Studies on the Chemical Kinetics of Bleaching Bamboo Pulp with Calcium Hypochlorite

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Dendrocalamus strictus pulp prepared on the pilot plant was bleached in the laboratory by calcium hypochlorite using 4, 6 *and* 8% *of chemicals calculated as available chlorine on oven-dry weight of the pulp at* 5% *consistency and* 30°C. *The time of reaction was varied as* 15, 30, 60, 120 *and* 180 *minutes and pH was varied from* 8 *to* 10. *The pentosan content and permanganate number of the resultant pulp was determined. Strength properties of the standard sheets were determined and brightness of the standard sheets before and after aging was also determined. It is observed that the pentosan content and permanganate number of these pulps usually fall with the increase in time of reaction and the fall is more pronounced at lower pH. Strength properties improve on bleaching till a certain time of reaction after which they tend to fall. Beating time is reduced with the increase in time of reaction and the amount of chemicals. The results also indicate that it is a fast reaction at the start followed by a slow second order reaction.*

INTRODUCTION

Use of calcium hypochlorite or sodium hypochlorite has continued as a bleaching agent for considerable time and shall continue because of the advantages of low cost and controlled degradation of cellulose. Hypochlorite bleaching is mainly on oxidation reaction which decolorizes and solubilizes the lignin, natural dyes and other impruities in the fibre. Under certain conditions, reactions other than oxidation predominate. Hypochlorite preferentially attacks lingnin but it also reacts with cellulose particularly if the reaction is not properly controlled. The following reactions are believed to occur in alkaline hypochlorite bleaching:

$$Ca(ClO)_2 + 2H_2O \longrightarrow Ca^{+} + 2OH^{-} + 2HClO$$

$$HClO + OH^{-} \rightleftharpoons ClO^{-} + H_2O$$

$$HClO + ClO^{-} \longrightarrow ClO + Cl^{-} + OH$$

$$ClO + ClO^{-} + OH^{-} \longrightarrow 2Cl^{-} + 2O + OH$$

$$ClO^{-} + CH \longrightarrow ClO + OH^{-}$$

Hypochlorites are alkaline in nature having a pH of eleven but pH decreases as bleaching proceeds because of the formation of carbon dioxide and organic acids and the hypochlorite is converted into calcium chloride. This changing pH during bleaching results in the decomposition of hypochlorite and degradation of the pulp. Higher pH reduces the rate of reaction considerably. Hence proper control of pH during hypochlorite bleaching is essential. Similarly consistency at which the bleaching is carried out also controls the rate of reation because higher the consistency higher is the concentration of the effctive hypochlorite resulting in increased rate of reaction. Besides pH and consistency, the other main variables are, duration of reaction, amount of hypochlorite used on the weight of the pulp and temperature. Generally in hypochlorite bleaching temperature is seldom raised beyond 40°C and is generally carried out at room temperature which is around 30°C in India. In the present set of experiments, 4, 6 and 8% of chemicals calculated as available chlorine on o.d. weight of the pulp at 5% consistency and 30°C were used. The time of reaction was varied as 15, 30, 60, 120 and 180 minutes. The pH was varied from 8 to 10. This study was carried out to find out the chemical kinetics of bleaching of bamboo pulp with calcium hypochlorite with the idea that it may throw some light on the order of reaction and also on the optimum conditions for partial bleaching.

Alongwith this the effect of these variables on the strength properties of the resultant pulp was also studied because the strength properties in a way reflect the quality of the pulp. Brightness of the standard sheets before and after aging was also determined to have an idea of the keeping quality of the pulp in relation to the chlorine demand.

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PRODUCTION OF THE PULP AND ITS EVALUATION

Dendroclamus strictus bamboo obtained from the demonstration area of the Forest Research Institute was pulped on the pilot plant after chipping and screening in the usual manner under the following conditions by the sulphate process :

1. Total chemicals on o.d. wt. of chips as Na_2O, %— 17.5
2. Sulphidity, % — 25
3. Bath ratio — 1:4
4. Maximum temperature, °C —162
5. Time (including 2½ hrs. t oraise to maximum), hrs. — 4½
6. Unbleached yield, % — 44

The dry sheets of this pulp were prepared on the pilot plant. This pulp was used in these investigations.

The permanganate number, copper number, lignin, pentosan and ash content of the pulp were determined according to TAPPI standards.

1. Permanganate number — 17.8
2. Copper number — 0.89
3. Lignin, % — 4.2
4. Pentosans, % — 15.1
5. Ash, % — 1.10

Standard sheets of this pulp were made after beating of the pulp in the Lampen Mill laboratory beater to a freeness of 250 ml. (C.S.F.) and strength properties of these sheets were determined

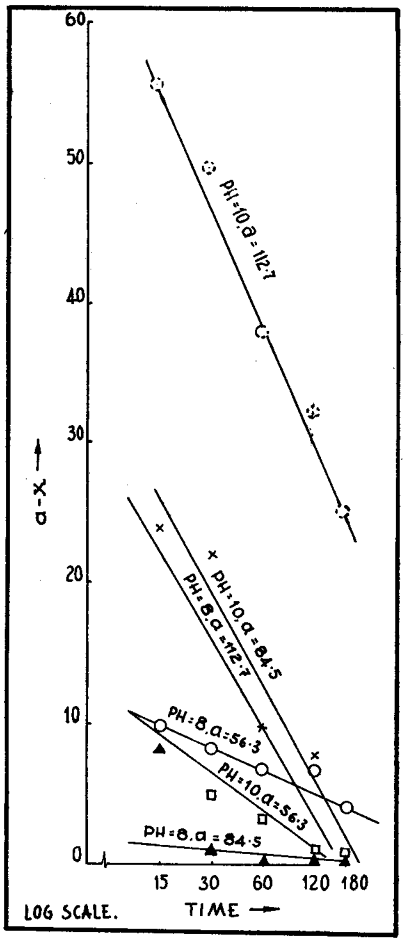

Fig. 1 Rate of Aqueous solution of calcium hypochlorite consumption with bamboo pulp at various conconcentration at pH 8 and 10.

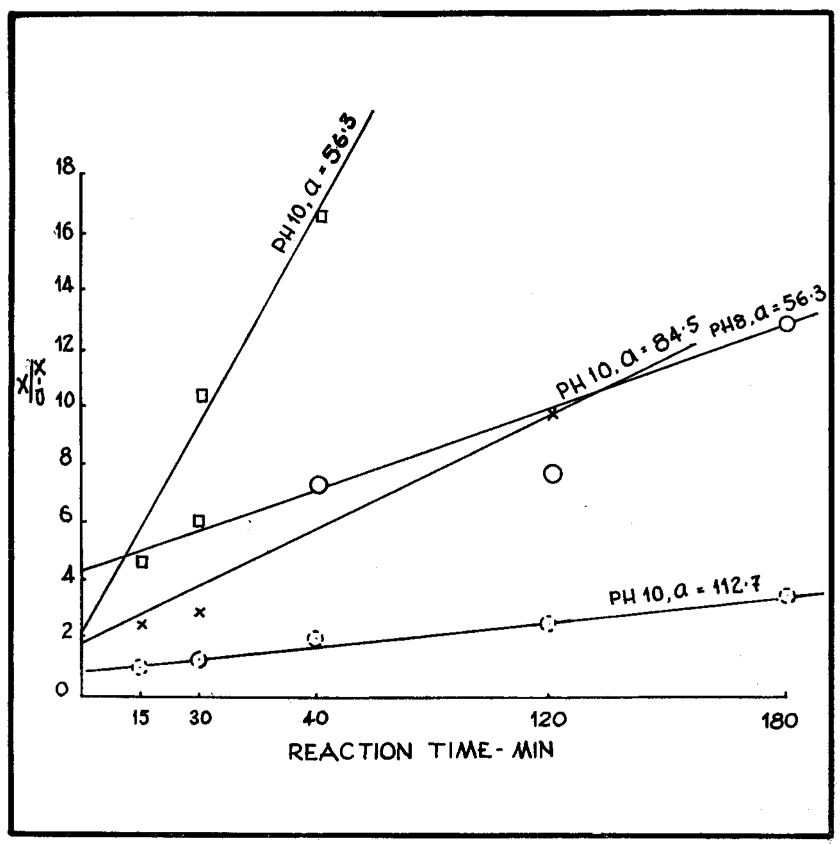

Fig. 2 Second order reaction curves showing reaction of Aqueous solution of calcium hypochlorite with bamboo pulp at various centration at pH 8 and 10.

after conditioning them at 65% R.H. and 27°C. The results are given below:

Breaking length, km	—	4.28
Burst fartor	—	31.8
Tear factor	—	101.0
Folding endurance (double folds)	—	45

EXPERIMENTAL AND DISCUSSIONS

100 gms. of o.d. pulp was taken and disintegrated for ½ hr. after soaking in water overnight. This disintegrated pulp was taken in a four litre erlenmeyer flask and bleached with calcium hypochlorite at 5% consistency and 30°C using the following variables:

1. Amount of calcium hypochlorite calculated as availaple chlorine on o.d. weight of the pulp, % — 4, 6 & 8
2. pH — 8 and 10
3. Time, minutes — 15. 30 60, 120 and 180,

The pulps were squeezed on a 65 mesh screen. The amount of chemical consumed was calculated by titrating the residual chlorine in the filtrate collected. The pulp was further washed and the yield of the semi-bleached pulp was determined. Standard sheets of this pulp were made after beating the pulp in laboratory Lampen Mill beater to a freeness of 250 ml. (C.S.F.). The strength properties were determined after conditioning them at 65% R.H. and 27°C. The brightness of these pulps was also determined using Photovolt meter 610 and taking Mg0 = 100. Permanganate number and pentosan content of these pulps were also determined. One standard sheet of each condition was aged in an oven kept at 102°C for 72 hrs. and the brightness of this sheet was also noted. All these results are tabulated in tables I, II, III, IV, V and VI.

From a scrutiny o fthe Tables I, II, III, IV, V and VI, it is observed that permanganate number and pentosan content generally decrease with the increase in time of reaction. It is also observed at lower pH the permanganate number is lower than at higher pH. Higher the amount of the chemicals lower is the permanganate number. Similarly the time of beating is also higher when bleaching is carried out at higher pH. It has also been observed in general that the strength properties improve till a certain time of reaction after which they tend to fall and improvement is more pronounced at higher pH.

To determine the rate of reaction and also to find out the order of the reaction, the values of the effective concentrations of chlorine at various periods of time are recorded in Table VII and are plotted against the logarithm of elapsed time (fig. 1). It is immediately clear that the reaction is characterised by a rapid consumption of chlorine during the first few minutes. On chlorination of phenol (1, 2), similar results have been observed and are long recognised in bleaching practice. Thereafter in agreement with the results of Curran and Baird(3), Yorston(4), and Hisey and Koon(5), the chlorine content decreases roughly in proportion to the logarithm of the elapsed time. The order of the reaction was considered using the usual equation and it was found only that using the 2nd order equation and plotting $\frac{x}{a-x}$ against time could in general approximate straight line be obtained for the several cases as in (fig. 2). On this curve it is of interest that on extension to zero time the extrapolated straight line does not pass through the origin as is expected for the 2nd order reaction which confirms the concept put forward by McCarthy Joseph L(6) and Carmody and Mears(7) that in aqueous solution reaction between chlorine and lignin two major changes occur namely a rapid initial process and a slow time-determined second order reaction. According to Herbest and Krassing(8) the residual lignin in pulp contains two structures (not necessarily located in different molecules), "a highly reactive structure which reacts with the oxidizing agent and a less reactive structure which reacts at a slower rate". This explains why the extrapolated values do not pass through the origin. The usual differential equation for a second order process is—

$$\frac{dx}{dt} = K_2(a-x)^2$$

which can be integrated to

$$K_3 = \frac{1}{at} \times \frac{x}{a-x}$$

and if it be assumed that in the chlorination of lignin two reactions occur, this latter equation can be corrected to allow extrapolation through the origin by means of insertion of the constant Z to give

$$K = \frac{1}{at} \left\{ \frac{x}{a-x} - Z \right.$$

where

a = initial active chlorine concentration (m.eq/litre)

t = time (minutes)

x = decrease in active chlorine concentration in time t. (m.eq/litres)

a-x = active chlorine concentration at time t (m.eq/litre)

also:

$Z = \frac{xo}{a-x}$ = graphically evaluated ratio.

$xo = \frac{aZ}{1+Z}$ = calculated active chlorine concentration decrease due to initial rapid reaction (m.eq/litre).

ao = a-xo = calculated intial active chlorine conecentration for slow second order reaction (m.eq/litre).

The second order reaction velocity constant K was evaluated by determining graphically, then calculating x as above, then ao.

It is clear from the summarised data in table VIII that the magnitude of K is an important function of the hydrogen ion concentration of the reaction mixture indicating that the slow 2nd order reaction is fastest in lower pH. It is not clear why the magnitude of the velocity constant increases as the concentration of active chlorine decreases. It seems probable that the slow 2nd order phase of the reaction between the pulp and bleach liquor is a reaction of oxidation.

CONCLUSIONS

1) Pentosan content and permanganate number decrease with the increase in time of reaction.

TABLE I Bleach consumption, bleach yield, permanganate number, pentosan content, beating time, strength properties of the standard sheets before and after aging of the pulps obtained by bleaching with 4% chemicals at pH 8 and different time intervals

Sl. No.	Time of bleaching	Bleach consumption *	Bleach yield	Permanganate number	Pentosans content	Time of beating	Breaking length	Burst factor	Tear factor	Brightness before aging	Brightness after aging
	Minutes	%	%	—	%	minutes	Km	—	—	Mgo=100	Mgo=100
1	2	3	4	5	6	7	8	9	10	11	12
1	0	0	100.00	17.8	15.1	80	4.28	31.8	101	—	—
2	15	3.30	96.5	10.5	14.8	55	4.88	34.7	116	36	35
3	30	3.42	96.1	10.0	14.4	45	5.61	34.8	121	37	35
4	60	3.52	94.7	9.7	14.3	45	5.54	35.8	135	37	32
5	120	3.54	93.5	9.3	14.0	40	5.51	36.3	134	37	33
6	180	3.71	92.7	9.0	13.1	40	5.31	34.2	131	37	32

* available chlorine on o.d. weight of the pulp.

TABLE II Bleach consumption, bleach yield, permanganate number, pentosan content, beating time, strength properties of the standard sheets before and after aging of the pulps obtained by bleaching with 4% chemicals at pH 10 and different time intervals.

Sl	Time of bleaching	Bleach consumption *	Bleach Yield	Permanganate number	Pentosans content	Time of beating	Breaking length	Burst factor	Tear factor	Brightness before aging	Brightness after aging
	Minutes	%	%	—	—	minutes	Km	—	—	Mgo=100	Mgo=100
1	0	0	100	17.8	15.1	80	4.28	31.8	101	—	—
2	15	3.29	92.5	11.7	13.4	70	5.32	38.3	118	36	33
3	30	3.65	92.0	11.6	14.0	50	5.66	38.7	131	40	35
4	60	3.77	92.0	9.9	14.5	40	5.67	38.7	140	41	39
5	120	3.92	92.0	9.7	14.8	40	5.80	39.1	140	41	36
6	180	3.95	92.0	9.4	12.6	35	6.35	39.0	130	41	36

* available chlorine on o.d. weight of the pulp.

TABLE III Bleach consumption, bleach yield, permanganate number, pentosan content, beating time, strength properties of the standard sheets before and after aging of the pulps obtained by bleaching with 6% chemicals, at pH 8 and different time intervals

Sl No.	Time of bleaching	Bleach consumption *	Bleach yield	Permanganate number	Pentosans content	Time of beating	Breaking length	Burst factor	Tear factor	Brightness before aging	Brightness after aging
	Minutes	%	%	—	—	minutes	Km	—	—	Mgo=100	Mgo=100
1	2	3	4	5	6	7	8	9	10	11	12
1	0	0	100	17.8	15.1	80	4.28	31.8	101	—	—
2	15	5.41	94.8	7.5	13.8	90	6.62	42.0	140	40	37
3	30	5.93	94.6	6.0	14.1	80	6.43	39.7	130	43	37
4	60	5.99	94.3	6.0	14.4	75	5.90	36.6	120	47	42
5	120	5.99	94.0	6.2	14.2	60	5.84	34.4	120	44	40
6	180	6.00	94.0	5.6	12.2	45	5.73	33.8	120	47	42

* available chlorine on o.d. weight of the pulp.

TABLE IV. Bleach consumption, bleach yield, permanganate number, pentasans content, beating time, strength properties of the standard sheets, before and after aging of the pulps obtained by the bleaching with 6% chemicals at pH 10 and different time intervals.

Sl No.	Time of bleaching	Bleach consumption *	Bleach yield	Permanganate number	Pentosans content	Time of beating	Breaking length	Burst factor	Tear factor	Brightness before aging	Brightness after aging
	Minutes	%	%	—	%	minutes	Km	—	—	Mgo=100	Mgo=100
1	2	3	4	5	6	7	8	9	10	11	12
1	0	0	100	17.8	15.1	80	4.28	31.8	101	—	—
2	15	4.30	96.5	11.4	14.4	110	5.00	32.3	132	38	36
3	30	4.44	95.5	8.4	14.3	85	5.46	36.3	123	46	41
4	60	5.31	95.5	6.2	14.3	60	5.50	40.0	145	45	41
5	120	5.46	95.0	6.2	14.8	45	5.28	37.0	128	47	43
6	180	5.88	94.5	5.8	14.8	35	5.00	32.0	128	49	43

* available chlorine on o.d. weight of the pulp

TABLE V Bleach consumption, bleach yield, permanganate number, pentosan content, beating time, strength properties of the standard sheets before and after aging of the pulps obtained by bleaching with 8% chemicals at pH 8 and different time intervals.

Sl No.	Time of bleaching	Bleach consumption *	Bleach Yield	Permanganate number	Pentosans content	Time of beating	Breaking length	Burst factor	Tear factor	Brightness before aging	Brightness after aging
	Minutes	%	%	—	%	minutes	Km	—	—	Mgo=100	Mgo=100
1	2	3	4	5	6	7	8	9	10	11	12
1	0	0	100.0	17.8	15.1	80	4.28	31.8	101	—	—
2	15	6.17	91.0	6.9	14.8	35	5.63	36.8	116	46	41
3	30	7.07	92.0	5.2	14.6	35	5.64	37.2	122	48	42
4	60	7.56	89.0	4.1	13.9	35	5.60	37.4	118	49	44
5	120	7.73	89.0	4.0	14.0	35	5.71	32.6	114	50	42
6	180	7.80	90.0	3.9	14.2	30	5.06	32.3	128	57	49

* available chlorine on o.d. weight of the pulp

TABLE VI Bleach consumption, bleach yield, permanganate number, pentosan content, beating time, strength properties of the standard sheets before and after aging of the pulps obtained by bleaching with 8% chemicals at pH 10 and different time intervals.

Sl No.	Time of bleaching	Bleach consumption	Bleach yield	Permanganate Number	Pentosans content	Time of beating	Breaking length	Burst factor	Tear factor	Brightness before aging	Brightness after aging
	Minutes	%	%	—	%	minutes	Km	—	—	MgO=100	MgO=100
1	2	3	4	5	6	7	8	9	10	11	12
1	0	0	100.0	17.8	15.1	80	4.28	31.8	101	—	—
2	15	4.10	92.6	9.8	10.8	40	6.30	42.8	140	39	37
3	30	4.49	92.0	8.3	11.0	40	5.85	38.2	133	41	38
4	60	5.33	90.2	7.9	11.0	35	5.51	36.6	125	48	41
5	120	5.73	90.0	7.6	11.0	35	5.22	36.5	125	51	43
6	180	6.23	87.6	7.4	11.5	30	5.47	32.5	109	53	43

* available chlorine on o.d. weight of the pulp

TABLE VII. Rate of reaction of bleach liquor with bamboo sulphate pulp.

Time (minutes)	(a—x) (m.eq./lit)	x (m.eq./lit)	x / a—x	K x 10⁶ *	Remarks
1	2	3	4	5	6
0	56.3	—	—	—	
15	9.9	46.4	4.69	461	
30	8.1	48.2	5.95	978	pH 8
60	6.7	49.6	7.41	922	K
120	6.5	49.8	7.67	500	avg. 745 x 10^6 *
180	4.0	52.3	13.08	865	
0	56.3	—	—	—	
15	10.0	46.3	4.63	2880	
30	4.9	51.4	10.48	4820	pH 10
60	3.2	53.1	16.60	4260	K
120	1.1	55.2	50.18	7100	avg. 5340x10^6 *
180	0.7	55.6	79.43	7630	
0	84.5	—	—	—	
15	8.1	76.4	9.43	—	
30	0.9	83.6	93.00	—	pH 8
60	0.1	84.4	884.00	—	
120	0.1	84.4	884.00	—	
180	0.0	84.5			
0	84.5	—	—	—	
15	23.9	60.6	2.54	585	
30	21.9	62.6	2.86	418	pH 10
60	9.6	74.9	7.80	1180	K
120	7.6	76.9	10.10	817	avg. 747 x 10^6 *
180	1.7	82.8	48.70	—	
0	112.7	—	—	—	
15	25.7	87.0	3.38	—	
30	13.1	99.6	7.61	—	
60	6.1	106.6	17.50	—	pH 8
120	3.7	109.0	29.40	—	
180	2.7	110.0	40.70	—	
0	112.7	—	—	—	
15	55.0	57.7	1.05	148	
30	49.4	63.3	1.28	142	
60	37.6	75.1	1.99	176	pH 10
120	31.9	80.8	2.54	128	K
180	24.8	87.9	3.54	135	avg. 146 x 10^6 *

* **Lower 6 is minus 6, (—6).**

TABLE VIII Summary of the kinetic data for bamboo sulphate pulp and aqueous bleach liquor at pH 8 and 10

pH of reaction	Permanganate of available chlorine on the o.d. wt. of the pulp	a m.eq/l.	XG / Z=a-xo graphically evaluated	XG / m.eq/l.	aO m.eq./l.	Oxidation Reaction Constant K_2
1	2	3	4	5	6	7
8	4	56.3	4.3	45.6	10.7	745 x 10-6
10	4	56.3	2.2	38.7	17.5	5340 x 10-6
8	6	84.5	—	—	—	—
10	6	84.5	1.8	54.4	30.1	747 x 10-6
8	8	112.7	—	—	—	—
10	8	112.7	0.8	50.1	62.6	146 x 10-6

Text to the Figures

2) Permanganate number at lower pH is lower than those at higher pH.

3) Higher the amount of the chemicals, lower is the permanganate number.

4) Time of beating is higher when bleaching is carried out at higher pH.

5) The strength properties improve till a certain time of reaction after which they tend to fall and improvement is more pronounced at higher pH

6) The results show that bleaching is fast reaction at the start followed by a slow second order reaction indicating that the residual lignin in pulp contains two structures (not necessarily located in different molecules) "a highly reactive structure" which reacts with the oxidizing agent and "a less reactive structure" which reacts at a slower rate.

7) The magnitude of velocity constant increases as the concentration of active chlorine decreases.

8) The second order reaction is fast at lower pH.

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