# Pulping of agricultural residues problems and suggestions

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SUMMARY

In the present investigations pulping of rice straw, by different processes like, Soda, Carbonate, sulfite and chemimechanical, have been studied. Extent of silica dissolution, pollution load, pulp and spent liquor qualities were investigated. Different methods to precipitate silica in spent liquors were also studied. Pulping experiments indicated that it is possible to produce pulps of satisfactory strength with milder cooking conditions. Sulfite and chemmechanical processes produced pulp of yield as high as 64% without significant loss in strength properties. For high yield pulps disc refiner was an ideal equipment for fiber separation. Soda spent liquor contained more silica than spent liquors from milder pulping processes. Spent liquors of low pH value and those containing fines showed high viscosity. By carbonation it was possible to precipitate out as high as 98% of silica in both spent and green liquors. Carbonation under pressure of about 3-5 kg/cm$^2$ after cooking was found to be effective in precipitating silica at the same time increasing the pulp yield by 6%. Carbonation of spent liquor in packed bed absorber showed satisfactory removal of silica. Carbonate spent liquor showed gradual settling of silica on storage due to low pH. Carbonate pulping in conjuction with green liquor desilication would help in incorporating the chemical recovery system.

Rice straw and wheat straw are the major fibrous raw materials, for paper making, among the agricultural residues. Straws contain significantly higher amounts of hemicelluloses and silica compared to woody fibrous raw materials[2]. Selection of pulping process and conditions are important in terms of pulp and spent liquor qualities. Most of the Indian mills are using soda pulping process for the straws. Other pulping processes which are capable of pulps of higher yields with satisfactory strength, have not been tried on commercial scale. The milder pulping conditions and processes would require less steam, energy and chemicals. Without chemical recovery unit the cost of cooking chemicals and steam would be higher. Presence of silica in the cereal straws is an irksome problem for incorporating the conventional chemical recovery system. The silica content in straws varies from region to region. Some straws contain as high as 14.5% silica[3]. The silica content reported in the straw spent liquor is as high as 16.5 g/l[3]. The adverse effect of the presence of silica in the spent liquor in various sections of the chemical recovery units is discussed by Panda A[4]. It is necessary to remove the major portion of this silica for smooth processing of the spent liquors from cereal straws. Pulping process should be adopted so as to have lower amounts of silica in the spent liquors, without affecting the quality of the pulp. The present paper discusses the quality of pulp, quality of spent liquors and extent of silica dissolution in different pulping processes for rice straw. Different methods studied for precipitation of silica in the spent liquor, are also discussed.

**Results and Discussions :**

Pulping : Alkaline pulping of straws is well established technology. The influence of sulfidity in straw pulping is less remarkable than in the pulping of woods[5]. Therefore the kraft process has not gained importance in case of straws. Most of the Indian mills passed on straws are adopting soda process for pulping. Table-1 shows the results of different pulping processes and their influence on strength properties. Cooking temperature of 140°C gave pulps of better strength than those obtained at 160°C. This may presumably be due to retention of more hemicellulose fraction. Increasing the cooking chemical from 6% to 12% reduced the yield

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TABLE—1 INFLUENCE OF PULPING PROCESS AND VARIABLES ON STRENGTH PROPERTIES OFISTRAW PULPS

| Expt. No. | 1 | 2 | 3 | 4 | 5 | 6 | 7* | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Soda process | | | | | Carbonate process (a) | | Sulfite | | Chemimechanical | | |
| 1. Cooking chemical | NaOH | | | | | $NaOH+Na_2CO_3$ | | $Na_2SO_3$ | | NaOH | | |
| 2. Chemical, % | 8 | 10 | 12 | 10 | 12 | 12 | 12 | 12 | 12 | 8 | 12 | 10.5 |
| 3. Cooking temp., °C | 160 | 160 | 160 | 140 | 140 | 160 | 160 | 160 | 140 | 90 (b) | 90(b) | Ambient (c) |
| 4. Refiner clearance, thou | — Not used — | | | | | 20 | 20 | 15 | 10+5 | 25 | 15 | 15 |
| 5. Total pulp yield, % | 50.4 | 48.0 | 46 3 | 50.13 | 48.21 | 52.8 | 50 6 | 55.1 | 64.9 | 63.8 | — | 84 |
| 6. Screen rejects, % | Nil | Nil | Nil | 0.60 | 0.50 | Nil | Nil | Nil | Nil | — | — | — |
| 7. Kappa Number pH | 33.7 | 26.3 | 21.4 | 28.5 | 22.4 | 34.4 | 29.6 | 29.5 | 48.3 | — | — | — |
| 8. Spent liquor pH | 8.1 | 9.8 | 9.4 | 9.9 | 9.6 | 8.9 | 8.9 | 6.7 | 6.8 | 10.4 | 10.4 | 11.0 |
| Solids, % | 8.8 | 9.3 | 10.4 | 9.2 | 9.8 | 9.4 | 8.9 | 8.9 | 7.3 | 8.4 | 6.8 | 4.8 |
| Residual chemical g/l | Nil | 1.2 | 3.1 | 2.1 | 3.3 | Nil | Nil | 4.3 | 6.0 | 4.9 | 8.6 | 7.5 |
| 9. pulp properties | | | | | | | | | | | | |
| i) Freeness, CSF, $ml_2$ | 155 | 145 | 145 | 180 | 155 | 110 | 135 | 110 | 115 | 200 | 120 | 115 |
| ii) Burst index, $kPam^2/g$ | 3.25 | 3.65 | 3.60 | 4.30 | 3.70 | 2.50 | 3.20 | 2.40 | 2.20 | 2.10 | 2.90 | 1.80 |
| iii) Tensile index, $N_2m/g$ | 51.0 | 59.5 | 62.0 | 67.5 | 66.5 | 45.0 | 60.5 | 45.5 | 46.0 | 38.0 | 46.0 | 53.5 |
| iv) Tear index, $mN.m^2/g$ | 4.90 | 5.10 | 5.20 | 5.50 | 4.80 | 4.51 | 3.95 | 4.65 | 3.30 | 4.65 | 5.35 | 3.30 |

a NaOH and $Na_2CO_3$ in the ratio 40 : 60 as NaOH
*0.1% AQ was added

b 60 min at 90°C

c Over night soaking at room temperature

by 4%, without significant gain in burst and tear. Kappa number did not differ at 160°C and 140°C. At lower temperature the residual alkali was on the higher side. In all the cases pulps were clean and did not require refining.

The carbonate process where a mixture of 40% NaOH and 60% $Na_2CO_3$ as NaOH was used also gave pulps of satisfactory strength with 12% chemical. Refiner was used after pulping for fibre separation. Carbonate spent liquor showed no residual sodium hydroxide.

Sulfite process gave yields as high as 65%, when 140°C temperature was used. The yield decreased to 55% when temperature was raised to 160°C. Refiner was used for fiber separation after pulping. There was no significant difference in the strength properties of the pulps produced at 160°C and 140°C. However the sulfite pulps had lower strengths compared to those of the pulps from soda and carbonate process. Sulfite spent liquor showed very low pH values.

Chemimechanical pulp produced by treatment of straw with 12% NaOH for one hour at 90°C gave good pulp which had tear comparable to that of chemical pulp. Burst and tensile were also satisfactory. Spent liquor showed high level of residual chemical. Cold soda pulps produced from the straw soaked in 15 g/l sodium hydroxide solution for over night had good tensile strength, burst and tear were on lower side.

The pulping results indicate that it is possible to produce satisfactory pulps with milder process conditions. This could held in saving of chemicals and steam energy. The pulps from different pulping processes did not show any remarkable variation in the strength properties.

Pollution loads : Small Paper mills based on agricultural residues are discharging spent liquors and washings into stream. At the present juncture small paper mills may not be able to set up techno-economically feasible chemical recovery system as capital investments involved are huge. Till suitable chemical recovery system emerges for these small mills it would be necessary to have some solution to reduce stream pollution load. Severe pulping conditions causes higher pollution loads. The pollution load exerted in different pulping processes is given in Table 2.

The COD load exerted in soda pulping was higher. Sulfite and carbonate pulping spent liquors had lower 'COD'. The chemimechanical pulp showed lowest pollution load. There was no significant change in the suspended solids load. Soda spent liquor had highest dissolved solids load. Milder pulping conditions could produce the spent liquor with low pollution loads. Further the overall pollution load could be reduced to a great extent by repeated recycling of spent liquors and washings[6].

TABLE—2
POLLUTION LOADS IN STRAW SPENT LIQUORS

| Pulping process | Total dissolved solids kg/t pulp | pH | Suspended solids kg/t pulp | COD kg/t pulp |
|---|---|---|---|---|
| 1. Soda process at 160°C. | 866 | 9.6 | 62 | 806 |
| 2. Soda process at 140°C | 770 | 9.9 | 67 | 804 |
| 3. Carbonate process | 734 | 8.4 | 77 | 767 |
| 4. Sulfite | 870 | 6.9 | — | 691 |
| 5. Chemimechanical (Cold soda) | 308 | 10.9 | 53 | 327 |

Properties of straw spent liquors : The properties of straw spent liquors during evaporation and combustion is given in Table-3.

The fluidity of the spent liquors from different pulping processes during evaporation showed wider variation. Straw spent liquors contain considerable amount of fines arising from the epidermis. These fines exert considerable effect on the viscosity. Soda liquor with fines showed very high viscosity. After removal of fines the viscosity dropped considerably. The pH or residual alkali level is another important factor which had influenced the fluidity. When the pH was raised to 9.0 by addition of fresh alkali, viscosity of concentrated liquors dropped remarkably in all the cases. The caustic required to raise the pH to 9.0 varied between 1.4 to 1.8 kg/m³ depending on initial pH. Carbonate and sulfite liquors showed higher viscosity compared to soda spent liquor, which was presumably due to formation of nuclei above 45% solids. Soda spent liquor showed tendency to precipitate above 53% solids. The heating value of soda spent liquor was higher compared to sulfite and carbonate spent liquors. In all the cases heating values were much below compared to liquors from woods, (3300-4000 cal/g). Soda carbonate spent liquors had good burning properties as measured by swelling volume. Sulfite liquor showed poor burning, which might be due to less dispersion of organic material. Results indicate that straw spent liquors, free from fines and with higher residual

alkali, could be evaporated without much problem. Suitable filtration equipment would be necessary to remove the fines from straw spent liquors.

Silica dissolution during pulping : Rice straw in particular contains high amounts of silica. Rice straw studied here had 4.2% silica in whole straw. It was observed that leaf portion contained 9.4% silica while stem had 5.07%. Most of the silica arises from epidermis of the leaves. The dissolution depends on cooking chemical and pulping conditions. Generally less than 50% of the silica in raw material dissolves out during pulping. Table-4 shows the extent of silica dissolution in different pulping processes. In soda pulping more amount of silica was dissolved. With increasing cooking chemical and cooking temperature dissolution was increased.

Carbonate and sulfite spent liquors had lower amounts of silica, which is attributed to lower alkalinity during pulping. Corresponding pulps had silica content depending on the amounts of silica dissolved during pulping. The milder cooking conditions also helped in retaining silica in the pulp rather than in the spent liquor.

**Precipitation of silica from the spent liquor :**

The silica present in the straw dissolves as soluble alkali silicates during alkaline cooking. Different methods for precipitation of dissolved silica is discussed by Panda.A.[7]. Extensive studies have been conducted on precipitation of silica involving addition of cations like lime and lowering of the pH. The lime treatment involves massive lime require-

TABLE–3 PROPERTIES OF STRAW SPENT LIQUORS

| Pulping process | Total solids % | pH | Calorific value K. cal/kg | Viscosity at 80° C Solids % | Viscosity cps | Swelling volume* | Observations |
|---|---|---|---|---|---|---|---|
| 1. Soda liquor with fines | 11.30 | 9.81 | | 48.96 | 455 | — | — |
| 2. Soda | 8.31 | 7.10 | 2739 | 58.93 | 100 | Good | Solids separation |
| | 9.19 | 9.00** | | 56.70 | 28 | Good | above 53% |
| | | | | | | | " " |
| 3. Sulfite | 7.57 | 6·91 | 2165 | 58.77 | 305 | Poor | Nuclei formation |
| | | | | | | | above 45% |
| | 7.18 | 9.00** | | 58.82 | 68 | " | " " |
| 4. Carbonate | 8.33 | 7.71 | 2490 | 50.86 | 145 | Good | Nuclei formation |
| | | | | | | | above 43% |
| | 8.41 | 9.00** | | 44.70 | 48 | Good | |

*SVR — Good — More than 30 ml/g.
Poor — Less than 10 ml/g.

** — pH was raised by external addition of sodium hydroxide

TABLE—4 EFFECT OF PULPING CONDITIONS ON DISSOLUTION OF SILICA

| Cooking process | Cooking temp. °C | Ash in pulp % | Acid insolubles in pulp % | Silica in spent liquor g/l |
|---|---|---|---|---|
| Soda (8%) | 160 | 9.03 | 8.35 | 1.14 |
| Soda (16%) | 160 | 8.24 | 6.96 | 1.59 |
| Soda (12%) | 160 | 7.67 | 6.33 | 2 30 |
| Soda (10%) | 140 | 7.50 | 7.01 | 1.65 |
| Carbonate (12%) | 160 | 10.50 | 9.80 | 1.03 |
| Sulfite | 160 | 9.52 | 8.70 | 0.89 |

* 12% ($NaOH$ : $Na_2CO_3$)
( 40 : 60 )

ment and also depends on the quality of the lime available. Lowering of the pH spent liquor to precipitate silica is another alternative. By lowering the pH silica precipitates as polymeric silica acid. The lowering pH could be achieved by using milder alkaline cooking chemicals like sodium carbonate, using acids and by carbonation of spent liquor.

In the present study it was observed that the spent liquor from carbonate pulping had pH which further depleted to around 7.0, by storing for 24 hours. There was precipitation of sludge in the carbonate spent liquors. The sludge quantity estimated was 7 to 9.5 g/l of black liquor. The sludge contained about 26% of the silica. Thus milder cooking chemicals during pulping could help in precipitation of silica after staring the spent liquor.

Silica precipitation using mineral and organic acids : The results of silica precipitation are given in Table-5. Silica precipitation involving lowering of pH by sulfuric acid, showed high amounts of organic matter coprecipitated alongwith silica. Organic matter loss was as high as 19g/l. The calorific value of supernatant liquor dropped to 2450 k cal/kg from 2740 k cal/kg.

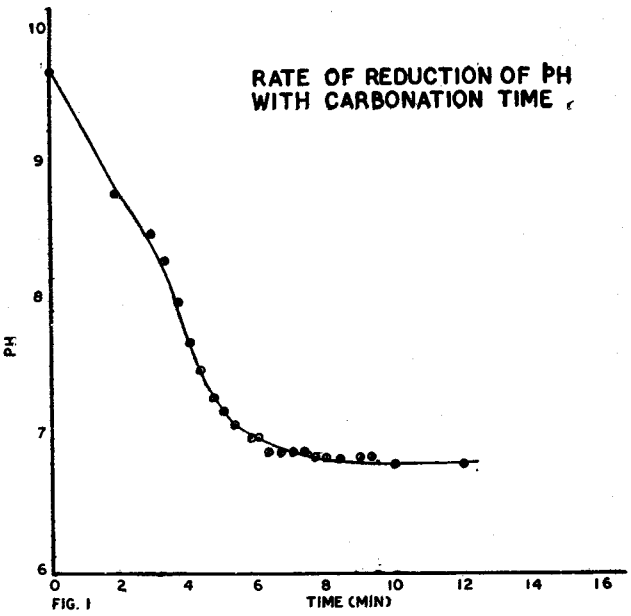

FIG. 1

TABLE--5 SILICA PRECIPITATION WITH MINERAL AND ORGANIC ACIDS

| Chemical | Temp. °C | Initial pH | Final pH | Sludge solids g/l | Organic matter lost g/l | $SiO_2$ in sludge % |
|---|---|---|---|---|---|---|
| 1. Sulfuric acid (14 g/l) | 63 | 9.74 | 4.03 | 25.20 | 19.10 | 7.50 |
| 2. Acetic* anhydride | 64 | 9.98 | 4.91 | 7.08 | 3.64 | 47.70 |
| 3. Aoetic anhydride + Polyethylene Oxide** | 64 | 10.02 | 4.98 | 7.40 | 3.30 | 49.00 |
| 4. ,, ,, | 23 | 9.98 | 4.96 | 40.30 | 31.20 | 9.75 |

* 13 g of $AC_2O$/litre of liquor.
** Polyethylene oxide solution used was 20 mg per litre of spent liquor

Acetic anhydride alongwith small dose of polyethylene oxide was effective in precipitating silica at 64°C. The organic matter loss was with silica-rich sludge. Another advantages of acetic anhydride is that the alkali is neutralised by forming organic sodium salts, which will not pose problems in recovery of chemicals. Use of mineral acids lead to formation of sulfates and chlorides.

Silica precipitation by carbonation : During carbonation the silica begins to precipitate when the free alkali has been neutralised. Carbonation helps in controlling the pH to the desired level which would be difficult in case acids are being used. Fig 1 shows the neutralization of spent liquor with increasing time of passing carbon dioxide.

Neutralization curve shows that pH drop was faster till 7.5 pH. In the later part of neutralization the pH drop was slow. It is evident that the neutralization of free alkali occurs around pH value of 7.5. Fig. 2 shows the effect of pH on silica precipitations. Maximum silica precipitation takes place between 8-9 pH. Further decrease in pH did not help in substantial silica precipitation. Carbon dioxide consumption was higher upto pH 8.0, which then dropped slowly. In the initial stage about 50% of $CO_2$ passed was absorbed while at pH 7.5 only 20% of $CO_2$ was absorbed.

Table-6 shows silica precipitation by carbonation at different temperatures.

Two sets of experiments were carried out. In one case silica in spent liquor was 1.05 g/l and in another case silica content of spent liquor was raised to 67.8 g/l. In both the sets high

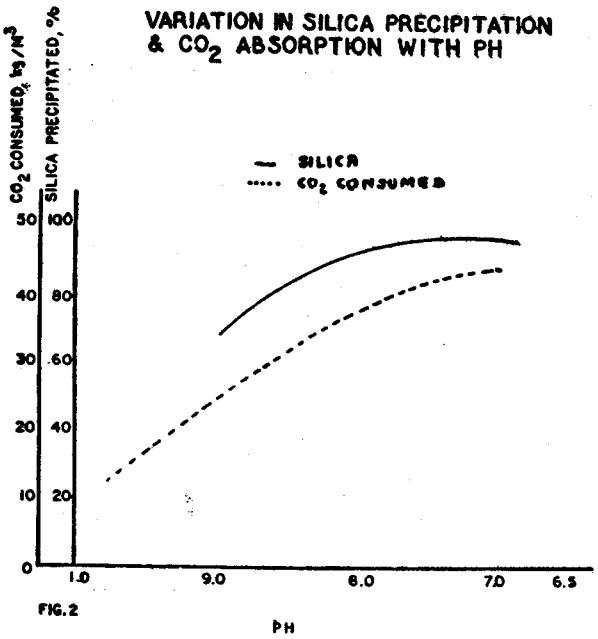

FIG.2

percentage of silica removal was achieved at the temperatures above 60°C. More than 95% of silica could be precipitated without significant loss of organic matter. At higher temperature organic matter losses are on lower side.

**Carbonation under pressure :**

Bratteberg T. reported a process for the manufacture of high yield kraft through precipitation and absorption of organic material by injecting the carbon dioxide[8]. Here silica precipitation studies were made by injecting carbon dioxide under pressure. The results are given in Table-7.

Results show that the pH of spent liquor reduced from 10.2 to 8.3 with increasing pressure of $CO_2$. About 74% of precipitation of silica was achieved at 5.3 kg/cm² pressure of $CO_2$. Sludge quantity was considerably low, compared to the sludge quantity obtained in carbonation of spent liquor, indicating sorption of precipitated material on the pulp fibres. The silica content and kappa numbers of the pulps in which $CO_2$ was injected were increased, indicating sorption of both silica and lignin on the pulp fibers. The pulp yield gain in the case of 5.3 kg/cm² $CO_2$ pressure was as high as 6%. High kappa number and sorption of silica did not affect the strength properties of the pulps. This carbonation under pressure could also help in easier filtration of precipitated silica in which pulp itself acts as filtering medium. This carbonation under pressure appears to be a promising method for silica removal.

**Carbonation in packed bed contact absorber :**

Packed bed contact absorber was fabricated to get the relevant data for carbonation of spent liquor. The liquor and carbon dioxide were passed in counter current direction. The column is illustrated in Fig. 3.

Results of silica precipitated by carbonation in this column are given in Table 8 Results show that it is possible to bring down the pH of the liquor from 11 to 7 in one stage. With thin spent liquors silica removal was not effective. Silica removal upto 69% was achieved with spent liquor having 7.3% solids. Approximate calculation worked out indicated that about 2 m³ of interfacial volume per cubic meter of spent liquor would be required. However the figures depend on type of packing, flow of liquor, and flow of gas. Experiments indicated that straw liquor containing lower amounts of free alkali would require only one stage.

Effect of temperature on silica precipitation and settling rate of precipitated silica :

TABLE 6. SILICA PRECIPITATION BY CARBONATION

| Expt. No. | Temp. | Initial | Final | Sludge solids | Organic matter | Silica in supernatant liquor | Silica removal |
|---|---|---|---|---|---|---|---|
| | °C | pH | pH | g/l | g/l | g/l | % |
| 1* | 20 | 9.74 | 6,79 | 7.34 | 5.3 | 0.150 | 85 7 |
| 2 | 33 | 9.24 | 6.79 | 6.44 | 4 5 | 0 005 | 99.5 |
| 3 | 62 | 8.97 | 6.81 | 7.66 | 5.4 | 0.004 | 99.6 |
| 4 | 73 | 8.58 | 6.86 | 7.20 | 5.3 | Traces | 100.0 |
| 5 (a) | 62 | 10.96 | 7.05 | 20.40 | 10.4 | 0.370 | 95.3 |
| 6 (a) | 74 | 10.72 | 7.32 | 16.60 | 8.4 | 0.2?0 | 97.1 |

*In experiments 1 to 4 original silica content was 1.05 g/l
(a) Original silica content was raised to 7.83 g/l by external addition of sodium silicate.

TABLE -7 SILICA PRECIPITATION BY CARBONATION UNDER PRESSURE

| Expt. No. / Particulars | 1 (control) | 2 | 3 | 4 |
|---|---|---|---|---|
| O. D. straw charge, g | 100 | 100 | 100 | 100 |
| $CO_2$ pressure, kg/cm² | Nil | 2.7 | 3.0 | 5.3 |
| Spent liquor | | | | |
| i) pH | 10.2 | 8.7 | 8.4 | 8.3 |
| ii) Residual NaOH, g/l | 2.4 | 2.3 | 2.3 | 1.7 |
| iii) Sludge solids, g/l | 4.7 | 5.1 | 5.2 | 5.5 |
| iv) Organic matterin sludge g/l | 3.6 | 3.9 | 3.7 | 4.1 |
| v) Silica g/l | 0.74 | 0.25 | 0.21 | 0.19 |
| Silica precipitated, % | Nil | 66.2 | 72.0 | 74.3 |
| Pulp properties | | | | |
| Pulp yield % | 53.6 | 55.7 | 57.8 | 59.5 |
| Silica % | 10.6 | 11.6 | 10.9 | 11.4 |
| Kappa Number | 30.8 | 54.4 | 56.9 | 49.5 |
| Freeness, CSF (ml) | 140 | 135 | 135 | 145 |
| Tensile index, N. m/g | 41.0 | 42.0 | 39.5 | 41.0 |
| Burst index, kPa.m²/g | 2.60 | 2.10 | 1.90 | 2.30 |
| Tear index, mN.m²/g | 3.10 | 2.45 | 2.85 | 3.20 |

Cooking conditions — 12% NaOH, 90 min at 160°C
Carbonation condition — 120°C, 60 min after terminating cook.

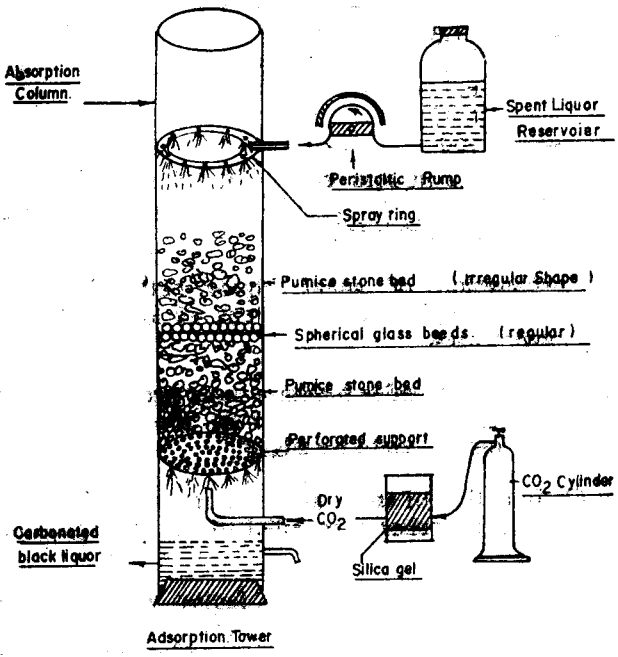


Fig. 3 - ILLUSTRATIVE DIAGRAM FOR CARBONATION OF BLACK LIQUOR

If silica is not removed prior to combustion will be carried over to green liquor. Silica presence in green liquor will have adverse effect on settling of slurry after causticization.

Results given in Table-9 show that temperature during carbonation of the green liquor had considerable impact on precipation and settling of silica.

Increasing the temperature from 32°C to 80°C, silica precipitation was increased from 92 to 98%. The settling of precipitated silica was fast at 80°C, which required only 3 minutes, while at 32°C it required about 45 minutes for 50% settling. Fig. 4 shows the influence of presence of silica on settling rates of causticized slurry.

Silica in the green liquor affects the settling rate due to coprecipitation of voluminous calcium silicate. After silica removal by carbonation the settling rate improved considerably.

**Conclusions :**

1. Milder cooking chemicals and pulping conditions can produce straw pulps of satisfactory quality with lower pollution loads, less chemical losses and with low silica content in spent liquors.

TABLE—8. SILICA PRECIPITATION BY CARBONATION IN PACKED BED CONTACT ABSORBER

| Particulars | 1 Drain spent liquor | 2 Liquor from chest pulp | 3 Liquor from chest pulp | 4 Concentracted liquor |
|---|---|---|---|---|
| Solid content, g/l | 3.4 | 4.1 | 4.1 | 7.3 |
| Temperature, °C | 21 | 22 | 64 | 56 |
| Flow of liquor, lit/min | 0.7 | 0.7 | 0.6 | 0.6 |
| Initial pH | 9.9 | 11.1 | 10.0 | 9.7 |
| Initial silica, g/l | 0.69 | 0.72 | 0.72 | 1.27 |
| pH after one stage | 6.60 | 6.96 | 7.0 | 7.04 |
| pH after two stage | 6.44 | 6.70 | — | 7.04 |
| Sludge solids, g/l* | 0.91 | 1.50 | 1.83 | 9.8 |
| Ash content of sludge, % | 41.3 | 46.1 | 40.1 | 38·8 |
| Final silica in liquor, g/l | 0.25 | 0.58 | 0.51 | 0.39 |
| Silica precipitated % | 64 | 20 | 30 | 69 |

Sample of spent liquor were collected from the mill
*Matarial precipitated per litre of spent liquor.

TABLE—9. EFFECT OF TEMPERATURE ON SILICA REMOVAL AND SETTLING RATE

| Temparature °C | 32 | 51 | 66 | 80 |
|---|---|---|---|---|
| Final pH | 9.6 | 9.4 | 9.4 | 9.2 |
| $SiO_2$ in carbonated green liquor | 0.52 | 0.42 | 0.18 | 0.11 |
| % $SiO_2$ Precipitated | 91.8 | 96.1 | 97.2 | 98.3 |
| Volume of precipitate, ml. | 50 | 52 | 48 | 43 |
| Total time for 50% settling, min. | 45 | 37 | 20 | 2.5 |

| | | |
|---|---|---|
| Green liquor initial pH | — | 11.3 |
| $Na_2Co_3$ g/l | — | 106 |
| XaOH, g/l | — | 6.4 |
| $SiO_2$, g/l | — | 6.35 |
| $CO_2$ flow — ml/min | — | 150 |

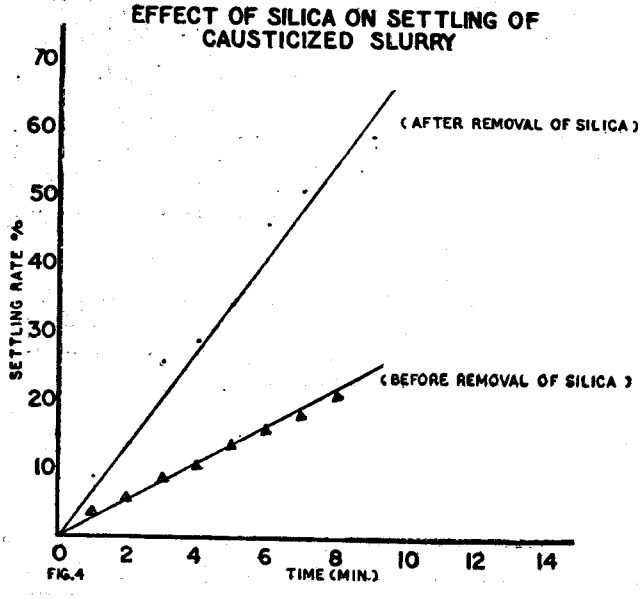

FIG.4

2. Straw spent liquors could be evaporated satisfactorily after removing the fines and increasing the residual alkali (pH 9.0).

3. Carbonation of spent liquor could help in removing silica to the extent of 98% at higher temperatures.

4. Carbonation under pressure was promising both in precipitating silica and at the same time increasing the yield by 6%.

5. Carbonation of straw spent liquor in packed bed contact absorber was efficient in precipitating silica.

6. Temperature was important factor while precipitating silica in the green liquor by carbonation. Temperatures above 60°C showed better desilication and settling rates.

7. Carbonate pulping could be a process where chemical recovery can be incorporated due to

following advantages.

i) Low amounts of silica in spent liquor.

ii) Dissolved silica precipitates on storing

iii) Causticization may not be required as 60% of the chemical is sodium carbonate.

iv) Silica build up in the system can be checked by green liquor desilication.

**Experimental :**

Raw material : The rice straw was procurred from farmers of local Dehra Dun area. The straw was made free from dust and then chopped to 2.5 to 3.0 cm length chops for pulping.

Pulping : The pulping experiments were carried out in series digester consisting of six bombs each of 2.5 litre capacity, heated in polyethylene glycol both material to liquor ratio was 1 : 7 in chemi-mechanical and 1 : 5 in other pulping processes. After pulping, cooked material was either disintegrated or refined depending on the pulping process. Finally pulps were washed on a funnel with recycling of washings to avoid the loss of fines. The strength properties of the pulps were carried out as per ISO standards given in the manual of laboratory research methods[1]. Analysis and properties of spent liquor were carried out according to methods mentioned in[1].

Carbonation of spent liquor : The carbonation experiments were carried out using commercial carbon dioxide, having 80-90% $CO_2$ content. The carbon dioxide was dried over silica gel before passing into spent liquor. The carbon dioxide was bubbled through spent liquor at the desired temperature, with vigorous agitation. Constant flow was maintained with the help of manometer. In all the experiments involving silica precipitations, the sludge was separated by centrifuging at 5000-6000 rpm. In the cases where silica in spent liquor was considerably low, sodium silicate was added externally to raise the silica content.

Carbonation under pressure : The carbonation was carried out by injecting carbon dioxide gas into the autoclaves after terminating the cooking. The autoclaves were cooled down to temperature below 100°C, and then carbon dioxide was injected at desired pressure. After gas injection the autoclaves were kept at 120°C for one hour. Pulps were washed with fixed quantity of water. The spent liquor collected was made free from the sludge by centrifuging.

Carbonations in packed bed contact absorber : The apparatus is shown in Fig. (3). The perspex tube was packed with pumico stone bed separated by spherical glass beeds. Packing was supported by a perforated grid. The liquor was sprayed on the top of bed through a peristaltic pump at constant flow.

The carbon dioxide was injected below the bed in counter current direction. The carbonated liquor was collected at the bottom. While studying at higher temperatures the column was heated by circulating hot spent liquor prior to carbonation. The dimensions of the packed bed column are given below :

| | | |
|---|---|---|
| Diameter of the column | = | 6.3 cms |
| Depth of packing | = | 64 cms |
| Interfacial volume | = | 770 $cm^3$ |
| Cross sectional area | = | 7.8 $cm^2$ |
| Flow of liquor | = | 42 lit/hr |
| Total volume of column upto packed height | = | 1995 $cm^3$ |

Carbonation of green liquor : The green liquor was prepared by mixing sodium carbonate and sodium hydroxide. Silica was introduced into green liquor by adding sodium silicate solutions. The green liquor was carbonated by passing carbon dioxide. The causticization experiments were carried out with green liquors before and after removal of silica. The green liquor to lime ratio was kept 8 : 1, during slaking period. Further causticization was completed by refluxing for one hour. The settling rates of causticized slurries was measured immediately.

Mill spent liquors : Mill spent liquors were collected from a mill operating on wheat straw. Sample of spent liquors were collected from the drain point and from the blow pit after squeezing the pulp. The spent liquors had following compositions.

| | pH | T.S.% | $SiO_2$ g/l | Residual alkali g/l |
|---|---|---|---|---|
| Drain spent liquor | 9.88 | 3.35 | 0.69 | 1.73 |
| Chest spent liquor | 11.11 | 4.10 | 0.72 | 3.84 |

One portion of chest spent liquor was concentrated in vacuum flash evaporator to solids content of about 7.3%.

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