Breakthrough in desilication technology–opens up opportunities for efficient processing of non-wood black liquor and lime sludge reburning

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ABSTRACT

Efforts for removal of silica from spent pulping liquors have been going on since last few decades. In India carbonation technique is extensively studied method for desilication. Ten years of continuous research on various carbonation methods, enabled Central Pulp & Paper Research Institute (CPPRI), to come out with a carbonation technique capable of selective precipitation of easily filterable silica Based on this process technology a mill scale desilication plant was designed and developed and became operational in May, 1989 at Hindustan Newsprint Limited (HNL), Kerala. The results of desilication on mill scale have been highly encouraging. More than 80% desilication was achieved with easily filterable silica containing less than 0.5% lignin. The plant has been working satisfactorily and indications of positive advantages of removal of silica are clearly felt. The present paper highlights the development and operational experience of commercial scale desilication plant.

Introduction :

The need for removal of silica before the black liquor enters the chemical recovery system, has been felt long back, with the experience of adverse effects of silica in pulping and recovery cycles Adverse effect have been critically analysed and discussed at length (1, 2, 3), Silica not only forms hard deposits on evaporator tubes & furnace walls, it also affects the causticization process adversely. Lime treatment method was extensively studied in India, however the technique could not become commercially attractive due to massive quantities of lime (200–400% on silica basis) and problems in filtration of resulting Ca-silicate sludge (4). Desilication of black liquor and green liquors using carbonation method is another widely accepted method. The precipitation of silica by carbonation dates back to 30's and since then efforts are continuing to achieve selective precipitation of silica.

Although silica starts precipitating first, but the pH ranges for silica precipitation and lignin precipitation are in close proximity (5). Thus quantitative & selective precipitation of silica before lignin starts precipitating. becomes the important criteria in desilication involving carbonation. Many researchers worked on carbonation technique in the past but could not succeed in achieving selective silica precipitation (6, 7). Rakta Pulp Mill in Alexandria, Egypt, has also set-up a desilication plant (8). However, there is no information about any commercial desilication plants based on Rakta Technology.

CPPRI initiated the work on desilication of bamboo black liquor employing carbonation method in early 80's and the project was assisted by UNIDO/SIDA. Extensive research work on basic chemical aspects of carbonation of black liquor: carbonation with different methods and filtration & characterization of silica sludge was carried out for more than five years. Based on semi pilot plant scale data, a mill size prototype desilication plant was designed, developed and commissioned in May 1989.

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each. The three tanks are in series. Black liquor from storage tank is pumped to first tank from where it overflows into second and then to the third tank. As high pH liquor enters the first tank, it has two reactors. Black liquor in each reactor tank is circulated by high capacity (1400m³/hr), low head and low rpm propeller centrifugal pumps having axial flow. Mixing of flue gas with black liquor takes place at the reactor heads situated on the delivery of the circulation pumps. The end of the delivery pipe remains immersed below the liquid level. The carbonation is done slowly in three stages. In the first stage the pH is brought to about 11.0 in first tank followed by pH 10.5 and around 10.1 in second and third tanks The low rpm circulation facilitates in avoiding the break-up of silica flocs. The carbonated liquor from last tank is taken to hot retention tank, where the size of the silica flocs is allowed to build-up at about 80°C. After hot retention the carbonated liquor goes to horizontal DELKOR Belt Filter. The liquor is separated from silica sludge on belt filter. The sludge washings and filtered black liquor are combined & taken to realkalization tank, where the pH of the carbonated and filtered black liquor is raised to about 12.0, before sending to evaporation. The operation of plant is controlled by Central control Panel.

Operating Experiences :

Although there are minor problems like foam formation, difficulties in on-line pH monitoring, the performance has been, by & large, highly satisfactory. One of the main task of achieving precipitation of selective and easily filterable silica mass has been achieved successfully. This washed silica contain significantly less quantities of lignin and sodium and almost white in color. The results in Table—4, show the performance of desilication plant with varying feed rates. Over all desilication efficiency was about 75—80% with silica sludge containing more than 90% SiO_2. The silica sludge on an average contained about 0.5% lignin and 1.0% sodium.

TABLE-4

Results of Desilication on Plant Scale*

Parameters	Run Numbers 1	2	3	4
Feed liquor				
Total solids, % w/w	20.9	17.0	17.6	16.4
RAA, g/l as Na_2O	7.8	5.3	5.2	6.1
SiO_2. % w/w	2.83	2.60	1 80	2.36
pH at 30°C	12.4	12.5	12.3	12.4
Filtration				
Feed, m³/hr	9	10	12	18
Temperature °C	62	65	68	66
Wash water, m³/hr	3.4	1.3	2.2	0 75
Belt speed, m/min	3.5	3.0	3.0	4.0
Silica sludge**				
Moisture, %	76.0	74.0	74.5	78.0
Ash at 600°C	92.0	92.0	91.9	89.0
SiO_2, %	91.0	91.0	91.0	87.6
Lignin, %	0.53	0.41	0.48	N.D.
Sodium, %	2.5	1.8	2.4	N.D.
Desilication, %	77.4	75.0	78.5	80.9

*Kraft black liquor from pulping of 80% bamboo and 20% reed.

**Expressed on o.d. sludge. Flue gas flow—400m³/hr having 8—10% CO_2.

TABLE-3

Result of Stepwise Carbonation in SBR

Expt. No.	Initial Liquor pH 30°C	SiO₂ g/l	Flow lit/min	Desilicated liquor pH 30°C	SiO_2 g/l	Desilication %	Sludge Filtration Sec. 500 ml.	Organics%*	SiO_2 %
1.	12.65	7.5	0 6	10 7	2.2	71	90	2 2	82
2.	12.29	7.9	0 4	10.5	1.2	85	17	1.3	90
3.	12 66	7 5	1.5	10 6	2.1	72	25	—	89
4.	12 30	8.5	1.3	10 7	2.4	71	30	1.7	84

* Determined by colorimeter (washed sludge).

New Opportunities in Black Liquor Processing and Lime Sludge Reburning through Desilication :

Considering the multifarious operational and environmental advantages, the desilication, in mills using silica rich fibrous raw materials, is going to provide new opportunities like efficient operation of chemical recovery system, reduction in solid waste through lime reburning etc. Mills hitherto not having equipped with chemical recovery system, due to problem of silica are now thinking of recovery installations. Lime reburning in mills using bamboo and other silica rich raw materials would enormously help in overcoming the solid waste disposal problems. The cost of reburnt lime has been calculated based on extensive economic calculation and is found to be at least 20% lower than the purchsed burnt lime, even of gains from sale of silica are not teken into account. Silica sludge can be purified and converted into a costly marketable product. The brief economics of desilication and lime reburning installation for a 100 tpd mill is given in Annexure—1, which clearly indicates that it is a profitable proposition with considerable profit and short pay back period.

ANNEXURE—1

Economics of Desilication and Lime Sludge Reburning Plant For 100 TPD Pulp Production

Capital costs :

Desilication plant	190 Lacs
Lime sludge reburning plant	400 ,,
Total capital cost	590 ,,

Operating costs :

Desilication plant	200 Lacs
Lime sludge reburning plant	150 ,,
Total operating cost	350 ,,

	No Desilication No Lime Sludge Reburning Plant	With Desilication & Lime Sludge Reburning Plant
Evaporators :		
Additional steam requirement due to scaling reduction in steam economy–0.5 steam cost Rs. 350/ton	37 Lacs	—
Downtime in evaporators & furnace due to cleaning of scale, soot blowing steam etc.	8 Lacs	—
Causticization :		
Lime requirement Lime purity—40% Cost Rs. 2000/ton	495 Lacs	—
Disposal of lime sludge (Excluding cost of land sludge generated at 65% dryness-50,000 t/yr Cost Rs 60/ton	30 Lacs	—
Chemical Losses :		
Sodium losses and Na_2O-2.2%	96 Lacs	9 Lacs (0.2% losses)
Operating Costs :		
Desilication plant	—	200 Lacs
Lime sludge reburning plant	—	150 Lacs
Depreciation :		
(11 8% of CAPITAL)	—	70 Lacs
Interest :		
(18% ON CAPITAL)	—	106 Lacs
TOTAL	666 Lacs	535 Lacs

Gain - 131 Lacs

Additional benefit due to silica sludge as a by-product for industrial application.

Nearly 2.2 t/day silica (Rs. 15/kg)	— 109 Lacs
Net expected profit	— 240 Lacs/annum
Payable period	— 30 months
Cost of lime regenerated with sale of silica	— Rs. 1030/ton
Cost of lime regenerated with out sale of silica	— Rs. 1470/ton

Combination of all these effects resulted in carbonated black liquor with very low pH values, below 10.0 and silica sludge difficult to filtre.

Concept of submerse bubble reactor (SBR) :

Most of the experiments in absorption column did not give satisfactory results and on continuous runs the carbonation rate was fluctuating widely resulting in variations of end–pH for identical operating conditions. Finally it was decided to use some other type of reactor where gas-liquid transfer is efficient as well as uniform and gentle. At this stage, the idea of submerse bubble reactor was conceived. In this reactor the liquid to be treated with gas is circulated in a tubular system by a pump, which on its downward path sucks the gas in the form of discreet bubbles. The shearing action of the flow works the gas bubble in kneading fashion continuously, exposing new gas-liquid interfaces. A typical layout for corbonation in SBR is illustrated in Figure–2.

Carbonation in two stage SBR :

It was decided to have two stage carbonation in SBR, to allow higher flow rates and also giving no chance for mixing of fresh alkaline liquor with carbonated black liquor. The arrangement for two stage carbonation is illustrated in Fig 3. In two stage carbonation, pH was reduced stepwise. The results of batch wise carbonation were highly encouraging and the results indicate (Table 3), that the filtration rate of carbonated black liquor showed remarkable improvement and silica precipitation was on higher side. With two stage carbonation continuous desilication became practically possible.

The Proto-type mill size desilication plant at Hindustan Newsprint Limited (HNL).

Repeated experiments employing semi-pilot plant scale trials, SBR carbonation technique was found to be ideal in achieving selective precipitation of silica. Based on the data obtained on pilot plant scale trials, mill size desilication plant was designed and developed.

The mill produces the required quantity of chemical pulp by kraft process and about 700 m^3/d, of black liquor is generated by chemical pulping. Although the mill practices cross recovery of chemical and mechanical pulping spent liquors, the storage of black liquors is done separately. Whenever there is a shortage of reeds, bamboo is used for producing chemical grade pulp. Both bamboo and reed liquors are rich in silica and mill often finds heavy scales in evaporators. The black liquor from chemical pulping process has following properties :

Total solids, % w/w	—	14–18
Temperature, °C	—	65–75
pH at 30°C	—	12.3–12.6
SiO_2, g/l	—	3–6
Residual active alkali (RAA), g/l	—	5-8

The lay-out of mill size desilication plant is illustrated in Figure—3. The erection of the desilication plant was done by HNL and the plant was commissioned jointly by HNL and CPPRI in May, 1989. The plant essentially consists of three tanks 3, 5 and 7. The first submer e bubble reactor tank has two reactors. while the second and third have one reactor head

TABLE—2
Results of Carbonation in Packed Bed Column

Trial No.	Initial liquor				Desilicated liquor				Silica sludge			
	pH 30°C	T.S. %w/w	SiO_2 g/l	RAA g/l	pH 30°C	T.S. %w/w	SiO_2 g/l	RAA g/l	Desilication %	Filtration min/ 500 ml.	Organics %	SiO_2 %
Bamboo,WBL	12.1	12.3	5.0	5.9	10.2	11.9	0.9	0.4	82	10	15	75
Bamboo,WBL	12.0	12.4	6.3	6.0	10.3	12.1	2 5	0.8	60	3	10	83
Bamboo,WBL	11.9	10.8	4.2	6.4	9.8	9.7	1.1	0 8	74	DNF	14	82
Bamboo,WBL	12 3	12.9	5.0	7.2	10.3	12.2	1.4	Nil	72	30	15	78

ND—Not determinad.
DNF—Did not filter.

Desilication :

Carbonation of the Black liquors :

Lignin constitutes 60% of the total organic residues of black liquor and exist as colloidal macro molecules. The pH of lignin precipitation lies in close proximity to that of silica precipitation so very slow and precise drop of pH is prerequisite of efficient desilication. When carbondioxide is introduced into the black liquor, the alkali (NaOH) converts to Na_2CO_3 and pH drop quickly. As a pH of the liquor drops silicates present in the black liquor convert to hydrosilicic acid monomers, which on further drop of pH coalase to form dimers & polymers. Several of these polymers join to form silicic acid gel which are large enough to precipitate out,

Typical chemical composition of black liquors is shown in Table—1. Lignin & saccharinic acid constitute the major portion of total organic residue of the black liquor which are likely to undergo chemical changes during carbonation. Inorganic portion show high salts concentration which favours silica gel formation rather than sol.

TABLE—1

Typical Composition of Black Liquors

S. No.	Component	Range, % on dry solids
	Inorganics as NaOH	**30–40**
1.	NaOH	2—4
2.	Na_2S	0.5—1
3.	$Na_2S_2O_3$	0.5—1.5
4.	Na_2SO_4	1.0—2.0
5.	Organic Na	10—20
6.	SiO_2	1.5—3.5
7.	Na_2CO_3	9—12
	Organics	**60—70**
1.	Lignin	35—45
2.	Hemicellulose	1—2
3.	Saccharinic acid	15—20
4.	Other organics acids (Acetic, formic, lactic)	3—5
5.	Extractives and Alcohols	3—5

Experience of Carbonation in Semi-production Absorption Column :

The efforts to carbonate black liquor by direct injection of carbondioxide into black liquor resulted in local over carbonation & ultimately to heavy lignin coprecipitation. Another classical method of gas liquid mass transfer is by counter current interaction of liquid and gas in packed bed columns where gas is injected from below. An elaborate arrangement for packed bed carbonation of black liquor was organised, using a column 8m in height & 1m in diameter & packed with ceramic saddles. Schematic lay out of packed bed column carbonation is given in Figure—1. Though more than 70% desilication could be achieved, there was a massive lignin coprecitation due to channelling & localised carbonation as indicated in Table—2.

The sludge analysis results, shows that although organic matter content was comparable with silica sludge obtained by direct carbonation, but it was difficult to filter the sludge obtained from packed bed column. Some times the sludge did not filter at all.

Some of the observation made on carbonation in packed bed column are—

— Heavy foam formation restricting the passage of flue gas leaving the column.

— Localized carbonation in some pockets of column leading to lignin and silica precipitation even at pH levels as high as 10.7.

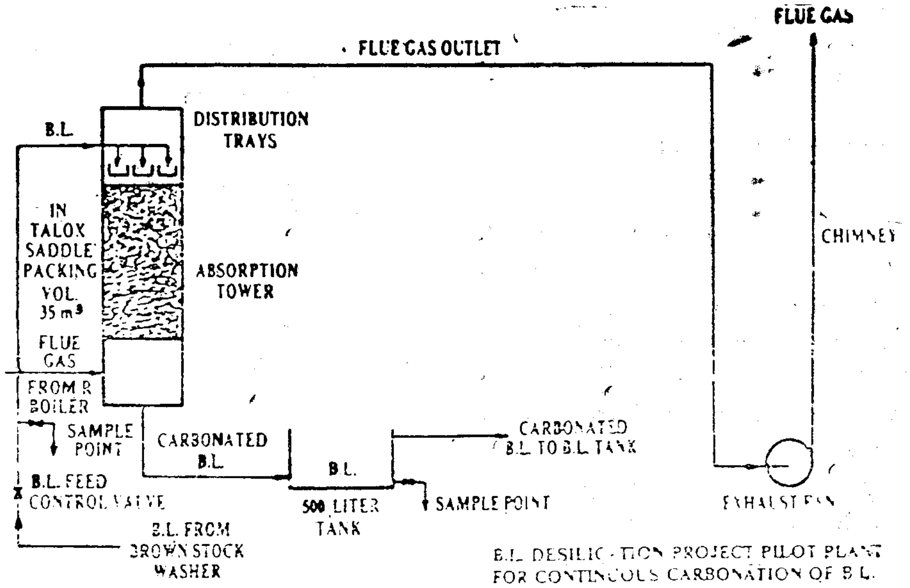

FIG. 1, SEMI PRODUCTION PACKED BED COLUMN

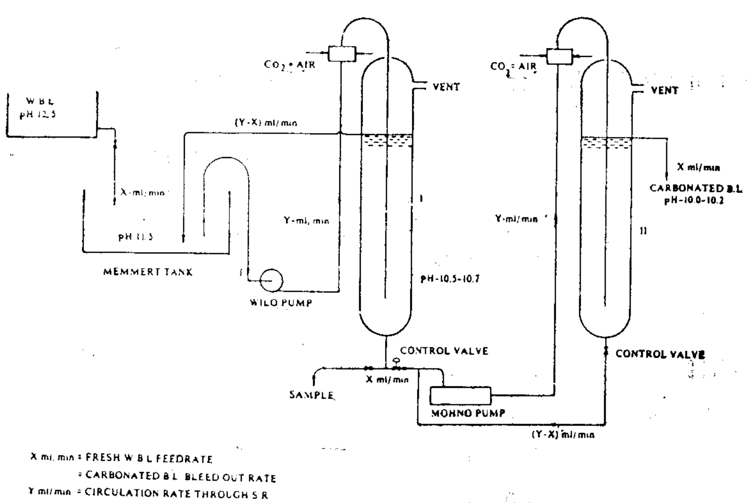

FIG. 2, STEPWISE CARBONATION IN SBR

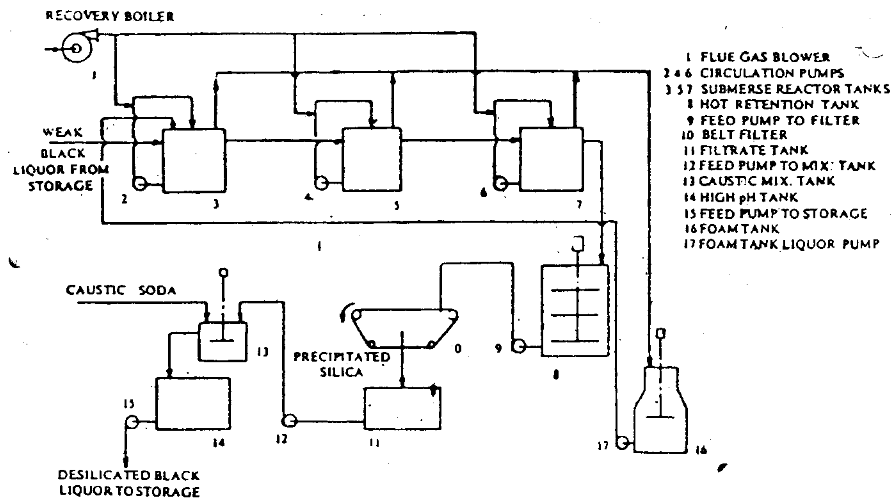

FIG-3, SCHEMATIC OF DESILICATION PLANT.

— Deposition of silica and lignin in packing materials.

— Carbonation was not gentle as desired end pH (10.0) was obtained in single pass ($5m^3/hr$), which is much faster as compared to direct carbonation ($0.5m^3/hr$).

— It was also observed that significant quantities of liquor fed to column drained along the column wall without carbonation.

— Large voids were observed, where there was no black liquor coming in contact with flue gas, indicating the type of packing material was not suitable.

Conclusion :

1. The commercial installation and operating experience made it clear that by slow carbonation, it is possible to desilicate the black liquors without precipitation of lignin.

2. The desilication technology developed is a break-through for commercial installation. The technology is economically viable for mills of medium and large size.

3. Considering the magnitude of benefits and financial gains expected through desilication, it is clear that the investment on commercial installation shall be genuine and realization may be faster than expected.

Reference :

1. Panda, A. Indian Pulp & Paper 16 (1) : 470 (1962).

2. Panda, A. Indian Pulp & Paper 16 (6) : 701 (1962).

3. Misra, D. K. Indian Pulp & Paper 26 (6) ; 701 (1972).

4. Kalyan Sundram, K; Ganesh, R; Jaspal, N.S. and Bhargava, R.L. Nonwood plant Fibre Pulping Progress (TAPPI) No. 3 : 81 (1972).

5. Kulkarni, A.G; Kolambe, R.L; Mathur, R.M; and Pant, R; IPPTA 20 (1984).

6. Ono, K; and Tsugi, H; APIPC 35 : 1157 (1963).

7. Marshak, A.B; Grabovskii and Perekal Suii, N.P. ABIPC, 38 : 1036 (1960).

8. Ibrahim, H; Proceedings of International Non-wood Fibre Pulping and Papermaking Conference: Beijing Vol. II : 877 (1988).