Removal of Soluble Silica From Sulphate Green Liquor

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SUMMARY

Laboratory studies on sulphate green liquor desilication showed that silica, 80-90% of the original, could be removed from the green liquor by carbonation at 75-95°C with subsequent settling and filteration. There was 94-99% sodium sulphide loss on carbonation of green liquor. The sulphur was lost as hydrogensulphide, which was found to be directly proportionel to silica removal at 75-95°C temperature range; while at lowcr temperature range (24-26°C) it was found to be 10-20% only at 80% silica removal.

Experiments were also carried out to re-utilize the lost sulphur, again in the system. Results chowed that escaped hydrogen sulphide gas can be absorbed, 40-55% in white liquor at 80-90% silica removal at a temperature range of 80-90°C. It was noted that Total Titrable Alkali of green liquor decreased by 6.7 gpl. while white liquor Total Titrable Alkali decreased by nearly 30% due to the formation of sodium Sulphate and sodium thiosulphate.

INTRODUCTION

In the manufacture of pulp, cellulose is separated from plant material by various digestion process in which alkali is employed as digesting medium. To make pulping process economical, it is very necessary to recover this alkali for re-utilization in the system. In recovery of alkali, however, certain difficulties are experienced when black liquor contains high silica content.

Silica in the form of soluble alkali compounds used to deposit as a hard scale on the inside of the evaporator tubes, pans and possibly also coating the tubes and walls of boilers and furnance (1-2). This decreases the heat economy (apart from it, it requires occasional shutdown for cleaning purpose).

In bamboo based paper mills the source of

silica entrance in chemical recovery is through bamboo and lime which contain 1.5-3.0 and 5-15% silica respectively. High concentration of the silica in lime sludge also creates serious problem during reburning in kiln for lime recovery. Thus nearly 0.5 T of lime sludge, per ton of paper, has to be disposed off by the Paper Mills.

There are some reports and patents on the silica removal from alkaline liquors by various investigators (3-9) but no information has been received as to operating the silica removing process in any factory practically.

EXPERIMENTAL

(a) Carbonation

Carbonation of green liquor was done by passing Carbon Dioxide gas at a rate of 2-3L/Min into green liquor kept in round bottom three necked flask. Carbon Dioxide gas was passed into green liquor through one side mouth while the escaping gases were released from the other side mouth of the flask. Green liquor containing flask was kept on hot plate and temperature of the reaction mix-

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ture was maintained by the help of an energy regulator connected in the line. For sulphur recovery released gases were passed into two white liquor containers, containing 1L of Sodium Hydroxide (100 gpl) solution each, counter-currently with the help of polythene tubings. Volume of the green liquor was maintained time to time during the experiment by adding distilled water into the green liquor.

(b) Green Liquor Analysis

After the experiment, silica, thus precipitated was filtered out and the clear filterate was analysed for silica and Na_2S (Sodium Sulphide) contents. End pH, Total Titrable Alkali and in some case Total Active Alkali and Sodium carbonate contents of green liquor were also found out. Silica content in green liquor was determined by calorimetric method. In this method, after dilution of reaction mixture, silica was determined as molybdnum blue, the transmittance of which can be read directly by the help of calorimeter. Silica content was thus calculated from standard curve of silica concentration Vs transmittance. Results are recorded in Table 1A-1D.

Sodium sulphide content was found out by the difference of total reducing compounds, "TRC" $(Na_2S+Na_2SO_3+Na_2S_2O_3)$ and sulphide free reducing compounds, "SFRC" $(Na_3SO_3+Na_2S_2O_3)$ according to Tappi standard method. "TRC" was found out by iodometric titratation while for "SFRC" Sodium Sulphide was first removed by precipitation which was done by freshly prepared suspension of Zinc carbonate made by mixing equal volumes of molar solutions of Zinc sulphate and sodium carbonate, pricipitate thus formed due to sodium sulphide was filtered out and "SFRC" was found out in the filtrate by iodometric titration. Results are recorded in Table 1A-1D.

TABLE-IA DESILICATION	OF SULPHATE GREEN	LIQUOR BY CARBONATION
Or Lig, initial silica &	Na Scontents were 878	24 47 and recnectively)

EXPT.	EXPT.	EXPT.	EXPT.	EXPT.
No. 1	No. 2	No. 3	No. 4	No. 5
····· , ········				11000
1000	1000	1000	1000	1000
2.0	2.0	20	2.0	20
90	90	90	90	90
1.0	2.0	3.0	4.0	50
10.95	10.95	10.95	10.95	10.95
10.90	10.50	10.25	10.10	9 90
			10110	5.50
8.00	7 80	3 40	7.00	7.12
2.44	4 88	58 53	2.90	2.15
	1,00	50.55	04.05	74.02
24.06	27.67	17 32	11.76	5 48
1.67	7.56	29.20	51.92	77.54
	EXPT. No. 1 1000 2.0 90 1.0 10.95 10.90 8.00 2.44 24.06 1.67	EXPT. EXPT. No. 2 1000 1000 2.0 2.0 90 90 1.0 2.0 10.95 10.95 10.90 10.50 8.00 7.80 2.44 4.88 24.06 22.62 1.67 7.56	EXPT. EXPT. EXPT. EXPT. No. 1 No. 2 No. 3 1000 1000 1000 2.0 2.0 2.0 90 90 90 1.0 2.0 3.0 10.95 10.95 10.95 10.90 10.50 10.25	EXPT.EXPT.EXPT.EXPT.EXPT.No. 1No. 2No. 3No. 410001000100010002.02.02.02.0909090901.02.03.04.010.9510.9510.9510.9510.9010.5010.2510.10 8.00 7.803.402.902.444.8858.5364.6324.0622.6217.3211.761.677.5629.2051.92

 TABLE—1B DESILICATION OF SULPHATE GREEN LIQUOR BY CARBONATION (Gr. Liq.initial silica & Na2S contents were 8.2 & 24.47 gpl respectively)

PARTICULARS	EXPT. No. 1	EXPT. No. 2	EXPT. No. 3	EXPT. No. 4	EXPT. No. 5	EXPT. No. 6
A-EXPT. CONDITION ;					· · · · · · · · · · · · · · · · · · ·	
(1) Green liquor, ml	1000	1000	1000	1000	1000	1000
(2) Co_2 gas flow, L/Min	2.0	2.0	2.0	2.0	2.0	2.0
(3) Temperature °C	75	75	75	75	75	75
(4) Time of carbonations, hrs.	1.0	2.0	3.0	4.0	5.0	6.0
(5) Initial pH	10.95	10.95	10.95	10.95	10.95	10.95
(6) Final pH	10.55	10.30	10.10	9.95	9,90	9.85
B-RESULTS						
I-Silica						
(a) Content, gpl	7.80	4.16	3.12	2.80	1.87	1.10
(D) Removal, %	4.88	49.26	61.95	65.85	77.19	86.70
(2) Sodium sulphide						
(a) Content as Na_2S , gpl.	19.79	18.21	12.05	7.62	5.02	0.975
(b) Loss %	19 09	25 58	50.74	68.8 5	79.48	96.01

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PARTICULARS	EXPT.	EXPT.	EXPT.
	No. 1	No. 2	No. 3
 A-Expt. condition Green liquor, ml CO₂ gas flow, L/Min. Temperature, °C Time of carbonation, hrs. Initial pH Final pH 	1200	1200	1200
	2.5	2.5	2.5
	85	85	85
	2.5	4.0	6.0
	10.95	10.95	10.95
	10.15	9.85	9.70
 B-Gr. liq, Analysis Silica Content, gpl Removal, % Sodium sulphide Content as Na₂O, gpl Loss, % 	1.30	1.10	1.10
	84.14	86.09	86.70
	11.72	5.27	1.39
	50.13	77.58	94.08
 C—Sulphur (as Na₂S) recovery (a) 1st container (1 L NaOH) (i) Na₂S as Na₂O, gpi (ii) Recovery, % (b) 2nd container, (1L NaOH) (i) Na₂S as Na₂O, gpl (ii) Recovery, % 	5.22	11.50	10.69
	36.92	52.56	40.29
	0.72	0.52	1.20
	5.09	2.38	4.52
(c) Total recovery	42.01	54.94	44.81
D-Net sulphur loss	29 .07	34.96	51.91

TABLE-1C DESILICATION OF SULPHATE GREEN LIQUOR BY CARBONATION (Gr. Liq. initial silica & Na₂S contents were 8.2 & 24.47 gpl respectively)

TABLE-1D DESILICATION OF SULPHATE GREEN LIQUOR BY CARBONATION (Gr. Liq. silica content was 8.2 gpl while T.T.A., T.A.A. Na₂CO₈ and N₂S contents were 109.12, 44.02, 65.10 and 23.78 respectively)

			-					
Particulars	Expt	Expt	Expt	Expt	Expt	Expt	Expt	Expt
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
 Expt. Condition Green liquor taken, ml CO₂ gas flow, L/Min. Temperature, °C Time of carbonation, hr. Initial pH Final pH 	1000	1000	1000	1000	1000	1000	1200	1200
	2.0	2.5	2.0	2 5	2.0	2.5	2.0	2.0
	95	95	85	85	75	75	26	24.5
	6.0	6.0	6.0	6 0	6.0	6.0	4.0	4.0
	10.95	10.95	10 95	10.95	10,95	10.95	10.95	10.95
	9.90	9.7	9.85	9.60	9.85	9.65	9.90	9.80
 Gr. Liq. Analysis: Silica (a) Content, gpl (b) Removal, % T.T.A. as Na₂O, gpl T.A.Ado- 4. Na₂CO₃ -do- 5. Sod. Sulphide (a) Content as Na₂O, gpl (b) Na₂S. Loss% 	1.20 85.30 104.78 4.34 100.44 1.414 94.00	0.84 89.7 109.12 4.96 104.16 0.399 98.30	1.10 86.70 106.64 4.34 102.30 1.076 95.40	0.72 91.20 106.02 4.96 101.06 0.300 98.70	1.10 86.70 106.64 4.34 102.30 0.975 96.04	0.80 90.20 102.30 4.34 97.96 0.206 99.00	1.46 81.77 102 92 17.97 23.53	1.33 83.78 102.30 19.44 17.28

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RESULTS & DISCUSSION

Silica, 80-90% of original, could be removed from the green liquor by lowering the pH to 9.5-10 at 75-95°C by carbonation (Fig-1, Table 1A-1C). It is observed that silica separates as easily filterable granules at lower pH, while at higher pH it forms gel like precipitate which takes time for settling.



Soda green liquor can effectively be desilicated by carbonation without any chemical loss while in the case of sulphate green liquors sulphidity is greatly affected (Fig 2). Optimum condition, at which sodium sulphide loss can be sacrified, cannot be found out as there is a leanear relation hip between sodium sulphide loss and silica removal from the sulphate green liquor by carbonation (Table 1A-1D)

Desilication of sulphate green liquor is only useful if the lost sulphur can be re-utilized again in the system. Experiments were also carried out in this respect. Results (Table 1C) showed that nearly 40-55% of the escaping, hydrogen sulphide gas, during carbonation of sulphate green liquor can be absorbed by white liquor at a temperature range of 80-90°C. The percent absorption of hydrogen sulphide gas, however, can be increased by decreasing carbonation or white liquor temperature (Table 1 D) although silica removal will remain the same (80-90%).

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