Conservation of Lime by Desilication of Kraft Green Liquor

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Carbonation of green liquor at 60-80°C with flue gas to pH=9.5 will remove 80-90% of silica in the liquor. Causticization of desilicated green liquor will give a lime sludge (1.5—2.5% SiO_2) suitable for reburning in a kiln. Reuse of reburned lime will reduce fresh lime requirement by 90-95% compared to present practice of once through use of lime. Preliminary design and cost estimates for a proposed green liquor desilication process favour further work on a pilot plant scale in a paper mill.

Silica enters the chemical recovery system in a paper mill through bamboo (1.5-2.5% SiO_2 o.d.) and lime (5-15% SiO_2). Silica will be present as sodium silicate in black liqour and green liquor and as calcium silicate in lime mud. In bamboo based paper mills the general range of silica concentration will be 0.5–2.5, 0.5–12.0, 7.0–43.0 and 9.0–14.0 g SiO_2/l for white liquor, weak black liquor, concentrated black liquor and green liquor respectively; concentration of silica in lime sludge will vary over the range 5–15%. The presence of high concentration of silica in lime sludge poses problems during reburning in a kiln for lime recovery. Silicate would melt at the usual calcination temperature levels in the kiln (1100-1300°C) and tend to seal the pores of the lime pellet by forming a glasslike coating enclosing a pellet with an overburned outer layer and an inner core of incompletely calcined lime. Partially calcined lime pellets from silica rich lime sludge will have less available calcium oxide and also give slow and incompletc slaking. Paper mills based on bamboo do not have lime reburning facilities because of the above problems. Instead lime is used in once-through operation. Fresh lime stone is calcined in a country kiln or rotary kiln and used for causticization. The resulting lime sludge rich in silica (5–15% SiO_2) is disposed off. Disposal of lime sludge (0.3–0.7 ton/ton of pulp) is a major and costly solid waste disposal problem at many plant sites.

Silicate in black liquor also deposits as a hard scale in digester walls and evaporator tubes and leads to beehive fomation in recovery boiler. Sodium silicate in green liquor decreases causticizing efficiency. Thus desilication of black liquor or green liquor would reduce the silica problem and also permit satisfactory calcination of lime and (1.5 —2.5% SiO_2) for reuse. Reburning of lime would reduce fresh lime requirement by 90-95%. Sodium silicate in alkaline process liquors can be precipitated by acidification as free silica and as silicate by calcium oxide, magnesium sulfate and aluminum sulfate. This investigation deals with desilication of green liquor by carbonation for tackling the silica problem at the green liquor stage.

Proposed Green Liquor Desilication Process:

Green liquor contains sodium carbonate, sodium sulfide, sodium hydroxide, sodium sulfate and sodium silicate. Silica can be precipitated from green liquor by carbonation with flue gases containing carbon dioxide from either the recovery boiler or lime kiln. During carbonation, the following principal reactions take place, equation (1,2,3).

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$$CO_2 + OH^- \rightleftharpoons HCO_3^- \quad (1)$$

$$CO_2 + CO_3^{=} + H_2O \rightleftharpoons 2HCO_3^- \quad (2)$$

$$SiO_3^{=} + 2HCO_3^- \rightleftharpoons 2CO_3^{=} + Sio_2 + H_2O \quad (3)$$

$$HS^- + HCO_3^- \rightleftharpoons H_2S + CO_3^{=} \quad (4)$$

Absorption of carbon dioxide by green liquor followed by reactions (1) and (2) decrease the pH of the liquor. Precipitation of silica takes place according to reaction (3). Carbon dioxide is released from carbonated green liquor by raising the liquor temperature to favour the reversal of reaction (2). Experimental studies using commercial and laboratory green liquor samples have shown that 80–90% of silica in green liquor can be removed by carbonation at 60-80°C to pH=9.5 with subsequent settling and filtration. The pH of carbonated green liquor should not decrease below 9.5; since reaction (4) becomes predominant below pH=9.5 and leads to sulfur loss from system as hydrogen sulfide. Temperature determines the nature of the silica precipitate which governs settling and filtration rates; silica separates as a gel below 44–46°C and as easily filtrable granules above 50°C during carbonation.

The results of laboratory experiments dealing with desilication efficiency and settling and filtration characteristics of the silica precipitate are incorporated in a proposed process[1]. Figure 1 gives a plausible flow diagram of the proposed process. The following additional units are required for the desilication of green liquor with flue gas carbonation.

1. Turbulent contact absorber for carbonation of green liquor by flue gas (absorber consists of hollow poly-propylene spheres maintained in a fluidized state between retaining grids for handling slurries).
2. Thickner for increasing the slurry concentration in carbonated green liquor.
3. Filter for the separation of silica precipitate.
4. Steam stripping column for decomposing bicarbonate in carbonated green liquor for satisfactory causticization, and
5. Kiln for reburning of lime mud.

Special Features of Proposed Process :

A summary of flow rates and compositions of themajor streams in the proposed desilication process is given in Tabie 1. Material balance for silica in various pulp mill streams is given in Table 2 for a hypothetical 250 ton per day bamboo kraft pulp mill along with the balance for the proposed desilication process.

The concentration of silica in green liquor decreases from 7.25 to 0.82 g SiO_2/l with the proposed desilication process which results in a lime sludge containning 1.2% SiO_2 compared to 5.7% SiO_2 in the conventional process. The concentration of silica in white liquor also decreases from 2.9 g SiO_2/l to 0.15 g SiO_2/l and this in turn gives a marginal decrease in the silica concentration of black liquor and green liquor streams over the values in conventional recovery plant.

A summary of design specifications and preliminary cost estimates for the units in the proposed desilication process is given in Table 3. The total fixed capital investment for the process will be Rs. 45.0 lakhs. Operating costs and saving from the modified process are given below :

Operating cost (daily basis) :

Utility and Power	
Fuel oil 22 t @ Rs. 1000/t	Rs. 22,000
Makeup lime 6 t @ Rs. 300/t	Rs. 1,800
Steam 10 t @ Rs. 60/t	Rs. 600
Power, 3000 kWh @ Rs. 0.2/kWh	Rs. 600
Labour, supervision and maintenance	Rs. 650
Depreciation, taxes and insurance, etc.	Rs. 1,380
Total operating cost	Rs. 27,030

Savings with desilication
=(Fresh lime consumption with no desilication+

Table 2—Material Balance for Silica In A 250 Ton Per Day Bamboo Kraft Pulp Mill*

Input			Output		
	Recovery Process**			Recovery process	
Source	Conventional	Modified	Source	Conventional	Modified
Bamboo chips (2.1%	11350	113 0	Scales:		
White liquor	3920	172	Digester	168	168
			Blow tank and		
Makeup salt cake	160	160	Storage tanks	504	410
			Evaporator	2500	2000
Fresh lime (6 5%	7330	450		450	350
			Lime kiln	—	202
Reburned lime (1.8%)	—	2040	Pulp	1590	1290
			Black liquor losses		300
			Slaker grits	3400	1000
			White liquor	3920	172
			Lime mud	10228	—
			Reburned lime	—	2040
			Silica byproduct	—	6240
Total	22760	14172		22760	14172

*kg SiO_2/day

** Conventional recovery process disposes sludge Modified recovery process removes 85% of silica in green liquor by carbonation and lime sludge is calcined and reused.

Table 3
Design Specifications And Cost of Units In Proposed Desilication Process

Unit Specifications	Cost, Rs. (Lakhs)
1. Turbulent contact absorber Diameter-0 9 m Number of stages—4 Total height—6.4 m Packing—35 mm hollow polypropylene spheres	4.0
2. Thickener* Diameter—11.5 m Height— 3.0 m	—
3. Steam Stripper Diameter—1.0 m Height —15.0 m Packing—50 mm polypropylene pall rings	5.0
4. Filter Diameter —1.8 m Length —1.2 m Filter area—7.0 m	2.0
5. Rotary kiln Diameter—2.75 m	16.0
6. Auxiliary facilities, pumps, pipelines, insulation, instrumentation and construction cost	18.0
Total fixed capital investment	45.0

*Green liquor clarifier can be used as a thickner and green liquor sent from smelt dissolver to carbonator.

silica byproduct+lime mud disposal cost—operating cost for desilication)
=(113×300 + 6.2×200 + 290×25—27030)
=Rs. 15360

(Fresh lime=300/ton, silica by-product=200/ton, Cost of lime mud disposal=Rs. 25/ton)

Saving per ton of pulp=Rs. 60

Desilication of green liquor by carbonation at 80°C to pH=9.5 will remove 80-85% of silica in liquor and improve causticization efficiency and white liquor clarity. The concentration of silica in lime mud will decrease to 1-2% SiO_2 and will allow satisfactory calcination in a rotary kiln. Reuse of reburned lime will reduce fresh lime requirement by 90-95% compared to present practice. Preliminary design and cost analyses favour further development work on pilot plant scale.

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Reference

1. Idrees, M., 'Desilication of Kraft Green Liquor by Carbonation', M. Tech. Thesis, Indian Institute of Technology, Kanpur. (April, 1975).

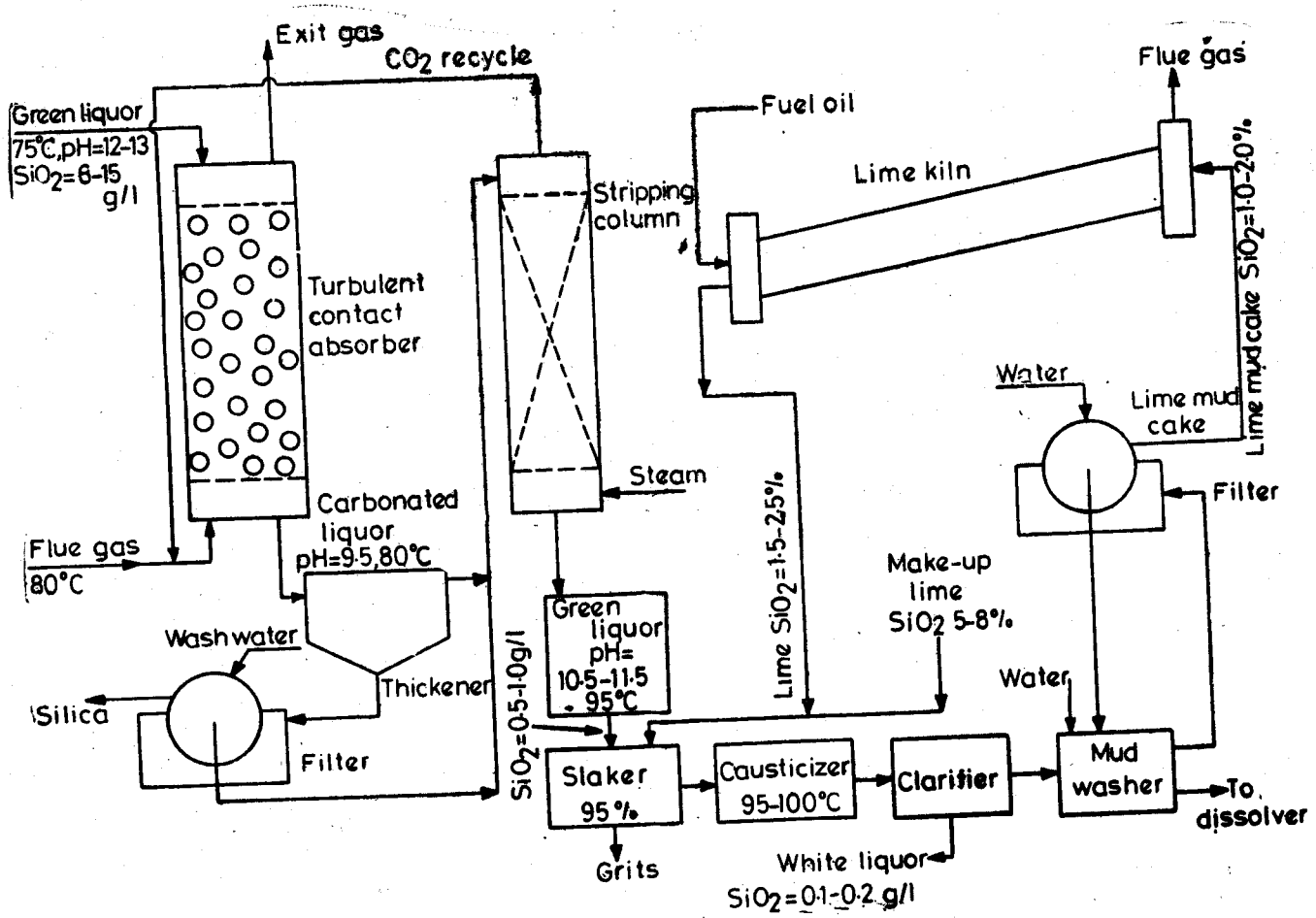

Fig. 1 Proposed process for silica removal from green liquor.

TABLE 1

Summary of Liquor Compositions And Flow Rates In The Modified Chemical Recovery Process

Sl. No.	Description	Flow rate h^{-1}				Composition, g/l							
		Volume m^3	Solids kg	Water kg.	Total kg.	NaOH	NaHS	Na_2S	Na_2Co_3	$NaHCO_3$	Na_2SO_4	Na_2SiO_3	SiO_2
1.	Green liquor	58.15	8445	55450	63895	13.6	—	19.4	99.2	—	1.80	11.40	5.60
2.	Carbonated green liquor	59.6	10480	55000	65480	—	12.63	1.9	94.5	64.4	1.80	1.67	0.78
3.	Silica	—	260	166	426	—	—	—	—	—	—	—	—
4.	Carbonated green liquor to stripper	60.7	10480	56150	66630	—	12.43	1.8	92.8	63.3	1.75	1.64	0.81
5.	Stripped green liquor	59.7	9045	56500	65545	—	12 62	1.9	134.8	—	1.75	1.67	0.82
6.	White liquor	47.7	5870	45600	51470	80.4	—	19.6	21.2	—	1.75	0.31	0.15