Effect of Sludge in Bleach Liquor on Bleaching and Papermaking

N. M. Pai—Asst. Research Officer and G. P. Saraf—Chemist
Research Centre, The West Coast Paper Mills Ltd., Dandeli, North Kanara, Karnataka State

This paper highlights the various problems experienced in commercial production of bleached pulp when turbid bleach liquor containing sludge is used for bleaching. This sludge containing mainly calcium compounds and silica was observed to cause some problems during papermaking as well. This study covers a series of bleaching experiments carried out in Research Centre by using bleach liquor containing 0-15% sludge on volume basis of the bleach liquor (0-6.9% on O.D. pulp). During bleaching of pulps the presence of sludge in the bleach liquor showed (i) Slow brightness development of the resultant pulp, (ii) Higher chlorine demand to achieve required brightness, (iii) Lower viscosity and increased ash content of the bleached pulps. The sludge in bleach liquor adversely affected the beatability of the bleached pulps resulting in inferior quality paper. Alum requirement of these pulps were higher to obtain a desired pH.

Introduction

Generally calcium hypochlorite or bleach liquor is used for bleaching unbleached sulphate pulp in our country. This bleach liquor is obtained on a commercial scale by reacting chlorine with calcium hydroxide or slaked lime. After the completion of the reaction, some quantity of sludge containing CaO, $CaCO_3$ and SiO_2 separates and settles down in the settling tanks. To obtain clear bleach liquor sufficient time and space are necessary. It was observed that settling properties of bleach liquor depend on size of slaked lime particles and temperature during chlorination (1). Laboratory investigation carried on settling properties of bleach liquor generally showed that settling properties of bleach liquor produced at high temperature and high concentration or with excess (insoluble) lime are not good. When milk of lime of initial high temperature was used for making bleach liquor, it was observed that due to internal disturbance, the column of the sludge already settled travelled to the top, making the entire bleach liquor turbid. This was in accordance with the experiences reported by Miller (2).

The bleach preparation plant in the West Coast Paper Mills consists of one reaction tank, one overflow tank, three settling chests and one clarifier. Although much care is being taken to supply clear bleach liquor to the bleach plant of the pulp mill, occasionally turbid liquor is used. The most probable reasons for the turbidity in bleach liquor may be insufficient time for settling the sludge whenever there is high production of bleach liqour and the high temperature of the bleach liquor.

Apart from this, lack of process control during bleach liquor preparation may also cause disturbance in settling of the sludge (2). The literature on this subject is limited as very little work was carried out on it. The purpose of this study was to highlight the various effects caused by the presence of sludge in bleach liquor during bleaching and papermaking. The notable problems associated with the presence in bleach liquor are :

i) Slow brightness development due to high pH (i.e. 10.8—11.2) (3).

ii) Higher chlorine demand to obtain a particular brightness of pulp.

iii) Increase in ash content of bleached pulp.

iv) Due to high pH of the washed bleached pulp, higher amounts of alum as well as sulphuric acid are necessary to neutralise the alkalinity during sizing for getting required pH.

v) Poor quality bleached pulp having low pulp viscosity and unsatisfactory strength properties.

vi) Frequent sludge troubles may lead to scale problems in the process equipments.

Experimental

About 5 Kgs. (O.D.) of alkali extracted pulp of bomboo and hardwood (70 : 30) were collected from the alkali washer of the bleach plant in pulp mill. This pulp was centrifuged in the hydro-extractor to bring the consistency to about 30 percent. Shredding of the pulp was carried out to determine its consistency exactly. The Kappa No. of this pulp was determined as per TAPPI Standards (T236m-60) and was found to be 7.3. Equivalent weight of the wet pulp was taken corresponding to 400 gms. of O.D. pulp to carry out the bleaching experiments. A series of bleaching experiments were carried out by adding different amounts of sludge (O to 15% on vol. basis of bleach liquor) to the clear bleach liquor. This corresponds to O to 6.9% of dry sludge on O.D. pulp. To obtain almost same brightness as obtained when clear bleach liquor was used, higher amounts of chlorine were added depending on the amount of sludge added in the bleaching experiments. The brightness, viscosity, bleached pulp yield (corrected for ash), ash in pulp and post colour number of bleached pulps were determined and the results are tabulated in Table No. I.

To confirm the figures of bleached pulp yield (corrected for ash) with the addition of sludge, as they were slightly higher than that of blank, some more experiments were planned with the addition of equivalent amounts of sodium hydroxide (caustic soda) for comparison. The lot of alkali extracted pulp used in this case was different and its Kappa No. was 8.7. The results are tabulated in Table No. II.

In order to study the effect of sludge on brightness development of pulp during bleaching, single stage hypochlorite bleaching was carried out with different amount of sludge using 3.0% chlorine. The brightness and residual chlorine of the pulps were recorded at different time intervals and the results are given in Table No. III.

The bleached pulps obtained in the earlier experiments were beaten in the Laboratory Valley Beater to different slowness levels. Rosin, alum, mixed with

TABLE I

Effect of increasing amounts of sludge in bleach liquor on bleaching of pulp

Kappa No. of alkali extracted pulp = 7.3
Pulp equivalent to 400 gms. O.D. was taken for bleaching.

Particulars	*Clear bleach liquor*	*Sludge in bleach liquor*		
Sludge in bleach liquor on volume basis, %	Nil	5.0	10.0	15.0
Dry sludge on pulp (O.D.), %	Nil	1.38	3.44	6.88
(i) **Hypochlorite Stage I :**				
Chlorine applied, %	2.0	2.38	3.15	3.8
Chlorine consumed, %	1.82	2.01	2.30	2.5
pH	7.45	9.95	11.0	11.2
(ii) **Hypochlorite Stage II :**				
Chlorine applied, %	1.0	2.0	1.8	2.1
Chlorine consumed, %	0.56	0.52	0.68	0.89
pH	7.75	11.25	11.2	11.25
Total chlorine applied, % (H_1 & H_2 stages)	3.0	4.28	4.95	5.9
Total chlorine consumed, % (H_1 & H_2 stages)	2.38	2.52	2.98	3.39
Brightness (Elrepho), %	79.9	76.8	76.4	75.0
Viscosity, (CED), cp.	4.9	4.3	3.5	3.1
Bleached pulp yield, % (Corrected for ash) (on alkali extracted pulp basis)	94.1	94.4	95.8	96.6
Ash in pulp, %	1.0	1.51	2.22	2.12
Post Colour Number	5.4	3.7	3.9	4.4

Constant Conditions :	*Hypo I*	*Hypo II*
Consistency, %	10.0	10.0
Temperature, °C.	45	45
Retention time, Mins.	90	60
Sulphamic acid (on pulp), %	0.07	0.07

TABLE II

Comparative study of bleaching of pulp by using bleach liquor with sludge/caustic soda

Experiment No. / *Particulars*	Kappa No. of alkali extracted pulp = 8.7						
	1	*2*	*3*	*4*	*5*	*6*	*7*
1. Hypochlorite Stage I :							
Chlorine applied, %	2.2	2.7	3.7	4.8	2.7	3.7	4.8
Chlorine consumed, %	2.16	2.64	3.46	4.32	2.7	3.3	4.3
Sludge on pulp (O.D), %	Nil	1.0	2.64	4.7	Nil	Nil	Nil
NaOH on pulp (O.D), %	Nil	Nil	Nil	Nil	0.66	1.6	3.2
Retention time, Mins.	90	90	90	90	90	90	90
pH	7.1	7.6	10.4	10·8	7.3	8.9	11.3
2. Hypochlorite Stage II :							
Chlorine applied, %	1.2	1.5	2.0	2.5	1.5	2.0	2.5
Chlorine consumed, %	1.02	1.26	1.56	2.1	1.48	1.7	1.94
Sludge on pulp (O.D), %	Nil	0.4	1.32	2.3	Nil	Nil	Nil
NaOH on pulp (O.D), %	Nil	Nil	Nil	Nil	0.33	0.9	1.7
Retention time, Mins.	90	90	90	90	90	90	90
pH	7.5	9.85	11.1	11.3	7.4	10.9	11.3
Total chlorine applied, %	3.4	4.2	5.7	7.3	4.2	5.7	7.3
Total chlorine consumed, %	3.2	3.9	4.0	6.4	4.2	5.0	6.2
Brightness (Elrepho), %	80.4	78.6	77.6	75.4	80.2	78.4	76.5
Viscosity (CED), cp.	7.9	6.8	5.2	4.1	5.7	4.6	3.8
Bleached pulp yield corrected for ash, %	96.4	98.7	97.2	96.9	96.6	96.2	95.9
Ash in bleached pulp, %	0.9	1.3	1.6	2.0	1.0	1.1	1.1
Total sludge added, % (on O.D. pulp)	Nil	1.4	3.96	7.0	Nil	Nil	Nil
Total NaOH added, % (on O.D. Pulp)	Nil	Nil	Nil	Nil	0.99	2.5	4.9

Constant Conditions : Pulp equivalent to 50 gms. O.D. was taken for bleaching.

	Hypochlorite Stage I	*Hypochlorite Stage II*
Consistency, %	10.0	10.0
Temperature, °C.	45	45
Sulphamic acid, % (on O.D. pulp)	0.07	0.07

N.B. — Sulphamic acid was not used where caustic soda was added.

TABLE III

Effect of increasing amounts of sludge in bleach liquor on brightness development of pulp

Bleaching was carried out by employing single stage hypochlorite. Kappa No. of alkali extracted pulp = 7.3

Retention time, mins.	30	60	90	120	150	300
1. Residual chlorine, GPL						
(a) Clear bleach liquor	0 33	0.20	0.13	0.11	0.11	—
(b) 5% sludge	0.38	0.17	0.13	0.10	0.07	0.04
(c) 10% sludge	0.47	0.18	0.10	0.09	0.06	0.05
Brightness of bleached pulp :						
(a) Clear bleach liguor	74.2	75.8	76.7	76.7	76.7	—
(b) 5% sludge	71.1	74.3	74.7	74.9	75.0	75.4
c) 10% sludge	68.0	71.1	71.5	72.1	72.3	72.7

Constant Conditions :

Chlorine, %	...	3.0
Consistency, %	...	10.0
Temperature, °C.	...	45
Sulphamic acid,% (on pulp), %	...	0.07

sulphuric acid were added to the beaten stock to get pH 4.5. The amounts of alum and sulphuric acid were recorded for different pulps. Standard sheets were prepared on Noble and Wood Sheetmaking machine with white water circulation. The sheets were evaluated for strength properties, sizing and one minute Cobb's test and the results are recorded in Table No. IV.

The results of Bauer McNett Fibre Classification of the pulps with and without sludge are given in Table No. V.

Results and Discussion

The increasing amounts of sludge in bleach liquor (O—15 per cent on volume basis of bleach liquor) directly affected the bleaching process. As shown in Fig. 1 higher amounts of chlorine were necessary to approach the brightness of the bleached pulp obtained in the case where clear bleach liquor was used. Because of high pH with the addition of sludge, with the limited retention time, lot of chlorine remained unreacted resulting in unnecessary waste of chlorine going to the drain.

The pH of the stock increased steadily with the increase in amounts of sludge resulting in decrease in bleached pulp brightness as well as viscosity. This is shown in Fig. 1. The ash in bleached pulp increased steadily and remained constant with the increase in sludge in bleach liquor. The figures of bleached pulp yield (corrected for ash) were slightly towards higher side with the addition of sludge. Hence, to confirm the results of bleached pulp yield on the addition of sludge, the bleaching experiments were repeated, where the sludge was replaced by equivalent amount of caustic soda. The ash in bleached pulp and bleached pulp yield with sludge are shown in Fig. 2.

The brightness development of the pulp during single stage hypochlorite bleaching using 3 per cent chlorine and with amounts of sludge in bleach liquor from 0-10 per cent became slower as shown in Fig. 3. With the use of 10 per cent sludge in bleach liquor on volume basis, the final brightness of the bleached pulp dropped to

72.3% (Elrepho) as against 76.7% (Elrepho) obtained in the blank experiment by using clear bleach liquor. However, there was no significant change in the residual chlorine content in the system when sludge upto 10 per cent was added to the bleach liquor on volume basis. This is shown in Fig. 3.

The Fig. 4 shows the effect of sludge on beating characteristics of the bleached pulps with the increase in sludge content in bleach liquor. The beating was progressively quicker with the addition of increasing amounts of sludge in bleach liquor.

Due to sludge in the bleached pulp obtained by using increasing amounts of sludge the requirement of higher doses of alum and sulphuric acid are necessary to obtain pH 4.5 at which sizing of the paper sheets are evaluated. This is shown in Fig. 5.

The effect of sludge on strength properties of the paper sheets is shown in Fig. 6. All the strength properties showed decreasing amounts of sludge were present in bleach liquor.

TABLE IV

Effect of sludge in bleach liquor on sizing and strength properties of sheets

Particulars	*Clear bleach liquor zero % sludge*			*Turbid bleach liquor 5% sludge*			*Turbid bleach liquor 10% sludge*			*Turbid bleach liquor 15% sludge*		
Initial slowness, °SR		17			17			18			20	
Final slowness, °SR	21	29	40	20	29	39	22	30	44	20	28	39
Beating period, Mins.	4	8	12	2	5	9	2	4	7	0	2	4
pH of the beaten pulp		7.4			8.8			8.8			9.2	
Rosin, %		1.0			1.0			1.0			1 0	
Alum, %		2.0			3.4			4.3			4.3	
H_2SO_4, %		1.4			1.4			1.7			2.5	
Final pH		4.5			4.5			4.5			4.5	
Basis weght, g/m²	62.5	64.4	63.6	64.2	60.7	59.4	62.0	64.3	63.8	62.0	64.0	63.4
Bulk, cc/g.	2.53	2.25	2.31	2.80	2.86	2.70	2.90	2.69	2.71	2.91	2.58	2.86
Bretakig length, km.	1.36	1.94	2.42	1.09	1.53	1.80	0.71	0.97	1.30	0.67	1.02	0.91
Stretch, %	2.2	2.4	2.6	1.9	2.5	2.5	1.4	1.4	1.7	1.6	1.4	1.1
Tear factor	89.0	82.5	73.6	79.8	70.5	65.4	58.8	40.5	37.6	32.9	25.8	21.4
Burst factor	15.7	20.6	25.2	13.6	17.8	20.2	11.1	10.9	11.6	6.8	9.0	6.8
Double folds (MIT)	3	7	12	2	3	4	1	1	1	1	1	1
Strength Index No.	875	1125	1270	690	845	935	300	265	260	210	215	180
Sizing, Seconds	10	23	25	10	27	28	8	28	25	8	23	23
One min. Cobb Test (Avg.) g/m²	15.8	17.3	16.4	14.6	14.5	15.3	14.7	13.3	12.7	12.5	16.0	14.1

Note : Sheets were prepared on Noble and Wood Sheetmaking machine.

TABLE V

Bauer McNett Fibre Classification of Bleached Pulps

Fraction retained on, %	*Clean liquor*	*5% Sludge*	*10% Sludge*	*15% Sludge*
35 mesh	39.38	39.97	38.22	38.98
50 ,,	11.01	10.95	11.19	11.10
100 ,,	5.01	4.40	4.03	4.43
150 ,,	13.06	11.26	14.49	13.72
Passing through 150 mesh	31.54	33.42	32.07	31.77

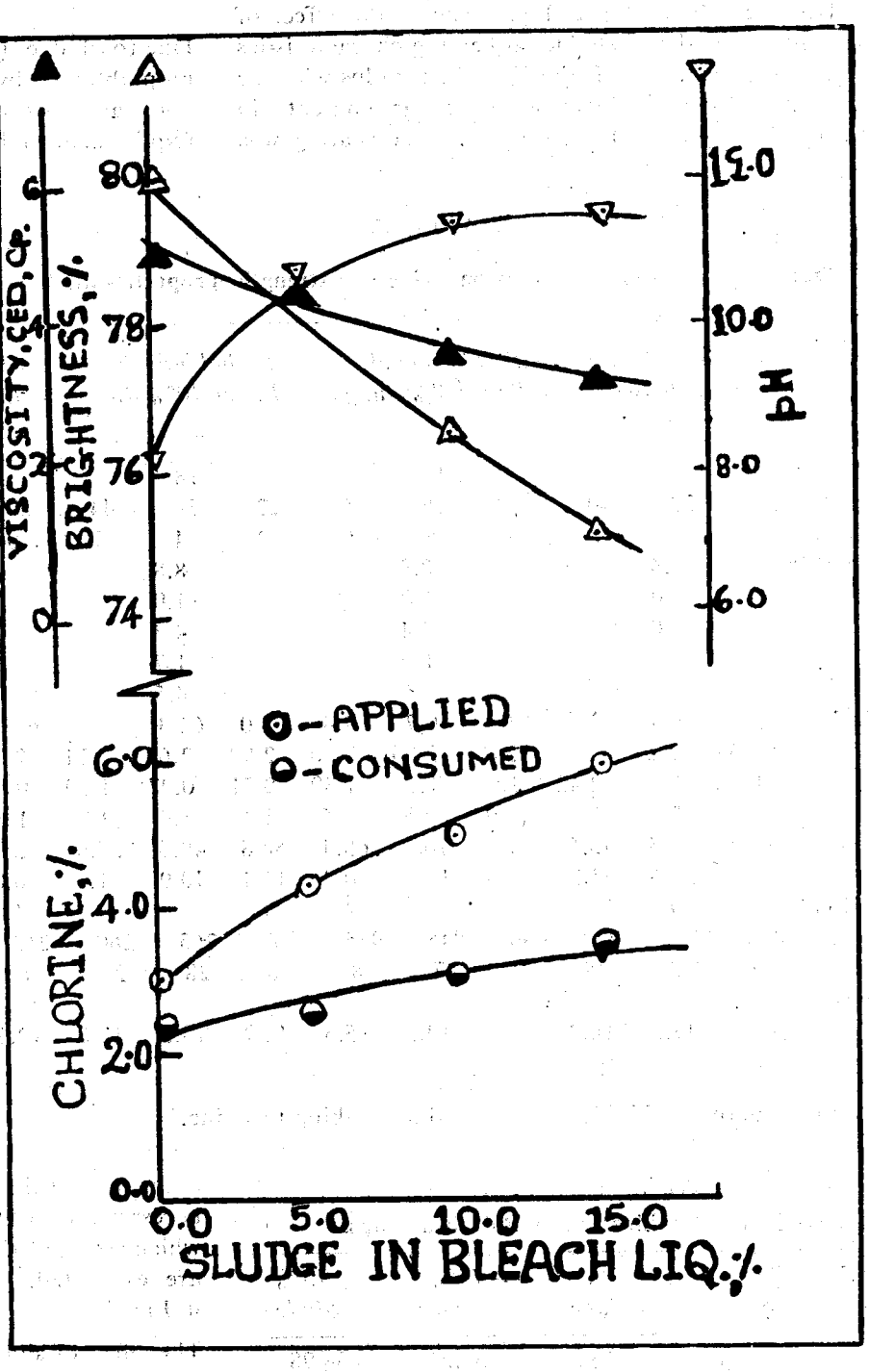
VISCOSITY, CP.
BRIGHTNESS, %
pH
80
78
76
74
12.0
10.0
8.0
6.0
6
4
2
0
APPLIED
CONSUMED
CHLORINE, %
6.0
4.0
2.0
0.0
0.0
5.0
10.0
15.0
SLUDGE IN BLEACH LIQ. %

Fig. 1

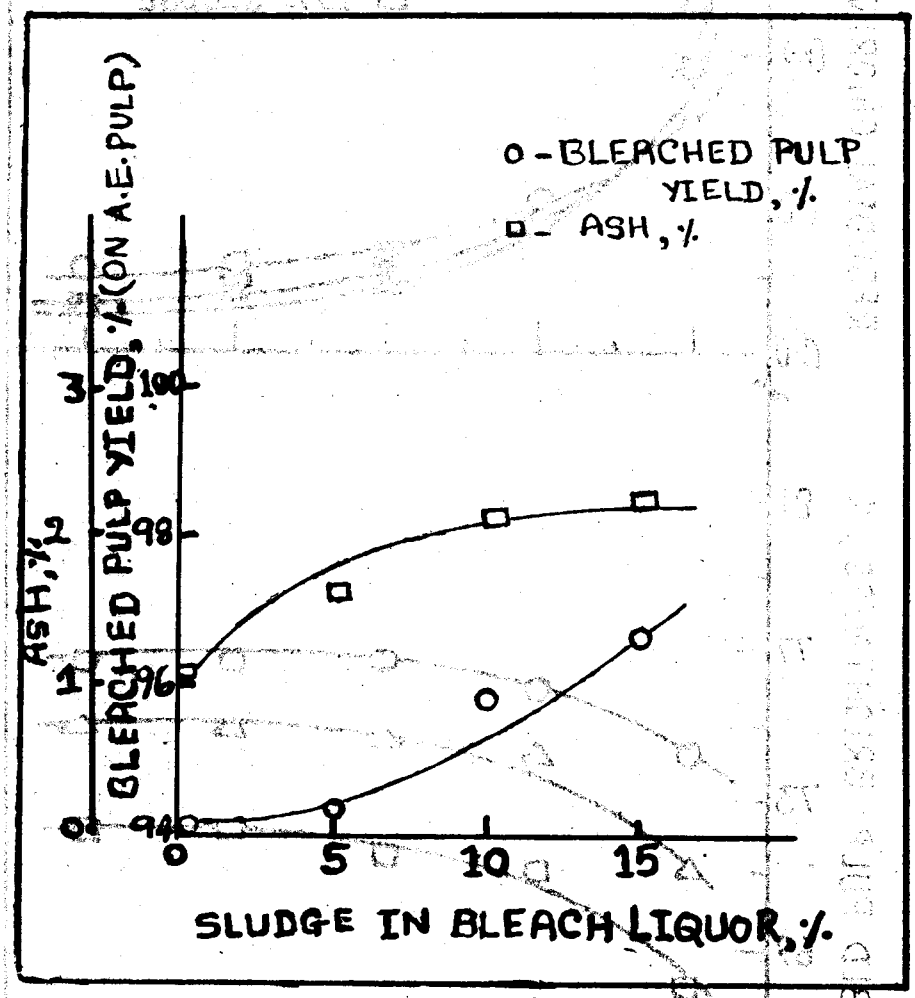
o - BLEACHED PULP YIELD, %
□ - ASH, %
BLEACHED PULP YIELD, % (ON A.E. PULP)
ASH, %
100
98
96
94
3
2
1
0
0
5
10
15
SLUDGE IN BLEACH LIQUOR, %

Fig. 2

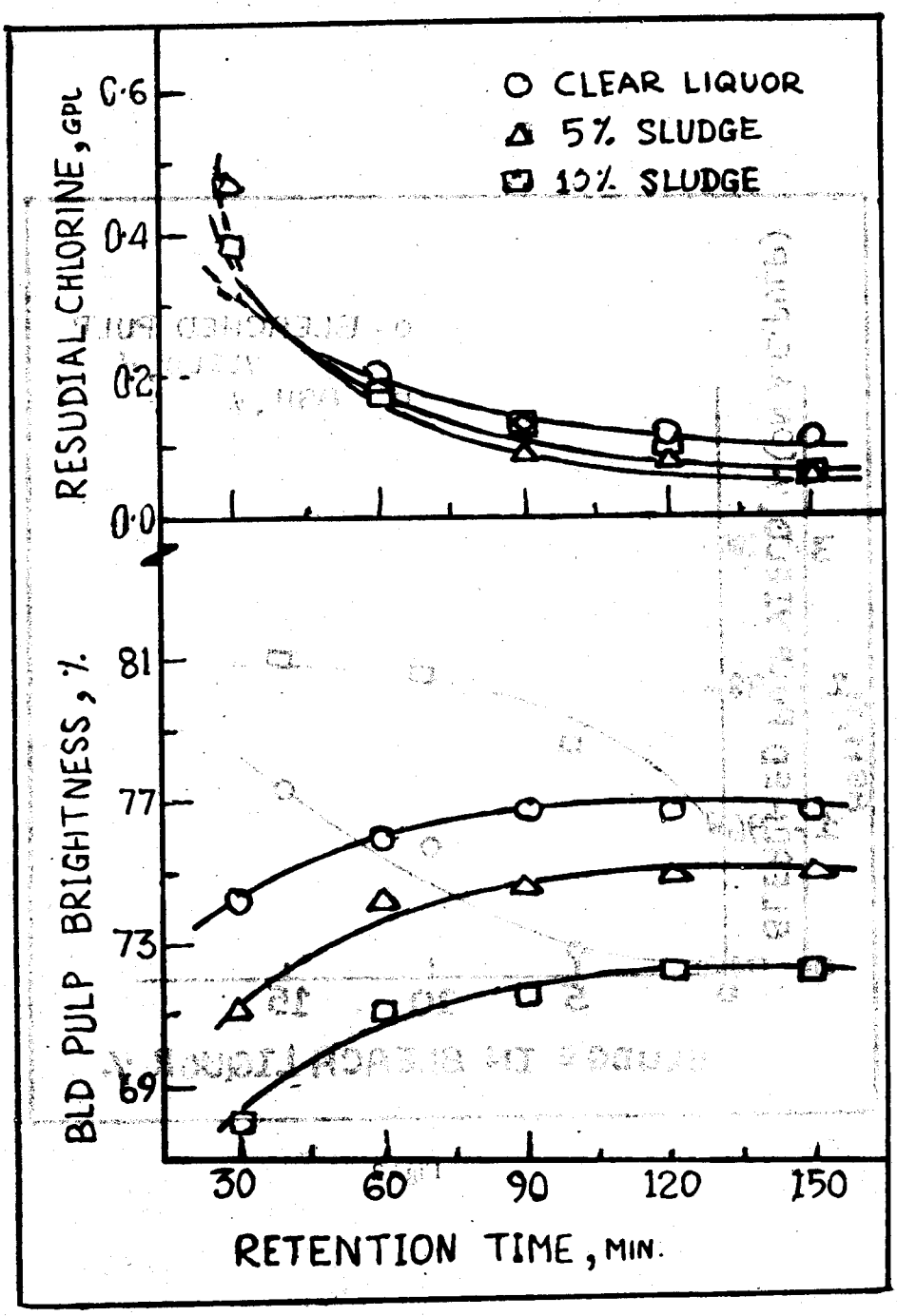
O CLEAR LIQUOR
Δ 5% SLUDGE
□ 10% SLUDGE
RESUDIAL CHLORINE, GPL
0·6
0·4
0·2
0·0
BLD PULP BRIGHTNESS, %
81
77
73
69
30
60
90
120
150
RETENTION TIME, MIN.

Fig. 3

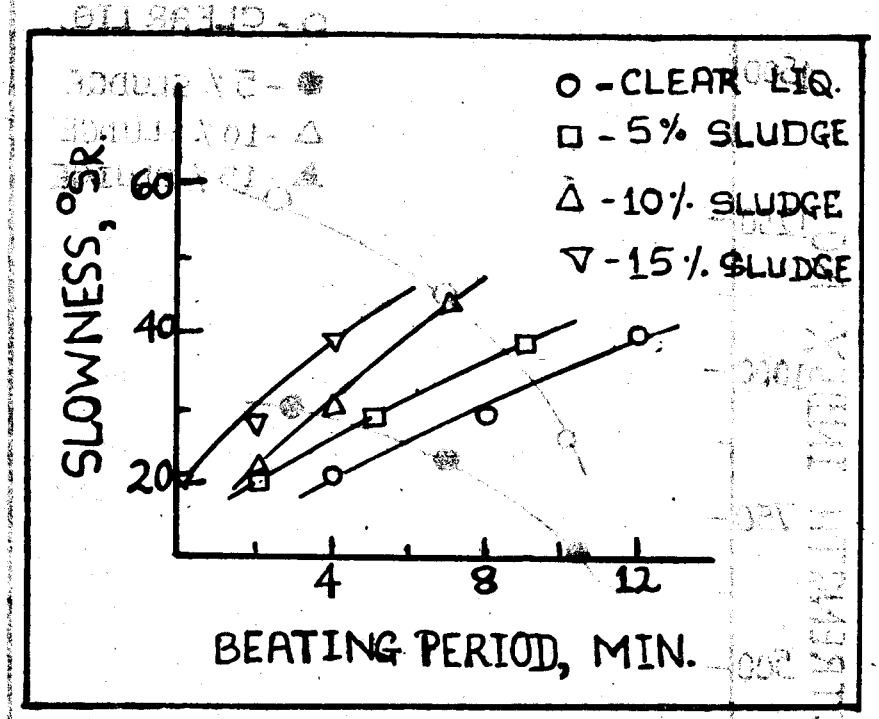
O - CLEAR LIQ.
□ - 5% SLUDGE
Δ - 10% SLUDGE
▽ - 15% SLUDGE
SLOWNESS, °SR.
60
40
20
4
8
12
BEATING PERIOD, MIN.

Fig. 4

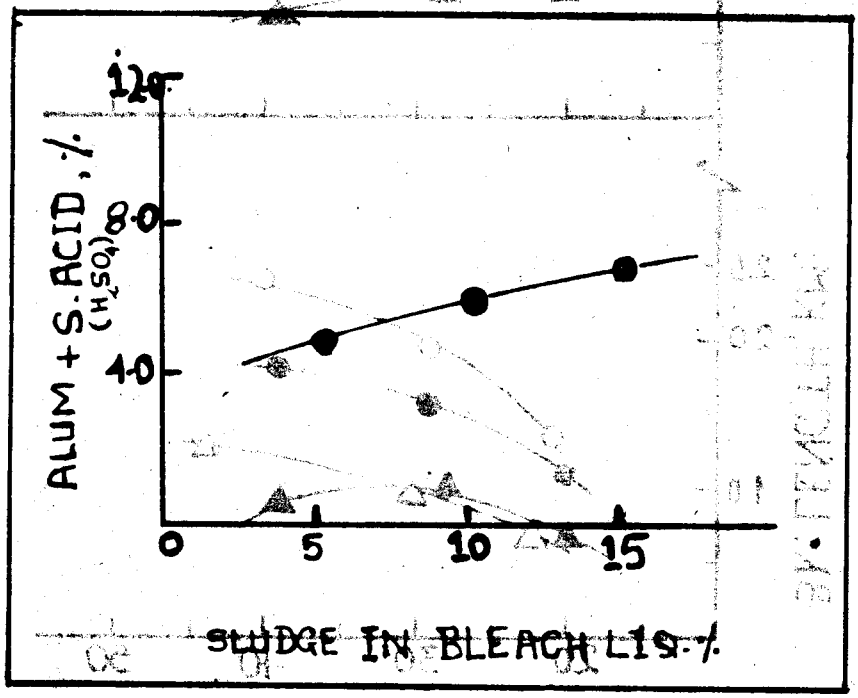
ALUM + S. ACID, % (H_2SO_4)
12.0
8.0
4.0
0
5
10
15
SLUDGE IN BLEACH LIQ. %

Fig. 5

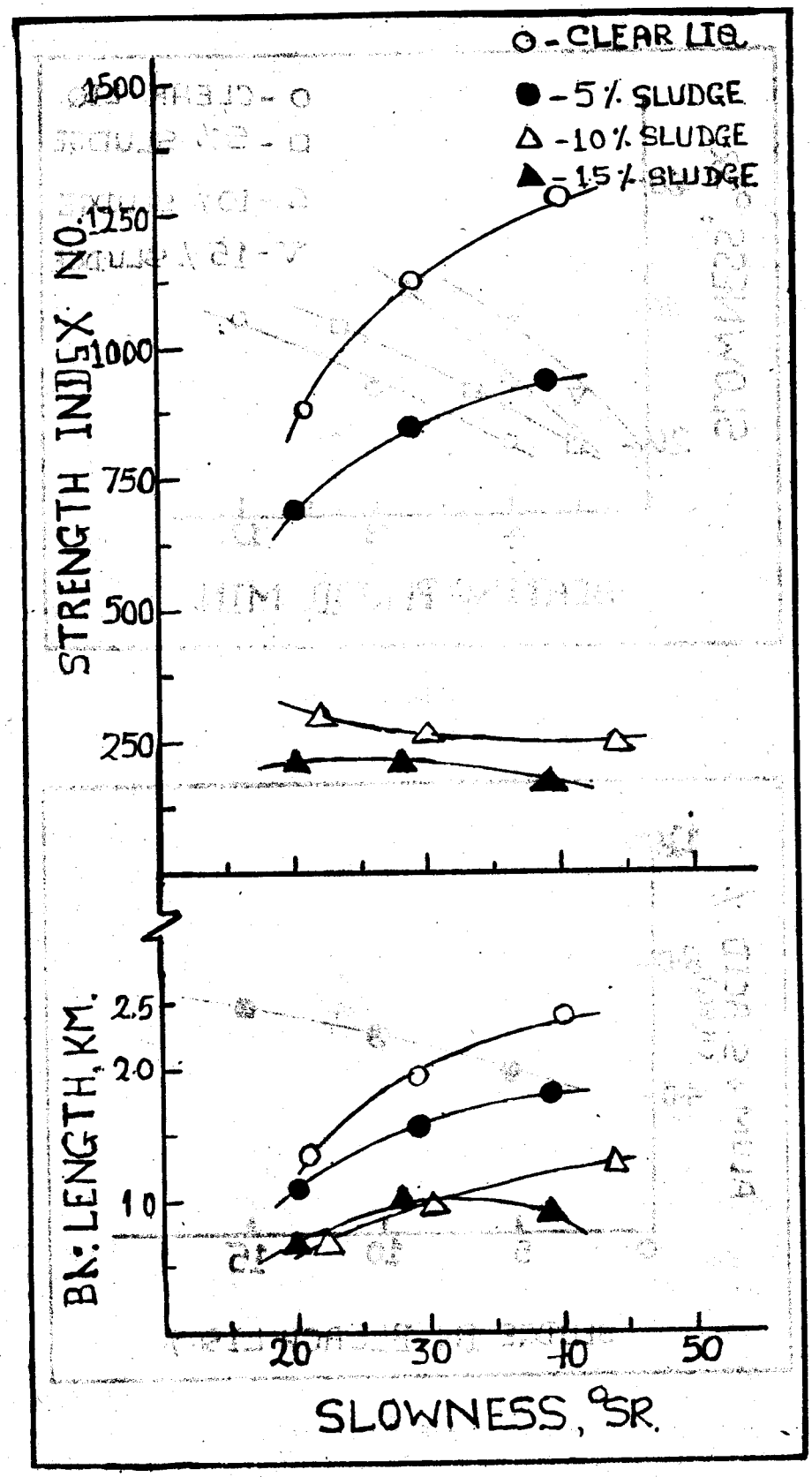
O - CLEAR LIQ.
● - 5 % SLUDGE
△ - 10 % SLUDGE
▲ - 15 % SLUDGE
STRENGTH INDEX NO.
1500
1250
1000
750
500
250
BN. LENGTH, KM.
2.5
2.0
1.0
20
30
40
50
SLOWNESS, °SR.

Fig. 6

Conclusions

It was observed that presence of sludge in bleach liquor would have the following adverse effects on bleaching of pulp and papermaking.

i) Slower brightness development of the resultant pulp as a result of inhibiting nature of calcium compounds present in the sludge.

ii) Higher chlorine demand to achieve desired pulp brightness.

iii) A substantial amount of residual chlorine would be left out in the system during bleaching, as a result of higher amounts of chlorine used. This would be a waste.

iv) The bleached pulps contain more dead load as ash.

v) The viscosity and strength properties of the bleached pulps would be lower.

vi) Alum requirement of these pulps would be higher for normal sizing of paper.

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