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

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ABSTRACT

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

INTRODUCTION

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

Technological status of Indian pulp & Paper Mills

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

Large Scale Mills (with chemical recovery process)

Small Scale Mills (without chemical recovery process)

The technological status of these mills is discussed below:

Scale of Operation

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

Level of Technology

Pulping process

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

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

Pulp washing system

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

Bleaching process

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

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

Status of AOX level in Pulp and Paper Mills Indian perspective

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

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

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

Source : Information available in literature and from association of mills

Table 2 Status of AOX in Indian Pulp and Paper Mills

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

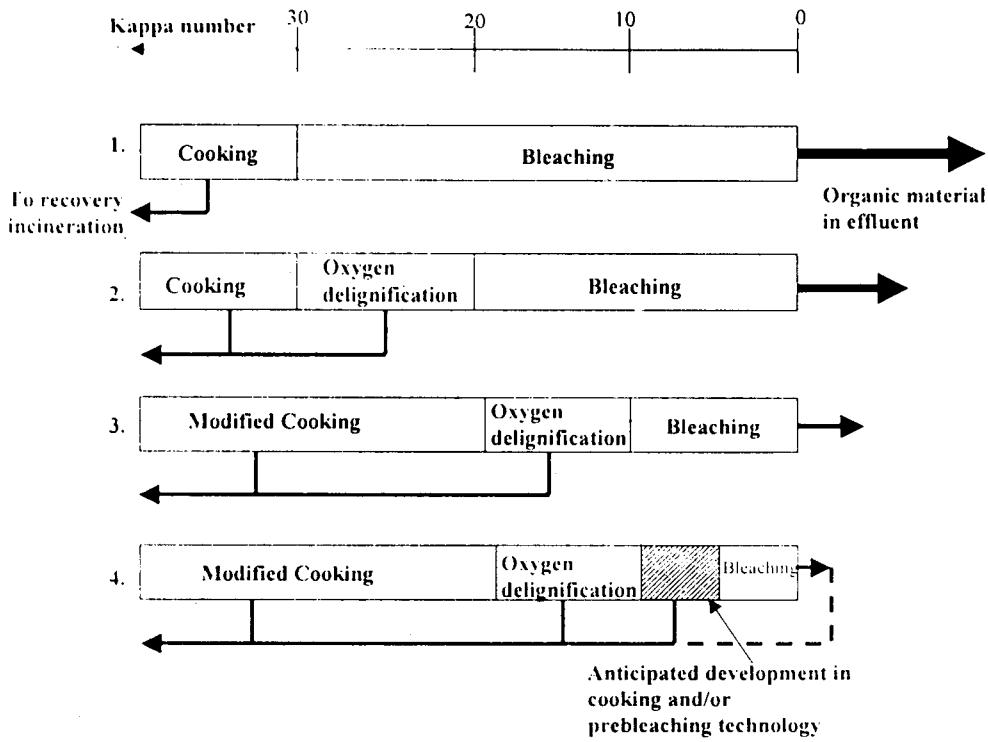

Fig. 1 Development of alternate pulping process

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

High kappa number of pulp due to absence of chemical recovery.

- High carryover of black liquor alongwith pulp going to bleaching plant.
- Use of high dosage of elemental chlorine.
- Obsolescence in technology & equipments.

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

Integrated approach to reduce AOX level

In view of increased global competitiveness, preference for eco-friendly paper products, imposition of stringent environmental regulations, Indian pulp and paper mills particularly large mills are required to adopt energy efficient and environmentally friendly new fibre line to

efficient and environmentally friendly new fibre line to become at par with the international status . This appear to be a difficult task primarily due to low scale of operation and use of mixed fibrous raw materials. However the level of AOX and other pollutants may be reduced to maximum extent in Indian paper mills by adoption of integrated approach involving better house keeping , process optimisation and other measures. These measures as given below, may be implemented with minor process modification and some capital investment to reduce the level of AOX :

Controlled Pulp Mill Operation

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

Imporved Pulp Washing

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

Substitution of Elemental Chlorine with Chlorine dioxdide

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

Oxidative Alkali Extraction Bleaching

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

Improved Chemical mixing in the bleach plant

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

Increased Use of Recycled Fibre

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

Post Digester leaching of pulp

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

Enzymatic prebleaching

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

enzyme used. Some of the large mills have started the use enzymatic pre bleaching to achieve high brightness of pulp.

Elimination of Chlorination Stage Filtrate Recycle.

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

Biological Treatment process

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

CONCLUSION

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