

# Effect of Green Liquor to Lime Ratio During Slaking on the Settling Rate of Causticized Slurry

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## Introduction

Many paper mills in India are faced with the problem of poor settling rate of the lime sludge, owing probably due to the inferior quality of lime used. Since the settling rate of the causticized slurry i. e. the precipitated calcium carbonate determines the production of white liquor, economics dictates that a slurry should be obtained which will give a fast settling sludge. It is known that the settling characteristics of the causticized slurry i. e. the precipitated calcium carbonate, depends on both the physical and process variables, however, in normal working, it is the former which determines greatly the settling properties of the sludge. Among the physical variables, besides the quality of lime, the method of slaking of lime with the green liquor is quite important. Since the effect of varying the ratios of green liquor to lime during slaking has been differently reported, it is desirable to study the effect of this important variable on the settling properties of the

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*Improved slaking as obtained through an increase in the liquid to lime ratio at the slaker inlet, enabled to produce causticized slurries, which gave the fast separation of the suspended particles of precipitated calcium carbonate resulting in increased production of the white liquor, higher consistencies of the underflow and white liquor overflow of significantly improved clarity. Initial experiments carried out in the laboratory, where the effect of liquid to lime ratios on the settling characteristics of the causticized slurry were studied, demonstrated that a ratio of 6:1 produces a slurry with significantly better settling characteristics of the sludge, compared to where the ratio was initially 3:1. Plant trials have confirmed this, and as a result the productivity of the causticizing section at the West Coast Paper Mills has significantly improved.*

sludge for individual conditions. Rai<sup>1</sup> reported that for efficient slaking 25% of total quantity of green liquor is added in the slaker and the balance added to the classifier. The liquor to solid ratio is kept at a practical minimum to give a maximum detention period in the slaker. Roth Rock<sup>2</sup> also believed that low ratios of green liquor to lime during slaking will produce larger mud particles, resulting in faster settling mud than high ratios. At the West Coast Paper Mills many times the production of white liquor has to be limited, as the settling rate of the lime sludge used to be poor. This was observed even when no change in the process conditions and the quality of lime as measured by the nature and extent of impurities was made.

This necessitated that a study of the effect of green liquor to lime ratios (volume by weight) during slaking on the settling rate or the lime sludge be made and the present paper describes these findings.

## Experimental :

Settling tests were carried out using causticized slurries obtained from the reaction of total quantity of 1.5 litre of green liquor with the required quantity of lime and further completing the causticization reaction under reflux for one hour. The contents at the end of the causticization reaction were transferred with sufficient agitation to a graduated one litre measuring cylinder and the volume of the supernatant obtained was recorded at different time intervals. The white liquor obtained in each case

was tested for total titrable alkali and causticity.

For varying the green liquor to lime ratio during slaking, the initial volume of the green liquor reacted with lime during the first 3 minutes was varied, and the balance of the preheated green liquor was added in either one or two instalments. Where the balance green liquor was added in two instalments a time interval of 3 minutes was followed.

At the West Coast Paper Mills the green liquor addition was earlier done in three stages. For a certain rate of green liquor addition, the quantities were equally proportioned ( $\frac{1}{3} + \frac{1}{3} + \frac{1}{3}$ ) at the slaker inlet, slaker outlet, (drum type slaker) and the rake classifier sump box. Preliminary experiments were carried out where the effectiveness of slaking by this method was compared with where  $\frac{2}{3}$ rd green liquor was added first and the balance  $\frac{1}{3}$ rd after 3 minutes. In another case all the green liquor was reacted with lime during the first 3 minutes only. The results are given in Table I. More experiments were carried out using the composite green liquor and the composite bin lime sample obtained from the plant daily for a few days, to show the effect of liquid (green liquor) to lime ratio during slaking on the settling characteristics of the lime sludge. The results are given in Table II. The composite green liquor and bin lime samples were subjected to detailed chemical analysis and the results are given in Table III and IV. The effect of varying the green liquor to lime ratios from 2.9 : 1

**TABLE I—Effect of Varying the Mode of Green Liquor Addition on the Settling of Causticized Slurry.**

Green Liquor

Na<sub>2</sub>CO<sub>3</sub> as such g/l 130.4

Burnt Lime

av. CaO, % 70

Lime used for 1.5

litres of green liquor 140 gms.

	Settling 5 mins.	rate 10 mins.	after 15 mins.	after 20 mins.	after 30 mins.	T.T.A. as Na <sub>2</sub> O g/l	Causti- city. %
A	4	8	13	19	24	116.0	81.5
B	22	40	55	58	59	116.2	80.8
C	42	58	65	65	65	116.2	81.1

A:—Green liquor added in three instalment (0.5+0.5+0.5 litres) liquid to solid ratio during slaking 3.6:1.

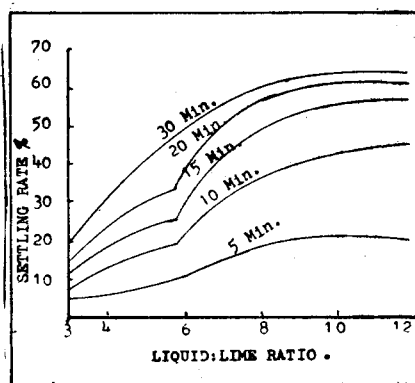
B:—Green liquor added in two instalments (1+0.5 litre) liquid to solid ratio during slaking 7.2:1.

C:—Green liquor added at one time (1.5:1) liquid to solid ratio during slaking 10.8:1.

Temperature of green liquor °C — 98

Temperature of causticization °C — 102

to 11.7 : 1 during slaking for a typical green liquor and the burnt lime produced in the mill, are shown graphically in Fig. 1. The effect of using burnt lime of various sizes and at varying green liquor to lime ratios was also studied and the results are given in



**Fig. 1—Effect of Green Liquor Lime Ratio on the Settling Rate of the Lime Mud.**

Table V.

Experiments were also carried out to study the :

- i) Effect of causticization time on the causticity of white liquor and the settling characteristics of the lime sludge. For this two sets of experiments were carried out using different green liquor and different lime. In each set of experiments, the causticization reaction was terminated at time intervals of 15, 30, 45 and 60 minutes by rapidly cooling a part of the slurry. This cooled slurry with supernatant white liquor was used for causticity determination. The settling rate determination was made as usual with another part of the hot slurry. The results are

**TABLE II—Settling Rate in Laboratory for the Composite Green Liquor  
and Composite Bin Lime Samples**

Date	A							B						
	Settling rates			% in minutes		TTA as Na <sub>2</sub> O g/l	Causti-city %	Settling rates			% in minutes		TTA as Na <sub>2</sub> O g/l	Causti-city %
	5	10	15	20	30			5	10	15	20	30		
12-11-70	8	17	24	31	47	126.5	80.8	4	8	12	16	26	119.4	82.1
13-11-70	8	17	24	34	42	131.7	82.3	4	8	15	24	31	131.4	82.1
14-11-70	—	—	—	—	—	—	—	—	—	—	—	—	—	—
15-11-70	14	28	40	52	61	127.1	80.8	5	12	18	25	36	126.5	80.4
16-11-70	10	20	30	38	52	126.2	84.7	6	11	18	22	32	127.4	83.8
17-11-70	10	19	29	39	54	124.3	82.2	6	10	—	—	25	127.1	82.6
18-11-70	20	45	58	63	67	127.1	79.5	5	10	15	20	28	131.1	79.3
19-11-70	25	58	68	71	73	122.4	79.0	6	12	18	23	32	124.2	79.0
20-11-70	12	24	35	44	57	129.9	83.3	5	9	14	17	25	130.8	83.3
21-11-70	13	24	36	45	57	129.9	83.3	5	9	13	17	25	131.4	83.3
22-11-70	12	23	32	41	55	118.7	83.5	5	10	14	18	26	121.7	83.6

A—Green liquor added in two instalments.  
Liquid to lime ratio during slaking: 7.8:1

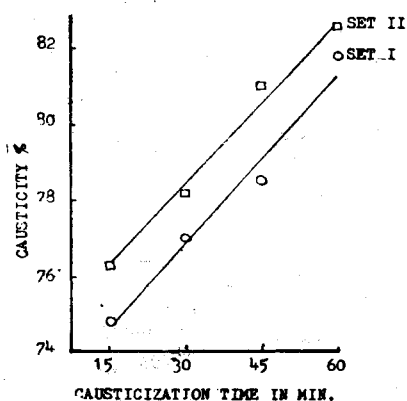
B—Green liquor added in three instalments.  
Liquid to lime ratio during slaking: 3.9:1

**TABLE III—Composite Green Liquor Analysis**

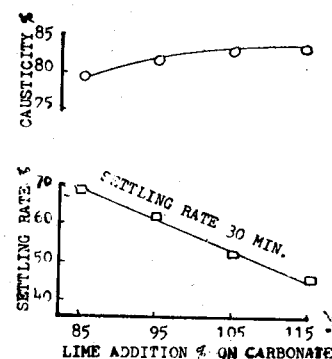
Date	T.T.A. as Na <sub>2</sub> O g/l	NaOH as Na <sub>2</sub> O, g/l	Na <sub>2</sub> S as Na <sub>2</sub> O, g/l	Na <sub>2</sub> CO <sub>3</sub> as Na <sub>2</sub> O, g/l	Na <sub>2</sub> CO <sub>3</sub> as such, g/l	Na <sub>2</sub> SO <sub>4</sub> as Na <sub>2</sub> O, g/l	Reduction, %	Suspended matter, ppm
12-11-70	124.6	35.3	18.6	70.7	120.8	1.52	92.5	20
13-11-70	125.2	32.8	19.8	72.6	124.0	1.55	92.7	24
14-11-70	124.0	34.7	18.6	70.7	120.8	1.62	92.0	46
15-11-70	124.0	37.8	18.6	67.6	115.5	1.69	91.7	50
16-11-70	123.1	38.8	18.6	65.7	112.4	1.40	93.0	156
17-11-70	121.5	37.5	19.8	64.2	109.7	1.40	93.0	90
18-11-70	123.4	36.6	19.2	67.6	115.5	2.66	87.8	—
19-11-70	121.1	41.5	22.9	56.7	110.2	2.07	91.7	102
20-11-70	121.8	37.2	21.7	62.9	100.7	1.45	93.8	70
21-11-70	124.0	45.0	13.6	65.4	102.3	1.78	88.4	82
22-11-70	123.4	32.8	23.6	67.0	114.5	1.11	95.5	34

given in the Table VI and graphically in Fig. 2.

- ii) Effect of addition of various amounts of lime on causticity of white liquor and settling characteristics of lime sludge. In this study also two sets of experiments were carried out using different green liquor and different lime. The lime addition (available CaO) on sodium carbonate was varied from 85% to 120%. The results are given in Table VII and graphically in Fig. 3.



**Fig. 2—Causticity Development  
Against Causticization  
Time.**



**Fig. 3—Effect of Adding Varying  
Amounts of Lime on Settling  
Rate and Causticity Increase**

TABLE IV-Composite Bin Lime Analysis

Date	Av. CaO %	Silica %	MgO %	Mixed oxides %	Loss on ignition %	CaCO <sub>3</sub> (Calculated from loss on ignition) %
12-11-70	71.0	9.0	3.11	2.73	5.04	11.4
13-11-70	70.5	7.28	1.61	2.45	5.75	12.7
14-11-70	71.0	7.2	0.81	2.00	7.8	17.7
15-11-70	69.0	9.4	1.10	1.82	6.9	15.7
16-11-70	66.5	6.43	1.83	2.22	8.11	18.4
17-11-70	69.5	6.67	0.50	2.31	6.00	13.6
18-11-70	68.0	6.00	1.57	2.64	7.96	18.0
19-11-70	66.0	6.38	1.08	1.00	10.59	24.0
20-11-70	69.8	5.7	0.93	2.97	8.1	18.4
21-11-70	65.0	10.0	1.61	2.73	10.0	22.7
22-11-70	65.0	5.81	0.87	0.81	9.2	20.9

TABLE V-Settling Rate With Particles of Different Sizes Isolated from the Composite Bin Lime Sample by Sieve Classification

Form of lime	Purity % Av. CaO	Settling rate in 30 mts. %	A		Settling rate in 30 mts. %	B	
			T.T.A. as Na <sub>2</sub> O g/l	Causticity %		T.T.A. as Na <sub>2</sub> O g/l	Causticity %
Composite	65	50	126.5	84.9	22	127.4	83.8
$\frac{1}{4}$ " to $\frac{1}{2}$ " pieces	66	60	127.1	83.8	30	123.4	83.4
+20 mesh	64.5	58	127.7	83.4	30	128.3	83.4
-20 mesh	64.0	55	127.1	83.0	34	127.4	83.0

A-Green liquor added in two instalments, green liquor : lime ratio 7.8:1

B-Green liquor added in three instalments, green liquor : lime ratio 3.9:1

iii) Effect of using starch on the settling rate of lime sludge. Since use of additives<sup>3</sup> is practised in the clarification of white liquor, a study of the use of starch<sup>4</sup> in improving the settling rate was also made. The results are given graphically in Fig. 4.

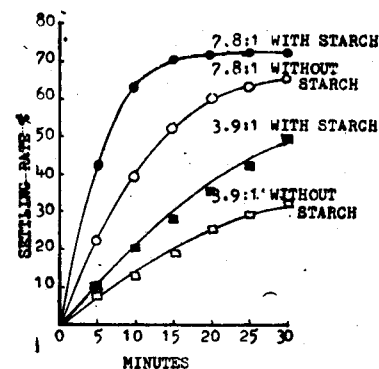


Fig. 4-Effectiveness of Starch in Improving the Settling Rate at Varying Green Liquor to Lime Ratio.

## Results And Discussion

The results in Table I show that when the slaking was carried out at a liquid to lime ratio above 3.6, a fast settling lime sludge was obtained. This has been further confirmed by the results given in Table II, where the composite green liquor and composite bin lime samples were treated daily (12.11.70 to 22.11.70) with different green liquor to lime ratios and every time the results of settling were found to be much better where the initial slaking was carried out at 7.8:1 compared to 3.9:1. Table III gives the chemical composition of the green liquor processed during the test period (12.11.70 to 22.11.70). It is seen that T.T.A. has not varied much and it ranged

**TABLE VI—Effect of Liquid to Lime Ratio on the Wet Sieve Analysis of the Lime Sludge.**

Green Liquor T.T.A. as  $\text{Na}_2\text{O}$ , g/l — 124.3  
 $\text{Na}_2\text{CO}_3$  as such, g/l — 115.0  
 Bin lime purity as av.  $\text{CaO}$ , % — 68

Liquid to lime ratio during slaking	Settling rate % in 30 mins. %	T.T.A. as $\text{Na}_2\text{O}$ g/l	Causticity, %	Wet sieve analysis of the lime sludge retained on		
				100 mesh	—100 +300 %	—300
11.7:1	65	127.1	81.8	37.4	12.8	49.8
7.8:1	63	123.4	81.8	29.0	10.2	60.8
5.8:1	47	127.1	83.1	17.8	16.2	66.0
3.9:1	32	126.5	83.1	10.1	12.1	77.8
2.9:1	20	129.1	83.1	12.1	8.0	79.9

**TABLE VII—Effect of Causticization Time on Causticity Development**

Green liquor : Lime ratio — 7.8:1.

Reaction time, min.	Settling rate in minutes						White Liquor	
	5	10	15	20	25	30	T.T.A. as $\text{Na}_2\text{O}$ , g/l	Causticity, %
<b>Set I</b>								
15	40	60	60	60	60	60	130.8	74.8
30	32	44	57	60	60	60	130.5	77.0
45	21	40	52	58	60	61	130.8	78.5
60	19	37	50	57	61	63	123.4	81.8
<b>Set II</b>								
15	26	44	54	54	54	54	127.7	76.3
30	20	36	50	58	58	58	128.3	78.2
45	20	34	47	55	60	60	130.8	81.0
60	11	23	32	41	48	52	129.0	82.6

between 121.1 to 125.2 gpl. However caustic soda, sodium sulphide and sodium carbonate varied widely. The reduction of sodium sulphate and the suspended matter in the green liquor has also varied much. This range of the green liquor constituents may be taken as the normal green liquor processed in the mill.

Table IV gives the purity (available lime content) and the chemical constituents of the bin lime used during the test period (12.11.70 to 22.11.70). It is seen that the available lime content varied from 65 to 71%, silica content varied from 5.7 to 10.0%. Similarly magnesium as magnesium oxide and oxides of iron and aluminium also varied much. The noncalcined portion in the lime as indicated by the calcium carbonate left in the lime also varied from 11.4% to 24.0%. It is thus seen that the lime used during the test period varied considerably in the chemical constituents and the calcination. However, it is of interest to note that the settling rate of the lime sludge improved considerably and remained high for all types of lime used and the green liquor processed when green liquor to lime ratio of 7.8:1 was maintained during the first 3 minutes. Here the settling in 30 minutes was in the range of 42 to 71%. The average settling is 56.5%. The same lime and the green liquor gave a poor settling lime sludge when the green liquor to lime ratio of 3.9:1 was used. The settling rate ranged between 25% and 36% and the average was 28.6%, a value 50% less when compared to 56.5% obtained

**TABLE VIII—Effect of Adding Varying Quantities of Lime on Causticity and Settling Rate of Lime Sludge.**

Lime added on the basis of conversion of Na <sub>2</sub> CO <sub>3</sub> %	Liquid: Lime ratio during first three minutes	Settling rate in minutes						White Liquor	
		5	10	15	20	25	30	T.T.A. as Na <sub>2</sub> O g/l	Causti- city, %
SET I									
85	9.7:1	32	55	65	69	71	71	128.0	80.0
95	8.6:1	31	54	65	68	70	70	127.7	80.4
105	7.8:1	19	31	50	51	61	63	123.4	81.8
120	6.8:1	11	22	32	40	47	51	128.0	84.1
SET II									
85	9.8:1	36	61	67	69	69	69	130.2	79.0
95	8.8:1	22	38	50	57	60	62	133.9	80.8
105	8:1	11	23	32	41	48	52	129.0	82.6
115	7:1	10	18	26	32	38	46	132.1	83.4

with a green liquor to lime ratio of 7.8:1.

It is thus clear from the above observations that the way the green liquor and lime are mixed in the slaker during slaking determines the settling rate characteristics of the sludge, the higher the liquid proportion during slaking, the faster is the settling rate.

In table V the settling rates were studied taking lime in different sizes, ranging from lumps,  $\frac{1}{4}$  to  $\frac{1}{2}$ " size, retained on 20 mesh and passing 20 mesh. For the same causticity all the lime samples gave a high settling rate (average 55%) when green liquor to lime ratio of 7.8:1 was used. The settling rate

was poor when green liquor to lime ratio of 3.9:1 was used and the average settling was 28%. It is thus clear that the form of lime used, whether in powder form or lump form has practically not affected the settling of sludge. The mode of addition of green liquor to the lime does effect the settling quality of sludge.

The effect of liquid to lime ratios during slaking on the settling characteristics of the causticized slurry were traced to differences in the particle size distribution of the sludge. When slaking was carried out at low liquid to lime ratios, the dimensions of the particles produced were finer compared to where the same operation was

carried out with increasing liquid to lime ratios. This is shown in the results given in Table VI. From the results given in Table VI, it will be seen that with decreasing liquid to lime ratios during slaking, the sludge produced contains more material passing through 300 mesh. Such a sludge will require much longer time (Fig. 1) for achieving maximum settling when compared to less time required for coarser particles. However, for practical considerations, it will not be desirable to work at very high liquid to lime ratios, as the intensity of the reaction will be reduced, and lime losses may go up because of the free lime content in mud. A liquid to lime ratio of 6:1 to 8:1 may be preferred for getting a good settling rate of the lime sludge.

The results in Table VII and Fig. 2 show that the relationship between reaction time (upto 60 minutes) and causticity obtained is almost linear. Further development of causticity may proceed in an asymptotic manner<sup>5</sup>, however this was not studied in the present case. The settling rate in 30 minutes was practically unaffected with increase in the causticity of white liquor.

The effect of adding varying amounts of lime was to decrease the settling rate of the lime sludge significantly for little increase in the causticity of white liquor (Fig. 3). This is in agreement with the observation of others wherein it is reported that a larger excess of lime will restrict the settling rate.

The effect of addition of starch

(0.2 gram/litre of green liquor) as shown in Fig. 4 was to further improve the settling rate. An observation of significance, as shown by the experiments was that, when the slaking was carried out at low liquid to lime ratio, the effectiveness of starch in improving the settling rate was poor. However, the same starch worked well at the green liquor to lime ratio of 7.8 : 1 during slaking.

#### Conclusions :

1) Green liquor to lime ratio during slaking is an important variable in determining the settling rate

of the lime sludge. A ratio of 6:1 to 8:1 may be preferred. However it is advisable to determine the optimum ratio for the individual conditions to achieve the best results.

2) Starch improves the settling rate of the lime sludge. However, to achieve the desired effect, it is important that the particle size distribution of the precipitated calcium carbonate should be such that it would flocculate.

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