Reinforced Oxidative Extraction Stage With Higher H_2O_2 Dosage- A Mill Experience To Reduce The Bleaching Chemical Cost And Chlorinated Compound For Cleaner Environment.

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ABSTRACT

In order to reduce the bleaching cost and problem of organochlorine compound during bleaching of pulp, it has become necessary to reduce the use of chlorine dioxide in existing bleaching sequence without affecting the pulp quality. This study examines the effect of higher dosage of hydrogen peroxide in oxidative extraction (Eop) stage of four stage C/DEopD_1D_2 bleaching sequence. The objective was to determine the impact of increased hydrogen peroxide dosage in Eop stage on chlorine dioxide reduction, final pulp brightness, brightness reversion and effect on effluent quality. Lab results showed that hydrogen peroxide found to be a promising bleaching chemical, increase in peroxide dosage from 0.5% to 1.0%(100%H_2O_2) in Eop stage reduced the usage of chlorine dioxide in subsequent D_1&D_2stage by approximately 4.0kg/MT with improved final pulp brightness and whiteness by 0.4 and 0.6 points respectively and reduced effluent color and AOX by approximately 15% and 6% respectively. However, COD and BOD of effluent were more or less similar. Based on the lab findings, a plant trial was taken by increasing the hydrogen peroxide dosage from 0.6% to 0.9% (100%H_2O_2). Similar observations were found, reduction in of ClO_2 from 14.5kg/MT to 12.0kg/MT with final pulp brightness and whiteness increase by 0.4 & 0.6 point respectively. It also helped in reducing effluent color about 19%.

Key Wards: Oxidative Extraction, H_2O_2 bleaching, AOX, Effluent color

Introduction:

Chlorine dioxide has been the most popular bleaching agent for pulp bleaching process worldwide. Chlorine dioxide overcomes the problem of generating organochlorine compounds over the elemental chlorine. In the current scenario, bleach plants are more focussed to improve effluent quality while maintaining the pulp quality at low bleaching chemical cost. Chlorine dioxide is having less potential of generating organochlorine compound. Mills are replacing the chlorine in chlorination stage with 100% chlorine dioxide (D_{100}) stage or replacing/reducing the use of hypochlorite in the final bleaching stage. However, use of chlorine dioxide in pre or final bleaching stages also produces some organochlorine compound during bleaching process as a result of chemical reaction of lignin structure and chlorine dioxide AOX [1].

There are several processes to reduce the organochlorine compound in effluent such as Oxygen delignification, Ozone, Proxyacids, Enzymatic bleaching etc. Some process needs equipments modification and are cost intensive. Many factors have to be considered for selecting effective and economical way to minimize the problem. Hydrogen peroxide is capable of decreasing the disposal problems posed by chlorine-containing bleaching agents since no chlorinated organics nor chlorides are formed during hydrogen peroxide bleaching. Interest in utilization of hydrogen peroxide in delignification during the first stage of bleaching has been very small, mainly because oxygen bleaching is much more economical.

Addition of oxygen and hydrogen peroxide in extraction stage has become an accepted technology for pulp mill. Hydrogen peroxide in oxidative (Eo) stage has synergistic effect on the brightness and reduction in chemical requirement in subsequent bleaching stage and reduced effluent color [2].

The optimal use of hydrogen peroxide in the alkaline extraction stage requires careful observation and control of various operating parameters involved in the bleach plant. Under the optimal conditions, hydrogen peroxide can provide numerous results. Use of hydrogen peroxide in bleaching produces better final pulp brightness or reduces the requirement of other bleaching chemicals, improve brightness stability of bleached pulp, reduces the level of chlorinated compound in mill effluent and reduces bleaching chemical cost [3].

Chemistry of H_2O_2 during bleaching of pulp

When hydrogen peroxide is applied in bleaching of kraft pulp is reacts via three intermediate species formed during bleaching reaction [3].These forms of chemical depend on the pulp pH and presence of certain metals ions with the pulp.

- Perhydroxyl anion (HOO^-) under alkaline conditions
- Hydroxyl radical ($HO^.$) in the presence of transition metal like manganese and iron.
- Hydroxonium ion (HO^+) under acidic conditions

As shown in Fig.1 desired result in pulp bleaching is delignification and chromophore elimination. These two

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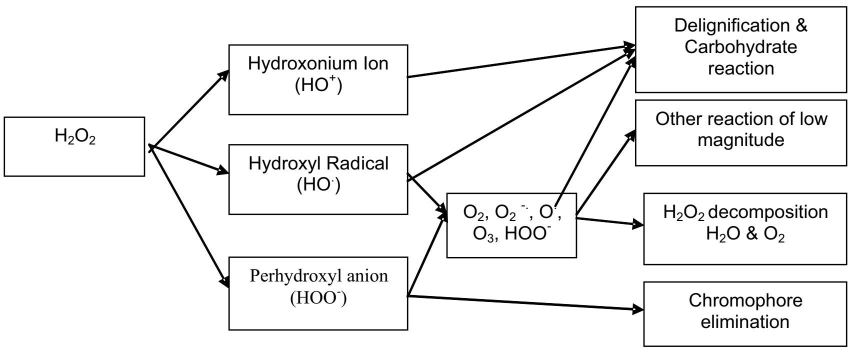

Fig.1: Hydrogen peroxide chemical reaction [3].

results are favoured under the alkaline conditions with limited or no transition metal present. Reaction with carbohydrate results in strength loss of pulp and other reaction can result in waste of hydrogen peroxide during bleaching process. Hans U. Soss et al [4] reported that higher alkalinity and temperature 75-90 °C favoured the generation active perhydroxyl anion for bleaching, however very high alkalinity and temperature both convert the hydrogen peroxide into hydroxyl radical and leads to decomposition of peroxide.

During this study, we have used the higher dosage of hydrogen peroxide more than 0.5% (100% H_2O_2) in Eo stage and determined its impact on bleaching cost / reduction in chlorine dioxide charge in subsequent D_1 and D_2 bleaching stage in C/DEopD_1D_2 bleaching sequence, final pulp brightness and brightness stability and bleach effluent characteristics.

Experimental Approach:

Lab Experiments were carried out on plant unbleached pulp of kappa number 18.1 having raw materials furnish (80-82% hard wood+18-20% bamboo). The unbleached pulp, collected from brown stock washer was centrifuged to a consistency of 30% so as to remove the free liquor from the pulp. The pulp was analysed for kappa number, unbleached viscosity and brightness according to Tappi test method T-236-om-99, T-230-om-99 and T-525-om-02 respectively. Results are shown in Table-I. The unbleached pulp was bleached by employing the C/DEopD_1D_2 bleaching sequence under bleaching conditions given in Table-II. Six set of experiments were designed with different dosage of H_2O_2 in Eop stage. Chlorination stage was performed in close lid plastic container by applying kappa factor 0.22 in C/D stage for chlorine dosing during chlorination stage. Hydrogen peroxide dosage in Eop stage was varied from 0.5 to 1.0% (100% H_2O_2) on BD pulp basis and correspondingly reduced the chlorine dioxide dosage in subsequent D_1 and D_2 bleaching stage.

Eop stage was performed in six bomb autoclave heated in oil bath at 75°C after adding the required caustic and hydrogen peroxide. The required oxygen pressure was maintained after achieving the desired temperature of 75°C, first 5.0kg/cm^2 pressure was given for 30- minute, which was then reduced to 2.5kg/cm^2 for remaining 90-mintute time.

Hydrogen peroxide was used 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 % (100% H_2O_2) of pulp in Eop stage in experiment No. I, II, III, IV, V and VI respectively under the same bleaching conditions as given in Table-II. After completion of bleaching time, bombs were taken out and cooled in a water tub. End pH & residuals H_2O_2 were determined and finally pulp was washed on buckner funnel with the help of demineralised water.

The D_1 and D_2 bleaching stage were carried out in plastic bag with different dosage of chlorine dioxide to achieve the same level of final pulp brightness. In the D_1 stage of experiment No.I, II, III and IV 0.9, 0.82, 0.74 and 0.66% ClO_2 was applied, keeping the same chlorine dioxide in D_2 stage (0.3% ClO_2) in all these experiments. In experiment No. V& VI, 0.68 and 0.60 % ClO_2 was used in D_1 stage, keeping the same chlorine dioxide 0.2% ClO_2 in D_2 stage. Final pH was maintained by adding the dilute H_2SO_4 in the pulp before adding ClO_2 in all the experiments. After completion of bleaching reaction time, end pH and residual chlorine were determined.

The final bleached pulps, obtained under the different sets of experiments were analysed for brightness, whiteness, brightness reversion and viscosity as per Tappi method T-525-om-02, T-260-om-60 and T-230-om-99 respectively. We have mixed the effluent generated under each bleaching stage of experiment No.-I in a ratio CD:Eop:D1:D2 :: 3.6:1:1:1 (on the basis of effluent generated per gram of pulp) after filtering & without washing. Similarly from experiment No.-V, the effluent from each stage of bleaching was mixed. These two effluent samples were analysed for pH, Color, COD, BOD and AOX, results are given in Table-IV.

Effect of higher hydrogen peroxide dosage on the CE permanganate number (CE P number), Eop brightness, chlorine dioxide consumption, brightness and whiteness of final bleached pulp are given in Fig-I, II, III and IV respectively.

Process trial:

Pulp mill is having 175-180MT/day bleached pulp production capacity. Mixed hard wood and bamboo is being used as a fibrous material for pulp production and pulp is bleached to brightness of 89+ ISO brightness by employing C/DEopD_1D_2 bleaching sequence with dosage of hydrogen

Table I Unbleached pulp properties

Particulars	Unit	
Kappa number		18.1
Viscosity	cps	17.6
Brightness	ISO %	29.8

Table II Bleaching conditions (C/DEopD$_1$D$_2$, lab experiment)

Particulars	Unit	Experiment No.					
CD STAGE		I	II	III	IV	V	VI
Kappa factor		0.22	0.22	0.22	0.22	0.22	0.22
Total Cl_2 (as Cl_2)	%	3.98	3.98	3.98	3.98	3.98	3.98
Cl_2:ClO_2		90:10	90:10	90:10	90:10	90:10	90:10
Retention Time	min.	45	45	45	45	45	45
Temperature	°C	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient
Consistency	%	3	3	3	3	3	3
Residual , Cl_2	%	0.034	0.034	0.034	0.034	0.034	0.034
Eop stage							
NaOH	%	2.5	2.5	2.5	2.5	2.55	2.6
H_2O_2 (100 %)	%	0.5	0.6	0.7	0.8	0.9	1.0
Oxygen pressure	kg/cm^2	5 for 30 min	5 for 30 min	5 for 30 min	5 for 30 min	5 for 30 min	5 for 30 min
	kg/cm^2	2.5-for 90 min	2.5 for 90 min	2.5 for 90 min	2.5 for 90 min	2.5 for 90 min	2.5 for 90 min
Temperature	°C	75	75	75	75	75	75
Consistency	%	10	10	10	10	10	10
pH Initial/Final		12/10.9	12/10.9	12/10.9	12/10.9	12/10.9	12/10.9
Residual H_2O_2	%	nil	nil	nil	Traces	0.012	0.018
CE P.Number		2.1	1.8	1.7	1.6	1.4	1.4
Eop Brightness, ISO	%	59.7	62.6	65.2	66.8	68.6	69.7
D_1 stage							
ClO_2 charge	%	0.9	0.82	0.74	0.66	0.68	0.60
Retention Time	min.	180	180	180	180	180	180
Consistency	%	10	10	10	10	10	10
pH final		4.0	3.8	4.0	3.9	4.0	4.0
Temperature	°C	70	70	70	70	70	70
Residual	%	0.031	0.028	0.036	0.015	0.015	0.016
D_2 stage							
ClO_2 charge	%	0.3	0.3	0.3	0.3	0.2	0.2
Retention Time	min.	180	180	180	180	180	180
Consistency	%	10	10	10	10	10	10
pH final		3.9	3.9	3.9	3.6	3.7	3.9
Temperature	°C	70	70	70	70	70	70
Residual	%	0.019	0.021	0.024	0.024	.024	0.021

Table-III Bleaching chemical consumption and bleached pulp properties (Lab experiment)

Particulars	Unit	Experiment No.					
Chemical		I	II	III	IV	V	VI
Chlorine	kg/MT	35.9	35.9	35.9	35.9	35.9	35.9
ClO_2	kg/MT	13.5	12.7	11.9	11.1	10.3	9.5
H_2O_2(100% H_2O_2)	kg/MT	5	6	7	8	9	10
NaOH	kg/MT	25	25	25	25.5	25.5	26.0
Bleached pulp							
Brightness, ISO	%	90.3	90.4	90.4	90.3	90.8	90.8
Whiteness, ISO	%	85.6	85.7	85.9	86.1	86.5	86.8
Viscosity (0.5% CED)	Cps	10.0	9.6	10.6	10.6	10.1	9.6
Post color number		0.40	0.34	0.32	0.29	0.27	0.26

Table - IV Bleaching effluent characteristics (Untreated, lab experiment)

Particulars	Unit	Experiment No.	
		I	V
pH		3.61	3.64
Color (Pt Co unit)	mg/l	473	403
COD	mg/l	640	650
BOD	mg/l	200	200
AOX	mg/l	43.5	40.9

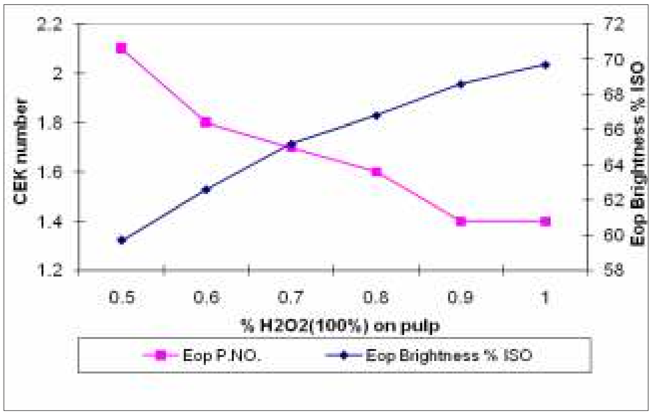

Fig.2: H_2O_2 Vs CEK number and Eop brightness

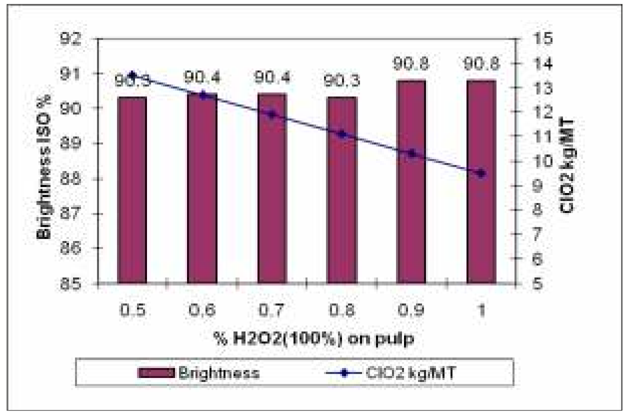

Fig.3: H_2O_2 Vs brightness and ClO2 usage

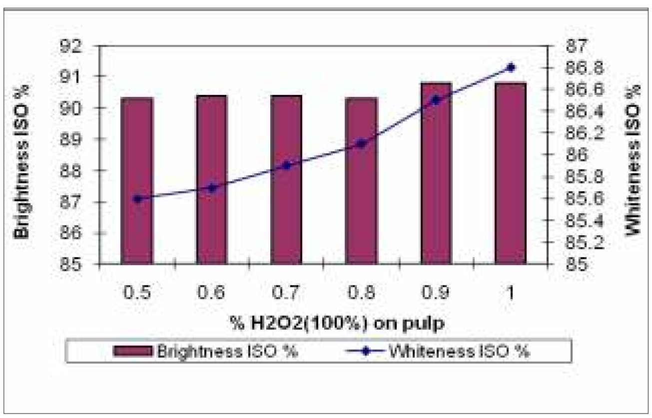

Fig.3: H_2O_2 Vs brightness and whiteness

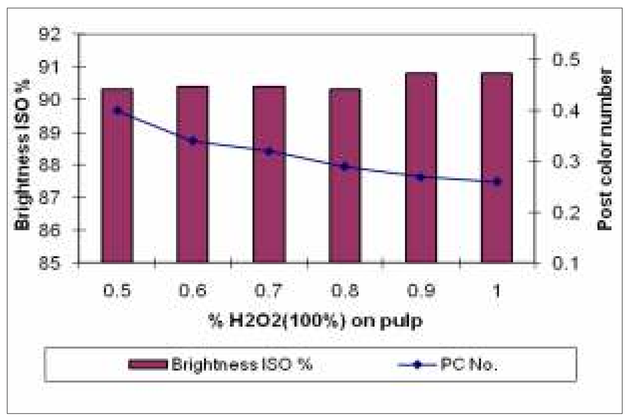

Fig.4: H_2O_2 Vs brightness and PC number

peroxide 0.6%(100% H_2O_2) in Eop stage. To improve pulp brightness, we have to increase the chlorine dioxide charge in D_1 or D_2 stage, which results higher bleaching cost and effluent load in term of organochlorine compound.

Based on laboratory results, plant trial was conducted using higher dosage of hydrogen peroxide to reinforce again the extraction stage to a maximum level. Dosage of H_2O_2 was increased from 0.6% to 0.9% (100% H_2O_2). Trial was taken for three weeks time and based on the encouraging results it was continuously adopted for regular use in plant. The chemical addition in C/D stage and bleaching conditions were kept same during the trial as shown in Table-V , only the chemical addition H_2O_2 in Eop stage increased from 0.6 to 0.9% (100% H_2O_2) and correspondingly addition of chlorine dioxide was reduced in subsequent D_1 and D_2 bleaching stage to achieve the same degree of final pulp brightness. The chemical used during bleaching process, brightness, whiteness, brightness reversion and viscosity of bleached pulp are shown in Table-VI.

In bleach plant, overflow of D_2 filtrate was going to D_1 filtrate tank and over flow from D1 filtrate tank was going to C/D stage filtrate tank and from where it goes to drain. The overflow of the Eop stage also going to drain. The Effluent generated during the bleaching process were mixed in the

Table-V Bleaching conditions (plant trial)

Particulars	Unit	Normal Run	Trial Run
Unbleached Kappa No.		17-18	17-18
CD STAGE			
Cl_2:ClO_2		92:8	92:8
Retention Time	min.	45	45
Temperature	°C	48-50	48-50
Consistency	%	7.5	7.5
Residual , Cl_2	gpl	0.050	0.051
Eop Stage			
Retention time	min	120	120
Temperature	°C	75	75
Consistency	%	10	10
pH Final		10.3	10.3
CE P. Number		1.9	1.5
Eop Brightness , ISO	%	58.5	63.3
D_1 Stage			
Retention Time	min.	180	180
Consistency	%	9	9
pH final		3.5-4.0	3.5-4.0
Temperature		70	70
Residual as Cl_2	gpl	0.052	0.048
D_2 Stage			
Retention Time	min.	180	180
Consistency	%	9.0	9.0
pH final		3.5-4.0	3.5-4.0
Temperature	°C	70	70
Residual as Cl_2	gpl	0.052	0.021

Table-VI Bleaching chemical consumption and bleached pulp properties (Plant trial)

Particulars	Unit	Normal Run	Trial Run
Chemical			
Chlorine	kg/MT	50.0	50.0
ClO_2	kg/MT	14.5	12.0
NaOH	kg/MT	32.0	32.0
H_2O_2 (100% H_2O_2)	kg/MT	6.0	9.0
Bleached pulp			
Brightness, ISO	%	89.0	89.4
Standard deviation, Brightness		0.81	0.72
Whiteness, ISO	%	82.0	82.6
Viscosity (0.5% CED)	Cps	10.0	10.2
Post color number		0.66	0.55

Table VII Pulp Mill bleach plant effluent characteristics (Untreated, plant trial)

Particulars	Unit	Normal run	Plant trial run
pH		2.8	2.8
Color Pt Co unit	mg/l	2300	1860
COD	mg/l	1443	1460
BOD	mg/l	460	450

Table- VIII Cost analysis

Chemical	Normal Run	Plant trial run
	Cost Rs/MT of pulp	Cost Rs/MT of pulp
Cl_2	440	440
ClO_2	1305	1080
NaOH	720	720
H_2O_2 (100% H_2O_2)	275	410
Total bleaching cost Rs/MT of pulp	2740	2650

ratio of 64:36 (CD:Eop) as same going in ETP drain. The mix effluent were analysed for color, BOD and COD results are given in Table-VII.

Results and discussion:

Lab study:

- As shown in Fig.2, with increased dosage of hydrogen peroxide in Eop stage from 0.5 to 1.0% (100% H_2O_2) on pulp, CE permanganate number decreased from 2.1 to 1.4, after which it was constant. Brightness of Eop pulp increases by 10 point, however increase in brightness was not linear.

- As shown in Fig.3, when the dosage of hydrogen peroxide increases from 0.5 to 1.0% (100% H_2O_2) in Eop stage, the consumption of chlorine dioxide decreases from 12.0 to 8.0kg/MT of pulp with improved brightness and whiteness of final bleached pulp by 0.5 and 1.2 point respectively.

- Results also showed the improvement in brightness stability means reduction in post color number of final bleached pulp. This has been due to the ability of hydrogen peroxide of removing the chomopore group from the pulp, results in improving the brightness and brightness stability of final bleached pulp. The viscosity of bleached pulp was more or less similar to that of normal hydrogen peroxide dosage pulp, which means there is no adverse effect on viscosity of bleached pulp.

- As shown in Table IV, at a dosage of 1.0% H_2O_2(100%) in Eop stage, color and AOX of effluent reduced by about 14-15 % and 6 % respectively, however the COD and BOD of effluent more or less similar to normal bleached pulp effluent. Use of higher hydrogen peroxide dosage in Eop stage helps to remove the color and AOX in effluent.

Process trial:

When hydrogen peroxide dosage increased from 0.6% to 0.9%(100%H_2O_2) in Eop stage in the plant, it resulted reduction in CE permanganate number (CE P number) and thus reduce the consumption of ClO_2 from 14.5 kg/MT to 12.0kg/MT in subsequent D1&D2 stages. This also reduced the variation in final pulp brightness with improved final bleached pulp brightness and whiteness by 0.4 and 0.6 point respectively. The post color number has decreased from 0.66 to 0.55 of final bleached pulp, which means improvement in brightness stability. Viscosity of final bleached pulp was more or less similar i.e. 9.7 Cps and 10.0 cps. Table V & VI show the results.

Effluent quality improved in terms of color of effluent, there was reduction in color of effluent by about 19 %, however, the COD and BOD was more or less similar with normal hydrogen peroxide dosage. Table-VII shows the results.

Conclusion:

- Reduced the chlorine dioxide by 2.5kg/MT by increasing from 0.6% to 0.9% (100%) H_2O_2 in extraction stage with final pulp brightness and whiteness improvement by 0.4 & 0.6 points respectively.
- Bleaching cost reduced about Rs. 90 /MT.
- Improvement in brightness stability.
- Reduction in color of the effluent.

Adopting this strategy mill could be able to reduce the use of chlorine compound during bleaching process of pulp with improved pulp quality. During this plant trial, improvement in final paper brightness has been observed. Use of optimised quantity of hydrogen peroxide might help to reduce the pollution load and improving the quality of paper.

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