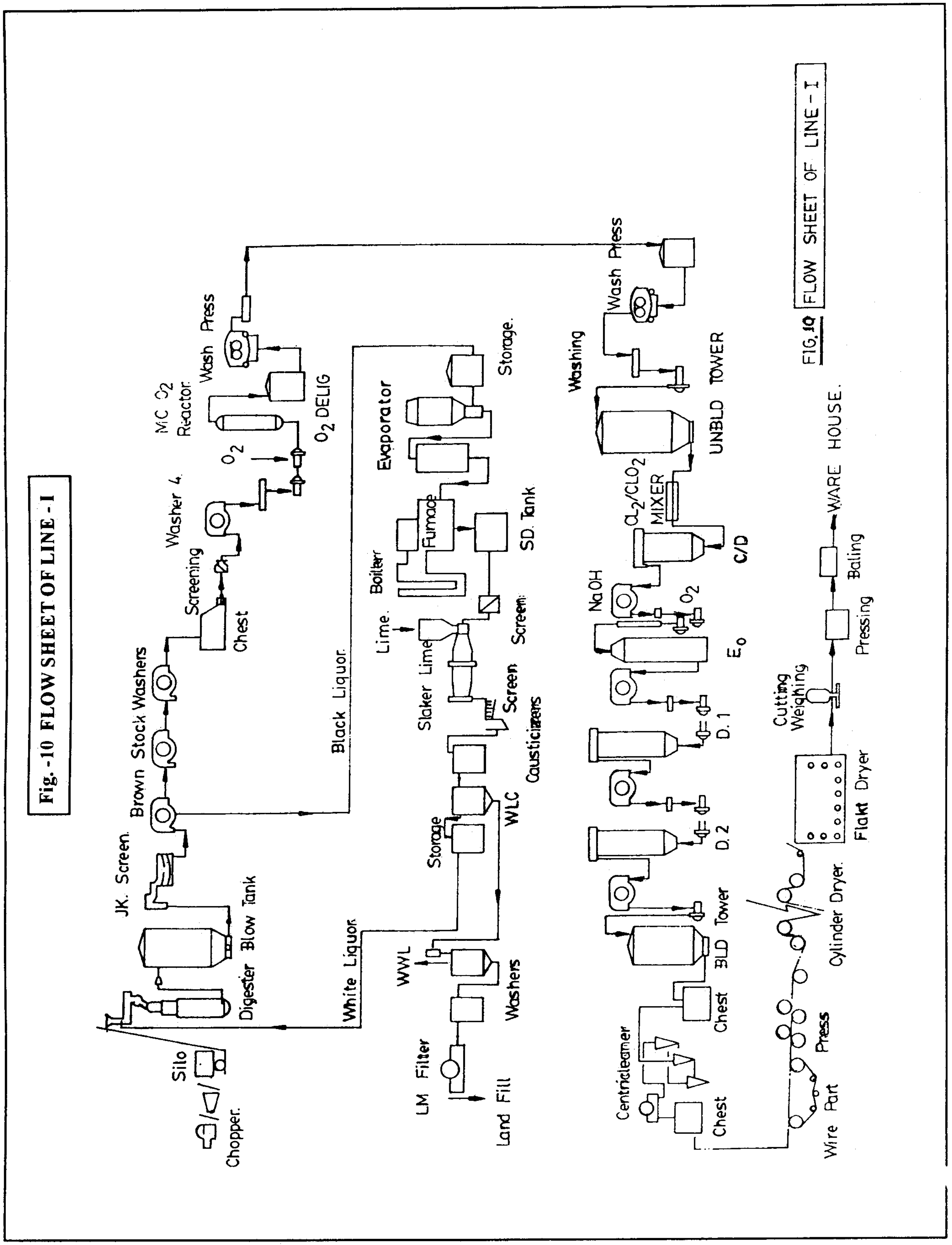


Fig.-10 FLOW SHEET OF LINE - I

FIG.10 FLOW SHEET OF LINE - I

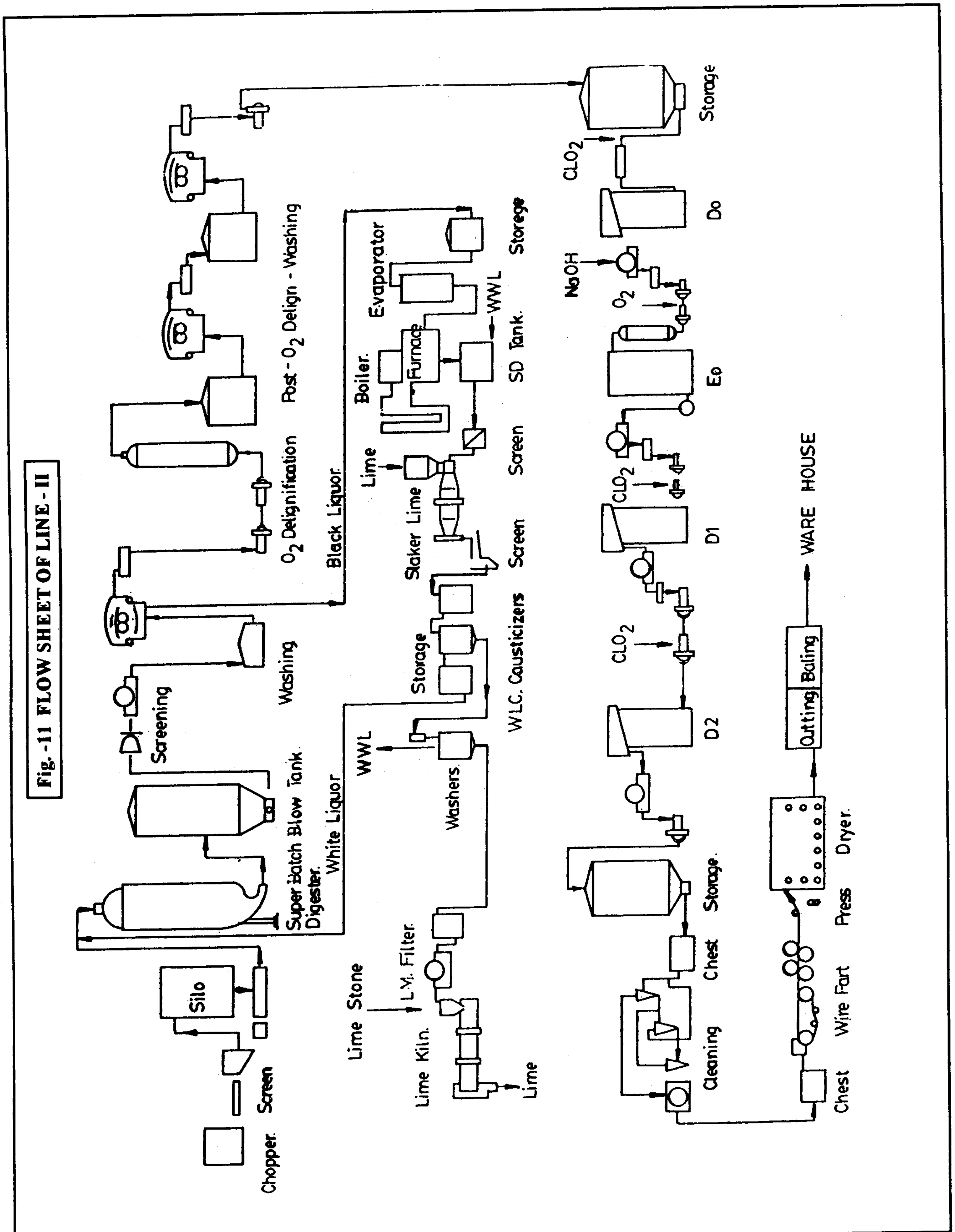


Fig. -11 FLOW SHEET OF LINE - II

TABLE-2 TYPICAL INVESTMENT COSTS

Basis : 100,000 TPA Pulp Mill

S. No.	System	Cost (M.USD)	Remarks
1.	Debarking Drum	3	- Disposal of bark
2.	Extended Delignification	12	- Higher recovery capacity
3.	Oxygen Delignification	10	- Higher recovery capacity
4.	Wash Press	2	
5.	ClO_2 generation plant	16	
6.	Oxygen Reactor for Eo stage	1	
7.	Activated Sludge Process-ETP	10	

is presented in Table-1 and Fig.-9 for comparison. A typical investment costs for installation of some of these systems individually are presented in Table-2.

PHOENIX EXPERIENCE

Phoenix Pulp and Paper Public Co., Ltd., Thailand, is a 200,000 TPA market pulp mill from Bamboo, Kenaf and Eucalyptus. Its line 1 started in 1982 and second line started in 1994. The present system in both the fiber line are briefly described below:

Process Details

Phoenix I (Fig. - 10)

- Raw material handling part debarking, chipping and screening.
- Convention kraft process with continuous Kamyr digester.
- Knotters, brown stock washer and screening.
- Medium consistency oxygen delignification (introduced in 1994).
- Bleaching sequence C/D Eo D D.
- Bleaching stage cleanliness and screening.
- Sheeting M/C.

Phoenix II (Fig.-11)

- Wood handling, debarking chipping and screening.
- Extended delignification - SuperBatch Cooking.
- Medium consistency oxygen bleaching.
- Element chlorine free bleaching sequence Do Eo $D_1 D_2$.
- Bleaching stage centricleaning and screening.
- Sheeting Machine.

WASTE WATER MANAGEMENT

The effluent from both lines is treated in Activated Sludge based effluent treatment plant. The treated effluent which meets all regulatory norms i.e. BOD, COD, TDS, SS, etc. All the treated effluent is used for irrigation of eucalyptus plantation.

A periodic check of Dioxin in treated effluent is done and the values are coming as not detectable level. Presently this is no regulation for AOX. However, the AOX values tested for treated effluent of mill are below 0.3 kg/tonne pulp. Further efforts are in progress to improve over all environmental performance with respect to utilization of resources and reduction of emissions.

ENVIRONMENTAL REGULATION

It is always advocated by most of the regulating authorities to adopt **best available economically achievable technology** with respect to address environmental concerns. US Environmental Protection Agency **(EPA)** is considered world over as a reference organization to adopt regulatory norms. EPA cluster rules phase-1 to control both effluent discharge and air emission from pulp, paper and paperboard. mill published in 1998. This was the first time EPA issued integrated, multi-media regulations. AOX limits for bleached kraft mills in the regulation are given as 0.95 kg/Tonne pulp for discharge maximum and 0.62 kg/Tonne pulp as monthly average. It may be mentioned that minimum three years compliance time frame has been given. The rule also provide individual mills with incentives to adopt Advanced Pollution Control Technologies that will lead to further reduction in toxic pollutants discharge beyond the water discharge limits set in the rule.

Many of the countries have also fixed with their norms for AOX discharge. It may be mentioned that after taking basic guide lines from the experience and information from advance countries and at the same time real environmental impacts, the regulatory authorities of the country has to undertake extensive study in cooperation with industry to evolve a logical and achievable guide lines and norms to address AOX issue. The environmental indicator setting up exercise for the country has to be taken up very seriously. The regulatory authorities should continue to offer incentives to adopt the advanced technologies to reduce the pollutants discharge.

CONCLUSIONS

Amid growing public, environmental and scientific concerns the generation and discharge of organically bound chlorides from a recognized as an important environmental indicator in many countries for monitoring the performance of bleached pulp mills using the chlorine compounds. Based on the various technological developments and as presented in the paper it can be concluded that mills have to identify most techno-economically viable configuration of process from cooking area, through bleached plant to effluent treatment and disposal. It may be mentioned that the regulations are to be based on overall structure of the indusrty and its environmental impacts. However, necessary considerations should be also given with regard to technological and environmental advancements in progress on global basis.

REFERENCE

1. Stringer, AM, Industrial Environmental Control - Pulp & Paper Industry, TAPPI Press, USA. 1993.
2. Reeve, DW, etal, Pulp Bleaching & Practices Tappi Press, 1996.
3. Patrick K.L., Bleaching Technology Chemical & Mechanical Pulp, Miller Freeman Publication, 1991.
4. Berry Rechard; World Pulp & Paper, International review 1992, Sterling Publication, UK.
5. Miner Reid, etal, Tappi Vol. 82 No. 4 Page 135-1999.
6. Vice K, Pulp & Paper Canada, Pulp & Paper Canada W 99, No. 12 T 456 (1998).
7. Hsich, S.J., etal, Tappi Vol 74 No. 11, P 117-1998.
8. Pryke, DC, etal, Pulp & Paper Canal, Vol. 96, 11 P 76-1995.
9. Chopped. D., etal, Tappi Vol 84, No. 2, P-26-2001.
10. Weber N, etal, Pulp & Paper Canada, Vol 101, No. 12, P-97-2000.
11. Matsukura. M, Tappi, Vol 77, No. 1, P176-1964.
12. EPA's Final Pulp, Paper and Paper board Cluster Rule-Overview, EPA Publication.