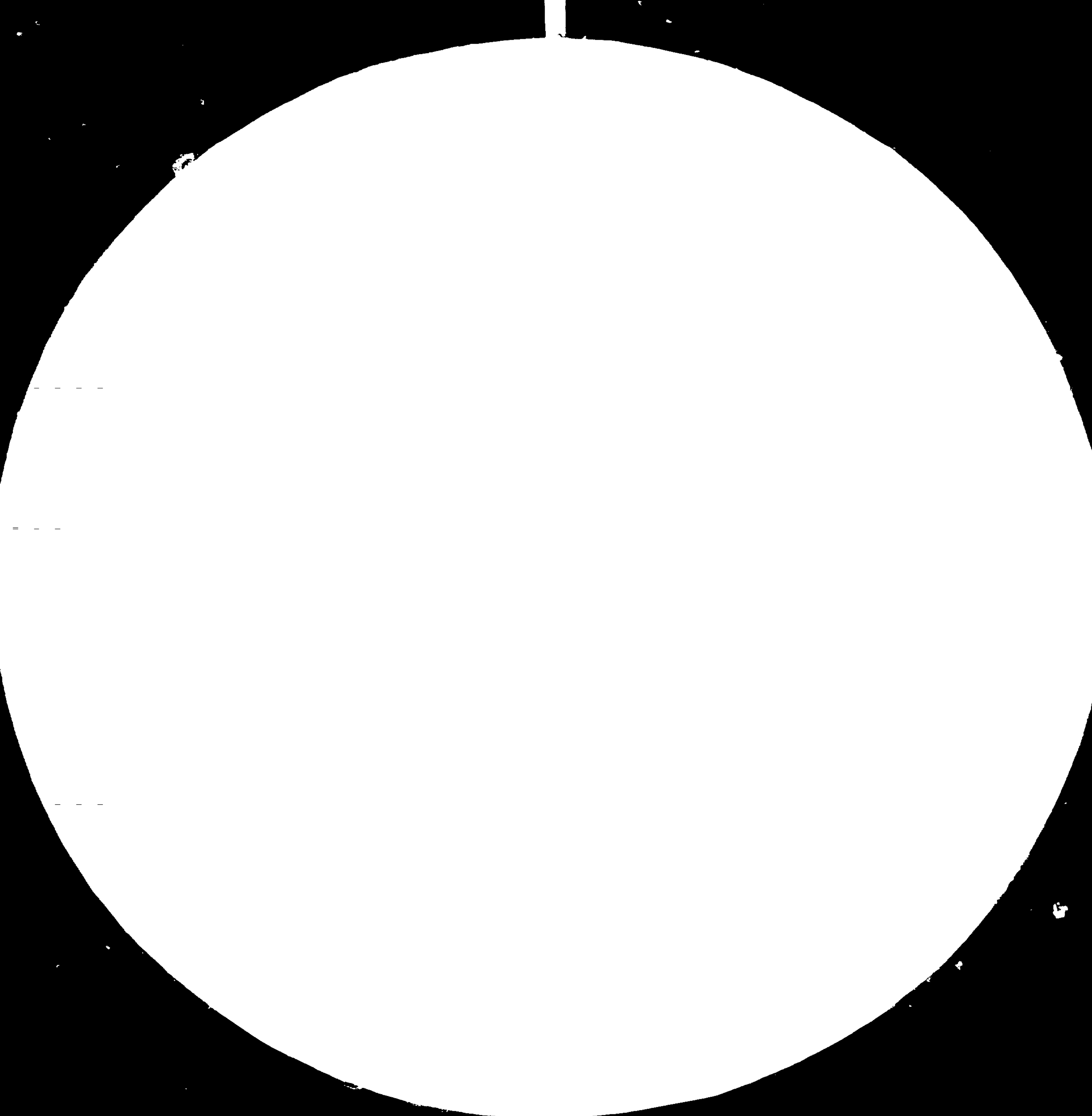

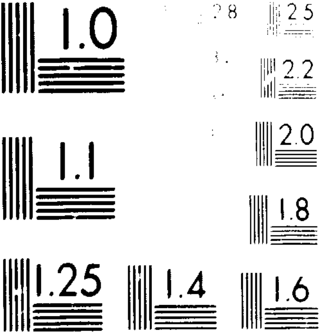
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REPORT ON THE RESEARCH WORK CARRIED OUT

ON

DESILICATION OF BAMBOO BLACK LIQUOR

AT THE ASHOK PAPER MILLS, JOGIGHOPA, ASSAM

FROM 1980 TO AUGUST 1982

UNDER PROJECT

US/IND/79/206

by

UNIDO Expert
P.G. Bleier

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I. THE PROJECT

The main raw material used for pulping in India and many other developing countries is bamboo, which contains an appreciable amount of silica. Most of the silica gets dissolved during cooking of this raw material and remains as an undesirable constituent in black liquor and causes the following problems at the subsequent stages of its process:

- Scale formation in evaporator tubes
- Hard smelt deposits on furnace walls of recovery boiler
- Slow settling characteristics of recaustisized white liquor
- Unsuitability of lime sludge for lime mud reburning.

As a result the recovery operation and economy are adversely affected because of unsuitability of lime sludge for reburning. In the near future, there will be more and more problems in disposing of lime sludge considering the stringent environmental regulations that the developing countries are going to formulate in the next decade.

there is, therefore, sufficient justification in undertaking projects for pilot plant trial based on knowledge available from various laboratories. This would increase not only the efficiency of the bamboo based mills but also will reduce their chemical cost considerably. Besides, it could provide extra steam and energy for the plant by burning the organic matter in furnaces and thus avoid large water pollution and environmental dangers.

The Ashok Paper Mills uses 100% bamboo as fibrous raw material. It has a recovery plant, but it does not return the lime as it cannot successfully reburn the lime needed in the causticising reaction for reclaiming the caustic soda in the chemical recovery plant. About 270 kg of burnt lime on 100% Cao basis per tonne of pulp produced is required for this reaction using 100% bamboo as raw material. In many parts of the world, huge quantities of lime mud is, therefore, removed from such pulp mills containing most of the silica in the lime mud, and the mud is dumped and used for land filling or is allowed to go into the streams and rivers polluting the water.

Although a number of valuable and apparently reliable technical papers are available on the subject of desilication, the uncertain economical and practical adoption of the desilication process by industries in the developing countries, and lack of finance to promote such a pilot scale project had been the main deterrent in venturing to invest substantial funds in a pilot plant to transform the laboratory results to practical applicability. International organizations like UNIDO can play an important role by undertaking to finance such a project which will be beneficial to most of the developing countries engaged in the manufacture of pulp using bamboo as raw material.

II. DETAILS ON THE ASHOK PAPER MILLS, JOGIGHOPA

1. Bamboo chips: The bulk of the raw material used in Jogighopa is bambusa tulda, a rather thin species, home grown in Lower Assam by peasants, with a content of only 3% SiO_2 (in unwashed chips). 1.15%
An occasional admixture is forest grown bambusa voluka, reaching considerable thickness on maturity.

The bamboo is chipped and digested either in a high moisture "green" condition (said to cause much foaming in WBL*) or as dry, brown culms. The product of two different multiknife chippers giving varying chip character is used according to requirement. There is no washing of the chips prior to pulping.

2. Pulping: Jogighopa works with a low sulfidity of 12% (normal 24%) so that the process really stands between soda and kraft pulping. This possibly explains the lack of any sulfate smell around Jogighopa also when handling and carbonating WBL. The rather high chemical losses usually are made up by sodium sulfate. Caustic soda is available from the electrolysis plant. Occasionally elemental sulfur is used.

3. WBL: The considerable variations in WBL concentration and composition is mainly caused by insufficient control over chip size, chip moisture, and digester filling. Solids content varies between 11 and 14%, free residual alkali between 5 and 10 g/1 Na_2O, and pH between 11.8 and over 13.

In order to secure WBL of the highest available temperature, experimental samples for carbonation were originally procured after the first brown stock washer. However, for decreased variability and possibly also for reduced contamination with suspended fibers and debris, WBL was drawn afterwards from a large storage tank with hardly any temperature loss. Although the WBL does not seem to contain much suspended solid material,

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* Abbreviations used in this report are
WBL - weak black liquor
TWBL - treated (or carbonated) weak black liquor

all attempts to filter WBL in the laboratory failed. The suspended material present would add to the loss on filtration after pH reduction.

When the pulping operation was shut down over a period of weeks, investigations were continued with WBL drawn from the hot storage tank. (Sulfuric acid was employed for pH reduction). No change of property resulting from aging could be observed. Also carbonated WBL did not seem to change on prolonged storage. Ordinary, but not too careful handling does not produce much foam in WBL.

4. Recovery boiler flue gas: The gas is obtained by tapping the main flue gas duct immediately after the recovery boiler exhaust fan. It is transported over about 15 m through a heat insulated 10 inch pipe and over a valve, a non-constricting Prandtltube measuring device, some bends, and a Pall Ring filled simple trap for condensate to the bottom inlet of the carbonation tower. A separate blower was provided but not required, as the pressure generated by the exhaust fan is sufficient to overcome all obstacles including a height of at least 340 cm Pall Ring packing in the column.

As it takes 24 hours for a restarted recovery boiler to reach equilibrium condition, there was not much chance to observe constancy in flue gas. It seems, however, that in normal conditions the flue gas contains 9 - 11% volume CO_2. To maintain the desired pH drop on carbonation short time variations in CO_2 content due to work on the recovery boiler do not seem to require adjustment of WBL flow. The flue gas arrives at the column with a temperature of about 73°C.

The condensate separating from flue gas is of brownish colour and has a pH of 8.5. It has no sulfidic smell nor a positive lead acetate reaction before or after passage through the carbonation tower. After passage through the carbonation tower the whitish, smoky appearance of the flue gas caused by dispersed alkali salts and/or droplets, (there is no electrostatic precipitator), is hardly changed.

III. THE STRATEGY OF RESEARCH

August 1980, survey of previous desilication work.

1. The study of literature available on desilication in alkaline pulping of annual crops resulted in the decision to aim at practical pilot-scale desilication by carbonating weak black liquors (WBL) with recovery boiler flue gases. This seemed the most promising method for the following reasons:

(a) Desilicating black rather than green liquors should permit overcoming difficulties in the evaporation and combustion stage as well as those in caustification and clarification.

(b) Work with weak rather than with semi-concentrated black liquors should reduce difficulties with co-precipitation of organic material and with viscosity.

(c) Of the two known methods, desilicating WBL by pH reduction is preferred to lime treatment. A large excess of lime is known to be required for effective desilication, even if an intricate plant with - say - 4 - 5 stages for counter-current treatment by lime should be chosen. (See reports by R.L. Bhargava also on the disused pilot plant of West Coast Paper Mill, Dandeli, Karnatak, India). Lime has to be bought (and in the case of Jogighopa transported over 1,000 km), whilst CO_2 is available in stack gases.

Lime treatment results in more sludge (calcium carbonate/calcium silicate) to be handled and to be disposed of than the silicious mud after carbonation, expected also to pose problems.

Also, energywise carbonation is likely to be cheaper than desilication by lime.

(d) Cheap flue gas of the recovery boiler was to be used rather than boiler stack gases because of higher CO_2 content, because of lower temperature, and because of its availability in vicinity to the recovery plant. In the absence of a lime kiln there is no option to use kiln stack gases.

2. For carbondioxide absorption a packed tower was suggested as a means for mass transfer for the following reasons:

(a) The foam problem could largely be surpressed by a system of distributing liquid in a continuous gas phase.

(b) Absorption columns are units of low or negligible energy demand. No energy is required to disperse the reacting phases.

(c) The thin films flowing over the packing of a column - particularly at low viscosities - are advantageous because of the short distances of transport for CO_2 from the gas/liquid interface into the bulk of the liquid. This reduces or completely avoids the danger of over-acidification on the phase interface and of irreversible precipitation.

(d) Being able to neglect considerations of foam and of energy, the operator can concentrate on optimum desilication rather than high absorption efficiency.

(e) An absorption column is the given unit for steam stripping trials; the same unit could be used for work on carbonation and for experimental CO_2 removal to raise the alkalinity in the preparation of TWBL for evaporation and combustion.

3. (a) The decision whether a clarification stage should precede filtration should be left for a later stage.

(b) To separate precipitated silica a filter press or rotary band filter is preferred to decanting centrifuges that are known to demand much energy, maintenance and outside servicing, difficult to obtain in developing countries.

4. Two central problems were expected to require attention in the desilication work:

(a) To find optimal conditions to precipitate a maximum of silica with minimum co-precipitation of valuable organic black liquor components and minimum loss of salts.

(b) To find conditions for solid/liquid separation (sedimentation and filtration) of precipitates known to be difficult.

5. Preliminary decisions were discussed and co-ordinated between the two experts working on the project.

IV. THE PILOT PLANT

1. WBL is drawn from a hot WBL storage tank and transported by gravity through a 3/4 inch pipeline to the top of the tower. The flow is controlled by a valve positioned for operation whilst observing the TWBL flowing into a receiver.

2. Flue gas is transported by the recovery boiler exhaust fan through a 10 inch pipe and a trap for condensate to the bottom inlet in the tower. The flow is regulated by a valve.

3. The absorption column. The tower is a heat insulated 510 mm Ø mild steel tube, fitted on both ends with cones that carry the in- and outlets for gas and for liquids. On the inside of the lower end of the shell, a mild steel grid is fitted to hold the packing. The upper end of the tube is fitted with a liquid distribution plate in horizontal position with many 3 mm holes for liquid passage and with some 3 cm Ø and 5 cm high tubes to allow the spent gas to pass (suggested by India Engineering Ltd, handling the know-how of Norton Int.). Minimum liquid flow to guarantee proper distribution was stated to be 8 l/min (India Engineering Ltd.). With a packed height of 190 cm it is estimated that less than 25 l are held in the column at any time.

The liquid exit is provided with a liquid seal. Liquid flow is determined by timing the filling of a standard volume. Prior to continuous pH monitoring final pH is frequently controlled in separate samples at temperatures of 30 A 60°C. ← Qnol

4. Tanks for flocculation and sedimentation. Carbonated WBL is collected in heat insulated tanks, so far not provided with means of agitation, although gentle agitation may assist in flocculation and should help in clarification.

5. Instrumentation of the pilot plant.

(a) Temperature is measured by normal mercury thermometers.

- WBL: at column entrance, at column exit, in hot retention and flocculation tank
- Flue gas: before and after Prandtl compression tube at column entrance and at column exit.

(b) Flow rate.

- WBL: by timing the filling of standard volume with WBL
- Flue gas: by conversion from pressure difference read by Lambrecht inclined tube manometer from Prandtl compression tube.

(c) pH is measured in samples of WBL and TWBL with a combined glass electrode of adequate resistance to temperature and to alkalinity. The transportable precision-pH meter reading digitally to two digits, has temperature compensation on electric supply by batteries.

(d) CO_2 is measured by the UNORM M 5861 measuring instrument on samples drawn from the gas supply line and from the central exhaust pipe on top of the absorption towers.

6. Analysis. Both wet combustion and gravimetric SiO_2 determination laid down in the Tappi Standard Method are lengthy and work-intensive procedures. For speedy follow-up of desilication trials, therefore, the well-known Molebdynum Blue colorimetric method for silica determination was adapted for use in WBL analysis. Destruction of the organic material and the required monomeric solution of silica are affected by low temperature fusion of dried WBL in a large nickel crucible with sodium hydroxide and sodiumperoxide. Contact of

alkaline solutions with glassware is avoided. Traces of nickel seem to have a beneficial effect on the development of Molebdynum Blue. In the absence of a photoelectric colorimeter colour matching was carried out visually.

Repeated analyses and ample repetition of determination of residual silica (silica solubility) in carbonated WBL have established a high degree of reliability of the method developed in Jogighopa, most useful also for future work.

7. pH determination. All pH values measured with a glass electrode in the course of the desilication work in Jogighopa have been determined at 30°C. Many measurements were also repeated at 60°C, where on the average a decreased value of 0.4 pH units was found. Rather wide variations of this difference do not permit - so far - numerical pH correction due to temperature change.

Temperature compensation of the pH-meter corrects only for potential change of the glass electrode due to temperature. The change of the hydrolytic equilibrium with temperature in the complex mixture of sodium salts in WBL has to be determined empirically. By titration only 30% of sodiumbicarbonate was found in WBL at pH 10, whilst in the pure system of a bicarbonate buffer, 50% bicarbonate is present at this pH; this demonstrates the considerable shifting of equilibrium from pure solutions to WBL. (It is somewhat surprising that the technical and patent literature seen does not state temperatures of pH determinations, nor is there any reference to the problem pointed out above.)

V. THE RESEARCH WORK

A. February 1981 (first mission to Jogighopa).

1. First attempts to blow mill RCFG*) through mill WBL resulted in the production of large quantities of obnoxious foam.

2. pH reduction to levels of 9.8 to 10.2 at 65°C (using WBL from the first pulp washer) resulted in a voluminous gelatinous, darkly coloured precipitate.

3. Retention at elevated temperatures of the precipitates over periods of hours brought about flocculation, i.e. change into a heavy, rather granular precipitate with improved sedimentation and acceptable filtration properties. The unwashed residues consisted mainly of nonsilica material.

4. An improvised carbonation tower 2 m high and 510 mm Ø, packed with 10 cm internodal sections of 2.5 cm Ø thin bamboo permitted a better controlled carbonation without foam formation. WBL was circulated counter-current to the flue gas; the quick initial pH reduction slowed considerably below a pH of 10 due to the buffering action of black liquor salts.

5. With pH reduction to 9.5 - 10.0 and with flocculation by hot retention and subsequent vacuum filtration, the silica in WBL was lowered and loss of WBL solids could be limited to 3 - 5 %. Primitive laboratory facilities made the obtaining of information on desilication tedious and insecure.

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*) Recovery boiler flue gas

6. Whilst lack of time and amenities prevented much optimization work, the preliminary trials had established the possibility of silica precipitation by carbonation and of flocculation with subsequent separation.

B. February to April 1982 (2nd mission to Jogighopa)

1. In the intervening year the carbonation tower was equipped with a liquid distributor, filled with 24 mm Pall Rings as packing and the flue gas pipe was enlarged. No progress was made as none of the programme prepared for further work had been implemented.

The Regional Research Laboratories at Jorhat, Assam, had omitted to adapt as promised, a colorimetric method of silica determination for WBL. Therefore, in order to permit intelligent dispositions for optimizing the carbonation procedure, a reliable but speedy analytical method for silica determination adapted to the laboratory amenities in Jogighopa had to be established first.

2. With the high alkalinity of the black liquor and low CO_2 content of the stack gases, the height of 190 cm packed with Pall Rings was hardly sufficient to reduce in one passage the pH to about 10, the minimum flow rate permissible being 8 l/min.

3. Repeated and lengthy interruptions of the operation of the pulp mill and of the chemical recovery plant unfortunately prevented an intensive study of WBL carbonation. Only at the end of the mission could the enlarged tower with a packed height of 350 mm be taken into operation. However, it became evident that regular flow through the column under a single WBL passage and lenient carbonation conditions, considerably reduced the amount of co-precipitated black liquor solids.

4. With the successful adaptation of a reliable and speedy silica determination, the reduction of retained dissolved silica to 0.7/0.8 g/l in WBL carbonated to a pH of about 10 at 60/70^{0} C was established. On cooling to an ambient temperature (25^{0}C +) regularly a further reduction to 0.3/0.4 g/l silica takes place; this secondary precipitate is pure white hydrated silica or silicate.

5. The thermal instability of the solution of organic salts (ligninate and carbohydrate derivatives) at lowered pH was noted, rendering heating of carbonated WBL almost impossible and causing incrustations and clogging and flooding of the packed tower. More concentrated 20% carbonated WBL seems to be even more unstable than 12-14% TWBL. Similar to hard wood lignin , bamboo sulfate lignin melts at low temperatures considerably aggravating crust formation.

6. The aim of providing design data for construction of a small production desilication plant was not achieved.

C. April - September 1982

1. During this period only 12 carbonation runs were carried out. The duration of the single runs are claimed to have been about 8 hours further stressing the utility of a carbonation column for desilicating WBL.

2. Variation of working conditions for optimization was not attempted. But the consistent results obtained also when using WBL of varying properties - a consequence of discontinuous operation of a pulp mill - greatly raise confidence in the earlier findings:

(a) Desilication to a level of 0.7/0.9 g/l residual silica in carbonated WBL, corresponding to a rate of desilication of 60%.

(b) Reduction of loss of solids to less than 3% of total WBL solids made possible lenient carbonation in regularly operated absorption tower.

(c) Flocculation time of 3 - 4 hours at 60 - 70°C.

(d) Satisfactory filtration rate of 3 $m^3/m^2/h$ (found with laboratory vacuum filtration as operation of the pilot filter press supplied has not yet been attempted).

VI. FINDINGS

1. The silica content of 1 - 1.5% (unwashed chips in Jogighopa) is lower than any value quoted for bamboc in literature. The management and technicians in Jogighopa however are convinced that reducing the silica content in WBL below 1.3 - 2.0 g/l would greatly benefit their operation in the field of chemical recovery.

2. Low sulfidity, batch type kraft pulping in Jogighopa dissolves practically all silica into WBL of high alkalinity. WBL and flue gas concentrations tend to be low and vary considerably so that continuous carbonation demands close control and resetting of flow to ensure a constant degree of carbonation.

3. The pressure generated by the recovery plant exhaust fan suffices to transport flue gas at least through a height of 350 cm of 24 mm Ø packed with Pall Rings. Together with gravity feed of WBL, the absorption column therefore is a no energy requiring unit for mass transfer.

4. The low efficiency in CO_2 absorption (average reduction from 11 to 9% CO_2) can probably be improved by reducing flue gas flow.

5. Aiming at a final pH of about 10, the capacity of a 350 cm column of 500 mm Ø lies around 0.8 m^3/h (treating high alkalinity WBL with recovery boiler flue gas of low concentration).

6. Further lowering pH considerably reduces the capacity.

7. For convenience and lack of opportunity, temperature, a most essential parameter in reactions, was kept invariant in carbonation trials.

The first material precipitating on careful carbonation is of orange coloration, being typical, probably, for bamboo lignin . On exposure to air - after filtration - the colour darkens.

8. pH reduction of bamboo WBL in Jogighopa will always result in coloured precipitates containing organic material (ligninates).

9. Carbonating WBL in a single passage through a packed column, retention in the column, and treatment time is certainly not more than 2 minutes.

10. The originally finely dispersed precipitate always flocculates; flocculation seems to continue over an extended time. During that period no further silica is precipitated.

11. Flocculants tried so far may speed up flocculation, however, without improving silica removal.

12. Although removal of hydrated silica from solution is a colloidal process, a "true solubility" is indicated by the repeatable values for retained silica.

13. Work in Jogighopa corroborates other findings that precipitated silica is "associated" with alkali or actually is sodium silicate. In the case of the low silica WBL in Jogighopa this however does not cause an appreciable alkali loss.

14. The presence of calcium ion has the tendency to lower the level of silica retained in solution. Larger amounts of lime redissolve the precipitate of carbonation due to rise in pH. Magnesium ion - in appreciable quantity - desilicates to a low level, also at higher pH, but produces very badly filtering precipitates.

15. Over-acification is to be avoided because of possibly irreversible insolubilization of organic material. Lenient and regular carbonation in a packed tower reduces or prevents over-acidification on the gas/liquid interface and therefore reduces organic co-precipitation.

16. Many carbonation trials have confirmed that on pH reduction to about 10 (measured at 30° C) the silica solubility at 60/70° C in WBL is 0.7/0.8 g/l and a total loss of black liquor solids of less than 3%. In the case of Jogighopa WBL the fairly low value of retained silica represents a desilication rate of 50/60% only.

17. On allowing the carbonated WBL to cool to 25/30° C the silica solubility is lowered to 0.2/0.4 g/l corresponding to a desilication rate of 80/90%. No further organic material coprecipitates on cooling so that this secondary precipitate is purely white and consist of hydrated silica associated with alkali. Work on cooling carbonated WBL has been discontinued inspite of interesting desilication attained, because it is not regarded to be technologically correct to lose the heat contained in WBL.

18. Preliminary trials with black liquor of 20% solids concentration again indicate a 60° C silica solubility of 0.7 g/l, i.e. considerably improved desilication.

19. Carbonated WBL cannot be reheated because of the known solution instability of organic material at reduced alkalinity. This problem is aggravated by the property of precipitated bamboo lignins to fuse at fairly low temperatures.

20. Seeding for better precipitation by recirculating TWBL as suggested in the preliminary report (August 1980) need not be considered:

(a) In the upper, more alkaline part of the column the precipitate redissolves and therefore would lose effectiveness.

(b) The development of a white silicious covering of the Pall Rings has been observed in the lower part of the absorption tower. This could act in promoting precipitation. The danger of the absorption tower being blocked by growing deposits can be checked by alkaline rinsing, which easily cleans the Pall Rings.

21. The mild steel absorption tower corrodes badly after only short use. The normal oxygen content of flue gas probably is increased by suction-side leaks (also due to corrosion) causing the known corrosivity of alkaline sulfidic solutions in the presence of oxygen. It was observed that corrosion was more severe on the lower, flue gas entrance side of the tower, which may indicate the removal of some of the alkali salts (mist) of the flue gas by the scrubbing action of the column. The multi-purpose use of the carbonation tower also for black liquor oxidation and for reducing losses of alkali through the stack is worth further study.

22. With established conditions for flocculation by hot retention the problem of solid/liquid separation of precipitates known to be "difficult" loses most of its menace. Satisfactory sedimentation rates of 0.6 m/hour are easily reached; a sediment volume of 5% or less of the total volume

of the carbonated WBL has also become commonplace. Insufficiently flocculated precipitates sediment quickly in a dense and dark layer and sediment slowly in a fine and light layer. The second fraction tends to block filter beds. There would be no problem in clarification before filtration.

23. Attained filtration rates of 3 $m^3/m^2/h$ must be regarded to be very satisfactory (laboratory vacuum filtration). Also filtration through thicker filter cakes are not likely to pose additional problems.

24. The flock structure of filter cakes seems to be very stable. Wet filter cakes are pseudoplastic when handled, i.e. they liquify under mechanical stress, but "dry up" when allowed to rest. Such filter cakes seem to retain an unimpeded capacity for further filtration and for washing.

25. Decanting centrifuges handling the precipitates after flocculation, are left out of consideration because of complications in developing countries.

26. Laboratory filter cakes have up to 40% solid content; it is likely that this value could be raised in technical operation.

27. On drying, filter cakes form a brownish powder. In the case of much precipitated ligninates dark crusts are formed due to fusion.

27. The attempt to replace the valuable WBL in the voids of the filter cake by wash water (neglecting diffusion of WBL out of the flocks) meets with difficulties. Small amounts of silica and of organic material redissolves on washing, probably by hydrolysis of precipitated sodium compounds; the dark coloured wash solution increases in pH with washing!

VII. FUTURE WORK

1. Transfer of the desilication work: Further trials of carbonating black liquors after pulping annual crops should be shifted to an easily accessible site (pulp mill) that holds promise of reliable and continuous operation and that is equipped with basic laboratory facilities and with adequate staff.

2. The Ashok Paper Mills should be encouraged and assisted to continue desilication work towards the planned small production size plant. The immobile equipment erected in Jogighopa, and the knowledge, experience and devotion of the Jogighopa management and staff, particularly Mr. Battacharria, should not be permitted to go waste.

3. For continuing development work to reach a stage permitting the design of an industrial desilication plant two alternatives are seen:

(a) Copy of the Jogighopa absorption tower 500 mm Ø but with increased height and constructed of stainless steel. For increased mobility such an expensive piece of equipment should be designed in a composite manner permitting easy dis- and reassembly. Construction should allow flexible use, also for CO_2 steam stripping trials. The equipment should be completed with clarifyer and with a new filter press with frames.

(b) Design of a mobile, smaller diameter (100 - 200 mm Ø) absorption column of prefabricated sections of alkali resistant glass. This would allow speedier delivery. Filtration investigations had to be continued on a laboratory scale. This unit would facilitate preliminary investigations on liquors sent in from different pulping operations because of the reduced quantities required.

4. Extension of desilication research on black liquors from different mills working with different annual crops and employing different pulping methods.

5. The principal follow-up investigations to confirm and to optimize the findings of Jogighopa would entail variations of the important parameters cf the system i.e.:

- Composition and concentration of black liquor
- Silica content in black liquor
- CO_2 and O_2 content of flue gas
- Flow rate of reaction components
- Reaction temperature
- Temperature and agitation during flocculation
- Washing of filter cake
- Eventual change of type of packing of absorption tower.

6. As an early opportunity for variation the possibility of co-operation with the continuous Kamyr, high sulfidity wheat straw pulp mill in Duna Ujvaros, Hungary, should be carefully considered. Preliminary work could be done in the laboratories of the Austrian engineering firm Waagner Biro with the testing of the Waagner Biro "Submerse Bubble Reactor" claimed to be of high efficiency and of lenient action (no foam because of only macro bubbles).

7. The multiple use of the carbonation column also for black liquor oxidation and for recovery of chemicals from stack gas should be investigated.

8. A literature search should be undertaken to uncover further information on fundamentals helpful to the understanding of the desilication process.

VIII. OTHER INTERNATIONAL ACTIVITIES

A. Thessalian Paper Mills, Larissa, Greece.

Greek Patent No. 63513 granted to D.K. Misra. (copy enclosed)

Dr. Misra, former General Director of the Thessalian Paper Mills, has done concentrated work on desilication of weak black liquors after continuous, Pandia, soda wheat straw pulping. After Dr. Misra was replaced as General Director in Larissa, activities in desilication seem to have come to a standstill.

Dr. Misra's idea is to desilicate in two stages:

1. In the first stage the pH of WBL is lowered by flue gas to about 10 in order to limit organic loss. The retained dissolved silica is reduced to 1.1 g/l corresponding to a desilication rate of 85%, organic loss 4% and alkali loss 2,7%.

2. Further desilication by lime (11 g CaO/1 WBL) to a claimed level of 0.2 g/l silica corresponding to a desilication rate of over 90%. Total organic loss 6%.

The precipitates formed in the two stages are concentrated separately by centrifuge, then mixed and filtered by rotary filter.

The lime of stage 2 brings the treated WBL back to high alkalinity as required for further processing.

Dr. Misra's method certainly deserves careful study. Our criticisms however are:

(a) Complicated plant layout with three filtrations, two of which as centrifuges with high demand for energy and for maintenance.

(b) Increased requirements for lime.

(c) Increased quantities of sludge to be disposed of.

(d) The precipitates after carbonation tends to remove inorganic material like calcium or aluminium with the likely benefit of further reduced crust formation in the evaporator tubes; in this respect Dr. Misra's reintroduction of calcium in organic solution (chelates) in the WBL may well outweigh advantageous desilication.

B. Activities at the Rice Straw Pulp Mill, Rakta, Alexandria, Egypt; development work by Lurgi and Babcock Krauss-Maffei (more details in forthcoming paper by Mr. El Ebiary, Tappi Pulping Conf. Oct. 1982)

A visit by the UNIDO expert to the discontinuously soda pulping rice straw mill in February 1982 permitted some insight into the progress of desilication work mainly by exchange of views with the head of research, Dr. Hassan Ibrahim, on the two pilot plants for desilication from Lurgi and BKMI.

1. The disused pilot plant erected by Lurgi, Germany, could be inspected. CO_2 was transferred from cold fuel boiler flue gases by means of a high speed mixer placed in a 4 m^3 reaction tank. Storage tanks; a rotary band filter; a loaned decanting centrifuge had been returned to the owner.

2. BMKI activities are farther advanced and results will be published in the near future (possibly in a paper announced by Mr. El Ebiary, Chairman of Rakta, for the Tappi Pulping Conference 1982). A sample of ignited bright white silica obtained in pilot scale work was shown. Rakta will not erect an industrial desilication plant in the foreseeable future (Mr. El Ebiary), bur intends to sell know-how together with BKMI to interested parties.

In order to prevent clogging of the washer screens BKMI would have to redesign the brown stock washing, which at the moment produces WBL of 3 - 5% solid concentration only, before a desilication plant could be erected.

In their pilot scale work WBL is "reconcentrated" which may - according to the views of the UNIDO expert - lead to changed properties of silica: In Rakta pulping a rather low pH results with partial precipitation of silica on to the fiber with the possible formation of polymeric silica in the WBL (this also could explain the precipitation of silica on the journey from Rakta to Lurgi, reported by Gavelin). On reconcentration by evaporation the state of solution is likely to be changed.

Although BKMI claims to successfully operate with three different methods of CO_2 transfer, it appears that all methods, basically, work as energy intensive "bubble reactors" producing obnoxious foam.

Dr. Ibrahim stresses the need for (physical and chemical) "after-treatment" to obtain well filtering precipitates. In the absence of a recovery boiler and with a distance of many hundred meters between fuel boiler and pilot plant, there only is the alternative of working with "synthetic" flue gas or with reheated fuel boiler gas.

No figures as to reaction temperature, flocculation time and temperature, pH levels and WBL concentration were divulged, but desilication was claimed to be successful and the work is in its terminal stage.

C. Fundamental research to back up practical desilication

Practical desilication involves a number of physical and chemical phenomena, some of them ill understood. Clearer insight should not only help in establishing industrial desilication but should also provide tools to tackle problems likely to crop up when adapting the basic process to different pulping materials and processes.

Within the framework of this report only some of the fields requiring further investigation can be pointed out - in a haphazard order rather than according to their significance.

Subjects to be studied:

1. The state of solution or dispersion of silica in WBL (monomeric or polymeric; what polymers) is likely to determine precipitating and flocculating properties. This state will depend on pulping parameters as temperatures, dwell time and alkalinity.

The pure system of alkali/silica/water is known to be complex and depending on prehistory of the sample; in WBL the presence of pulping chemicals, in particular also the sodium salts of carboxylated organic breakdown products , the hydrolysis with temperature, and the ionic strength, further complicates the situation. Reaching further back, there are open points as to the chemical and the morphological nature of silica in the plant tissue and still further back as to the mode of transport of silica from the soil to its point of deposition.

2. Degree of order of precipitated silica. Not well considered statements are occasionally met with not based on factual evidence, as to the "crystallinity" of flocculated silica precipitates. The Regional Research Laboratories at Jorhat, Assam, have applied X-ray analysis to a single non-representative Jogighopa precipitate and found a low degree of order only.

3. Influence of lignates and of aliphatic salts on the properties of alkaline silica solutions or dispersions (colloid solutions).

4. Influence of co-precipitated organic material on flocculation of the total precipitate.

5. The nature of alkali associated with the flocculated silica precipitates.

6. The nature (and possible utilization) of the first organic fraction, co-precipitated with silica.

It can be seen that the wide fields of the chemistry of black liquors and of hydrated silica could be involved in background investigations on desilication. Basic research on these issues beyond some few selected problems is certainly beyond the UNIDO/SIDA project. The search for knowledge already in existence but dispersed in various publications is however to be recommended. The writer of this report has found that this will also take determined effort, as he has spent many hours in university central and institute libraries with only very limited gain in information having some bearing on the problems posed by desilication.