Desilication of Bamboo Kraft Green Liquor and Installation of Lime Kiln

C S Kashikar, Rajeev Goel and Ashok Kumar

To meet the CREP requirement to burn lime sludge with high silica content in lime kiln, a process has been developed to reduce silica in lime mud through two-stage causticisation process. Unclarified green liquor from predominantly bamboo as fibrous raw material has been desilicated using partial causticizing process by adding 25 to 30 % of lime in the first stage to achieve residual silica in desilicated green liquor at the level of about 1.9 gpl. Residual silica in desilicated liquor was found almost to be the same for clarified or unclarified green liquor. Silicated mud settling rate both for clarified and unclarified green liquor was also the same. First stage silicated mud filterability was marginally better in case of clarified green liquor mud. Soda loss was also similar in silicated mud generated either in clarified liquor silicated mud or unclarified liquor silicated mud.

The study reveals that with green liquor desilication, about 60 - 65 % of the lime mud generated can be burnt in the kiln and thus reduce the solid waste to the extent of about 35 - 40 % of the present level.

Bilt Ballarpur has already started work for installing two stage causticising plant with rotary limekiln which will be completed by March 2007.

INTRODUCTION

Charter on Corporate Responsibility for Environment Protection (CREP) is an agreed time bound program to improve upon the environmental performance of the pulp and paper industry. Increasing environmental awareness and other issues have forced the industry to look for alternatives for the lime mud reburning. Lime mud generated during causticizing process poses disposal problem. Lime mud reburning allows the conversion of solid waste into useful product by removing silica from the system through two-stage causticising process.

An integrated paper mill like Ballarpur generates large quantity of lime mud as solid waste which has to be disposed off. The major constraint in reburning lime mud from bamboo as a raw material is the presence of high amount of silica in the black liquor.

Higher silica content of the lime mud prevents the conversion of $CaCO_3$ to available CaO. This may be due the formation of tricalcium silicate. It also induces uneven burning of the lime and increases furnace oil consumption.

Bench scale studies have been carried out for both the alternatives, i.e. Black Liquor Desilication and Green Liquor Desilication. In this paper, the findings of Green Liquor Desilication, are given. Similar studies with bagasse liquor using 2 stage causticizing process of green liquor were published by Marimuthu et al (1).

The studies on black liquor desilication have also been published earlier (2,3) .

DESILICATION BY TWO STAGE CAUSTICIZING

In paper industry, during conventional causticising process, quick lime (CaO) is added to green liquor to convert sodium carbonate to sodium hydroxide.

When lime is added to the green liquor, it preferentially reacts with sodium silicate and forms calcium silicate because the reaction (2) is faster than the reaction (1). This situation can be used to preferentially precipitate the silicate in early stages. Thus, lime can be used in two stages -

First stage : To remove bulk of the silica and for part causticizing.

Second Stage : For causticizing efficiency up to 80%.

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3 \quad ...(1)$$

$$Na_2SiO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaSiO_3 \quad ....(2)$$

1st stage lime addition preferentially

Ballarpur Industries Limited, Unit Ballarpur P.O. Ballarpur Paper Mills, Distt.Chandrapur (M.S.)

reacts with the silica in green liquor (reaction 2) and precipitated silica sludge is removed by settling and supernatant liquid is taken for recausticizing (reaction 1). Lime mud generated in 2nd stage has less silica which may be recycled in the system after reburning.

TERMINOLOGIES USED FOR PROCESS INTERMEDIATES

To facilitate discussion on the subject matter, following terminology have been adopted :

Other terminologies remain as per the present convention.

Desilication	Is the process of removing silica from the green liquor by first stage partial causticization.
Silicated Mud	Is the lime mud generated after desilication of green liquor, which is to be discarded.
Desilicated Liquor	Is the desilicated liquor remaining after clarification and separation of above silicated mud,
Desilicated Weak Liquor	Is the weak liquor generated from the mud washing and filtration of silicated mud.

EXPERIMENTAL DETAILS:

Causticizing experiments were carried out in stainless steel container using a geared stirrer paddle at 150 rpm at 90°C in the constant temperature water bath for 30 min. After the reaction, the mixture was settled for 30 min in an oven at 80°C. The supernatant liquid was thereafter decanted. The remaining mud slurry was then filtered through leaf filter and mud cake formed on the leaf filter was subsequently washed with hot water. Filtration and washing were carried out under vacuum of 360 mm of Hg. Leaf filter was used to simulate the plant condition with the drum filter at the rate of 2 rpm. (Leaf filter was immersed in the mud slurry for 10 sec, drained for 3 sec and after that, dipped in hot water for 7 sec and again drained for 3 sec.)

Hot water (80°C) was used for the washing of mud cake to get displacement ratio of 1.2 during washing through the leaf filter.

In laboratory desilication study, the first stage causticizing experiments were carried out with clarified as well as unclarified green liquor. Experiments were carried out with lime having 60.8 % available CaO and 7.0 % silica content.

First stage lime addition was carried out at two different levels i.e. 25 & 30 % of total lime required for the 80 % causticizing efficiency.

EXPERIMENTAL CONDITIONS:

In the laboratory, the experimental conditions were maintained as in Table-1.

Lime Quality Used

Lime used for the desilication experiments was analysed for the available CaO and silica. Detailed analysis is given in Table-2. All experiments were carried out using same quality of lime. The whole lime (composite) was crushed to coarse powder, -10 mesh, and added.

Lime was at room temperature at the time of adding to hot green liquor.

Table 2: Lime Analysis

Parameter	Unit	Result
Available CaO,	%	60.8
Total CaO,	%	80.5
Silica, (SiO_2)	%	7.0
MgO	%	3.6

Green Liquor Source:

Clarified green liquor and unclarified green liquor were collected from the plant on different days and used as such in the laboratory. The detailed analysis of green liquors are given in Table-3.

Table-1: Experimental Conditions *Clarified green liquor*

Set No.	Unit	1	2	3	4	5	6	7	8	9	10
Temperature	°C	90	90	90	90	90	90	90	90	90	90
Time	min	90	90	90	90	90	90	90	90	90	90
Lime added, % of total	%	25	30	25	30	25	30	25	30	25	30
Volume of GL taken	Litre	12	12	12	12	12	12	12	12	12	12
Lime added	g	198.2	237.8	231.4	277.6	208.6	250.2	210.0	252.0	218.6	262.

Unclarified green liquor

Set No.	Unit	1	2	3	4	5	6	7
Temperature	°C	90	90	90	90	90	90	90
Time	min	90	90	90	90	90	90	90
Lime added, % of total	%	25	30	25	30	25	25	30
Volume of green liquor taken	litre	12	12	12	12	12	12	12
Lime added	g	195.8	235.0	204.6	246.0	212.2	182.2	218.6

Table-3 : Analysis of green liquor Clarified green liquor

Set No.	Unit	1	2	3	4	5	6	7	8	9	10
TTA	gpl	115.6	115.6	121.6	121.6	114.8	114.8	111.2	111.2	114.4	114.4
NaOH	gpl	28.8	28.8	26.8	26.8	25.2	25.2	24.0	24.0	25.2	25.2
Na2S	gpl	24.0	24.0	23.2	23.2	24.8	24.8	22.4	22.4	21.6	21.6
Na2CO3	gpl	62.8	62.8	71.6	71.6	64.8	64.8	64.8	64.8	67.6	67.6
Na2SO4	gpl	2.86	2.86	2.36	2.36	3.92	3.92	3.90	3.90	10.56	10.56
CE	%	31.4	31.4	27.2	27.2	28.0	28.0	27.0	27.0	27.2	27.2
SiO2	gpl	3.8	3.8	4.2	4.2	3.5	3.5	4.0	4.0	5.6	5.6

Unclarified green liquor

Set No.	Unit	1	2	3	4	5	6
TTA	gpl	113.6	113.6	114.0	114.0	120.0	106
NaOH	gpl	25.2	25.2	24.8	24.8	26.0	22.8
Na2S	gpl	27.2	27.2	25.6	25.6	28.0	26.4
Na2CO3	gpl	61.2	61.2	63.3	63.3	66.0	56.8
Na2SO4	gpl	2.07	2.07	3.3	3.3	7.7	3.9
CE	%	26.0	26.0	28.1	28.1	28.3	28.6
SiO2	gpl	3.6	3.6	3.7	3.7	3.9	3.0

Table-4 : Desilicated Liquor Analysis Clarified green liquor

Set No	Unit	1	2	3	4	5	6	7	8	9	10
Volume generated	ml	10585	10510	10660	10575	10745	10675	10815	10515	10550	10350
Volume of liquor generated, % of initial	%	88.2	87.6	88.8	88.1	89.5	89.0	90.1	87.6	87.9	86.3
TTA	gpl	120.4	121.2	127.2	128.8	120.0	120.4	116.0	119.6	118.4	120.0
NaOH	gpl	41.6	43.6	40.4	42.8	36.0	40.4	34.8	39.6	36.0	40.0
Na_2S	gpl	25.6	24.8	26.4	27.2	27.2	25.6	24.8	23.2	24.0	22.4
Na_2CO_3	gpl	53.2	52.8	60.4	58.8	56.8	54.4	56.4	56.8	58.4	57.6
Na_2SO_4	gpl	3.3	2.7	2.8	2.9	3.9	3.8	4.3	4.5	11.7	11.2
SiO_2	**gpl**	1.4	1.8	2.4	1.9	1.9	1.9	2.4	1.9	2.4	2.2
CE	%	43.9	45.2	40.1	42.1	38.8	42.6	38.2	41.1	38.1	41.0
Desilication	%	63.2	52.6	42.9	54.8	45.7	45.7	40.0	52.5	57.1	60.7

Unclarified green liquor

Set No.	Unit	1	2	3	4	5	6	7
Volume generated	ml	10640	10550	10735	10485	10625	10940	10890
Volume of desilicated liquor generated, % of initial	%	88.7	87.9	89.5	87.4	88.5	91.2	90.8
TTA	gpl	124.0	119.6	122.0	125.6	128.8	110.4	110.8
NaOH	gpl	38.0	38.4	37.6	40.8	40.0	35.2	36.0
Na_2S	gpl	28.0	28.8	26.4	28.0	28.0	26.4	28.0
Na_2CO_3	gpl	58.0	52.4	58.0	56.8	60.8	48.8	46.8
Na_2SO_4	gpl	2.65	2.58	3.65	3.85	8.31	4.24	4.31
SiO_2	**gpl**	1.3	2.0	2.1	1.8	2.6	1.8	1.9
CE	%	39.6	42.3	39.3	41.8	39.7	41.9	43.5
Desilication	%	63.9	44.4	43.2	51.4	33.3	40.0	36.7

OBSERVATIONS:

- Initial silica level in green liquor varied from 3.0 to 5.6 gpl irrespective of clarified or unclarified liquor with average of 4.22 % in clarified and 3.5 % in unclarified green liquor.
- Causticizing efficiency (CE) of green liquor was in the range of 26 to 31 % with average of 28 %.
- Sodium sulfate in green liquor varied from 2 to 4 gpl.

RESULTS AND DISCUSSION

Desilicated Liquor

After settling for 30 minutes, desilicated green liquor was decanted and the mud slurry used for the filtration. Decanted desilicated green liquor was analysed for TTA and Silica. Detailed analysis is given in Table -4.

SILICATED MUD SETTLING CHARACTERISTICS

Mud settling was carried out in one-liter glass cylinder for 30, 60 and 120 min at 80°C in oven. Mud height was recorded as given below.

Silicated mud from clarified green liquor

Set No.	Unit	1	2	3	4	5	6	7	8	9	10
Mud vol settled in 30 min.	ml	75	60	65	80	60	75	65	75	60	75

* Settled height remained unchanged at the end of 30, 60 & 120 min. Silicated mud actually settledin 5 - 10 min.

Silicated mud from unclarified green liquor

Set No.	Unit	1	2	3	4	5	6	7
Mud volume settled in 30 min.	ml	65	80	70	80	70	75	90

* Settled height remained unchanged at the end of 30, 60 & 120 min. Silicated Mud during the experiments actually settled in 5 - 10 min

OBSERVATIONS AND COMMENTS:

DESILICATED LIQUOR

- Total volume generated after Desilication was around 88 to 91% of initial green liquor.
- Silicated Mud settling rate in desilication stage green liquor was good. In all silicated mud height remained same after 30, 60 or 120 min.
- In general silicated mud, settling rate was marginally faster for clarified green liquor. Silicated mud settling rate being high, this marginal difference is not of any consequence.
- Clarity of desilicated green liquor was good.
- Total alkali of the desilicated green liquor increased by 5 to 7 gpl due to water evaporation/flashing.
- CE achieved in desilicated green liquor during Desilication stage was 39 to 45 %. CE increased by 12 to 15 %.
- Desilication achieved was in the range of 42 to 60 % in clarified liquor and 33 to 51 % in unclarified liquor. The removal of silica with 25 % or 30 % lime addition did not make much difference.
- Silica level in desilicated green liquor was in the range of 1.4 to 2.4 gpl.
- Higher the silica level in green liquor, higher was the percent desilication achieved. But the final residual silica in desilicated green liquor was in the same range irrespective of initial silica content.

SILICATED MUD FILTRATION CHARACTERISTICS

Silicated Mud slurry was filtered through leaf filter. The mud cake formed was washed in hot water as per the time schedule given in the Table-5. 360 mm of Hg vacuum was applied during the filtration and displacement washing.

Details of experimental conditions during filtration, properties of the silicated mud slurry and silicated mud cake are given in Table-5.

Table-5 : Silicated Mud Slurry and Silicated Mud Filtration

Clarified green liquor

Set No.	Unit	1	2	3	4	5	6	7	8	9	10
Filtration washing time (pick up-washing-drain)	sec	10-10-3		8-3-5-3		10-10-3		10-10-3		10-10-3	
Vacuum applied	mm	360	360	360	360	360	360	360	360	360	360
Weight of mud slurry	g	1243	1370	1302	1530	1151	1356	1079	1401	1466	1676
Consistency of slurry	%	23.7	25.7	26.9	26.8	-	-	-	-	-	23.3
Volume of mud slurry	ml	900	1020	950	1110	870	990	870	1030	1110	1260
Volume of hot wash water	ml	2000	2000	2000	2000	-	-	-	2000	-	2000
Filtrate collected during suction	ml	185	145	145	127	-	-	-	132	-	220
Filtrate collected during washing	ml	488	390	335	380	-	-	-	440	-	450
Cake thickness	cm	3.5	2.5	3.5	4.3	-	-	-	3.5	-	4.0
Cake uniformity		OK	OK	OK	OK	-	-	-	OK	-	OK
Crack in the cake		No	No	No	No	-	-	-	No	-	No
Volume of final mud slurry	ml	210	230	210	240	-	-	-	140	-	330
Volume of final hot water	ml	1705	1760	1800	1825	-	-	-	1850	-	1820
Weight of OD grits, through 20 mesh	g	16.7	18.8	23.7	25.4	16.3	19.3	15.6	19.8	18.9	28.5

Unclarified green liquor

Set No.	Unit	1	2	3	4	5	6	7
Filtration washing time (pick up-washing-drain)	sec	10-10-3		10-10-3		10-10-3		
Vacuum applied	mm	360	360	360	360	360	360	360
Weight of mud slurry	g	1261	1453	1229	1389	1272	986	1169
Consistency of slurry	%	23.6	24.3	-	-	-	26.9	26.8
Volume of mud slurry	ml	950	1110	910	1010	1010	740	885
Volume of hot wash water	ml	2000	2000	2000	2000	2000	2000	2000
Filtrate collected during suction	ml	200	95	102	110	115	80	55
Filtrate collected during washing	ml	360	360	285	320	370	215	195
Cake thickness	cm	-	3.0	3.2	3.4	2.0	2.0	1.5
Cake uniformity		-	OK	OK	OK	OK	OK	OK
Crack in the cake		-	No	Yes	No	Yes	No	No
Volume of final mud slurry	ml	270	425	275	275	600	270	480
Volume of final hot water	ml	-	1850	1920	1950	1730	1900	1950
Weight of OD grits, through 20 mesh	g	15.6	18.8	15.8	18.5	20.3	16.1	18.0

OBSERVATIONS & COMMENTS:

- In case of clarified green liquor, while washing the silicated mud, some times cake had fallen off while lifting the leaf filter cake from the hot wash water bath. In such cases, the analysis results has not been given.

It may be noted that such disengagement of cake experienced in the lab will not be a concern in the plant operation due to physical configuration of washing shower exit zone.

- The consistency of silicated mud slurry remaining after decanting desilicated liquor was in the range of 21 - 26 %.
- Silicated mud filtration rate was marginally better in case of clarified liquor.
- In case of clarified green liquor, cake cracked during drying performed after displacement washing with hot water.

Unclarified green liquor**

Set No.		1	2	3	4	5	6	7
Cake weight	g	-	475	445	566	255	317	242
Cake consistency	%	-	48.4	47.7	52.5	42.0	53.1	51.7
Total alkali as Na_2O	%	-	9.11	9.98	10.04	8.74	7.81	7.94
Available CaO	%	-	1.01	1.07	1.85	1.20	1.35	0.95
SiO_2	%	-	7.8	8.6	7.8	13.6	8.5	7.4
Soda Loss	%	-	1.6	1.7	2.0	0.9	0.9	0.7

*Sample no. 1 was not analyzed due to dislodging of mud cake from leaf filter during filtration.

Clarified green liquor*

Filtrate Analysis (with washing)	Unit	1	2	3	4	5	6	7	8	9	10
Suspended solids	ppm	1480	1550	2090	2500	-	-	-	4550	-	1870
TTA	gpl	98.0	119.2	121.9	118.8	-	-	-	113.4	-	118.0
NaOH	gpl	38.0	47.2	42.4	42	-	-	-	41.6	-	48.0
Na_2S	gpl	20.0	24.8	25.6	24.8	-	-	-	23.2	-	20.0
Na_2CO_3	gpl	40.0	47.2	53.6	52	-	-	-	53.6	-	50.0
SiO_2	gpl	1.1	1.3	1.9	1.6	-	-		1.2	-	1.4

*Sample no. 5, 6, 7 and 9 were not analyzed due to dislodging of mud cake from leaf filter during filtration.

SILICATED MUD CAKE QUALITY:

- Cake dryness was in the range of 46 to 52 % for both types of green liquors.
- Soda loss in case of unclarified or clarified green liquor mud cake was almost same.
- Silica in mud was in the range of 7 to 10 % on the OD basis.
- Displacement ratio in the laboratory washing was in the range of 1 : 1.2.
- Soda could be lower than the laboratory values as silicated mud washing will be carried out in 3-stages in the plant operation.

Detailed analysis is given in Table-6.

DESILICATED WEAK LIQUOR QUALITY

The combined filtrate collected during filtration was analysed. The results are given in Table-7.

Hot water (80°C) was used to wash the mud cake to achieve displacement ratio of about 1.2 during washing through the leaf filter.

Table-6 : Silicated Mud Cake Analysis
Clarified green liquor*

Set No.	Unit	1	2	3	4	5	6	7	8	9	10
Cake weight	g	514	542	586	760	-	-	-	718	-	631
Cake consistency	%	46.6	48.6	51.4	50.3	-	-	-	52.2	-	46.9
Total alkali as Na_2O	%	9.86	9.11	10.8	11.5	-	-	-	10.1	-	11.2
Available CaO	%	1.46	1.29	2.02	1.12	-	-	-	0.67	-	1.07
SiO_2	%	9.71	9.35	9.23	8.18	-	-	-	8.94	-	11.7
Soda Loss	%	2.0	1.8	3.0	3.0	-	-		2.6	-	2.7

*Sample no. 5, 6, 7 and 9 were not analyzed due to dislodging of mud cake from leaf filter during filtration.

Table-7 : Filtrate Analysis
Unclarified green liquor**

Filtrate Analysis (with washing)	Unit	1	2	3	4	5	6	7
Suspended solids	ppm	-	2980	5300	4880	10230	6490	9740
TTA	gpl	-	114.0	120.0	124	108.8	108.0	108.0
NaOH	gpl	-	40.0	38.8	43.6	36.8	39.2	40.0
Na_2S	gpl	-	26.4	26.4	26.4	24.8	25.6	25.6
Na_2CO_3	gpl	-	47.6	54.8	54.0	47.2	43.2	42.4
SiO_2	gpl	-	1.6	1.5	1.7	1.6	1.5	1.7

**Sample no. 1 was not analyzed due to dislodging of mud cake from leaf filter during filtration.

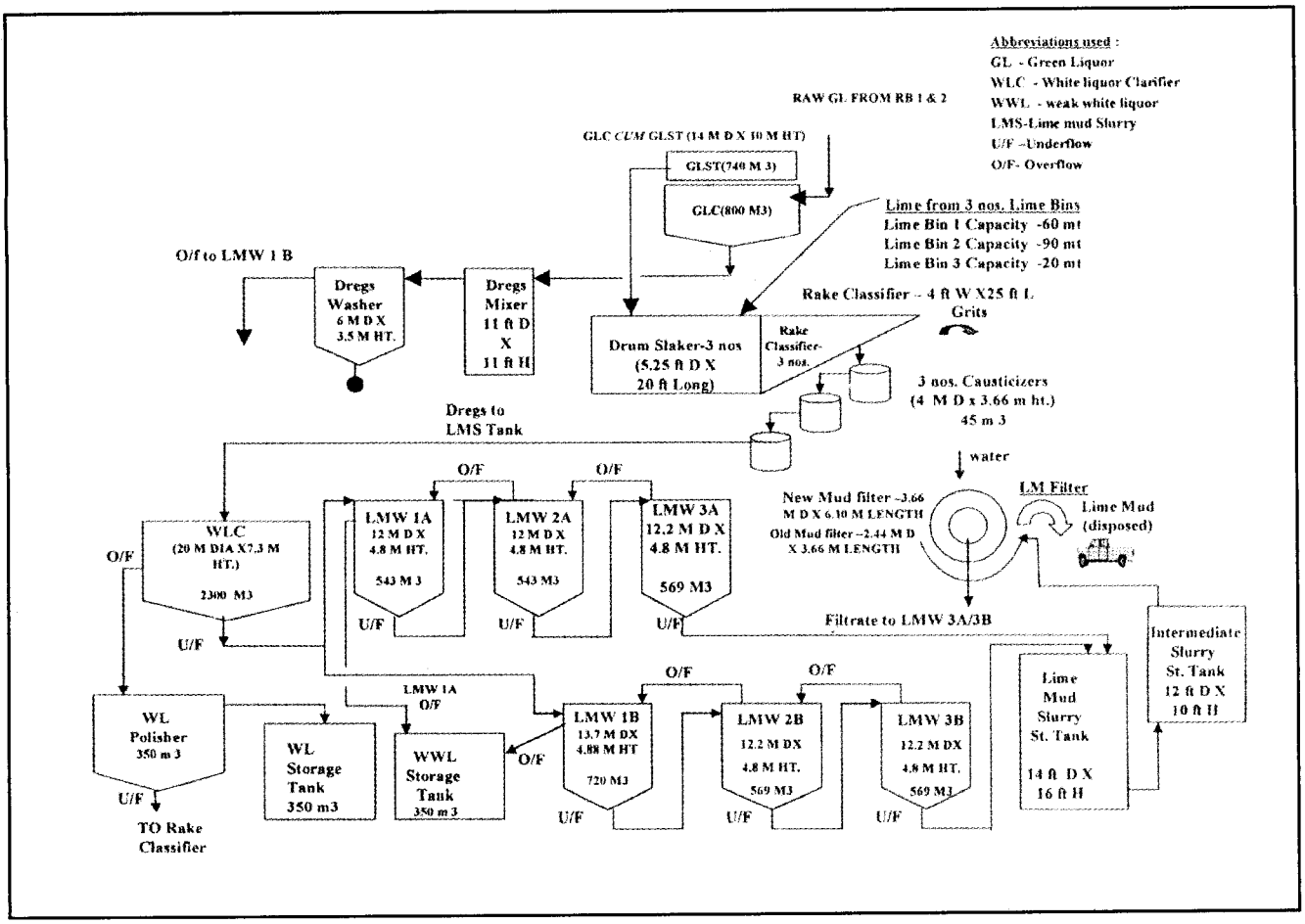

Figure-1: Flow diagram of existing causticising process.

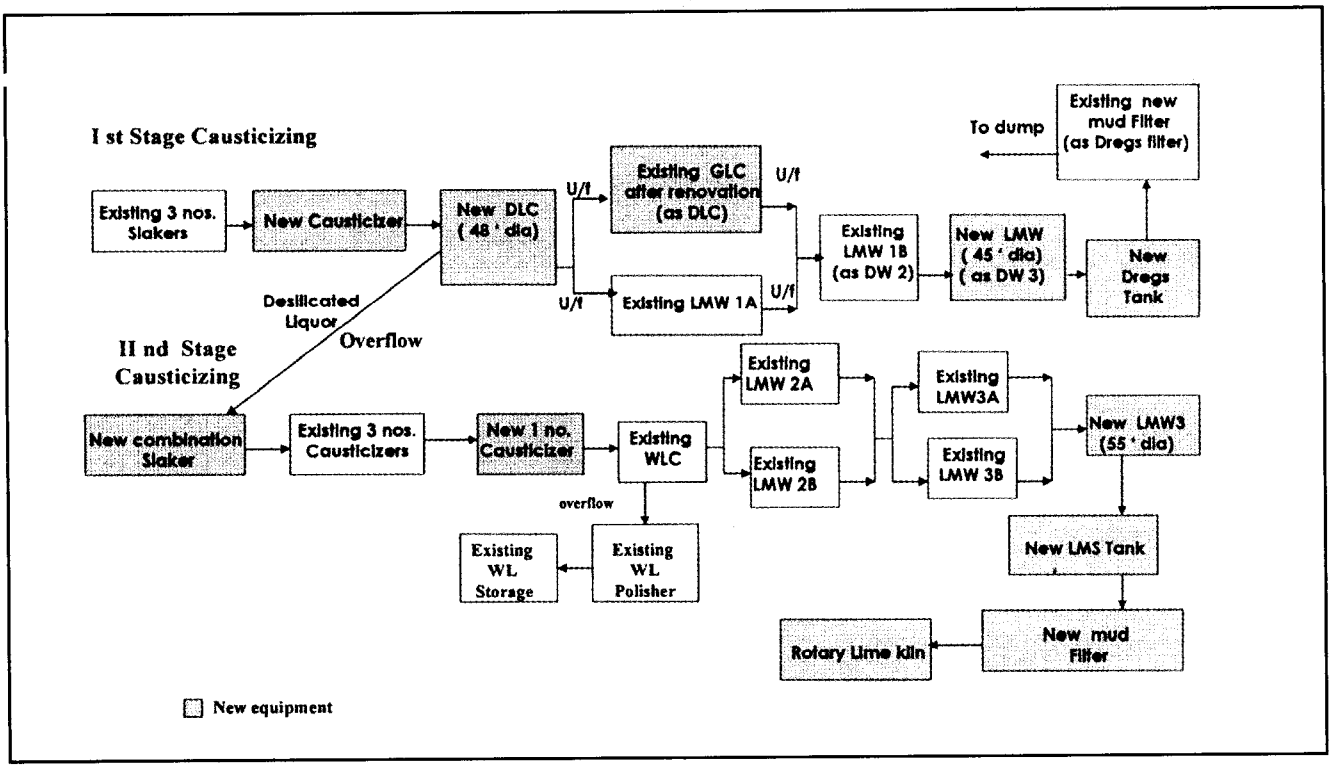

Figure-2: Flow diagram of proposed 2-stage causticising process.

OBSERVATIONS AND COMMENTS:

- Laboratory Filtrate along with washing had the higher concentration than the present weak white liquor from the plant.
- In the actual plant practice, the concentration of weak desilicated liquor is expected to be higher due to silicated mud washer stage.

CONCLUSION

- Unclarified green liquor is the preferred choice for desilication using part causticizing process with the lime addition of 25 to 30 % in the first stage to achieve residual silica level of 1.9 gpl.
- Residual silica in desilicated green liquor remains about the same for both clarified and unclarified green liquors.
- Lime mud settling rate in first stage in case of clarified and unclarified green liquor was almost the same.
- Silicated mud filterability remains similar for both unclarified green liquor and clarified liquor silicated mud.
- Mud cake soda loss was also same in lime mud generated either in case of clarified liquor lime mud or unclarified liquor lime mud.
- Laboratory data has been confirmed by two plant scale trials for green liquor desilication at Ballarpur existing causticising plant.

ACTION PLAN AT BALLARPUR

- Bilt Management is installing two-stage causticisation plant with 180 TPD lime capacity. This will reduce lime mud disposal to the extent of 60 65%. Flow diagram of existing causticising plant and proposed causticising plant is given in figure-1 and figure-2 respectively. Care has been taken to utilize the existing equipment to the maximum possible extent.
- Limekiln is being designed for higher lime mud cake purging to the tune of 40% for maintaining 5-6% silica level in the mud entering kiln.
- Mills operating cost will increase as lime cost expected from the kiln is expected to be Rs. 5400/MT against existing lime cost of Rs. 2650/MT.
- The installation of producer gas plant to reduce fuel oil consumption is under study and will be installed to reduce the lime cost, by about 20-25%
- The recently developed technology in mud filtration (Dorr Oliver Eimco Continuous Cleaner, DOCC) will be adopted for getting maximum mud cake dryness which is critical in view of higher silica content in mud. The expected mud dryness after two-stage causticisation is about 50%.
- Limekiln oil burner is designed for burning Non-Condensable Gases (NCG) in the kiln.

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