Two Stage Causticizing At TNPL For Effective Limekiln Operation And To Reduce Silica Build-Up In Recovery Cycle

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ABSTRACT

Rotary Lime kiln is an integral part of modern Soda Recovery plant in large scale pulp and paper mills. When the lime sludge is recycled, the non process element built up in the lime sludge will increase. The Silica is one of the major non process elements in the lime sludge which adversely affect the operation of limekiln. The Silica buildup in the recovery cycle is more predominant in the mills using agricultural residue like Bagasse and Wheat Straw etc. Two stage causticizing is an apt method to control the Silica level in the system for optimizing the operation of Rotary Limekiln. TNPL is producing 500 TPD of bleached Bagasse pulp and 300 TPD of bleached hardwood pulp. Two stage causticizing has been operated successfully for more than a decade in the mill. In this paper, operation of two stage causticizing system in TNPL and its benefits are discussed along with material balance of causticizing plant and Silica.

Introduction

Chemical recovery operations are the heart of the modern pulp and paper making process. Pulp mill operation totally depends upon the chemical recovery plant. Its availability and efficient operation are of utmost importance to recover energy and to meet the environmental standards. In India, most of the paper mills are wood based and many mills also use agricultural residues as a primary source of raw material. TNPL is the World's largest manufacturer of paper using Bagasse as a primary and predominant raw material which makes TNPL unique in terms of the technology used. The Black Liquor generated at TNPL is non-wood (Bagasse – agro based) type, which poses several challenges in terms of the recovery plant performance.

Table - 1 Black Liquor Characteristics of Bagasse and Hardwood

Parameters	Unit	Bagasse	Hardwood
Na	%	18.2	17.8
K	%	1.65	1.5
Cl	%	2	1.7
C	%	31.6	33.5
S	%	2.2	1.9
SiO2	%	1.6	0.22
Fe2O3	%	0.06	0.04
Fibre	PPM	150	50

The composition and characteristics of non-wood (Bagasse) based black liquor generated is different from that of normal hardwood black liquor (Table - 1). Presence of high amount of non-process elements and poor thermal & rheological properties of these non-wood black liquors limit both energy & chemical recovery (1 & 2). The chemical pulping of agricultural residues poses no problem. However, major difficulty arises in recovery of heat and chemicals from cooking chemical at every stage of recovery due to presence of silica (3). Robert and Hurter (4) stated that Silica in non-wood fibers enters the black liquor and causes many problems in conventional chemical recovery systems. Also, non-wood black liquors have viscosity problems that make it difficult to achieve high solids content. Geoff Covey et al (4) reviewed the bagasse pulping potential in Australia, and reported that Silica present in the Bagasse is a major obstacle for chemical recovery. They discussed several Silica removal methods and concluded that there is no commercially proven method to remove Silica. Purging of Silica along with lime sludge could be carried out, but, leads to generation of solid waste which would pose a disposal problem. The authors also said that compared to wood based black liquor, Bagasse based black liquor is very viscous with high Silica content and lower heat value. Its use is limited to small scale mills with low pressure boilers or mills that follow the soda process and not the Kraft process.

Concept of Two stage causticizing

Function of the recausticising plant is to convert the green liquor generated from recovery boiler to white liquor i.e. conversion of Sodium Carbonate to Sodium Hydroxide to produce white liquor and it is reused in the cooking process in digester. The function of the primary stage slaking is to reduce the amount of Silica present in the green liquor and to remove separately the high Silica Lime mud. The lime mud from second stage slaking with less silica is used in Limekiln for Burnt lime production.

In conventional causticizing, burnt lime is added with green liquor to convert Sodium Carbonate to Sodium Hydroxide.

$$Na_2CO_3 + CaO + H_2O = 2NaOH + CaSiO_3$$

However, this depends on the Silica content in green liquor. The lime added will first react with Silica present in raw green liquor to form Sodium Silicate.

$$Na_2SiO_3 + CaO + H_2O = 2NaOH + CaSiO_3$$

The reaction of burnt lime with Sodium Silicate is faster than the reaction with Sodium Carbonate in raw green liquor and thus Calcium Silicate would be produced first and precipitated. The two stage causticizing concept exploits the faster reaction of Burnt lime with Sodium Silicate than Sodium Carbonate which will remove considerable quantity of silica from the green liquor.

Experience of TNPL with bagasse based BLS

Composition and characteristics of the Bagasse based black liquor generated at TNPL is different from that of the normal hardwood black liquor generated in other paper mills. TNPL is operating two streets of FFFF evaporator and a high pressure 1300 TPD Recovery Boilers firing the black liquor solids at 70% concentration. Scaling due to silica is a major problem in the operation of FFFF Evaporators. Though on line washing is done in high concentration effects, mechanical cleaning of evaporator tubes is carried out periodically to remove the silica scales.

High concentration of Silica present in the recovery cycle causes problem in the operation of limekiln due to increase in lime sludge moisture which leads to increase in oil consumption and also affects the purity of burnt lime.

The recausticizing plant supplied by Hindustan Dorr Oliver (HDO) was installed in 1985 during commissioning of the mill and with the White Liquor (WL) production capacity of 800 M^3/day for the pulping capacity of 200 TPD Bagasse pulp & 80 TPD of Hardwood pulp. In 1995 pulping capacity of the mill was increased to 400 TPD of Bagasse & 100 TPD of Hardwood pulp. The Causticizing plant was augmented to 2000 M^3 of WL production with two stage Causticizing. Rotary lime kiln - 1 to 170 TPD supplied by Fuller-KCP was installed during the same period. During mill Development plan (MDP) in 2008 the hardwood pulp production was increased to 300 TPD and chemical Bagasse pulp production was increased to 500 TPD. The Causticizing plant was augmented with Dorr Oliver Eimo Equipment to 3600 M^3 WL production per day. Second Lime Kiln of 170 TPD supplied by ENMAS ANDRITZ was installed to meet the requirement of MDP and operated at full capacity with two stage causticizing system.

As stated earlier, Silica build up in the recovery cycle is one of the major problems for the mills using agricultural residue. Effective removal of Silica in green liquor can be carried out by adapting two stage causticizing (5, 6). Our experience and benefits of operating two stage causticizing are presented in this paper.

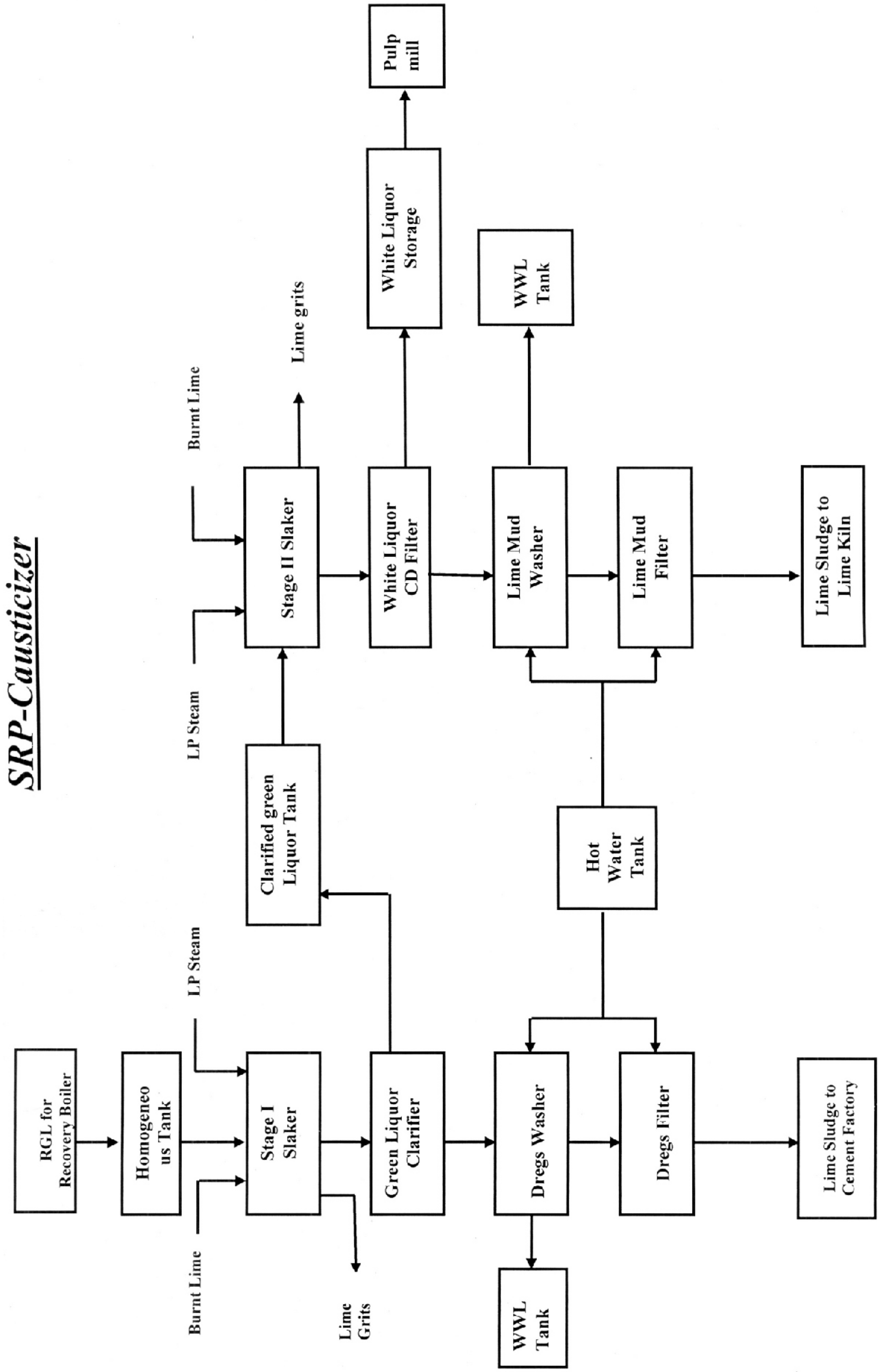
Process description of system

The raw green liquor from recovery boiler is received in the homogeneous tank. The homogeneous tank is provided with agitator to even-out concentration variation of green liquor received from recovery boiler. The green liquor is then heated in a shell and tube heat exchanger to increase the temperature of green liquor to 93°C, using steam as the heating medium and fed into two stationary slakers. Burnt lime is fed to the slaker through weigh belt feeder. About 40% of total lime required is used in first stage causticizing for maximum removal of Silica from raw green liquor. The partially slaked green liquor is passed through first stage causticizers and then fed to green liquor clarifiers. The clarified green liquor is taken to clarified green liquor storage tank (Figure - 1)

The lime mud from green liquor clarifier is washed through three stage washing and then filtered out in Dregs filler. The first stage lime mud at 40% moisture is disposed at present. In near future the lime mud will be pumped to TNPL cement plant. The green liquor from clarified green liquor storage tank is taken through on line heater for raising the green liquor temperature to 94°C then fed to stationary slaker. The balance 60% of burnt lime required from total lime is fed through weigh belt feeder. The caustisized slurry is passed through four numbers of causticizers and filtered in White Liquor Clari Disc (WLCD) filter. The white liquor produced is stored in WL storage tanks.

The lime sludge generated from second stage causticizing contains less Silica. The lime mud from WLCD filter is washed in a single stage lime mud washing system consisting of two lime mud washers in parallel operation. The lime mud from lime mud washer

Figure - 1
Process Fow Diagram Of Caustizing Plant In TNPL



is filtered in the lime mud filters. The filtered lime mud cake, at a moisture level of 45% is burnt in Lime Kiln to produce burnt lime.

Results and Discussion

The properties of both hardwood and bagasse black liquor is presented in the Table-1 and it clearly indicates that bagasse black liquor contains more Silica than the hardwood. Generally, Silica present in the non wood fiber is classified as internal and external. The internal or inherent Silica which form part of the plant structure will vary depending on soil conditions, climate and farming practices (4, 5). Whereas, the external Silica enter in through raw material during harvesting, handling, and storage. During pulping, the Silica is dissolved and enters recovery cycle through black liquor. High Silica content in the black liquor results in various problems in the chemical recovery loop, such as, increased black liquor viscosity at high solids concentrations, hard scales in the evaporator and hard deposits at various points in the recovery boiler, lower heat of combustion, formation of colloidal gels in the recausticizing system that lower the setting rate, reduced lime mud dewatering, formation of glassy material in lime kilns and reduced slaking rate (4, 5). Therefore, it is necessary to purge the Silica from the recovery loop to reduce the Silica buildup more specifically in the non wood fiber plants. By practicing two stage causticizing, a portion of Silica is purged through the first stage lime mud. However, we need to find out environmentally friendly method to dispose first stage lime mud to avoid the solid waste build-up (6).

The composition of Raw Green Liquor, Clarified Green Liquor and White Liquor from the two stage causticizing operations was analyzed and the results are presented in the Table - 2. The Silica content is found to be 4.1 gpl 2.0 gpl and 0.55 gpl for Raw Green Liquor, Clarified Green Liquor and White Liquor respectively. Similarly, composition of 1^{st} & 2^{nd} stage lime sludge and burnt lime was also analyzed and the results are presented in the Table - 3.

Table - 2
Characteristics of Liquor from Chemical Recovery Operation

S. No	Parameters	UOM	Raw Green Liquor	Clarified Green Liquor	White Liquor
1	TTA as Na_2O	gpl	106.02	105.4	101.68
2	NaOH as Na_2O	gpl	13.02	35.3	67.58
3	Na_2S as Na_2O	gpl	18.6	18.6	17.36
4	TTA as Na_2O	gpl	31.62	53.9	84.94
5	Na_2CO_3 as Na_2O	gpl	74.4	51.5	16.74
6	TSS	PPm	390	150	40
7	Silica as SiO_2	gpl	4.1	2.0	0.54
8	Conversion Efficiency	%	NA	NA	80.01
9	Sulphidity	%	NA	NA	20.44

Table - 3
Characteristics of Lime Sludge and Burnt Lime

S. No	Parameters	UOM	1^{st} Stage Lime Sludge	2^{nd} Stage Lime Sludge	Burnt Lime
1	Moisture	%	39.6	44.73	NA
2	Loss on ignition	%	38.3	39.5	0.64
3	Acid insolubles	%	7.17	5.2	4.6
4	Silica as SiO_2	%	6.98	5.0	4.5
5	Mixed oxides ($R2O_3$)	%	0.82	0.81	1.23
6	Total calcium as CaO	%	88.0	89.7	90.8
7	Magnesium as MgO	%	2.01	1.68	1.29
8	Available CaO	%	0.92	1.09	77.2
9	Sodium as Na_2O	%	0.88	1.19	1.34

Table - 4
Quantitative Material Balance of Causticizing Operation at TNPL

S. No	Parameters	UOM	Quantity
1	TTA production as Na_2O	tpd	300
2	Sulphidity	%	20.44
3	NaOH production as Na_2O	tpd	239
4	NaOH production as NaOH	tpd	308
5	Theoretical lime requirement at 100% CaO	tpd	216
6	Theoretical lime requirement at 75% CaO	tpd	287
7	Excess lime required	%	5.0
8	Actual lime required at 75% CaO	tpd	302
9	WL total active alkali	gpl	84.94
10	WL production	cu.m/day	3532
11	WL production as TTA	tpd	359
12	GL to WL conversion	%	85
13	GL production as TTA	tpd	422
14	GL concentration as TTA	gpl	106
15	GL production as TTA	cu.m/day	3985
16	Lime mud production as 100% $CaCO_3$	tpd	385
17	Inerts in the LIme	tpd	86
18	Lime grits generation	%	12.0
		tpd	10
19	Inerts carried over lime mud	tpd	76
20	Lime mud generated on OD basis	tpd	461
21	Lime used in the first stage	%	40.0
		tpd	121
22	Lime mud purged in the first stage	tpd	184
23	Lime used in second stage	%	60
		tpd	181
24	Second stage lime mud for kiln	tpd	277
25	Lime consumed MOL preparation	tpd	10
26	Lime production from kiln	tpd	312
27	Lime from Lime sludge	tpd	180
28	Lime from Lime stone	tpd	132
29	Lime stone makeup	tpd	213

Table - 5
Computation of Quantitative Silica Balance at TNPL Recovery Operation

S. No	Parameters	UOM	Quantity
1	RGL processed	cu.m/day	3985
2	Silica in RGL	gpl	4.1
3	**Silica input through RGL**	**tpd**	**16.34**
4	Lime used in the first stage	tpd	121
5	Silica in burnt lime	%	4.5
6	Silica input through burnt lime used in first stage	tpd	5.43
7	Lime mud purged in the first stage	tpd	184
8	Silica in first stage lime mud	%	6.98
9	***Silica purged through first stage***	***tpd***	**12.87**
10	Silica in clarified green liquor	gpl	2.0
11	Silica in clarified green liquor to second stage	tpd	8.0
12	Lime used in second stage	tpd	181
13	Silica input through burnt lime used in second stage	tpd	8.15
14	Second stage lime mud for Kiln	tpd	277
15	Silica in second stage mud	%	5.0
16	Silica output through second stage mud	tpd	13.83
17	WL production	cu.m/day	3532
18	Silica in WL	gpl	0.54
19	***Silica output through WL***	***tpd***	**1.91**
20	***Silica output through WWL***	***tpd***	**0.34**
21	Lime grits generation	tpd	10
22	Silica in lime grits	%	9.70
23	***Silica output through lime grits***	***tpd***	**1.00**
24	Lime consumed MOL preparation	tpd	10
25	***Silica purged through MOL***	***tpd***	**0.45**
26	Lime stone makeup	tpd	213
27	Silica in lime stone	%	0.22
28	***Silica input through lime stone***	***tpd***	**0.47**
29	Lime production from kiln	tpd	312
30	Silica in Burnt lime produced	tpd	14.03
31	**Silica input (S.No. 3+27)**	**tpd**	**16.81**
32	***Silica output (S.No. 9+19+21+24+30)***	***tpd***	**16.57**

Desilication efficiency

1	Silica in RGL	tpd	16.34
2	Silica in RGL	tpd	7.97
3	Silica in WL	tpd	1.91
4	Silica removed from RGL to CGL	tpd	8.37
5	Silica removed from CGL to Wl	tpd	6.06
6	Total silica removed from RGL to WL	tpd	14.43
7	Efficiency of silica removal in first stage	%	58.0
8	Efficiency of silica removal in second stage	%	42.0
9	Silica in first stage mud	%	6.98
10	Silica in second stage mud	%	5.0

The Silica content is found to be 6.98%, 5.0% and 4.5% for 1^{st} & 2^{nd} stage lime sludge and burnt lime respectively. The quantitative material balance of causticizer operations at TNPL is presented in Table - 4. From the Table it clear that about 184 TPD lime mud generated from the first stage is disposed off as solid waste and it will be utilized in Lime Sludge and Fly ash Management (LSFM) plant to produce Cement.

Over all Silica balance is presented in the Table - 5. The lime mud generated from the first stage is either disposed off as solid waste or sold to cement plants. As an innovative measure, TNPL installed LSFM plant to utilize the solid wastes, such as, lime mud from chemical recovery process and fly ash from power boilers. This is the unique solution to dispose off industrial inorganic solid waste and produce the value added products.

Adaptation of two stage causticizing process resulted in the following benefits

- The capacity of WLCD filter filtration is improved.
- The acid wash frrequency of WLCD filter is reduced.
- Silica in the lime mud to the lime kiln is reduced.
- The lime sludge dryness is improved.
- The purity of Burnt lime improved.
- The furnace oil consumption is optimized.
- Silica build-up in the system is avoided.
- Scaling due to silica in the evaporators can be reduced.

Conclusion

Two stage causticizing is being operated successfully in TNPL for more than a decade. It is estimated that about 16.18 TPD Silica enter the recovery system while processing 3985 M^3 of predominately bagasse based Green liquor and to produce around 3532 M^3 of white liquor. About 16.65 TPD Silica is removed from the system out of that about 1.91 TPD Silica carried to pulp mill through WL, 13.87 TPD is purged through first stage lime mud, 1.0 TPD is sent along with lime grits and 0.45 TPD through MOL. Two stage causticizing helped to improve WLCD performance, Lime sludge dryness, Lime purity, optimized fuel oil use and reduced silica buildup in the chemical recovery system.

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