Problems in B L Evaporation In Indian Raw Materials

R. C. BHARADWAJ*

Due to the acute shortage of Bamboo and soft woods in our country we are forced to cook the following additional raw materials, to meet with the demand of paper :—

i) Eucalyptus
ii) Wheat-straw
iii) Rice-straw
iv) Grass
v) Kahi, Khar & Kanna
vi) Bagasse

We are cooking these raw materials purely as well as after mixing in different ratios. The hard woods & agricultural residues, when cooked origin black liquor which contain high percentage of Silica content and high viscosity. The analysis of black liquor from different raw materials cooked and viscosities are given below :

1. **Rice straw Black Liquor (Sulphate cook)**

Strength	19.79° Tw/20°C
Total solids	175.3 grams/litre
O : I	1 : 0.935
T.T.A.	37.82 grams/litre as Na_2O
Silica	**16.64 grams**/litre
Na_2SO_4	9.748 ,, ,, as such

2. **Wheat-straw Black Liquor** (soda cook)

Strength	13.75 °Tw/31°C
Total solids	133.46 grams/litre
O : I	1 : 1.057
T.T.A	30.225 grams/litre as Na_2O
Silica	**19.48** grams/litre
Na_2SO_4 as such	0.523 grams/litre

3. Percentage ash & Moisture of the raw materials is given below :

1 **Wheat Straw sample**

Wheat straw as such

Ash%	8.8%—10.4%
Moisture	13.8%

Wheat straw accepted

Ash %	7.0%
Moisture	11.0%

2. **Grass sample**

Ash	9.052%
Moisture	14.6%

3. **Khar Sample**

Ash	3.73%
Moisture	15.0%

4. **Rice-Straw**

Ash	15.32%
Moisture	11.38%

5. **Bagasse (as such)**

Ash	52.26%
Moisture	11.46%

4. **Thick Black Liquor analysis (sulphate cook)**

(i)	Percentage of total solids contents	54 to 61%
(ii)	Specific gravity	1.28 to 1.4 at 110° to 130°C
(iii)	Ratio of organic to inorganic matter of thick B. Liquor	1 : 0.97 to 1 : 0.91
(iv)	Total Titrable alkali as Na_2O on Black Liq. total solids basis	23 to 24.2%
(v)	Silica (Si_2O) on B.L. Total solids basis	2.2 to 3.0%
(vi)	Na_2SO_4 on B.L. TS basis	3.6 to 3.8%
(vii)	Free alkali as NaOH on BL TS basis	0.42 to 0.47%

BLACK LIQUOR SCREENING

The black liquor received from the Pulp Mill contain considerable and varying percentages of pulp fines, because of the inherent nature of the short fibered raw materials cooked. The total suspended solids in the black liquor vary from 300 mgs/litre to 800 mgs/litre, depending upon the raw materials cooked.

In order to obtain a satisfactory performance of the Evaporators Plant, it is first and formost thing to effectively screen out the liquor so that screened liquor should have fibres not exceeding 5 mgs/litre of the liquor.

*Superitendent Recovery
Shree Gopal Paper Mills

1. Inclined Stationary Screen

This type of screen has provided to be very effective. We have in operation one inclined stationary screen with 5½% angle of inclination, and 100 mesh stainless steel wire cloth and screening area of 252-7 ft², where primary screening is done i. e. 4 M³/sq. ft./24 hrs.

Secondary screening is done in another inclined stationary screen with 5½% angle of inclination and 200 mesh stainless steel wire cloth and screening area of 208.4 ft.². Accept of this secondary screen is final—liquor ready for Evaporator feed. The rejects and overflow of both the screens are further screened in a vibratory screen fitted with 60 mesh wire stainless screen. Screened liquor from this vibratory screen is recycled back to primary screen and rejects i. e. pulp fines are discarded off.

2. Malone Filter

It is a rotary filter drum with self cleaning by steam jets and fitted with 100 mesh stainless steel wire cloth. Its performance was found unsatisfactory as the rate of filteration of black liquor remained v. low.

Russel Separator

It is an inclined vibratory screen with gyratory motion and fitted with 100 mesh wire cloth. It too failed to give satisfactory performance.

4. Two Deck Vibratory Inclined Screen

It was tried with 100 and 125 mesh stainless steel wire cloth and even with careful adjustments of the frequency, amplitude of vibrations and the angle of inclination of the Screen, the performance was far from satisfactory. Further, mechanical wear & tear of the wire cloths was abnormally frequent.

5. Sharple's Vibro shaker Screen

Its performance was also far from satisfaction.

SILICA REMOVAL

Silica removal from black liquor, prior to its feeding to Evaporators is a must for better performance of the Plant. Lot of work is being done for the removal of soluble silica. Recently we have sent a sample of black liquor to the Govt. expertise for Silica removal at the following address :—

The Director
Govt. of India, Ministry of Defence
Research & Dev. Organisation,
Defence Science Laboratory
Metcalfe House
Delhi 110054

So far as the removal of suspended solids is concerned, it has been easily got rid of by settling the Black Liquor in huge capacity tanks and by maintaining regularly the B. L. storage tanks cleaning schedule.

ACK LIQUOR OXIDATION

Black liquor oxidation, which was suggested by Hilding Bergstrom and K. G. Trobeck in 1939, has become of great importance for the sulphur economy of sulphate pulp Mills. When unoxidised black liquor is going through the evaporating process, it has been stated that the loss of sulphur may amount to as much as 12 kg. per 1000 kg. sulphate pulp. The oxidation of Black liquor converts the volatile sulphur compounds into substances, which will remain in solution. The oxidation is carried out in a specially constructed system where the black liquor is brought into intimate contact with air.

The oxidation of black liquor has the following advantages :

1. Corrosion in the black liquor evaporators is considerably reduced. Ordinary steel tubes last at least twenty times longer than without the oxidation process.
2. Greater evaporator capacity, since the oxidised black liquor gives off only insignificant amount of volatile gases.
3. Sulphidity in white liquor is appreciably increased.
4. The increase in sulphidity is accompanied by a decrease in consumption of lime.
5. The evaporator condensate will be much purer. This means reduced air and water pollution.
6. Evaporators heating tubes remain almost unrusted.
7. Efficiency of Recovery system increases considerably.
8. Water gets evaporated from the black liquor during its oxidation process. It obviously results in reduced steam demand for black liq. concentration.

FREE ALKALI AND BOOSTER DOSING OF LIQ. CAUSTIC

Free alkali in Black Liq. feed to Evaporators should be maintained at 6-8 gm/litre as NaOH. Corresponding pH should vary between 11-12.5. Because at lower free alkali level, lignin precipitation starts, thus fouling the tubes seriously. To maintain this free alkali level, booster dose of Liquid caustic of 250-300 grams/litre as Na_2O was practiced and found to be very effective, in comparison to continuous dosing of alkali to black liquor.

(BROOKE FIELD)—UNIT—CENTIPOISE

Viscosity Results of various raw materials Black Liquor at Different Concentrations & Temperatures

Sl. No.	Total solids %	Wheat Straw cP			Grass cP			Bagasse cP			Eucalyptus cP			Black Liq. 75% sabai grass + Khar.			Thick Black Liquor		
		30°C	60°C	90°C	30°C	60°C	90°C	30°C	60°C	90°C	30°C	60°C	90°C	30°C	60°C	90°C	30°C	60°C	90°C
1.	11.64	12.5	8.75	6.25	—	—	—	—	—	—	6.5	4.0	3.5	8.5	5.0	5.0	—	—	—
2.	13.00	—	—	—	11.25	8.75	6.25	—	—	—	—	—	—	—	—	—	—	—	—
3.	15.00	—	—	—	—	—	—	12.5	8.75	6.25	8	5	4	14	9.5	7.5	—	—	—
4.	25.90	—	—	—	45.0	20.0	12.5	—	—	—	13	8	6	42	20	14	—	—	—
5.	31.15	—	—	—	—	—	—	108.75	47.5	25.25	19.5	11	7	—	35	20	—	—	—
6.	40.4	—	—	—	960 0	195.0	75.0	—	—	—	—	44	22	—	—	43.5	—	—	—
7.	45.16	—	—	—	—	—	—	1365.0	311.25	126.25	—	—	37	—	—	—	—	—	—
8.	52.10	5900	880	237.5	—	—	—	—	—	—	—	—							
9.	54.08	—	—	—	—	—	—	33250	1862.5	1225.0	—	—							
10.	60.66	—	—	—	—	—	—	—	5700.0	1225.0	—	—					82000	9250	1000
11.	62.34	44500	5400	780	—	—	1640	—	—	—	—	—					1550	640	80
12.	67.2	Beyond the range	22500	2675	—	—	—	—	—	—	—	—					112000	13000	1900
13.	63.00																	4600	140

BLACK LIQUOR SOAP PROBLEM

The resin soaps formed in the cooking reaction are more or less insoluble in the black liquor and tend to separate and float on the surface. This separation is hastened as the concentration increases. At a point in the Evaporator system where the liquor concentration is about 25 to 28% total solids and at a temp. from 160 to 180°F the separation of soap is maximum. Since it tends to foul the heating surfaces and reduce capacity, it is advisable to skim off the soap at the intermediate stage for which an intermediate tank is provided. The liquor is removed to settling tanks and the soap skimmed off and sent to Tall—oil plant.

CARBONACEOUS DEPOSITS

In some cases there is a tendency towards formation of a coating of organic matter on surface of the Evaporator tubes. This generally a result of a slow polymerization and carbonization during the destructive distillation reaction, which occurs on heating in the presence of caustic soda. This sort of deposit is a gummy black, carbonaceous material which greatly reduces the rate of heat transfer. It can be easily removed by boiling the evaporator with water or with weak alkali work or white liquor solutions.

SCALE FORMATION AND ITS REMOVAL

Scales may be considered from the standpoint of their chemical properties according to the following classifications :

1. **Water soluble scales;** which can be removed by boiling out the evaporator.

2. **Insoluble scales;** which can be removed by mechanical means.

3. **Insoluble scales;** which are too hard to be removed by mechanical means and hence chemical cleaning is needed.

1. Water soluble scales are usually found to be of Sodium sulphate from an excess of unreduced salt cake, carried in the liquor from the sulphate process. The scale on the tubes result from the inverted solubility curve property of sodium sulphate.

2. Scales insoluble in water, but removable by mechanical means, are usually a combination of Calcium Carbonate and organic compounds resulting from an excessive amount of lime in the liquor. In some cases it is necessary to use an inhibited solution of 2 to 4% HCl in order to remove carbonate scale, following by drilling.

3. Scales of 3rd class are the hard and obstinate scales which form a glass line structure on the tube surfaces and are very difficult to clean by mechanical cleaning. It is due to formation of complex compound of sodium-Aluminium Silicate. The cause of its formation appears to be the presence of excessive alumina in the liquor circulation, which results from the use of certain types of refractory in Recovery furnace. A certain amount of Silica is always present in the liquor as it is present in the wood and bamboo and Agricultural residues as well as an impurity in the lime or salt cake.

The alumina content of the liquor tends to increase over a period of time, since there is no place in the system where aluminium compounds are precipitated as the hydroxides, as is the case with chromium and magnesium whose hydroxides are precipitated in the causticizing operation. Gradually a stage comes when serious problems of this scale formation starts resulting in marked reduction in the Evaporator capacity.

For the removal of such type of scales 10-20% $NaHSO_4$ acid (Sodium Hydrogen sulphate acid has been found to be very effective. This special acid is prepared from equimolecular ratios of salt cake and sulphuric acid which was circulated through tubes for 6—8 hrs. at 65—75°C.

RESULTS ACHIEVED

a) TECHNICAL

Due to this acid circulation, downtime for tubes descaling by mechanical means has been reduced a lot. Earlier frequency of bypassing the bodies for tubes descaling was high, due to the excessive hard and obstinate scale encountered on the tubes of the Evaporator bodies. Frequency of tubes descaling, prior to acid circulation was as under :—

Effects	% total solids handled	Frequency of bypassing for tubes descaling
Body No. I	40-42%	10-15 days
Body No. II	14-15%	20 ,,
Body No. III	18-20%	30 ,,
Body No. IV	24 26%	60 ,,
Body No. V	32-35%	90 ,,
Additional bodies (3A, 4A, & 5A)	3A—18 20% 4A—24-26% 5A—32-35%	45 ,,

The present frequency of tubes descaling of bodies after circulating 20% inhibited Sodium Bisulphate acid is as follows :—

		Frequency of bypassing
Body No. I	14-42% solids	35-36 days
Body No. II	14-15%	50-55 ,,
Body No. III	18-20%	90 ,,
Body No. IV	24-26%	90 ,,
Body No. V	32-35%	90 ,,
Additional bodies (3A, 4A & 5A)	3A—18-20% 4A—24-26% 5A—32-35%	90 ,,

We have observed that after the $NaHSO_4$ acid circulation, the scale formation, inside the tubes is normal and can be easily removed by conventional equipment.

The performance of the Evaporation Plant has increased because of the increase rate of Evapo ation.

Vapour Side Scale

Vapour side scaling of the Evaporator tubes normally occurs in the later effects. This is due to the presence of sulphur compounds i.e. Methyl mercaptans, Ethyl mercaptans and hydrogen sulphide etc. which reacts with steel tubes to form iron sulphite scale. Methyl mercaptans, an extremely foul smelling and weekly acidic gas is liberated from the sodium methyl mercaptide present in the black liq. during evaporation.

$$\underset{\text{Sodium Methyl mercaptide}}{CH_3SNa} + H_2O \rightarrow \underset{\text{Methyl mercaptan}}{CH_3SH} + NaOH$$

This is generally removed by circulating 15 to 20% NaOH on the outside surface of the tubes for 20–24 hrs at 70–75°C Temp.

METHOD OF FEEDING BLACK LIQUOR

Due to the excessive use of hardwoods, bagasse, wheat-straw and other agricultural residues, the black liquor is highly viscous and silicous in nature. High viscous black liquor has detrimental effect on the performance of B.L. Evaporator Plant. In this type of black liquor, *MIXED FEED* in Evaporator has proved to be successful.

MIXED FEED

In this case the thin black liquor is fed to the second effect and passed in forward feed from the second to the last effect and their pumping it from the last effect to first and finishing in the first effect. This will not seriously handicap the later effect but will finish the viscous liquid at the highest temperature, where its viscosity is the least and heat transfer coefficient the largest.

This type of 'mixed feed' is a compromise for a viscous thick black liquor, between the operational advantage of forward feed and the greater economy of backward feed.

Forward feed : is not suitable, as the most concentrated liquor is in the last effect (at highest vacuum) where the temp. is lowest and the viscosity highest. Under such conditions, the capacity of the last effect is low because of low overall coefficient. This results in a lower capacity of the multiple effect system as a whole.

Bakward feed : Under condition of backward feed, the concentrated liquor is in the effect where the temp is the highest and the viscosity the lowest and the co-efficient can be high inspite of viscosity. But because of pumping the thin black liquor into the last effect (high vacuum) a little carelessness or mechanical defects in the pump—heavy entrainment of black liquor can take place—causing alkali losses.

Hence Mixed feed is preferable.

QUINTUPLE EFFECT & FORCED CIRCULATION EVAPORATOR

In quintuple effect, we concentrate the thin black liq. of 14% total solids to 40% total solids only, as above this concentration, the capacity of Evaporator fail, because of falling heat transfer coefficient, on account of characteristics of black liquor. Black Liquor from 40% total solids to 60% total solids is concentrated in the Forced Circulation Evaporator and from there it is pumped to Recovery Boiler.

We are operating the quintuple effect Evaporator alongwith Forced Circulation as per flow sheet appended below:

Thin Liquor — Preheater — Preheater — Preheater
No. 3 No. 2 No. 2A
—Body No.2—Body No. 3—Body No.4—Body No. 5
3A 4A 5A
(Additional bodies)
Intermediate tank—Preheater—Preheater-Preheater
No. 4 No. 1 No. 1A
—Body No. I—Forced Circulation—Thick Liquor
Effect to Rec. Boiler

We have our spare body which can be connected in line, for disconnecting any of the five bodies.

FORCED CIRCULATION EVAPORATOR

In the forced circulation Evaporator, liquid is pumped through tubes of the heating element at

reasonably high velocities with little or no evaporation in the tubes. The liquid vapour mixture is fed through nozzle into the Evaporator body which becomes nothing but a flash chamber where the vapour bubbles are separated from the liquid.

In this case relative elevations are so designed that the hydrostatic heat of liquid on the heater outlet is enough to prevent any liquid boiling in the tubes and boiling only takes place as the pressure is relieved in discharging the liquid into the evaporator body.

The selection of a Forced Circulation Evaporator for an installation depends upon a favourable balance between the cost of energy to circulate the liquid versus the improved co-efficient which is secured by the greater velocities.

This type is particularly applicable to highly viscous and highly concentrated liquid at 60% to 65% total solids at high temperature.

With scaling liquors, the rate of formation of scale is retarded, but scaling is not entirely prevented except at relatively high liquid velocities.

Entrainment is reduced to the vanishing point by the working action of the high velocity, downward curtain of liquor and foamy liquor handled with care.

We have got 3 Heat Exchanger—with a total heating area of 216 m^2. Heat transfer co-efficient is 550 k. cal./hr m^2 °C. Velocity of B. Liq. is 4·6 ft/second.