New Bleaching Sequences to Eliminate Elemental Chlorine Usage

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ABSTRACT

Laboratory Experiments were carried out to eliminate use of Elemental Chlorine. Earlier work carried out in many Laboratories indicate that maximum AOX gets generated in chlorination and Extraction Stage (after chlorination stage). Hence any reduction or elimination of chlorine usage will reduce AOX formation. Though AOX was not tested in our Experiments, the sequences have been developed by eliminating chlorine usage and it is expected that AOX would get reduced.

The conventional bleaching sequence used in India by many mills is CEHH. However, some mills also use the sequences CEpHH & CE_p HHP.

The above three conventional sequences were compare with the four new sequences namely OP_XEHH, OP_XEHHP, OP_XEpHH & OP_XEpHHP. In the new sequences developed it was found necessary to use 1st oxygen stage to reduce Kappa Number to a reasonable level so that further reduction could be achieved in P_XE or P_XEp stage.

With an unbleached pulp of Kappa Number - 22, for Conventional Sequences, the total available chlorine consumed was 6.5 to 7.5% while for the new sequences it was 3.0 to 3.7 because no chlorine was used in chlorination stage. The brightness level achieved for conventional and New sequences were 78.5 to 80.0°GE. The Viscosity values for conventional sequences were between 6.6 to 7.41 m Pa s while it was 8.7 to 9.0 m pas for new sequences indicating less degradation.

As expected, the P.C. Numbers were low (both for conventional & New sequences) if the last stage is a P-stage.

The strength properties of pulps of New Sequences were better (strength Index 1995 to 2003) as compared to conventional sequences (1858 to 1945).

These experiments indicate that P_X Stage can be a simple bleaching stage to reduce Kappa Number which can be easily incorporated into conventional sequences.

INTRODUCTION:

With the chlorine based bleaching processes currently used in India, the environmental impact of Pulp Mill effluents carrying AOX content has gained considerable attention.

In the developed countries, most of the mills have already stopped using chlorine in 1st stage which has been completely replaced by chlorine dioxide. This technology is the so called 'ECF' technology and

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TABLE-1

Bleaching with non-conventional bleaching sequences compared to conventional bleaching sequences

Unbleached pulp of Kappa Number = 22.0

Sl. No.	1	2	3	4	5	6	7	8
1 to 4 control sequences 5 to 8 test sequences	**CEHH**	**CEHHP**	**CE_PHH**	**CE_PHHP**	**OP_XEHH**	**OP_XEHHP**	**OP_XE_PHH**	**OP_XE_PHHP**
Chlorination:					Oxygen Stage : 2.5% NaOH ; 0.5% Mg SO_4;			
% dosage of Cl_2 as A.Cl_2 in chlorine water	3.85	3.85	3.85	3.85	10% consistency; 98 ± 2°C Temperature; 5 kgs/cm² O_2 pressure; 60 Minutes Retention.			
% consistency	3.0	3.0	3.0	3.0	Kappa Number achieved after O_2 stage = 14.44			
Initial pH	2.80	2.80	2.81	2.81	Peracid Stage (P_x): Active Oxygen, % =0.2;			
Temperature, °C	--------- Ambient----------				10% consistency; 80± 2°C Temperature;			
Retnetion Time, hrs.,	--------- 1.0 ----------				60 minutes Retention time.			
Final pH	3.36	3.36	3.42	3.72	Kappa Number Achieved : After P_X Stage = 10.28			
Extraction Stage :								
% dosage of NaOH	1.5	1.5	1.5	15.	1.5	1.5	1.5	1.5
% dosage of H_2O_2 (as rec'd basis)	--	--	0.5	0.5	--	--	0.5	0.5
% Consistency	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Initial pH	10.54	10.54	10.21	10.21	10.92	10.92	10.47	10.47
Temperature, °C	---------- 65-70 ----------							
Retnetion Time, minutes,	---------- 45 ----------							
Initial pH	8.57	8.57	8.30	8.30	8.54	8.54	8.21	8.21
Kappa Number of Alkali Extracted pulp	11.3	11.3	9.4	9.4	8.67	8.67	8.54	8.54
Hypochlorite Stage-I:								
% dosage of Cl_2 as A-Cl_2 in Hypo	2.31	2.31	2.31	2.31	2.31	2.31	2.31	2.31
% dosage of sulphamic acid	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
% dosage of NaOH	0.75	0.75	0.75	0.75	--		--	--
% consistency	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Initial pH	9.64	9.64	9.82	9.82	8.74	8.74	8.98	8.98

Sl. No.	1	2	3	4	5	6	7	8
Temperature, °C	---------- 35-40 ----------							
Retnetion Time, hrs.,	---------- 2½ ----------							
Initial pH	8.21	8.21	8.51	8.51	7.82	7.82	7.69	7.69
% Residual chlorine	0.11	0.11	0.35	0.35	---------- Nil ----------			
% Chlorine consumed in H1	2.20	2.20	1.96	1.96	2.31	2.31	2.31	2.31
Brigthness achieved, °GE	76.5	76.5	77.0	77.0	77.0	77.0	77.5	77.5
P.C. Number	8.59	8.59	8.21	8.21	11.56	11.56	10.79	10.79
Hypochlorite Stage-II:								
% dosage of Cl_2 as A-Cl_2 in Hypo	1.54	1.16	1.16	0.77	1.54	1.16	1.16	0.77
% dosage of sulphamic acid	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
% dosage of NaOH	0.2	0.2	0.2	0.2	--	--	--	--
% consistency	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Initial pH	9.44	9.62	9.68	9.48	8.56	8.62	8.71	8.62
Temperature, °C	---------- 35-40 ----------							
Retnetion Time, hrs.,	---------- 2 ----------							
Initial pH	8.89	8.91	8.65	8.54	7.74	7.79	7.42	7.69
% Residual chlorine	0.12	0.08	0.14	0.07	0.14	0.06	0.08	0.05
% Cl_2 consumed in H_2	1.42	1.08	1.02	0.70	1.40	1.10	1.08	0.72
Total % Cl_2 consumed in bleaching	7.47	7.13	6.83	6.51	3.71	3.41	3.39	3.03
Brigthness achieved, °GE	80.0	78.0	80.0	78.5	80.0	78.5	80.5	78.5
P.C. Number	9.65	4.89	8.69	5.42	10.21	4.92	9.92	5.84
Final H_2O_2 Stage :	0.05% Mg SO_4-$7H_2O$; 0.75% Sodium Silicate ; 0.75% NaOH; 0.5% H_2O_2 (As received) : 10% consistency; 55 to 60°C Temp. ; Retention time 3 hours.							
Brigthness achieved, °GE	--	80.5	--	80.5	--	80.0	--	80.0
P.C. Number	--	2.54	--	2.32	--	2.92	--	2.24
Viscosity, m. Pas (0.5% CED at 20°C)	7.41	7.18	6.93	6.62	8.84	8.69	8.96	8.84

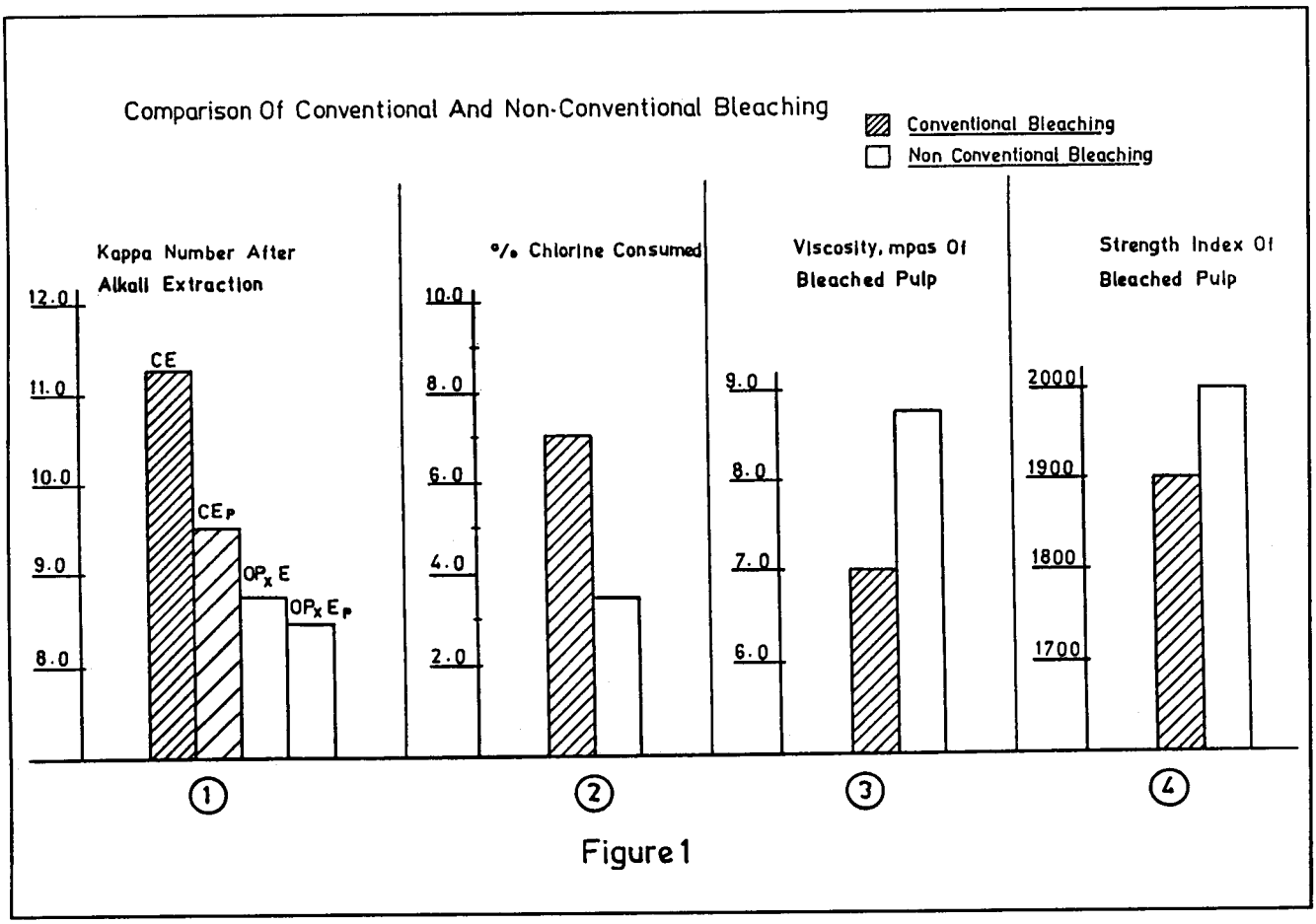


Figure 1

another competing Technology is the 'TCF' technology which does not use any chlorine compounds.

However, among other methods to eliminate or minimize chlorine, 1st stage oxygen treatment is a well developed technology. To be selective, this process has to be done in two steps and this involved additional capital investment.

Recently methods have been developed to prepare peroxymonosulphuric acid just before use (1, 2) and an additional P_X stage followed by alkali extraction can bring down the Kappa Number further and hence chlorination can be completely eliminated.

The present work describes sequences where chlorination is completely eliminated.

EXPERIMENTAL

Pulp used for Experiments :

Screened Unbleached Kraft Chemical pulp collected from Pulp Mill : Kappa Number 22.0.

Peroxymonosulphuric Acid (Caros Acid) Preparation:

Addition of concentrated sulphuric acid to 50% w/w hydrogen peroxide in the mole ratio of 1.5:1 and maintaining the reaction temperature between 30 and 35°C. The prepared acid was stored in refrigerator for further use. Caro's acid has the formula H_2SO_5, $\overset{O}{\overset{\|}{HO}}\!-\!O\!-\!\overset{O}{\overset{\|}{SO}}\!-\!H$. The active oxygen of Caro's acid is 14% (based on mass by mass basis), as only one oxygen of O-O linkage permole is considered active.

BLEACHING (MULTISTATE)

Bleaching experiments were carried out on small batches of 400 g in water tight polythene bags. Temperature of reaction was maintained by immersing the polythene bags containing pulp & added bleaching agents in water bath whose temperature was maintained by immersing the polythene bags containing pulp & added bleaching agents in water bath whose temperature was maintained.

TABLE-2

Strength Evaluation of Bleached Pulp

Sl. No.	1	2	3	4	5	6	7	8
1 to 4 control sequences 5 to 8 test sequences	CEHH	CEHHP	CE_pHH	CE_pHHP	OP_XEHH	OP_XEHHP	OP_XE_pHH	OP_XE_pHHP
Initial Freeness, °SR	15	14	15	15	13	14	13	13
Beating Time, min.	55	50	50	55	60	65	65	65
Final Freeness, °SR	41	40	40	41	40	41	40	41
Grammage, g/m^2	61	60	62	61	61	60	61	60
Caliper, µm	78	75	78	78	80	80	80	78
Bulk, cm^3/g	1.28	1.25	1.26	1.28	1.31	1.33	1.31	1.31
Breaking Length, m	8142	8090	7942	7984	8411	8601	8809	8421
Tear Factor	56.42	56.96	54.49	55.19	58.24	57.92	59.05	58.11
Burst Factor	49.71	49.54	47.12	47.92	52.18	51.84	53.21	51.89
Double Fold	422	384	315	390	440	421	456	430
Strength Index	1945	1939	1858	1899	2003	1990	2029	1995

Note :- Strength Index is calculated by the formula - { (Burst Factor) X (Tear Factor) X (Log D F)} X½ 100

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 DISCUSSIONS

Bleaching conditions and bleaching results are given in Table-1 and Figure-1. From the results it is observed that after E or EP stage, the Kappa Number is 9.4 to 11.3 for conventional sequences. For non-conventional sequence it is 8.54 to 8.67. This helps in reducing hypochlorite dosage to achieve same level of final brightness.

The total available chlorine consumed for conventional sequence is 6.51% to 7.47% whereas it is 3.03 to 3.71% for non-conventional sequences for final brightness of 78.5 to 80.0°GE showing a substantial reduction.

Final pulp brightness of 84-84°GE can also be achieved by slightly increasing the dosage of available chlorine. Accordingly to bleach a pulp of Kappa Number 22.4 (Table-3) total available chlorine consumed for conventional sequences is 7.60 to 8.73% whereas is 3.54 to 4.37 for non conventional sequences for final pulp brightness of 84-85°GE.

From Table-2, the bleached pulps of non conventional sequences are found to be stonger (Strength Index 1995 to 2003) as compared to conventional sequences (1858 to 1945). This is borne by higher final viscosity achieved (Table-1). as expected (based on our earlier work and plant operation) the pulps bleached with P-Stage as last stage have lower P.C. Number as compared to sequences without last P-Stage, irrespective of whether the sequence used is conventional or non-conventional.

Effluent characteristics for different bleaching sequences are given in Table-1. Comparatively COD, BOD and Colour values of Peracid Stage effluent (P_X) are lower than the effluent of chlorination stage (C) indicating a substantial reduction in effluent treatment load. Accordingly AOX generation would also be low for the new sequences as no elemental chlorine is used in bleaching.

TABLE-3

Bleaching with non-conventional bleaching sequences compared to conventional bleaching sequences

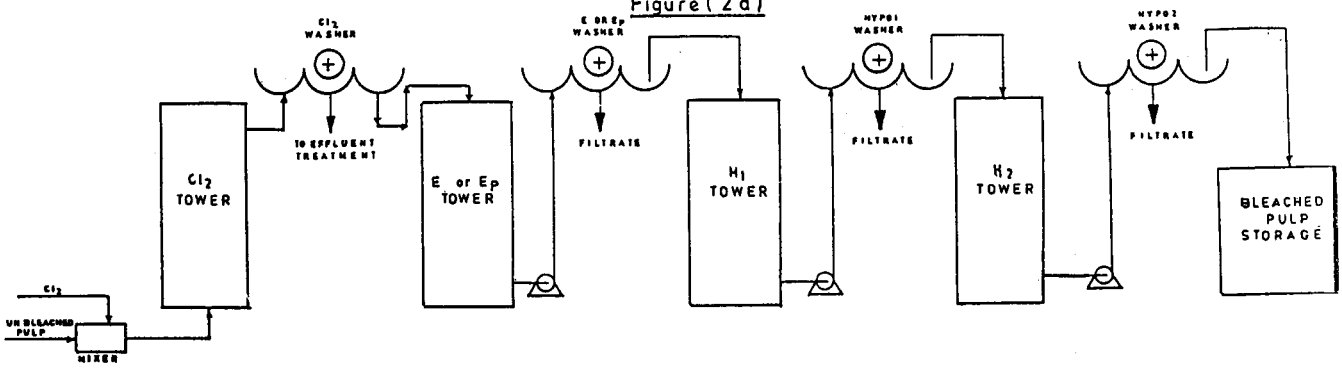
Unbleached pulp of Kappa Number = 22.5

Sl. No.	1	2	3	4	5	6	7	8
1 to 4 control sequences 5 to 8 test sequences	**CEHH**	**CEHHP**	**CE_PHH**	**CE_PHHP**	**OP_XEHH**	**OP_XEHHP**	**OP_XE_PHH**	**OP_XE_PHHP**
Chlorination:					**Oxygen Stage :** 2.5% NaOH ; 0.5% Mg SO_4;			
% dosage of Cl_2 as A-Cl_2 in chlorine water	4.5	4.5	4.5	4.5	10% consistency; 98 ± 2°C Temperature: 5 kgs/cm^2 O_2 pressure; 60 Minutes Retention.			
% consitency	3.0	3.0	3.0	3.0	**Kappa Number achieved** after O_2 stage = 13.4			
Initial pH	2.72	2.72	2.72	2.72	**Peracid Stage** (P_x): Active Oxygen, % =0.2;			
Temperature, °C	--------- Ambient----------				10% consistency; 80± 2°C Temperature;			
Retnetion Time, hrs.,	--------- 1.0 ----------				60 minutes Retention time.			
Final pH	3.92	3.92	3.92	3.92	**Kappa Number Achieved** : After P_x Stage = 9.73			
Extraction Stage :								
% dosage of NaOH	1.5	1.5	1.5	15.	1.5	1.5	1.5	1.5
% dosage of H_2O_2 (as rec'd basis)	--	--	0.5	0.5	--	--	0.5	0.5
% Consistency	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Initial pH	10.93	10.93	10.86	10.86	11.05	11.05	10.97	10.97
Temperature, °C	---------- 65-70 ----------							
Retnetion Time, minutes,	---------- 45 ----------							
Initial pH	8.71	8.71	8.57	8.57	8.62	8.62	8.50	8.50
Kappa Number of Alkali Extracted pulp	10.22	10.22	9.35	9.35	8.58	8.58	8.20	8.20
Hypochlorite Stage-I:								
% dosage of Cl_2 as A-Cl_2 in Hypo	2.70	2.70	2.70	2.70	2.70	2.70	2.70	2.70
% dosage of sulphamic acid	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
% dosage of NaOH	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
% consistency	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Initial pH	10.67	10.67	10.75	10.75	10.60	10.60	10.50	10.50

Sl. No.	1	2	3	4	5	6	7	8
Temperature, °C	---------- 35-40 ----------							
Retnetion Time, hrs.,	---------- 2½ ----------							
Initial pH	8.75	8.75	8.32	8.32	8.40	8.40	8.77	8.77
% Residual chlorine	0.15	0.15	0.39	0.39	---------- Nil ----------			
% Chlorine consumed in H1	2.55	2.55	2.31	2.31	2.70	2.70	2.70	2.70
Brigthness achieved, °GE	79.5	79.5	80.0	80.0	80.0	80.0	80.5	80.5
Hypochlorite Stage-II:								
% dosage of Cl_2 as A-Cl_2 in Hypo	1.80	1.35	1.35	0.9	1.80	1.35	1.35	0.9
% dosage of sulphamic acid	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
% dosage of NaOH	0.2	0.2	0.2	0.2	--	--	--	--
% consistency	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Initial pH	10.10	10.10	10.25	10.37	10.37	10.37	10.25	10.25
Temperature, °C	---------- 35-40 ----------							
Retnetion Time, hrs.,	---------- 2 ----------							
Initial pH	8.94	8.94	8.86	8.86	8.71	8.71	8.89	8.89
% Residual chlorine	0.12	0.07	0.18	0.11	0.13	0.05	0.09	0.06
% Cl_2 consumed in H_2	1.68	1.28	1.17	0.79	1.67	1.30	1.26	0.84
Total % Cl_2 consumed in bleaching	8.73	8.33	7.98	7.60	4.37	4.00	3.96	3.54
Brigthness achieved, °GE	84.0	83.0	84.5	83.5	84.5	84.0	84.5	84.0
P.C. Number	8.39	5.42	8.34	4.91	6.39	4.98	5.43	4.68
Final H_2O_2 Stage :	0.05% Mg SO_4-$7H_2O$; 0.75% Sodium Silicate ; 0.75% NaOH; 0.5% H_2O_2 (As received) : 10% consistency; 55 to 60°C Temp. ; Retention time 3 hours.							
Brigthness achieved, °GE	--	84.5	--	85.0	--	85.0	--	85.5
P.C. Number	--	3.18	--	3.22	--	3.12	--	3.24
Viscosity, m. Pas (0.5% CED at 20°C)	7.22	7.01	7.12	7.11	7.88	7.81	7.97	7.84

FLOW DIAGRAM SHOWING CONVENTIONAL BLEACHING SEQUENCE

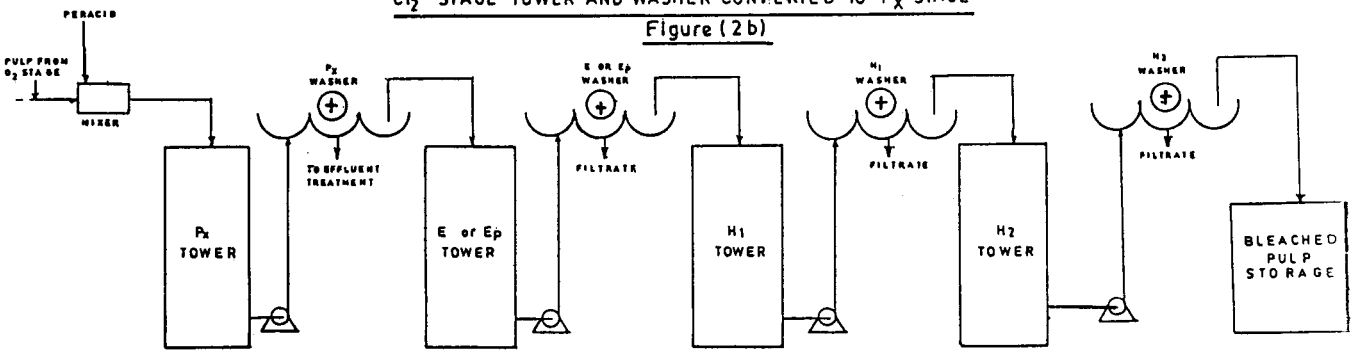
Figure (2 a)



FLOW DIAGRAM SHOWING NEW BLEACHING SEQUENCE

Cl_2 STAGE TOWER AND WASHER CONVERTED TO P_X STAGE

Figure (2 b)



CONCLUSIONS

1. It is possible to incorporate a P_X-Stage in the present bleach plants (The chlorination Stage with its tower and washer being converted to P_X-Stage). P_X can easily be prepared and dosed without additional equipment (Figure-2).

2. To completely eliminate chlorination stage a pre-oxygen stage bleaching is required to bring down the Kappa Number to desired level for further bleaching.

3. The new sequences developed have a potential to completely eliminate first stage chlorination thereby reducing AOX generation.

4. The cost of chemicals for P_x Stage at dosage level of 0.2% (as Active oxygen) on pulp would be Rs. 556 per tonne pulp.

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LEGEND

Abreviation used for Bleaching Stages

C : Chlorination

E : Alkali extratcion

E_P : Alkali extraction augmented with Hydrogen peroxide

H : Calcium Hypochlorite

P_X : Peroxymono sulphuric Acid

O : Oxygen.

TABLE-4
COD and BOD Load each stage, kg/t

Conventional Bleaching Sequence	CEHH			CEHHP			CEpHH			CEpHHP		
	COD	BOD	COLOR H. unit	COD	BOD	COLOR H. unit	COD	BOD	COLOR H. unit	COD	BOD	COLOR H. unit
C-stage	20.3	9.6	1000	20.3	9.6	1000	20.3	9.6	1000	20.3	9.6	1000
E- ,,	18.2	10.8	4000	18.2	10.8	4000	--	--	--	--	--	--
Ep- ,,	--	--	--	--	--	--	19.9	3.1	5000	19.9	3.1	5000
H_1 ,,	11.9	4.3	150	11.9	4.3	150	5.8	5.5	150	5.8	5.5	150
H_2 ,,	4.1	8.6	50	4.1	8.6	50	4.3	4.8	50	4.3	4.8	50
P- stage	--	--	--	6.5	5.9	50	--	--	--	6.3	4.1	50
New Sequence	**OP_XEHH**			**OP_XEHHP**			**OP_XE_PHH**			**OP_XE_PHHP**		
	COD	BOD	COLOR H. unit	COD	BOD	COLOR H. unit	COD	BOD	COLOR H. unit	COD	BOD	COLOR H. unit
O_2-stage	31.5	12.9	2500	31.5	12.9	2500	31.5	12.9	2500	31.5	12.9	2500
P_X- ,,	7.7	8.2	100	7.5	8.2	100	7.5	8.2	100	7.5	8.2	100
E- ,,	13.1	2.6	600	13.1	2.6	600	--	--	--	--	--	--
E_P- ,,	--	--	--	--	--	--	14.3	4.9	600	14.3	4.9	600
H_1- ,,	7.2	6.2	100	7.2	6.2	100	4.2	5.2	100	4.2	5.2	100
H_2- ,,	3.6	0.9	50	3.6	0.9	50	2.2	0.4	50	2.2	0.4	50
P-stage	--	--	--	4.3	0.36	50	--	--	--	6.1	0.42	50

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