Desilication Of Green Liquor By Two Stage Causticizing

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ABSTRACT

This paper deals with the efficient removal of silica from the green liquor and to make the resulting lime sludge suitable for reburning. Generally non-wood fibrous raw materials contain nearly 10 times higher silica content when compared to wood based raw materials. In bagasse silica content is about 1.5-2.0%. In Kraft process it is converted into sodium silicate and enters into green liquor. Green liquor is the spent liquor from pulping process in the Paper manufacturing process, which can be reused by converting it into white liquor by Causticizing process by addition of lime. In this process the reacted lime can also be reused by calcination process in a lime kiln without any major problem, if the silica content of reacted lime sludge is low. In this process the lime is added in 2 stages as 25% in 1st stage and remaining 75% in the 2nd stage. The analyses of sludge and liquor samples are carried out at TNPL, Karur. From the results the percentage removal of silica in each stage is determined.
Keywords: Desilication, Causticizing, Green liquor, White liquor, Lime sludge.

INTRODUCTION

Nowadays the environment and production cost of the process makes industries to be conscious. In paper making process the cost and environmental impact is stabilized mainly in Chemical recovery plant [1]. This is because of the recycling of the reacted chemicals like Sodium hydroxide and lime. Kraft pulping would not be economical without chemical recovery. The cooking chemicals, NaOH and Na_2S are too expensive to be used on a once-through basis [2]. Viewed as a whole, the Kraft pulp industry is a major inorganic chemical industry, producing NaOH and Na_2S. The fuel value of the black liquor is a major part of the industry energy resources [3].

The green liquor is obtained from black liquor which is the spent liquor from the cooking process in wood pulping. The Black liquor is concentrated and ignited in a furnace to separate the organic and inorganic materials. The inorganic materials are dissolved in weak white liquor and thus green liquor is produced. The composition of green liquor is 80% of Na_2CO_3, 15% of NaOH and 5% of Na_2S [4].

Besides the main cooking chemicals, green liquor contains considerable amount of dissolved and suspended solids [5]. They originate from raw material, bleaching or make up chemical or process water and enter the causticizing through the recovery boiler.

Normally the green liquor is converted to white liquor by Causticizing in single stage. Since most of the raw material for paper manufacturing contains high silica content [6], Silica will enter the system in a large quantity and leads to many problems in lime reburning [7]. The silica present in the Green liquor is more reactive with lime than Na_2CO_3. The reactions are given below.

Reaction of Silica with lime

$Na_2SiO_3 + CaO + H_2O \rightarrow 2NaOH + CaSiO_3\downarrow$ (Undesirable fast reaction)

Reaction of Na_2CO_3 with lime

$Na_2CO_3 + CaO + H_2O \longrightarrow 2NaOH + CaCO_3\downarrow$ (Causticizing slow reaction)

Since the process is done in one stage the sludge will contain both $CasiO_3$ and $CaCO_3$. $CasiO_3$ in sludge makes unsuitable for reburning, since it cannot convert to CaO.

Reusing of lime sludge in soda recovery plant is essential on account of two reasons, it reduces the solid waste pollution load, saves natural resources of lime stone deposits.

This study deals with the effective removal of silica from the system by adding lime in 2 stages as 25% in 1st stage and remaining 75% in the 2nd stage. The analysis of liquor and sludge were done to determine the percentage removal of silica in each stage.

LITERATURE REVIEW

TWO STAGE CAUSTICIZING

By this process the silica can be removed separately and can make the lime sludge suitable for reburning by adding lime in 2 stages. The preferential reaction of lime with silica in green liquor is first allowed to take place by adding 25% of total lime required for conversion. Thereby the precipitating sludge will contain higher amount of $CaSiO_3$ complex which can be discarded from the system.

The supernatant liquor is then recausticized with remaining 75% lime. Since the silicates are removed in 1st stage, the lime will react only with Na_2CO_3. The precipitation in this stage contains only $CaCO_3$ which can be reburned by following Calcination reaction.

$CaCO_3 + \text{Heat} \rightarrow CaO + CO_2\uparrow$

RESULTS AND DISCUSSION

LIQUOR:

The chemical composition of raw green liquor, Clarified green liquor (1st stage) and white liquor (2nd stage) are tabulated in the Table-1.

From the above table it is clear that Na_2CO_3 content is more than NaOH since Na_2CO_3 has to be converted into

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Table-1 Composition of liquor

S.No	Liquor Sample	Na_2CO_3 (gpl)	NaOH (gpl)	Na_2S (gpl)
1.	Raw green liquor	72.22	17.22	20.44
2.	Clarified green liquor	53.69	29.02	21.31
3.	White liquor	14.76	67.32	18.11

Table-2 Composition of Sludge

S.No	Sludge Sample	Loss on ignition (%)	Mixed oxides (%)	Available CaO (%)	Sodium as Na_2O (%)
1.	First stage sludge	34.96	2.00	84.90	1.4
2.	Second stage sludge	38.14	1.76	90.32	0.60

NaOH. Also it shows decreasing of Na_2CO_3 and increasing NaOH content, since in first stage itself some conversion takes place. It explains the total conversion of the Na_2CO_3 into NaOH. This White liquor is used for cooking of wood in pulping operation done in paper industry.

SLUDGE:

The chemical composition of first and second stage sludge is analyzed and the results are tabulated in the Table-2.

ACID INSOLUBLE SILICA ANALYSIS:

The acid insoluble silica content in raw green liquor, Clarified green liquor (1st stage), white liquor (2nd stage) are tabulated in the Table-3. The acid insoluble silica content in first and second stage sludge is analyzed and the results are tabulated in the Table-4.

From these tables the silica content of the liquor decreasing in successive stages is evidently shown.

In table-4 the silica content in first stage is higher due to silicates complex segregation. Since most of the silica is removed in first stage itself the second stage sludge contains lower amount of silica.

SILICA MATERIAL BALANCE

Input to first stage causticizing

Silica in raw green liquor = 3.73 gpl
Silica in lime (25%) = 1.51 kg/m^3
Total silica input to first stage= 5.24 kg/m^3

Table-3 Silica content in liquor

S.No	Component	Value (gpl)
1.	Raw green liquor	3.73
2.	Clarified green liquor	1.71
3.	White liquor	0.28

Table-4 Silica content in sludge

S.No	Component	Value (%)
1.	First stage sludge	8.38
2.	Second stage sludge	4.50

Table-5 Percentage Silica removal in each stage

S.No	Component	Value (%)
1.	Removal in 1st stage	54.15
2.	Removal in 2nd stage	38.34
3.	Carryover in WL	7.51

Output from first stage causticizing

Silica in clarified green liquor = 1.71 gpl
Silica in dregs = 3.53 kg/m^3
Total silica output from first stage = 5.24 kg/m^3

Input to second stage causticizing

Silica in clarified green liquor = 1.71 gpl
Silica in lime (75%) = 4.53 kg/m^3
Total silica input to second stage = 6.24 kg/m^3

Output from second stage causticizing

Silica in white liquor = 0.28 gpl
Silica in lime sludge = 5.96 kg/m^3
Silica output from second stage = 6.24 kg/m^3

(% Silica removal in 1St and 2Nd stAge liquors)

% Silica removal in Green liquor = (Difference in Silica content of entering and Leaving liquor/ Silica in Raw Green liquor) x100

(% Silica carryover in white liquor)

% Silica Carryover in White liquor = (Silica in White liquor/ Silica in Raw Green liquor) x100

Table-5 shows the silica removal pattern in each stage. From this graph its evident that most of the silica is removed in 1st stage and remaining is removed in 2nd stage. It is clear from the results 92.5% of silica is removed from the system; only 7.5% is carried over as extra load. This gives lower silica content lime sludge in 2nd stage of 4.5% silica, which is more suitable for converting into CaO by reburning it.

CONCLUSION

Thus Two-stage causticizing is a very good economical solution for minimizing the silica content in the mud. Since this process is very simple, easy to adopt on plant scale and eliminates disposal problem of the lime sludge, it is a suitable for economic consideration. Also this process greatly enhanced the performance of lime kiln operations and thus the production cost of the burnt lime is reduced.
Second stage lime sludge can be used for reburning without any major

problem. First stage sludge can be used for Land filling, Cement industries. (TNPL is planning to use this sludge for cement production), controlling the pH of agricultural land, spreading on the land where effluent is being treated by using top soil.

EXPERIMENTAL

LIQUOR ANALYSIS:

The raw green liquor, Clarified green liquor (1st stage) and white liquor (2nd stage) are subjected to chemical analysis. The compositions of Na_2CO_3, NaOH, and Na2S are determined by standard methods of CPPRI TM IV-A1 [8].

SLUDGE ANALYSIS:

The 1st & 2nd stage sludge is analyzed. Loss on ignition, mixed oxides, Available CaO & Na_2O is determined by standard methods of CPPRI TM IV-A19, TM IV-A22, TM IV-A18 & TM IV-A20 respectively.

ACID INSOLUBLE SILICA ANALYSIS:

The silica content of the raw green liquor, Clarified green liquor (1st stage) and white liquor (2nd stage) are determined by standard methods of CPPRI TM IV-A3. The first and second stage sludge is determined by standard methods of CPPRI TM IV-A21.

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