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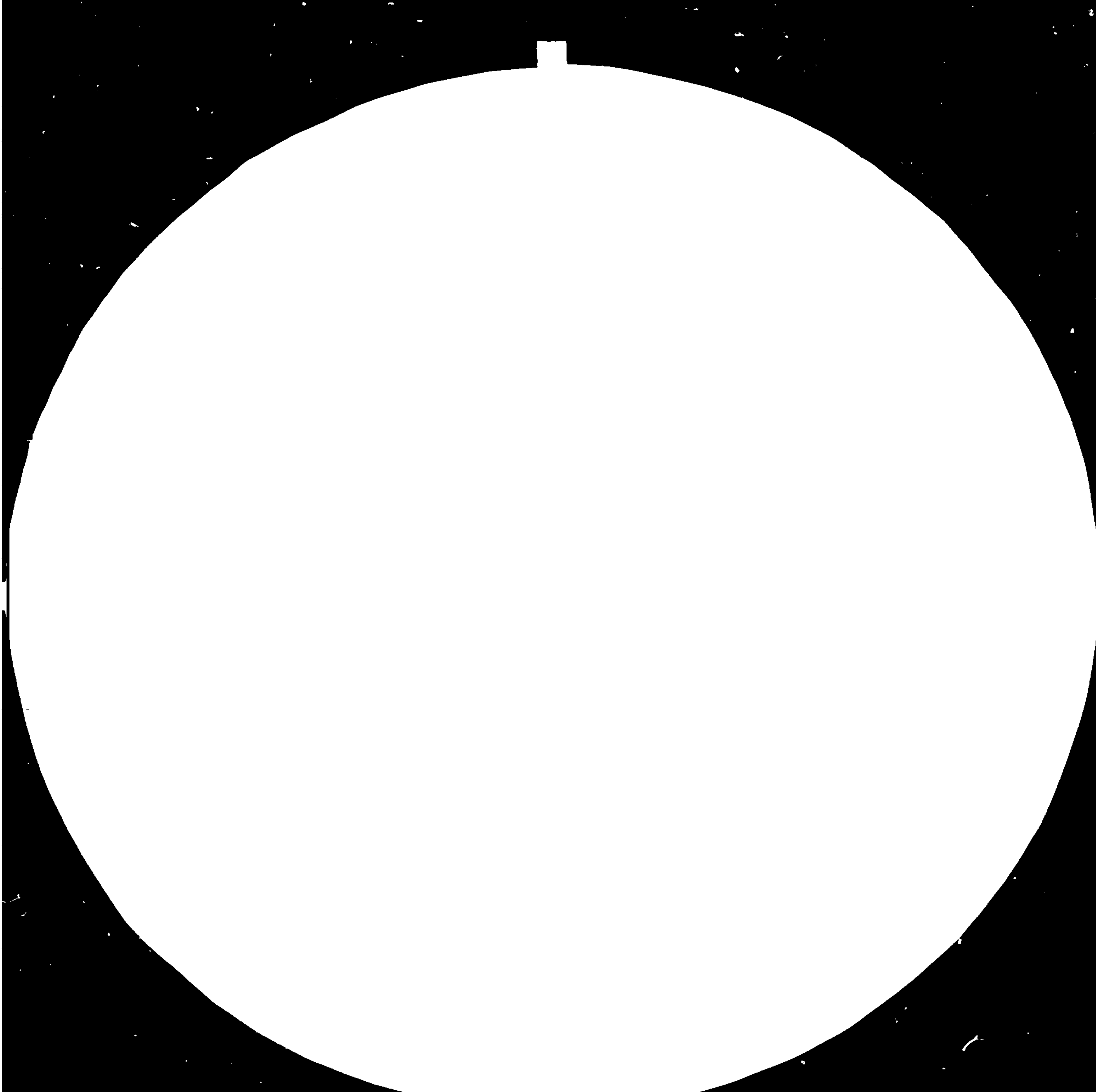

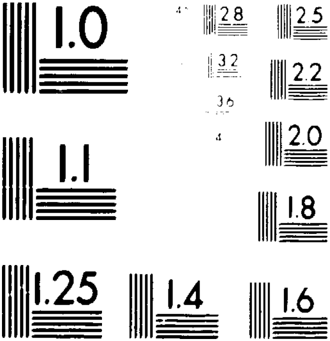

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UNITED NATIONS INDUSTRIAL
DEVELOPMENT ORGANIZATION

October 1984

14190

India

DESILICATION PILOT PLANT FOR BAMBOO BLACK LIQUOR

(US/IND/79/206)

Mission Report

by

P.G. Bleier
UNIDO Expert

3024

UNIDO DESILICATION PROJECT US/IND/79/206

Mission to India of Mr P.G. Bleier, September s984

To terminate the R&D phase I of pilot desilication by submerse carbonation, the original intention was to quantify the operation by installation of metering and control equipment in the pilot submerse reactor erected and operated during Bleier's work in Fort Songadh, March 1984. This was made impossible by delay in delivery of the metering equipment. Bleier however traveled to Songadh on September 13 to join the co-expert Mr J. Leffler, who had gone to Songadh at the begin of the month in order to attend to flowsheet and site selection for the phase II, erection of a mill size demonstration desilication plant.

The ensuing pilot plant work resulted in additional confirmation of the viability of the chosen desilication procedure and in deeper understanding of the underlying chemistry. Improved desilication, improved filterability and improved chances of realkalization by vacuum decarbonation was achieved.

1) Mode of Carbonation; Two Stage Submerse Reactor.

The importance of well controlled, gentle carbonation was again proved. Carbonation trials during monsoon time (June to August, Songadh report XIII, exp 11 - 26) under basically unchanged operating conditions (unchecked because of lacking control gauges) miscarried, because of inevitable lignin coprecipitation. This unwelcome phenomenon was never properly elucidated; pulping of bamboo, partially decomposed by wet storage under admixture of local hardwood was however suspected. Subsequently carbonation proceedure was changed to a batchtype operation in order to avoid direct and sudden interaction of fresh alkaline liquor with carbonated pH 10 liquor, containing flocculated silica precipitate. Now, without improved pulping raw material, light coloured, quick filtering silica mud was obtained; the critical pH/30° of visible precipitation was lowered from 11.1 (!) to 10.3 and without brown coprecipitate, the pH could be lowered to 9.8 (!) with consequent excellent desilication.

Proceeding from batchtype to continuous operation by carefully bleeding fresh liquor into the thermostatic circulation (Mehmert) tank and withrawing carbonated material from the outer shell of the submerse reactor -both at the rate of 700 ml/min (40 l/h)- it was also possible to obtain light coloured, quick filtering silica mud; the process was run for a length of time, sufficient to replace the carbonated liquor produced in the initial "batchtype" operation.

To realize a longstanding desire for multistage carbonation (see earlier reports), also circumventing the impact of fresh liquor on acidified liquor, it was decided to add a second submerse reaction stage, utilizing available glass sections supplemented by sections produced and fitted by the Songadh workshop. Both stages were alike, circulation of the first stage being provided by a centrifugal pump, the Mohno pump being used for the second stage. The first stage was operated well above the pH of visible precipitation. (It can be supposed, that submicroscopic precipitation of silica and possibly also of organic material takes place well above the "visible" precipitation pH).

Two stage carbonation results in unusually bulky floccs and consequently rapid filterability. The preciptated silica mud is of light greyish colour. pH can be lowered below pH/30° of 10 without brown coprecipitation and with good desilication.

All carbonation trials refered to above were carried out on black liquors from bamboo/hardwood mixtures of 40/60 to 50/50, showing that gentle carbonation permits selective silica precipitation even in presence of rather unstable hardwood lignin.

Earlier experience is confirmed that, the gentler carbonation, the lower is the pH of visible precipitation and the lower is the permissible final pH before lignin coprecipitation !!

2) Limit of desilication.

With lowering the final precipitation pH/30^{0} to or below 10.0 the retained silica (at 70^{0}C!) in the filtrate was reduced to 0.6/0.7 gpl and even to 0.46 gpl (exp 34). This repeats the desilication level attained in early work at Ashok Pulp Mills/Assam whilst all previous work in Fort Songadh stopped at a minimal barrier of 1.1/1.2 gpl dissolved silica at 70^{0}C.

The now established silica solubility is in good agreement with data published by K. Goto (J. Chem. Soc. Jap., Pure Chem Sect. 76, 1364, (1959)) as reported by R.K. Iler, Chemistry of Silica, Wiley, 1979, p 84.

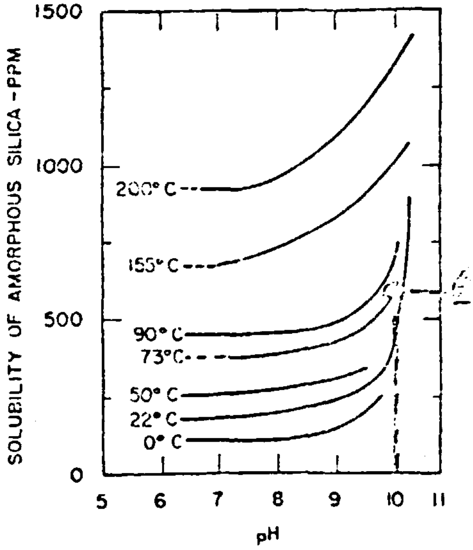


Figure 1.7. Solubility of amorphous silica versus pH at different temperature [from Goto (167a)].

A further improvement of desilication by lowering silica solubility further by judicious addition of polyvalant metal ions can be hoped for. (Cf. silica removal from boiler feed water). However all trials run so far with lime, slaked lime alumn or small amounts of magnesium have not succeeded in improving desilication of black liquor.

Silica solubility is independent of initial silica concentration and does not seem to vary with black liquor solids content; therefore higher initial silica content improves the rate of desilication by pH reduction.

3) Additional Information on Carbonation.

The adaptation by CPPRI of a rapid colourimetric method for CO2 determination for black liquor analysis was of much help to study the relationship between the degree of carbonation, pH reduction and desilication. This method served in place of measurement of CO2 quantities entering and leaving the submerse reactor; the available colourimeter was of insufficient accuracy to permit detailed investigations.

Earlier acidimetry of black liquor was confirmed. Black liquors from Fort Songadh mill 1983 and 1984 (as well as European wood and wheat straw black liquors) have similar acid requirements for pH/30° reduction from over 12 to abut 10. With good agreement between sulfuric acidification (H_2SO_4: dibasic) and carbonation (CO_2:monobasic) the present acid demand for desilication by pH reduction was found to be 0.275 equivalent/liter.

Independently of the acid used, the rate of pH reduction decreases as pH reduction proceeds,probably because of the buffering action of organic salts and of ligninates.

However, whilst sulfuric acidification will continue also beyond the point of lignin precipitation,CO2 sorption practically comes to a **standstill** at a pH/30° of 10.2 (corresponding to a pH of about 9.9 at 70°). On continuing carbonation, the resistance towards CO2 sorption results in a very slow (gentle) acidification, which we have learned is the precondition for selective precipitation of clean silica. In fact, in the submerse reactor, it was possible to reduce pH/30° to 9.7 (!), at the same time reducing -without lignin coprecipitation- the 70°silica solubility to 0.5 gpl by almost completely suppressing the ionic silica species ($H^+ + HSiO_3^- \rightleftharpoons SiO_2 + H_2O$)

The phenomenon described can best be interpreted by approaching of the equilibrium of bicarbonate formation/dissociation: $Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2\ NaHCO_3$. With this understanding it will be possible to choose such working conditions that permit optimizing carbonation as well as decarbonation.

Analysis shows that on approaching the equilibrium there is four times as much bicarbonate present than carbonate. This would mean that all of the free alkali,almost all of the sodium silicate and some of the carbonate of the initial liquor is transformed into bicarbonate.However, it must be assumed that CO2 also frees some of the weak organic acids and some phenolic groups from the sodium compounds formed during pulping, a process that is not likely to be completely reversible on realkalization.

4) Sedimentation and Filtration.

Both sedimentation and filtration depend on proper flocculation. It has been stated before that submerse carbonation, particularily when performed in two stages, results in coarse and stable floccs. It is possibly the rapid primary circulation and slow secondary circulation in the submerse reactor, that is beneficial to the aggregation of silica floccs.

The rate of sedimentation and of filtration had increased. Also the sediment volume increased somewhat to a silica content in the sediment of only 15 gpl.

Sedimentation in a 500 ml measuring cylinder (about 35 cm) was complete after one hour. However -repeating earlier results- the decantate contained somewhat more silica than the filtrate (exp 38: 1.1 gpl instead of 0.8 gpl SiO2), indicating, that some very finely divided silica had not been collected by the large **sedimenting** floccs. Unless this problem can be solved, the inclusion of clarification -before filtration- in the flow sheet of the large demonstration plant is not advisable.

Filtration was speedier than ever before. On building a 8 mm filtercake by filtering 4.5 liter carbonated black liquor through a 11 cm Ø Buchner funnel over paper, the intial filtration speed was 25 $m^3/m^2/h$, the final speed was 3 $m^3/m^2/h$ and the average 6 $m^3/m^2/h$.

First experiments showed that medium dense monofil wire screen retained the filtercake like filterpaper.

Earlier work with packed column carbonation indicated improved filterability after hot retention of the carbonated liquor. In the recent desilication trials, however, filterability severely deteriorated when the hot carbonated liquor was kept for more than 30 minutes. In some cases excellent initial filterability of light coloured floccs turned into non filtering material of darker colour. It seems that some postprecipitation of lignins occurs, whilst pH and degree of desilication remain unchanged. The obseved phenomenon needs further elucidation but must be taken as a warning against large scale indermediate clarification.
Note was taken of the fact observed since the begin of experimental project work, that whenever some vacuum builds up in the filtering flask due to filtration resistance, the filtrate coming from the stem of the filter funnel is bubbling and foamy. This is probably due to degasing rather than to boiling; the filtrate collected in the flask does not "boil". Black liquor foam at pH 10 is not stable.

5) Decarbonation and realkalization.

Vacuum treatment of desilicated hot carbonated black liquor strips some of the CO2 and reduces the alkali demand on backtitration and on realkalization to the point of normal viscosity of the concentrated black liquor.
Hot laboratory viscometry on realkalized carbonated liquor shows, that considerably more caustic soda is required for adequate fluidity after evaporation to 50% solids content, than corresponds to CO2 required for desilication (about 0.4 equivalents alkali after carbonation with 0275 equ/liter). Some condensation reactions that take place during carbonation apparently are not reversible. In respect of thick liquor viscosity, there is no difference between immediate and delayed realkalisation. The amount of alkali required at present exceeds the quantity required to make up present alkali losses. Further investigations will have to show how far realkalisation requirements can be reduced by more careful carbonation and by optimized CO2 stripping by steam or by vacuum.

6) Acknowledgement and Future Work

The carbonation work since the Unido Mission, March 1984, by the Ford Songadh team guided by Mr Gopinath Rao, has to be gratefully acknowledged. (See Annexe I) Equally thanks are due to CPPRI, in particular to Dr R.M. Mathur assisted by Mr S Nai-thani who spent an extended time in Songadh cooperating in carbonation work and operating the CPPRI laboratory evaporation and hot viscometry equipment. (See also Annexe II on CPPRI work on realkalization).
Collaboration with the Unido co-expert Mr J Leffler and with all members of the team was pleasant and constructive.

A list of urgent problems to be attended to by the Songadh and CPPRI teams (the latter preferably also continuing to work in Songadh) is enclosed as Annexe III.

At a final meeting with Mr Gopinath Rao and Dr Shenoy (Parkhe Research Institute), the following points were covered:

1) The pilot submerse reactor is to be expanded to a full glass 3-stage unit. The additional glass sections (Schott, Mainz) and rotameters to measure the gas flow to the three stages are to be selected by Mr G.Rao, to be ordered by Unido. The possibility to dismantle the pilot plant into its modular sections has to be maintained for tranfer to a new location at a later date.
2) A new equipment for laboratory evaporation and for hot viscometry will be procured. Dr Mathur will advise on design and on type of viscometer.
3) Dr Mathur CPPRI will also advise on precision required of a new colourimeter for determination of the degree of carbonation.
4) It was suggested that submerse carbonation work on model solutions should include sulfate and soda green liquors.
5) Investigating the ageing of carbonate black liquor (Annexe II/c) attention should be given to lignin postprecipitation.
6) Attempts should be made to find conditions of carbonation and of aftertreatment permitting the lowering of the silica content of decantates to the silica level of the corresponding filtrates.

7) Dr Shenoy suggested that the study of temperature as carbonation variable (Annexe II, A2) should be undertaken with the understanding, that under practical operation conditions temperature cannot be kept constant.

8) Finally it was stressed, that in the past it had been unwarranted to neglect CO_2 stripping as an important part measure of realkalization. Whilst degassing vacuum equipment is available in Songadh on entry of black liquor into the evaporation sector, sophisticated and highly efficient and sophisticated degassing equipment also is available.

9) **Summary** of Meeting with Government of India Officials, New Delhi, 1 October.

25.10.84

Annexe I

DESILICATION OF BAMBOO BLACK LIQUOR UNIDO PROJECT AT CENTRAL PULP MILLS

REPORT No. [illegible].

TECHNICAL DEPARTMENT
THE CENTRAL PULP MILLS LIMITED.,
FORT SONGADH
OCTOBER, [illegible].

CENPULP - FACTORY :

Date : 3.10.1984

REPORT No.XIII

DESILICATION OF BAMBOO BLACK LIQUOR BY CARBONATION.

CONTENTS:

1. Desilication of W.B.L. in submerse reactor with increased circulation rate.
2. Desilication of semi-concentrated B.L. in submerse reactor.
3. Desilication of W.B.L. in submerse reactor with batch carbonation system.
4. Desilication of W.B.L. in submerse reactor with continuous carbonation system.
5. Two stage carbonation of W.B.L. in primary and secondary [illegible] reactors.

1. Desilication of W.B.L. in submerse reactor with increased circulation rate.

1.1 W.B.L. trials were taken in S.R. by increasing the circulation rate e to study its effect on carbonation, silica removal percentage and subsequent filterability characteristics.

1.2 The arrangement of the equipment was in the same order as for the regular S.R. Only the Mohno pump gear reading was switched over to 280 RPM so as to get a throughput flow of 7.5 lits/min instead of 5 lit/min at 187 rpm.

The trials were run at two different rates, viz. slow ([illegible]) carbonation and fast carbonation. The carbonation rate was adjusted by adjusting the CO_2 valve pressure inaccordance with the fresh W.B.L. input flow.

The results and findings of these trials are enlisted in table No.1 trial Nos. 15, 16, 17 & 18.

1.3 The observations and conclusions are as follows :-

1.3.1 It has been proved by these experiments that high circulation [illegible] high turbulence in the system which deflocculates the silica floc yielding very fine dispersed silica particles causing [illegible] colloidal charge.

1.3.2 Filterability was fair to poor throughout the pH range.

1.3.3 At higher circulation rate carbonation rate ( ) also should be higher (650 and 1000 ml/min. flow respectively) to achieve good filterability and fair colloidal charge.

1.3.4 From the tabulation column it is obvious that filtration is very sensitive towards turbulence in the system. More gentle the carbonation better will be the filterability. The results also reveal the carrying capacity of a S.R. and that above a certain rate of carbonation of the W.B.L. cannot be successfully processed in a particular S.R.unit or In the unit under trial, the maximum [illegible] capacity is observed to be around 650 ml/min. input rate.

1.3.5 Excessive foam was observed throughout the trial. It could be controlled only by closing the air valve. Even the slightest amount of air could cause heavy foam.

2. Desilication of Semiconcentrated Black Liquor (S.C.B.L.) in S.R.

2.1 The trials were taken on S.C.B.L. for desilication by carbonation. S.C.B.L. at a T.S. of 25-26%, collected from the 3rd effect of evaporator was carbonated in S.R. to evaluate the filtrability characteristics and extent of desilication.

2.2 Arrangement of the equipment was exactly similar to the regular S.R.

The results of these experiments are discussed in table No.1, trial No. 20-23.

2.3 Observation and [illegible] conclusions.

2.3.1 With respect to the filtrability and white sludge it was found that S.C.B.L. is unsuitable for desilication by carbonation. Throughout the pH range sludge was brown and organic matter in the sludge upto the extent of [illegible] though the filtration was poor (filtration time 3-4 minutes for 100 ml. compared to less than 60 seconds for good filtration).

2.3.2 Foam problem was less than regular trials. The foam observed in the foam chamber was very thick and dense.

2.3.3 Critical visible precipitation point was on a higher side than that of W.B.L. Apparently silica precipitation could be seen at a high higher pH of 11.25 - 11.5. Silica particles were of granular nature on the glass wall of the beaker.

2.3.4 Further these trials were discontinued because of the unsuitability of S.C.B.L. for desilication.

3. Desilication of W.B.L. in S.R. with batch carbonation system.

3.1 After the breakage of monsoon the trials were continued with W.B.L. in regular S.R. The problem encountered was that even at higher pH of 10.4 - 10.5 silica sludge used to turn brown with poor filtration properties because of the co-precipitation of organic matter with sludge. It was concluded that the brown sludge may be due to the presence of hard wood lignins in the B.L. or may be due to the addition of fresh B.L. to the highly carbonated B.L. whereby the fresh B.L. could destablise the equilibrium achieved and deflocculate the silica flocs in the B.L. suspension.

To confirm the hypothesis, further trials were continued with batch carbonation system.

3.2 The equipments were arranged in the same usual manner. The overflow from the S.R. was directly taken up to the [illegible] heater. The addition of fresh B.L. was cut-off. The W.B.L. was slowly carbonated at a CO_2/Air pressure of 0.3 - 0.4 Kg/Cm². At every time interval of 10 mins. the samples were collected to test the silica removal and filtrability.

The results are tabulated in the table No.1, trial No.[illegible], 33, 34,& 35.

3.3 The outcome of the trials are listed below:-

3.3.1 The batch carbonation system gave highly promising results and filterability was good even at a fairly low pH of 9.0 with a fluffy white silica precipitation.

3.3.2 The silica removal was to the extent of 86% at a pH of [illegible].

3.3.3 The rate of drop in pH (Delta pH) could be controlled very easily by adjusting the CO_2 /Air valve.

3.3.4 The above results confirm the hypothesis that the direct addition of fresh B.L. is one of the main reasons which causes a brown sludge. The explanation is that the carbonated B.L. with highly granulated and nice filtering silica particles get the shock when directly mixed with fresh B.L. thereby disturbing the equilibrium which in turn deflocculates the silica flocs causing very fine precipitate which adheres to the organic particles and precipitates as brown sludge. To eliminate this problem either the direct addition of fresh B.L. to the fully carbonate B.L. should be avoided or it should be slowly diffused into the system through gradual mixing.

4. Desilication of W.B.L. in S.R. with continuous carbonation system.

4.1 In these particular trial W.B.L. was processed continuously in the S.R. The overflow from the S.R. was directly taken out as a product without recirculating it back to the mamartø heater.

4.2 The equipments were arranged in the similar manner as that of regular S.R. The only alteration made was that a 'T' was provided on the delivery side of the Mohno pump before the CO_2 injector, to bifurcate its flow. Only 800-1200 ml/min. B.L. flow was passed through the S.R. and rest was taken back to mamarty heater. The fresh B.L. was added to the mamart heater in the rate same as that of product output. The CO_2/Air was adjusted according to the B.L. flow to achieve the product pH 10.1 - 2 10.2 .

The results are tabulated in the table No.1, trial No.32, 33 & 36.

4.3 The observations and conclusions are as follows :-

4.3.1 Due to the wide fluctuations in W.B.L. flow in S.R. and high pressure of CO_2 (0.9 - 1 Kg/Cm^2) it was found difficult to maintain a constant pH. [illegible] [illegible] obvious that because of the flow variation, over and under [illegible] was taking place with consequent poor filtrability of carbonated B.L. Also sudden acidification can cause disturbance in the development of granular precipitation.

4.3.2 Foam problem was less severe may be because of reduced throughput in S.R.

4.3.3 These trials also confirm the theory that it is only by gradual carbonation that a nicely filtering white silica precipitate can be obtained.

5. Desilication of W.B.L. in two stage carbonation.

5.1 In the single stage continuous operation as the product pH of B.L. was difficult to control it was further decided that the carbontation should be devided into two stages using different S.R.S. in order to carryout slow carbontation.

5.2 Arrangement of the equipments:-

The arrangement resembles the system shown in Drawing No.PR-61-491-03-03 annexed. One S.S. submerse reactor was fabricated in C.P.D. workshop and was connected in series with the old glass bubble reactor.

The CO_2/Air supply was divided into two streams with separate control valves to achieve better process control. The circulation rates through the 1st and 2nd S.R. was kept nearly the same at 5 Lit/min. To get a 5.0 Lit/min. flow in 1st stage S.R.'T' was provided to the delivery side of [illegible] Pump and only desired amount was passed through the 1st stage S.R. The product carbonated B.L. flow was maintained at 500 ml/min. by adjusting the control valves as shown in the drawings.

In the 1st stage S.R. the system was maintained at a pH of 10.6 - 10.7 and only 500 ml/min. partially carbonated B.L. flow was fed to the second stage S.R. to achieve the product pH of 10.0 - 10.1 .

Fresh B.L. addition rate was adjusted at the same rate as that of the product output rate. The CO_2/Air valves were operated separately to control the pH in both the S.R.S.

The results are tabulated in the table No.1. Exhl No.37[illegible]

5.3 Observations and conclusions.

5.3.1 The concept of two stage carbonation has brought an evolutionary change in the continuous desilication process yielding good filterable and fair silica sludge.

5.3.2 Contrary to the earlier apprehension, the product B.L. pH control could be satisfactorily achieved by adjusting the CO_2/Air valve in accordance with B.L. flow.

5.3.3 Foam problem was tolerable and less severe but still persisting.

... 2

5.3.4 The present trials gave encouraging results. Further detailed studies on feasibility and flexibility of this system for desilication are going on.

5.3.5 From these results, it can be safely concluded that slow carbonation of B.L. without giving shocks to the final product B.L. or mixing the final product B.L. with fresh B.L. are the most essential requirements for getting good desilication efficiency as well as a silica sludge having good filteration characteristics.

5.3.6 These observations have a given rise to the thinking that the prototype Mill size demonstration unit being planned, a minimum of thereeestages for carbonation in S.R.units are required.

......

[illegible]

[illegible]t. o.	Initial SI [illegible]/ [illegible]	Initial & concentrated [illegible] at [illegible]	[illegible] in [illegible] gpl	Gpy/Incre in SL gpl	Pump [illegible]/ SL Input-outlet flow [illegible]/cc/min	Filtration & colour of silica sludge	Silica in [illegible] gpl
([illegible])	([illegible])	(3)	([illegible])	(5)	([illegible])	(7)	([illegible])
1[illegible] [illegible].7.[illegible]	22.[illegible]/53	22.[illegible] [illegible]* 10.[illegible] [illegible].5 [illegible] [illegible].37			107/100cc	Poor Fair Good) light Good) coloured Good) [illegible]	6.2 2.56 2.46 1.6[illegible] 1.[illegible] 1.24
[illegible]	[illegible]	[illegible].37 [illegible]* [illegible] [illegible] 10.[illegible] 10.[illegible] [illegible] (Fixed [illegible])			107/1.5 lit	Poor [illegible]) light Good) coloured Good) gyle Good) Good)	5.6 2.3[illegible]
[illegible] [illegible].7.84	[illegible]	[illegible] [illegible]* [illegible] [illegible] [illegible] [illegible] 10.[illegible] (Fixed [illegible])			[illegible]/[illegible] cc	Good) [illegible]) brown Fair) gyle Poor) Poor) Poor)	6.3[illegible] 0.[illegible]
[illegible] [illegible].7.[illegible]	[illegible]	[illegible].37 [illegible]* [illegible] [illegible].[illegible]6 [illegible] (Fixed [illegible])			- -	Good Poor) brown Poor) gyle Poor-brown gyle	[illegible] 1.[illegible]
17 [illegible].7.84	25/60	[illegible] [illegible].1[illegible]* 1[illegible] [illegible] [illegible]			-	Poor) Poor) brown Fair) sludge Poor)	6.65 2.[illegible] 1.[illegible]
[illegible].7.84	22/75	[illegible].6 [illegible].1[illegible] [illegible]* [illegible] [illegible] 20.[illegible] 10.[illegible] [illegible] [illegible]			-	Poor Poor) light Good) coloured [illegible]) sludge Poor) brown Poor) sludge Poor)	5.75 2.[illegible] 2.3[illegible]

Cenpulp Technical Dept.

Date: [illegible]

Silica removal %	Org. content in sludge %	CO2 content in BL as Na2CO3 g/l	Remarks
(9)	(10)	(11)	(12)
		15.2	Filtration of mixed carbonated BL was carried out. About 40 litres filtered at 6 l/min rate. But washing could not be done due to pressure differential in filter (5 kg/cm2)
56.7		40.6	
60		45.0	
74.2		33.5	
75.7		28.6	
60		32.5	
			Filtration of mixed carbonated BL was carried out. About 40 litres BL filtered at 6 litre/min. Washing done.
55.5			
		14.0	Poor filtration of mixed carbonated BL.
[illegible]			
		30.0	
		11.0	Poor filtration of mixed carbonated BL
		26.0	
		32.0	
74.0		21.0	
		15.0	Poor filtration & brown coloured sludge.
53.4		30.0	
71.6		27.0	
			Poor filtration of mixed carbonated BL. Brown coloured sludge.
27.4			
37.9			

1	2	3	4	5	6	7	8	9	10	11	(12)
[illegible] [illegible].7.64	[illegible]/69	10.[illegible] 11.[illegible]* 10.[illegible] 10.[illegible] 10.40 10.5 10.7 10.6 (Mixed SL)			260/1600 cc	Good) Light Good) coloured Good) Good) Fair) Good) Fair)	7.3 1.7 1.3	76.7 62.[illegible]		11.0 24.0 26.0	Filtration of mixed carbonated SL was carried out. About 20 lits SL was filtered and then pressure developed in pressure gauge (5 kg/cm2) and further filtration could not be done.
2[illegible] [illegible].54	12.[illegible]/60	1[illegible].[illegible] 10.17 11.[illegible] 11.[illegible]* 10.[illegible] 10.[illegible]7 10.[illegible] 10.[illegible] 10.[illegible] 10.[illegible] 1[illegible].[illegible] (neutralised with lime) 1[illegible].[illegible] (neutralised with [illegible])	170.2 1[illegible].4 1[illegible].8 1[illegible].6 1[illegible].6 125.52 (Mixed SL filtered) 25[illegible]	66.7/ 52.[illegible] 65.1/ 51.6 63.9/ 45.7 60.4/ 45.2 [illegible]/55.1 10[illegible]/69.1	167/900 cc	Good) Light Good) coloured Good) sludge Fair) Dark coloured sludge V.Poor	5.2 2.9 2.6 1.02 1.[illegible] 1.44	34.2 50.0 60.4 73.5 72.2	3.5 ([illegible]) 73 (43.5% [illegible])	9.5 15.0 13.5 [illegible] 24 24.0 30.0 [illegible] 13.5 35.5	Filtration of mixed carbonated SL was carried out. Only 5-6 lits SL filtered through filter press. Further filtration and could not be done due to pressure increased in pressure gauge (5 kgm/cm2)
2[illegible] 27.[illegible]	1[illegible]/52	10.[illegible]7 11.1[illegible] 10.[illegible] 10.[illegible] 10.[illegible] 10.[illegible] 10.[illegible] 10.[illegible] (Mixed SL)	1[illegible].5 127.0 1[illegible].5 174.4	6[illegible]/46.5 60.[illegible]/47.6 64.6/41.9 67.2/42.2	167/800 cc	Good) Light Good) coloured Poor) sludge V.Poor) Dark " coloured " sludge	5.3 5.5 2.0 1.75	43.4 6[illegible] 67.3		14.0 17.5 22.0 [illegible]	Poor filtration of mixed carbonated SL and dark coloured sludge.
2 27.[illegible]	14.5/57	13.6 11.1* 10.85 10.[illegible] 10.[illegible] 10.[illegible] 10.[illegible]			167	Poor) Dark Poor) coloured Poor) sludge Fair [illegible] Good) [illegible] Good) coloured sludge [illegible]			34[illegible]		Poor filtration & dark coloured sludge.
2[illegible]/11	11.5/55	10.15 10.24 10.[illegible]1 10.[illegible]				Poor) Dark Poor) coloured Poor) sludge					

* Precipitation [illegible] point at 70°C.

[illegible] OF [illegible] IN [illegible] BUBBLE REACTOR

Run No.	Initial pH/Temp °C	Initial & corrected pH at 20°C	Pump MIT/ pH input-output flow ml/cc/min	Filtration & colour of sludge
31 [illegible]	23/47	12.67 11.24* 11.1 10.90 10.41 10.71 10.60 10.43	187/900 cc	Poor Poor Poor Poor Poor Poor Brown coloured sludge
32 [illegible]	[illegible]	11.[illegible] 12.[illegible]* 11.07 10.47 10.70 [illegible] 10.35 10.0[illegible] 10.35 10.62 (fixed pH)	187/1000 cc	Poor Fair Fair Good [illegible] Fair Fair Fair Brown coloured sludge
[illegible]	27/45	[illegible] [illegible]* [illegible] [illegible] [illegible] [illegible] 10.48 10.37	187/1000 cc	Poor Poor Fair Fair Fair Fair Fair Brown coloured sludge
[illegible]	23/[illegible]	12.71 [illegible]* 11.0[illegible] [illegible] [illegible] [illegible] [illegible] 10.52 10.[illegible] (fixed pH)	187/500 cc	Poor Poor Poor Fair Fair Good Fair Poor Poor Brown coloured sludge Brown sludge
[illegible] [illegible]	23/[illegible]	12.25 11.1[illegible]* [illegible] 10.[illegible] [illegible] [illegible] 10.[illegible] (fixed pH)	[illegible]/1500 cc	Fair Fair Good Poor Poor Brown coloured sludge

* Precipitation pH point at 20°C

ilica in BL g/l	Silica removal %	Org. content in sludge %	CO2 content in BL as Na2CO3, g/l	Remarks
				Poor filtration throughout the expt. Carbonated BL rejected.
12.2			26.0 31.0	Poor filtration & dark coloured sludge.
5.6	54.0		54.0	
2.8 2.4	77.0 80.3		53.0 55.[illegible]	
			40.0	
13.6			26 25	Very poor filtration & dark coloured sludge.
3.7 3.6 2.[illegible]	72.7 73.5 [illegible]	44.0	57.5 57.5 53.5	
2.40	82.3	46.0	46.0	
11.5				Poor filtration & dark coloured sludge.
2.68 2.24 1.60	76.7 80.5 86.1	52.0 47.0		
2.2	80.9			
11.0			30.0	Poor filtration & dark coloured of sludge.
2.50 1.[illegible] 1.10	76.7 [illegible] [illegible]		37.5 47.5 50.0	

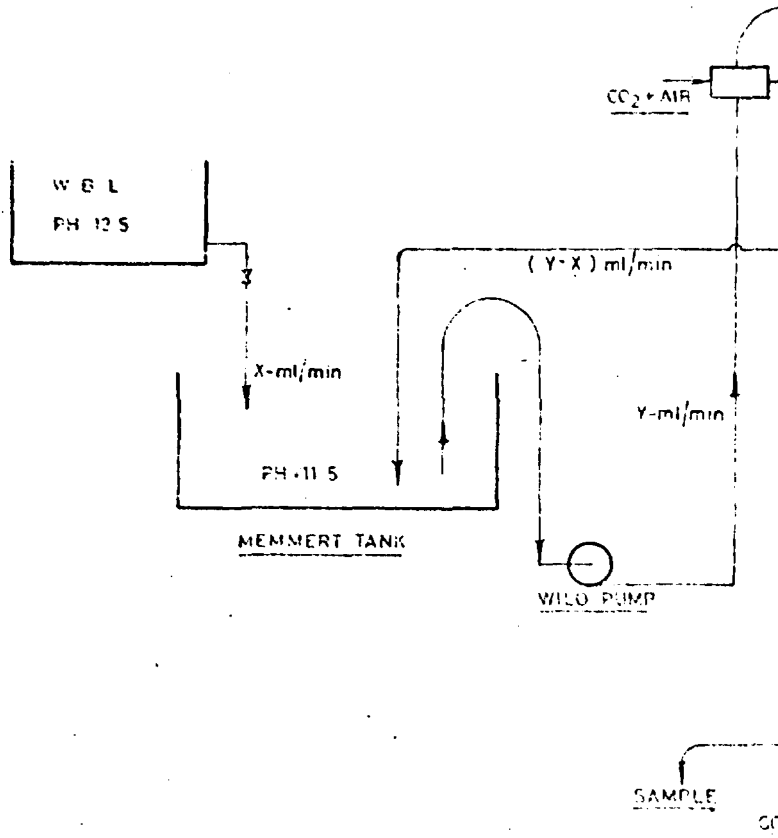
TABLE [illegible]

[illegible] BUBBLE REACTOR

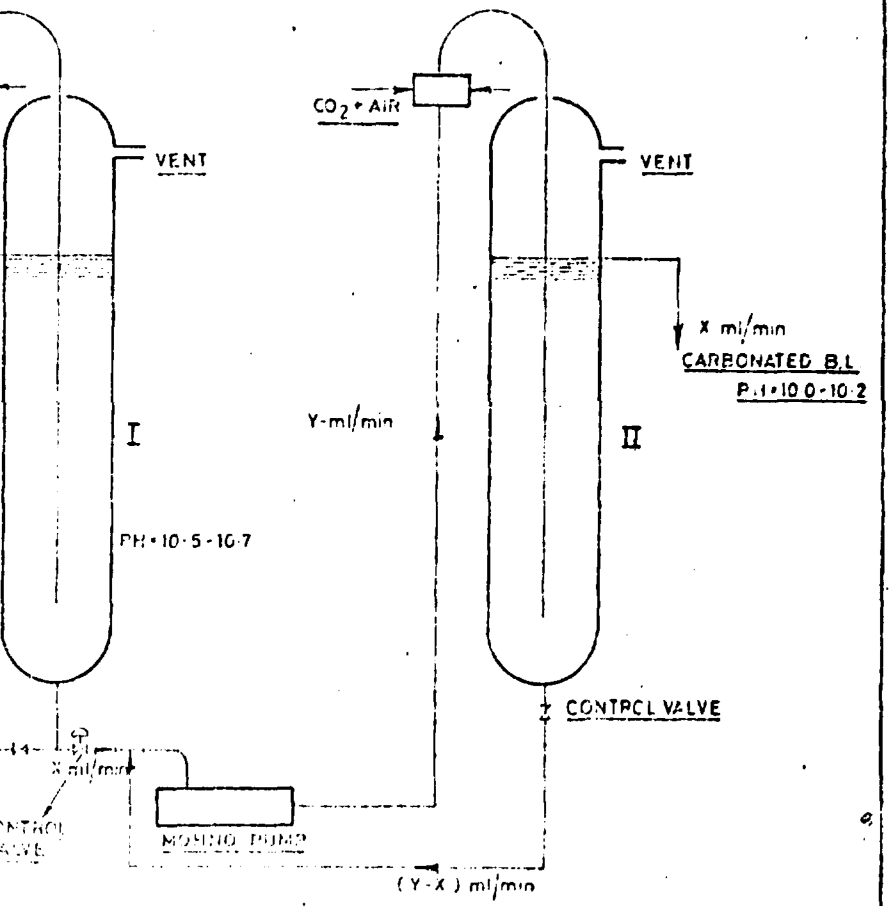
Expt. No & Date	Initial BL Tw/Temp. °/°C	Initial & carbonated BL pH at 30°C	Analysis of BL TS g/gpl	 Org. g/gpl	 Inorg. g/gpl	Filtration & colour of silica sludge	Silica as SiO$_2$ gpl	Silica removal	Carbonate as Na$_2$CO$_3$ in BL gpl	Loss on ignition %	Organic content %	Remarks
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
27 7.[illegible].64	12/34	12.0	12.5/155.7	63.1/84.4	36.4/49.6		5.0					
		10.93	11.9/127	62/78.8	38/48.2	Fair grey-white	2.4	52.0	16	White sludge	White sludge	
		10.9	11.9/127.6	64/81.7	36/45.9	Good white	1.65	67.0	23	10.7 !	1.3	
		10.76	11.4/121.6	66.3/80.7	33.7/40.9	Good white	1.30	74.0	23			
		10.65	12/12[illegible]	64.9/83.3	35.1/45.1	Good-white	1.2	76.0	24			
		10.67	11.7/125.2	62.6/78.4	37.4/46.8	Fair-brown	0.75 !	85.0	24 !		Brown sludge 93	
		10.72	11.5/122.6	65.8/80.7	34.2/41.9	Fair-brown	0.76 !	84.8				
28 5.9.64	13/62	12.67	13.8/147.5	65.2/96.1	34.8/51.3		5.7		12			
		11.05	12.3/129.6	65.3/81.8	34.7/47.8	Poor-white	4.0	29.8	16			
		10.95	12.7/135.6	65.6/[illegible].9	34.4/46.7	Good-light brown	2.8	50.9	16			
		10.88	12.8/136.1	67.9/92.5	32.1/43.6	Good-brown	2.6	54.4	16	35.8 (sludge washed with cold water)	19.9	
		10.81	12.4/132	66/87.2	33.9/44.8	Fair-brown	2.4	57.8	19			
		10.78	12.3/133.5	70/93.5	30/40	Fair-brown	[illegible]	60.1	19	21.5 (sludge washed with hot water)	17.3	
		10.87	12.4/131.6	68/83.6	32/42	Fair-brown	2.2	61.4				
29 7.[illegible].64	11.5/60	12.26	11.6/124.2	62.6/77.7	37.4/46.5		5.0		9			
		11.65							15			
		10.44							18			
		10.15				Poor			19			
		10.12	11.5/122.7	64.9/79.6	35.1/43.1	Good-white	0.9	82.0	27	15.3	1.3	
		10.04	11.4/121.2	64.9/78.7	35.1/42.5	Good-white	0.65 !	87.0	27			
		10.02	11.6/123.1	65/79.9	35/43.1	Fair-brown	0.75 !	85.0	-	36.4	17.8	

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
70 [illegible]	12/66	12.5	13.4/144.0	61.9/83.1	30.1/54.8		5.3		9.0			Batch process
		11.02							15			
		10.49	12.7/135.6	65.3/88.5	34.7/47.1	Good-white	2.4	54.7	23			
		10.2	12.8/137.1	65.3/89.5	34.7/47.6	Good-white	1.92	63.0	31.5			
		10.0	12.6/135.2	66.9/90.4	33.1/44.7	Good-white	0.84	84.1	33.5	13.8	3.4	
		9.63	12.1/129.3	65/84.1	35/45.4	Good-brown	0.70	86.0	34	50	24.4	
71 12.9.64	13/62	12.22	13.2/141.8	64.2/91	35.8/50.0		6.1					-do-
		10.40	12.9/139	66.6/92.9	33.7/46.2	Fair-white	3.5	42.6				
		10.25	12.7/135.5			Good-white	2.4	60.6				
		10.18	12.9/137.6			Fair-grey	1.82	70.2				
		10.10	13.1/140.2			Good-grey	1.48	75.7		45.2	23.3	
		10.04	12.8/136.7			"	2.22	80.0		52.6	31.6	
		9.95	12.6/134.9			Good-brown	1.20	69.3				
		9.80	12.7/135.9			"	1.05	87.8				
		9.67	12.3/131.3			Good-brown	0.87	85.7				
		9.44	11.9/127.3			"	0.80	80.9		67.6	59.9	
		9.22	12.3/132	61/80.8	30/51	"	0.60	86.9		75.12	66.5	
72 [illegible]	11.[illegible]/67	[illegible]	[illegible]	[illegible]/83.7	37.1/49.5		7.5					Continuous with modification
		10.4	[illegible]/131.[illegible]	67.7/90.6	32.8/43.2	Good-grey	2.0	73.3				
73 16.9.64	9.5/67	12.4					4.4					-do-
		10.25					1.4	68.2				
		10.15					1.02	76.8				
		10.0					1.74	[illegible]				
74 [illegible]	10/65	10.72	12.2/129				4.0					Batch system
		10.47	10.8/114.5				3.2	20.0				
		10.77					2.20	45.0				
		10.7[illegible]	11.3/120.5				2.0	50.0				
		10.0					0.55	86.2				
		9.62	11.5/123.1				0.46	86.5				

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
55 20.9.64	10/65	12.26					3.9					**Batch**
		10.4					2.7	30.7				
		10.25 10.09					2.4 1.6	38.4 55.8				
		10.15 (Cement tank)					0.6	64.6				
56 21.9.64	10/60	12.44	11.1/117.4				3.9					**Two days sedimentation in 50 ml cylinder.**
		10.71	10.5/109.18				2.4	38.5				**<u>silica</u>**
		10.22	10.4/110.1				1.9	51.5				**Top 0.67 g/l** **Middle 0.67 g/l** **Bottom 0.66 g/l**
		10.07	10.4/100.9				1.28	57.2				**Batch and continuous**
57 24.9.64	10/45	12.7	12.2/128.9				3.6					**Two-stage carbonation**
		9.9					0.6	83.3				
58 27.9.64	13/52	12.79					4.5					**2-stage carbonation. 1 hr sedimentation in 500 ml cylinder**
		10.20					1.0	77.9				
		9.9					0.73	82.6				**<u>silica</u>**
												Top 1.1 g/l **Middle 1.1 g/l** **Bottom 1.16 g/l**



X ml/min = FRESH W.B.L. FEEDRATE,
= CARBONATED B.L. BLEED OUT RATE
Y ml/min = CIRCULATION RATE THROUGH S.R



P NO	DESCRIPTION & SIZE	MATERIAL	QTY	REMARKS

THE CENTRAL PULP MILLS LTD
FORT SONGADH DIST. SURAT, INDIA.

DESIGNED BY	C G R	2-10-84
DRAWN BY	D G PATEL	2-10-84
TRACED BY		
CHECKED BY		
APPROVED BY		

Pilot Plant For Two-Stage Carbonation Of Bamboo B.L. In Submerse Bubble Reactor

SCALE

DRG. NO. PR_{61}-491-03-03

Annexe II

UNIDO Project US/IND/79/206
Desilication of bamboo BL

Further work on Desilication Project to be carried out by CPM & CPPRI as prepared by Mr. P G Bleier before his deparature from Fort Songadh on 28.09.1984.

A) CARBONATION:

1. Quantification, running 2-stage SR with flow meters, measuring CO_2 content before and after passage through SR (Orsat).

2. Influence of temperature on carbonation (critical visible precipitation pH, final precipitation pH, retained dissolved SiO_2 in filtrate).

3. Influence of CO_2 concentration on above parameter (12% CO_2 + 30% CO_2).

4. Completing acidification with H_2SO_4. Commencing of acidification with H_2SO_4.

5. Carbonation of model solution with 8 gpl NaOH, 28 gpl Na_2CO_3 & 6 gpl SiO_2 (~~or~~ as $NaHSiO_3$) varying temperature & CO_2 concentration.

6. Measurement of pH carbonate/model solution at different temperatures.

7. Partial acidification by SO_2 in CO_2/air (stabilization of lignin).

B) **DECARBONATION (AT 100°C):**

1. In vacuum/100°C/optimizing
2. By steam under pressure.
3. Decarbonation of model solution.

C) **AGING OF CARBONATED BL:**

1. Precipitation & viscosity on evaporation after different lengths of hot storage (lignin & silica).
2. pH change on hot storage.
3. Aging in dependance of final pH and on speed of acidification.

D) **SILICA SOLUBILITY:**

1. In dependance of pH, CO_2 content and temperature in WBL and in model inorganic solution (by carbonation and also by addition of wet silica precipitate).

E) FILTRATION & WASHING:

1. Test different monofil filter cloth from 'Delco' (building 8 mm wet filter cakes).

2. Determine void volume in wet filter cake).

3. Investigate backsolving of lignin silica and absorbed alkali by washing with hot and cold water.

4. Try to characterise non silica contamination in silica mud (lignin, carbohydrate, Al_2O_3, Fe_2O_3, CaO, Na_2O ....).

5. Determine H_2O content of air dry (105°C) silica mud.

F) REALKALISATION:

1. Continue CPPRI work on investigating cause for increased alkali demand of carbonated BL.

Annexe III

DESILICATION PROJECT - US/IND/79/206.

STUDIES ON REALKALIZATION OF CARBONATED BLACK LIQUORS

Realkalization of carbonated black liquor has now been considered as an integral part of desilication process. It would be necessary to keep certain optimum level of free alkali for smooth evaporation of black liquor. Results of caustic soda and lime realkalization of carbonated black liquors are discussed below.

The carbonated black liquor was collected from Central Pulp Mills Ltd after the filtration stage. Different dosages of NaOH were added to carbonated liquor and refluxed for 30 minutes. Residual active alkali (R.A.A) was determined after cooling the liquor. Similarly different lime dosages were added and refluxed for 60 minutes. The results of lime realkalization & caustic realkalization are given below:-

Carbonated weak black liquor:

Solids	-	13.4%
R.A.A	-	3·6 9440 g/l as Na_2O
pH at 30°C	-	9.65 (Decrease in pH due to storage for about one week)

Lime samples :

Lime samples were collected from CPM and also from local lime kilns. The purity of lime sample as CaO was determined.

Realkalization by caustic addition :

Sl. No.	Caustic addn. as NaOH, g/l	pH of the black liquor 30°C	R.A.A. g/l as Na_2O		Caustic consumed g/l	Causticizing efficiency %
			Calculated	Actual		
1	NIL	9.65	-	2.6	-	-
2	2.4	10.02	6.0	5.0	1.0	41.7
3	3.4	10.04	7.0	5.2	2.2	41.1
4	4.4	10.14	8.0	5.6	3.6	45.5
5	5.4	10.21	9.0	5.8	4.2	40.7
6	6.4	10.43	10.0	7.2	2.8	56.3

The caustic added was in the form of concentrated solution of known strength. From the results it is clear that there is a difference in calculated and actual values of R.A.A. Difference is attributed to the consumption of sodium hydroxide by some phenolic hydroxide and carboxyl groups liberated by reduction in pH during carbonation (- ONa $\xrightarrow{}$ CO2 - OH), (-COONa CO2 COOH). The hydroxide consumption reached a maximum and then decreased slowly similar observations were made in lime realkalization. The results of lime realkalization are given below:

Realkalization by lime (Local Dehradun lime)

S.No.	Lime dosage g/l	Lime, g/l (corrected for purity*)	End pH	R.A.A as Na_2O g/l Calculated	R.A.A as Na_2O g/l Actual	Causticizing efficiency %
1	3.5	7.77	9.77	9.0	4.2	4.0
2	5.0	11.35	9.88	11.1	6.4	23.8
3	7.5	17.03	10.53	14.1	7.4	31.3
4	10.5	23.04	10.72	19.0	9.0	55.3

* Available lime index = 44.0%

Realkalization using CPM lime sample

S.No.	Lime dosage g/l as CaO	Lime, g/l (corrected for purity*)	End pH	R.A.A as Na_2O g/l Calculated	R.A.A as Na_2O g/l Actual	Causticizing efficiency %
1	5	11.22	10.28	2.52	8.74	12.98
2	7	15.71	10.66	4.16	11.6	25.6
3	8	17.95	10.90	5.16	13.0	31.22
4	10	22.44	11.01	7.32	15.88	40.05
5	12	26.93	11.03	8.44	10.74	39.91

* Available lime index = 44.56%

The results of lime realkalization show that the causticizing efficiency of lime at the initial stages is very low. The maximum causticizing efficiency of lime in the case of carbonated black liquor is less than 40%. The lime samples showed 98% causticizing efficiency with pure Na_2CO_3 solution.

From the results it is evident that the sodium hydroxide liberated by lime causticization is readily consumed by some organic components leading to lower value of R.A.A. compared to theoritical values. Even the causticizing efficiency, which was calculated based on actual increase in residual active alkali, is not the exact efficiency of the conversion. It can be concluded that both in caustic as well as lime realkalization part of the added or liberated NaOH has been consumed by organic components. Futher studies would be required to investigate the amount of free carboxyl and phenolic - OH groups before and after carbonation. An attempt was made to find out the phenolic hydroxyl groups by differential spectroscopic (U.V). Some results are given below :

Sample	ph-OH gps % on T.S.	ph-OH gps % on organic matter
Initial B.L	1.18	2.09
Carbonated B.L	1.16	2.06

There is no significant difference in-OH gps. Some alternate methods for -OH & -COOH group determination will be tried.

SOLUBILITY OF LIME DURING REALKALIZATION

Investigation, on solubility of calcium during realkalization by lime was also made. Increased amount of lime is not desirable for evaporation process. During lime realkalization the amount of calcium, going through black liquor evaporator units, would depend on the settling rate of precipitated CaCO3. In the present study the dissolved as well as suspended calcium was determined. For suspended calcium the realkalized black liquor was allowed to stand for one hour and black liquor sample from different levels of supernatant zone was pipetted. For dissolved calcium. A portion of realkalized black liquor was centriferged at 7000 rpm. and clear liquor free from suspended calcium was taken. The calcium was estimated by flame photometer. The results are given below.

Lime dosage g/l as CaO	R.A.A g/l as Na_2O	Dissolved calcium mg/l	Suspend calcium* mg/l	Total Calcium mg/l
Nil	1.88	-	-	-
5	1.30	120	290	410
7	3.30	120	350	470
8	4.30	120	390	510
10	7.60	120	490	610
12	9.05	120	720	840

* After one hour settling.

From the results it was evidenced that the dissolved calcium remained constant irrespective of the dosage. The suspended calcium increased with the increased amount of lime dose.

Results of viscosity of realkalized black liquor

(Caustic realkalization)

Black liquor sample	NaOH added g/l as Na_2O	Calculated R.A.A g/l as Na_2O	Actual R.A.A g/l as Na_2O	Brookfied viscosi mpa,sec.at 80°C solids	
				50%	55%
Initial B.L	NIL	-	9.76	24	95
Carbonated B.L	NIL	-	2.79	52	*
Realkalized B.L	4.20	6.99	4.49	60	479
Realkalized B.L	6.31	9.30	6.05	30	120

* Could not be determined due to separation & precipitation.

From the results it can be concluded that the R.A.A level over 6.0 g/l should be sufficient to have reasonable viscosity value.

Viscosity of lime realkalized black liquors

R.A.A 6.02 g/l		R.A.A 9.06 g/l	
B.L. solids %	Viscosity mPa. sec at 80°C	B.L.solids %	Viscosity mPa.sec. at 80°C
18.95	0.6	18.23	1.3
34.95	1.6	36.10	3.0
42.50	7.5	39.30	–
53.60	65	56.0	48.0