Lime Sludge Reburning - A Promising Approach Towards Solid Waste Utilisation

Marimuthu. P., Gunasekaran J.P. and Mohan Rao N.R.

ABSTRACT

Growing environmental awareness and increasing competitiveness in the pulp and paper industry has forced the industry to look for viable alternatives. Lime sludge generated during the causticizing process poses disposal problems. Exploring the lime sludge reburning, to convert it back to useful lime is a promising approach to convert solid waste into an useful product and taking care of 'Silica' build-up in the system through two stage causticizing, makes the lime sludge reburning an attractive proposition which will be cost effective.

INTRODUCTION

An integrated pulp and paper industry generates huge quantity of solid wastes that pose disposal problem. The prominent one among them is lime sludge, the by product generated in soda recovery process. Where ever possible, few mills sell this to Cement industry where it is used as raw material. Other mills dispose this waste as land fill. But the deliterious impact on environment forced more mills to reuse the lime sludge in the soda recovery process.

NEED FOR PROCESS MODIFICATION WITH TWO STAGE CAUSTICIZING IN THE PLACE OF CONVENTIONAL CAUSTICIZING

Reusing of lime sludge in soda recovery is an excellent positive alternate for disposal, because it reduces the pollution and saves natural resources of limestone deposits. The major constraint in reusing lime sludge in the non-wood based paper industry is the presence of higher amount of Silica in the agricultural residues. The kraft cooking process dissolves the silica content of raw materials and this becomes an undesirable constituent in the black liquor. The silica content of the bagasse black liquor is about 2%. The silica in the Black liquor is the source of many difficulties that are encountered in various stages of the recovery process. The major troubles that originate with silica in the black liquor, compels plant shut downs are scale formation in evaporates and digester preheater tubes and hard smelt deposits on the furnace walls and boiler super heater tubes. Apart from this, Silica causes slow settling of lime slurry during causticising operation when the lime sludge is taken for reburning in kiln. Silica present in lime sludge induces in the uneven burning of lime and increases furnace oil consumption. Further, the main trouble caused by the silica and inerts in lime sludge is prevention of $CaCO_3$ to available CaO conversion. This may be due to the formation of tricalcium silicate during the calcination process. Calcium silicate can not be changed in to quick lime when it is burnt.

Tamilnadu Newsprint and Papers Limited
Kagithapuram, - 639136
Distt. Trichy (T.N.)

The above discusssed factors necessitates the reduction of silica content from the lime sludge before the process of reburning.

CONCEPT OF TWO STAGE CAUSTICIZING

In conventional causticizing quick lime is added with green liquor to covert sodium carbonate to sodium hydroxide.

$$Na_2CO_3 + CaO + H_2O \Leftrightarrow 2\ NaOH + CaCO_3$$

However, this depends on the silica content in the green liquor. The lime added will first react with the silica present in the form of sodium silicate in the green liquor to form siliceous complex compounds and this retards the causticizing resulting in poor causticizing efficiency and quality of lime sludge.

$$Na_2SiO_3 + CaO + H_2O \Rightarrow 2\ NaOH + CaSiO_3$$

The reaction of quick lime with sodium solicate is faster than the reaction with sodium carbonate in green liquor and thus calcium silicate would be firstly produced and precipitated. The Two stage Causticizing concept exploits the faster reaction of quick lime with sodium silicate than sodium carbonate which remove considerable quantity of silica from the lime sludge. If the raw green liquor silica is removed before recausticizing, the lime mud can be recycled in the lime kiln at lower cost. Therefore, the preferential reaction of CaO with the silica in green liquor is first allowed to take place and thereby precipitating the silica as calcium silicate complex. The precipitated silica sludge is removed by settling and the supernatant with remaining lime is taken for recausticizing reaction. This principle was used in our studies.

EXPERIMENTAL

Causticizing experiments were carried out in laboratory by single and two stage causticizing. The following conditions were maintained during the causticizing experiments. For each experiment 1000 ml of raw green liquor (Table-1) from plant was treated with the required quantity of lime (Table-2) of known purity. After the first stage the liquor was filtered and causticizing was continued with the filtrate

Table-1

GREEN LIQUOR ANALYSIS

PARTICULARS	Unit	RAW GREEN LIQUOR (1)	RAW GREEN LIQUOR (2)
TTA as Na_2O	gpl	124.0	115.3
NaOH as Na_2O	gpl	21.1	19.2
Na_2S as Na_2O	gpl	27.3	24.8
Na_2CO_3 as Na_2O	gpl	75.6	71.3
Total Suspended Solids	ppm	700	420
Acid Insoluble Silica as SiO_2	gpl	3.80	4.10

Table-2

LIME ANALYSIS

PARTICULARS	UNIT	80% CaO LIME	70% CaO LIME
Loss on Ignition	%	6.4	0.4
Acid Insoluble Silica as SiO_2	%	4.5	8.3
Mixed Oxides	%	1.6	2.0
Total Calcium as CaO	%	84.3	83.6
Available CaO	%	81.0	73.0
Magnesium as MgO	%	2.1	2.0

adding the remaining dosage of lime. For single stage experiments 100% lime was added with green liquor. For heating the causticizing medium a laboratory water bath was used.

Parameter	I stage	II stage
Time, min	30	90
Temperature, C	95	95
Lime Addition, %	25	75

Results & Discussion

OPTIMISATION OF LIME QUANTITY IN THE FIRST STAGE

In the optimisation experiment the minimum quantity of lime required to get a good clarity of first stage liquor with the minimum reaction in the green liquor is optimised. The experiments with different dosages of lime are shown in Table-3. Twenty five percent of the total requirement of known purity lime was needed to get a reasonably clear supernatant solution. Consequently 25% of total lime requirement was added in the first stage in all our experiments in further studies.

TWO STAGE CAUSTICIZING EXPERIMENTS

Two stage causticizing experiments were carried out with 70% purity with 8% silica lime. The results of the filtrate liquor and the sludge are given in Table 4. The results indicate that causticizing efficiency and the quality of the filtrate are same for the two stage final liquor and the single stage liquor. The settling rate of the first stage was remarkably faster and the clarity of the second stage is also good. This reduces load to a great extent in lime mud washers. The sludge volume of second stage was considerably lower than the single stage causticizing.

Table-3

LIQUOR AND LIMESLUDGE ANALYSIS

(in optimisation of lime requirement)

PARTICULARS	Unit	LIME ADDITION TO GREEN LIQUOR (Qty.) 20%	25%	30%
TTA as Na_2O	gpl	122.8	124.0	124.6
NaOH as Na_2O	gpl	36.6	39.7	43.4
Na_2S as Na_2O	gpl	28.5	29.8	29.8
TAA as Na_2O	gpl	65.1	69.5	73.2
Na_2CO_3 as Na_2O	gpl	57.7	54.5	51.4
Causticizing Efficiency	%	38.8	42.1	45.8
Acid Insoluble Silica	gpl	2.3	1.8	1.7
Clarirty of filtrate	---	poor	clear	clear
SETTLED SLUDGE VOLUME				
for 30 min in 1000 ml slurry	ml	110	120	130
LIMESLUDGE ANALYSIS				
Loss on Ignition	%	38.8	38.2	37.5
Acid Insoluble Silica as SiO_2	%	6.0	6.4	6.3
Mixed Oxides	%	1.9	2.0	2.1
Total Calcium as $CaCO_3$	%	86.8	87.3	87.0
Magnesium as $MgCO_3$	%	3.6	3.2	3.6

Table-4
LIQUOR and SLUDGE ANALYSIS with 70% CaO LIME
(in two stage causticizing)

PARTICULARS		TWO STAGE CAUSTICIZING Ist Stage LIQUOR	2nd Stage LIQUOR	SINGLE Causticizing LIQUOR
TTA as Na_2O	gpl	114.1	112.8	112.8
NaOH as Na_2O	gpl	34.1	80.6	79.4
Na_2S as Na_2O	gpl	21.1	19.8	21.1
TAA as Na_2O	gpl	55.2	100.4	100.5
Na_2CO_3 as Na_2O	gpl	58.9	12.4	12.3
SULPHIDITY	%	35.8	19.7	21.0
Causticizing Efficiency	%	36.7	86.7	86.6
Acid Insoluble Silica	gpl	1.9	0.40	0.50
SETTLED SLUDGE VOLUME for 30 min in 1000 ml slurry	ml	140	460	590
LIME SLUDGE ANALYSIS				
Loss on Ignition	%	32.0	37.9	35.2
Acid Insoluble Silica	%	10.8	5.4	8.1
Mixed Oxides	%	1.8	2.0	1.9
Total Calcium as $CaCO_3$	%	84.0	90.4	86.4
Magnesium as $MgCO_3$	%	3.1	2.8	3.0

SLUDGE QUALITY

The chemical analysis of the primary and secondary sludge of the two stage and of the single stage shows that the silica reduction in second stage sludge by 30% when compared to the single stage. This is due to the efficient removal of silica in the first stage itself by precipitation silica as calcium silicate with lime. The silica content of the second stage sludge was 5%. When this sludge is mixed with low silica lime stone the net silica content will be less than 4% which is very much desired to get good calcination in lime burning kiln. This lime mud of low silica content produced in 2nd stage recausticising would be recycled almost all in the kiln.

PLANT TRIALS WITH TWO STAGE CAUSTICIZING

Tamilnadu Newsprint and Papers Ltd. is one of the largest integrated paper mill producing 1,80,000 MT of fine paper and newsprint with bagasse as the chief raw material. TNPL consumes lime of 140 T/Day and generates 200 T of lime sludge per day. Based on the laboratory trials, plant trials were carried out at our plant. The following conditions were maintained during the plant trials. In reguler single stage causticizing 40-45 M^3 of green liquor flow was kept with 4.0-4.5T of lime addition with 65-70% available CaO. The first stage causticizing was carried out in a separate slacker with 1.0-1.3 T of lime, which amounts to 25-30% of the total lime requirement followed by the precausticizing with a time duration of 30 min at 90 deg °C.

This slurry was taken to a clarrifier. The overflow of the clarifier was taken to another slacker where the remaining quantity 2.5-3.0.T of lime added. The slurry was subjected to the regular causticizing and washing. The first stage sludge which settled quickly was taken to a dregs washer and then washed

Table-5

PLANT TRIAL RESULTS LIQUOR ANALYSIS

PARTICULARS		(1)	(2)	(3)	(4)	AVG
GREEN LIQUOR ANALYSIS						
TTA as Na_2O	gpl	112.8	114.7	109.7	111.6	112.2
NaOH as Na_2O	gpl	20.5	19.2	19.2	18.6	19.4
Na_2S as Na_2O	gpl	24.8	23.6	23.6	22.4	23.6
Na_2CO_3 as Na_2O	gpl	67.5	71.9	66.9	70.6	69.2
Total Suspended Solids	ppm	460	340	375	410	400
Acid Insoluble Silica	gpl	4.6	4.1	4.7	4.3	4.4
GREEN LIQUOR CLARRIFIER O/F (Ist stage liquor)						
TTA as Na_2O	gpl	101.1	102.9	102.3	94.9	100.3
NaOH as Na_2O	gpl	34.7	35.3	39.1	34.1	35.8
Na_2S as Na_2O	gpl	21.1	22.3	18.6	17.4	19.9
TAA as Na_2O	gpl	55.8	57.6	57.7	51.5	55.7
Na_2CO_3 as Na_2O	gpl	45.3	45.3	44.6	43.4	44.7
Causticizing Efficiency	%	43.4	43.8	46.7	44.0	44.5
Acid Insoluble Silica	gpl	2.1	2.4	2.3	2.1	2.2
Settled Sludge Volume						
at 30 min for 1000 ml	ml	120	100	150	120	125
WHITE LIQUOR CLARRIFIER O/F (2nd Stage Liquor)						
TTA as Na_2O	gpl	86.8	82.5	81.8	82.4	83.4
NaOH as Na_2O	gpl	59.5	57.0	58.3	57.0	58.0
Na_2S as Na_2O	gpl	17.4	17.4	16.1	16.1	16.8
TAA as Na_2O	gpl	76.9	74.4	74.4	73.1	74.7
Na_2CO_3 as Na_2O	gpl	9.9	8.1	7.4	9.3	8.7
SULPHIDITY	%	22.6	23.8	21.6	22.0	22.5
Causticizing Efficiency	%	85.7	87.6	88.7	86.0	87.0
Acid Insoluble Silica	gpl	0.60	0.50	0.40	0.50	0.50
Settled Sludge Volume						
at 30 min for 1000 ml	ml	450	430	420	400	425

Table-6

LIME & LIME SLUDGE ANALYSIS

PARTICULARS		(1)	(2)	(3)	(4)	AVG
FEED LIME ANALYSIS						
Loss on Ignition	%	1.2	0.9	0.5	0.5	0.8
Acid Insoluble Silica	%	8.6	7.6	7.2	7.8	7.8
Mixed Oxides	%	1.7	1.8	2.2	1.9	1.9
Total Calcium as CaO	%	83.4	85.3	83.4	84.0	84.0
Magnesium as $MgCO_3$	%	2.0	2.4	1.8	2.1	2.1
Available CaO	%	71.4	76.4	73.5	74.0	73.8
Ist STAGE LIMESLUDGE						
Moisture	%	43.3	42.0	41.4	43.7	42.6
Loss on Ignition	%	35.8	34.5	34.6	34.9	35.0
Acid Insoluble Silica	%	9.4	9.5	9.6	9.0	9.4
Mixed Oxides	%	1.9	1.7	2.2	2.2	2.0
Total Calcium as $CaCO_3$	%	85.2	84.2	85.0	84.7	85.4
Magnesium as $MgCO_3$	%	2.8	3.3	3.5	3.1	3.2
Sodium as Na_2O	%	1.2	1.4	1.7	1.3	1.4
2nd STAGE LIME SLUDGE						
Moisture	%	47.0	48.8	47.2	46.7	47.4
Loss on Ignition	%	38.8	38.0	37.4	38.4	38.2
Acid Insoluble Silica	%	5.2	5.6	6.0	5.2	5.5
Mixed Oxides	%	1.8	1.7	1.7	1.8	1.8
Total Calcium as $CaCO_3$	%	91.0	89.7	90.0	90.6	90.3
Magnesium as $MgCO_3$	%	2.6	3.0	2.8	2.6	2.8
Sodium as Na_2O	%	0.6	0.7	0.5	0.6	0.6

thoroughly and disposed off.

The second stage sludge was taken into regular mud washers and finally filtered through mud filters and then fed to lime kiln. The analysis results of the liquors and sludge are given in Table-5 & 6. The results show that two stage causticizing brings down the silica to 5% from 8% in the single stage sludge.

LIME KILN

In TNPL Rotary kiln with a capacity of 170 MT of Burnt lime per day was installed in Aug. 97. The technical details of kiln and variable cost of burnt lime from kiln is given in Annexture-1. At present, plant modification are under way to reduce the soda loss in the first stage sludge. Therefore, presently single sludge comprising of 30% lime stone is being used for reburning. The chemical analysis of input that is possible to obtain 70-75% purity lime can be obtained by reducing the siliça through two stage causticizing and the same is expected in the plant scale.

Table-7

KILN FEED SLUDGE, LIMESTONE and BURNT LIME ANALYSIS

PARTICULARS		LIME SLUDGE	LIMESTONE	BURNTLIME
Moisture	%	50 - 55	0.2 - 0.6	---
Loss on Ignition	%	35 - 37	41 - 43	0.5 - 1.3
Acid Insoluble Silica	%	7.5 - 8.5	0.5 - 2.0	8.0 - 9.0
Mixed Oxides	%	1.5 -2.5	1.0 - 2.0	1.5 - 2.5
Total Calcium as $CaCO_3$	%	85 - 87	94 - 96	83-84 as CaO
Magnesium as $MgCO_3$	%	2.0 - 3.0	2.0 - 3.0	2 - 3 as MgO
Sodium as Na_2O	%	0.4 - 0.7	------	0.2 - 0.3
Available CaO	%	1.0 - 2.0	------	70 - 75

Note : Ratio of feed to kiln : 70% Sludge : 30% Limestone

ANNEXURE -1

TECHNICAL DETAILS OF LIME KILN

Supplier	:	Fuller KCP, Chennai.
Capacity	:	170 MT of Burnt Lime per Day.
Type	:	Rotary Kiln with Alumina Brick lined.
Size	:	Length : 82 meter, Effective diameter : 3.2 m
Speed	:	0.5 to 1.5 RPM., Retntion time : 193 min
Temperature	:	Feed end : 180 C, Burning zone : 1100 - 1150 C
Fuel	:	Furnace oil.
Drive	:	DC motor Supported by Diesel Generator.

VARIABLE COST OF BURNT LIME From KILN

PARTICULARS	UOM	Consumption / MT of Burnt Lime JUL 98	Consumption / MT of Burnt Lime AUG 98	Cost Rs/MT of Burnt Lime JUL 98	Cost Rs/MT of Burnt Lime AUG 98
Lime sludge	Kgs	2011	1818	0	0
Lime stone	Kgs	793	716	716	790
Furnace oil	Lits	210	238	1344	1504
Power	Kwh	28	36	58	89
Steam MP	Kg	107	109	47	50
Diesel & Others	--	--	--	4	32
COST/Ton of BURNT LIME			=	**2168**	**2465**
Quantity of Lime produced	MT			2680	670
Avg Purity of lime produced (CaO%)				72.02	73.86

CONCLUSION

The disilication concept works well in the plant in proportion to the laboratory trial. The continuous operation of two stage causticizing and sludge reburning greatly reduces the cost of lime production and at the same time saves as a workable solution for the disposal of lime sludge.

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