

New Bleaching Sequences using Chlorine Dioxide to Bleach Bamboo and Hardwood Kraft Pulps

MD. Wasi Ahmed and Dathathreya C.T.

The Sirpur Paper Mills Limited, Sirpur, Kaghaznagar-504 296 (A.P.)

ABSTRACT

Laboratory scale bleaching studies carried out by using 1.5% Chlorine dioxide in the last stage after CEH or CEHH sequences had indicated that final bleached pulp brightness could be increased by 4 to 8 points. The pulp strength is preserved and P.C. Numbers are reduced. Using chlorine dioxide in one stage in addition to conventional bleaching agents to bleach blends of Bamboo and Plantation hardwood Kraft pulps of 20.0 Kappa number, laboratory scale experimental studies had indicated that lower initial Kappa number of unbleached pulp is beneficial when ClO_2 is used in bleaching. Total chlorine required is substantially lower and that the strength levels of pulp are well preserved. Bleached pulp of higher brightness can be produced by CEHD of CE_pHD sequences with good strength and good brightness stability. Moreover response to ClO_2 in D stage is better if hypo bleaching is stopped at a lower brightness ($68 \pm 1^\circ\text{GE}$). In new bleaching sequences using chlorine dioxide in two stages, unbleached pulp of lower kappa number can be bleached by sequences D/C.E.D. ; $\text{D/C.E}_p\text{D}$ and $\text{D/CE}_p\text{D}$. By optimising the $\text{D/CE}_p\text{D}$ sequence and by slightly increasing elemental chlorine in 1st stage, bleached pulp of 88.0°GE could be achieved. Also by incorporating a 1st stage oxygen delignification, bleached pulp of 88.0°GE could be achieved by the sequences O.D. C.E.D. ; $\text{O.D/C.E}_p\text{D}$ and $\text{O.D/CE}_p\text{D}$. Data indicates that the pulps bleached by DCE_pD and $\text{O.D/C.E}_p\text{D}$ sequences to 88.0°GE . are stronger than CEHH bleached pulp of 80.0°GE with good viscosity (10.3 and 10.5 mpas) and low P.C. Number (1.09 and 1.12).

INTRODUCTION

The first continuous mill use of chlorine dioxide by site manufacture using Rapson-Wayman process began in 1946 in Canada (1). The use of chlorine dioxide for bleaching is increasing continuously and standard sequence of CEDED has given way to DE_pDD sequence in the present day ECF Mills (2). Today the leading bleaching sequence for Kraft Pulps is DE_pDD with some modifications. The competitive sequence for EDF process is TCF process. However it has been found that ECF process is better than TCF process with respect to strength preservation. Research work to ascertain whether ECF process is better or TCF process is better with respect to environmental pollution, has indicated that TCF has no additional advantages as compared to ECF (3). Also, it has been found by Life Cycle Analysis that TCF pulps have lower recyclability as compared to ECF pulp (4).

From the above, it is clear that chlorine dioxide as a bleaching agent has a future. Hence laboratory works was carried out to bleach Kraft Pulp (of Plantation Hardwood with small percentage of bamboo) by sequences using chlorine dioxide in one or two stage

along with conventional bleaching agents like chlorine and hypochlorite to develop sequences which would produce pulp of good brightness, good brightness stability and good strength.

EXPERIMENTAL

Pulp used for experimental studies

Unbleached pulp of Kappa Number 20.0 attained by cooking blend of Bamboo and Plantation hardwood in laboratory rotary Digester.

Chlorine dioxide preparation

Chlorine dioxide was generated in laboratory by heating a mixture of Sodium Chlorate, Oxalic acid dehydrate and 33% sulphuric acid at $30-60^\circ\text{C}$ in all glass apparatus. The evolving gas after scrubbing with sodium chlorite solution was absorbed in ice cold water. Chlorine dioxide thus prepared was stored in refrigerator.

Bleaching

Bleaching experiments were carried out on small batches equivalent to 400 grams OD pulp in water tight polythene bags. Reaction temperature was maintained

Table 1. Bleaching of unbleached pulp of Kappa No. 20.0 by using chlorine dioxide in one stage

Bleaching sequence	CEHD	CE ₀ HD
Chlorination		
% dosage of Cl ₂ as A.Cl ₂ in Cl ₂ water	3.0	3.0
% consistency	3.0	3.0
Initial pH	3.52	3.52
Temperature °C	Ambient	Ambient
Retention time, hrs.	1.0	1.0
Final pH	3.72	3.72
Extraction Stage		
% dosage of NaOH	1.5	1.5
% dosage of MgSO ₄ .7H ₂ O	-	0.05
O ₂ pressure, kg/sq. cm.	-	5.0
% consistency	7.0	10.0
Initial pH	11.12	11.27
Temperature °C	65-70	100±2
Retention time, hrs.	1.0	1.0
Final pH	9.49	9.23
Kappa Number	9.4	6.31
Hypo Stage -I		
% dosage of Cl ₂ as A.Cl ₂ in Hypochlorite	1.75	1.0
% dosage of sulphuric acid	0.15	0.15
% consistency	7.0	7.0
Initial pH	8.14	8.25
Temperature °C	35-40	35-40
Retention time, hrs	21/2	21/2
Final pH	6.84	7.04
Residual Cl ₂	0.10	0.15
% Cl ₂ consumed	1.65	0.85
Brightness achieved °GE	67.0	67.5
PC Number	14.96	7.61
D- Stage		
% dosage of ClO ₂	1.5	1.5
% consistency	10.0	10.0
Initial pH	7.04	6.92
Temperature °C	70.0	70.0
Retention time, hrs.	3.0	3.0
Final pH	5.94	5.98
ClO ₂ consumed %	1.22	1.21
Total A. Chlorine applied/consumed %	8.70/7.86	7.95/7.05
Brightness achieved °GE	83.0	83.0
P.C. Number	3.46	2.89
Viscosity mpas (0.5% CED at 20.0°C)	8.72	8.54

by immersing the polythene bags containing pulp and added bleaching chemicals in water bath whose temperature was maintained.

Oxygen Bleaching

This was carried out in a laboratory autoclave of 2½ litre capacity whose temperature could be maintained by steam jacket indirect heating. The autoclave is equipped with a stirrer to mix the contents manually, periodically to ensure proper reaction with oxygen.

RESULTS AND DISCUSSION

Bleaching of unbleached pulp of Kappa Number 20.0 by using ClO₂ in one stage in addition to conventional bleaching agents.

From the results it is observed that lower initial Kappa Number is beneficial when a final ClO₂ stage is used. The total chlorine required is substantially lower and that the strength levels of pulp is well preserved.

Table 2. Strength properties of standard handsheets of 60 gsm of bleached pulps beaten to 40°SR in Valley beater

Bleaching sequence	CEHD	CE ₀ HD
Initial Freeness °SR	14	16
Beating time, min	50	50
Final freeness °SR	40	40
Breaking Length, m	8389	8602
Tear Factor	83.33	75.26
Burst Factor	56.46	58.87
Double Folds	394	328
Strength Index	2303	2234

Table 1 and 2. Moreover response to ClO₂ is better if hypo bleaching is stopped at a lower brightness level of 68±°GE. Total chlorine consumed was 7.86% and 7.05% of CEHD and CE₀HD sequences respectively and a pulp brightness of 83.0°GE was achieved. By optimizing further, bleached pulp of 85+ brightness can be attained with good brightness stability and good strength preservation.

Bleaching of unbleached pulp of Kappa Number 20.0 by using ClO₂ in two stages in new bleaching sequences

Here the objective is to have final target brightness of 88.0°GE using ClO₂ in two stages, the sequences used

Table 3. Bleaching of unbleached pulp of Kappa No. 20.0, using ClO₂ in two stage optimization studies

Bleaching sequence	D/C.E.D.		D/C,E ₀ .D		D/C.E _p .D	
	a	b	a	b	a	b
D/C Stage						
% dosage of Cl ₂ as A.Cl ₂	0.9	1.2	0.9	1.2	0.9	1.2
% dosage of ClO ₂	0.8	1.1	0.8	1.1	0.8	1.1
% consistency	12.0	12.0	12.0	12.0	12.0	12.0
Initial pH	4.98	4.34	4.98	4.34	4.94	4.23
Temperature °C	55.0	55.0	55.0	55.0	55.0	55.0
Retention time, hrs.	3/4	3/4	3/4	3/4	3/4	3/4
Final pH	6.18	5.74	6.18	5.74	6.18	5.57
Kappa Number	9.5	5.73	9.5	5.73	9.5	5.73
Extraction Stage						
% dosage of NaOH	2.0	2.0	1.8	1.8	2.0	2.0
% dosage of MgSO ₄ .7H ₂ O	-	-	0.05	0.05	-	-
% dosage of H ₂ O ₂ (on 100% basis)	-	-	-	-	0.3	0.3
O ₂ pressure, kgs/cm ²	-	-	5.0	5.0	-	-
% consistency	12.0	12.0	12.0	12.0	12.0	12.0
Initial pH	11.47	11.64	11.38	11.56	11.69	11.74
Temperature °C	85.0	85.0	85.0	85.0	85.0	85.0
Retention time, min.	75.0	75.0	75.0	75.0	75.0	75.0
Final pH	10.35	10.70	9.28	9.34	10.21	10.34
Kappa Number	4.98	2.49	3.86	1.96	4.90	2.54
D-Stage						
% dosage of Cl ₂	0.65	1.0	0.65	1.0	0.65	1.0
% consistency	12.0	12.0	12.0	12.0	12.0	12.0
Initial pH	6.96	6.84	7.02	6.93	6.96	6.86
Temperature °C	75.0	75.0	75.0	75.0	75.0	75.0
Retention time, min	200	200	200	200	200	200
Brightness °GE	59.0	63.5	66.5	74.0	70.0	74.5
P.C. Number	3.1	2.80	2.46	2.39	1.70	2.07
Viscosity mPas (0.5% CED at 20°C)	10.2	10.2	9.8	8.4	8.4	9.8

Table 4. Optimization of Cl₂ dosage in D/C stage of D/C.E_p.D bleaching sequence by fixing ClO₂ dosage at 0.8%

Bleaching sequence	D/C.E _p .D					
	1		2		3	
D/C Stage						
% dosage of Cl ₂ as A.Cl ₂	1.4		1.8		2.2	
% dosage of ClO ₂	0.8		0.8		0.8	
% consistency	10.0		10.0		10.0	
Initial pH	4.12		3.62		3.20	
Temperature °C	55		55		55	
Retention time, hrs.	45		45		45	
Final pH	5.78		4.86		4.34	
E_p Satage						
% dosage of NaOH	2.0		2.0			
% dosage of H ₂ O ₂ (on 100% basis)	0.3		0.3		0.3	
% consistency	12.0		12.0		12.0	
Initial pH	10.94		11.32		11.15	
Temperature °C	85		85		85	
Retention time, min.	75		75		75	
Final pH	10.16		10.34		10.04	
Kappa Number	2.54		1.45		2.2	
D-Stage	a	b	a	b	a	b
% dosage of ClO ₂	0.65	1.00	0.65	1.00	0.65	1.00
% consistency	12.0	12.0	12.0	12.0	12.0	12.0
Initial pH	7.07	6.84	6.94	6.24	7.27	7.04
Temperature °C	75	75	75	75	75	75
Retention time, hrs.	200	200	200	200	200	200
Final pH	6.95	6.76	6.83	6.12	6.72	6.43
Brightness °GE	74.00	81.0	81.0	85.0	85.5	88.0
P.C. Number	1.35	1.04	0.87	0.81	0.51	0.7
Viscosity mPas (0.5% CED at 20°C)	9.8	8.1	8.2	8.0	8.0	7.9

were D/C.E.D.; D/C.E_o.D and D/C/E_p.D Table 3. The bleaching conditions were maintained at levels as suggested. As these experiments were carried out without a 1st Oxygen stage, dosage in 1st stage was carried out at level suggested in the proposal and also at a higher level. These experiments indicate that the pulp could be bleached to 86.5°GE by the sequence D/C.E_p.D with total chlorine consumption of 8.04%. The ClO₂ consumed was 2.6% (6.84% as chlorine equivalent).

D/C.E_p.D sequence was optimized to achieve the target brightness of 88.0°GE by confining ClO₂ addition as suggested but increasing chlorine in 1st stage Table 4. However in the last stage ClO₂ applied had to be increased to 1.0% to achieve the target brightness. It is found that the pulp could be bleached to 88.0°GE with total chlorine application of 6.93%

with ClO₂ addition of 1.8% (4.73% as active chlorine).

Further studies were carried out by incorporating a 1st oxygen delignification also. In this series the sequences studied were O.D/C.E.D.; O.D/C E_o.D and O.D/CE_p.D Table 5. ClO₂ applied was confined to 0.8% in D/C stage and 1.0% in the final D stage. Results indicate that the final bleached pulp brightness of 88±1°GE could be achieved by O.D/C.E_o.D and O.D/C.E_p.D sequences with good final viscosity and low P.C. Number.

Based on the optimum conditions evolved a concluding set of experimental studies was carried out and the unbleached pulp of 20.0 Kappa Number was bleached by the sequences CEHH, D/C.E_p.D and O.D/C.E_p.D Table 6. For CEHH sequence, the brightness was confined to 80.0°GE. With D/C.E_p.D and O.D/C.E_p.D sequences, 88.0°GE brightness could be

Table 5. Bleaching of unbleached pulp of Kappa No. 20.0, using in two stages after oxygen delignification

Bleaching sequence	O.D/C.E.D.	O.D/C.E _o .D	O.D/C.E _p .D
Oxygen Stage			
% dosage of NaOH		1.8	
% dosage of MgSO ₄ .7H ₂ O		0.05	
% consistency		12.0	
Initial pH		11.29	
Temperature °C		100 ± 2	
% pressure, kgs/cm ²		3.0	
Final pH		1.0	
Kappa Number		8.1	
D/C. Stage			
% dosage of Cl ₂ as A.Cl ₂		0.9	
% dosage of ClO ₂		0.8	
% consistency		12.0	
Initial pH		5.32	
Temperature °C		55.0	
Retention time, min.		45	
Final pH		6.22	
Kappa Number		4.48	
Extraction Stage			
% dosage of NaOH	2.0	1.8	2.0
% dosage of H ₂ O ₂ (on 100% basis)	-	-	0.3
% of dosage of MgSO ₄ .7H ₂ O	-	0.05	-
Oxygen pressure kg/cm ²	-	5.0	-
% consistency	12.0	12.0	12.0
Initial pH	11.54	11.52	11.34
Temperature °C	85	85	85
Retention time, min.	75	75	75
Final pH	10.85	9.51	10.74
Kappa Number	2.94	0.98	1.57
D- Stage			
% dosage of ClO ₂	1.0	1.0	1.0
% consistency	12.0	12.0	12.0
Initial pH	7.14	7.42	7.32
Temperature °C	75	75	75
Retention time, min.	200	200	200
Final pH	6.58	6.53	6.68
Brightness °GE	82.0	87.5	86.5
P.C. Number	1.37	1.36	1.38
Viscosity mPas (0.5% CED at 20°C)	10.22	9.0	9.70

achieved with good viscosity (10.3 to 10.5 maps) and low P.C. Number (1.09 to 1.12). Total chlorine consumed for D/C.E_p.D sequences is 6.93% and for O.D/C.E_p.D it is 5.63%.

Strength properties of these pulps (along with CEHH bleached pulp) are given in Table 7. The data indicates that the pulps bleached with D/C.E_p.D and O.D/C.E_p.D sequences to 88.0°GE brightness are stronger than CEHH pulp of 80.0°GE brightness.

CONCLUSION

By incorporating one chlorine dioxide stage at the end of CEH sequence, stronger pulp with good brightness stability (low P.C. Number) and better viscosity can be attained by CEHD or CE_oHD sequences. By stopping hypo bleaching at a lower brightness level (68±1°GE) and further bleaching with chlorine dioxide, responses

Table 6. Bleaching studies to compare the sequences CEHH, D/C.E_p.D and O.D/C.E_p.D unbleached pulp of Kappa No. 20.0

Bleaching sequence	CEH				D/C.E _p .D			O.D/C.E _p .D			
Bleaching conditions											
% dosage of Cl ₂ as A.Cl ₂ in Cl ₂ water	3.0	-	-	-	2.2	-	-	-	0.9	-	-
% dosage of ClO ₂	-	-	-	-	0.8	-	1.0	-	0.8	-	1.0
% dosage of NaOH	-	1.5	-	-	-	2.0	-	1.8	-	2.0	-
% dosage of H ₂ O ₂ (on 100% basis)	-	-	-	-	-	0.5	-	-	-	0.5	-
% dosage of Cl ₂ as A.Cl ₂ in hypo	-	-	-	1.3	1.2	-	-	-	-	-	-
% dosage of Sulphamic acid	-	-	0.15	01	-	-	-	-	-	-	-
% dosage of MgSO ₄ .7H ₂ O ₂	-	-	-	-	-	-	-	0.05	-	-	-
Oxygen pressure, kgs/cm ²	-	-	-	-	-	-	-	3.0	-	-	-
% consistency	3.0	7.0	7.0	7.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0
Temperature °C	Ambient	65-70	35.40	35-40	55	85	75	100±2	55	85	75
Retention time, min.	45	60	160	60	45	75	200	60	45	75	200
End ph	3.45	10.13	7.62	7.21	4.56	10.65	6.42	9.45	6.46	10.42	6.46
Kappa Number	-	4.72	-	-	5.12	2.2	-	9.85	4.24	1.88	-
Brightness °GE	-	-	75	8	-	67.5	88	-	-	68.5	88
P.C. Number	-	-	9.13	5.63	-	-	1.09	-	-	-	1.12
Viscosity mpas (0.5% CED at 20°C)	-	-	-	9	-	-	10.58	-	-	-	10.32
Total chlorine consumed in bleaching (all as A.Cl ₂) %	3.0+1.58+0.81 = 5.39				2.2+ 0.8+2.63 + 1.02x2.63 = 6.93			0.9+0.8x2.63+1.0x2.63= 563			

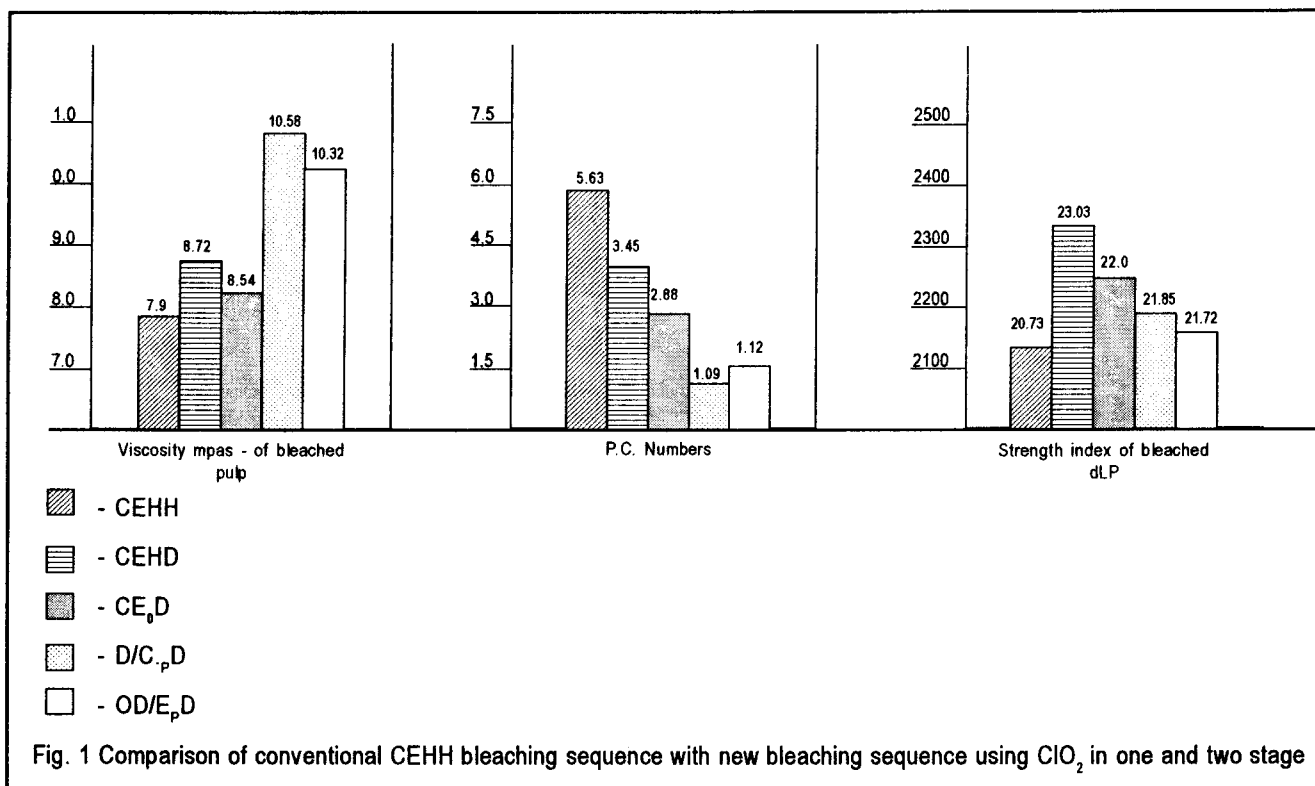


Fig. 1 Comparison of conventional CEHH bleaching sequence with new bleaching sequence using ClO₂ in one and two stage

Table 7. Strength properties of standard handsheets of 60 gsm of bleached pulps beaten to 40 °SR in valley beater

Bleaching sequence	CEHH	D/C.E _p .D	O.D/C.E _p .D
Breaking Length, m	8250	8248	8112
Tear Factor	72.22	75.61	76.67
Burst Factor	54.17	57.42	56.28
Double Folds. No.	190	253	238
Strength index	2073	2185	2172

to ClO₂ is better. Using unbleached pulp of lower Kappa Number is beneficial when a final ClO₂ stage is used because the total chlorine required is substantially lower and that the strength levels of final bleached pulp is well preserved. Good quality bleached pulp of 88.0°GE brightness, good viscosity (10.3 to 10.5 mPas) and low P.C. Number (1.09 to 1.12) can be produced by the sequences D/C.E_p.D and O.D/C.E_p.D using unbleached pulp of 20.0 Kappa Number.

LEGEND

C - Chlorination,
 E - Alkali Extraction,
 E_p - Alkali extraction augmented with hydrogen peroxide
 H - Calcium hypochlorite
 O - Oxygen.
 E_o - Alkali extraction augmented with oxygen
 D - Chlorine dioxide

D/C - Chlorine dioxide with Chlorination

P.C. - Post Colour Number

ACKNOWLEDGEMENT

We thank the Management of The Sirpur Paper Mills Limited, Sirpur Kaghaznagar for permitting us to publish this paper.

REFERENCES

1. Singh R.P. Tappi Press Journal "The Bleaching of Pulp" 3rd Edn. (1979)
2. Johnson P.A. et al, Tappi Journal, 79, (7) 61, (1996).
3. Reeve, Douglas, World Paper, p 34 (July 1995).
4. Ebellig, K Trans. 10th Fundamental Res. Symp. Products of Paper making, 3, Oxford (1993).