Desilication Efficiency versus Sulfide Loss in the Carbonation of Green Liquor

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SUMMARY

The desilication of Green liquor by carbondioxide has been investigated at different pHs ranging from 10.25 to 9.35. It has been found that maximum desilication is achieved at pH below 9.6. A sharp decrease in sulfide concentration with concurrent drop in sulfidity has also been observed below pH 9.6. The mode of sulfide loss has been studied and it has been found that most of the sulfide is converted to sulfur. The various factors connected to this has been discussed and an attempt has been made to delineate the mechanism of conversion of sodium sulfide to sulfur. The effect of desilication on other constituents of green liquor, on the efficiency of subsequent causticization and the sludge composition has also been studied.

INTRODUCTION

The fibrous raw materials of Indian origin, like bamboo, bagasse etc. contain a high percentage of silica (2–4%) which is carried over in the kraft liquors in the soluble form of sodium silicate. The accumulation of silica in the recovery system poses many problems such as :

1. Hard scale formation on evaporator tubes, furnace walls etc.
2. Beehive formation in the recovery boiler.
3. Poor settling of lime mud in the causticizing process.
4. Improper burning of lime mud in the reburning process.

Therefore, the removal of silica from black and green liquors will reduce these operational problems to a considerable extent and also improve the over-all economy of the process as a result of the reburning of the sludge. Various methods have been suggested by many of the desilication of weak black liquor and green liquors (1–6).

As a part of our comprehensive scheme on desilication studies of spent liquors, with the ultimate view of improving the overall economy of the process by obtaining a reburnable sludge, we have started investigations on all the aspects of green liquor desilication. In this communication, we present results of part of our studies conducted in this direction.

In an interesting recent publication by Veeramani and Idress(7) it has been claimed that effective desilication of green liquor can be achieved by carbonation. The authors have demonstrated in this publication that 80–90% of silica can be removed by carbonation at 60–80°C at a pH of 9.5. The silica residue did not pose any problems from point of view of filtration. Desilication of green liquor was also found to improve the causticizing efficiency. The authors had also suggested the reburning the lime sludge in view of the reduced silica content of the sludge. It has also been pointed out by these investigators that it was necessary to limit carbonation to pH 9.5, since H_2S is released in appreciable concentration at lower pH levels. However, not much of experimental data on this important aspect viz. pH effect on sulfur losses was provided by them in the paper.

We have carried out a detailed investigation on the carbonation of green liquor at various pH values and its effect (a) on the extent of desilication (b) on the concentrations of various components of green liquor including sulfites (c) on the causticizing efficiency and (d) on the composition of lime mud, have been thoroughly examined and the results of this study are presented in this paper. The probe on the effect of pH in the carbonation of green liquor has been conducted in a detailed way, so that a point of proper balance between desilication efficiency and sulfidity loss can be found out. This becomes especially important, when there is a decrease in input silica as well be the case when increased amounts of hardwoods, which contain less of slilica, are used

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in the process. The basic chemistry aspects of this process has been also looked into in this paper.

EXPERIMENTAL

The clarified Green liquor from the causticizing section of our mills was collected and analysed for its constituents. The green liquor was preheated to a temperature range of 60–80°C and carbon-dioxide gas from the gas cylinder was bubbled through it (130–140 bubbles per minute) with intermittant shaking so as to bring down the pH to the different levels (viz. 10.1, 10.0, 9.9, 9.75, 9.7, 9.6, 9.45 and 9.35). The carbonated liquors were filtered and the filtrates were causticized at 85–90°C using a lime of purity 71.3% as CaO added 10.0% more than the stoichiometric requirement. The results pertaining to the green liquor analysis before and after carbonation and of their corresponding white liquors and lime mud are presented in the Tables—I to IV.

The composition of individual sulfur compounds in green liquor were found out as per standard TAPPI method (T-624-0S-68).

RESULTS AND DISCUSSION

The results of the studies are presented in Tables—I, II and IV.

The following facts emerge from our study :

1. Effective desilication is achieved below pH of 9.6

2. Considerable loss of sulfidity of the green liquor (as shown by the loss of sulfides) is noted, especially below pH 9.6.

3. As a result of carbonation, the free sodium hydroxide present in green liquor is converted into sodium carbonate the reby increasing the lime requirement for causticization.

From this, it is clear that although desilication is achieved, it is at the cost of sulfidity. Thus the sulfidity of uncarbonated green liquor which was 11.90% drops down to 4.96% for the carbonated green liquor (after causticization). As is evident from the data the decrease in sulfidity is marginal upto pH 9.7 and a very sharp decrease occurs when the pH is below 9.6. We have also examined the mode of sulfidity loss. We found that there was not much difference in the total sulfur content in the untreated green liquor as well as carbonated green liquor at pH 9.45 (vide Table—IV), although there is a considerable decrease in the sodium sulfide concentration.

In their paper on carbonation of green liquor, Veeramani and Idress have proposed that at the pH of 9.5 and below, the loss in sulfidity occurs, because of release of considerable quantities of H_2S which escapes into the atmosphere. This proposal does not appear to be consistent with the accepted tenets of the theory of Acids and Bases. The pka of

hydrogen sulfide (the dissociation of both the steps), carbonic acid, and silicic acid are presented in Table-V.

It follows from the pka data that the concentration of free H_2S will be very much negligible (approx. 0.3%) at pH 9.5, since the first pka of H_2S is about 7.0. The concentration of both free H_2S and $(SH)^-$ at various pH values can be calculated from Henderson equation. No doubt free H_2S will be liberated from green liquor solution in appreciable quantities by passing carbondioxide through it. It is not at a pH of 9.5 but only when the pH comes down below 6.5.

Pomeroy has calculated a series of factors showing the amount of total sulfides-existing as H_2S at various pH values at 20°C in aqueous solution vide Table—V [8]. The pH profile of H_2S dissociation given in Rydholm is also in conformity with this[9].

It would also be pertinent here to refer to the observations made by Nordell[10] on the treatment of waters containing hydrogen sulfide. "In treating sulfur waters, the important and unfortunate fact is that carbon dioxide comes out much more easily than the more soluble hydrogen sulfide. Also as it comes out, the pH value, (assuming a normally alkaline water), rises, this upsets the equilibrium between alkaline sulfides and hydrogen sulfide so that the reaction proceeds in the wrong direction for the removal as hydrogen sulfide....if the water had a pH value of 9.0 only a little over one-half of one percent would be present as hydrogen sulfide and the reminder would be present as an alkaline or alkaline earth sulfide "[10].

On the basis of these data the possibilities of the formation of H_2S and its subsequent escape into the atmosphere cannot be rationally explained. We feel in view of the facile oxidisability of some of these sulfur compounds, part of which may be oxidised to colloidal elemental sulfur and therefore not lost fully. The fact that there is not much difference in the total sulfur content of untreated and carbonated green liquor lends support to our proposal.

We could not, however, exactly estimate the colloidal sulfur present in the supernatint liquor, as extraction, with carbon disulfide did not give reproducible results. But the increase in polysulfide concentration observed clearly points out to the formation of elemental sulfur. A microscopic examination of the CS_2 extract also revealed the presence of needle like crystalling sulfur. Further in the precipitated sludge we have found out that sulfur is present. The carbonated sludge at pH 9.45 (Wherein maximum desilication was observed) contained 71% silica (equivalent to 92–95% silica in the original liquor), 17% sodium carbonate and rest was mostly elemental sulfur. We have extracted this with carbon disulfide and on evaporation recovered most of it. We have also estimated the sulfur by gravimetric estimation in the sludge by oxidising it. Thus it follows that observed sulfidity loss at pH 9.45 is not due to conversion of sodium sulfide to the free-

112

hydrogen sulfide but due to the oxidation of part sodium sulfide to elemental sulfur.

We have also tried to delineate some aspects of the mechanism of oxidation of sodium sulfide in green liquor at pH 9.45 to elemental sulfur. A perusal of the oxidation-reduction potential data reveals that the reduction of carbon-dioxide to oxalic acid has a negative potential of 0.490 while for the oxidation of sulfideion to elemental sulfur the potential is 0.508 volts (equations (1) and (2)).

$$S^{-2} \rightleftharpoons S^{\circ} + 2e \qquad .. \quad (1)$$
$$2Co_2 + 2H^+ + 2e \rightleftharpoons H_2C_2O_4 \qquad .. \quad (2)$$
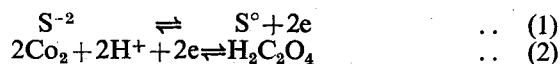
Thus it is possible that the two electrons released by oxidation of sulfide to sulfur will reduce CO_2 to oxalic acid. We have indeed found the presence of oxalate ions in the system. Further work on the mechanistic aspects is underway.

Thus it is quite obvious that the proposal of sulfide loss through H_2S evolution at pH 9.5 is not found to be correct but the sulfide loss is actually due to the precipitation of elemental sulfur.

In our studies we have also found out that as a result of carbonation, beyond pH of 9.45 significant amount of sodium carbonate was also precipitated along with the sludge. This is evident clearly from the decrease in TTA of carbonated green liquor and also the presence of Na_2CO_3 in the sludge.

Moreover, as is obvious, as a result of carbonation, all free sodium hydroxide in green liquor is converted into sodium carbonate which will increase the lime requirement in the causticizing stage.

A perusal of our data further reveals, that inspite of desilication of green liquor, the sludge obtained by causticizing with lime still contain about 3% silica which is obviously from the lime used for causticizing (approx. 6.3%). The presence of silica in these quantities in the lime mud may affect the reburning process. Further studies to evaluate the economics of reburning of this sludge is being undertaken.

However, this points out to the fact, if reburning is to be successful the lime used for causticizing as well as the make up lime should as well also contain minimum amount of silica.

In this study, therefore, we have confined ourselves to the pH profile in the carbonation of green liquor and its effect on the concentrations of various components of green liquor.

TABLE—I

ANALYSIS OF GREEN LIQUOR

Particulars	Plant Green Liquor	Carbonated Green Liquor							
		1	2	3	4	5	6	7	8
pH at 60 °C	10.25	10.10	10.00	9.90	9.75	9.70	9.60	9.45	9.35
T T A as Na_2O, gpl	119.04	119.80	117.80	119.04	119.04	118.42	115.94	113.46	96.30
Na_2CO_3 as Na_2O, gpl	76.88	99.20	106.64	107.82	109.12	108.50	108.50	109.74	93.20
NaOH as Na_2O, gpl	29.76	8.68	—	—	—	—	—	—	Nil
Na_2S „	12.40	11.16	11.16	9.92	9.92	9.92	7.44	3.72	3.10
Acid Insolubles gpl	7.10	7.14	6.66	6.636	2.01	1.32	0.66	0.448	0.448

TABLE—II

CAUSTICIZING OF GREEN LIQUOR

Particulars	1	2	3	4	5	6	7	8
pH of Green liquor at 60° C	10.25	10.1	10.0	9.9	9.75	9.7	9.6	9.45
Settling rate, %	17.0	17.0	17.5	18.0	24.0	25.0	29.0	30.0
Suspended solids, gpl	191.37	185.52	206.17	209.17	211.53	205.53	213.33	193.77
SiO_2 in the sludge, %	8.76	7.87	6.98	6.71	4.85	4.0	3.62	3.36
Analysis of White Liquor								
T T A as Na_2O, gpl	121.60	119.04	119.04	114.08	115.32	114.70	116.56	112.84
NaOH ,,	94.94	91.14	89.90	89.28	89.90	80.60	81.22	71.30
Na_2CO_3 ,,	15.50	16.74	17.36	14.88	15.50	24.18	27.90	37.82
Na_2S ,,	11.16	11.16	11.16	9.92	9.92	9.92	7.44	3.72
Causticizing Efficiency	84.61	84.55	83.79	85.70	85.29	76.51	74.46	65.31
Sulphidity, %	11.90	10.90	11.40	10.00	10.00	10.96	8.40	4.96
Silica, gpl	0.640	0.472	0.46	0.452	1.276	1.32	1.76	1.812

Lime purity = 72.0% CaO,   Silica = 6.3%

TABLE—III

LIME SLUDGE ANALYSIS

Particulars	Plant Green Liquor	1	2	3	4	5	6	7
Moisture, %	13.72	—	0.61	0.44	0.35	0.47	0.87	0.07
Losson Ignition, %	31.12	37.34	38.25	37.70	35.79	41.79	41.25	40.96
Free CaO, %	12.80	15.60	1.10	2.20	—	0.60	0.60	0.60
Total CaO, %	54.79	52.42	49.68	50.96	54.87	52.95	56.06	51.31
MgO, %	4.17	1.68	2.80	2.82	2.80	—	—	3.63
R_2O_3, %	0.28	—	0.22	0.62	0.35	0.28	0.50	—
Acid Insolubles, %	8.76	7.87	6.98	6.71	4.85	4.00	3.62	3.36

TABLE–IV

SULFUR COMPOUNDS IN GREEN LIQUOR

S. No.	Particulars	Normal Green liquor	Desilicated liquor
1.	pH at 60°C	10.25	9.45
2.	Na_2S as Na_2O, gpl	12.40	3.72
3.	$Na_2S_2O_3$ "	1.019	1.019
4.	Na_2S "	0.4367	0.946
5.	Na_2SO_4 "	2.81	2.833
6.	Na_2SO_3 "	0.859	0.466
7.	Total sulfur as sulfur, gpl	7.99	7.11

TABLE–V

FREE HYDROGEN SULFIDE CONCENTRATIONS AT VARIOUS pH VALUES IN AQUEOUS SOLUTIONS OF ALKALI AND ALKALINE EARTH SULFIDES[8]

pH	% of free H_2S
5.0	98.0
6.0	86.0
6.5	67.0
7.0	39.0
7.5	17.0
8.0	6.0
9.0	0.63

TABLE–VI

Particulars	pka 1	pka 2	Temp·
Silicic acid (H_2siO_3)*	9.38	12.0	
Hydrogen sulfide (H_2S)*	6.88	14.15	20°C
Carobnic acid (H_2CO_3)**	6.37	10.25	
Water (H_2O)***	15.70	—	

* Comprehensive inorganic chemistry, volume I, J.C. Bailer, Pergamon Press, 1973.

** Hand Book of Chemistry and Physics, 50th Edition, 1969–70, D-119, The Chemical Rubber Co. Cleveland, Ohio.

** Organic chemistry, J.B. Handrickson, D.J. Cram and G.S. Hommond Mcgrawhill, London (1970) P.304.

REFERENCES

1. Indian Patent—Chemical Abstracts **56**, 3126 (1962).
2. Indian Patent—ibid **60**, 761 (1964).
3. Panda A., Das, Papier **18**(4), 169 (April 1964).
4. Tsuji, H., and Ono, K. Chemical Abstracts **66**, 3980 (1967).
5. Isono, Z., and Ono. K, ibid **68**, 88335 (1968).
6. Srivastava, P.B., and Mandal, G., "Research and Industry" **22**(2) 80 (1977) and papers cited therein.
7. Veeramani, H., and Idrees, M., Indian Pulp and Paper **31**, 17 (April-May) 1977.
8. Pomeroy, R. J.Am. Water Works Assoc. **33**, 943 (1941).
9. Rydholm, S. Pulping Process, Wiley Interscience, N.Y. (1965) p. 584.
10. Nordell, E., "Water treatment for Industrial and other uses", Reinhold Book Corporation, New York (1961), Second Edition p-110.