Chlorine Dioxide Bleaching-A Case Study

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INTRODUCTION

It is difficult to achieve brightness of more than 82/83% with conventional C-E-H-H sequence without pulp degradation. To obtain high degree of pulp brightness with minimum fibre degradation, bleaching agents like chlorine dioxide and or peroxide are suggested. In addition to this, it is becoming necessary for the paper Industry to replace hypo and chlorine in bleaching from pollution control point of view. Hence, to meet current and futuristic challenges, several bleaching experiments (1) with C-E-H-D-E-D, C-E-H-D-Ep-D, C-E-D-E-D and C-E-D-Ep-D sequences with SO_2 washing were done using Dioxide/Peroxide in our R&D laboratory to find out suitable sequence to achieve 88% pulp brightness, less pollution load and less strength loss because of usage of higher percentage i.e., 80-85% short fiber furnish.

Based on the In-House R&D experiments and overall advantages of Chlorine dioxide in pulp bleaching, THE ANDHRA PRADESH PAPER MILLS LIMITED decided to adopt C-E-D-E-D as bleaching sequence and installed a 3 TPD ClO_2 generation plant for captive generation of chlorine dioxide which was commissioned in September 1995.

This article deals with the various practical difficulties encountered in change over from conventional C-Ep-H-H sequence to C-Ep-D-E-D sequence and the measures taken in surmounting some of the difficulties to meet that set targets of higher pulp brightness with better brightness stability, lesser pollution and product quality upgradation.

DESCRIPTION OF CHLORINE DIOXIDE PLANT

The Andhra Pradesh Paper Mills opted for an integrated process of ClO_2 generation plant of 3.0 TPD capacity, based on the UHDE-MUNICH technology. It is having the environmental advantage (zero effluent) i.e., it does not produce any toxic effluent and is absolutely safe for chlorine dioxide water storage.

ClO_2 is generated by MUNICH PROCESS, with HCl as reducing agent.

$$NaClO_3 + 2\ HCl \longrightarrow ClO_2 + 1/2\ Cl_2 + H_2O + NaCl$$

The ClO_2 water contains about 7.0 gpl ClO_2, 1.0 gpl Cl_2 (max) and 1.0 gpl HCl (max) and pH is around 2.0-2.5.

The plant was commissioned in September 95.

CHLORINE DIOXIDE BLEACHING SYSTEM

Presently the mill is using 80% farm grown tropical hard woods which include Casurina (Casurina Equistifolia), Subabul (Leucaena leucocephala), Eucalyptus (Eucalyptus grandis), Mango (Mangofera indica), Cashew (Anacardium occidentle) and 20% Bamboo (Dendracalmus Strictus) as the fibrous raw material. Kraft process is used for pulping.

There are two streets of bleach plant namely Bleach plant II (BP_2) of capacity 150 TPD and Bleach plant III (BP_3) of capacity 150 TPD. In BP_2, pulp is bleached using C-Ep-H-H sequence, Where as BP_3 is designed for the bleaching sequence of C-E-D-E-D. The Chlorine tower is an upward flow tower and the Alkali and dioxide towers are downward flow towers. The D_1 & D_2 towers are provided with FRP vents.

To mitigate chlorine dioxide emissions from D stage towers, scrubbers were installed with process/ chilled water as scrubbing medium and also a condenser was installed in vapours line before scrubber with fresh water connection.

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MILL TRIALS WITH CHLORINE DIOXIDE

Mill trials with chlorine dioxide were started in October 95 in BP_3 plant to achieve bleached pulp of 85% brightness.

The incoming unbleached pulp has an average permanganate number of 14.7 and viscosity 17.7 Cps. The average gaseous chlorine consumption was 47.1 Kg/T with an average viscosity of 13.7 Cps. With the addition of peroxide at 7.5 Kg/T of pulp there is an improvement in brightness of the pulp (49.4 Vs 45.7%) as seen in **Table-1.**

TABLE-1

Chemical Consumption, Conditions and Extracted Pulp Characteristics with out and with peroxide

UNBLD PULP PERMANGANATE No.		
KAPPA No.	14.7/20.5	
VISCOSITY, Cps (0.5 M CED)	17.7	
TOTAL CHLORINE Kg/admt	47.1	
VISCOSITY, Cps	13.7	
	WITH H_2O_2	WITHOUT H_2O_2
ALKALI, Kg/admt	26.4	26.2
PEROXIDE, Kg/admt	7.5	--
FLOW BOX pH	10.6	10.7
TOWER TEMPERATURE^{0}C	63.6	60.7
BRIGHTNESS, % ELREPHO	49.4	45.7

Laboratory experiments were conducted to optimise the bleaching conditions.

Laboratory trials

A series of bleaching experiments were carried out with Ep pulp produced in BP_3. The conditions (temperature, retention time and pH) and chemical charges were varied to optimise the D_1 & D_2 stages. The results are given in **Tables-2 and 3.** The laboratory results indicated that

- # In D_1 stage, at lower dosages of dioxide (12kg/T), lower pulp temperature and pH in the range of 3.0 to 4.0 improve the brightness to a level of 78.5%.
- # At higher dosage 14Kgs/T in D_1 stage and lower retention time, higher pulp temperature 67-68^{0}C and pH 3.3 improve the brightness.
- # In D_2 stage, higher pulp temperature (75-76^{0}C) is preferable in improving the brightness of the pulp.
- # SO_2 washing improves the brightness and whiteness of the final pulp.

However, on plant scale we observed that even when the D_1 pH is 2.5-2.9, we could able to get about 77.0% brightness after D_1 stage. Initially, pulp bleaching with C-E-D-E-D sequence was started. Due to ClO_2 emissions we could not able to achieve 85% pulp brightness. Hence, to get targetted brightness, peroxide was added in first alkali extraction stage and second alkali extraction (E_2) stage was converted to oxidative extraction

TABLE-2

Effect of temperature, alkali addition and retention time in D_1 stage

Ep PULP COLLECTED FROM BP_3 PLANT; DIOXIDE COLLECTED FROM DIOXIDE PLANT

Consistency, %	11.84	ClO_2 gpl	6.56	pH 3.9	
Brightness, %	47.9	HCl gpl	0.57		
Viscosity, Cps	11.1	Cl_2 gpl	1.81		

S.No.	Particulars	SET 1	SET 2	SET 3	SET 4	SET 5	SET 6	SET 7	SET 8
1.	DOSAGE AS ClO_2, Kg/T	14	14	14	14	14	14	12	12
2.	ALKALI, Kg/T	-	-	4.0	4.0	4.0	4.0	4.0	3.0
3.	PULP TEMP, ^{0}C	67-68	57-59	67-68	67-68	57-59	57-59	67-68	57-59
4.	RETENTION TIME, mts	180	180	180	130	180	130	180	180
5.	pH FINAL	2.5	2.8	3.1	3.3	3.6	4.0	4.2	4.0
6.	BRIGHTNESS, % ELREPHO	73.7	73.5	78.5	80.5	79.5	79.0	78.0	78.5
7.	VISCOSITY, Cps (0.5M CED)	11.0	11.3	11.3	11.4	11.4	11.4	10.8	11.1

TABLE-3

BLEACHING OF Ep PULP WITH C-Ep-D-E/H-D SEQUENCE

Ep pulp pH 8.0; K.No. 2.6; Brightness 47.3%; Viscosity 10.2 Cps ClO_2 gpl 6.83; pH 2.6

S.No.	PARTICULARS				
I D_1 STAGE					
1	ClO_2 ADDED, Kgs/T	13.0			
2	PULP TEMP, °C	62-63			
3	pH FINAL	3.9			
4	RETENTION TIME, mts	130			
5	BRIGHTNESS, %	79.0			
6	VISCOSITY, Cps	10.3			
II E/H STAGE					
1	ALKALI ADDED, Kgs/T	5.0			
2	HYPO ADDED, Kgs/T	3.0			
3	RETENTION TIME, mts	90			
4	PULP TEMP, °C	62-63			
5	pH FINAL	10.7			
6	BRIGHTNESS, % ELREPHO	82.6			
7	VISCOSITY, Cps (O.5M CED)	8.5			
III D_2 STAGE					
1	DIOXIDE ADDED, Kgs/T	1.0		1.0	
2	PULP TEMP, °C	70		75-76	
3	pH FINAL	8.3		7.5	
4	RETENTION TIME, mts	120		120	
		WITHOUT SO_2	**WITH SO_2**	**WITHOUT SO_2**	**WITH SO_2**
5	SO_2 ADDED, Kgs/T	-	1.0	-	1.0
6	pH AT 1% Consistency	-	6.9	-	7.2
7	BRIGHTNESS, % ELREPHO	84.1	85.8	86.0	86.5
8	VISCOSITY, Cps	8.5	8.5	8.2	8.2
9	WHITENESS, % (BERGER)	68.1	71.2	74.2	74.9

stage with hypo chlorite (E/H). The average dosage of hypo is 3-4 Kg/T of pulp. With C-Ep-D-E/H-D sequence, at a total dioxide dosage of about 9.5 Kg/T, we could able to get a brightness of about 83.0%. As SO_2 treatment (2) helps to improve the brightness further, besides acting as an antichlor, addition of SO_2 has been started since February 1996 at a dosage of 0.9-1.0 Kg/T in back water of final washer which inturn used for dilution of D_2 pulp before washing.

After improving the scrubbing system an attempt was made to avoid peroxide and hypo addition to get the targetted 85.0% pulp brightness with higher dosage of chlorine dioxide in D_1 & D_2 stage with SO_2 washing i.e., with C-E-D-E-D-SO_2 sequence instead of C-Ep-D-E-/H-D-SO_2 sequence. But we could not achieve more than 81.0% pulp for brightness inspite of dosing 13.9Kg chlorine dioxide per ton of pulp in D_1 stage and 2.3Kg chlorine dioxide per ton of pulp in D_2 stage. This could be due to the downward flow system as the chlorine dioxide is not getting mixed thoroughly and reacted completely with the pulp resulting chlorine dioxide loss through emissions.

With a view to achieve 85.0% brightness and to avoid chlorine dioxide emission losses, the

TABLE-4

THE CHEMICAL CONSUMPTION, CONDITIONS OF D_1, E_2/H & D_2 STAGES

PARTICULARS	CEpDE/HD	CEDED-SO_2	CEpDE/HD-SO_2
DIOXIDE (D_1), Kg/admt	8.3	13.9	11.8
VAT PULP pH	3.4	-	-
(% values)	(avg)		
<2.9	-	87.2	87.4
3.0-4.0	-	12.8	12.6
TOWER TEMP °C	64.4	66.0	64.0
BRIGHTNESS, % ELREPHO	71.3	75.0	77.9
VISCOSITY, Cps (O.5M CED)	10.6	8.9	9.9
E/H STAGE			
ALKALI, Kg/admt	3.8	5.4	5.2
pH	8.9	9.7	9.7
TEMP °C	47.5	51.0	52.0
HYPO, Kg/admt	4.2	-	3-4
DIOXIDE (D_2), Kg/admt	1.05	2.3	0.7
VAT PULP pH	7.7	-	8.1
TEMP °C	45.0	64.2	53.3
SO_2 Kg/admt	-	0.9-1.0	0.9-1.0
TOTAL DIOXIDE Kg/T	9.35	16.2	12.5

sequence was again changed to C-Ep-D-E/H-D with SO_2 washing. The chemical consumption and conditions are presented in **Table-4.**

BENEFITS DERIVED OUT OF ClO_2 BLEACHING

Pulp quality improvement

There is an overall improvement in optical properties of bleached pulp. Brightness is improved by about 4 units (84.1 vs 80.5) and whiteness by about 7 units (68.5 vs 61.1) compared to C-Ep-H-H pulp. No adverse affect on strength properties as seen in **Table-5.**

Paper quality improvement-Product upgradation

The introduction of dioxide in the bleaching sequence helped to manufacture high brightness (85-87%) range products like copier, Diary and Printing varieties. And also the general brightness level is improved to 80-82% from 74-76% level.

TABLE-5

OPTICAL AND STRENGTH PROPERTIES OF FINAL PULP (AVERAGE)

S.No.	PARTICULARS	CEpDE/HD	CEDED-SO_2	CEpDE/HD-SO_2	CEpHH
1	BRIGHTNESS, % ELREPHO	82.9	81.1	84.1	80.5
2	VISCOSITY, Cps (O.5M CED)	7.8	7.7	7.9	7.4
3	WHITENESS, % (BERGER)	65.8	61.5	68.5	61.1
	STRENGTH PROPERTIES AT 40 °SR				
1	BURST FACTOR	35.1	34.2	35.6	33.0
2	BREAKING LENGTH, mtrs	5920	5895	6025	5775
3	TEAR FACTOR	62	63	63	60
4	DOUBLE FOLDS, Nos	12	10	13	12

Environmental effect-Pollution load

Though we do not have the plant scale data of AOX, our laboratory study results (3) indicates a reduction in AOX, BOD and COD values. The results are given in **Table-7.**

TABLE-7

R&D LAB STUDY RESULTS

Characteristics of bleach effluents

S.No.	SEQUENCE	AOX* Kg/T	BOD_3 Kg/T	COD Kg/T
1	CEHH	1.771	13.27	38.00
2	CEDED	1.650	11.83	33.70
3	CEpDED	1.577	11.77	33.20
4	C/D EpDED	1.002	9.37	28.07

Combined effluent values derived at by averaging the individual stage determined values.

* AOX values got tested at CPPRI on Dohrmann TOX Analyser.

FUTURE PLANS

To further improve the pulp quality and AOX, there is a proposal to go in dioxide addition in chlorination stage (C/D). Also measures are being planned to provide more efficient mixers and upward retention tubes to reduce chlorine dioxide losses and improve pulp brightness level to 86-88%.

CONCLUSIONS

In down ward tower design, absorption of the chlorine dioxide in pulp at higher dosages is less and leads to chlorine dioxide emissions. In such a situation pulp brightness 84.0% + with better strength properties can be obtained with C-Ep-D-E/H-D-SO_2 sequence. This facilitates to use this high bright pulp for high brightness grades of paper.

By introducing peroxide in E_1 stage and hypo in E_2 stage, saving of chlorine dioxide chemical and reduction of colour in alkali backwater effluent could be achieved. Further trials are underway to achieve 87 + % brightness, with the substitution of chlorine by chlorine dioxide (C/D) in chlorine stage and incorporation of upward flow tube with ONLINE MIXER in D_1 & D_2 stages. This leads to further optical quality improvement of paper and pollution abatement.

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REFERENCES

1. **"High Brightness Pulps from Bamboo-Mixed Hard woods." Sarkar P.K., Murthy N.V.S.R., Sagar CH. V.V. & Rao P.V.V.S.** IPPTA Vol. 6 No.3. September 1994. Paper presented in IPPTA zonal seminar, 1994.

2. **Britt, II Edition p 278.**

3. **"Modification of Bleaching Technology for Environmental Management at APPM". Murthy N.V.S.R., Sarkar P.K. & Khare S.K.** in IPPTA convention issue 1994., P-13. Paper Presented in Annual seminar, 1994.