

# Possibility of reburning lime sludge by reduction of silica in green liquor with two stage causticization

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## ABSTRACT

Disposal of solid wastes from paper industry is a major problem in India. As a measure for the abatement of Pollution, the Reburning of lime sludge generated in soda recovery plant is a must. This will also help to improve the mill economy. The problems during reburning of lime sludge are high alkali and silica contents. Alkali can be brought down by efficient washing and filtration process whereas Silica is a major problem for reburning. In the past, attempts have been made to reduce the silica in the black liquor, green liquor and sludge. In the present study an attempt has been made to bring down  $\text{SiO}_2$  level by two stage causticizing process without affecting Causticizing efficiency, alkali losses, total Causticizing time and total settling time. The laboratory experiments were conducted to study all these aspects and the plant trial was also taken on the same line successfully to study the development of the same process with minimum requirement of plant equipment.

Reburning of lime sludge in paper industry is crucial to its economy and reducing the pollution hazards. Most pulp and paper mills in the world having recovery process are burning lime sludge but in India very few paper mills based on Bamboo as its raw material is doing so. The reasons are that certain parameters are necessary for its reburning i.e. Silica should be less than 5.0% and  $\text{Na}_2\text{O}$  less than 0.3%. In India lime sludge generated from paper industry contains high silica because of the raw material used which is bamboo having  $\text{SiO}_2$  of 0.5 to 1.5% and lime quality ( $\text{SiO}_2$  in lime varies from 3.0 to 6.0%) in general.

In the process of lime sludge calcination where time period is more in the rotary lime kiln, higher amounts of Silica and alkali lead to the formation of clinkers and rings in the rotary kiln and make it difficult to reburn the sludge. The silicates having low melting point hinders the calcination of calcium carbonate and quality of lime produced is also poor. Such lime with higher percentage of silica also affects the settling rate of sludge in the causticizing process with higher alkali loss.

The production of quick lime ( $\text{CaO}$ ) from lime sludge is the best way to combat the pollution as it can be reused in the mill itself.

The main problems in reburning the lime sludge are impurities like silica, alkali and superfine granulometry of lime sludge.

In the process of calcination, the lime sludge is subjected to the thermodynamic changes (8). The differential thermal analysis (DTA) studies on the lime sludge sample indicate the beginning of endothermic reaction at  $700^\circ\text{C}$ , which obtains its peak at  $804^\circ\text{C}$  and reaches its completion at  $860^\circ\text{C}$ . However, final temperature has been taken as  $900^\circ\text{C}$ . The burning of lime sludge will be possible by the fast reaction rate of calcination which is controlled by efficient extraction of  $\text{CO}_2$ . The alkalis which volatilise between  $700^\circ\text{C}$  to  $800^\circ\text{C}$  are trapped to avoid ring formation. The high silica content will cause problem.

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To solve this problem, silica removal from the green liquor in the stepwise causticization results in lesser amount of silica in the final sludge which is within the limit for reburning.

The green liquor from bamboo based raw material contains  $\text{SiO}_2$  (5-15 gpl.) and it should be brought to 2.0 gpl  $\text{SiO}_2$ . In the process of causticizing,  $\text{Na}_2\text{CO}_3$ ,  $\text{SiO}_2$  and  $\text{Ca}(\text{OH})_2$  are the reactants (1). The thermal analysis of these reactions indicate the formation of calcium Silicate of unimolar composition. The rate of formation of Calcium Silicate is faster in the initial stage than Calcium Carbonate where  $\text{NaOH}$  % is less. The rate of formation of Calcium Silicate slows down with increasing percentage of  $\text{NaOH}$  in green liquor. The 75% of  $\text{SiO}_2$  is removed by 30% of lime added out of total lime requirement for Causticization (6). In this study, an attempt has been made to study and understand (a) the quality of lime that is to be used in both the stages, (b) the time and temperature during Causticization, (c) settling properties of the Causticized lime muds and (d) the Causticizing efficiency of the final liquor.

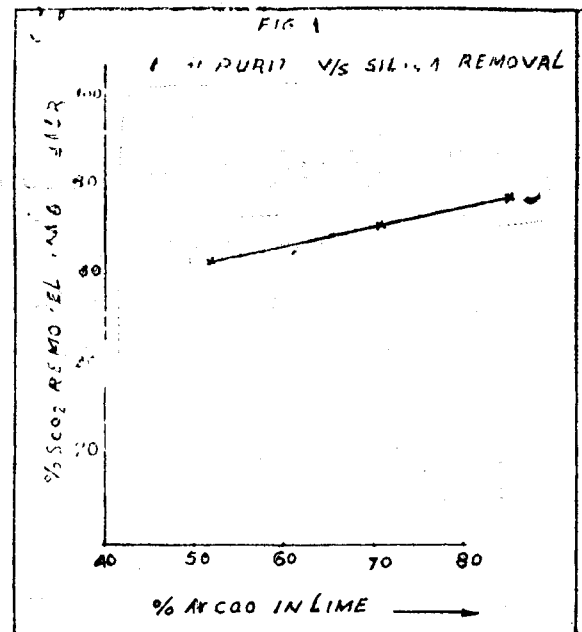
**(a) Effect of Quality of lime :**

The quality of lime affects the removal of  $\text{SiO}_2$  from green liquor in the first Causticization stage. The temperature and time maintained during experiments were  $90^\circ\text{C}$  and 30 minutes respectively and the quantity of lime was used 35% of the total lime required for the green liquor.

Table—I shows that the rate of reaction depends on the amount of  $\text{SiO}_2$  and  $\text{Ca}(\text{OH})_2$  in lime. For lime containing more  $\text{SiO}_2$ , desilication will be less and higher % of  $\text{Ca}(\text{OH})_2$  will help. Removal of  $\text{SiO}_2$  from green liquor is by precipitation : as  $\text{CaSiO}_3$  which is formed by the reaction of  $\text{Ca}(\text{OH})_2$  with  $\text{SiO}_2$  present in the green liquor.

TABLE—I  
Effect of Lime quality variation during first Causticization stage

LIME ANALYSIS		$\text{SiO}_2$ in Overflow liquor (G/L)	% Silica Removal from G/L.
$\text{SiO}_2$ %	CaO (avg.)		
2.2	85.0	1.20	78.2
4.9	71.0	1.54	72.0
7.6	62.0	1.90	65.5
4.3	48.0	2.00	63.5



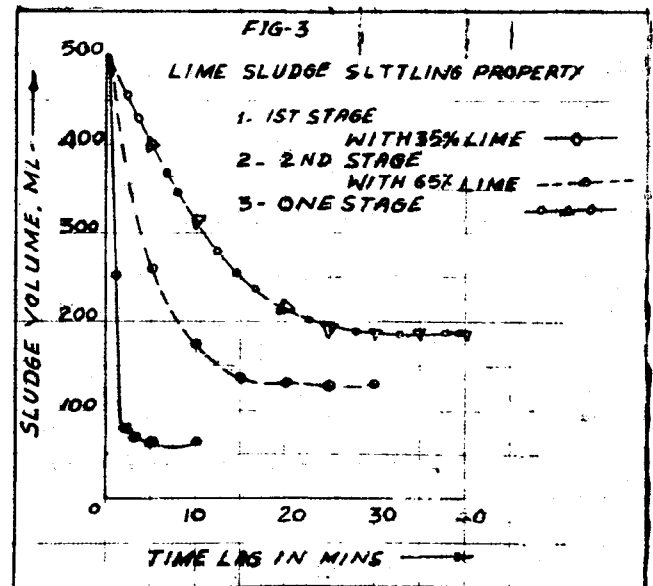
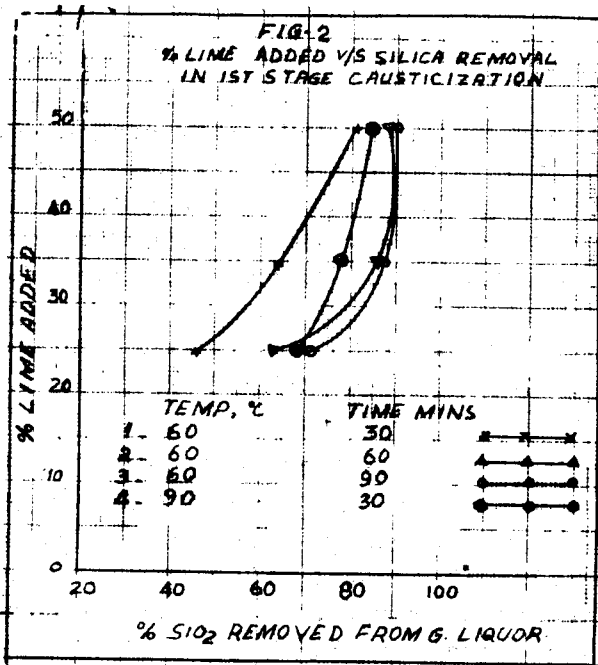
**(b) Effect of Time and Temperature :**

Experiments were conducted to find out the effect of temperature as well as reaction time in Silica removal from green liquor.

It can be seen that desilication is faster with higher percentage of lime taken, and with longer reaction time. At a temperature of  $90^\circ\text{C}$  with same quantity of lime and time, desilication is faster than at  $60^\circ\text{C}$ . Hence for first stage desilication the conditions of 25-30% of total lime at  $90^\circ\text{C}$  and 30 minutes are suitable. In the second stage, time will be 90 minutes keeping the total Causticizing time constant both in single as well as in two stages.

**TABLE—II**  
**Effect of Lime %, Reaction Time and Temperature during**  
**Ist Causticization stage**

% Lime	Reaction Time (Min.)	Reaction Temp. °C	SiO <sub>2</sub> in G/L. gpl.	SiO <sub>2</sub> in Lime mud	% SiO <sub>2</sub> Removal from G/L
25	30	60	2.42	13.1	46.1
25	60	60	1.74	15.4	62.8
25	90	60	1.34	15.3	71.4
25	30	90	1.50	14.3	68.0
35	30	60	1.76	10.1	62.4
35	60	60	0.68	12.8	85.5
35	90	60	0.62	12.4	86.7
35	30	90	1.08	11.0	76.9
50	30	60	0.90	10.0	80.8
50	60	60	0.62	9.7	86.7
50	90	60	0.52	9.8	88.9
50	30	90	0.74	9.6	84.2



TABLE—III

Settling Rate of Lime Sludge in case same quantity of Lime added in single stage and two stage Causticization

Time Lag (In min.)	SETTLING RATE OF LIME SLUDGE VOLUME OCCUPIED BY LIME SLUDGE, ml.		
	Ist stage with 35% Lime	2nd stage with rest 65% Lime	One stage with 100% Lime
0	500	500	500
1	250	455	485
2	80	400	465
3	70	340	440
4	68	300	420
5	67	260	400
7	67	215	360
10	67	175	315
12	—	145	290
15	—	135	255
20	—	132	215
25	—	131	195
30	—	131	180
35	—	131	180
40	—	—	180
45	—	—	180

(c) Settling properties of Causticized sludge :

The settling properties of lime sludge at different stages were also studied and compared with single stage Causticization as reported in Table-III and Fig. 3

The settling rate of Causticized sludge in first stage is about six times faster as compared to single stage Causticized sludge. The settling rate of Causticized sludge obtained in 2nd. stage is about one and a half times faster than single stage Causticized sludge. Total time of settling is same in two stages and single stage Causticization.

(b) Causticizing Efficiency :

The Causticizing efficiency in two stage Causticization and single stage Causticization are found to be more or less same as reported in Table - IV.

Plant Trial :

A plant trial was conducted by using 15 to 27% lime in the first stage out of total lime requirement and the lime sludge was discarded after washing to recover the alkali. The remaining quantity of lime was added to clarified liquor obtained from first stage Causticization. The reduction of silica content in clarified liquor from first stage was determined and the results obtained are reported in Table - V.

To minimize the  $\text{SiO}_2\%$  in sludge to the limit of reburning possibility, the Silica in the green liquor should be less than 2 gpl. This is possible by using lime 25% to 30% of the total lime in first stage Causticization by using more quantity of lime, desilication is also more in green liquor with higher amount of Silica, the sludge will also contain more silica. On average, 65.0% silica could be removed from green

**TABLE—IV**  
**Causticized Liquor Analysis**

Sl. No.	Tests	Ist Stage	2nd Stage	Single Stage
1.	NaOH (G/L)	44.00	81.60	84.60
2.	Na <sub>2</sub> S „	24.96	24.96	24.96
3.	Na <sub>2</sub> CO <sub>3</sub> „	63.60	13.78	12.72
4.	Na <sub>2</sub> O „	91.76	91.14	92.34
5.	SiO <sub>2</sub> „	2.02	0.20	0.21
6.	Causticizing Efficiency %	—	88.70	89.80
7.	SiO <sub>2</sub> in Lime Mud %	13.20	6.10	8.00

**TABLE—V**  
**Plant Trial Data During Ist Stage Causticization**

Table Lime %	Feeder Avg. CaO %	Lime Analysis SiO <sub>2</sub> %	SiO <sub>2</sub> in Feed G/L (g/lit)	SiO <sub>2</sub> in G/L after Ist stage (g/lit)	SiO <sub>2</sub> % in mud	SiO <sub>2</sub> % removed after Ist stage
25.0	64.8	5.4	5.20	1.60	10.7	69.0
14.8	46.0	5.6	5.10	3.10	12.5	40.0
20.4	61.0	5.4	4.94	1.96	13.7	60.0
23.3	66.2	5.3	4.96	1.70	13.8	66.0
27.2	62.0	5.4	6.02	1.42	12.0	76.5
26.6	64.0	5.2	5.54	1.38	13.0	73.0
24.1	65.2	5.6	5.62	1.74	12.8	69.0
18.6	61.0	5.6	5.86	2.44	12.0	58.4
19.8	64.0	5.2	5.64	2.68	11.9	53.0
26.3	67.0	5.2	5.70	1.62	10.0	71.6
20.9	60.0	6.1	5.68	2.12	13.6	62.7

liquor during the plant trial with the addition of 22.5% of total lime requirement in first stage Causticization.

**Conclusions :**

1) Silica content in green liquor can be brought to 2 gpl. by adding 25% lime in the first stage Causticization with 90°C temperature and 30 minutes detention time without affecting Causticizing efficiency in the final stage. First stage sludge containing about 14%

Silica can be used for land filling Cement Industry, to control pH of agricultural land, to spread on the land where the effluent is being treated by using top soil as living filter etc. The second stage lime sludge can be used for reburning without any major problem.

2) Quality of lime affects the efficiency of SiO<sub>2</sub> removal from green liquor. Higher percentage of CaO and less SiO<sub>2</sub> content in lime improves SiO<sub>2</sub> removal from green liquor.

3) The settling rate of sludge in first stage is very fast. As a result, the size of clarifier for first stage lime liquor will be small. The size of second stage clarifier for lime liquor will be less than single stage white liquor clarifier.

To get better quality lime sludge after the second stage, one can use better quality of lime which contains more than 70% avg. CaO and less SiO<sub>2</sub> contents and lower grade lime with avg. CaO 60-70% in the first stage of green liquor Causticization.

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