

# Reduction of Chloride Dioxide in Paper Bleaching using Peroxide Activation

Ayo Afolabi, Rudzani Sigwadi, Ambali Abdulkareem

**Abstract**—All around the world pulp and paper industries are the biggest plant production with the environmental pollution as the biggest challenge facing the pulp manufacturing operations. The concern among these industries is to produce a high volume of papers with the high quality standard and of low cost without affecting the environment. This result obtained from this bleaching study show that the activation of peroxide was an effective method of reducing the total applied charge of chlorine dioxide which is harmful to our environment and also show that softwood and hardwood Kraft pulps responded linearly to the peroxide treatments. During the bleaching process the production plant produce chlorines. Under the trial stages chloride dioxide has been reduced by 3 kg/ton to reduce the brightness from 65% ISO to 60% ISO of pulp and the dosing point returned to the E stage charges by pre-treating Kraft pulps with hydrogen peroxide. The pulp and paper industry has developed elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching, in their quest for being environmental friendly, they have been looking at ways to turn their ECF process into a TCF process while still being competitive. This prompted the research to investigate the capability of the hydrogen peroxide as catalyst to reduce chloride dioxide.

**Keywords**—bleaching, chloride dioxide, elemental chlorine free (ECF), hydrogen peroxide, totally chlorine free (TCF).

## I. INTRODUCTION

PAPER is a major product that can be found from the plant, and is the most valuable product to the society. Paper products are not only used for the publishing industry and for writing on, but also in a variety of specialty papers, cardboards, brown papers etc. It is made by pulping wood, bleaching this pulp and then spreading it out into sheets to make it into paper. In order to obtain the paper production there's some chemical process to be followed.

It was discovered over a decade ago that the previous widespread use of  $\text{Cl}_2$  contributed to the production and subsequent release to the environment. Chloride dioxide has achieved significant commercial attention in the field of water disinfection, pulp bleaching and waste water treatment. Pulp bleaching is the prime use of chlorine dioxide as it is a unique selective oxidizer for lignin [1]. Lignin is a three dimensional polymer with a complex structure, present in all woody plants and other lignocelluloses residues which are used as raw material for paper manufacturing [2]. Fibers in pulp may be further treated to remove residual lignin and further brighten the resultant papers [3]. In recent years, ECF and TCF bleaching systems have become widely used alternatives for conventional chlorine bleaching with elemental chlorine in pulp production [3, 4].

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Currently, ECF and TCF bleaching systems are widely used for pulp production [5]. These bleaching processes are based in oxygen-derived compounds, among which, hydrogen peroxide has received much attention [6]. Due to environmental effect the pulp and paper industry has forced to explore alternatives to chlorine based bleaching practices of the bleached Kraft pulp production. Various technologies and bleaching chemicals such as oxygen, ozone and peroxides have been suggested to be used on Kraft pulp bleaching [7]. Unfortunately, these bleaching chemicals have some drawbacks. Oxygen delignification is effective but its delignification effectiveness is limited to about 50% after which severe loss of pulp strength occurs. Hydrogen peroxide under alkaline or acidic conditions is not an effective delignifying agent while ozone is considerably more effective but it promotes aggressive radical reactions which cause undesirable carbohydrate degradation [7,8].

Many researchers have lodged a research and development activity in the design and implementation of new environmentally processes for bleached chemical pulp manufacture. Environmental consciousness is evident not only in the market place but also in increasingly stringent government regulation of the industry's waste streams, processes, and products [9]. This problem of chlorine dioxide replacement as a brightening agent must be tackled to improve environmental quality and human health. The new process technology of using hydrogen peroxide as catalyst is being proposed to prevent the production of toxic effluents. This study also investigates the possibility of eliminating the effluent of chloride dioxide during paper bleaching by using hydrogen peroxide as the catalyst to prevent the production of this toxic effluent.

## II. MATERIALS AND METHODS

The main apparatus used for this experiment was the pulp mill bleach plant. This plant consists of 3 bleaching sequence stages, which are briefly described below:

*D-stage:* The D stage uses chlorine dioxide as the reducing agent and is termed the delignification stage. This is where most of the delignification takes place and the rest of the bleaching stages are brightening stages with caustic used as the extraction and pH correction stage. The plant does not use a sequestering stage as the D stage pH is 3 and most of the metals are treated in that stage. The chlorine dioxide reactor is a 30 m long reactor that could process 250 tons/day pulp at 10% consistency. The chlorine dioxide used at this stage was at 6 g/l and the pulp consistency to the stage was 10%. The reactor is a vertical up flow tower that uses plug flow as the pulp goes up the tower. Chlorine dioxide was dosed via a chlorine dioxide mixer prior to entering the tower upon which the pulp retention time was approximately 1 hour through the reactor.

*E-stage:* The E stage is a down flow tower which uses 5% caustic to correct the pH and at concentration of 60%. The caustic helps to further increase delignification and to extract

more lignin. The amount of caustic dosed can also be attributed to the amount of chlorine dioxide dosed in the previous section. Dosing was done via the steam mixer to the E tower.

*P-stage:* The P stage reactor is a 50 m up flow tower similar to the D tower where pulp is retained for 4 hours at the maximum flow rate. Only peroxide is dosed at this stage. The pulp at the top of the tower is scraped off and diluted with the same filtrate.

Each stage was preceded by a washing stage and counter current washing was employed. Fresh process water was used in the P washer and the filtrate from the P stage was used as wash water on the E washer, the filtrate from the E washer was used as wash water for the D washer and the D washer filtrate containing sulphates and impurities was sent to the mill effluent. A titration method was used to measure residual peroxide on the P stage and peroxide strips were used on the E stage due to its colour. The brightness meter was used to measure the brightness.

TABLE I  
DETAILS OF BLEACHING SCHEME

Kappa number initial			10
D <sub>0</sub> stage	ClO <sub>2</sub> charge	kg/ton	16
	Consistency	%	10
	Retention time	min	80
	Temperature	°C	60
	pH	11	11
E <sub>p</sub> stage	NaOH charge	%	3
	H <sub>2</sub> O <sub>2</sub> charge	kg/ton	6
	Consistency	%	10
	Retention time	min	80
	Temperature	°C	65
P stage	H <sub>2</sub> O <sub>2</sub> charge	kg/ton	6
	Consistency	%	10
	Retention time	min	300
	Temperature	°C	65

### III. RESULTS AND DISCUSSION

Table I shows the three different stages that were involved on the bleaching milling plant. The first run was performed with a pulp production of 150 tons/hr. The chlorine dioxide dosing rate was 16 kg/ton and the peroxide in the E-stage was 4 kg/ton while the peroxide in the P-stage was 6 kg/ton at 60%. The catalysts of 2 ppm were added to the feed. It can be seen from Table II that the 68% ISO brightness can be achieved at the D-stage with the addition of chlorine dioxide whereas more than 80% ISO brightness can be achieved at the P-stage with the addition of hydrogen peroxide.

Fig. 1 shows the summarized results of all the three stages at the first bleaching trial including the specific time taken during the observation period. These results compare all stages of bleaching, and it can be seen that all the three stages ISO brightness is quite close to one another.

The results indicate that the brightness was pretty high for the whole first trial and the D-stage brightness was nearing 70% ISO brightness. The dip in brightness at time 21:30 was as a result of the plant being down for that time period.

TABLE II  
FIRST BLEACHING TRIAL

Time	Catalyst	ClO <sub>2</sub>	D - stage Brightness	pH stat E	H <sub>2</sub> O <sub>2</sub>	E - stage Brightness	H <sub>2</sub> O <sub>2</sub>	P - stage Brightness	Residual H <sub>2</sub> O <sub>2</sub>
06:00		16.00	64.90	10.28	4	75.30	6	79.00	
08:00		16.00	64.60	10.36	4	74.90	6	79.30	
10:00		16.00	65.00	10.16	4	75.20	6	79.70	
12:00	2	16.00	65.60	10.88	4	78.20	6	81.10	130
12:30	2	15.15			4	76.10	6		
13:00	2	15.00	65.80		4	77.20	6	81.60	
13:30	2	15.00			4	77.10	6		
14:00	2	15.00	66.50	11.04	4	77.10	6	81.60	
14:30	2	15.00	66.30		4	77.60	6	82.30	
15:00	2	15.00	66.20	12.14	4	78.00	6	81.90	
15:30		15.00	66.40		4	77.80	6	81.10	
16:00		15.00	66.30	12.00	4	77.60	6	81.50	120
17:00		15.00	64.60	11.74	4	77.20	6	81.70	
17:30		15.00	68.30		4	76.20	6	82.50	
18:00		17.00	67.40	11.69	4	77.00	6	81.50	
19:00		17.00	68.00	11.83	4	78.20	6	81.00	
20:00		16.50	67.80	11.72	4	78.00	6	80.80	
21:00		16.50		11.20	4	0.00	6		
22:00		16.50	64.70	10.87	4	75.80	6	80.10	
00:00		16.50	63.50	10.75	4	74.70	6	79.70	

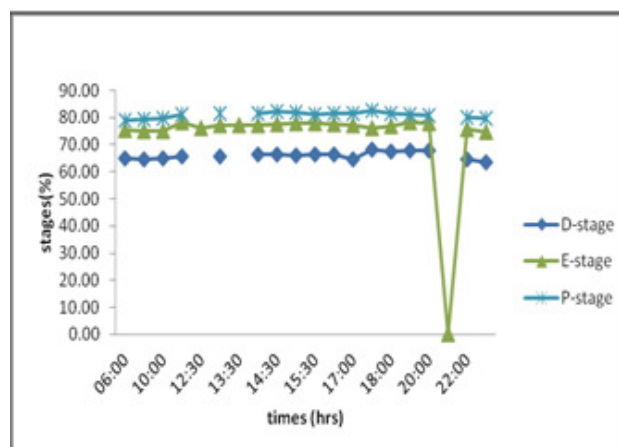


Fig. 1 First bleaching trial

The second trial of bleaching with the addition of sodium hydroxide and the residual peroxide is represented in Table III. Initially 2 ppm manganese based catalyst was dosed into the feed but due to lack of improvement in the results the catalyst dosage was increased to 4 ppm. It can be seen that no change in brightness was observed in the E-stage for the first 6 hours. The results appear that no changes occurred when comparing with the first bleaching trial because the sodium hydroxide was not effective on the E-stage. A change in dosing point was then employed. The initial dosing point was unto the E-stage and the dosing point was changed unto the P-stage. The retention time on the D-stage was 1 hour 30 minutes and that of the E-stage was the same as the D-stage. The retention time on the p-stage was 4 hours. Due to this it was then decided that the manganese based catalyst dosage should be decreased to 3 ppm.

At 3 ppm to the E-stage no significant increase in brightness was observed although the amount of residual peroxide decreased. The decrease in pulp residual peroxide may have been due to either the decomposition of hydrogen peroxide with the catalyst in the system or could have been due to the peroxide consumption due to a reaction with some chromophores and carbonyl groups that did not have much impact on the brightness. It can be seen in Fig. 2 that the difference in time follows the trend at D-stage. Due to lack of any improvement on the pulp brightness on the E-stage, it was decided that the dosage point be changed under the suspicion that the peroxide being used in the stage was all already being consumed as the initial residual peroxide was 30 mg/l from 60% at 4 kg/ton.

TABLE III  
SECOND BLEACHING TRIAL

Time	Catalyst	ClO <sub>2</sub>	D-stage Brightness	pH start E	NaOH	H <sub>2</sub> O <sub>2</sub>	R-H <sub>2</sub> O <sub>2</sub>	E-stage Brightness	H <sub>2</sub> O <sub>2</sub>	P-stage Brightness	Residual H <sub>2</sub> O <sub>2</sub>
02:00		17.00	64.40	10.54		4		74.10	6	79.00	
04:00		17.00	64.80	10.90		4		74.60	6	80.00	
06:00		17.00	64.00	8.40	48.00	4		74.20	6	79.10	
08:00		17.00	64.30	11.10	48.00	4		74.40	6	79.40	
09:10	2	17.00				4			6		
10:00	2	17.00	64.70	11.15	41.00	4		74.70	6		177
10:30	2	17.00	0.00			4		73.90	6		
11:00	2	17.00	0.00			4		73.90	6		
11:30	2	17.00	0.00			4		74.40	6		
12:00	2	16.50	67.30	10.61	45.00	4		74.60	6	79.50	
12:30	2	16.00	0.00			4		75.60	6		
13:00	2	16.00	65.00			4		76.10	6	79.90	157
13:15	4	16.00	0.00			4			6		
13:30	4	16.00	0.00			4		75.40	6		
14:00	4	16.00	65.50	11.45		4		76.00	6	80.00	
14:30	4	16.00	0.00			4		75.00	6		
15:00	4	16.00	63.60			4		74.70	6	79.80	
15:30	4	16.00	0.00			4			6		
16:00	4	16.00	62.00			4		75.20	6	79.90	
16:30	4	16.00	0.00			4			6		
16:40	3	16.00	0.00			4			6		
17:00	3	16.00	63.40			4	3-10	76.00	6	80.00	50-100
17:30	3	16.00	0.00			4			6		
18:00	3	16.00	0.00			4			6		
20:00	3	16.00	63.80	10.94		4		75.80	6	80.10	
21:00	3	16.00	63.80			4		0.00	6	81.30	
22:00	3	16.00	64.26	11.60		4	100	74.80	6	80.70	30-60

The manganese based catalyst was therefore dosed to the P-stage at 3 ppm. This was done for 6 hours again and there was no significant increase in brightness to justify the usefulness of the catalyst but again there was a decrease in residual peroxide. The reduction in residual peroxide suggested that the peroxide was either decomposing or consumed but was not doing any work towards brightening the pulp.

The data of the final trial of bleaching with trial pulp are presented in Table IV. It can be observed from this Table that the peroxide complex should be given more lignin to help with delignification as there was very little lignin left in pulp after the D-stage with the kappa number known to be around 2 and indicates the trial pulp that denotes the effect of reducing chlorine dioxide.

The chloride dioxide was reduced by 3 kg/ton of pulp and the dosing point returned to the E-stage. Due to the nature of the catalyst complex and the ability it gives the peroxide better selectivity during delignification the third trial was done under reduced D-stage brightness conditions.

The theory behind this change was to increase the delignification requirement for the pulp due to contact the catalyzed peroxide to allow the complex to react with lignin as opposed to the brightening effect the two stages predominantly do.

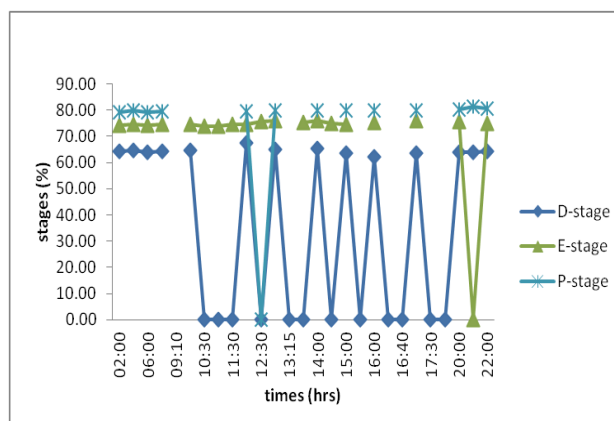


Fig. 2 Second bleaching trial

The peroxide dosage on the E-stage was increased to 6 kg/ton as the residual peroxide was already too low, and this was to see the effect of the catalyst when reacting with pulp at an already high kappa number and having more lignin to react with. The decline in brightness on the D-stage was from 65 to 58 while brightness on the E stage only declined by 2 brightness points, from 76 to 74 with the catalyst at a dosage of 3 ppm. This constitutes a 16 point brightness gain using catalyst as opposed to an 11 point brightness increase when no catalyst was employed. When comparing the bleaching without the catalyst and bleaching with the catalyst the possible brightness increase with catalyst could be 5 brightness points which signifies a reduction in ClO<sub>2</sub> of 5 kg/ton.

Fig. 3 shows that the difference in time will follow the trend at D-stage. D-stage employed around 16% charge of chlorine dioxide while the E-stage and P-stage employed around 6% charge of H<sub>2</sub>O<sub>2</sub>. The brightness results for the D-stages, E-stages and P-stages are summarized in Fig. 3. An examination of these results indicates that the D-stages pretreatment, combined with the addition of H<sub>2</sub>O<sub>2</sub>, significantly raises the brightness of the pulps. For target brightness values of more than 80% ISO with the use of peroxide reduces the totally applied chlorine dioxide by 3 kg/ton. A comparison of E-stage and P-stage of ISO bleaching with the hydrogen peroxide is nearly the same.

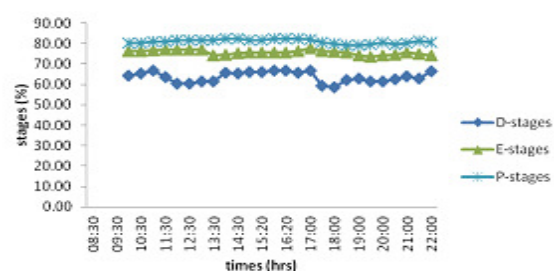


Fig. 3 Final bleaching trial

TABLE IV  
FINAL BLEACHING TRIAL

Time	Catalyst	ClO <sub>2</sub>	D - stage Brightness	E - stage pH	H <sub>2</sub> O <sub>2</sub>	Trial pulp	Trial pulp	Residual H <sub>2</sub> O <sub>2</sub>	E - stage Brightness	P - stage Brightness
08:30	3	16.00			4.00					
09:00	3	16.00			4.00					
09:30	3	13.00			4.00			30.00		
10:00	3	13.00	64.20	10.20	4.00				76.40	80.40
10:30	3	13.00	65.20		6.00				76.50	80.40
11:00	3	13.00	66.90		6.00			30.00	76.80	80.90
11:30	3	16.00	63.50		6.00	63.50			77.00	80.80
12:00	3	16.00	60.50	11.22	6.00	60.50			77.00	81.60
12:30	3	16.00	60.50		6.00	60.50	77.00	20.00	77.00	81.60
13:00	3	16.00	61.30		6.00	61.30	77.00		77.00	81.70
13:30	3	16.00	61.30		4.00	74.10			74.10	81.70
14:00	3	16.00	65.70	10.96	4.00	74.50			74.50	82.40
14:30	3	16.00	65.20		4.00			30.00	75.20	82.20
15:00	3	16.00	65.90		4.00				75.50	81.60
15:20	3	13.00	65.90		4.00				75.50	81.60
16:00	3	13.00	66.70	10.60	4.00				75.80	82.20
16:20	3	13.00	66.70		6.00				75.80	82.20
16:30	3	13.00	65.60		6.00			30.00	76.50	82.40
17:00	3	13.00	66.90		6.00				77.70	81.90
17:30	3	13.00	59.20		6.00	80.50	59.20		76.40	80.50
18:00	3	13.00	58.50	10.42	6.00	79.90	58.50		76.10	79.90
18:30	3	13.00	62.30		6.00	79.30	62.30	30.00	75.80	79.30
19:00	3	13.00	62.70		6.00	79.00	62.70		74.10	79.00
19:27	3	13.00	61.30		6.00	73.50	61.30		73.50	79.40
20:00	3	16.00	61.40	10.00	6.00	74.50	61.40		74.10	80.70
20:30	3	16.00	62.50		6.00	75.80	62.50		74.50	79.60
21:00	3	16.00	64.00		6.00	74.90	64.00		75.80	80.30
21:30	3	16.00	62.90	10.97	6.00	74.10	62.90		74.90	81.20
22:00		16.00	66.40		4.00				74.10	80.50

## IV. CONCLUSIONS

The analyses of the results obtained from this study show that the manganese based catalyst was efficient in the reduction of chloride dioxide required to bleach pulp. In the same vein, the use of hydrogen peroxide allowed for more than 80% ISO brightness gains in Kraft pulps. In pulp and paper bleaching, it is clear that the use of hydrogen peroxide as a bleaching agent results in the environment free chlorine. Alternatives to the use of catalyst, such as manganese, result in reductions in the quantities of chlorines produced. However, sufficient evidence exists from responses observed at NaOH addition show the reduction in residual peroxide and can it can be inferred that the peroxide was either decomposed or consumed but was not performing any work towards brightening the pulp. It is clear that the hydrogen peroxide as the bleaching agent can reduce the chlorine oxide production as the result indicate the decline in brightness on the D-stage was from 65 to 58 while brightness on the E stage only declined by 2 brightness points, from 76 to 74 with the catalyst at a dosage of 3 ppm. This constitutes a 16-point brightness gain using catalyst as opposed to an 11-point brightness increase when using no catalyst. When comparing the bleaching without the catalyst and bleaching with the catalyst the possible brightness increase with catalyst could be 5 brightness points which indicates a reduction in ClO<sub>2</sub> of 5 kg/ton.

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