Chlorine Dioxide Substitution During Bleaching of Pulp - An Attempt Towards AOX Reduction in Effluent.

Sanjay Kumar Yadav, Nirmal Singh, K.D Prasad and S.S Arora

In the last 2-3 decades, environmental issues have been the dominant driving force for development of both pulping and bleaching processes. The bleach plant effluents have traditionally been the major contributors to polluting discharge. Proposed regulations of adsorbable organic halide (AOX) and the consumer's desire to buy environmentally friendly products have led pulp mills to implement AOX reduction strategies. The level of AOX can be decreased by extended delignification, oxygen delignification, substitution of Chlorine dioxide for chlorine, ECF Bleaching and TCF bleaching. The present paper highlights the effects of chlorine dioxide (ClO_2) substitution in sequence $C/DE_{OP}D_{||}D_2$ applied to Kraft pulp of mixture of hardwoods and bamboo. Based on lab study, process scale trial up to 40% substitution was conducted. BOD_{3}, COO, AOX and color were monitored for the effluent generated from bleach plant besides the regular parameters like brightness, reverted brightness and CED viscosity. Chlorine dioxide substitution reduced load of BOD_{3}, COD and Color with large reduction in AOX with substantial increase in 0.5% CED viscosity and reduction in P.C No. of pulp. 40% substitution in plant has resulted approx. 37% reduction in AOX in mill effluent.

INTRODUCTION

In the present scenario of strict new environmental regulations, the Indian pulp and paper industries have to adopt the new technologies for reducing the discharge of the group parameters like BOD, COD, AOX and color in effluent. Several mills, mostly in Scandinavia and Western Europe have opted to produce TCF pulp, while nearly all mills in North America use elemental chlorine free (ECF) processes (1). During these days, the effect of the pulp and paper industry on the environment is being closely examined. Mills that bleach pulp with chlorine-based compounds discharge chlorinated organics into the environment. Most of the effluent load of organic substances, particularly of chlorinated organic substances in a bleach kraft pulp mills originates from the chlorine and alkali stages (2). Approximately 80% of chlorine is contained in high molecular weight material and the remainder is contained in discrete compounds. Over 200 chlorinated organic compounds have been identified (3). A simple and economical method for estimating the amount of chlorinated organic material is AOX (adsorbable organic halide). AOX is easy to analyse. Adsorption of the halides on active carbon directly from the water solution is done. The carbon is washed and burnt to detect HCl. The following empirical relationship exists between the charge of chlorine containing bleach chemicals as active chlorine and AOX value for bleach plant effluent (5).

$$AOX = K [Cl_2 + ClO_2/5 + Hypo/2]$$

K = 0.11-0.14 for kraft pulps

Today it is generally accepted that the formation of chlorinated organics is a function of the consumption of elemental chlorine and thus AOX is linearly proportional to the consumption of elemental chlorine (6). Axegard showed that AOX decreases as chlorine dioxide substitution increases and varies linearly with the elemental Cl_2 used in the first stage as shown in fig. (1) (4).

An increasingly attractive means to reduce the discharge of chlorinated organics content is to improve brown stock washing, use of extended delignification techniques for removing as much lignin as possible before the pulp enters to bleach plant and to modify the bleaching process either by use of oxygen delignification or substitution of ClO_2 for chlorine (7). These techniques serve to reduce chlorinated organics as well as BOD (biochemical oxygen demand), COD (chemical oxygen demand), and toxicity. BOD and acute toxicity are caused by biodegradable, low-molecular-weight compounds, high-molecular-weight compounds are the primary cause of COD, color, and chronic toxicity (8,12). ClO_2 substitution reduces BOD 20-30% and color by 5080% at 90-100% substitution (8). Douglas C.Pyrke has shown that Color & AOX can be reduced by increasing ClO_2 substitution (9). Not only ClO_2

Ballarpur Industries Ltd., Unit Shree Gopal Yamunanagar -135001 (Haryana)

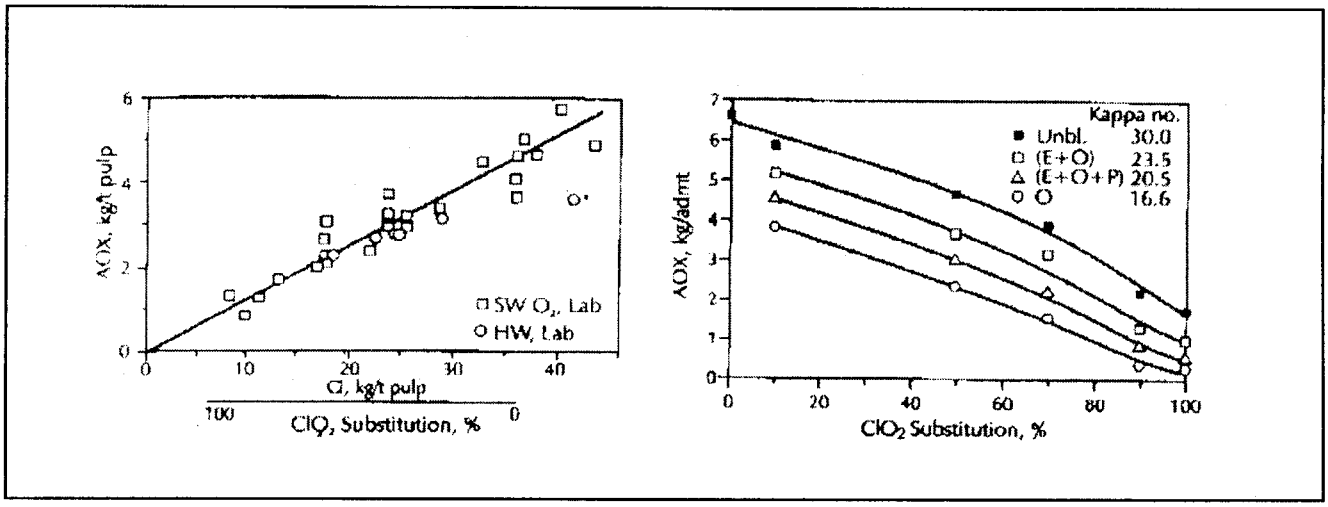

Figure 1 Axegard charts showing relationship between AOX formation and ClO_2 substitution

substitution reduces the pollution load, but also it is fully compatible for producing market pulps of 89-90% ISO brightness (10).

Industrial use of chlorine dioxide to replace chlorine was at first only a means of protecting the strength of the pulp; 5-10% of the chlorine was replaced with equivalent chlorine dioxide. ClO_2 substitution did not gain wide acceptance until the late 1980s when environmental concerns about chlorinated organic matter led the industry to decrease chlorine use and adopt substantial and later complete replacement with chlorine dioxide (12).

Chlorine dioxide is an oxidant, which accepts five electrons per molecule in being reduced to chloride ion:

$$ClO_2 + 4\,H^+ + 5\,e^- \rightarrow Cl^- + 2\,H_2 \quad (1)$$

The molecular weight of chlorine dioxide is 67.5 and so its equivalent weight is 13.5 (67.5/5). Chlorine accepts two electrons, so its equivalent weight is 35.5 (71/2)

$$Cl_2 + 2\,e^- \rightarrow 2\,Cl^- \quad (2)$$

Therefore, in substituting chlorine dioxide for chlorine to provide equivalent electron transfer, one kg of chlorine dioxide is equivalent to 2.63 kg (35.5/13.5) of chlorine. ClO_2 substitution expressed in percent and is based on equivalent chlorine. Equivalent chlorine applied on pulp is expressed as Kappa factor also known as Chlorine multiple:

Chlorine as % equivalent chlorine = kappa factor x unbleached pulp Kappa No.

In view of reducing of AOX level, we studied the effect of chlorine dioxide substitution on bleach plant effluent in laboratory and taken a process trial with 30 & 40% chlorine dioxide substitution in the first stage of bleaching. The main objective was to study the effectiveness of substitution in reducing AOX level in effluent to meet the statuary requirement in the future.

Experimental Approach

Laboratory studies were conducted with plant washed unbleached pulp (bamboo 20% + mixed hard wood 80%) of Kappa no.17.5 by following the plant bleaching sequence C/ $DE_{OP}D_1D_2$ with 10, 30, 40 & 100% substitution. Each bleaching stage, except E_{OP}, was carried out by taking pulp in polythene bags with required amount of chemicals and kept for required time at constant temperature water bath as per the conditions given in table-1. Eop stage was performed in tumbling type digester at 75°C by adding required caustic, hydrogen peroxide and oxygen. First oxygen pressure at 5 kg/cm^2 was given for 30min. thereafter it was reduced to 2.5 kg/cm^2 for rest 90-minute time. Dewatering was done on Buckner funnel in all the stages and collected the effluent, thereafter washing was done by filtered mill water.

Laboratory studies were also extended to oxygen delignification in order to reduce the kappa no. before bleaching stage and to reduce the use of bleaching chemicals. Oxygen delignified pulp was further bleached by bleaching sequence $D_0E_{OP}D_1D_2$ The details of bleaching chemicals and conditions are given in table-2.

The final bleached pulps, obtained from all experiments under different chlorine dioxide substitution and oxygen delignification followed by $D_0E_{OP}D_1D_2$ sequence, were analyzed for brightness, Viscosity & P.C No. The results are tabulated in table-3. The effluent generated from each stage was finally mixed in ratio C/ $D:E_{OP}:D_1:D_2$::43:23:24:10 on the basis of plant back water utilization and combined effluent was analyzed for pH, BOD, COD, color and AOX. The results are indicated in table-4.

PROCESS TRIAL

The mill is producing 220 mt/day of superior varieties of writing printing

Table 1

Bleaching conditions

Particular	Unit	$C/DE_{OP}D_1D_2$	$C/DE_{OP}D_1D_2$	$C/DE_{OP}D_1D_2$	$D0E_{OP}D_1D_2$
C/O STAGE					
Unbld. Kappa No		17.5	17.5	17.5	17.5
Kappa factor		0.22	0.25	0.26	0.3
Cl_2 (as Cl_2)	%	3.85	4.37	4.55	5.25
Cl_2:ClO_2		90:10	70:30	60:40	0:100
Retention time	min.	45	45	45	45
Temperature	°C	Ambient	58-60	58-60	60-62
Consistency	%	3	10	10	10
pH Initial		2.3	3.4	3.5	3.4
Residual Chlorine	g/l	0.02	0.0021	0.002	0.0032
E_{OP} STAGE					
Alkali charge	%	2.5	2.5	2.5	2.5
H_2O_2 charge	%	0.5	0.5	0.5	0.5
Oxygen pressure	kg/cm²	5 for 30 min. 2.5 for 90min.	5 for 30 min. 2.5 for 90min.	5 for 30 min. 2.5 for 90min.	5 for 30 min. 2.5 for 90min.
Temperature	°C	75	75	75	75
Consistency	%	10	10	10	10
pH Initial/Final		11.9/10.9	11.8/11.6	11.9/11.6	12.1/11.5
D_1STAGE					
ClO_2 charge	%	0.8	0.8	0.8	0.8
Retention time	min.	180	180	180	180
Consistency	%	10	10	10	10
pH final		4.4	4	4.1	4.2
Temperature	°C	70	70	70	70
Residual ClO_2	g/l	0.051	0.019	0.018	0.038
D_2 STAGE					
ClO_2 charge	%	0.4	0.2	0.2	0.2
Retention time	min.	180	180	180	180
Consistency	%	10	10	10	10
pH final		3.9	4.1	4.2	4.2
Temperature	°C	70	70	70	70
Residual ClO_2	g/l	0.055	0.022	0.028	0.018

paper, industrial paper and coated papers & boards. The mill has modern DCS controlled bleach plant having a capacity of 180 mt/day bleached pulp. The unbleached pulp is bleached to a brightness level of 90% ISO by employing four stage $C/DE_{OP}D_1D_2$ bleaching sequence with 8% ClO_2 substitution of chlorine with chlorine dioxide. Chlorine dioxide plant is having enough capacity of 5 mt/day and is based on latest R-8 process a state of art technology. Switch over to elemental chlorine free (ECF) bleaching will not be a constraint at any points of time.

Based on laboratory findings, process scale trial was planned with 30 and 40% substitution in first stage of bleaching sequence in order to explore the possibility for reducing the AOX level in mill effluent. The trial was conducted for two weeks. The chlorine and chlorine dioxide addition during C/D stage have been indicated in table-5.

The bleaching conditions in Eop, D_1 & O_2 stage more or less on the same line as given in table-1. The bleaching chemicals consumption during normal run i.e. with 8% substitution and with 30% & 40% substitution of chlorine dioxide are given in table-6.

The bleached pulp was evaluated for

Table 2

Oxygen Delignification Conditions (Laboratory experiments) Kappa no. of unbleached pulp: 17.5

Kappa no. of pulp after oxygen delignification : 10.5

Particular	Unit	O	D_0	Eop	D_1	D_2
Kappa factor		-	0.3	-	-	-
Alkali charge	%	2.5	-	2.5	-	-
H_2O_2 charge	%	-	-	0.5	-	-
ClO_2 charge	%	-	1.19	-	0.8	0.2
Oxygen pressure	kg/cm²	7	-	5 for 30 min.	-	-
		-	-	2.5 for 90min.	-	-
Temperature	°C	90-95	60-62	75	70	70
Consistency	%	10	10	10	10	10
Retention time	min.	60	45	-	180	180
pH Initial/Final	cp	11.9/11.1	3.6	12/11.1	3.9	3.7
Residual Chlorine	g/1	-	0.0032	-	0.012	0.006

Table 3

Pulp Quality (Laboratory experiments)

Particular	Unit	$C/DE_{OP}D_1D_2$	$C/DE_{OP}D_1D_2$	$C/DE_{OP}D_1D_2$	$D_0E_{OP}D_1D_2$	$OD_0E_{OP}D_1D_2$
Unbld. Kappa No.		17.5	17.5	17.5	17.5	10.5
Kappa factor		0.22	0.25	0.26	0.3	0.3
Cl_2 : ClO_2	%	90:10	70:30	60:40	0:100	0:100
ISO Brightness	%	90	90.2	90.4	90.8	91.2
0.5 % CED Viscosity	cp	13.8	14.9	15.3	17.8	15.5
P.C No.		0.36	0.35	0.34	0.32	0.31

Table 4

Effluent Characteristics (Laboratory experiments, untreated effluent)

Particular	Unit	$C/DE_{OP}D_1D_2$	$C/DE_{OP}D_1D_2$	$C/DE_{OP}D_1D_2$	$D0E_{OP}D_1D_2$	$OD_0E_{OP}D_1D_2$
Cl_2 : ClO_2	%	90:10	70:30	60:40	0:100	0:100
pH		10.1	9.6	9.5	9.4	9.9
COD	Kg/t	33.7	33.2	33	28.2	18
BOD	Kg/t	12.8	11.2	10.8	8.3	6.7
COLOR	Kg/t	22.2	16.5	14.9	10.6	5.5
AOX	Kg/t	1.47	1.2	1.01	0.72	0.47

brightness, Viscosity, P.C No and also for strength properties at 300 deg CSF under different chlorine dioxide substitution. The average results have been given in table-7. The mills effluent was also analyzed for its characteristics like pH, BOD, COD, color and AOX. The average results have been tabulated in table-8.

RESULT & DISCUSSIONS

A. Lab studies

The effect of ClO_2 substitution in 1st stage of bleaching sequence on bleached pulp quality based on laboratory studies have been given in table-3. With increased substitution of chlorine dioxide, the viscosity of final bleached pulp increases and brightness reversion of pulp decreases as indicated by lower post color number (P.C No.). It means brightness stability is superior. This is due to the high oxidizing power (giving 5 electrons in reducing to chloride ion as compared to 1 electron in case of Cl_2) and more selective in removing lignin from pulp without degrading cellulose. Approx. 0.4 & 0.8% brightness, 1.5 & 4.0 cp viscosity

Table 5

C/D Stage Plant Conditions

Particular	Unit	8% Substitution	30% Substitution	40% Substitution
Unbld. Kappa No.		17-19	17-19	17-19
Cl_2 (as Cl_2)	%	4.35	3.23	2.85
ClO_2	%	0.14	0.56	0.74
Retention time	min.	45	45	45
Consistency	%	7.1	7.1	7.1
Temperature	°C	51-55	56-58	56-58
pH Final		1.8	2.2	2.1
Residual chlorine	%	0.054	0.009	0.004

Table 6

Bleach Chemicals Consumption (Plant trial), Kg/t of Pulp

Particular	Cl_2	ClO_2	NaOH	H_2O_2	O_2	SO_2
Normal run	43.50	14.00	33.20	9.00	5.10	1.40
8% substitution of ClO_2						
Trial run	32.30	19.90	29.50	9.00	4.60	1.40
30% substitution of ClO_2						
Trial run	28.50	21.00	25.60	9.10	4.50	1.40
40% substitution of ClO_2						

Table 7

Pulp Quality (Plant trial)

Particular	Unit	8% Substitution	30% Substitution	40% Substitution
Unbld. Kappa No.		17-19	17-19	17-19
ISO Brightness	%	89.6	89.7	89.8
0.5 % CED Viscosity	Cp	13.3	16.0	17.0
PC No.		0.88	0.57	0.56
Breaking length	km	8.6	8.8	9.0
Tear factor		70	74.1	76.2
Burst factor		62	66	67

gain with 0.02 & 0.04 reduction in P. C No were measured on 40 and 100% substitution respectively as compared to 10% substitution, where as 1.2% brightness and 1.7 cp viscosity gain with 0.05 reduction in P.C No were noticed on oxygen delignification before bleaching.

Effluent characteristics such as pH, COD, BOD, Color and AOX for all experiments have been tabulated in table-4. Results clearly indicates that 40 & 100% ClO_2 substitution reduces 2 & 6 % COD, 15 & 35 % BOD, 7 & 21% Color and 31 & 51% AOX in bleach effluent as compared to 10% substitution respectively, while oxygen delignification with 100% substitution of ClO_2 reduces approx. 47% COD, 48% BOD, 75% Color and 68% AOX as compared to 10% substitution. It means that kappa no. reduction before bleaching by oxygen delignification is helpful in reducing AOX level to a great extent. There is significant reduction in bleaching chemical consumption with oxygen delignified pulp. There is saving of approx. 8 kg chlorine dioxide per tonne of pulp with 1 % higher brightness of bleached pulp.

b. Process trial

Results of pulp quality from 30 and 40% substitution of ClO_2 as compared to normal 8% substitution have been given in table-7. Process trial also shows the same trend in CED Viscosity and P. C No. as obtained in laboratory. Although no significant increase in brightness was noted in plant but there was significant increase in CED

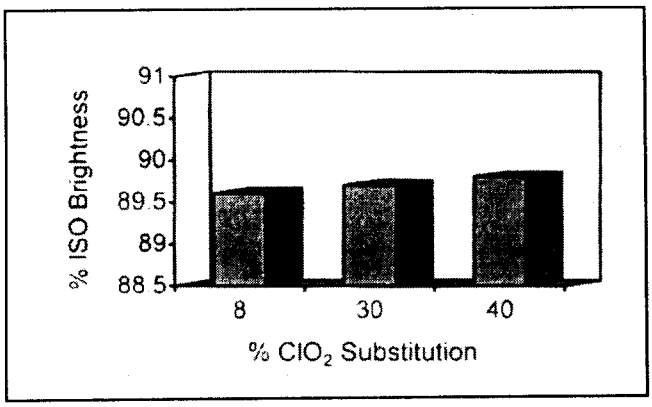

Figure 2 % ISO Brightness of pulp in plant trial versus ClO_2-substitution.

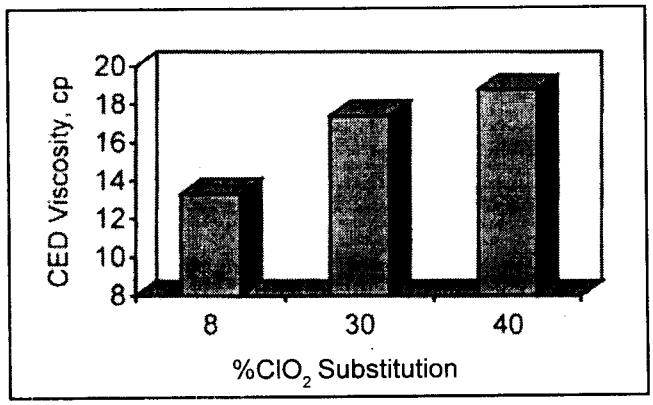

Figure 3 CEO Viscosity of pulp in plant trial versus ClO_2-substitution.

Table 8

Treated Effluent Characteristics (Plant Trial, sample taken from ETP plant)

Particular	Unit	8% Substitution	30% Substitution	40% Substitution
pH	7.6	7.5	7.5	
COD	mg/l	66	60	46
BOD	mg/l	11.5	10.0	9.6
COLOR	pt-co unit	156	134	120
AOX	mg/l	4.7	3.4	2.8
AOX	kg/t	0.75	0.56	0.47

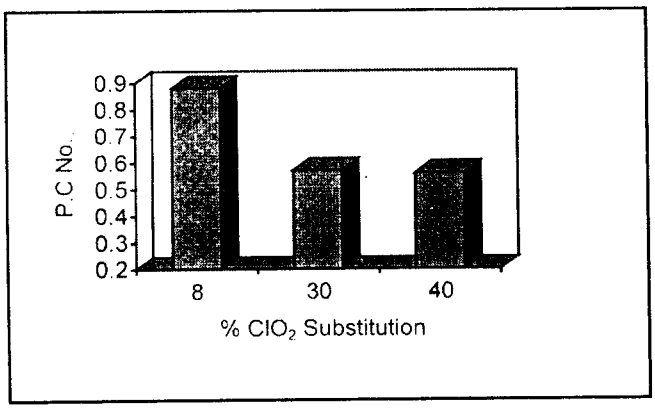

Fig.4: P.C No. of pulp in plant trial versus ClO_2-substitution

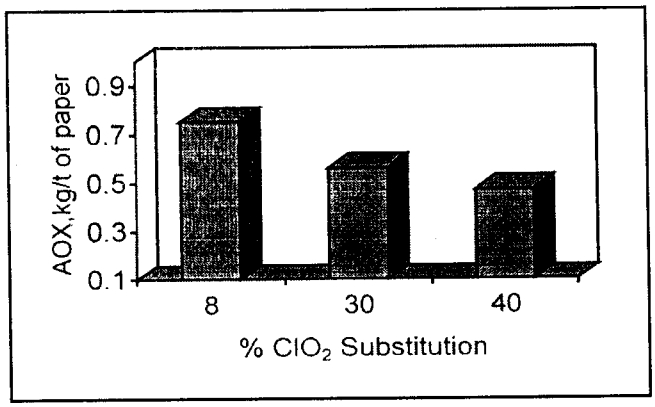

Fig.5: AOX of treated Mills Effluent during plant trial versus ClO_2-substitution.

Viscosity i.e from 13.3 to 17.0 cp and reduction in P.C No. i.e from 0.88 to 0.56 on 40% replacement of Cl_2 by ClO_2 in first stage of bleaching.

Fig-2, Fig-3 & Fig-4 illustrates the effect of ClO_2 substitution on % Brightness, Viscosity and P.C No. respectively.

Treated mills effluent characteristics have been given in table-8. Plant scale data also reveals the fact that ClO_2 substitution reduces the effluent load in terms of COD, BOD, Color and AOX. Although 30-40% substitution has marginal effect on COD, BOD and Color, but there is significant reduction of AOX level in effluent. Fig-5 illustrates the effects of ClO_2 substitution on AOX of treated mill effluent.

40% substitution of ClO_2 decreased the amount of discharge of Chlorinated compounds measured as AOX in mill effluent i.e. from 0.75 to 0.47 kg/t. Approx. 25 & 37 % AOX level is reduced in mill effluent on 30 & 40% replacement of Cl_2 by ClO_2 in first stage of bleaching as compared to present level of 8 % substitution respectively.

CONCLUSION

The substitution of chlorine dioxide for chlorine in the first stage of

bleaching is fully compatible for producing pulp of 89-90% ISO brightness. The laboratory studies and mill trial gave almost same trend of reducing the pollutant load like COD, BOD, Color, & AOX. Chlorine dioxide substitution results in superior pulp quality in terms of viscosity, brightness stability and strength properties. AOX can be largely reduced by the increased substitution of chlorine dioxide in first stage of bleaching sequence in place of chlorine. The present bleaching process has no adverse affect/impact on environment in regards to treated effluent. The present level of 0.75 kg/t of paper AOX in treated effluent is even below 1 kg/t of paper and with 40% substitution, it only 0.47 kg/t of paper. With such low value, the mill will never be under environmental constraint for AOX level.

The mill is also geared up with 100% substitution i.e. towards elemental chlorine free (ECF) bleaching.

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