

Trends in ASH content of straw pulps-an explanation

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It is well known that straw contains a high percentage of ash, which is mostly silica (SiO_2), and is located in special epithelial cells called silica cells¹. It is also reported that most of ash is retained throughout the washing of straw², thus indicating that the silica is chemically bound in the structure

During alkaline pulping of straws, an interesting trend in the ash content of the pulp has been observed by the authors viz. ash in the pulp (a) decreases with increase in the concentration of alkali added during pulping at constant H factor and (b) increases with increase in H-factor at a constant alkali charge (Table II). Such a trend has also been reported by other workers^(3,4,5,6), although no satisfactory explanation has been offered so far. According to Hopner⁵, the increase in ash content, with increase in H-factor is due to the precipitation of silicic acid in the later part of the pulping operation. However, the formation of silicic acid appears doubtful in alkaline pulping. In this communication, the various reaction products of silica in presence of alkali (NaOH) and their overall influence on the ash content of the pulp are discussed, thus offering a possible explanation for the anomalous behaviour of silica during alkaline pulping of straw.

The structure of a SiO_2 macromolecule is represented is presumed to be hypothetically present in straws.

The electronegativity difference between 'Si' and as in fig. 1. and the same 'O' is 1.7 (E.N. of 'Si' is 1.8 and that of 'O' is 3.57. In spite of the fact that the Si-O bond is a polar bond, it is a very strong bond (Bond energy is 108 K. Cals⁸. Because of this high bond energy, SiO_2 is not effected either by the polar nature or by the high dielectric constant of water (as the polar molecules will be usually ionised when placed in water).

But when silica reacts with a strong alkali such as NaOH (as in the case of pulping), the charged Na^+ and OH^- ions will influence the polar bonds of SiO_2 causing the cleavage of some of the Si-O

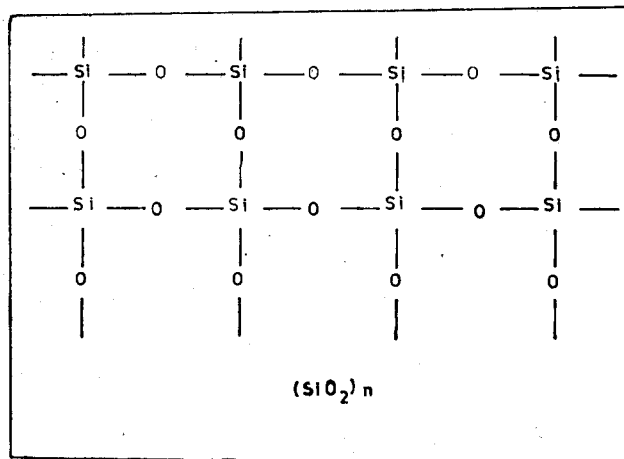
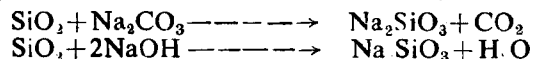


FIG. 1

bonds. The reactions between silica and alkalis are reported to be as below^{9,10}.

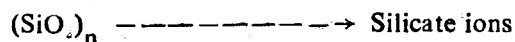


These reactions indicate the acidic nature of silica and the product of an acid-base reaction, viz. a salt is expected to be soluble in aqueous system. However, the reaction between silica and alkali is not so simple as shown above, and is mainly a function of the total alkalinity of the system. With increasing alkalinity, more and more Si-O bonds will be ruptured. Thus the size and formation of silicate ions is dependant upon the alkalinity. If the system is rich in alkali, the mixture mainly contains SiO_4^{4-} , SiO_3^{2-} , $\text{Si}_2\text{O}_7^{6-}$ and $\text{Si}_3\text{O}_9^{6-}$ ions. These silicate ions will form corresponding sodium silicates which are unstable and get dissolved during pulping. If low in alkali, relatively few Si-O bonds are broken and polymeric anions such as $(\text{SiO}_3)_n^{2n-}$

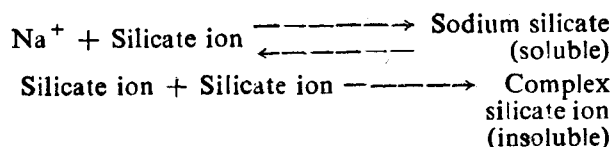
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are formed, the sodium salts of which are quite stable and will not be dissolved¹¹.

In a pulping system, the first step concerning silica is the dissociation of $(\text{SiO}_2)_n$ to silicate ions:



These silicate ions, will further form either simple sodium silicates or complex insoluble silicate ions, thus:—



Both the reactions will be occurring at the same time, but their relative rates will depend upon the alkalinity and H-factor of the system. By nature every change proceeds towards stability. Thus when the alkalinity is low, the formation of complex silicate ions is favoured. In addition, some of the simple silicate ions also condense to form insoluble complex ions, under the low alkalinity of the system. Thus the later reaction predominates resulting in higher ash content of the pulp. When the alkalinity is high, the formation of simple silicate ions increases and due to the increased concentration of OH^- and Na^+ ions, their condensation is inhibited. Thus the first reaction dominates resulting in more solubilization of silica and hence less ash in the pulp.

The affect of increase in H-factor at constant alkali charge can also be explained similarly. As H-factor increases, the consumption of alkali during

pulping increases, reducing the total alkalinity of the system. When there is a dearth of alkalinity, dissociation of the formed complex insoluble silicate ions is less and the tendency is towards the formation of insoluble silicates, increasing the ash content of the pulp.

It may also be mentioned that in the first case when the H-factor is constant and the alkalinity of the system is increased, the relative rates of delignification as well as reaction with silica are both enhanced, favouring the formation of soluble sodium silicates, resulting in reduced ash content in the pulp. The ash reduces from 18.0% to 10.3% by increasing alkali from 8-12% at constant H-factor of 82 (Table II).

In the latter case, when the H-factor is increased at a constant alkali charge, the rate of delignification is enhanced, but due to the resultant depletion in the alkali concentration, formation of insoluble silicate ions, is favoured. Thus, by increasing H-factor from 82 to 1032 18.0% ash in pulp increases to 20.2% at the same alkali charge of 8.0% and so on (Table II).

TABLE—I. PROXIMATE CHEMICAL ANALYSIS OF RICE STRAW

Ash	%	18.0
Cold Water Solubility	%	11.0
Hot Water Solubility	%	13.49
1% NaOH Solubility	%	44.31
Alcohol-Benzene Solubility	%	5.89
Holocellulose*	%	81.03
Lignin*	%	11.8

*Both extracted dust and final material are ash corrected.

TABLE—II. EFFECT OF NaOH PERCENTAGE AND TEMPERATURE ON ASH CONTENT OF RICE STRAW PULP

			Set I				Set II	
1.	NaOH on O.D. Straw	%	8.0	10.0	12.0	8.0	10.0	12.0
2.	Temperature	°C	140	140	140	170	170	170
3.	Time to Temperature	hrs.	1.5	1.5	1.5	1.5	1.5	1.5
4.	Time at Temperature	hrs.	0.5	0.5	0.5	0.5	0.5	0.5
5.	H-Factor*		82	82	82	1032	1032	1032
6.	Ash in pulp	%	18.0	15.2	10.3	20.2	18.0	15.9

*As the relative rate of reaction figures during straw pulping are not available, the H factor was calculated based on relative rate figures of bamboo.

EXPERIMENTAL

For experiments on pulping, a typical rice straw sample of 18% ash and 11.8% Lignin was used. The proximate chemical analysis of this straw is given in Table I. The straw was pulped in 800 ml bombs in a 15 litres capacity electrically heated rotary digester as per conditions in Table-II keeping two different H-factors and other cooking conditions constant, alkali charges were varied from 8 to 12% in each set to study the effect of chemical charge as well as H-factor on ash content of the pulps.

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