Relation Between Sulphate Loss of Washed Brown Pulp And Chlorine Consumption in CEH Bleaching & Generation of Pollution Load

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ABSTRACT

Bamboo and mixed Hard woods still continue to be the major fibrous raw materials for producing different grades of papers in India. During the process, major source of pollutants generated are from Pulp Mill and that too from Pulp washing and bleaching stages. While pre-bleaching stages also generate high pollution load which have a direct bearing on Chlorine and alkali consumption in subsequent bleaching stages.

Brown Stock Washer and Decker Washer are important stages of pre-bleaching and their performance at the optimum efficiency is essential to reduce pollution load in the bleaching stages.

In order to assess the co-relation of carryover alkali in the form of black liquor at pre-bleaching vis-avis Chlorine consumption in a conventional CEH bleaching, laboratory studies were carried out with two samples of Decker Pulp collected on different dates. Aliquots of black liquor of known concentration were added to the squeezed black liquor from Decker pulp in order to increase carryover alkali content as Na_2SO_4 kgs/ Ton of pulp in the range of 15 to 50 (with minimum difference of 5.0 kgs/Ton of pulp between two consecutive observations). It is observed that there almost exists a linear relationship between alkali loss and Chlorine consumption as depicted in Fig.2 & 3 Decker squeezed & unsqueezed pulps of Kappa No. 24.0 and 28.0 were bleached under C/E/H sequence for pulp brightness 79-80% P.V. The total chlorine consumption with Decker pulp of kappa no. 28.0 is higher than lower Kappa No. 24.0 pulp as expected. Squeezed Decker pulps of Kappa No. 24 & 28 consume lower amount of total chlorine by 0.34% and 0.6% respectively than their unsqueezed pulps. The final brightness of squeezed pulp is higher by 2-3 degress than unsqueezed pulp.

Pollution load of COD, Chlorided, total solids and colour per ton of unsqueezed pulp is more than the squeezed pulp under C/E/H bleaching sequence. Pollution load from higher kappa no. (28.0) pulp is more than the lower Kappa no. 24.0 pulp.

INTRODUCTION

Spent cooking liquor to a large extent is separated from pulp in washing operation. However even small amount of spent liquor still remaining in the pulp does influence considerably the consumption of chlorine and the characteristics of bleach effluent[1, 2].

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Table 1

Relationship between Alkali Loss from Decker Washer and Corresponding Chlorine Consumption

Decker Pulp consistency = 20.3%

Squeezed liquor collected = 1.82 M^3/Ton of pulp.

S. No.	Black liquor added ml/50ml of squeezed liquor	pH of squeezed liquor	Conductivity of squeezed liquor from Decker pulp m.mhos.	Alkali loss with squeezed liquor kgs, Na_2SO_4/ton of pulp	Addition of chlorine gms/litre of squeezed liquor	Chlorine water concentration g/l	Total Chlorine addition with squeezed liquor,kgs/ton of pulp	Conductivity (m.mhos) of chlorine treated liquor for pH 2.5
1.	Blank Expt.	7.95	1600	9.0	0.95	1.704	1.7	4200
2.	0.45	9.40	3000	15.0	1.27	1.704	2.3	5450
3.	0.65	9.85	4900	20.0	1.78	1.704	3.2	5800
4.	1.40	9.95	6200	25.4	2.14	1.704	3.9	6700
5.	2.00	10.05	7450	30.0	2.89	1.704	5.3	7000
6.	2.55	10.15	8700	35.3	3.27	1.704	6.0	7300
7.	3.50	10.25	10250	40.5	4.48	1.704	8.2	7500
8.	4.80	10.35	11650	45.6	5.57	1.704	10.1	7600
9.	5.75	10.40	13200	51.5	6.48	1.704	11.8	7800

* Black Liquor from pulp mill of 13.0 g/l as Na_2O was added to simulate the conditions of alkali loss/ton of pulp.

Retained cooking liquor has an effect on process control similar to variation in lignin content of pulp. Further more, it decreases the reaction rate in case of Kraft pulp by increasing the chlorination pH. The increase in Chlorine consumption resulting from retention of black liquor has been claimed to be 1.0-1.3 kg/kg of so-called Sodium Sulphate losses resulting from the black liquor during the washing stage.

The pulp slurry going into the Bleach Plant is usually alkaline, whereas the Chlorine dispersion is an acid treatment. The very first part of chlorination is therefore carried out at fairly high pH. After only a few seconds, the pH of free liquid drops almost to its final level due to formation of acids in various reactions. Chlorine reacts smoothly and rapidly with non-Carbohydrate component of chemical pulps to form a highly coloured partially water soluble meterial usually referred to as chlorolignin[3]. The chlorinated phenolic material becomes readily removable by the action of alkali and oxidants in subsequent bleaching stages. The amount of Chlorine applied depends on characteristics of pulp, the lignin content and the number of stages in the bleaching sequence[4,5,6]

Reduction in Chlorine consumption on account of reduced alkali loss at Brown Stock Washer/Decker Washer is helpful in minimising the impact final Brown Stock Washer followed by a Decker Washer, the Chlorine consumption becomes higher. This is partly because Chlorine is consumed to bring down pH of adhereing liquor with Decker Washer pulp from 8.5-10.5 to 2.5 and secondly to react with pulp to form chlorophenolic lignins which are removed in the Caustic extraction stage.

EXPERIMENTAL DETAILS

Two pulp samples from Decker Washer were collected on different dates when Bamboo and mixed hard woods proportion was 65:35. The pulp consistency, squeezed liquor quantity M^3/ton of pulp and condctivity (by uranyl zinc acctate method) were determined to findout alkali loss kg Na_2SO_4/Ton of pulp. Mill black liquor was then added in small aliquots with fixed quantity of squeezed liquor in order to increase alkali loss as Na_2SO_4 kgs/Ton of pulp in the range from 15 to 50 kg/Ton of pulp with a minimum difference of 5.0 kg/ton of pulp between two consecutive observations. The increase in pH was also recorded. The findings are given in

Retained colling liquor has an effect on process

Particulars	pulpconsistency%	Squeezed liquor M^3/ ton of pulp	pH of squeezed liquor	Alkali loss kgs. Na_2SO_4/ ton of pulp	conductivity m.mhos.
Table -1	20.3	1.82	7.95	9.0	1600
Table -2	16.1	2.73	10.1	15.0	3000
Table - 3					
(i) Lower Kappa No. 24.0 Pulp	16.1	2.80	10.1	14.2	2800
(ii) Higher Kappa No. 28.0 Pulp	14.8	3.70	10.5	17.0	4030

Table 1 & 2.

To know the impact of black liquor (concentration 13.0 g/L as Na_2O) addition on Decker squeezed liquor, chlorine water of known concentration was added gradually to bring down pH to 2.5. The total Chlorine consumption/ton of pulp with respect to black liquor addition is given in Table 1 & 2. Graphs (Fig. No. 2 & 3) were plotted between alkali loss in the squeezed liquor/ton of pulp versus Chlorine consumption.

Decker pulp (squeezed and unsqueezed) of Kappa No. 24 and 28 were bleached under C/E/H sequence for pulp brightness 79-80% P.V. bleaching conditions and results are reported in Table - 3. Pollution load generated at each stage of bleaching viz. COD, total solids, colour and chloride with squeezed and unsqueezed pulps is recorded in Table -4.

DISCUSSIONS

Washing of pulp at the Decker Washer : The

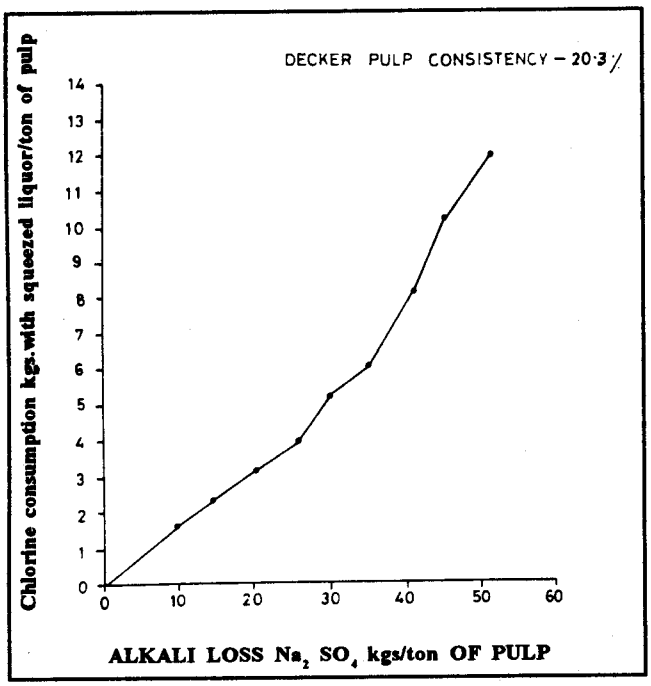

Fig.- 2 Effect of alkali loss at Decker washer on chlorine consumption in chlorination stage.

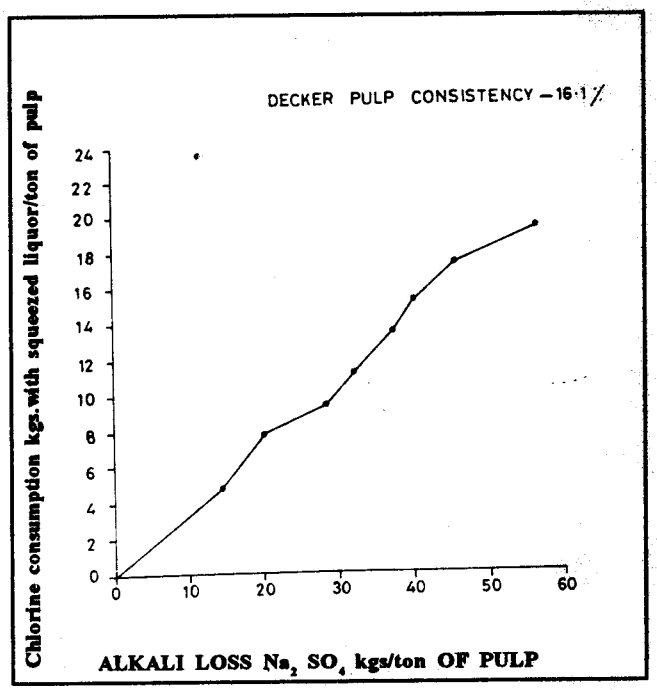

Fig.- 3 Effect of alkali loss at Decker washer on chlorine consumption in chlorination stage.

Table 2

Relationship between Alkali Loss from Decker Washer and Corresponding Chlorine Consumption

Decker Pulp consistency = 16.06%

Squeezed liquor collected = 2.73 M^3/Ton of pulp.

S. No.	Black liquor added ml/50ml of squeezed liquor	pH of squeezed liquor	Conductivity of squeezed liquor from Decker pulp m.mhos.	Alkali loss with squeezed liquor kgs, Na_2SO_4/ton of pulp	Addition of chlorine gms/litre of squeezed liquor	Chlorine water concentration g/l	Total Chlorine addition with squeezed liquor,kgs/ton of pulp	Conductivity (m.mhos) of chlorine treated liquor for pH 2.5
1.	Blank Expt.	10.10	3000	15.0	1.80	1.385	4.5	5300
2.	0.7	10.15	4950	20.0	2.81	1.385	7.7	5800
3.	1.35	10.20	6300	25.7	3.37	1.385	9.2	6100
4.	2.30	10.20	7450	30.2	4.45	1.210	11.1	6700
5.	2.70	10.30	8700	36.2	4.80	1.210	13.1	7000
6.	3.80	10.35	10200	40.0	5.49	1.120	15.0	7200
7.	475	10.40	11450	45.0	6.30	1.030	17.2	7400
8.	6.0	10.50	12710	50.8	6.97	1.030	19.0	7600

* Black Liquor from pulp mill of 13.0 g/l as Na_2O was added to simulate the conditions of alkali loss/ton of pulp.

composition of Bamboo and mixed hardwoods for the whole day on different dates was 65:35 for carrying out cooking at the Pulp Mill under normal pulping conditions. The pulps were having kappa No. in the range of 24-28.

Following were the observations of Decker Washer Pulps on different dates :

Washing of the pulp at the brown Stock Washer and Decker Washer depends upon Dilution factor, feed consistency, Vat consistency, shower temperature, drum speed, sheet thickness, actual composition of raw material in the pulp and vacuum maintained at the washers etc.

It is evident from Tabes 1 & 2 that at lower mat consistency of the Decker washer, the alkali loss, pH, conductivity and squeezed liquor quantity are on higher side. No two pulps have same consistency because of raw material composition in the mixed cooking, quality of pulp and other process conditions maintained at the plant. Conventional cooking of Bamboo & mixed hardwoods, washing & bleaching operation followed in paper industry is depicted in Fig. 1.

EFFECT OF BLACK LIQUOR ADDITION ON ALKALI LOSS & HIGHER CHLORINE CONSUMPTION

Mill black liquor of 13.0 g/L as Na_2O was added with the squeezed liquor from Decker Washer pulp in order to maintain alkali loss between 15 to 50 kg Na_2SO_4/ton & pulp (with minimum difference of 5 kg/ton of pulp between two consecutive observations). Chlorine water was added to bring down the pH around 2.5. The consumption of Chlorine kgs with squeezed liquor/ton of pulp is depicted in figures 2 & 3 and the findings are reported in Tables 1 & 2. In order to bring pH 2.5 by addition of Chlorine, conductivity was also measured. Chlorination stage often leaves considerable amount of acid spent Chlorine liquor with the pulp going to alkali extraction stage, which increases the consumption of the alkali in the extraction stage[7].

BLEACHING OF DECKER SQUEEZED & UNSQUEEZED PULPS UNDER C/E/H SEQUENCE.

Decker (squeezed and unsqueezed) pulps at kappa

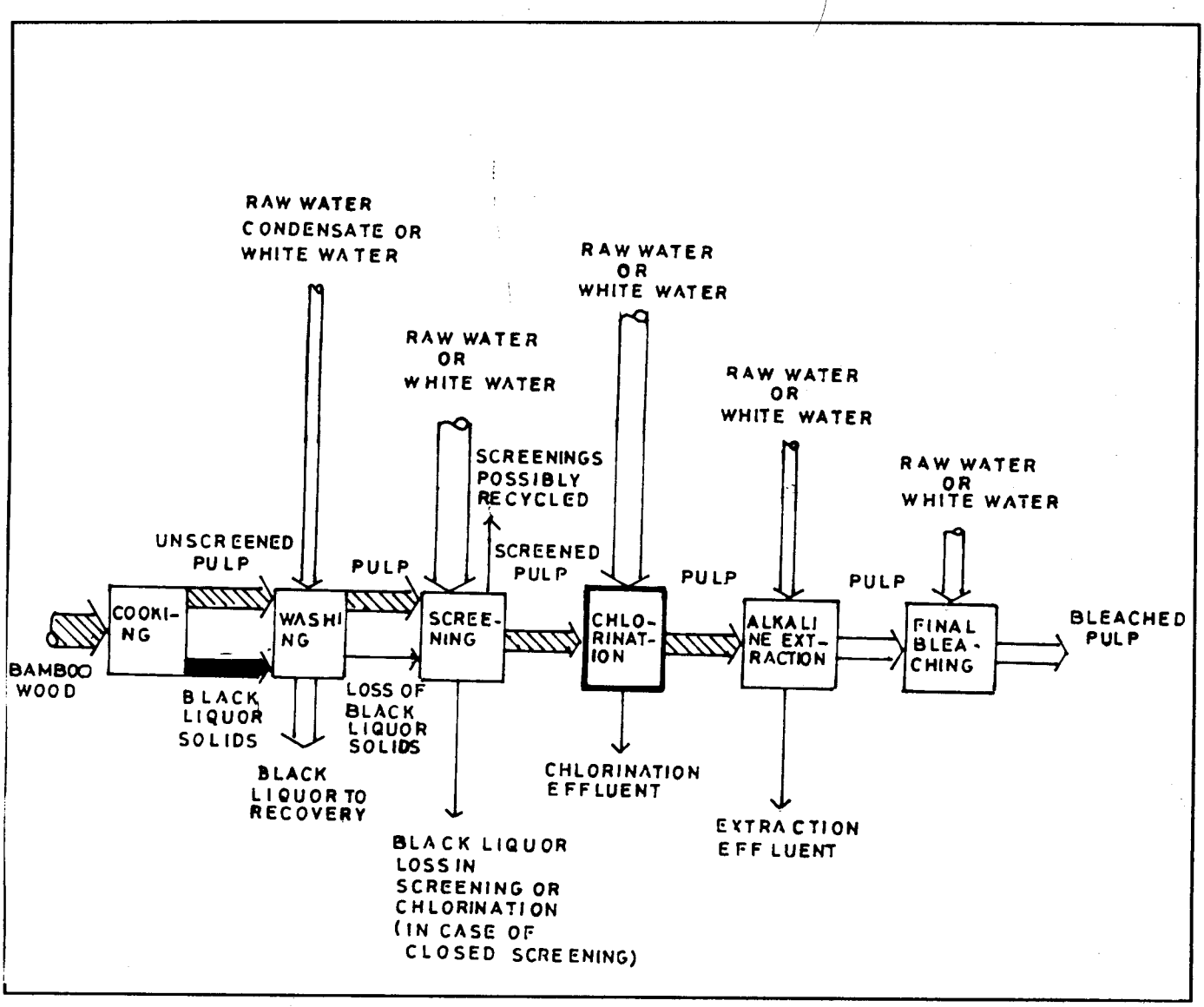

Fig.- 1 Sequence for the production of fully bleached chemical pulps

No. 24.0 and 28.0 were bleached under C/E/H sequence for a pulp brighten 79-80% PV (Table - 3). The total chlorine dosages in chlorine and hypochlorite stages for squeezed and unsqueezed pulps was kept same for a particular kappa No. in order to know the effect of squeezed liquor removed from pulp. The total chlorine consumption with Decker Pulp of Kappa no. 28.0 is higher than lower Kappa No. (24.0) Pulp as expected. Squeezed Decker pulps of kappa No. 24 & 28 consumed lower amount of total chlorine by 0.34% and 0.6% respectively than their unsqueezed pulps. The final brightness of squeezed pulp is higher by 2-3 degrees than unsqueezed pulps.

POLLUTION LOAD GENERATED IN C/E/H SEQUENCE BLEACHING

Pollution load generated from Decker squeezed and unsqueezed pulp while bleaching under C/E/H sequence is reported in table - 4. Pollution load in each stage of bleaching has been calculated for comparing different parameters and to find out total pollution load.

Table 3

Bleaching of Decker Squeezed and Unsqueezed pulps under C/E/H Bleaching sequence.

S.No.	Particulars	Decker Pulp (Kappa No. 24.0)		Decker Pulp (Kappa No. 28.0)	
		Squeezed	Unsqueezed	Squeezed	Unsqueezed
Chlorination Stage					
i)	Chlorine applied % /Chlorine Consumed %	4.5/4.36	4.5/4.4	6.0/5.7	6.0/5.8
ii)	End pH	2.1	2.3	1.85	2.0
Caustic Extraction					
i)	Caustic applied %	2.0	2.0	2.5	2.5
ii)	End pH	10.9	10.7	11.0	10.8
Calcium Hypochlorate stage					
i)	Hypochlorate applied % / Hypochlorate Consumed	3.0/2.5	3.0/2.8	3.0/2.3	3.0/2.8
ii)	Buffer added %	0.7	0.7	0.8	0.8
iii)	End pH	8.3	8.3	8.5	8.4
Final Results					
i)	Total Chlorine applied %/ Total Chlorine Consumed %	7.5/6.86	7.5/7.20	9.0/8.00	9.0/8.6
ii)	Pulp birghtness % PV	79.5	77.5	82.0	79.0
iii)	Pulp Viscosity (0.5% CED); cps	6.7	7.8	6.2	7.1

Constant Bleaching Condition

S. No.	Particulars	C	E	H
1.	Consistency, %	3.0	10.0	10.0
2.	Temperature, °C	Room	60 ± 1	40 ± 1
3.	Retention time, mts	60	60	120

Table 4

Pollution Load generated from Decker squeezed and Unsqueezed pulps bleached under C/E/H sequence.

S.No.	Particulars	Decker Pulp (Kappa No. 24.0)		Decker Pulp (Kappa No. 28.0)	
		Squeezed	Unsqueezed	Squeezed	Unsqueezed
	Effluent Load				
i)	Effluent volume generated, litre	2.58	2.65	2.56	2.62
ii)	pH	2.1	2.3	1.85	2.0
iii)	COD, kg/ton of pulp	34.7	38.3	38.8	41.8
iv)	Chloride, kg/ton of pulp	23.2	23.9	31.2	32.2
v)	Total solids, kg/ton of pulp	83.1	87.9	85.5	92.0
vi)	Colour, kg.ton of pulp	10.8	11.8	11.5	13.1
	Effluent load in extraction stage				
i)	Effluent volume, generated, litre	0.65	0.67	0.67	0.64
ii)	pH	10.9	10.7	11.0	10.8
iii)	COD, kg/ ton of pulp	14.8	16.3	16.6	17.5
iv)	Chloride, kg / ton of pulp	3.6	3.0	4.9	4.0
v)	Total solids, kg/ ton of pulp	30.4	34.3	40.1	43.4
vi)	Colour, kg/ ton of pulp	20.8	26.8	23.7	29.1
	Effluent Load in Hypo stage				
i)	Effluent volume, generated, litre	0.7	0.7	0.7	0.7
ii)	pH	8.3	8.3	8.5	8.3
iii)	COD, kg/ton of pulp	4.5	4.8	5.4	8.4
iv)	Chloride, kg/ton of pulp	24.8	25.2	25.2	25.9
v)	Total solids, kg/ton of pulp	57.5	59.7	59.5	62.5
	Total Pollution Load generated in C/E/H.sequence				
i)	COD, kg/ton of pulp	54.0	59.4	60.8	65.6
ii)	Chloride, kg/ton of pulp	51.6	52.1	61.3	62.1
iii)	Total solids, kg/ton of pulp	171.0	181.9	185.1	197.9
iv)	Colour, kg/ton of pulp	31.6	38.6	35.2	42.2

Note : Pollution load of various parameters has been calculated on squeezed liquor generated from each stage of bleaching

COMPARISON OF POLLUTION LOAD GENERATED FROM LOWER KAPPA NO. (24.0) SQUEEZED AND UNSQUEEZED PULP

Total pollution load generated from Decker unsqueezed pulp under C/E/H bleaching sequence is higher than squeezed pulp as detailed below :

	Total Pollution Load kg/ton of Pulp	Squeezed Decker Pulp	Unsqueezed Decker Pulp
(i)	COD	60.8	55.2
(ii)	Chloride	61.3	62.1
(ii)	Total solids	185.1	197.9
(iv)	Colour	35.2	42.2

COMPARISON OF POLLUTION LOAD GENERATED FROM HIGHER KAPPA NO. (28.0) SQUEEZED AND UNSQUEEZED PULP

Total pollution load generated from Decker pulp of higher Kappa No. (unsqueezed pulp) under C/E/H bleaching sequence is higher than squeezed pulp as detailed below:

	Total Pollution Load kg/ton of Pulp	Squeezed Decker Pulp	Unsqueezed Decker Pulp
(i)	COD	54.0	59.4
(ii)	Chloride	51.6	52.1
(ii)	Total solids	171	181.9
(iv)	Colour	31.6	38.6

It is evident from above that pollution load generated from higher Kappa No. pulp is more than lower Kappa No. Decker pulp bleached under C/E/H sequence.

CONCLUSION

Pre-stages of bleaching are important to reduce pollution load at the bleaching stages. There exists almost a linear relationship between alkali loss and chlorine consumption which will further need higher dosage of alkali treatment at the caustic extraction stage.

It has been experimentally found that Squeezed Decker pulp consumed lower amount of total chlorine than unsqueezed pulp to get the desired pulp brighten 79-80% P.V. Pollution load generated from Higher kappa No. pulp is more than lower Kappa No. of pulp. Squeezed pulp generate lower amount of pollution load than unsqueezed pulp. To minimise the pollution load during bleaching the kappa No. of unbleached pulp should be reduced to the extent so that it does not affect the pulp yield and physical strength properties significantly.

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