Loss of Chemicals in the Pulp and Paper Industry

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SUMMARY

The paper gives details of alkali losses in alkali recovery system with particular reference to their experience with two types of systems available at Ballarpur Industries Limited, Ballarpur. The losses have been grouped into two groups; (1) process losses due to equipment efficiency and operating parameters and (2) additional losses due state supervision and preventive maintenance in the mill.

The progress made by the sulphate pulping process and the soda pulping process can be mainly attributed to the availability of an efficient chemical recovery system for these processes. Sulphite process though older than the sulphate process, is no longer being employed due to non-availability of a satisfactory recovery system. In the acid sulphide process where calcium-bi-sulphite and sulphur dioxide are employed as pulping chemicals, the cost of the chemicals was so low that nobody was interested in recovering the base chemicals and the spent liquors were discharged into streams and oceans causing a high degree of pollution. With the stringent pollution laws enacted by various countries, Pulp and

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Paper Mills can not afford to discharge their effluents into the streams.

The recovery system in the sulphate and soda process is very essential both from the point of view of recovering the cooking chemicals which are much costlier as compared to those of sulphite pulping process and, to meet the stringent regulations of discharging the effluents into the inland surface waters or on land for irrigation purposes. The cost of external treatment of effluents so as to meet the ISI specifications IS:2490 for discharging of the effluents into the inland surface waters is quite prohibitive. It is not only capital internsive to instal a treatment plant but most of the treatment methods are also power intensive. The best method to meet these specifications is to have better recovery system for the spent liquors.

The alkali loss in a recovery system can be divided into two parts namely (i) the ordinary process losses influenced by the equipment efficiency and operating parameters and (ii) sometimes a considerable additional loss which is independant of these but is influenced by the efficiency of supervision and preventive maintenance systems.

The losses of alkali in the recovery system are from:

i) Brown stock washing
ii) Collection of spent liquor and its concentration
iii) Incineration of black liquors solids in the furnaces
iv) Causticizing of green liquor

The overall the recovery efficiency at Ballarpur Industries Ltd., (BILT) is 87–88%. This includes the operation of recovery boiler and roaster/smelter units.

BROWN STOCK WASHING

The recovery of chemicals start from the brown stock washing system. Some of the alkali lost with the knotter rejects. Every care should be taken to collect the rejects alongwith the entrained black liquor and returning the same to the digester for recooking. In a well operated mill the alkali losses with the knotter rejects are about 1–2 kg/t of pulp. At BILT it is about 0.5 kg/t pulp.

Efficiency of the brown stock washing system is governed by (i) washing area per ton of b.d. washed pulp per washer, (ii) dilution factor and (iii) foam characteristics of the brown stock foaming reduces the drainage rate of the pulp due to the entrainment of the air. Application of suitable type of defoamer results in an improvement.

It is clear that at the same percentage of washing efficiency if the alkali charged to the digester per ton of pulp is higher, it will result in a higher soda loss. Most of the wash plants in India operate at an efficiency of 95–98% with a corresponding soda loss of about 20–35 kgs/t of washed pulp. To reduce a soda loss still further either a much greater dilution factor has to be employed or the diffusion washing system will be an improvement.

At BILT soda loss with washed pulp is 30kg/ton on average.

COLLECTION OF SPENT LIQUORS AND ITS CONCENTRATION

The spent liquor recovered from the washing of the pulp is concentrated in M.E.E. i.e. Multiple Effect Evaporators before it is incinerated either in the Recovery Boiler or Roaster/Smelter Unit. There are two methods of concentrating the black liquor, namely Scandenavian Countries method and the method followed in U.S.A. In both the methods a concentration upto 48–50% solids is achieved in M.E.E. where its further concentration to 60–62% solids is raised in forced circulation evaporator in Scandenivian design and in direct contact evaporators in American design.

The most of the Indian paper mills are using bamboo and hardwoods for meeting the requirement of their fibrous raw material. We at BILT are using 30% hardwood and 70% bamboo as our raw material.

We started using hardwoods in the year 1968 and in the beginning we were processing mixed black liquors in M.E.E. But lot of difficulties were encountered in achieving the concentration due to severe scale forming tendency. The viscosity was also higher. To overcome these difficulties we resorted to separate cooking and separate processing of bamboo and hardwood black liquors. Also certain varieties of hardwoods posed great problems in this processing black liquor produced from them. These liquors had poor burning characteristic, ring forming tendency in roasters and heavy scaling nature in evaporators. Hence the following species of hardwoods are not used for pulping in our mill.

Botancial name	Local name	Density gm/cc
1. Terminalia tomentosa	Ain	0.70
2. Madhuea latifolia	Mahua	0.80
3. Terminalia chebula	Hirda	0.75
4. Anogeissus latifolia	Dhawda	0.75
5. Diospyros melenoxylon	Tendu	0.80
6. Dalbergia paniculata	Dhoban	0.78

Both liquors are separately screened before feeding to evaporators. By doing so evaporator tubes fouling due to fibrous and suspended material is greatly reduced.

Bamboo liquor is concentrated in M.E.E. having five bodies. The lower concentration effects are provided with dimister pads. A concentration upto 48% solids is carried out in M.E.E. and its further

concentration is achieved in Forced Circulation Evaporator upto 60% solids.

Hardwoods black liquor is concentrated only upto 35–40% solids in M.E.E. It is experienced at BILT that any attempt to achieve more than 40% solids concentration in M.E.E. greatly reduces the run period. The further concentration is raised either in cascade evaporator or forced circulation evaporator upto 56–57% solids. This is the limiting concentration. The free alkali in both liquors is 4–4.5 gpl. The difficulty encountered in concentrating the hardwood black liquor can be attributed to its higher viscosity and highly scaling nature. The scaling tendency of the hardwood black liquor is due to the nature of the extractives and Ca^{++} content of the hardwoods (>1%).

The scale samples of hardwood liquor and bamboo liquor have been analysed and the results are given in Table–I.

It can be observed from the analysis that the hardwood scales are rich in Ca^{++} content where as the bamboo scale are rich in silica content. The Ca^{++} scale in case of hardwood black liquor is both due to to higher Ca^{++} content of hardwoods and Ca^{++} carryover from causticizing section. The silica scale in case of bamboo black liquor is due to high silica content of the chips (4–5%). However, the Ca^{++} content of the bamboo liquor scale is only due to inefficient clarification of white liquor.

Due to highly scaling nature of hardwood liquors, the steaming effect is required to bypass for tubes cleaning after seven days of run as against 15–20 days in case of bamboo black liquor. Similar schedule is maintained for forced circulation evaporators. Though the literature advocates the boiling of evaporator tube with 20% sodium bisulphate solution for easy removal of silica scale, it is our experience that an inhibited hydrochloric acid (.05% conc.) boiling for 12 hrs. at 80°C once in a year proves useful.

In general in the recovery plants where direct contact evaporators are used, black liquor oxidiation proves useful both from the point of view of odor reduction as well as reducing the sulphur losses. Maladorous gases such as methyl inscaption, Hydrogen sulphide produced during concentration in cascade evaporator, can be represented by following reaction:

$$CO_2 + Na_2S + H_2O \longrightarrow H_2S + Na_2CO_3$$
$$CO_2 + 2\ CH_3SNa + H_2O \longrightarrow CH_3SH + Na_2CO_3$$

However, black liquor oxidation results in lovering the calorific value of black liquor solids by 2–4% depending upon the degree of oxidation employed. This reduction is due to exothermic nature of the reactions occuring during oxidation.

Use of dimister pads greatly help in arresting the enterainment of the liquor during evaporation. The surface condenser instead of barrometric condenser facilitates the recirculation of cooling water. For efficient operation of evaporators, every care should be taken to vent individual bodies separately and all noncondensables to be carried by a common header to condenser so that they are easily removed out of the system.

Finally it is to be kept in mind that any leakages through pump glands, unforseen drainages and overflow of liquor through tanks will add to dead loss of alkali.

INCINERATION OF BLACK LIQUOR SOLIDS

The concentrated black liquor is burnt either in the recovery boiler or roaster/smelter unit as the case may be. The calorific value of hardwood and bamboo black liquor solids as determined by Bomb's calorimeter has been found to be 3400 Kcal/kg and 3200-3300 Kcal/kg dry solids respectively.

The elemental analysis of bamboo black liquor solids on average is as follows : (BILT Sample)

C	—	35-36%
S	—	3- 4%
Na	—	20-21%
Si	—	2- 2.5%
H	—	3- 4%
O	—	37-32.5% (By diff.).

The main source of alkali losses in the recovery furnace are through (i) stack loss and (ii) dissolving tank chimney. The stack losses are due to inefficient performance of the precipitator. The optimum performnace of the precipitator is achieved only if the furnace condition is stable. It is well known that in the same furnace two opposite reactions i.e. oxidation and reduction are to be carried out so that the complete combustion takes place and the required reduction of salt cake is obtained. Therefore the distribution of total air at primary and secondary zone plays very important role. The other operating parameters like black liquor spray droplet size, ratio of secondary air to black liquor solids, percent excess oxygen in the flue gas and the turbulance within the recovery furnace has significant effect as furnace condition stability. The optimum operating conditions are to be reached by various trials.

At BILT, when our recovery boiler (JMW type) was commissioned, many problems like blackout in the furnace, chocking of the gas passage in superheater zone and economizer, were encountered. By various trials of firing gun angle, nozzle lip angles, firing pressures etc. we have reached stable operation by introduction of 'Twin Nozzle Spray' system. Now our recovery boiler runs for 90 days after which cold shut of 4 days is undertaken to clean the fluegas passages and maintenance jobs are carried out. After every 20-25 days of operation, a short duration (8 hrs.) shut is taken for cleaning the flue gas passage by handlancing.

The mechanically entrained fume particles are recovered in precipitations. The various factors flue gas temperature, density and dust concentration, velocity through precipitator play important role in achieving good collection efficiency of the precipitators. Apart from this scrappers, rapping mechanisms are found many times creating troubles due to which electrostatic precipitator run bypassed causing dead loss of alkali and particulars emission too. Normally precipitaotrs are working on 94-95% collection efficiency. To meet the particulate emission regulations, 99% collection efficiency precipitators are being used in America. But it is to be noted that the cost of the 99% efficiency precipitator is approximately double of the cost of 90% efficiency precipitators. Our precipitator is working with 94% collection efficiency and ash collection is 30 kgs/t of solids fired.

The alkali loss through dissolving tank chimney is reduced by providing efficient scrubbing system.

CAUSTICIZING OF GREEN LIQUOR

The alkali loss in causticizing section is through (i) final mud cake (ii) green liquor clarifier dregs, (iii) slaker classifier grits and (iv) through slaker chimney.

The final alkali content of the green mud can be reduced if efficient mud washing system is installed. Addition of a "Belt type Filter" as well as modifying the mud washers to two stage mud washing in the same mud washer found helpful in reducing the final total alkali content of green mud cake to 0.5%. Earlier it was 1.2%.

The green liquor clarifier dregs are of the order of 1.5 tons/day in our mills.

The dregs analysis is as under :

Na_2O	:	44.7%
SiO_2	:	22.3%
$Al_2O_3 + Fe_2O_3$	:	8.2%
CaO	:	26.1%
Mgo	:	8.6%

Therefore if efficient washing system is employed, about 2 kgs Na_2O alkali/t of pulp can be recovered.

However, efficient operation of mud washers will depend upon quality of lime and other operating parameters.

TABLE I.

SCALE ANALYSIS

S.No.	Particulars	Bamboo liq.	Hardwood liq.
1.	Source	Steaming effect	Steaming effect
2.	Concentration—°TW	52°TW	34°TW
	—Temp	96°C	94°C
3.	Silica as SiO_2 by HF %	52.1	1.3
4.	$Al_2O_3 + Fe_2O_3$ %	2.9	9.1
5.	Calcium as CaO%	13.6	36.1
6.	Magnesium as MgO%	1.1	3.5
7.	Sulphate as Na_2O%	nil	0.4
8.	Titratable Alkali Na_2O %	0.8	0.4
9.	Loss as Ignition%	17.0	31.2

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