Studies on Bleaching of Bamboo Pulp

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The author gives a brief description of prehydrolysed-kraft bamboo pulp bleaching with a particular emphasis on the contribution and importance of variables in the important purification and refining steps and includes studies on hypochlorite bleaching (with and without sulphamic acid). Salient features are also described as to why it is necessary to incorporate dioxide stage for preservation of viscosity, uniformity and better characteristics of bleached pulps.

Introduction :

Bamboo fibres are long cylindrical with tapered ends in shape and have inherent draw back of high length to lumen ratio. The fibrers lack in scalariform perforations typical of hardwood vessel elements or pitted structure of tracheids in softwoods. In the bleaching operations the diffusion of chemical takes place through the tapered ends of the lumen and the mode of reaction basically differs from the homogeneous diffusion and the uniform access of chemicals through the pitted perforations of wood fibres. A factor which further contributes significantly towards a relatively poorer response to bleaching is the presence of condensed lignins in bamboo pulp, which amounts to nearly 25 percent of the total lignin present. Most of these lignins are entrapped in the less accessible zones of the fibers. As a result of partial delignification the " hemicelluloses swell and diffusion of chemicals through the narrow lumen is hindered. This phenomenon is quite significant for paper grade bamboo pulps containing high proportion of both hemicelluloses and lignins. The fact that pulps of similar lignin contents obtained from other species, under identical conditions of purification and bleaching, undergo high degree of depolymerisation explains the basic difference between them and bamboo. Thus, sulphite pulps can be bleached readily to high brightness in few stages at low bleach consumption. Hardwood sulphate pulps can be bleached satisfactorily in four stages to +80 brightness, without much loss of strength. For Bamboo pulps the brightness can seldom be raised beyond 78 degrees in four stage

CEHH sequence without deterioration in strength of fibres—as measured by viscosity.

The success in bleaching kraft bamboo pulp will, therefore, be determined by an approach to remove, necessarily, maximum amount of condensed lignins enveloping fibers in one operation and subsequent removal of the remaining present inside the fiber structure, without appreciably affecting the cellulose in as many successive operations as would be economically feasible.

Chlorination :

The degradation and solubilization of lignins in chlorination stage could be regarded as continuation of purification of pulp which commences in pulping. Chlorine reacts with lignins by addition, substitution or oxidation depending upon its ratio with other constituents like hypochlorous or hypochlorite ions. The high initial alkalinity or pH of kraft pulp favours the formation of hypochlorite in the initial phases as a result oxidation reaction dominates. Addition reaction follow thereafter when the pH of the system drops down below 3. The success of purifying action of chlorine could best be judged by pH—which gives a picture of the other ionic species present.

The chlorination of bamboo kraft pulp with increasing concentration of chlorine shows that the consumption of chlorine increases upto certain limit depending upon the lignin content of pulp. Reaction of chlorine with pulp is very rapid in the initial period and thereafter the reaction velocity

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considerably subsides. Higher dosage of chlorine beyond a permissible chlorine demand which corresponds to nearly 60% of the total bleach requirement, results in appreciable degradation of pulp as measured by drop in viscosity. Results show that at 30-35°C increasing amount of chlorine decreases the residual P. No. and beyond (60% of 1/2 P. No.) Cl₂ no further reduction in hard...ess takes place.

The effect of pH keeping other factors constant. has a clear influence upon the degree of delignification and pulp viscosity. At the same level of chlorine consumption, whereas the P. No. attains an optimum value, the increasing pH decreases the viscosity and the percentage drop is most significant in the range of 2-3. In all probabilities the depolymerisation is caused by substantial increase in hypochlorous and hypochlorite ion concentrations. During purification of kraft pulp by chlorine, the system actually orients itself successively in the following order: Chlorine-(Hypochlorite)-pulpwater ; Chlorine — (Hypochlorite — Hypochlorous acid)-pulp-water; Chlorine-(Hypochlorous acid) ---pulp-water; and chlorine---pulp-water. Lignins and carbohydrates are accordingly exposed to three types of oxidizing agents each reacting and contributing in its own way towards delignification and depolymerisation. The reaction of these constituents of chlorine water with cellulose is non-specific and there are evidences of both oxidative and hydrolytic processes. The outcome is that both carboxyl and carbonyl contents are increased.

The influence of temperature is dependent upon the level of chlorine applied. The effect of temperature on delignification has shown that reaction rate is accelerated at higher temperatures (>40°C) thereby simultaneously favouring delignification and degradation of cellulose. At higher temperature there is a tendency for chlorine-water to be transformed into hypochlorous acid-a plausible cause of pulp degradation. At higher temperature the chlorine consumption increases and it is an indication that a part of available chlorine is consumed to render the degraded lignins in solution and the rest is consumed by susceptible cellulosic parts which are oxidized. The substitution reaction is facilitated under the conditions of low temperatures and the carbohydrates undergo less damage.

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Use of aditives in chlorination stage: The beneficial effects derived from Nitrogen compounds such as Ammonia, Urea, Ammonium chloride, sulphamic acid, etc. when added in small amounts in chlorination stage have been described in literature. On incorporating sulphamic acid (S.A.) at an optimum charge of chlorine during chlorination it was found that the viscosity drop of bamboo pulp can be markedly lessened. However, its effectiveness lies over a certain range only. Based on several experiments, it appears that for bamboo pulp, an amount equivalent to 1.8 percent based on chloride charge would be optimum. The fact that the detrimental effect of high pH and temperature during chlorination is lessened by the presence or addition of S.A. makes it a chemical of great utility. Though, the mechanism of reaction of S.A. is not yet established, but it appears likely that the detrimental action of hypochlorous acid is inhibited by its combination with S.A. forming chloro-sulphamic acid and or di-chlorosulphamic acid-both possessing low oxidation potential.

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As discussed in the foregoing paragraphs oxidation of cellulose occurs under all conditions of chlorination its rate increasing with concentration, pH and temperature. From experiments to determine the advantage of including small amounts of chlorine-dioxide during chlorination, it has been observed that the viscosity of pulp increases and the increase is directly related to the amount of chlorine dioxide applied at constant level of chlorine. The combinations of fixed amount of chlorine and varying amounts of chlorine divide have shown that viscosity of pulp increases sharply upto 0.6% ClO_a (expressed as Cl⁻) beyond which it has a tendency to drop down. Degree of delignification, as measured by P. No. increases with increasing amounts of dioxide however, once again the decrease becomes relatively insignificant beyond 0.6% doxide. With respect to delignification and preservation of viscosity this mode of treatment surpasses all other treatments. The rate of attack on carbohydrates is diminished perhaps due to decrease in concentration of chlorine by dioxide for which Rapson proposed the following mechanism. Chlorine dioxide reacts with lignins forming chlorite-the chlorite is cleaved to dioxide by chlorine and the process, nearly resembling dioxide treatment, continues.

A summary of what has been said in the foregoing paragraphs is given in Table 1. It will be

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observed from the table that a mixture of $Cl_2 + ClO_2$ give most satisfactory results with respect to degree of delignification and preservation in viscosity. The effect of S.A. and of other variables on viscosity and P. No. can be grouped in the following pattern.

With respect to % Preservation in Viscosity. low temperature supersedes sulphamic acid supersedes $Cl_2 + ClO_2$ supersedes low pH supersedes normal chlorination.

With respect to % reduction in P. No. Sulphamic acid supersedes $Cl_2 + ClO_2$ supersedes low pH supersedes low temperature supersedes normal chlorination.

S. No.	Variable	Chemical as Cl on pulp. %	Consis- tency.	Time min.	Temp. C	Initial pH	Free Cl g.p.l.	Reduction in P. No.	% Preservation of viscosity (based on unbleached pulp)
1.	Normal chlorinatio	n 3.0	2.5	35	31	7.95	0.185	41.1	38.7
2.	Low pH	3.5	2.5	35	30	8.4	0.188	56.5	40.0
3.	Low Temp.	4.5	2.5	35	18.5	7.9	0.178	53.1	· 72.3
4.	Sulphamic acid on Cl-1.84%	3.25	2.5	30	31	8.5	0.015	61.5	56.0
5.	ClO_2 as Cl —on	3.0	35	30	33 5	85	1 1 3 6	577	54 1
6.	Only ClO_2	3.0	3.5	60	.30	4.0		64.3	97.5

Alkaline extraction :

Chlorination:

3.		NaOH on	Consisten	cy. Time	Tem.	Free alkali	Reduction in P. No.	% Preservation	
No.	Variable ref.	pulp %	%	Min.	°C	g. p. l.	(based on unbleached pulp)	(based on un- bleached puip).	
1.	Normal Chlorination	2.5	12	80	70	1.60	71.3	30.2	
2.	Low pH	2.5	11	120	70 ·		76.7	35.5	
3.	Low Temp.	2.5	12	80	70	1.40	76.6	65.5	
4.	Sulphamic acid on Cl-1.84%	2.0	10	120	60	0.88	75.5	48.6	
5.	ClO, as Cl—on pulp 0.6%	2.5	9	150	80	1.088	81.0	45.3	
6.	Only ClO.	2.5	9	150	80	~	79.8	94.7	

Alkaline Extraction :

The hydrophobic lignins are rendered hydrophilic by chlorination as a result the whole interfibrillar material swell and hinder the passage of oxidizing agents in the subsequent purification stages. It becomes therefore necessary to treat the pulp with alkali to dissolve the chlorinated and oxidized lignins and lower chain hemicellulosic fractions. The causes of degradation of cellulose during alkaline

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extraction could be primarily attributed to peeling reaction rather than hydrolysis. The latter is known to occur under severe conditions of extraction beyond 100°C and alkaline extraction is rarely practised beyond 80°C. In the peeling reaction the end carbonyl group in cellulose molecule is cleaved and transformed to soluble gluco-iso saccharinic acid and the reaction proceeds stepwise with the newly formed adjacent carbonyl group until a stabilization reaction-in which the end structure rearranges to resistant configuration of gluco-metasaccharinic acid-stop the cleavage. Peeling reaction is more pronounced with pulps containing high percentage of carbonyl groups. Unfavourable conditions-like higher pH, higher chlorine charge or higher temperatures, during chlorination of pulp invariably give rise to hydrolysis reaction-a factor contributing towards high carbonyl contents in the pulp. Hydrolysed pulps exhibit maximum drop of viscosity during alkaline extraction.

The data presented in Table 1 show that on alkaline extraction the percentage reduction in **P**. No. is maximum for (C.D.), E pulp whereas the viscosity preservation is most satisfactory for (C-low temperature). E. and (C-S-A). E. pulps. (C D). E. pulp would supersede other pulps—if the results are computed at equal level of % reduction in **P**. No. Pulp purified by chlorine-dioxide

alone, undergoes minimum hydrolysis and acquires lesser number of functional reducing groups. As a result, it exhibits relatively small degradation compared to other pulps during alkaline extraction.

The effect of varying alkali charge, temperature and time on residual P. No. and viscosity has been shown in Table 2. For these studies unbleached bamboo pulp was chlorinated under following conditions:

 Cl_2 on pulp=3.2%; Initial pH=8.5; Consistency=3.0% 35 minutes at 22°C.

It will be seen from the table that with rise in concentration of NaOH viscosity decreases and beyond 4 percent alkali charge the percentage reduction is appreciable. More or less similar trend was revealed at temperature higher than 60°C. Higher retention time at 70°C brings more lignins in solution and results in proportionately less damage to cellulose. Losses of carbohydrates occur under all conditions of extraction and the percentage losses increase under the extreme conditions of alkali extraction and temperature. Surface active agent Lissapol NX, at higher concentrations, can also be advantageously used in alkaline extraction stage (Table II). Under similar conditions Ammonium hydroxide was found to be equally effective and capable of diminishing lignin contents. Few of the data are summarised below :

TABLE 2

Effect of alkali charge, temperature and time on viscosity and Permanganate Number (P. No.)

Sl. No.	Stage	Losses based on chlorinated pulp %	% Reduction in Viscosity	% Reduction in P. No.
1.	2% NaOH: 80 min. at 70°C	2.62	58.14	74.36
2.	3% NaOH : 80 min. at 70°C	3,29	58.85	75.65
3.	4% NaOH; 80 min. at 70°C	5.27	59.68	76.93
4.	5% NaOH; 80 min. at 70°C		70.88	76.93
5.	6% NaOH; 80 min. at 70°C	6.83	75.83	75.65
6.	2.5% NaOH'; 80 min. at 90°C	6.63	76.69	80.77
7.	2.5% NaOH; 80 min. at 60°C	3.08	57.81	75.65
8.	2.5% NaOH: 80 min. at 50°C	2.93	56.71	75.08
9.	2.5% NaOH; 150 min. at 70°C	3.65	58.41	82.06
10.	2.5% NaOH ;'240 min at 70°C	3.88	77.04	84.62
11.	2.5% NaOH; 300 min. at 70°C	2.74	77.16	84.62
12.	2.5% NaOH; 80 min. at 70°C			
	1.0 g.p.l. Lissapol NX	2.40	57.81	75.65
13.	2.5% NaOH; 80 min. at 70°C			15.05
	2.0 g.p.l. Lissapol NX	2.45	58.36	82.06
14.	2.5% NaOH; 150 min. at 60°C		55.75	78.21

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Consistency 10 percent; 80 minutes at 70°C

	N	HOH	on pulp) %	NaOH on pulp%
^{10/} Deduction in	2.5	3.0	3.5	4.0	2.5
P. No.	76.3	77.6	78.2	78.9	80.8
% Reduction in Viscosity	49.2	47.2	49.5	52.1	51.8

The experiments described in the preceding sections give a sufficient indication of the fact that, irrespective of the ideal conditions of chlorination and extraction, a theoretical level of 100 percent reduction in P. No. can never be accomplished. The maximum reduction in P. No. that can be affected seldom exceeds 80 percent. At this level the viscosity can be well preserved to an extent of 45 percent by use of additives in chlorination stage.

Real problem in the ensuing bleaching steps is posed by residual lingins. To affect degradation and dissolution of the residual lignins, amounting to 25% of unbleached pulp P. No., takes a longer bleaching time and higher amounts of bleaching chemicals. There could be two reasons for this, (i) The ligning are present inside the fiber structure and (ii) the lignins have very high molecular weight. Furthermore, the cellulose is susceptible to attack by oxidising chemical because in the preceding purification operations a majority of impurities have been removed as a consequence the external surface of the fibre is exposed and cellulose left in a more accessible state. These are the factors i.e. removal of impurities without seriously degrading cellulose, which would influence and determine the success of bleaching.

During the course of investigation on hypochlorite bleaching of C.E. pulp it was observed that the pulp degradation of such a high magnitude occurred which marred all the advantages brought forth from the previous steps. Can the degradation be checked by use of additives? The following paragraphs give a summary of the effect of Hypochlorite SA combination and hypochlorite alone on variation in oxidation potential, pH, reduction in P. No. and viscosity with reaction time.

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Hypochlorite bleaching of CSAE. Pulp:

In figure 1 is shown the effect of pH on oxidation Potential (O.P.) of sodium hypochlorite and for the sake of comparison—the results of chlorite and chlorine water have also been included. The results are in harmony with those already reported in literature and confirm that O.P. of hypochlorite or chlorine water is very much influenced by change in pH unlike chlorite which has a fairly constant value in a wider range of pH. In hypochlorite system with decreasing pH the O.P. increases and the difference is well marked between pH 7 to 8.5. Most of the damage to cellulose is done in this range.



Data presented in Table 3 show that the exhaustion of Cl—and the rise in O.P. is very quick in the first 30 minutes of reaction and preceeds some what slowly in the next 60 minutes. The decrease in pH

values-responsible for increasing O.P.-during the course of reaction is quite an expected trend in that the free alkali of the system is neutralised in the process of dissolution of oxidised lignins and like compounds. With increasing reaction time the percentage drop in viscosity and P. No. almost go parallel to each other. The sharp decline in viscosity and P. No. in the initial phase could be attributed to rise in O.P. and fast consumption of Cl--. Increasing proportions of S.A. decrease the overall rise in O.P. and results in slightly better viscosity preservation. Several other experiments have shown that the extent of molecular breakdown is appreciable with C.E. pulps having higher viscosities.

The facts described in the foregoing section substantiate that it is but essential to resort to some other specific bleaching chemical, in place of hypochlorite following C.E. treatments, which would prevent susceptible cellulosic part from oxidative and hydrolytic attack.

As has been shown in figure 1—in a wider range of pH Chlorine-dioxide possesses low oxidation potential compared to hypochlorite. This fact coupled with its ability to degrade lignins to colourless low molecular weight products without affecting carbohydrates makes it a bleaching agent of great importance. The results emerging out on treating C.E.—bamboo pulps with chlorine dioxide were encouraging in all respects. Further, by addition of chlorine dioxide stage to a four stage bleaching the total chlorine consumption can be reduced primarily owing to small amounts of chlorine required for final bleaching with hypochlorite.

There are other reasons of including dioxide in place of hypochlorite for the bleaching of C. 5.

TABLE 3

Hypochlorite treatment of C E Pulp: Effect of sulphamic acid on O.P., pH, P. No., Viscosity, etc.

Sulphamic acid on C		d on Cl=	Nil	Sulphamic acid on Cl=0.85%						Sulphamic acid on $Cl = 5.1\%$					
S. No	Time (Min)	0.	P. pl	H % Drop in Vis- cosity Cp	%Reduc- tion in P. No.	Free Cl g.p.l.	0. P	. pH	% Drop in Vis- cosity Cp	% Reduc- tion in P. No.	Free Cl g.p.l.	C. P.	% Drop in Vis- cosity Cp.	% Reduc- tion in P. No.	· Free C g.p.l.
1.	1	496	9.5			0.8875	530	9.65	5		0.8875	518			0.8165
2.	30	630	9.2	61.73	88.71	0.3195	642	9.0	59.02	2 91.13	0.2840	620	58.89	91.13	0.2485
3.	60	680	8.8	5 65.07	91.94	0.1175	682	9.9	61.98	8 92.34	0.1420	646	61.86	91.94	0.2130
4.	90	108		- 65.99	92.75	0.1065	694		63.2	1 92.75	0.1065	660	62.97	92.95	0.1775
5.	120	740	8.5	0 67.54	93.55	0.0710	726	8.55	66.42	2 93.15	0.0355	682	63.21	93.55	0.1420
6.	150	740	8.4	5 67.91	93.96	0.0516	722	8.5	66.67	7 93.55	0.0355	680	63.09	94.36	0.1065
7.	170	690	-8,5:	5 67.66	94.36	0.0355	682	8.4	67.54	4 94.36	0.0355	634	63.96	94.36	0.0710
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TABLE 4

S. No.	Pulp Characteristics	C	(1) EDH	C _{SA} EDH	С ₍₂₎ ЕDН	(CD) EDH	Ceh _{sa} d	(CD)E (HE) D
1.	Brightness (Colourimetrically) %			81	83	82	83
2.	≺ Cellulose, %	• • • •	93.09	95.2	97.4	98.30	95.75	97.21
3.	β Cellulose, %	•••			1.88	1.88	4.86	2 45
4.	¢Cellulose, %				1.05	0.94	0.474	0.80
5.	1% NaOH Solubility, %	• ••	5.22	2.79	1.61	0.36	2.06	1 33
6.	7.14% NaOH Solubility, %	•••			5.88	2.98	7.96	5.46
7.	Copper Number	•••	0.88	0.52	0.20	0.25	0.47	0.22
8.	Kappa Number	• ••			0.674	0.427	0.994	0.736
9.	Viscosity, Cp.					*		0.700
	(1% Cuprammonium)		9.5	14.5	16.2	19.2	10.2	13 44
10.	% Reduction in Viscosity							10.11
	during bleaching	· • •	77.9	66.2	64.8	58.3	68.6	70.8

4 Stage Bleached Bamboo Pulp Characteristics

3.6% Cl₂ on unbleached pulp;
 2.5% Cl₂ on unbleached Pulp;

pulps. The entrapped lignins in fibers are easily accessible to fast diffusing chlorine dioxide—a fair proportion of which is available in gaseous phase at higher temperatures. The diffusion occurs through the fiber walls and lumen, and in fact differs from the diffusion of hypochlorite which appear to take place through the lumen only. The percentage reduction in Permanganate Number i.e. reduction in lignin contents—a function of brightness of pulp, is always more for dioxide treated pulps and less for pulps treated with hypochlorite. minimum for C (High dose of chlorine), E.D.H. pulp. By use of additives i.e. sulphamic acid or chlorine dioxide, and Dioxide trea.ment following E. the \prec -cellulose content could be potentially raised and improvement in characteristics like 1%NaOH solubility (a measure of oxidative degradation of cellulose during bleaching), Copper number (a measure of functional reducing groups), 7.14%NaOH solubility (a measure of maximum cellulose solubility), etc. could be satisfactorily accomplished.

		 C. E. P Hypochlorite	ulp Dioxide	(CD). E. Hypochlorite	Pulp) Dioxide
1. % Reduction in viscosity	•••	 87	76	79	56
2. % Reduction in P. No.		 86	88	89	92

Bleaching of C.E.D., (CD). E.D. and CSA E.D. pulps continued with small amounts of hypochlorite, under controlled conditions of pH, yielded pulps of high brightness and improved characteristics. The data have been summarised, alongwith other pulp data, in Table 4. The figures show that viscosity preservation is maximum for (CD), E.D.H. pulp and

Summary and Conclusions :

Fiber morphology plays a significant role during purification and bleaching of kraft bamboo pulp. The inacessible lignins entrapped within the fiber structure account for lower brightness of conventionally purified and bleached C.E.H.H. pulp. Much of the

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success of bleaching depends upon the extent of lignin removal during purification i.e. C. E. operations without damaging fiber strength. For improving the effectiveness of chlorination use of slightly higher done of chlorine than the normal demand at low pH or low temperature or both combined should prove advantageous. The results of chlorination could be improved by judicious use of additives during chlorination.

The depolymerisation of cellulose during alkaline extraction has been found to be dependent upon the damage incurred to cellulose in the chlorination step. All the extreme conditions of time, temperature and alkali charge result in more losses of useful carbohydrate part. For alkaline extraction the exact choice of conditions depend upon the properties desired in the final pulp. However, an optimum alkali charge-capable of diminishing the unbleached P. No. to about 75 percent should form the basis. For better brightness and high viscosity preservation of C. E. pulps it would be necessary to replace first hypochlorite stage by chlorine-dioxide in the sequence C.E.H.H. The results of bleaching in all respects, can be improved by such a treatment.

Hypochlorite treatment, carried out under mild and controlled conditions, raises the brightness to + 80 units without degrading the viscosity of (CD). E.D. pulp. purified and bleached by such a sequence possess good end characteristics and has lower value of micro kappa number-a measure of residual lignins-compared to pulps of other sequences.

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