

# Desilication of Bamboo and Straw Black Liquors

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## ABSTRACT

Although wood is the most widely used raw material for pulp and paper industry, its availability is limited in many forest deficient countries. With the shortage of forest based raw material and to preserve the forest, the paper industry in Asia and other parts of the world is forced to use the non-woody fibrous raw materials. India is also one of the leading countries using substantial proportion of non-wood raw materials such as bamboo, cereal straws, bagasse, etc. Non-wood raw materials are characterized by high silica content. Silica content in non-wood varies between 1.5 to 20%. Most of this silica present in the raw material passes into black liquor during alkaline pulping. Presence of silica in relatively high concentration in spent liquors produced from pulping of non-wood raw materials creates numerous problems in operating a chemical recovery system efficiently. Evaporator, Recovery furnace, causticization and lime kiln operations are adversely affected by the presence of silica in black liquor. (1). Efforts on removal of silica from pulping and chemical recovery loop are going on for last five decades. Research work was carried out on desilication of black liquor and green liquor using different techniques like addition of cations (lime and alumina) and reduction of pH. None of the methods tried by earlier researchers succeeded at plant level. CPPRI initiated extensive research work on desilication of bamboo and reeds black liquor in early eighties and finally came out with a technology highly successful at commercial level. Due to mounting pressure of environmentalist and pollution control authorities installation of lime kiln is mandatory and land filling of lime sludge is not allowed any longer. In present context, desilication of black liquor will be an integral part of chemical recovery in pulp mills based on silica rich fibrous raw materials.

The present paper highlights the basics of Desilication technology developed by CPPRI and results obtained on pilot and commercial scale desilication of bamboo and rice straw black liquor. The successful demonstration of desilication both bamboo and rice straw black liquor have further confirmed the efficacy of CPPRI desilication technology in wide range of silica content (2-15 gpl).

## Introduction

In the last 5-6 decades a number of technologies and processes were studied, at different scales to get rid of silica from the recovery system. The methods developed earlier did not live up to the expectations and none of the technique was scaled up to commercial level. Attempts have been made by well-known companies like Lurgi GmbH, and BKMI, but none of these techniques were successful on a commercial scale. Controlled carbonation of black liquor in specially designed reactors by CPPRI has shown satisfactory desilication without lignin co-precipitation. Studies conducted on Bamboo, reeds, Wheat straw and Rice straw on pilot plant level have shown more than 90% desilication with 0.5 gpl residual silica in desilicated black liquor. Recently a mill scale desilication plant based on Rice straw black liquor has been commissioned in one of the mill in Southern part of India. The plant is running successfully since last four years.

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## Technology Developed by CPPRI

Central Pulp & Paper Research Institute initiated work on desilication in early eighties and did extensive basic research on mechanism of silica precipitation and reactions involved in desilication by carbonation. CPPRI adapted the carbonation technique essentially because the process does not produce sludge like lime treatment method where massive quantities of sludge is generated.

Further with CPPRI's basic knowledge, it became possible to evolve a technology for selective precipitation of silica without co-precipitation of lignin by adapting step wise, gentle carbonation technique. Concept of submerge Bubble reactor was developed by CPPRI for desilication of black liquor.

## Concept of Submerge Bubble Reactor

In this reactor the liquor to be treated with gas in a tubular system by a pump, which on its downward path sucks the

gas in the form of discreet bubbles. The shearing action of the flow works the gas bubble in kneading fashion continuously, exposing new gas liquid interfaces. Mohno pump was used for circulation of the black liquor and carbonated black liquor was collected from the bottom of the column.

The method was successfully tested on semi-pilot scale for more than three years and subsequently scaled up by more than 1000 times (30 lit/hr to 40m<sup>3</sup>/hr) and a commercial prototype mill size desilication plant at Hindustan Newsprints Ltd., Kerala became operational in June, 1989. Based on the technology another commercial scale plant with a capacity of 25M<sup>3</sup> was commissioned in a rice straw based mill in Andhra Pradesh Paper Mills Limited (Unit CP) in 2006. Silica content in original black liquor is in the range of 6-7% whereas desilicated black liquor contains silica in the range of 0.5-0.6% indicating more than 90% desilication efficiency

## Process Details

The process involves stepwise carbonation in Three reactors for

reduction of pH to desired level. In reactor 1 pH is dropped from 12.5 to 11.5 and in reactor 2 pH is further dropped to 10.7 and finally in reactor 3 the pH is reduced to desired level as optimized. Carbonated black liquor is taken in a clarifier for settling of precipitated silica. Underflow of

clarifier is taken to filter press whereas overflow mixed with press filtrate is taken into realkalisation tank to raise the pH by addition of alkali. This realkalised black liquor is sent for evaporation.

Schematic desilication Technology developed by CPPRI is shown in Fig. 1.

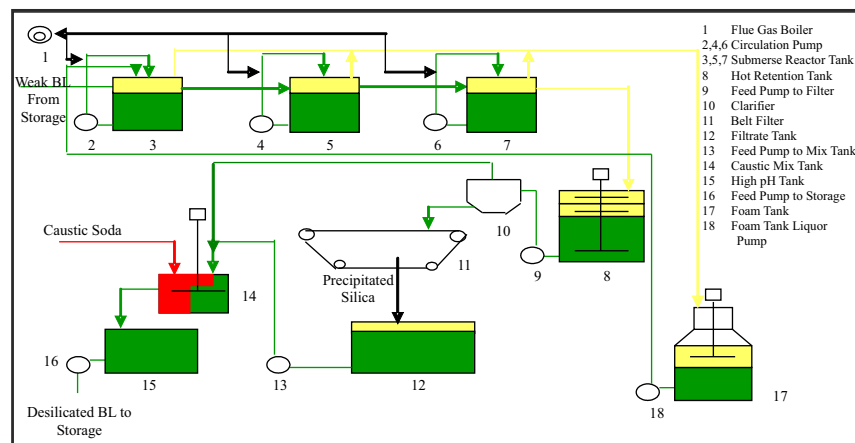


Fig 1 Schematic of CPPRI Desilication Technology

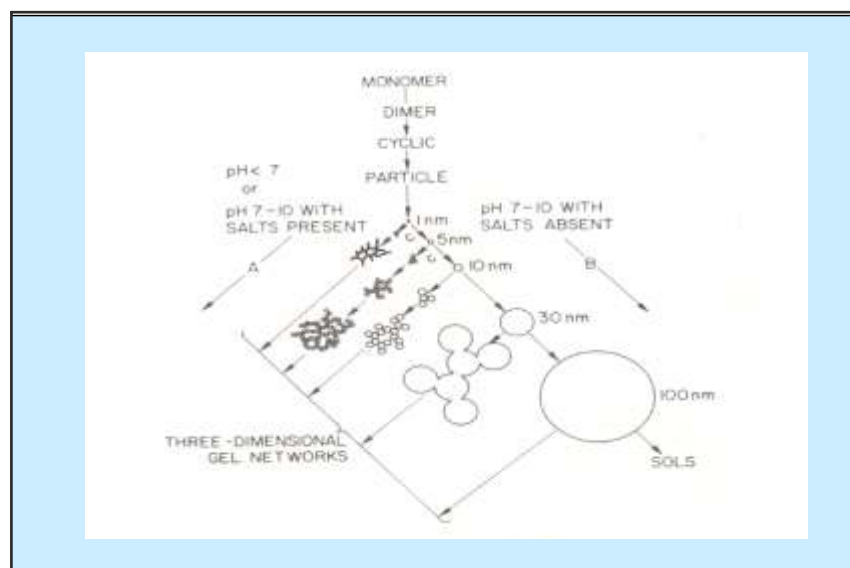


Fig.- 2 Mechanism of Precipitation of Silica

TABLE 1  
Results of Desilication of Bamboo Black Liquor at Different pH

Black Liquor Characteristics				Desilication (%)
Before Desilication		After Desilication		
pH	SiO <sub>2</sub> , g/l	PH	SiO <sub>2</sub> , g/l	
12.8	4.2	10.5	2.1	48.8
		10.4	1.5	64.3
		10.3	1.2	71.4
		10.2	0.8	80.9
		10.1	0.5	88.9
		10.0	0.4	90.5
		9.8	0.4	90.5

## Mechanism of Silica Precipitation by lowering of pH

Silica is present in black liquor in the form of Na<sub>2</sub>SiO<sub>3</sub>(2). Lowering the pH of black liquor converts silicates into insoluble polymeric anhydrides of silicic acid. The solution in equilibrium with amorphous silica at ordinary temperatures contains monomeric-silicic acid, Si(OH)<sub>4</sub>. Lowering the pH of alkali silicate solutions results first in formation of monosilicic acid. (3). This monomer undergoes polymerization, at a concentration greater than the solubility of amorphous silica (100-200 ppm), forming higher molecular weight species. The mechanism of polymerisation is ionic and is proportional to OH concentration, above pH 2. The mechanism of polymerization is shown in Fig. 2. Above pH7 stabilized particles (Sols) grow to a size of about 100 nm. On the contrary, when salts are present, to neutralize the charge on growing particles, aggregation of particles occur with the formation of chains and ultimately, three dimensional gel network. Thus the gel or sol formation depends on the medium containing silicic acid monomer. Black liquor contains silica in the form of sodium silicate and due to high salt concentration gel formation is favoured.

## Experimental

Studies were carried out on desilication of Bamboo black liquor on Pilot Plant at a mill site using flue gas from chemical recovery boiler. Rice straw black liquor desilication was carried at commercial plant using flue gas from power boiler of the mill. Extent of desilication was evaluated at different pH levels.

## Results and Discussions

### Desilication of Bamboo Black Liquor

Bamboo black liquor was carbonated at different pH levels to optimize the pH for maximum desilication efficiency. Results obtained are depicted in Table 1.

The results recorded in Table 1 show that silica precipitation starts at a pH around 10.5. 90% desilication is achieved at a pH of 10.1. Results show that residual silica content is almost same after pH level of 10.0. This indicate that carbonation of black liquor

beyond pH 10.1 does not facilitate silica precipitation. The above results indicate that optimum pH range for precipitation of silica in bamboo black liquor is 10.1-10.0. Residual silica content in black liquor is 0.4 g/l in this pH range. It is difficult to remove this residual silica by carbonation.

### Desilication of Rice Straw Black Liquor

Desilication trials were conducted on pilot plant in a Rice straw based mill to optimize process parameters prior to installation of commercial plant. Carbonation was carried out at different pH levels. Results obtained are shown in Table 2. silica content in black liquor showed a wide variation in the range of 4-13 gpl and therefore pilot studies were conducted at different initial silica levels

### Results Obtained on Commercial Scale Desilication of Rice Straw

Based on the desilication pilot plant process conditions for desilication of rice straw were freeze-dried. A full mill scale desilication plant on rice straw black liquor was installed and successfully commissioned by Enmas Andritz private limited, Chennai in a mill situated in Andhra Pradesh. Results obtained in the 25m<sup>3</sup>/hr plant are highly satisfactory and the plant is running satisfactorily since last four years.

### Impact of Desilication on Black Liquor Properties

Black liquor properties were evaluated before and after desilication. Following observations were made:-

- The black liquor was found to be

However there is no change in calorific value when calculated on the basis of organic content of the black liquor. Calorific value however increased in case of rice straw black liquor.

- There is a remarkable improvement in the swelling volume ratio (SVR) of carbonated & realkalized black liquor when compared to the original black liquor, which is a pointer towards better combustibility of desilicated black liquor.

### Conclusion

Pilot plant and full commercial scale plant trials have shown that the both Bamboo and straw black liquor which contains 2.0 to 14 gpl silica can be desilicated to a residual silica content of 0.5gpl. Black liquor properties were improved which shows that burning behaviour of black liquor is better after desilication. Successful operation of full commercial scale plant since last four years have created confidence among the industry. Adoption of desilication process in bamboo and straw based chemical recovery will help in reducing operational problems caused by silica, will save energy during evaporation and protect environment by reducing solid waste by making lime sludge suitable for reburning.

### References

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**TABLE 2**

**Results of Desilication of Rice Straw Black Liquor at Different pH**

Black Liquor Characteristics				Desilication (%)
Before Desilication		After Desilication		
pH	SiO <sub>2</sub> , g/l	pH	SiO <sub>2</sub> , g/l	
12.0	13.3	10.5	6.9	48.1
		10.4	5.8	56.3
		10.3	1.5	88.7
		10.2	1.0	92.5
		10.1	0.7	94.7
		10.0	0.4	97.0
		9.9	0.30	97.7
		9.7	0.30	97.7

The results shown in Table 2 reveal that silica precipitation in rice straw black liquor starts at pH around 10.5. Around 97% desilication is achieved at pH 10.0. Below pH 10.0 there is only marginal improvement in desilication efficiency. Residual silica content is 0.4 gpl at this pH and 0.3 gpl at pH levels 9.9 to 9.7. The above results indicates that optimum pH range for silica precipitation in rice straw black liquor is 10.0 - 9.9. Around 98% silica is precipitated in this pH range. One of the interesting observation made during the above experiments is that residual silica in desilicated black liquor is around 0.3-0.4 gpl in both the cases in spite of wide variation (4.2 and 13.3 gpl) in initial silica content of the black liquors. This shows that desilication technology developed by CPPRI is suitable for both high and moderate silica rich black liquor.

- highly colloiddally stable & no lignin co precipitation was observed.
- Foam generation during gas liquid interaction was found to be moderate and lie in highly manageable limits.
- Highly encouraging results were obtained during settling studies on carbonated black liquor. After three hours of settling the sludge volume stands at only 20% of total liquor volume and supernatant black liquor has less than 20 ppm suspended solids.
- The viscosity of the desilicated and realkalized black liquor is fairly close to the original black liquor.
- There is only a marginal reduction in the calorific value of realkalized black liquor in bamboo black liquor, due to increase in the concentration of inorganics during realkalisation.