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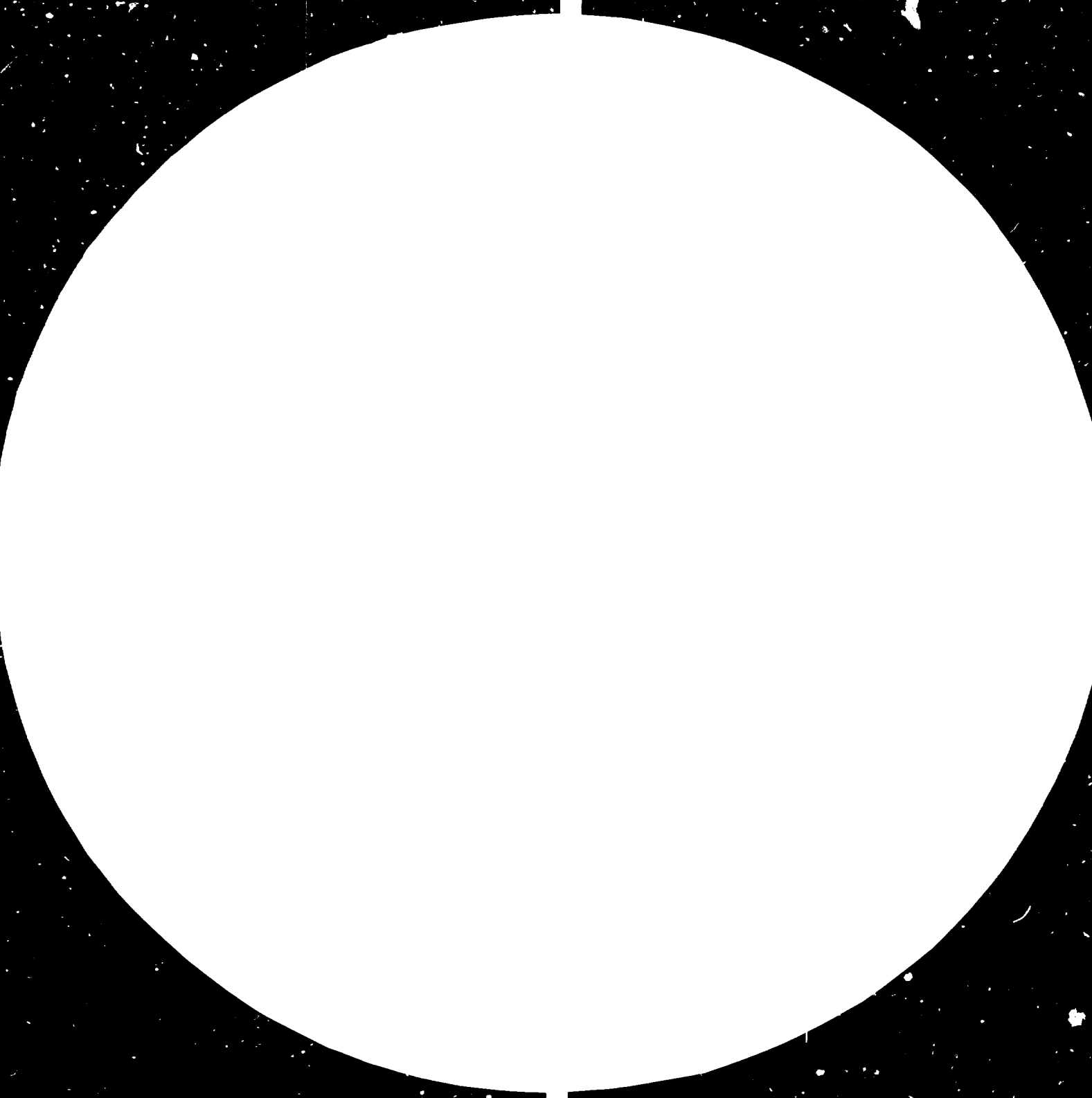

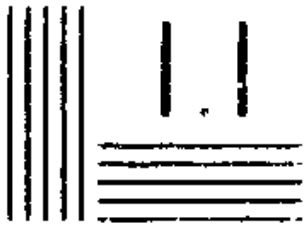

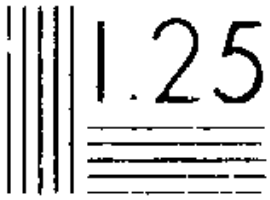

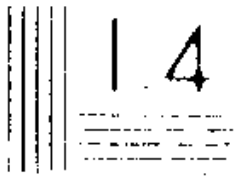

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March 1983

India

DESILICATION PILOT PLANT FOR BAMBOO BLACK LIQUOR

US/IND/79/206

Report on the third mission of the expert,
Mr. P. G. Bleier, 30 Jan 1983 - 3 March 1983

by

Paul G. Bleier
UNIDO Expert

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1. State of progress in desilication prior to mission to India

The progress made in desilication by carbonation trials at the Ashok Paper Mills (APM), Assam, was reviewed in the intermediate report by Mr. P.C. Bleier dated September 1982.

In repeated trial runs of a small, packed carbonation column (0.5 - 1 m^3/hour black liquor (BL) flow rate) the reduction of silica dissolved in weak black liquor (WBL) at about 60°C to about 0.6 gpl was accomplished. The precipitated "silica acid gel" (SAG), with some organic coprecipitate (less than 3% of total organic content of WBL) flocculated after hot retention of not less than 1 hour, subsequently the granular material sedimented rapidly and densely and showed good filterability with laboratory filtration equipment. Without lowering the temperature of the carbonated WBL, no method was found to further lower the level of residual dissolved silica. Optimal precipitation pH: about 10.0.

The repeatability of desilication results permitted a fair degree of confidence into the feasibility of large scale desilication of WBL. For increased confidence and to obtain design data for a larger pilot desilication unit, more trial carbonations of longer duration were planned but could not be effected because of operational difficulties of APM.

2. Transfer of the desilication project. Purpose of mission.

For continued desilication work UNIDO/SIDA decided to transfer activites to the 120 tpd bamboo sulfate pulp mill of the Central Pulp Mills Ltd, Fort Songadh, Gujarat, proposed by the Government of India as the new location for the project.

It was decided to visit the new project site in order to discuss with the Central Pulp Mill management and team of technicians a re-erection of the pilot carbonation unit, to select a convenient site for this unit and to decide upon an agreed mode of procedure.

On the occasion of this visit, UNIDO expert Mr. Bleier decided to attempt some practical carbonation so as to gain some information on carbonation response of the Central Pulp Mill WBL as compared to APM - WBL. With a different pulping procedure applied to different bamboo species of higher silica content leading to a different chemical milieu (higher sulfidity!) of the WBL one could expect either confirmation of results obtained in Assam, or otherwise information that the results obtained were of local significance only and that new reaction conditions had to be found under which a separation of silica would become possible.

For the purpose of practical trials the Central Pulp Mills was asked to prepare a reaction vessel and a pipe supplying flue gas to the reactor. Delayed delivery times prevented the realization of the original plan to carry out these trials with a transportable glass exchange column ordered for these and for similar purposes.

3. The Central Pulp Mills Operations

A. Normal bamboo operation

230 daily tons of local bamboo (dendrocalamus strictus) corresponding to 110 a.d. tons of bleached kraft pulp are chipped, screened (dry) and pulped in discontinuous digester for 4 hours with maximum temperature of 158°C, a liquid ratio of 2.8 and 12% sulfidity. Silica in bamboo 3%; 30% of silica stay with the (unbleached) pulp, the rest i.e. 5 daily tons dissolve in the black liquor. The weak black liquor collected after the first of three (countercurrent) brown stock washers - about 8 m^3 for each ton of a.d. screened unbleached pulp - has an average concentration of about 14% T.S. with 49% inorganic material and 5-6 gpl silica and 7-8 gpl residual free alkali as NaOH. WBL temperature 60/70°C. In the first of 5 evaporator effects the percentage of T.S. is raised to 22%, in the second to 26% and reaches finally 42%; further concentration by direct contact with flue gases in a cascade to 62%.

The flue gas - after an electrostatic precipitator - is available at about 85°C with an average content of 13.5% CO_2 and 7% O_2.

Lime burned in a local shaft furnace is used for causticification; CaO availability is only 60% (!) and the silica content 5-6% SiO_2. 70 daily tons of lime mud (containing 7.4 tons of silica) with a low (40%) solid content have to be transported for landfill; high lime mud alkalinity precludes utilization for soil amelioration.

The difficulties arising from siliceous lime mud (high moisture and vitrification of silicates on burning) together with high fuel costs have caused the Central Pulp Mills some years ago to discontinue the operation of the rotary lime kiln designed for lime recycling.

B. Bagasse

The Central Pulp Mills presently is running trials with bagasse to develop an adequate operation using available equipment for the following reasons: Limited bamboo supply; the bamboo alloted to the Central Pulp Mills for cutting is expected to flower within the next few years resulting in interrupted raw material supply; local abundance of sugar cane and technological advances of the sugar industry making a bagasse surplus available for fibre production.

Sulfate pulping of bagasse with 24% bamboo admixture is technically advantageous for reasons of good yield and good bleachability; bagasse pulping is encouraged by the authorities by means of taxation benefits for the paper produced with fibre mixture. About 25% fines are removed by dry screening; the residual material contains about 7% silica. The bulky nature of bagasse considerably reduces mill capacity and requires a higher liquid ratio.

Bagasse pulping inserted in the normal bamboo operation during the February 1983 UNIDO/SIDA mission permitted first desilication trials with this interesting fibre source.

4. Experimental Work

Trial carbonations were carried out with two different reaction units:

A. Bubble reactor

A mild steel cylindrical 800 l tank fitted with a high speed agitator with two 2" diameter propellers and with a supply pipe line (4" reduced to 2") admitting at the bottom of the tank and tangentially in direction of the agitator rotation flue gas for better distribution through a screen plate at the open end.

B. Exchange column

A stainless steel 8 m high, 1 m diameter column (Lundberg, USA) packed with 5 m^3 ceramic 2" "Inverlox Saddles" for countercurrent gas/liquid exchange, with liquid distributor on top and a 14" admission opening for flue gas at the lower end. The column belonging to different chemical units was made available for trial carbonations by the Central Pulp Mills, moved near to recovery boiler and fitted with about 20 m of a 14" steel supply pipe for flue gas.

The gas is drawn through the packing by a blower connected to the column exhaust with a plastic pipe reinforced with glassfiber.

Gas and liquid flow could be adjusted manually with valves and dampers that however did not permit precise adjustments.

No provisions were made for heating or cooling. With the given temperatures of black liquor and of flue gas the actual reaction temperature remained pretty stable at $62^{\circ}C \pm 5^{\circ}C$.

Industrial practice requires - if possible - work at process temperatures to utilize the heat content available without additional energy expenditure for heating or cooling. Still, the study of temperature variation may well contribute to the understanding of the chemistry of silica precipitation and flocculation. Rather than with the Fort Songadh large exchange column, these studies should be conducted with the more flexible, transportable glass column shortly to be delivered.

5. pH Measurement

Experience in Fort Songadh mill confirmed earlier formulated ideas that pH probably is not the critical magnitude either for precipitation of silica (alkalisilicate) nor for lignin (alkalilignin). pH still constitutes an important and easy to measure parameter that repeatably indicates a certain precipitation behaviour under defined carbonation conditions.

Like in other desilication work, the small portable digital pH-meter (WTW, West Germany) rendered invaluable assistance by giving repeatable indications even to the second place behind the decimal point (!).

To have a comparable base, all pH values were recorded at 30°C; in the pH range of 10.0/10.5, the pH values measured at about 60°C are about 0.3 units lower than at 30°C (in spite of potentiometric temperature correction on the pH meter); at higher pH values, this difference is somewhat larger.

It has been convened, that all pH values reported and discussed - unless temperature of measurement is specifically stated - refer to measurements taken at 30°C.

6. The differential silica precipitation by carbonation

Results and observations during the trials

All trial carbonations - about 15 experiments with the bubble reactor and about 10 runs with the large exchange column - established beyond doubt that silica can be separated by the precipitation of a granular, highly hydrated gel of greyish colour, contaminated with only minor amounts of organic coprecipitate. Apprehensions, that the Central Pulp Mill WBL might be more tricky in respect to differential precipitation proved to be unfounded. On the contrary, it is felt that in the Central Pulp Mill WBL SAG flocculates with greater ease and with lessened organic contamination than the liquors studied in Assam. Although there is no ready explanation for this advantageous fact, the higher silica content in WBL might be held responsible or the higher pulping sulfidity that gives rise to more stable sulfoligninates of lower molecular size. The presence of a destabilized form of dissolved silica cannot serve as an explanation: Agreement of direct molybdenum blue colorimetry with gravimetric analytical results proves silica to exist in WBL in monomolecular form only i.e. as $SiO_2(OH)_2^{--}$ or $SiO(OH)_3^-$ or $Si(OH)_4$.

The silica solubility of 0.6 gpl in carbonated WBL of 60 - 70°C as found in previous desilication work was confirmed in Fort Songadh experiments. This interesting fact could be interpreted by the presence in similar proportion in both Jogighopa and Fort Songadh carbonated BL of the three molecular silica species given above and accepted to be present in alkaline siliceous solutions.

The decrease of silica solubility on cooling carbonated BL reported and studied in Jogighopa also was found to occur in Fort Songadh. This phenomenon that seems to be anomalous, considering the rise of pH with reduced temperature, might find an explanation by studies of the temperature dependence of the hydrolytic equilibria of the silica species named above and of the other salts present in carbonated WBL.

7. Comparison of carbonation in different reactors

The observation made in earlier desilication work that the differential silica precipitation from BL is largely dependent on the "mode of carbonation" was extensively confirmed by work with Central Pulp Mill equipment and material.

Speed of pH reduction governed by the effectivity of CO_2 transfer determines the sol - gel transition of silica and of ligninates.

In the bubble reactor pH reduction to SAG precipitation was accomplished in about 30 minutes (treating charges of about 300 l i.e. a rate of 10 l/min), whilst in the exchange column carbonation was accomplished during the passage of (estimated) only 2 minutes (flow rate about 100 l/min). In the bubble reactor silica precipitation started in some cases at a pH 10.8 (!) and seemed to be optimal in the range of pH 10.6 - 10.4; even after prolonged carbonation (2 hours) to a pH of 9.7 no appreciable organic coprecipitation occurred. This was true not only for bamboo WBL but equally for bagasse WBl and for semiconcentrated liquors of 22% TS and 26% TS.

On the other hand, rapid carbonation in the exchange column yielded different results. No SAG precipitated above pH 10.45 - 10.50; however at this pH the presence of small amounts of chocolate brown and filter-clogging precipitate was observed indicating some local overacidifcation.

In the range of pH 10.4 - 10.1 good filtering SAG separated, with some indication of better desilication at lower pH. Below pH 10.1/10/0 heavy chocolate brown organic precipitation commenced, again causing bad filtration properties.

Comparing APM with Central Pulp Mill column carbonation it is remarkable that under APM conditions a finely dispersed "milky" precipitation appears first in the treated WBL that turns after some

retention into heavy yellowish floccs, whilst in Fort Songadh granular jellylike transparent floccs immediately form at the column exit and also in the bubble reactor carbonation. Also the orange coloured organic coprecipitate of APM was not observed in Central Pulp Mill desilication.

It is also important to stress the fact that when using pure CO_2 gas for BL carbonation (Kulkarni, CPPR, Dehra Dun, Jaspal, WPM, Dandeli, Konolka, Parkhe R.I., Khopoli) heavy brown organic sludge invariably precipitates, whilst utilization of flue gas with 10-15% CO_2 permits differential SAG separation (Kunar, Budapest University, Franzreb, West Dürkheim, El Ebiary and Hackl, Rakta Alexandria, and UNIDO/SIDA.)

8. Desilication of semiconcentrated black liquor

Trials of carbonating BL from the first two concentration stages from the BL evaporators at 22% and 26% TS solids in the bubble reactor were most successful. Differential SAG precipitation occurred after shorter treatment time, but at a similar pH. The resulting SAG floccs seemed to be somewhat smaller and filtration proved to be more difficult. Silica mud was unchanged with the usual greyish colour.

A first analysis disappointed by showing higher residual silica in the filtrate after carbonation, so that the hoped for better overall desilication did not materialize. This has to be checked; it is however not likely that a more concentrated salt solution should increase silica solubility.

An increased sodium loss, however, might be incurred, not only because of physical retention of the more concentrated liquor in the filter cake voids, but also because the higher sodium ion concentration (the "common ion") may cause increased insolubilization and retention of some sodium silicate species.

Carbonating semiconcentrated BL instead of WBL would double the capacity of carbonating equipment.

Trial carbonations of semiconcentrated material with the exchange column could not be carried out because of lacking provision for extraction of the material from the evaporators under vacuum.

9. Desilication of bagasse black liquors

A number of trial carbonations with bagasse WBL and one trial with bagasse semiconcentrated BL in the bubble reactor demonstrated - contrary to expectations - a response to carbonation and SAG precipitation very similar to bamboo BL; the small variations observed may only be accidental. Foaming tendency, however, seemed definitely to be increased.

The sulfate process employed in bagasse pulping on Fort Songadh differs from the mainly adopted soda bagasse pulping. Countercurrent brown stock washing (on three washers) proved more difficult because of the slimy nature of the stock; However bagasse WBL contained only minor amounts of susperded solids. BL filtration is not practised in Fort Songadh.

This successful bagasse desilication is somewhat of a novelty; in spite of a fairly comprehensive study of desilication literature no reported instance of bagasse desilication is known to the UNIDO expert.

10. Plugging of carbonation column

During the trial period with the big exchange column the original flow rate of 10/12 m^3/hour reduced to 4/5 m^3/hour with visible reduction of flue gas quantity leaving the blower exhaust. (The density of the white flue gas fume does not appear to be reduced by the scrubbing action of the column).

The plugged column was freed by rinsing with white liquor. Although plugging may have resulted only from overacidification that occurred because of the difficult adjustment of a correct BL flow, it was decided to reduce the risks of repeated plugging in the future by adjusting pH reduction within the column to the non-precipitation limit (pH 10.5/10.6), and to complete carbonation in a non-packed reactor. This will also increase carbonation capacity.

11. Foam

As expected, the carbonation of WBL in the bubble reactor produces obnoxious quantities of foam. Semiconcentrated BL of 22% TS and higher does not pose foam problems, probably because of the insolubilisation of sodium soaps at high sodium ion concentration.

Contrary to expectations and to APM experience, foam also was a problem with the carbonated WBL leaving the exchange column. The probable cause for this is seen in the unhampered fall over 2 m of the liquid from the support holding the packing to the liquid level underneath.

To reduce foam, foam killer was used for simplicity's sake, rather than other known and cheaper methods like liquid spraying. The type of foam encountered is a rather coarse"external" foam that surfaces rapidly and is not very stable.

12. Sedimentation of precipitated silica

Well flocculated SAG sediments rapidly and densely. Coprecipitated brown ligninous material interferes with sedimentation.

Sediment volumes between 15% and 25% of the total carbonated WBL volume were observed. The variation in sediment volumes indicates that flocculation (or even precipitation) are as yet not under good control. This and the appearance of two layered (coarse and fine) sediments might be remedied, once hot retention with or without gentle agitation can be practised.

For technical operation, the clarification of carbonated BL by sedimentation prior to filtration seems to be indicated.

13. Filtration of precipitated silica

Like sedimentation, and for similar reasons, filtrability of SAG proved to be somewhat variable. In absence of brown ligninous matter good or excellent filterability was encountered in the majority of cases. All filtration tests so far were carried out by vacuum filtration through a buchner funnel equipped with open filter paper. There is no doubt that good filterability will be independent of the filter medium used.

The floccs building the filtercake are stable and withstand mechanical action. Smoothing a cracked filtercake with a spatula does not destroy filterability.

The greyish colour of the filtercake is variable. The colouration (also reported by other authors) may be caused by flue gas impurities or by coprecipitated inorganic or organic contaminations. Iron oxide

(and R_2O_3) is present in the silica mud. The extent of organic coprecipitation - judged to be rather low, has not yet been determined. The presence of a lightly coloured fractionation of alkalilignin is suspected.

With 30%, the solids content of silica mud obtained in laboratory filtration is rather low.

Airdry silica mud loses 15% on ignition. The ignited material contains 85% SiO_2 and some alkali (first analyses).

14. The washing of silica mud

The strange phenomena observed when washing silica with water in Jogighopa/Assam again occurred in Fort Songadh.

The filtercake easily washes free of adhering dark coloured WBL. However the washings, when collected separately, are of an unexpected dark colouration and show higher alkalinity than the carbonated WBL filtered (!).

A plausible explanation for the now confirmed phenomenon could be as follows: In presence of high sodium ion ("common ion") concentration the solubility of $Na(SiO(OH)_3)$ or $Na_2(SiO_2(OH)_2)$ is lowered sufficiently, so that these compounds separate with the rest of the precipitate. On dilution with washwater these compounds redissolve, ionise and hydrolyse: $Na(SiO(OH_3) + H_2O = Si(OH)_4 = NaOH$. The caustic soda formed by hydrolysis in turn redissolves some of the precipitated lignins.

Unfortunately also some silica is likely to be redissolved. Optimal washing of silica mud has to be found by experimentation in order to balance desilication, organic loss and soda loss.

15. Recaustification

Carbonated black liquor has to be recaustified for reasons of solution stability prior to evaporation and to combustion. Although it was agreed to exclude this problem from the scope of the present UNIDO project, its urgent nature necessitated immediate attention. On irregular return, even of small quantities of carbonated BL to the main WBL stream before evaporation, ligninates destabilized by pH reduction caused operational difficulties in evaporation.

A first trial of steam stripping showed this to be ineffective for CO_2 removal.

First backtritrations with caustic soda or with burned lime of carbonated WBL to the original pH indicated that CO_2 uptake to the point of silica precipitation roughly corresponds to the "residual free alkali" (TAPPI method, titration to pH 8.3) present in the original WBL.

16. Detailed experimental report; Analysis

This report concentrates on the essentials of progress and new findings in desilication. Detailed notes of all the trial work are being kept in the Central Pulp Mill laboratories by Mr. Gopinath Rao, Chief of the laboratory and nominated by the Central Pulp Mill to be their representative in the common R + D work.

At the time of departure of the UNIDO expert a number of analytical results were not yet available and at the time of writing this report have not reached Vienna.

Desilication results could be obtained rapidly (within 20 min) by direct molebdynum blue colorimetry of diluted black liquors. Visual colorimetry used so far will be replaced by the more accurate electrophotometric colorimetry as soon as possible.

17. Future work

Appendix I contains the minutes of the concluding meeting at the end of the UNIDO mission outlining items to be studied in the near future (written by Shri Gopinath Rao).

18. Conclusion

After a month's work considerable growth of confidence into the viability of carbonation for desilication of black liquors can be recorded. Realistic chances for industrial application of desilication are opening up. The favourable availability of a large packed column permitted the scaling of carbonation up to a semi-industrial operation. For continuous semi-industrial work clarifiers and an adequate filter have to be provided. The success so far calls for a determined effort to complete the work and to overcome difficulties as may arise.

19. Expression of thanks

All official bodies, SIDA, UNIDO and the Ministry of Industry, Government of India, must be thanked for their efforts that contributed to the progress made. Equally valuable is the interest taken in technical matters by CPPR, Dehra Dun and Parkhe Research Institute, Khopoli. Most of all, the co-operative spirit and dedication must be appreciated of the Central Pulp Mills management and of the team of qualified technicians and consultant with their essential aid in opening up new avenues for more economic pulping of non-woods and for the protection of the environment.

Personal kindness and Indian hospitality experienced by the UNIDO expert rendered work easy and enjoyable.

Abbreviations used in this report

BL	=	black liquor
WBL	=	weak black liquor
APM	=	Ashok Paper Mill
SAG	=	silica acid gel
TS	=	total solids
tpd	=	metric tons per day
gpl	=	grams per litre

ANNEX I

CENPULP : FACTORY
DATE:- 04.03.1983

MINUTES OF THE MEETING ON DESILICATION PROJECT

A meeting was held at the Directors bungalow on 27.2.83 to discuss further work to be carried out on the Black Liquor Desilication. Following were present:

1. Mr. Paul G Bleier - UNIDO Expert
2. Mr. N S Sadawarte - Jt. Managing Director
3. Mr. P G Nemade - General Manager (Mfg)
4. Mr. C Gopinath Rao
5. Mr. S H Abnyankar
6. Dr. S C Shenoy

At the instance of Mr. Sadawarte, Mr. Bleier explained that the work on the project may be carried out further on the following lines during his absence as he was scheduled to leave Fort Songadh on 28th Feb to return to Vienna.

1. To establish optimum conditions of pH, and WBL flow in the pilot plant and to study their effect on desilication in terms of residual SiO_2 in grams per litre; also to study the dependence of hot retention time on WBL quality. He felt that the optimum pH could be 10.2 to 10.4.

2. To study in the laboratory the ideal condition required for good flocculation for filtration and sedimentation, He emphasised the need for carrying out all filtration and sedimentation tests at 60-70°C.

3. He expressed the need for having a more sensitive valve and flow indicator for BL control for the pilot plant.

4. He felt that the foam problem, which is very acute now can be reduced by providing suitable baffles inside the packed column to reduce the height through which the liquor at present is falling.

5. He promised that the pH recorder and pitot tube would be brought from Ashoka Paper Mills, Jogighopa. This will be necessary to provide better control in plant operation.

6. Mr. Bleier suggested that trial with semi-concentrated BL of 20-30% concentration also may be taken up in the absorbtion tower.

7. In order to eliminate the problem of jamming in the packed column due to silica sludge, he suggested that a 2-stage carbonation - 1st stage in the packed tower upto 10.5 to 10.6 pH followed by carbonation in an open pot provided with agitator and flue gas connection upto 10.1-10.2 pH may be carried out.

8. It was also suggested that a 2-stage treatment, 1st by carbonation upto a pH of 10.6 followed by treatment with acids like Acetic Acid or Sulphuric Acid may also be tried. Sulphuric Acid will have additional advantage of providing a source for sulphur make up.

9. Mr. Bleier indicated that the experiment on steam stripping for decarbonisation, tried in the batch carbonation pot was not a success, since there was no increase in the pH.

10. It is necessary to correlate WBL quality with behaviour in carbonation and filterability. For this, full analysis of the BL to find out silica R_2O_3, calcium, total ~~solid~~ alkali, etc will have to be carried out.

11. Mr. Bleier observed that during the sedimentation test after carbonation, he found two layers of sludge, a coarser one at the bottom and a finer one just above that. This can only mean that it is the finer one which is causing problem in filteration.

12. He stressed the need for carrying out some more test on realkalisation with NaOH and lime. He suggested that lime treatment for desilicated BL may be given in the carbonation pot after proving indirect steam coil. In case of lime treatment, it is necessary to test the filtered BL for CaO.

13. Mr. Bleier stressed the need for finding out carbon dioxide in original as well as desilicated liquor to find out the degree of carbonation. For this, he suggested that different mixtures of $CO_2 + N_2$ or CO_2 + air may be tried on WBL and model solutions of NaOH, Na_2CO_3, Na_2SiO_3 and different salts similar to those present in WBL. It was felt that this work may be carried out at PRI as better facilities are available there.

14. Mr. Bleier suggested that filtration test may be carried out by using flocculating agents like aluminate, polyacrylamides etc. Also, retaining the carbonised black liquor in a hot water bath for one or two hours will also improve filtration characteristics.

15. It is necessary to test for silica in the filtrate immediately after filtration in the hot condition as otherwise silica analysis could be wrong if the BL is allowed to cool.

16. It is necessary to standardise filter cake washing and to find out the wet weight and dry weight of silica sludge collected from a known volume of desilicated BL (500 cc is taken as our standard).

17. Mr. Bleier expressed a need to find out whether the effect of oxidation of BL during carbonisation on desilication.

18. Mr. Bleier also felt it necessary to investigate the effect of silica on lime mud burning in the laboratory.

19. Mr. Sadawarte indicated that progress report on desilication should be sent to Mr. Bleier every week.