Ferrite Recovery Process-A Promising Alternate For Small Paper Mills

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1. Introduction :

In small paper mills (10–50 TPD mostly use secondary fibers such as bagasse, rice/wheat straws, Jute. These mills adapt soda process requiring 250–350 kg pulping chemicals per tonne of pulp with 40–50% yield. The remaining constituents of the fibrous raw materials are dissolved in black liquor as sodium salts by the pulping reactions. Process economics necessitate the recovery of pulping chemicals from weak black liquor.

Black liquor from pulping is an exceedingly complex aqueous solution containing sodium salts of polydisperse lignins, carbo hydrate degradation products, extractives and several inorganic sodium compounds. The quantity of total dissolved solids in weak black liquor is 1 3–1.8 tonne per tonne of pulp and the concentration is 12–18% T.S. from the digester house operations. The organic constituents representing 55–65% of the total BLS contribute to the calorific value. A conventional plant accomplishes chemical recovery in three steps : concentration in MEE system, combustion in recovery boiler to generate steam and to separate the inorganics as smelt and causticization for regeneration of white liquor. These operations are very efficient with soft wood pulping black liquor but with non–wood pulping black liquor, the physico–chemical characteristics of the black liquors, significantly off–set the efficient continuous operation of the chemical units. Silica in non-wood and higher viscosity of non–wood black liquor limit the capacity of the evaporation plant and also affect combustion in recovery furnace. Silica in green liquor decreases the causticization efficiency and lime mud reburning is inefficient and incomplete which necessitate the disposal as a solid waste.

TABLE No. 1 : CHARACTERISTICS OF WASTE WATER FROM SMALL PAPER MILLS[41]

CHARACTERISTICS	RANGE	WEIGHTED AVG.
Volume, m^3/ tonne	208–330	223
Colour	Dark Brown	Dark Brown
pH	7.0–9.4	–
Total solids, mg/1.	3550–5395	5129
Suspended solids, mg/1	860–1510	1293
BOD_5, mg/1	320–1020	782
OCD, mg/1	2160–3470	2608
Pollution load kg/tonne paper (based on weight (Average value)		
Suspeneded solids, 288		
BOD_5, 174		
COD, 580		

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Small paper mills with no chemical recovery are discharging a large amount of pollutants to the water course if no effluent treatment process is employed. Table—1 indicates such data to use the effluent treatment process to meet the Minimal National Standards (MINAS). For liquid effluents from small paper mills have been set by government which are BOD_5: 50 mg/1, suspended solids : 100 mg/1 and pH : 6-9. For COD and colour, as yet there is no MINAS. To meet these standards heavy investment is necessary in effluent treatment facilities.

A review of the above problems together with the current awareness for conservation of energy, water and chemical resources and the need to reduce/eliminate the release of pollutants to the atmosphere/receiving waters, would serve as a guide line to consider and develop alternate chemical recovery systems.

The black liquor treatment in small pulp and paper mills can be discussed under the following hea s :-

2. a) Processes to treat black liquor to recover caustic soda.

b) Processes to treat black liquor to produce various value added lignin by products.

c) Processes where black liquor is treated to reduce pollution load.

d) Process modifications where black liquor is not generated or is generated in small quantities.

2. a) Processes to treat black liquor to recover caustic soda :—

i) Simplified regeneration scheme based on carbonation of black liquor and Eletrophoretic sedimentation scheme[1] :

Both the processes are suitable to recover the caustic soda from the black liquor available from 10-15 T.P.D paper plant based on straw/bagasse raw materials. The soda recovery is reported as 65 and 80% respectively for both the processes.

ii) Membrane Techniques : Reverse Osmosis (RO)/ Ultrafiltration (UF)[5] :—

A cost effective technique for concentration and separation of free soda as permeate through membrane as more than 60% of the total soda contents of black liquor is present as low molecular weight compounds. Lignin fraction (colour bearing compounds) are rejected at membrane interface as concentrate. This technique is used for straw black liquor for 30 T.P.D. plant which has concentration 4% T.S. The details of the results are given as below :—

		RO	UF
1.	Rejection of colours (%)	95	80
2.	Rejection of soda compounds (%)	85-90	50
3.	Optimum feed pressure, (kg/cm^2)	40	10
4.	Permeate Recovery (%)	35	48

iii) Broby Recovery Process[6] :—

A conventional recovery process, suitable for black liquor available from soda process (Straw/bagasse based), complete chemical recovery and about 1.5 tonne steam/Tonne of D.S. is also formed.

iv) Wet Air Oxidation Process[6,7,8] —

An effective process for destruction of toxic and hazardous organics in black liquor, suitable for straw/bagasse black liquor. eliminate the conventional evaporation and combustion steps, % Destruction in COD and toxic compounds are reported as 90-96 and more than 99 respectively; Initial investment is higher than the conventional system.

(v) Direct Alkali Recovery System (DARS) :

Ferrite Recovery Process[11, 12] :—

Suitable for small/medium sized pulp mill using soda process, elimination of lime circuit, Inherently very stable, and disturbances tend to be localized and do not spread throughout the system, Fluidization is very stable with little agglomeration or scale formation, no supplimentry fuel is required except during start up and combustion performance is excellent, NaOH can be regenerated at more than 300 gpl with 90-95% causticity which allows a lower dead load, reduce digester steam consumption and permit higher evaporator feed concentration, formation of pellets keeps fines to a useful form, no explosion risk in absence of smelt formation, no sludge disposal problem.

There is substantial reduction in capital investment and operating cost as compared to the conventional recovery system. The process can be used with Al_2O_3 and TiO_2 also.

(vi) **Wet Cracking of Black Liquor [15] :—**

Wet cracking of B/L (10% solids) of agricultural residue at 360°C and high pressure (200 atm) in absence of O_2 results in carbohydrate conversion to charpowder, organics becoming a gas (mixture of CH_4, C_2H_6, H_2 and CO_2). The process is claimed to be economic and helpful in controlling the pollution.

2(b) **Processes to treat black liquor to produce various value added lignin products[2,3] :—**

Soda lignin and its derivatives like chloro-sulphonated lignin, Nitrosulphonated lignin and nitrated alkali lignin can be produced by treating black liquor with acids H_2SO_4 HCl, HNO_3 and Na_2SO_3, SO_2, etc. These products can be used as dispersant in oil-well drilling, grinding aids in cement and concrete, oil well cementing aid, dispersant in clay and ceremic industries and floatation agent in ores refining.

2(c) **Processes where black liquor is treated to reduce the POLLUTION load [15] :—**

(i) Conventional effluent treatment processes can be used to meet the MINAS values which includes various operations like screening, primary treatment, secondary treatment etc.

(ii) Desilication process for black liquor will help in increasing causticizing efficiency and lime mud reburning, thereby reducing pollution.

(iii) Black liquor oxidation, changes in evaporator configuration, fluid bed combustion, thin film evaporation, oil flash evaporation will help in energy conservation and pollution control.

2(d) **Process modifications where black liquor is not generated or is generated in small quantities[15] :—**

(i) Use of organosolv. process with different alcohols or phenols or ammonia-ketone solvents to reduce water pollution and help to recover lignin.

(ii) Use of bio pulping methods hold promise for abating pollution arising out of chemicals.

(iii) Use of oxygen delignification, continuous cooking with high pressure/impregnation, use of anthroquinone and poly sulphides to increase yield are likely to reduce pollution load significantly.

(iv) Holopulping at atmospheric pressure by using selective delignification oxidents like ClO_2 is likely to give 70% yield, reduced colour and pollution load, with possibilities in chemical regeneration.

(v) Explosion pulping of bagasse using soda at 200°C and 13.8 MPa. N_2-pressure and explosive discharge through multiple bar nozzles reduces alkali consumption by 30-40%, improves drainage and reduces pollution load.

(vi) Vapour phase pulping of bagasse, with presoaking with alkali, cooked after removal of alkali at 160°C give 5% more yield than conventional liquid phase cooking. The volume of liquid effluents is reduced by half and had a COD of 992 kg/t against COD of 1964 kg/t in conventional liquid phase pulping.

From the above discussion the choice before the small paper mills are wide but the alternatives viable are limited by the level of proven technology one hand and economic viability on the other. The modification in pulping processes do not appear promising at this stage due to limited experimental investigation. Addition of "add on" pollution reatment unit of conventional type will be manadatory to meet MINAS values but is likely to be costly. In view of this, the alternatives to be the following :—

(i) Conventional chemical recovery.

(ii) Ferrite Recovery (DARS Process) where technology is fairly well established.

(iii) End of the unit add on effluent treatment plant.

An attempt has been made to make an economic analysis of the first two of the alternatives for small capacities in the range of 30-50 TPD to establish economic viability on the assumption that technology is available.

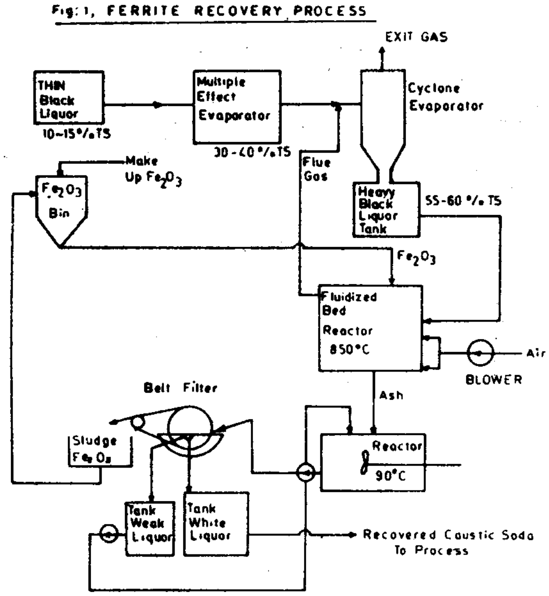
3. Economic Analysis :

An attempt has been made to estimate the chemical requirements, black liquor generation on the basis given in Table No. 3 for plant capacities 30, 40 and 50 T.P.D. bleached A.D. pulp production. The results are shown in Table No. 4. Capital investment as well as operating costs for the conventional recovery system have been calculated which are shown in Table No. 5. It can be seen from the cost analysis that conventional recovery system appears to be economical viable for the pulp mill capacity 30 T.P.D. or more at the present juncture The indegenous equipment capability may have to be examined.

Further capital investment and operating costs are calculated for the Ferrite Recovery Process which are shown in Table No. 6. It is assumed that process is technically feasible. The flow sheet and chemical reaction for the process are given in fig. no. 1 and operating results are shown in Table No. 2. The econòmic analysis indicates that there is substantial reduction in capital investment as well as operating cost as compared to conventional recovery system which are shown in Table No. 7.

Looking into the profitability analysis, it will be noticed that the conventional recovery system has pay out period from 9. 4 years to 4.5 years for the pulp mill capacity ranging from 30 to 50 T.P.D. which seems to be on the higher side. But in case of Ferrite recovery process the pay-out period is ranging from 3.0 to 1.9 years for pulp mill capacity 30 to 50 T.P.D. which-quite encouraging.

Fig: 1, FERRITE RECOVERY PROCESS



CHEMICAL REACTIONS:-

(i) $Na_2R + O_2 \longrightarrow Na_2CO_3 + CO_2$ —— (I)

(ii) $Na_2CO_3 + Fe_2O_3 \longrightarrow Na_2O\,Fe_2O_3$ (or) $2NaFeO_2 + CO_2\uparrow$ (II)

(iii) $2NaFeO_2 + H_2O \longrightarrow 2NaOH + Fe_2O_3\downarrow$ —— (III)

PROCESS ALTERNATIVES

(I) INSTEAD OF FLUIDIZED BED REACTOR, MULTIPLE HEARTH FURNACE OR ROTARY KILN CAN ALSO BE USED

(II) INSTEAD OF BELT FILTER, CENTRIFUGE CAN ALSO BE USED.

TABLE No. 2

Results of Experimental Studies Carried Out By Kulkarni et al[11] on Ferrite Recovery Process

1.	Straw Soda $B/L+Fe_2O_3$ (based on stoichiometric ratio 1:1 of Na_2CO_3/Fe_2O_3)	—1:0.3 ratio
2.	Combustion condition, Temperature,°C	—850
3.	,, ,, Time, minutes	—15
4.	Causticity*, %	—80 5
5.	Sodium Recovery, %	—86 0
6.	Nature of combustion product	—Soft Brown Mass
7.	Hydrolysis condition, Temperature,°C	—90
8.	,, ,, Time, minutes	—15

* Causticity is defined as ratio of NaOH as Na_2O to ($NaOH + Na_2CO_3$) as Na_2O in gpl in a white liquor sample.

Therefore, it is necessary that there is a urgent need to have a pilot/semi-commercial plant for ferrite recovery process to establish technical and economic viability of the scheme. It is hoped that this will reduce the cost of production of the paper as well as the effluent load on treatment system, thereby helping the small units to meet the pollution standards.

4. Conclusions :

The following can be concluded from the above analysis that :-

(a) There is an urgent think in terms of installation chemical recovery system for the small paper mills having capacity 30 T.P.D. or more. For this purpose a working pilot semi commercial model should be installed as a model unit.

(b) The detailed economic analysis must be carried out for the conventional as well as Ferrite Recovery Process.

(c) Technical feasibility should also be studied for Al_2O_3/TiO_2 instead of Fe_2O_3 in DARS.

(d) For small paper mills having production capacity less then 30 T.P.D., the critical economic analysis should be carried out to justify installation of reco: very units.

TABLE No. 3

Typical Data Used for the Economic Analysis of Small Paper Mills Based on Straw/Bagasse Pulp[10,11]

Sl. No.	Parameters	Unit	Unit	Value
1.	Pulp Mill capacity,	T.P.D	—	30, 40, & 50
2.	Alkali used for pulping,	%	— 10	based on B. D.
3.	Average B.L.S. based on bleached T/T A.D. pulp.		— 1.60	Raw Material.
4.	Over-all recovery efficiency			
	(a) with conventional system,	%	— 77	
	(b) with ferrite recovery	%	— 85	
5.	Working days, per year	—	— 330	
6.	Purchased NaOH cost,	Rs/T	— 7000	
7.	Inlet concentration of B/L.	%	— 10	
8.	Outlet ,, ,,	%	— 30	
9.	Steam cost	Rs/T	— 150	
10.	Lime cost (6.0% pure)	,,	— 600	
11.	Power cost,	,,/KWH	— 1.00	
12.	Ferrite cost (90% Pure)	Rs/T	— 800	
13.	Steam economy (5 effect evaporator)		— 3.5	
14.	Steam for dissolver & causticizing		— 0.4T/T A.D. Pulp	
15.	Lime required (60% purity)		— 1.3 T/T NaOH	
16.	Power Losses (based on consumption)		— 10%	
17.	Make up Fe_2O_3 required.		— 30kg/T of A.D. Pulp.	

TABLE No. 4.

Estimation of Alkali Requirement, Recovered Alkali, Black Liquor Solids, Steam and Power Requirement. (Conventional Recovery Unit).

Sl. No.	Description	Unit	Pulp	Mill	Size
1.	Capacity of pulp mill	T.P.D.	30	40	50
2.	A.D. Bleached pulp yield	%	35	35	35
3.	Straw required AD	T.P.D.	85.8	114.4	143.0
4.	,, ,, BD	T.P.D.	77.22	102.96	128.7
5.	Caustic soda used (")	T.P.D.	7.72	10.3	12.9
6.	B.L. Solids to recovery	T.P.D.	48	60	72
7.	Quantity of alkali recovered	T.P.D.	6.0	8.0	10.0
8.	Yearly recovery (based on 330 working days)	T.P.Y.	1980	2640	3300
9.	Equivalent value of recovered alkali at purchased caustic rate of Rs. 7000/-per tonne,	Rs/day (Thousand)	42	56	70
		Rs/yr. (in lacs)	138.6	184.8	231.0
10.	Evaporation rate, (5 effect evap.)	T.P.D.	321	428	535
11.	Steam consumed	T.P.D.	91.8	122.4	153.0
12.	Steam consumed in evap. (add. 5% for water boiling)	T.P.D.	96.3	128.4	160.5
13.	Steam for disolver and causticizing	T.P.D.	12.0	16.0	20.0
14.	Total steam consumed	T.P.D.	108.3	144.4	180.5
15.	Lime required,	T.P.D.	7.8	10.4	13.0
16.	Electricity consumed, KWH/day	KWH/Day	8400	9600	10800

TABLE No. 5

ECONOMICS OF INSTALLATION OF A RECOVERY UNIT.

Capacity of Mill, T.P.D.			30	40	50
CAPITAL INVESTMENET REQUIRED :					
i)	Evaporator Plant	Rs. (in lacs)	42	48	54
ii)	Smelter & cyclone unit	,,	48	54	60
iii)	Causticizing plant	,,	42	48	54
iv)	Tanks, civil etc.	,,	12	18	24
	Total capital investment	,,	144	168	192
	Amount of caustic required.	TPY	1980	2640	3300
COST OF PRODUCTION OF ALKALI IN RECOVERY SECTION :					
i)	Steam consumed,	TPY	35739	47652	59565
ii)	Steam cost,	Rs (in lacs) PY	53.6	71.5	89.4
iii)	Lime consumed,	TPY	2574	3432	4290
v)	Lime cost,	Rs (in lacs) PY	15.4	20.6	25.7
v)	Power consumed,	MWH/yr.	3050	3485	3920
vi)	Power cost,	Rs (in lace) PY	30.5	34.9	39.2
vii)	Auxiliary fuel,	--do--	2.6	4.0	5.4
viii)	Maintenance,	--do--	1.3	2.0	2.3
ix)	Wages,	--do--	1.1	1.3	1.5
x)	Total operating cost	--do--	104.5	134.3	163.5
xi)	Cost of recovered caustic before interest & Rs/T depreciation.		5278/-	5087/-	4955/-
xii)	Interest @ 13%	Rs.(in lacs)/yr	18.7	21.8	25.0
xiii)	Depreciation @ 7%	--do--	10.1	11.8	13.4
xiv)	Total interest & depreciaton on	--do--	28.8	33.6	38.4
xv)	Interest & Depreciation on NaOH recovered.	Rs/T of NaOH recovered	1455/-	1273/-	1164/-
xvi)	Total cost of recovered NaOH,	Rs./T	6733/-	6360/-	6119/-

TABLE—6

APPROXIMATE CAPITAL COST OF EQUIPMENTS AND OPERATING COSTS FOR FERRITE RECOVERY PROCESS

			PULP MILL CAPACITY (TPD)		
(A)	CAPITAL COST :		30	40	50
	(a) Evaporator,	Rs. (in lacs)	42	48	54
	(b) Fluid bed reactor	,,	34	40	46
	(c) Piping valves, instrumentation etc.	,,	21	27	33
	Total Capital investment.	,,	97	115	133
(B)	OPERATING COST :				
	i) Quantity of alkali recovered, TPD (based on 85 % recovery eff.)		6.6	8 8	11.0
	ii) Quantity of alkali recovered. TPY		2178	2904	3630
	iii) Quantity of steam consumed. TPD		96.3	128 4	160.5
	iv) Steam cost, Rs. (in lacs) year		47.7	63 6	79.5
	v) Electricity consumed kWH/day		8400	9600	10800
	vi) Electricity cost Rs. in lacs/yr.		30 5	34.9	39.2
	vii) Fe_2O_3 required. TPD		0.9	1.2	1.5
	viii) Cost of Fe_2O_3 Rs. (in lacs)/yr.		2 2	2.9	3 6
	ix) Auxiliary fuel, Rs. in lacs/yr.		2 6	4 0	5.4
	x) Maintenance	,,	1.3	2 0	2.3
	xi) Wages	,,	1.1	1.3	1 5
	xii) Total operating cost	,,	85.4	108.7	131.5
	xiii) Cost of recovered caustic before interest & depreciation, Rs./tonne		3921/–	3743/–	3622/–
	xvi) Interest @ 13%, Rs. (lacs)/yr.		12 6	15 0	17 3
	xv) depreciation @ 7%		6.8	8.00	9.3
	xvi) Total interest & depreciation Rs. (in lacs) / yr.		19.4	23.0	26 6
	xvii) Interest and depreciation of alkali recovered. Rs./tonne		891/–	792/–	733/–
	xviii) Total cost of recovered caustic Soda Rs./tonne.		4812/–	4535/–	4355/–

TABLE NO. 7

Costs Comparision of conventional and Ferrite Recovery Process

	Description	Conventional Recovery System			Ferrite Recovery System		
i)	Pulp Mill Capacity TPD	30	40	50	30	40	50
ii)	Capital Investment, Rs. (in lacs)	144	168	192	97	115	133
iii)	Cost of NaOH Production, Rs/tonne	6733/-	6360/-	6119/-	4812/-	4535/-	4355/-
iv)	% reduction in capital investments.	—	—	—	32.6	31.5	30.7
v)	% reduction in operating costs.	—	—	—	28.5	28.7	28.8
vi)	Depreciation, Rs. (in lacs) P.Y.	10.1	11.8	13.4	6.8	8.0	9.3
vii)	Profit, Rs. (in lacs) P.Y.	5.3	16.90	29.10	25.90	42.50	59.70
viii)	Payout period (years)	9.4	5.9	4.5	3.0	2.3	1.9

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