Desilication of Green Liquor by Modified Plant Trial Strategies

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Rice and Wheat Straw are most commonly used raw materials in pulp and paper industries. These raw materials contain high silica contents and silica concentration even reaches as high as 20g/l. Major portion of this silica enters into black liquor during pulping and rest remains adhered with the fibers and travels into paper machine. This silica poses serious problems in its chemical recovery. Chemical composition of the black liquor particularly the extant of lignin and its stability and hemmicellulosic contents have profound influence on the selective separation of silica.

In this research attempt has been made to improve the desilication process by implementation of modified continuous lime feeding system. Laboratory trials for desilication were performed with H_2SO_4, CO_2 and lime addition which gave 89%, 83% and 90% silica reduction respectively. H_2SO_4 and CO_2 were not selected for plant trials due to operational problems and high cost. Plant trials were carried out with hydrated lime which gave reasonable silica reduction but not as better as obtained by the lab trials. Addition of lime was carried out by modified continuous lime feeding system which bypasses the problems encountered by lime settling and results in significant reduction in soluble silica in green liquor.

Key Words : desilication, lime treatment, black liquor, green liquor, reduction, modified lime addition.

INTRODUCTION

Due to high availability of non-wood raw materials and lack of forest, wheat and rice straw are major raw materials of the pulping industry. More than 60% of pulping in Pakistan is carried out from non-wood raw materials. Silica contents vary from 1.5 to 20% in these raw materials [1]. Many measures are carried for the reduction of silica before entering into pulping process. Most common among those are dry and wet cleaning process. Around 10% silica is removed through dry cleaning process. Wet cleaning process removes all sand and grains, which owes to 5-10% silica reduction [2].

Silicates in the raw materials dissolve in alkaline solutions easily and form sodium silicates. In the presence of calcium salts they tend to form calcium silicates. The calcium silicates and calcium sulfates form scales in liquor heat exchangers of the indirectly heated digesters. Scale formation in heat exchangers in a continuous digester system limits heat economy i.e. increases steam consumption of the digester system [4].

Desilication

The desilication of the black liquor has been reported by carbonation. Black liquor is an alkaline solution containing dissolved organics and inorganic components. The free alkali (NaOH and Na_2S) present in the black liquor undergoes neutralization during carbonation resulting in the lowering of the pH of the black liquor which is key step for precipitation of silica. The other inorganic components particularly the sulfur compounds like Na_2S and Na_2SO_3 also undergo chemical changes during carbonation. For instance part of Na_2S may get established by oxidation to $Na_2S_2O_3$ and

part of the sulfur from Na_2S may be stripped off in the form of H_2S due to lowering of pH. The later reaction takes place only in the final stages of the carbonation process and the former reaction takes palce in the initial stages of the carbonation.

The most important organic components of the black liquor are the sodium salts of lignin and organic acids. These components also undergo chemical changes due to neutralization and oxidation reactions which take place concomitantly during carbonation with flue gas containing 10-12 % CO_2 and 5 - 8% O_2. In oxidation process mostly slow condensation reactions take place due to free hydroxyl groups created by lowering of pH.

Basically there are two main methods for desilication of the green liquor. Where silica concentration is approximately 6gm/l. They are

1. By addition of cations e.g. lime treatment and

2. pH reduction (by passing carbon dioxide or flue gas).

Lime Treatment of Green Liquor :

Clarified green liquor is treated with slaked lime (Lime with 90% available CaO) at 90°C for 5-10 min. silica precipitates calcium silicates as per reaction:

$$Na_2SiO_3 + Cao + H_2O \rightarrow CaSiO_3 + 2NaOH$$

The precipitate is filtered in a battery leaf filters and it separates as a white precipitate containing over 90% calcium silicate. This method has been developed by Lurgi AG and adopted in a Italian wheat straw pulp mill using a NACO pulping process. The mill maintains a SiO_2 level of 80% in lime sludge. The mill does not hava yet a lime re-burning plant [4].

In year 1953, Gruen patented his so called Gruco Process for precipitating silica form black liquor by addition of lime or milk of lime. The lime treatment in this process is carried out for 5 - 10 min at 90 - 200°C with dilute black liquor with silica content of 7 - 10 gm per liter. The desilication efficiency is 90%. The precipitation reaction is rapid. However, with longer reaction period, the organic acids in black liquor also react with lime forming calcium organic compounds and tend to precipitate with calcium silicates. Apart of lime also react with sodium carbonate and sodium sulfate. The side reactions are thus.

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

$$Na_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2NaOH$$

In this process lime must be added in considerable access of the stochiometric quantity.

EXPERIMENTAL

Laboratory desilication with Sulfuric Acid :

Selective precipitation of silica from black liquor is possible by pH reduction; even some ligninates also precipitate first due to weaker acidic function than silicic acid. The phenol group of lignin in black liquor have an acidity of pK = 9.4 to 10.5 while silicic acid acidity is intermediate between these values i.e. pK = 9.8 [3]. Desiccation at the lab scale was planned with the addition of Sulfuric acid. Following parameters were selected for the sulfuric acid addition to the green liquor;

Table 1 : Sulfuric acid addition data

Parameters	Values
Sample Volume	1000ml
Initial pH of the sample	10.92
Initial carbonate concentration in the sample	250g/l
Final carbonate in the sample	86g/l
Sodium Sulfide in the sample	15g/l
Total acid added	85ml
Concentration of acid	98%

Table 2. Desilication results with time with sulfuric acid

Time Minutes	pH	Silica as SiO_2 g/l	Reduction in silica %
Blank	10.92	8.40	0
0.00	9.48	1.50	82
15.00	9.53	1.29	85
30.00	9.63	1.15	86
45.00	9.57	0.96	89
60.00	9.73	0.92	90
48(Hours)	9.84	0.43	96

Laboratory desilication with Carbon Dioxide:

Desilication by pH reduction is also carried out by carbon dioxide addition (carbonation). Pure CO_2 was added to the green liquor and its desilication characteristics were observed.

Table 3. Desilication with Carbon Dioxide

Green Liquid taken	pH		Silica		
ml	Initial	Final	Initial g/l	Final g/l	Reduction %
1000	10.69	9.49	4.00	0.67	83
1000	10.78	10.04	4.00	1.44	64
1000	10.74	9.74	4.00	1.08	73

Laboratory desilication with Hydrated Lime

Lime addition is the most common desilication method of desilication due to availability and low cost of lime. Lime treatment was first carried out at laboratory basis. Trials were planned at pilot plant basis and yielded following results:

Table 4 : Lime treatment Trial No. 1

Weak Black Liquor	100 Liters
Temperature	80 °C
Lime added	500 gm
Lime Index	60 %
Stirring time	20 minutes

Table 5 : Finding of Trial # 1

Parameters	Black Liquor	Lime addition & four Hours settling
Temperature °C	80	65
Total Solids %	8.9	9.0
Silica as SiO2%	0.59	0.21
Desilication %	00	64.5

Plant Scale desilication with Hydrated Lime

Lime addition at plant scale was carried out by modified lime addition process. If lime is added at conventional process, the lime settles in the lime slurry tanks. But by the modified lime with uniform consistency was added to the green liquor. The system is modified by installing variable speed screw pump for feeding of lime into dissolver and dilution water line with Rota meter. Fresh lime sample for high lime index was chosen for the plant trials. Lime was used in 1:3 and 1:4 ratios of slurry. Followings were the finding of the plant trial.

Table 6 : Lime treatment Trial # 2

Weak Black Liquor	100 Liters
Temperature	85 ° C
Lime added	150 gm
Lime Index	60 %
Stirring time	20 minutes

RESULTS AND DISCUSSION

Desilication with sulfuric acid gives best

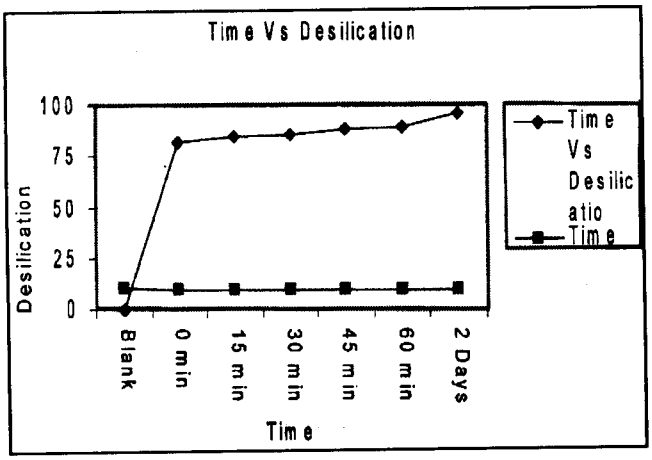
Table 7 : Finding of Trial # 2

Parameters	Black Liquor	Lime addition & settling 4Hrs	Lime addition & settling 24 Hrs
Temperature °C	85	65	26
Total Solids %	8.7	8.9	9
Silica as SiO_2%	0.485	0.270	0.222
Desilication %	00	44	44.6

Table 8 : Lime treatment Trial No. 3

Weak Black Liquor	100 Liters
Temperature	80 ° C
Lime added	1500 gm
Lime Index	60 %
Stirring time	20 minutes

results at the setting time of 48 hrs. the results are satisfactory even at 60 minutes settling and gives 90% desilication which is enough for any of the process but if applicable at the plant scale. If we plot a graph for the desiccation by sulfuric acid we find the following curve.



Desilication by sulfuric acid gives encouraging results even at the settling time of 15 min. i.e. 85% which is raised to 90% if the settling time is increased by 60 minutes.

Table 10 : Lime treatment plant Trial

Green liquor density	1.13 to 1.15
Lime Index	74%
Slurry concentration	30%
Lime to silica ratio	Variable
Settling time	10-12 Hours
Silica in green liquor	~ 7.0 g/l

Advantages and Disadvantages of Sulfuric acid desilication

Major advantage of desilication by sulfuric acid is that the deposition of silica and its application is rather simple. It causes desilication by both means of pH reduction and forming insoluble sulfates of silica. Its disadvantages include high cost of sulfuric acid at plant scale and Sodium losses due to the formation of Sodium Sulfate which acts as inert material in the recovery loop.

Desilication with carbon dioxide have not given some extra-ordinary results. Up to 83% desilication have been achieved by carbonation. One advantage of this process is the utilization of the flue gases which are costless. But this method of desilication has been developed for black liquors and it requires filtration and causes foaming in the

Table 9 : Finding of Trial # 3

Parameters	Black Liquor	Lime addition & settling 1Hr	Lime addition & settling 4 Hrs	Lime addition & settling 24 Hrs.
Temperature °C	80	70	55	26
Total Solids %	8	8.4	8	8
Silica as SiO_2%	0.46	0.362	0.113	0.075
Desilication %	00	22.6	76	84

Table 11. Finding of Plant Trial

Sr. No.	Lime feeding rate	Density of Green Liquor	Lime/Silica ratio	Silica Results	Reduction
	1/h	g/l	times	g/l	%
1	696	1.14	5.4	1.5	79
2	400	1.18	3.1	5.8	17
3	400	1.21	3.1	5.2	26
4	433	1.15	3.53	5.5	21
5	390	1.15	3.18	5.0	29

carbonation column and restricts the passage of flue gases leaving the column.

Finally the desilication with lime have given significant results. Desilication have been found up to 84%. Lime addition have many advantages like low cost, less lime requirements. less lime sludge generation, less loss of organics, loss of sulfate ions is reduced as side reactions are suppressed. Therefore lime treatment has been selected for the plant trials. By considering work of previous scientists and plant base lime addition problems new method for lime addition has been developed. Lime addition have not proven as better results as that by laboratory trials but this method subsidizes better lime addition and desilication and can be adopted for future plant development particularly lime treatment and ordinarily additions of setting chemicals like lime.

Modified Lime Feeding System

Lime feeding system already in practice comprises of mixing tanks and centrifugal pumps. Plant trials and even regular desilication had to be stopped due to the blockage in lime feeding pump and lines. For the recent plant trials the system is modified by installing variable speed screw pump for feeding of lime into the dissolver and the dilution water line with Rota meter. 30% slurry was made by addition lime powder and water into the mixing tanks. Lime mixing and concentration is maintained by the evolution of high pressure from the bottom of the tanks.

CONCLUSION

Laboratory trials and plant trial with lime and modified lime feeding system have revealed following conclusions.

1. Desilication of green liquor can be achieved up to 90% with sulfuric acid but their plant applications have some limitations.
2. Desilication with carbon dioxide addition can produce results up to 83% but its plant application faces problems like foaming, lignin settling and localized carbonation.
3. Lime addition with modified lime addition process have many advantages and can be adopted for future lime addition developments.

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