

## *Mechanism of Silica Precipitation by lowering pH in Chemi-thermomechanical Pulping Black Liquors:*

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### **Abstract:**

Black liquor is a complex colloidal system obtained by chemical pulping process. It comprises of lignin, nearly 50% of the total organic and Silica approx. 2-3% (OD basis) of the total inorganic components. Black liquor is fed to chemical recovery plant where silica causes scales in the channels and concentrators. Mechanism of silica precipitation, from black liquor, by lowering pH has been investigated in this research. Lowering of pH results in charge neutralization, affecting the precipitation of silica molecules. Silica starts agglomeration at pH 10. At lower pH levels, in the presence of other salts, small colonies of silica start precipitating. Large colonies, rich in silica are obtained at pH 9.8. Below this pH precipitation of lignin is increased. It is evident that the pH values at which silica precipitates (9.8) almost quantitatively, is close to the pH value at which lignin starts precipitating, however, maximum desilication can be achieved at pH 9.8.

### **Key Words:**

Black Liquors, lignin, silica, desilication and concentrators.

### **Introduction:**

Wheat and rice straw is being used in pulp and paper industry. Chemical and chemi-thermo-mechanical pulping are mostly applied. Silica is present in the raw materials and it goes into the black liquor generated as a waste material. This silica causes scaling when this liquor is fed into the recovery boiler. Straw pulping black liquor usually contains a high level of silica<sup>1</sup>. However, a cheap industrial byproduct consisting mainly of aluminum compounds can be used as a desilication agent and produces black liquor with over 90% of the silica removed. The process is relatively simple. Yield, permanganate number and beatability are not adversely affected, nor are sharp changes in pH, total alkalinity or heat value recorded. The resulting increase in viscosity has favorable implications for the

evaporation and combustion of weak black liquor in the chemical recovery system. In a joint venture with Lurgi Co., the company has developed an efficient silica removal system that allows the subsequent recovery of heat and chemicals from rice straw black liquor<sup>2</sup>.

Silica poses several problems in all unit operations of the chemical recovery cycle i.e. evaporation, combustion and causticization. Multiple effect evaporation and causticization are mostly affected by the presence of silica in the system. The average black liquor flow rate in the evaporator was observed to be only 85% of the design capacity due to silica scaling. <sup>3</sup>

Previous research work designed to overcome the problems of silica in black liquor is briefly reviewed. Carbon dioxide in flue gases has been used to reduce the pH of black liquor. Because of fear of decreased

heating value of the desilicated black liquor due to co-precipitation of the organic matter, the pH drop was limited to a pH window; where silica was suppose to precipitate without significant precipitation of organic matter<sup>4</sup>. A project undertaken in this field by the Egyptian company, RAKTA, and the German firm, BKMI Industrieranlagen GmbH is described<sup>5</sup>. Criteria to be satisfied by the project are outlined, and the pilot plant process developed which has successfully treated 4 m<sup>3</sup>/hr of black liquor from non-wood fiber pulping operations is reported. Results achieved are outlined, and said to be so successful that a large scale (150 m<sup>3</sup>/hr) desilication plant is now under construction for the treatment of mixed black liquor from bagasse and rice straw pulp at RAKTA's Alexandria mill.

As long the black liquor is in diluted form (weak black liquor), the silica scaling is low but as the weak black liquor is concentrated gradually, precipitation occurs and the scaling appears as the major problem of the recovery plant.

The problems of recovering chemicals from the spent black liquor in nonwood pulping are discussed. So far, hardly any pulp mill using rice straw has successfully operated a recovery plant.<sup>6</sup> Investigations into the desilication of rice straw black liquor have been carried out in co-operation with the Ratka General Co. of Alexandria, Egypt, which

runs the world's largest rice straw pulp and paper mill. Details are given of a semi-industrial scale pilot-plant, which was put into operation in 1985 on the basis of the results of the investigations. Experience with the pilot-plant has shown that it is technically feasible to desilicate black liquor from rice straw and that it is an economic proposition.

### Reagents and Techniques:

Following research was carried out on plant scale as well as in the laboratory. In quantitation silica and other salts; TAPPI standard procedures were employed and all reagents used were of AR grade. Silica determination involves  $\lambda_{\max}$  determination, which was performed at calibrated UV/VIS spectrophotometer in Packages Research Laboratories.

### Results and Discussion:

Black liquor with very little active alkali results in sludge formation which can become a source of scale in the evaporator units. Wheat Straw undergoing pulping process has the following composition:

Ash:	7.2%
Silica:	3.2%
Lignin (ash free):	18.5%
1% NaOH solubility:	46.5%

Higher, 1% NaOH solubility, in straws indicates the high proportion of low molecular weight carbohydrates and higher decay. Nearly 45% of the silica from black liquor gets deposited in evaporator tubes

Table 1; Influence of washing on silica reduction:

Raw material	Ash, %	Silica, %	% SiO <sub>2</sub> on black liquor solids
Wheat straw (unwashed)	6.4	2.7	2.9
Wheat straw (washed)	4.6	1.9	2.1

Less than 50% of the silica in the raw material gets dissolved during

pulping, in the case of straws as the pulping conditions employed are milder,

i.e., lower alkali concentration (20 g/dm<sup>3</sup>) and lower cooking temperature (150°C). With white liquor concentration of 120 g/dm<sup>3</sup> the evaporator cleaning was to be done every week. When the concentration was brought down to 80 g/dm<sup>3</sup> the evaporator cleaning was needed once in 20 days.

Silica may be precipitated in one of the two ways; either by the addition of metal ions like aluminium, magnesium or calcium in soluble forms as hydroxides or oxides, or by the lowering of the pH of the black liquor by adding acids. Except for the use of anhydride CO<sub>2</sub> from carbonic acid all these methods need additional chemicals and produce more waste than necessary to purge the silica<sup>7</sup>.

Lime treatment is highly expensive, high organic and alkaline loss and calcium solubility causes calcium scaling and difficult deposition of large calcium mud quantities. Calcium carbonate solubility in black liquor is ~0.3 g/l, i.e., 20 times as high as solubility in water.

Amorphous silica is surprisingly soluble, the solubility depending somewhat on the size of the primary particles. At pH 7 (and below) and at room temperature the solution contains about 0.15 g/l silica rising at 90°C to about 0.3 g/l all in the form of monomolecular silicic acid. Such material can easily pass through cell membranes of plant or animal. At pH 10, solubility rises from 0.28 g/l at room temperature to 0.4 at 90°C.

Silica solubility in black liquor is hardly different from water solubility. In fact almost everybody working on desilication has arrived at the limit of

0.3-0.4 g/l residual dissolved silica, independently of the starting concentration of silica. With the same lower limit the degree of desilication achieved, solely depends on the initial silica content. *With the critical lignin precipitation pH varying somewhat, we achieved best results at demonstration plant, final pH 9.8. Thus one of the main tasks of desilication by carbonation was to attain the end-pH very close to silica precipitation without over-carbonating the black liquor, which would lead to the beginning of lignin precipitation.*

Laboratory trials have shown straw lignin to be very stable, so that excellent desilication is possible. Aluminum considerably lowers silica content in well water, in soil solutions and boiler feed water at least around neutral pH. However, under no circumstances must soluble aluminum is left in black liquor, in order not to cause aluminum silicate scaling on evaporator tubes, which causes the most dread form of scaling.

Silica precipitation by pH reduction is only possible if silica is present in monomolecular form dispersion and at least partly in the ionic form i.e., in black liquor with a pH over 10.6. Similar to silica sols, the lignin stability in dilute and in concentrated black liquor depends on the negative electric charge of its colloidal particles resulting from ionization of its sodium salts. About 90% of the acidic function of black liquor lignin is phenolic, the rest is carboxylic.

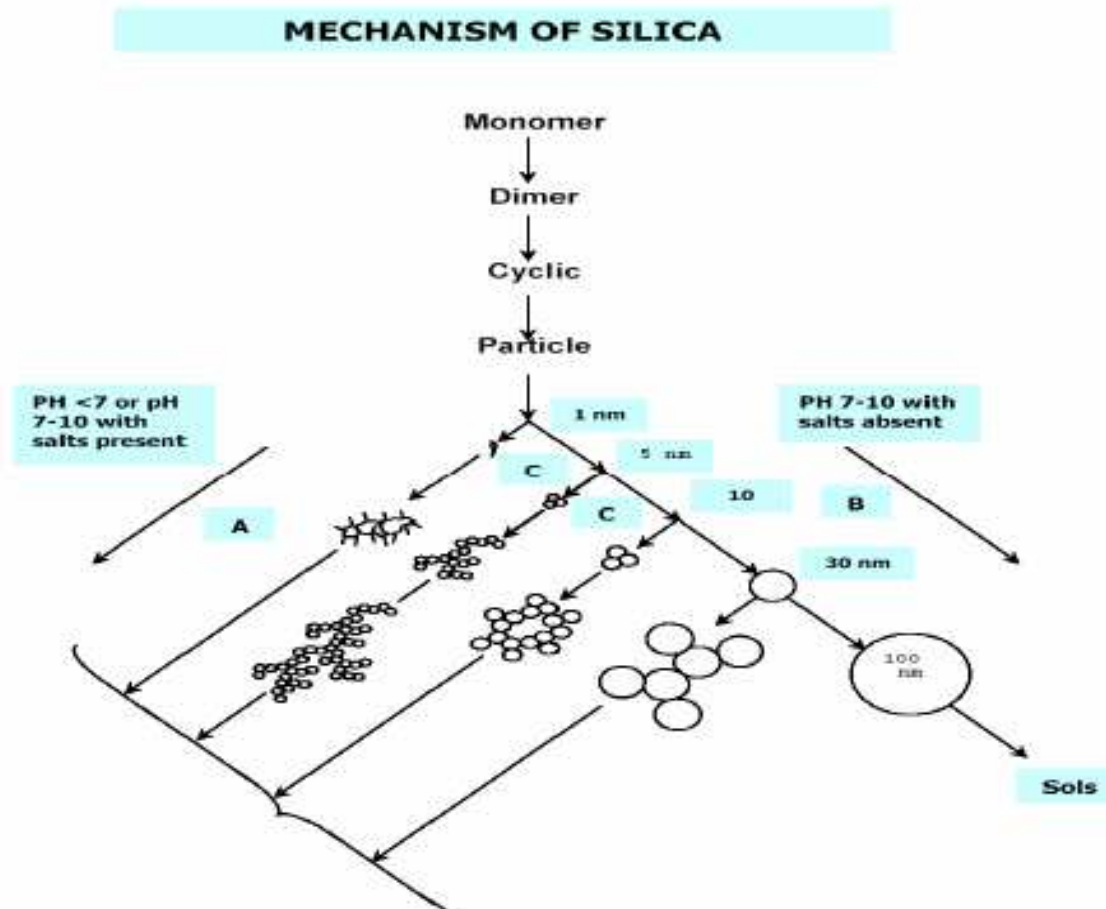


Figure 1: Schematic diagram showing silica precipitation.

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-monosilicic acid,  $\text{Si}(\text{OH})_4$ . Lowering the pH of alkali silicate solutions results first in formation of monosilicic acid. 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 polymerization is ionic and is proportional to  $-\text{OH}$  concentration, above pH-2. Above pH-7 stabilized

particles (Sols) grow to a size of about 100 nm (Fig 1).

On the contrary, when salts are present, to neutralize the charge on growing particles, aggregation of particles occurs with the formation of chains and ultimately, three dimensional gel networks. Thus the gel or sol formation depends on the medium containing silicic acid monomer.

With the surface silanol groups having acidic character, the primary particles are negatively charged and repel each other forming a stable sol. Further particle growth takes place by condensation, this time by primary particles forming chains and networks. Finally solid or semi-solid gels are

formed enclosing the whole aqueous phase, even at silica concentrations lower than 1%.

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