Studies on desilication of bamboo kraft black liquor

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SUMMARY

In the present study an attempt was made for desilication by th method of lowering the pH of the black liquor by carbonation. The bamboo kraft black liqour usually contains silica in the range of 5–8 g/l as SiO_2. Main objective of the study was to see the effect of PH and temperature on silica precipitation and also to achieve selective precipitation of silica. Studies revealed that temperature and pH are the two imp rtant parameters to be optimized. The pH range for silica precipitation is largely influenced by the temperature during carbonation. Studies revealed that at all temperature and pH levels there was a coprecipitation of lignin. Studies were also made for achieving selective precipitation of silica.

Treatment of sludge with calcium oxide or aluminium hydroxide at 80° C helps in redissolution of coprecipitated lignin without dissolving silica portion. Leaf filter studies indicated that the carbonated black liquor could be filtered easily on 600 mesh nylon cloth under reduced pressure of about 0.3 kg/cm^2.

INTRODUCTION

Bamboo is a major component of raw material furnish in Indian mills. Bamboo contains silica in the range of 2.5 to 3.5%. Most of this silica dissolves during pulping and remains in the black liquor as silicates. Silica in the raw material contributes to about 70% of the total silica input in the system (1) Various troubles in the chemical recovery operation, due to the presence of silica, had been discussed in the literature (1) Silica removal from the black liquor is necessary for smooth running of chemical recovery unit. Panda (2) has discussed various patents and methods of the removal of silica and observed that the best way to overcome the problems, due to silica in various sections of chemical recovery units would be to remove the silica before it enters the recovery system.

Methods available in the literature, and patents have been divided into following three groups for desilication of black liquors :—

(a) Method of addition of cations :

Method involves addition of cations like Ca^{++},Mg^{++} and Al^{+++} to precipitate silica as insoluble silicates. Among the cations, addition of lime (CaO) is economic and efficient. Exhaustive work has been done on desilication by lime treatment method both on laboratory and pilot plant scale. In India also intensive work has been done on this method. However, the method has not gained the place on commercial scale, as the quality of lime is not pure enough and reburning of sludge produced is not possible as it contains abont 20-25% silica (3) and also due to formation of voluminous and slow settling calcium silicate precipitate, which makes filtration difficult.

(b) Method of lowering the pH of the black liquor :

The lowering of the pH of the black liquor converts the silicates into insoluble polymeric anhydrides of silicic acid. The lowering of the pH could be effected either by addition of the acids or by the use of carbon dioxide. Use of acids leads to over acidification and hence heavy lignin precipitation. Use of carbon dioxide is efficient in bringing down the pH slowly without much over-acidification. Flue gas after removing moisture and dust is a good source of carbon dioxide and air mixture (about 14-20% CO_2).

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(c) Combined methd by lowering pH and addition of cations :

Not much work has been done on this method. Some work done by this method involves lowering of the pH and then precipitating silicic acid as silicates by addition of $MgSO_4$ (2).

With this back ground, study was undertaken for desilication using carbonation method. Studies were directed towards :—

i) achieving the selective precipitation of silica with lesser losses of organic matter with sludge.

ii) Easily filterable mass of silica precipitate.

iii) Retaining almost the same chemical nature of black liquor after carbonation and filtration to avoid lesser active alkali in evaporators.

MATERIALS

1) Black liquor

The Bamboo (Dendrocalamus strictus) from Bastar forests was used in this study. The Bamboo had 4.61% ash and 1.64% SiO_2 in raw material. The black liquor was produced by cooking bamboo by sulfate process uisng 16% A.A. as Na_2O for 90 minutes at 170°C. Three lots of black liquor produced for these investigations had following properties :—

Cook No.	1	2	3
pH	11.2	11.6	11.5
R.A.A. as Na_2O, g/l	10.39	9.24	8.34
Total solids,% w/w	19.46	19.48	19.48
SiO_2, g/l	7.2	7.18	5.2

2) Carbon dioxide

Carbon dioxide was obtained in cylinder. The CO_2 content was about 90% as analysed by KOH absorption method.

EXPERIMENTAL

1) Carbonation of the black liquor

The carbon dioxide from cylinder was passed into black liquor after drying over silica gel. The black liquor was agitated continuously by magnetic stirrer. The electrodes of pH meter and thermometer were immersed in black liquor during carbonation. The flow of carbon dioxide was between 40-50 ml/min. throughout the study.

2) Separation of sludge after carbonation

The sludge was separated by centrifuging for quantitative purposes. Centrifuging was done at 5000 rev/minutes. for 20 minutes. After centrifuging the supernatant liquor was taken out by slow decantation.

3) Analytical methods

Silica content of black liquor was estimated according to Tappi Standard Method T-625.

Silica content in sludge was estimated after ashing at 700°C. The ash was subsequently treated with HCl.

In this study HCl insolubles was taken as silica as the difference between HCl insolubles and HF insolubles was in traces.

The residual active alkali content in the black liquor was determined frequently as R.A.A. changed slowly with time.

RESULTS AND DISCUSSIONS

1) Rate of carbon dioxide absorption

Table 1 shows the reduction in pH with time at 17°C after carbonation. About 9.8 pH could be achieved in 30 minutes under atmospheric pressure at 17°C. It was found that there was heavy lignin precipitation below 9.8 pH. It is complicated to calculate the amount of CO_2 required for silica precipitation. However, some figures are available based on our laboratory calculations for the rate of absorption of CO_2 and the amount of CO_2 required to bring down the pH. These figures are limited only to laboratory purposes. Table 2 gives some data on the rate of absorption of carbon dioxide. Absorption of CO_2 decreases slowly with time. About 3.6 to 8.1 kg of CO_2/m^3 of black liqur is required to lower the pH in the range of 10 to 9.4 from an initial/pH of 10.9 under specified conditions. The volume of supernatant black liquor was reduced after separating the sludge. When the pH of 100 ml. black liquor was brought down from 11.1 to 9.9 the final volume. of supernatant liquor after sludge separation was 62 ml. The solids content of resulting liquor was reduced from 212 g/l to 185 g/l after carbonation.

2) Effect of pH and temperature on silica precipitation

Table 3 gives data on desilication carried out over different pH and temperature ranges. Temperature was varied from 21°C to 75°C. Perusal of results shows that the pH range for silica precipitation varied sharply with temperature. At lower temperature it is possible to precipitate silica at higher pH range, while at high temperature lower pH ranges are required. The residual active

alkali of the supernant liquor dropped considerably at all temperature ranges. The residual alkali drop was high in the initial stage. The pH values required for 90% desilication were 10.4, 9.5 ard 9.4 for 21°C, 64°C and 75°C respectively. In all the cases sludge contained considerable amounts of organics and inorganics along with silica. Thus, it would be difficult to achieve selective precipitation of silica by lowering the pH. This may be attributed to the reason that the threshold pH values for silica and lignin precipitation may not vary much. More studies are required to find the ways for selective precipitation of silica. Here the organics in the sludge is more because the colloidal lignin particles are also being settled during centrifuging which might have passed through some filtering media. The solids precipitated during carbonation varied from 6 to 90 g/l black liquor at different pH. The sludge solids for 90% desilication increases slightly with temperature. At higher temperatures it was observed that silica precipitation was sensitive to sligh- change in pH value. It would be difficult to maintain close range of pH on industrial scale. Thus the pH value cannot be used for controlling desired level of silica precipitation. Suitability of the parameters like residual carbonate content or reaction time might be used for controlling the desilication and needs more study.

3) Effect of temperature on solubility of precipitated silica

Effect of temperature on solubility was studied by precipitating silica at 17°C and pH of about 10 4 25 ml. samples of carbonated liquor was heated to different temperatures and silica content in supernatant liquor after centrifuging was estimated. The results are recorded in Table 4. The results indicate that the solubility of silica precipitated at lower temperatures increased with the increase in temperature. 94.4% silica precipitated at 17°C. When heated to 70°C about 36% of precipitated silica goes back into black liquor. The ash content of sludges at different temperatures is constant indicating proportional solubility of silica, organics and other inorganics. Tendency of the silica to dissolve at elevated temperature indicates that efficient precipitation could be achieved at lower tempera'ures. Preliminary experiments on relative settling on precipitated silica and lignin show slow settling characteristics of lignin. The results are given in table 5. In the initial stages of centrifuging, silica settled first as indicated by higher percentage of silica in sludge. In the later stages the silica content decreased due to the settling of lignin. Thus lignin settles more slowly compared to silica precipitate. Further detailed investigations are required on settling characteristics of precipitated silica.

4) Effect of addition of NaOH on the solubility of precipitated silica and lignin

The alkali level of carbonated black liquor was increased by adding sodium hydroxide. The objectivg was to dissolve the precipitated lignin leaving silica precipitate in the liquor. The black liquor was carbonated at 65°C and the pH was brought down from 11.5 to 9.7. Then different doses of NaOH was added to the samples of carbonated liquor and was agitated for 10 min. at 65°C The results given in Table 6 indicated that precipitated silica redissolved on increasing the residual active alkali level. Sludge solids decreased from 29 6 g/l to 13.2 g/l. Sludge shows more or less same ash content indicating solubiliiy of both silica and organics. Thus increasing the residual alkali level did not help in achieving the selective solubility of lignin alone.

5) Treatment of sludge with lime

The objective of the lime treatment of the sludge obtained after carbonation, was to convert the precipitated silica into insoluble calcium silicate. Thus the lime treated sludge when heated would dissolve only lignin portion. The black liquor was carbonated to a pH of 9.9 at 24°C. The sludge was separated by centrifuging and treated with 60% CaO based on sludge solids. The sludge solid concentration was kept at about 75 g/l. Slurry was heated to 75°C for 10 minutes. It was found that only about 14.4% of the precipitated silica was dissolvd back from the sludge. In case of sludge sample without lime treatment about 22.8% silica was dissolved. In both the cases about 85% material was dissolved. Thus when the sludge is heated with lime major portion of lignin could be dissolved retaining about 85% silica in the sludge.

6) Lime treatment followed by carbonation

The partially carbonated black liquor was treated with lime. The objective was to convert silica into silicic acid during carbonation and then to insoluble silicate by lime treatment. The black liquor was carbonated to different pH ranges at different temperatures. One portion of black liquor was then treated with 4.7% CaO on the basis of black liquor solids and the other portion was not treated. The results are given in table 7. The results indicate that silica precipitation was more dependent on pH rather than subsequent lime treatment. The subsequent lime addition after carbonation did not enhance the silica preciptation. The difference in silica preicpitation with and without lime is not significant. Lime addition did increase the sludge quantity.

7) Treatment of sludge with Al $(OH)_3$

Studies were carried out on disolution of lignin from the sludge obtained after carbonation of black liquor. As reported in section 5 it is evident that even water digestion of suldge leads to dissolution of about 22% of precipitated silica. In this investigation the treatment of sludge with lime and aluminium hydroxide were compared. CaO and $Al(OH)_3$ were used in stoichiometric quantities i. e. 93% CaO and 270% Al $(OH)_3$ on silica content basis respectively. Black liquor (150ml) was carbonated to 9.5 pH. The carbonated black liquor was centrifuged and the sludge was separated. The sludge was then converted to slurry having solids concentration of about 26 g/l. 40 ml of the slurry was treated with CaO and $Al(OH)_3$ separately at 85°C for 10 minutes. After treatment the slurry was again centrifuged. The supernatant liquor and sludges in all the cases were analysed. The results indicate that in all the three cases of digestion nearly 64% of the material get dissolved, most of which is precipitated lignin and other inorganics. But in case of digestion with only water nearly 16.4% of the precipited silica redisolved, while in case of the suldge when digested with CaO or Al $(OH)_3$ the redissolution of silica was considerably less; which might be presumbly due to formation of insoluble Ca^{+2} and Al^{+3} silicates. Thus the sludge digestion with eithter CaO or $Al(OH)_3$ helped in redissolution of precipited silica. Hower intensive pilot plant studies would be required to find out the economic feasibility aspects.

8) Treatment of sludge with NaOH

The sludge was treated with dilute alkali (0.1 N) at 80°C, to see the selective dissolution of lignin. However it was found that about 35% silica was redissolved alongwith lignin, after digestion. Thus the caustic treatment was not found to be favourable to achieve the relative solubility of lignin.

9) Carbonation of Black lipuor in adsorption column

An adsorption column was fabricated in our laboratory to study the carbonation conditions. The adsorption column is illustrated in fig 1. About 58 cms packed bed column was prepared with both regular shape glass beeds and irregular shape stones. The spent liquor quantity held between the voids of packing was about 770 ml. The black liquor was sprayed on the top of bed and gas was allowed to flow from bottom. It was found that the carbonation was efficient with lower amounts even less than 10% losses of carbon dioxide. The pH value dropped from 10.9 to 10.1 in one pass with the black liquor flow of 0 5 lit/min. However, due to lack of equipment for accurate measurement of flow of gas and also due to non-uniform spraying the mass transfer coefficients could not be estimated:

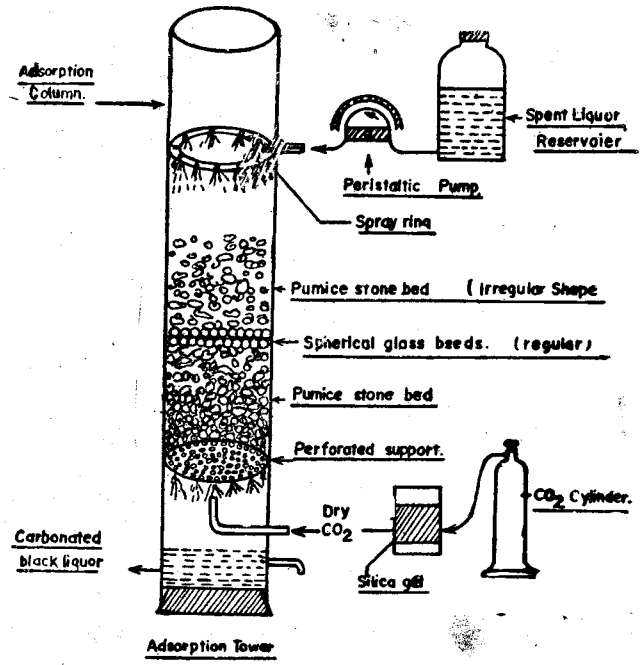

Fig I

ILLUSTRATIVE DIAGRAM FOR CARBONATION OF BLACK LIQUOR

10) Filtering characteristics of sludge

Studies were also made on the filtering characteristics of the carbonated black liquor. The leaf filter apparatus which was fabricated in laboratory according to dorr-oliver method (4) illustrated in fig. 2 was used for this study. Studies were carried out at different pH and temperature ranges. The leaf filter was dipped in carbonated liquor and reduced pressure of about 0.3 Kg/cm^2 was applied. The carbonated liquor was stirred continuously to avoid the settling of solids. The filter medium was 600 mesh nylon cloth. The results are recorded in Table 9 and table 10. The results in table 9 indicate that filtration is more efficient at lower temperature. The solids retention on filter medium was 81.3% at 24°C as compared to 45.6% at 79°C. Further the results in table 10 reveal that with increase in the pH, solids retention on filter medium goes on decreasing The decreased solids retention is due to precipitation of high amounts of lignin at lower pH ranges. It was also observed that it would be difficult to filter the carbonated black liquor which will have more than 50 g/l sludge

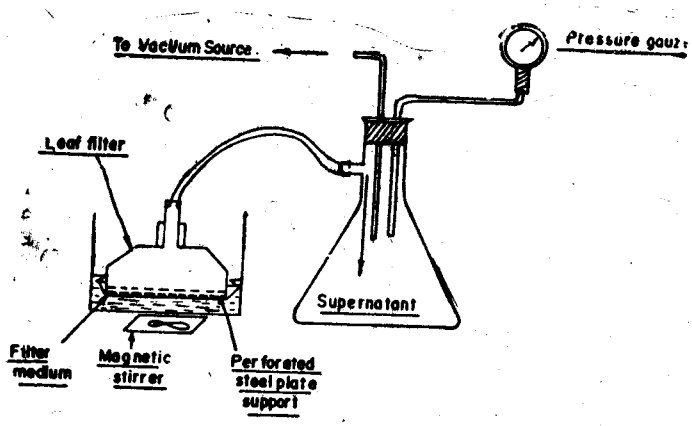

Fig 2- LEAF FILTER APPARATUS

solids. At pH 8.03 it was difficult to filter the carbonated black liquor. From the leaf filtration studies it appears that it will not be difficult to filter the carbonated liquor upto 50 g/l sludge solids concentration.

CONCLUSIONS

1. By carbonation of black liquor as high as 98% of silica could be precipitated.
2. The pH range for silica precipitation is dependent on chemical composition of black liquor and also on the temperature during carbonation.
3. At all temperature ranges the silica precipitation starts when about 50% of alkali had been neutralised.
4. At temperature below 50°C about 90% desilication could be achieved in the pH range of 9.5 to 10.3. For temperatures above 50°C pH range was below 9.5.
5. Silica precipitation is very sensitive to pH changes at higher temperature. Thus pH cannot be used as a parameter for controlling the silica precipitation.
6. Precipitated silica has a tendency to redissolve at elevated temperatures. Precipitation should preferably be carried out at lower temperatures.
7. At all temperature and pH ranges, lignin was coprecipitated with silica.
8. Lime treatment followed by partial carbonation and increasing the residual alkali level after carbonation did not help in selective separation of the silica.
9. Heating of concentrated sludge with either lime or $Al(OH)_3$, helped in redissolving precipitated lignin without dissolving the silica portion.
10. The carbonated black liquor having sludge solids of 50 g/l could be filtered easily under reduced pressure of about 0.3 Kg/cm^2 with 600 mesh nylon cloth.

REFERENCES

1. Panda, A.; Indian Pulp and Paper, Vol. 16 No. 1 (1962).
2. Panda, A.; Indian Pulp and Paper, Vol. 16 No. 6. 701-6 (1962).
3. Farnandes, J. D.; Recovery of silica from black liquor; paper presented at IPPTA Zonal Seminar at Calcutta, Sept., 1978.
4. John Perry "Filtration" Chemical Engineers' Hand Book McGraw-Hill Publication-969, 1950 (Ed).

TABLE—1 EFFECT ON CARBONATION TIME ON pH OF BLACK LIQUOR AT 17°C UNDER ATMOSPHERIC PRESSURE

Carbonation time min.	pH of black liquor
0	11.2
5	10.7
10	10.4
15	10.2
20	10.0
30	9.8

TABLE—2

Black liquor —100 ml.
Initial pH—10.9
of B. L.

Temperature—30°C, Atmospheric Pressure—743 mm Hg

Time Sec.	CO_2 passed ml	pH	Unabsorbed CO_2 (ml)	% of CO_2 absorbed	CO_2 absorbed kg/m³
380	252	10.05	10	9.60	3.6
605	400	9.83	40	90.0	5.5
730	483	9.55	56	88.6	6.4
990	730	9.37	188	74.2	8.1

TABLE—3 DESILICATION OF DIFFERENT TEMPERATURES

Initial pH of B. L.=11.9 SiO_2=5.2g/l, R.A.A.=7.9 g/l as Na_2O

Temp. °C	pH	Supernatant liquor SiO_2 g/l	R.A.A. as NaO g/l	$S.O_2$ removed %	Solids g/l[a]	Sludge (Centrifuged) SiO_2* %	Organics* %	Other Inorganics* %[b]
21	10.90	2.60	3.64	50.0	12.1	21.5	36.4	42.1
	10.65	1.10	2.71	78.8	33.0	9.5	73.3	17.2
	10.40	0.50	1.94	90.4	57.9	8.1	44.5	47.4
	10.30	0.50	2.00	90.4	64.8	7.3	42.7	50.0
52	10.10	4.10	4.03	21.2	6.6	16.7	41.4	41.9
	9.90	3.00	2.70	42.3	53.7	4.1	49.4	46.5
	9.75	2.65	2.33	49.0	61.9	4.1	50.7	45.2
	9.65	1 45	1.70	72.1	74.3	5.1	51.1	43.8
64	9.80	4.60	4.40	11.5	20.1	3.0	37.0	60.0
	9.60	0.90	2.30	82.7	46.4	9.3	74.7	16.0
	9.50	0.55	3.60	89.4	64.4	7.2	67.7	25.1
75	9.60	3.30	1.86	36.5	28.2	6.7	44.5	48.8
	9.40	0.55	1.55	89.4	82.7	5.6	30.9	63.5
	2.30	0.10	1.24	98.1	90.7	5.6	44.9	59.5

* Expressed on dry sludge solids.
a-'g' solids precipitated per litre of black liquor
b-calculated by difference.

TABLE—4 EFFECT OF TEMPERATURE ON SOLUBILITY OF PRECIPITATED SILICA

Test	Temp°C	17	38	45	55	70
SiO_2 g/l*		0.40	1.96	2.10	2.40	3.0
SiO_2 removed, %		94.4	72.8	70.8	66.7	58.3
Ash % in sludge		34.8	34.6	34.1	33.0	34.9

* Residual silica in supernatant liquor after centrifuging.

TABLE—5 RELATIVE SETTLING OF PRECIPITATED SILICA AND LIGNIN

Centrifuging time min.	Solids settled g/l	SiO_2% on sludge
3	18.04	17.3
5	19.40	17.7
7	18.84	15.9
9	34.04	11.6
11	50.84	5.7

Centrifuging was done at 5000 rpm.
The final pH was 10.7 at 24°C after carbonation.

TABLE—6 EFFECT OF ALKALI LEVEL ON SOLUBILITY OF PRECIPITATED SILICA AND LIGNIN

Initial black liquor — pH-11.5; R.A.A. - 8.34 g/l; SiO_2-5.2 g/l
Carbonated black liquor — pH- 9.7; R.A.A. - 2.71 g/l; SiO_2-3.4 g/l
Temperature during carbonation - 65°C.

NaOH added g/l as Na_2O	Final pH	R.A.A. as Na_2O g/l	Supernatant liquor		Sludge (centrifuged)		
			SiO_2 g/l	SiO_2 removed %	Solids g/l	Ash %	Sio_2 %
Nil	9.7	2.71	3.4	34.6	29.6	34.7	6.1
1.86	9.9	3.10	4.0	23.1	16.7	36.4	7.2
3.41	10.3	3.88	5.1	1.90	15.1	37.3	0.7
4.65	10.4	4.26	—	—	13.2	34.2	—

TABLE—7 RESULTS OF CARBONATION AND LIME TREATMENT

initial black liquor : pH-11.5; SiO_2-5.2 g/l

Temp. °C.	pH	CaO added g/l*	Supernatant liquor		Sludge (centrifuged)		
			SiO_2 g/l	SiO_2 removed %	Solids g/l**	SiO_2 %	Ash %
50	30·1	Nil	3.40	34.6	35.3	4.71	31.7
50	10.1	4.7	3.30	36.5	47.7	4.9	56.2
50	9.9	Nil	2.65	49.0	48.8	—	32.4
50	9.9	4.7	2.40	53.9	52.1	11.1	76.4
75	9.7	Nil	3.90	25.0	29.1	—	32.9
75	9.7	4.7	3.90	25.0	36.9	7.2	54.2
75	9.5	Nil	1.40	73.1	49.7	4.7	32.6
75	9.5	4.7	1.90	63.5	67.0	6.0	46.9

* On dry black liquor solids.
** On initial black iiquor volume.

TABLE—8 RESULTS OF SLUDGE TREATMENT WITH CaO AND $Al(OH)_3$

Treatment method	Amount of (a) material solubilized, %	Amount of SiO_2 dissolved	SiO_2 % in final sludge
Control	65.3	16.4	38.0
Digestion with CaO*	64.4	5.0	41.7
Digestion with Al $(OH)_3$**	63.7	1.0	48.6

Original sludge solids —26 g/l

Original sludge silica content —15.6%

*CaO, 93% on silica

**$Al(OH)_3$ 270% on silica

(a) Amount of the sludge material dissolved.

TABLE—9 FILTRATION CHARACTERISTICS OF CARBONATED BLACK LIQUORS AT DIFFERENT TEMPERATURES

Temp. °C	Initial pH	Final pH	Sludge solids (a) g/l before leaf filter	Sludge solids (b) g/l after leaf filter	Ash % of sludge (a)	Ash % of sludge (b)	% retention of solids on filter medium
24	10.8	9.8	21.9	4.1	41.1	37.0	81.3
79	9.4	8.5	21.5	11.7	34.9	42.3	45.6

a) Sludge solids in carbonated black liquor before leaf filtration.

b) Solids concentration in the supernatant liquor obtained after leaf filtration.

TABLE—10 FILTRATION CHARACTERISTICS AT DIFFERENT pH VALUES

pH* values	Sludge solids before leaf filter g/l	Sludge solids after leaf filter g/l	% retention of solids on filter medium	Ash content of leaf filtered sludge %	SiO_2 g/l in leaf filtered supernatant liquor
8.87	20.6	5.9	71.4	42.3	2.20
8.31	23.2	7.12	69.3	31.8	1.60
8.03	72.0	27.6	61.7	30.8	0.88

* pH values of carbonated liquor at 80°C.