Studies in Bleach Liquor Preparation

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SUMMARY

Bleach liquor preparation constitutes an important part of the Pulp Mill operation. This project was undertaken as a part of the Research Programme to study the reasons for fluctuations in chlorine losses, in bleach making, and the turbidity of the liquor in our mill. In the past no systematic investigations in this direction were undertaken. Experiments on slaking lime, settling characteristics of milk of lime, chlorination etc. were carried out at the Research Centre, and coupled with the plant experiments and observations. Experiments were also carried out on the recovery of chlorine by washing of the bleach sludge. This work is divided into three parts, namely, (i) preparation and control of milk of lime, for improvement in hypochlorite production, (ii) optimum conditions for chlorination of milk of lime and (iii) bleach sludge and the recovery of chlorine, which supplements the economy of the process. Suggestions based on the above studies have also been given.

INTRODUCTION

Calcium hypochlorite, or bleach liquor as it is commercially known is an important bleaching chemical widely used in Paper Industry. The properties of bleach liquor directly depend on the choice of lime, preparation and characteristics of calcium hydroxide its chlorination etc. These facts have been generally overlooked, and the problems or difficulties associated with the use of bleach liquor have been contributed to bad quality of lime, and to some unknown factors, which is not always necessarily true. It is needless to stress that the entire economy and efficiency of bleach liquor manufacture depends upon the right type of lime, the control of slaking and chlorination of milk of lime, bleach sludge, and its washing. This project was undertaken as a part of the Research Programme to study the reasons for the fluctuations in chlorine losses in bleach liquor preparation, and turbidity of the liquor in our mill. This work has been divided into three parts, namely:

I) Preparation and control of milk of lime, for improvement in hypochlorite production.
II) Optimum conditions for chlorination of the milk of lime.
III) Bleach sludge and recovery of chlorine which supplements the economy of the process.

EXPERIMENTAL

I) PREPARATION AND CONTROL OF LIME FOR IMPROVEMENT IN HYPOCHLORITE PRODUCTION

At the outset it was anticipated that the mode of chlorine absorption by the milk of lime and the settling characteristics of the bleach liquor prepared from it are related to the characteristics of milk of lime, the particle size of calcium hydroxide, impurities and its temperature etc. These (except the impurities) in turn are governed by the type of quicklime the method of its slaking, the ratio of water to quicklime and the amount, temperature of water for dilution, to the required concentration, and the temperature suitable for chlorine absorption.

In the beginning, experiments were conducted in the Research Centre, to study the settling characteristics of the milk of lime, prepared by slaking lime with different water/lime ratios, at constant temperature 50°C and afterwards diluting to the same concentrations i.e. 45.0 gpl. Settling characteristics were found by the usual 1-litre cylinder method. The results of the experiments are given in Figure-1.

Having done these laboratory experiments, samples of milk of lime were collected from Pulp Mill lime slaker, after the vibrating screen, keeping the lime feeding rate and the amount of water for slaking constant i.e. ratio of 6:1 was maintained. The results of these plant experiments are given in Table—1 and Figure-2.

II) OPTIMUM CONDITIONS FOR CHLORINATION OF THE MILK OF LIME

Experiments were conducted to find out the optimum conditions for chlorination of the milk of lime, to produce bleach liquor of suitable strength with good stability and clarity.

(i) After taking trials at the Lime Slaker, with water/lime ratio, 6 : 1 it was decided to conduct

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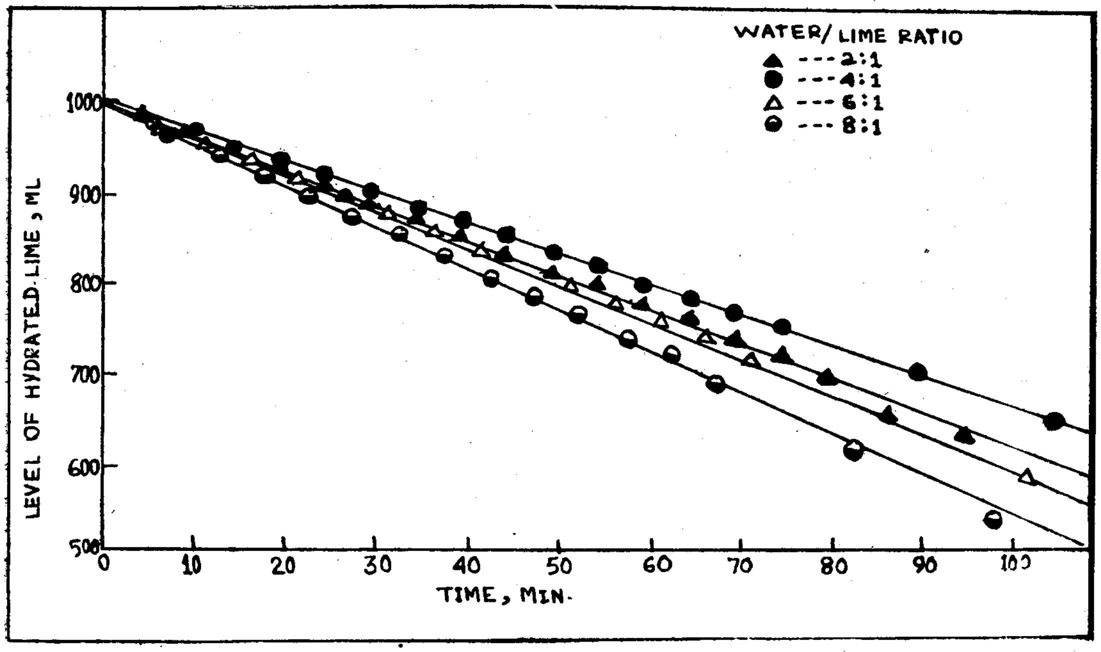

Fig.—1 : Settling Characteristics of Lime Slurries.

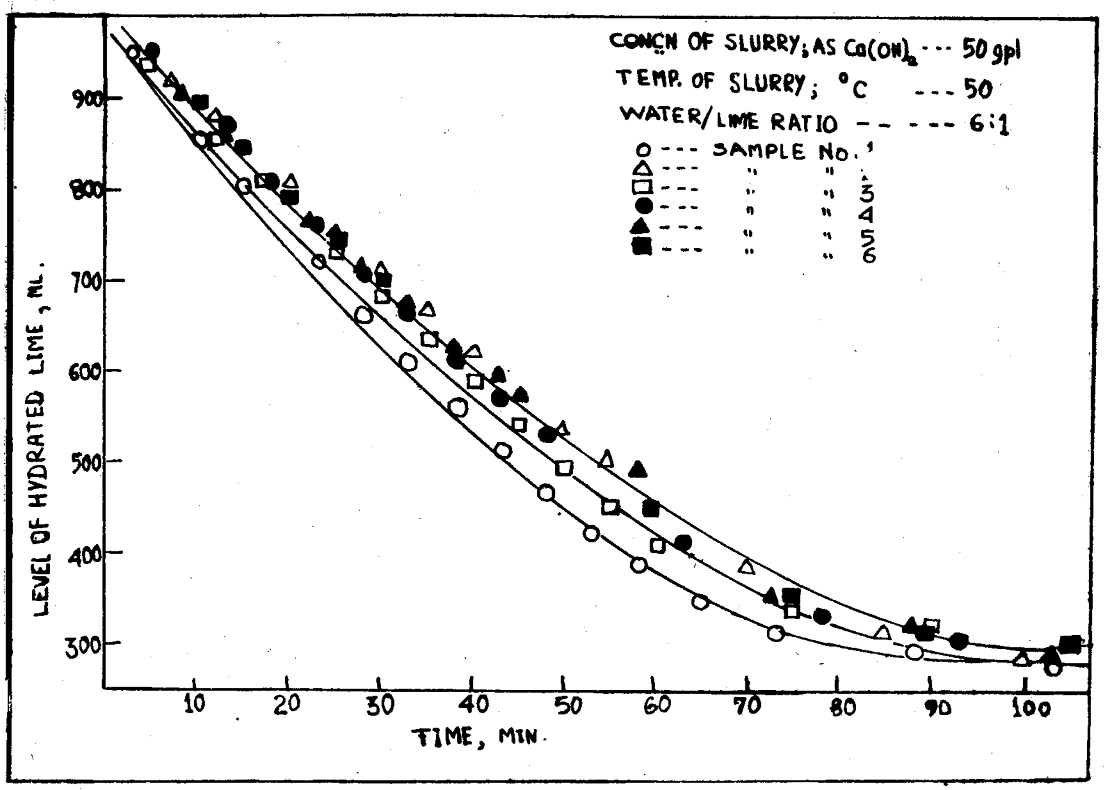

Fig.—2 : Settling Characteristics of Lime Slurry Samples From Lime Slaker.

TABLE—I

ANALYSIS OF LIME SLURRIES TAKEN FROM PULP MILL LIME SLAKER WITH WATER/LIME RATIO=6 : 1

Sample No.	Rate of lime feed, Kg/min.	Amount of water for slaking, Lit./Min.	Temp. of water for slaking, °C	Average Temp. of after slaker, °C	Average Temp. of after Rake class, °C	Average Temp. of slurry after vibrating screen, °C	Conc. of slurry as $Ca(OH)_2$ gpl (From outlet of vibrating screen)
1	15	90	51	70	62	60	93.24
2	15	90	48	65	59	56	76.96
3	15	90	48	66	59	56	81.03
4	15	90	51	72	64	61	103.2
5	15	90	51	71	64	62	99.1
6	15	90	52	71	66	63	107.3
7	15	90	53	72	65.5	64	107.3

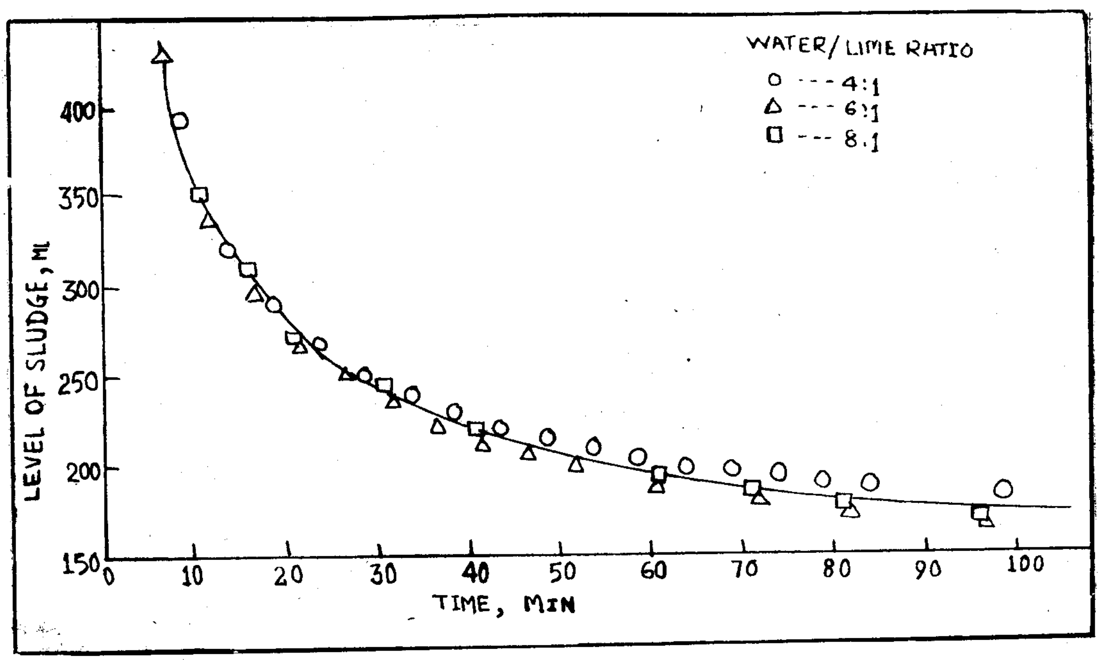

Fig. 3 : Settling Characteristics of Bleach Liquor Prepared In Laboratory.

some laboratory experiments with an intention of studying the effect of different water/lime ratios on the chlorine absorption and settling characteristics of the resultant bleach liquor. The results are given in Table II and Figure-3. In the above experiments, bleach liquor was prepared from 1 litre of 50 gpl concentration at room temperature. Constant agitation of the milk of lime was done by a magnetic stirrer. Three sets of bleach liquor were prepared in the laboratory under the same conditions of concentration chlorine flow, chlorination time etc. Analysis of the resultant bleach liquor was done for available chlorine excess $Ca(OH)_2$ of settled liquor pH and calcium chlorate.

TABLE—II

BLEACH LIQUOR PRODUCED IN LABORATORY FROM LIME SLAKED WITH DIFFERENT WATER/LIME RATIOS*

Set No.	Water/ Lime Ratio	Initial temp. of lime slurry, °C	Final temp. of lime slurry, °C	Chlori- nation time, Min.	Analysis of resultant bleach liquor			
					Available chlorine, gpl	Excess $Ca(OH)_2$, gpl	$CaClO_3$, gpl	pH
1	4:1	32	45	15	38.9	2.40	0	11.30
2	6:1	32	45	15	38.1	2.41	0	11.38
3	8:1	32	45	15	37.3	2.40	0	11.40

*Lime slurry was diluted to 50 gpl conc. as $Ca(OH)_2$ in all the three cases before chlorination.

(ii) Having done these laboratory experiments, the process in our mill was studied and samples of bleach liquor, lime slurry etc. were collected under different process conditions. Bleach liquor samples were analysed for available chlorine, total chlorine, calcium chlorate, excess lime, pH etc. and their settling characteristics were observed. Excess chlorine, which is the difference between total chlorine+chlorate chlorine and the available chlorine has been calculated in each case, and the percent excess chlorine on available chlorine has also been mentioned. Results are given in Table—III.

(iii) As mentioned previously, experiments were conducted in the laboratory, to study the formation of bleach liquor from milk of lime at higher temperatures, to simulate plant conditions.

III) BLEACH SLUDGE AND RECOVERY OF CHLORINE

As sludge in bleach liquor is always associated with appreciable quantity of available chlorine, and active lime to some extent, it is desirable to study the recovery of these chemicals from sludge through an economic process, easy for operation and yet with minimum losses. It has been found that recovery of chlorine from sludge, by washing with water is a convenient method, easy for operation.

(i) In the beginning two preliminary experiments were conducted to study the recovery of chlorine from sludge through washing. The settling characteristics of these sludge samples collected from different places were found out and their suspended solids content (after washing free of chlorine and chloride) were found out. Available chlorine, and excess lime, were determined by Tappi Standard T611 os-41. Washings were done in beakers, with fresh water. For thorough mixing of the water and sludge, electric and magnetic stirrers were used. The clear liquors, after settling for 3 hours were decanted in measuring cylinders, and their available chlorine contents were found for. calculating the percent chlorine recovery, based on original available arbitrary quantity and continued in stages. The experiment repeated wtih equal quantity of water which was split in three and two stages instead of five. Results are given in Table—5. IV and V.

(ii) Another bleach sludge sample was collected from the plant and washing experiments were carried out. Washing of the sludge was done only in two stages, and settling time of 3 hrs. was given. Details regarding splitting of the wash water quantity are given in Table—V Set IA. The same experiment was repeated with the same conditions, except that continuous stirring was done on magnetic stirrer for 1 hour, and then allowed to settle. Results of this experiment under Set IB are given in Table—V. This experiment was repeated with continued stirring for hour but splitting the quantity of water in different proportion. Results are given under Set II. For set III, warm water at 40°C. was used to observe the effect of temperature of wash water.

(iii) Experiments on sludge washing were modified, as it was felt that the suspended solids in sludge should be the basis for calculating the quantity of water for washing. Firstly washing was done in two successive stages. Ratio of suspended solids/water was calculated, and for each stage of washing two hours settling time was given, after thoroughly mixing bleach sludge with water. Results are given in Table–VI, giving total recovery with different solids/water ratio, and the total percent chlorine recovery.

Another sample of sludge was brought, and the washing experiment was done, using solids/water ratios, 1 : 10, 1:30 1:40 and 1:50. The levels of the settled liquor were noted after 1 hour, 2 hours, 3 hours and overnight. Available chlorine in these were determined and percent chlorine recovery calculated at different solids/water ratios, and with

TABLE—IV

Unwashed sludge from the drain line of a Chest in bleach liquor preparation plant was collected. Its settling characteristics were determined and are as follows :

Time, Min.	0	15	30	45	60	90	120	150	180
Level of sludge, ml	1000	990	985	980	978	975	970	965	965

Available chlorine of the sludge and excess alkali : This was determined as per Tappi Standard (T611 os-47)

1) Available Cl_2 = 25.31 gpl

2) Excess alkali = 73.0 gpl as $Ca(OH)_2$

Total solids in the sludge

Total solids 115.12 gm/litre (after washing free of Cl_2) i.e., the sludge contains 63.4% active lime.

WASHING OF THE SLUDGE IN LABORATORY

500 ml sludge was taken for expt. for each set. Water for washing taken for each wash as given below, stirred with electric stirrer for 1 min. Allowed to settle for atleast 3 hrs. Clear liquor decanted and analysed.

Set I	Water for washing, ml.	Water on sludge volume, %	Decanted clear liquor, ml.	Available chlorine of clear liquor, gpl.	Available chlorine contents of clear liquor, gm.	Chlorine recovery on original avl. Cl_2 contents, %
First wash	200	40	210	15.03	3.15	24.5
Second wash	300	60	285	9.5	2.71	21.5
Third wash	300	60	350	5.85	2.04	16.10
Fourth wash	300	60	320	3.70	1.18	9.28
Fifth wash	400	80	400	2.01	0.80	6.30
					Total :	77.68%
First wash	500	100	500	10.7	5.35	42.1
Second wash	500	100	520	5.3	2.75	21.7
Third wash	500	100	510	2.75	1.40	11.0
					Total :	74.8%

TABLE—III

DATA ON BLEACH LIQUOR PREPARATION IN THE PLANT

Sl. No.	Chlorine gas pressure, Kg/cm_2	Feed of lime slurry, l/m	Temp. of lime slurry, °C.	Conc. of lime slurry $Ca(OH)_2$, gpl	Flow of fresh water to R.T., l/m	Temp. of fresh water to R.T., °C	Temp. of Reaction Tank, °C.	Sludge wash to Reaction Tank, l/m	Avg. conc. of lime slurry In R.T. $Ca(OH)_2$, gpl	Analysis of the bleach liquor samples: Source	Available Cl_2, gpl	Total Cl_2, gpl	Calcium chlorate (as Cl), gpl	Total Cl_2 + chlorate Cl_2, gpl	Excess Cl_2 on available Cl_2, gpl	Excess chlorine, %	Excess (insoluble) lime as $Ca(OH)_2$, gpl
1.	2.0	210	42	70.0	115	25	52	182	—	Reaction tank	38.03	41.41	0.47	41.88	3.85	10.12	—
2.	2.0	210	45	71.0	110	25	52	180	—	Overflow to Transfer Tank	35.72	41.06	0.67	41.73	6.03	16.82	—
3.	2.0	210	46	79.8	110	25	50	180	—	Chest No.2 inlet	35.33	41.34	0.71	42.05	6.72	19.01	—
										Reaction Tank	33.38	37.16	0.61	37.77	4.39	13.17	—
										Transfer tank	34.11	37.65	0.52	38.17	4.06	11.85	—
										Chest No. 2 inlet	35.80	39.33	0.59	39.92	4.12	11.49	—
4.	2.0	220	43	76.96 (composite)	200	26	48	Nil	35–40.5	Reaction tank (composite)	32.20	34.11	0.35	34.46	2.26	7.0	—
5.	2.0	220	43		180+70	26	46	,,		Chest No. 3 inlet (composite)	31.91	35.05	0.44	35.47	3.55	11.11	—
6.	2.0	220	43		180+70	26	47	,,									
7.	2.5	220	43	88.8 (composite)	150+80	25	50	Nil	40–42	Reaction tank (composite)	38.03	39.91	0.38	40.29	2.26	5.92	—
8.	2.4	220	43		200+65	25	50	,,		Chest No. 2 inlet (composite)	36.5	39.02	0.47	39.49	2.99	8.09	—
9.	2.4	220	44		200+65	25	50	,,									
10.	2.4	220	45		180+65	25	50	,,									
11.	2.5	180	51	93.6 (composite)	190	27	50	300	46–33	Reaction tank 52°C.	39.84	42.18	0.006	42.186	2.346	5.87	1.46
										Transfer tank at 53°C.	38.91	41.33	0.0	41.33	2.42	6.21	3.40
12.	2.5	195	52		180	27	52	Nil		Sample from settling test (Transfer tank) 53°C.	34.2	37.22	0.006	37.226	3.026	8.82	5.66
										Sludge wash 38°C. (Settled liquor)	18.0	21.62	0.100	21.72	3.72	20.64	17.37
13.	2.5	200	53	80.66	200+70	28	48	Nil	34	Reaction tank	25.52	26.66	0.0	27.66	1.14	4.45	4.40
										Transfer tank (49°C.)	24.74	26.30	0.007	26.307	1.566	6.33	3.88
										Settling test liquor (49°C) (Transfer tank)	24.95	26.09	0.006	26.097	1.146	4.58	3.21
14.	2.5	120	53	104.3	200+40	28	52	Nil	34.5	Reaction tank	36.58	40.2	0.402	40.602	4.022	10.99	2.77
15.	3.0	180	53		200+40	28	51	Nil	44.5	Transfer tank (50°C.)	33.85	37.83	0.370	38.20	4.35	12.83	4.1
										Chest No. 1 inlet (50°C)	33.43	36.5	0.735	38.565	5.135	15.33	3.51

TABLE—V

WASHING OF THE SLUDGE IN LABORATORY

A composite sample of washed sludge, was collected in a bucket, from the drain line of sludge washing tank in Pulp Mill.

Its settling characteristics are as follows :

Time, Min.	0	5	20	35	50	80	110	140	200
Level of sludge, ml.	1000	920	840	800	780	755	740	730	725

Available Cl_2 in the sludge = 21.62 gpl
Excess alkali in the sludge = 47.54 gpl
Total solids in the sludge = 86.32 gpl (after washing free of Cl_2) i.e., the sludge contains 55% active lime.

This sludge, collected from the drain line of the sludge washing tank was taken for washing, as it contained good amount of available chlorine.

WASHING OF THE SLUDGE

500 ml sludge was taken for each set of experiment. Water for washing taken for each wash as given below, stirred for 2 min. Then allowed to settle for 3 hrs. Clear liquor decanted and analysed.

Set IA	Water for washing ml. (1)	% on sludge volume (2)	Decanted clear liquor ml. (3)	Available chlorine of clear liquor gpl. (4)	Available chlorine contents of clear liquor, g. (5)	Chlorine recovery on original available Cl_2 contents, % (6)
First wash	500	100	555	9.78	5.42	50.10
Second wash	500	100	505	4.75	2.40	22.22
					Total :	72.32

All conditions same as above, except, that after addition of water continuous stirring was done on magnetic stirrer for 1 hour and then allowed to settle.

Set IB	(1)	(2)	(3)	(4)	(5)	(6)
First wash	500	100	540	9.80	5.29	48.90
Second wash	500	100	560	4.78	2.67	24.52
					Total :	73.42

Set II	(1)	(2)	(3)	(4)	(5)	(6)
First wash	750	150	765	7.70	5.9	54.57
Second wash	250	50	320	5.10	1.63	15.10
					Total :	69.67

Set III	(1)	(2)	(3)	(4)	(5)	(6)
Warm water at 40°C.	500	100	560	9.57	5.35	4.93

TABLE—VI

BLEACH SLUDGE WASHING WITH WATER IN TWO SUCCESSIVE STAGES

Characteristics of the bleach sludge collected from plant.

I) Available Cl_2 = 29.63 gpl

II) Excess lime = 43.0 gpl as $Ca(OH)_2$

III) Suspended solids = 71.0 gpl

Experiment No.		1	2	3	4
Volume of sludge taken, ml		500	500	500	500
F_1 ml of fresh water added	I stage	250	500	750	1000
Suspended solids water ratio	I stage	7.1	14.2	21.3	28.6
W_1 ml of clear settled liquor recovered	I stage	195	360	610	835
F_2 ml of fresh water added	II stage	750	500	250	IInd Stage not done
Suspended solids : water ratio	II stage	21.5	14.4	7.3	
W_2 ml of clear settled liquor recovered	II stage	660	470	340	
Available Cl_2 gpl in W_1		19.2	14.5	11.5	9.63
Available Cl_2 gpl in W_2		7.55	7.73	7.79	—
Available Cl_2 in W_1, %		3.75	5.22	7.01	8.05
Available Cl_2 in W_2, %		4.98	3.63	2.65	—
Recovery in W_1, %		25.32	35.24	47.30	54.3
Recovery in W_2, %		33.65	24.51	17.81	—
Total Cl_2 recovery, %		58.97	59.75	65.11	54.3

For each stage of washing, a settling time of 2 hours was provided after mixing of bleach liquor sludge with fresh water.

increasing settling times. The results are given in Table—VII. A graph of settling time in hours vs. percent chlorine recovery, for each set of solids/water ratio has been plotted and represented in Figure-5.

Single stage washing, and two stage counter current washing were studied with another sample of bleach sludge. The results are given in Table—VIII.

RESULTS AND DISCUSSION

I. Results of the laboratory experiments (Figure-1) on slaking and settling characteristics showed that at constant temperature i.e. 50°C. as the water/lime ratio increased, the settling characteristics of lime slurry improved. This observation is in agreement with that reported by Miller[1]. It appears that, at constant temperature with increasing ratio of water/lime, the particle diameter of calcium hydroxide increases, resulting in quicker settling. However, these results are not in agreement with those reported by Boynton[8]. It is also expected that at constant water/lime ratio, increasing the temperature would result in finer particles with lower settling properties.

Results of the plant experiments shown in Table–I and Figure–2 indicated that keeping the lime feeding rate, and the amount of slaking water constant, i.e. water/lime ratio, 6:1 the settling properties of lime slurries were almost similar, after diluting to 50 gpl. This is probably due to the same size of calcium hydroxide particles, at constant water/lime ratio. Although slight changes in temperature, have affected, the concentration of lime slurries, these temperature changes are inadequate, to affect the particle size and consequent settling rates.

The degree of calcination has also an important bearing on the properties of resultant oxide. The difference in calcination will produce oxides of diffe-

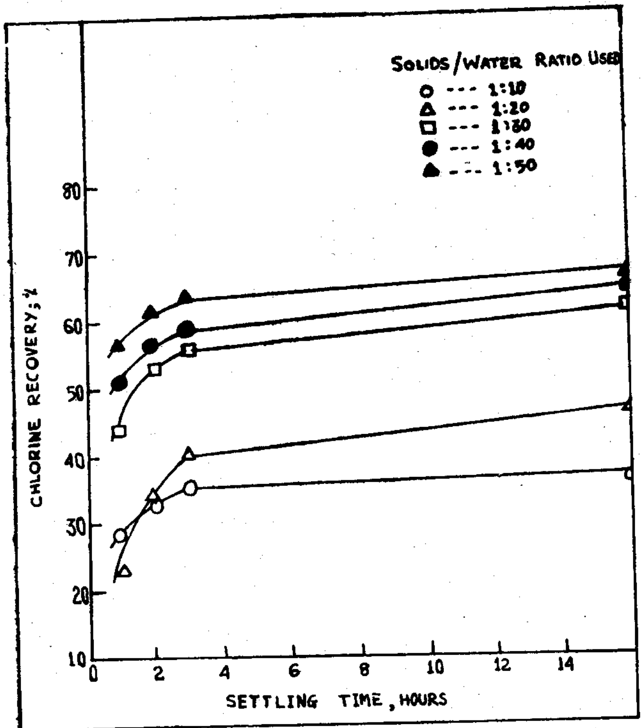

Fig. 5. Recovery of Chlorine from Bleach Sludge

rent types such as soft burned oxide, overburned oxide, or the mixture of the two. The nature of calcium oxide consequently plays an important role in slaking. The soft burned calcium oxide reacts with water instantaneously and vigorously, while the overburned calcium oxide reacts with water slowly, and produces crystalling products. The overburned type also requires water at high temperature for completion of slaking and produces extremely fine hydroxide which result in turbid liquor although the hydroxide may be of large diameter as determined by low specific surface. Miller(1) has dealt with these characteristic phenomenon in his comprehensive study. It is imparative that overburned or hard-burned oxides, containing cystallites should not be accepted for bleach making, as particle size control is not possible with these types. For highly reactive lime, lower ratios of water/lime with high temperatures of water favour formation of crystalline and very fine particles of calcium hydroxide, which are difficult to settle quickly. The crystalline particles are associated with higher specific surface and lower settling rates and do not react with chloiine readily. The particle size and nature like crystallinity can be controlled by a suitable combination of water/lime ratio, and water temperature for slaking, thorough agitation, or dissipation of slaking heat quickiy.

TABLE—VII

BLEACH SLUDGE WASHING IN THE LABORATORY

A composite sample of unwashed sludge brought from sludge washing tank.

Characteristics of the sludge

i) Available Cl_2 = 21.87 gpl)
ii) Excess lime = 28.67 gpl) As per Tappi Method
iii) Suspended solids = 58.26 gpl)

500 ml sludge samples taken for each washing with various solids to solids : water ratios. Thorough mixing of sludge and water was done with the help of magnetic stirrer and then poured in cylinder to determine settling.

Ml. of fresh water added for washing	Ratio solids to water	No.	Settiing time, hours	Clear liquor, ml.	Available Cl_2, gpl	Cl_2 contents, gms	Cl_2 recovery, %
291.6	1:10	1	1	245	12.62	3.09	28.24
		2	2	290	,,	3.65	33.50
		3	3	310	,,	3.91	35.73
		4	Overnight	310	,,	3.91	35.73
582.6	1:20	1	1	280	9.19	2.58	23.52
		2	2	415	,,	3.81	34.90
		3	3	485	,,	4.45	40.08
		4	Overnight	550	,,	5.05	46.25
874	1:30	1	1	620	7.73	4.79	43.82
		2	2	750	,,	5.80	53.04
		3	3	800	,,	6.20	56.50
		4	Overnight	870	,,	6.72	61.52
1165.2	1:40	1	1	930	6.03	5.6	51.30
		2	2	1035	,,	6.21	56.90
		3	3	1075	,,	6.45	59.20
		4	Overnight	1130	,,	6.82	62.30
1456.5	1:50	1	1	1210	5.17	6.25	57.20
		2	2	1315	,,	6.75	61.90
		3	3	1355	,,	7.09	64.75
		4	Overnight	1610	,,	7.28	66.50

TABLE—VIII

SLUDGE WASHING EXPERIMENT IN THE LABORATORY

Composite sample of sludge was collected from the plant.

Sludge characteristics :

i)	Total solids	=	60 gpl
ii)	Free Lime	=	32 gpl as $Ca(OH)_2$
iii)	Available Cl_2	=	20.26 gpl.

I. 500 ml sludge + 900 ml water fresh (solids/water ratio = 1:30)

↓ 2 hrs. settling after agitation.

Cl_2 recovery = 57.4% (in single stage washing)

II. Two stage countercurrent washing :

a) 500 ml sludge + 300 ml fresh water

↓ 1 hr. settling

W_1 and Cl_2 recovery in W_1 = 23.39%

b) Sludge from previous stage 'a' + 600 ml fresh water

↓ 1 hr. settling

W_2 and Cl_2 recovery in W_2 = 37.85%

∴Total Cl_2 recovered in Stage a & b = 23.39 + 37.85%

Sludge after the stage 'b' discarded = 61.24%

c) Fresh sludge 500 ml + W_2

↓ 1 hr. settling

W_3 and Cl_2 recovery in W_3 = 38.3%

d) Sludge from previous step (c) + 300 ml fresh water

↓ 1 hr. settling

W_4 and Cl_2 recovery in W_4 = 19.9%

∴Total Cl_2 recovery in steps c + d = 38.3 + 19.9 = 58.2%

W_1, W_2, W_3, & W_4 ———→ ml. of clear settled liquor

Based on this study, the following suggestions have been given :

1) For our Lime Slaker, it has been suggested to take trials with water/lime ratio, 4:1 and temperature of water prior to slaking 50–55°C. At present, there is no fixed water/lime ratio, at the Lime Slaker. Lower temperatures, than mentioned above, may be tried for better particle size. This is expected to prevent formation of very fine $Ca(OH)_2$ particles.

2) The showers at the outlet of Lime Slaker, as well as those on Rake Classifier, should be of fresh water, instead of hot water, to dissipate heat of slaking quickly and prevent crystallisation of calcium hydroxide particles.

Thus, with the existing conditions, such as rate of the lime feed, final concentration of lime slurry to Lime Storage Tank etc. these changes are expected to result in the following :

A. Control the formation of very fine, as well as crystalline calcium hydroxide particles. For better hypochlorite production, the particles of calcium hydroxide should be relatively coarse, as they absorb chlorine better than the fine particles, and also, they selltle fast. On the other hand, crystalline particles of calcium hydroxide are not desirable in milk of lime, as they are slow in the reaction with chlorine, and increase turbidity of the calcium hypochlorite solution due to slow settling.

B. Fresh water instead of hot water in showers, at the Slaker outlet and on Rake Classifier is expected to reduce the temperature of milk of lime. This would help in rapid chlorine absorption, and reduce mechanical losses, during chlorination at high temperature.

C. Saving in steam as fresh water to be used instead of hot water on showers.

D. With this water/lime ratio of 4:1, it is expected that retention time in slaker will increase without modifying its speed etc.

II (i) It is seen from Table—II and Figure-3 that the bleach liquor prepared from milk of lime with water/lime ratios 6:1 and 8:1 have almost similar settling properties. However, they don't have marked advantage over the one from water/lime ratio 4:1. It is very difficult to reproduce the conditions in the laboratory similar to those on plant. It was found that the reaction of chlorine with milk of lime at higher temperature is very difficult to control, in the absence of pressure gauge or rotameter for chlorine.

(ii) The process variables under the plant conditions can be easily seen from Table-III, in which percent excess chlorine on the available chlorine had been calculated. Theoretically, available chlorine and total chlorine of a sample of bleach liquor should be the same. Hence, the excess on the available chlorine, may be taken as the loss occurring during the process. It can be seen from Table-III that the percent excess chlorine varied between 4.45% to 19.01% depending upon the process conditions. The lowest value of 4.45% for Sample No. 13 may be attributed to the lower available chlorine i.e., 25.52 gpl and the lowering of the temperature of the Reaction Tank i.e., 48°C, although the initial temperature of the lime slurry was 53°C. The highest value of 19.01% excess chlorine for Sample No. 2 can be attributed to the fact that starting with a lime slurry of 42°C the temperature of the Reaction Tank raised to 52'C. which is quite enormous. The results of Sample No. 11 were rather surprising, as the amount of calcium chlorate formed was quite negligible or zero, and excess chlorine was only 5–6%, although the temperature of Reaction Tank was 52°C, and available chlorine 38–39 gpl. A possible explanation is a large amount of sludge wash from Sludge Washing Tank with available chlorine 18 gpl was put in the Reaction Tank and also starting with a lime slurry of 51–52°C, the temperature of Reaction Tank was also 50–52°C. The conditions favourablefor chlorate formation as given in the literature are :

(a) High temperature of alkali

(b) Introducing excess chlorine

(c) High concentration of alkali

It is mentioned in the literature that calcium chlorate is an unstable compound, so it is quite possible that it gets decomposed after its formation, thereby resulting in higher amount of total chlorine, as compared to the available chlorine. The conditions, such as high temperature and concentration of milk of lime should be controlled, so as to suppress the chlorate formation, or the resultant higher amount of total chlorine.

(iii) Bleach liquor prepared in the laboratory, from milk of lime at increasingly higher temperatures, show that there was a difference of only 0.5 to 0.7 gpl between total chlorine and available chlorine, with zero or negligible amounts of calcium chlorate. Moreover, a significant fact observed was that the chlorine absorption reduced with the increase in the initial temperature of milk of lime, indicating thereby, mechanical losses in proportion with the initial temperature. It was not possible to estimate the mechanical losses of chlorine, in these laboratory experiments. Another noteworthy observation was that bleach liquor prepared from milk of lime at room temperature, had good settling propeities. But with higher initial temperatures of milk of lime, the resultant bleach liquor samples had poor settling properties, in proportion with temperatures. It was also noticed during the settling tests on bleach liquor samples in cylinders, that internal disturbance without any external source takes place, when milk of lime of initial high temperatures are used. This is similar to the experiences reported by Miller(2). Due to this internal disturbance, the column of sludge already settled, travels to the top, making the intire bleah liquor turbid. This did not happen with bleach liquor samples prepared from milk of lime at room temperature. Moreover, it was observed that the bleach liquor made from milk of lime at room temperature, had pale pink colour. But as the temperatures of milk of lime increased the colour of the resultant liquors also became dark pink, probably due to the reaction of chlorine, with the impurities of lime at high temperatures.

The settling characteristics of the bleach liquor samples from plant are graphically represented (Figure-4). There is no exact relationship between excess lime (insoluble) content, and the settling properties. It is a general observation, that the settling properties of bleach liquor produced at high temperature and higher concentration of excess (insoluble) lime are not good. Correlating the data obtained from the laboratory experiments, with the observations and results from the plant, it is suggested that a separate tank, which would serve as Dilute Lime Slurry Storage is suggested in which dilution of lime slurry to uniform concentration is done, and at

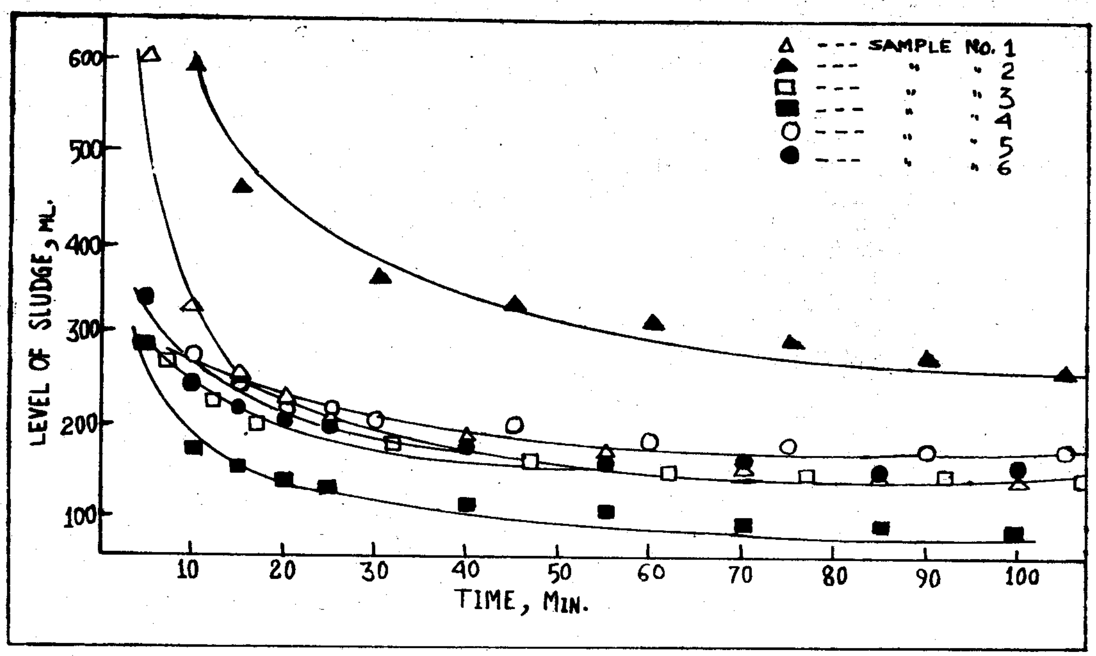

Fig.—4. Settling Characteristics of Bleach Liquor Samples

the same time, lowering of the lime slurry temperature can be achieved. The equipment for cooling the lime slurry through heat exchanger etc. would need more capital investment. Dilute Lime Slurry Storage Tank would serve both the purposes i.e., dilution and lowering of the temperature. The dilution in Reaction Tank is to be avoided.

The expected advantages are as follows :

1) Further dilution with fresh water or sludge wash from Sludge Washing Tank will help to reduce chlorine losses occurring at high temperatures, as mentioned in this place as percent excess chlorine would be less at lower temperatures. Also mechanical losses of chlorine, associated with high temperature of lime slurry would be minimised.

2) At present there is no control over the concentration of lime slurry fed to Reaction Tank. Uniform concentration of milk of lime as 35–37 gpl $Ca(OH)_2$ will help to reduce lime losses going with the sludge. Also uniform concentration milk of lime will help to maintain uniformly the available chlorine content of the bleach liquor.

3) The turbidity of the resulting bleach liquor will reduce, if milk of lime of lower temperature and lower uniform concentration is fed to the Reaction Tank.

4) It will prevent the high excess of calcium hydrocide in the Reaction Tank. High excess of calcium hydroxide increases its solubility in bleach liquor, which is reprecipitated during bleaching(2). An excess of 4–7 gpl calcium hydroxide results in a bleach with more than 1 gpl dissolved calcium hydroxide. It is necessary to accurately control the concentration calcium hydroxide suspension prior to chlorination to maintain maximum 1 gpl excess for stability at economic level. This may reduce the scaling trouble in the hypochlorite tower feed line and the hypo tower in our Bleach Plant.

III Results in Tables—IV and V show that for maximum recovery of chlorine, it is the quantity of water added, that matters rather than the number of washing stages, where limited quantity of water was split and transferred in two or three stages.

Results of Table-V, Set IA, Set IB, Set II & III show that prolonged stirring or use of warm water does not improve chlorine recovery.

The maximum amount of chlorine which could be recovered will normally depend on the volume of the clear, settled liquor obtained, after mixing the sludge with water, and allowing it to settle the concentration of available chlorine in settled liquor, and the compactness of the solid phase.

Since the same sludge cannot be preserved for long, for experimental purposes, fresh composite samples, were brought from Pulp Mill, frequently.

Results of the Table—VI, indicated that, where the same quantity of water was added in two stages, the chlorine recovery was little higher. However, since in two stages the settling time for solid-liquid separation is just double of that given in single stage, it seems that even in single stage, chlorine recovery will improve if somewhat longer time for settling the solids is given. Since single stage washing of bleach sludge, is a more practical proposition in the mill these experiments were aimed at constant conditions of settling time, temperature, the effect of various suspended solids : water ratios, on percent chlorine recovery etc. With continuous increase in this ratio, chlorine recovery also showed continuous increase. However, a distinct improvement in chlorine recovery was noticed when the ratio was changed from 1:20 to 1:30, which implies that for achieving acceptable levels of chlorine recovery without unnecessary lowering available chlorine concentration, and producing sludge washings much in excess than that could be used in the system, a ratio of suspended solids/water, to be maintained between 1:20 and 1:30 (Figure–5).

In order to compare the effectiveness, for maximum chlorine recovery, two stage countercurrent washing was carried out and was compared with single stage washing. It is seen from the results included in Table VIII, that the chlorine recovery for single stage washing was 57.4% and in two stage counter-current washing it was 61.2% and 58.2%. This implies that the two stage countercurrent washing is not really advantageous over single stage washing.

It was suggested that the capacity of the present Sludge Washing Tank may be increased, or it may be remodified, so as to accommodate, wash water and bleach sludge, as per the optimum ratio of suspended solids/water, for maximum chlorine recovery. Bleach liquor preparation plant may be run continuously as far as possible to utlise the washings.

The total suspended solids in bleach sludge were found to contain 50–60% of active lime, which at present goes to drain after washing. This may be utilised as a supplementary material with lime, in case lime treatment of alkali extraction stage effluent is adopted.

The washings from Sludge Washing Tank should be always clear when taken to Reaction Tank, as the calcium hydroxide in sludge is converted to calcium carbonate during chlorination, and makes the resultant liquor turbid.

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