Pollution Abatement and Effluent Recycle Through Oxygen Delignification and Bleaching Processes

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ABSTRACT

Pure oxygen/enriched air is increasingly used since seventies in several process industries to comply with stringent environmental norms to reduce pollution at the source with concurrent benefits of higher through-put and savings in recurring expenses. Paper mills in N. American and Scandinavian countries have readily adopted oxygen delignification and bleach sequences and achieved significantly improved environmental performance. Indian paper industry has also recognized these tangible benefits and some mills have installed oxygen pulping and bleaching systems.

A comparative assessment of the pollution potentials of a conventional [CEHH] sequence and ECF sequence of [OD(EOP)D] and the tangible benefits of the oxygen based delignification/bleaching processes are illustrated for mill capacities of 200 and 450 TPD with 75:25 furnish of mixed hardwoods: bamboo.

A higher target kappa number (30 vs. 15) for the unbleached pulp for use in the oxygen based bleach system also has the concurrent benefits of higher pulp yields (+4%), lower digester furnish (-8%), saving in alkali requirement for pulping (-13%) and a higher proportion of recycle of weak black liquor (15%) to the digester to maintain the desired liquor : wood ratio.

The total BOD and COD loads released by the oxygen based plant are 51 kg BOD and 102 kg COD per ton of pulp compared to bleach plant loads of 178 kg BOD and 250 kg COD per ton of pulp for conventional CEHH plant. These represent substantial reductions of pollution potential by 70% BOD and 60% COD by adopting the oxygen based processes. The latter also enables the recycling of organic pollutant load equivalent to 100 kg COD per ton of pulp through the recycle of oxygen delignification stage effluent to the Chemical Recovery system. The total oxygen requirement is estamated to be 5 and 12 TPD for 200 and 450 TPD paper mills respectively.

NTRODUCTION

There are about 300 paper mills in India with 34 units in the large-scale sector (>100 TPD), 30 in the medium (50-100 TPD), 50 in mini (20-50 TPD) and 186 in small - scale (<15 TPD) categories. The primary aim of papermaking is to separate the cellulosic fibres from the raw material like softwood/hardwood, bamboo, bagasse, straws, etc. With no softwood resources available, Indian paper industry has developed during the past century, utilizing all other locally available fiber resources.

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Paper industry is considered as one of the sectors contributing to large-scale air and water emissions. Stringent environmental norms have forced the sector to develop and adopt various technological innovations for pollution abatement. Technologies based on pure oxygen/enriched air are being increasingly used in this sector at various stages of pulping (cooking), bleaching (prebleaching and extraction), chemical recovery (black liquor oxidation) and wastewater treatment (activated sludge process) [1].

The bleach section contributes to the major pollution load in an integrated paper mill. Chlorine, caustic and hypochlorite are used in conventional sequence (CEHH) and a few mills have adopted chlorine dioxide (D) and peroxide (P) stages. Mills operating abroad have adopted novel bleach sequence eliminating the use of chlorine and have evolved eco-friendly ECF and TCF (Elemental chlorine free and Total chlorine free) processes based on the use of enzymes (xylanases), peroxide, oxygen, and ozone.

Oxygen bleaching/delignification was developed as a commercially feasible process during the late 1970s overcoming the major limitations of cellulose degradation and poor strength properties with the incorporation of certain magnesium salts [2]. Currently, Sweden ranks at the top and oxygen is an inherent feature in most of its paper mills for better environmental performance. Japanese mills also employ oxygen widely since it is inexpensive in relation to chlorine, caustic and chlorate. A large quantity of oxygen is available as a byproduct of nitrogen required in the manufacture of integrated circuits [3]. In 1996, nearly 160,000 daily tons of world's bleached kraft pulp production was based on oxygen delignification and Scandinavia and Europe together accounted for largest installed capacity in the world [2]. Indian paper industry has also recognized these tangible benefits and some mills have installed oxygen pulping and bleaching systems.

Numerous benefits accrue from the use of oxygen in predelignification and bleaching stages. Significant reductions are obtainable in pollutant loads (COD, BOD, and AOX) [4], power [5], water consumption, and wastewater generation [6]. Tangible benefits include savings through reduced chemicals for pulping and bleaching [7], higher pulp yield and wastewater treatment costs. Other significant benefits can be realized through partial closure of fiberline by recycle of the oxygen pre-bleach stage effluent to the chemical recovery system. Oxygen based systems in combination with peroxide, caustic, ozone, chlorine dioxide and enzymes can lead to ecologically acceptable bleach sequences like TCF and ECF pulps.

OXYGEN BASED PROCESSES

Conventional pulp bleach plants are based on the use of chlorine chemicals such as chlorine (Cl_2) and hypochlorite (OCI) as oxidizing agents for the removal of residual lignin from unbleached pulp. This practice has been in vogue for several decades until the advent of more powerful oxidizing agents like chlorine dioxide and peroxide which enabled the production of high brightness pulps. Recognizing the carcinogenic potential of chlorolignins in the spent bleach effluents of chlorination/extraction (CE) stages and the recalcitrant nature, chlorine is no longer preferred as a primary bleach chemical.

The global trend is in favor of ECF and TCF bleach sequences and the use of chlorine and chlorine compounds have been greatly curtailed or eliminated altogether by incorporating enzymes and pure oxygen processes. Delignification achieved during early stages of bleaching is a continuation of pulping reactions employing lignin specific chemicals to preserve the yield and strength attributes of unbleached pulp . The ability of oxygen stages to give upto 50% delignification also gives an opportunity to raise target kappa number of unbleached pulp with some savings in alkali charge [8].

If the bleach sequence is started with oxygen stage, the effluent from this stage will be chloride free and consist mainly of degraded lignin and carbohydrate compounds dissolved in residual alkali. The spent liquor from oxygen stage can be recycled to be mixed with weak black liquor and evaporated and burned in the chemical recovery boiler. Recycling of the oxygen stage effluent to the mill recovery system has the potential to reduce the overall pollution load by nearly one-half [6]. The benefits of oxygen as a prebleach stage are also realized in the main bleach plant through savings in bleach chemicals and the release of environmentally compatible residual pollutants.

This presentation highlights the potential opportunities of oxygen based technologies for pollution abatement and cleaner production with significant savings in chemical inputs. The presentation, therefore, aims at achieving the following objectives:

- Assessing the pollution potential of conventional (CEHH) processes based on literature and material balance calculations.

- Evaluating the corresponding pollution attributes of the proposed oxygen based process [OD (EOP) D] for the desired pulp brightness and capacity.
- A comparative assessment of the above in terms of inputs (chemicals, oxygen demand, energy, water, etc.) and outputs (contribution to pollution load) and associated cost aspects.
- Verify/supplement/validate the assessments using feedback from select installations in response to a questionnaire.
- Highlight the potential opportunity for replication of these processes in the Indian industries.

COMPARATIVE ASSESSMENT

A large integrated paper mill (capacity - 450 TPD) is considered to assess the pollution potential of both conventional (CEHH) and proposed oxygen based [OD (EOP)D] bleach plant sequences.

Pulping section

A summary of the mass balance calculations for the pulping section is given in Table 1. A higher target kappa number (30 vs. 15) for the unbleached pulp for use in the oxygen based bleach system also has the concurrent benefits of higher pulp yields, lower digester furnish, savings in alkali requirement for pulping and a higher proportion of recycle of week black liquor to the digester to maintain the desired liquor: wood ratio (4:1). The extent to which these benefits can accrue is also evident from the comparative values of the various input and output parameters listed in Table 1 for the two different bleaching scenarios considered in this paper.

TABLE 1.

DIGESTER INPUT/OUTPUT PARAMETERS AND TANGIBLE BENEFITS OF OXYGEN DELIGNIFICATION AND BLEACHING

PARAMETERS	BLEACH SEQUENCE		BENEFIT (%)
	CEHH	OD (EOP)D	
A. IN PUTS			
Mill Capacity, TPD	450	450	-
Digester Furnish, T	978	900	-8
Hardwood: bamboo	75:25	75:25	-
Hardwood, T	734	675	-8
Bamboo, T	244	225	-8
Alkali charge, % as Na_2O	18	17	-5
Active alkali strength, g/L as Na_2O	50	50	-
Sulfidity, %	20	20	-
Chemical Charge, T as Na_2O	176	153	-13
White liquor, m^3	3522	3060	-13
Liquor: wood ratio	4:1	4:1	-
Liquor volume, m^3	3913	3600	-8
Black liquor recycle, m^3 (%)	391 (10)	540 (15)	+5
B. OUTPUTS			
Kappa number	14.5	30	15
Unbleached Pulp Yield, %	55	57	+2
Bleached pulp yield, %	46	50	+4

TABLE 2.

ESTIMATED COMPOSITION OF UNBLEACHED PULP BLEND FOR BLEACHING

Wood Type	Component	Raw chips, tons	Unbleached pulp content tons (%)	Black Liquor content tons (%)	Composition of pulp	
					Average (%)	Overall average (%)
CASE I. PULP FOR CONVENTIONAL PROCESS (CEHH)						
Hardwood Eucalyptus (75%)	Cellulose	352.42[9]	323.05 (91.6)[9]	29.37 (8.4)[9]	80.0	78.5
	Hemicellulose	190.89[9]	73.42 (38.0)[9]	117.47 (62)[9]	18.2	19.6
	Lignin	176.21[9]	7.34 (4.16)[9]	168.87 (95.84)[9]	1.8	1.9
	Extractives	14.68[9]	-	14.68 (100)[9]	-	-
	Total Content	**734.2**	**403.8 (55)**	**330.4 (45)**	**100.0**	**100.0**
Bamboo (25%)	Cellulose	115.02[10]	103.51 (90)[10]	11.45 (10)[10]	76.9	-
	Hemicellulose	56.29[10]	28.19 (50)[10]	28.19 (50)[10]	20.9	-
	Lignin	66.08[10]	2.84 (4.29)[10]	63.24 (95.71)[10]	2.1	-
	Ash	7.34[10]	-	7.34(100)[10]	-	-
	Total Content	**244.7**	**134.6 (55)**	**110.2 (45)**	**100.0**	
CASE II. PULP FOR OXYGEN BASED PROCESS [OD (EOP) D]						
Hardwood Eucalyptus (75%)	Cellulose	324.00	302.22 (93.27)	21.78 (6.72)	78.6	77.2
	Hemicellulose	175.50	67.50 (38)	108.00 (62)	17.5	18.9
	Lignin	162.00	15.03 (9.27)	146.97 (90.72)	3.9	3.9
	Extractives	13.50	-	13.50 (100)	-	-
	Total Content	**675**	**384.7 (57)**	**290.2 (43)**	**100.0**	**100.0**
Bamboo (25%)	Cellulose	105.75	97.29 (92)	8.46 (8)	75.9	-
	Hemicellulose	51.75	25.92 (50)	25.92 (50)	20.2	-
	Lignin	60.75	5.04 (8.29)	55.71 (91.71)	3.9	-
	Ash	6.75	-	6.75 (100)	-	-
	Total Content	**225.00**	**128.2 (57)**	**90.1 (43)**	**100.0**	-

Capacity = 450 TPD

(Digester furnish = hardwoods: bamboo = 75:25)

Unbleached pulp

a) CEHH : Kappa number = 14.5; yield = 55%

b) OD(EOP)D : Kappa number = 30; yield = 57%

Success of pulping reactions during kraft cook depends on several important variables like wood species and chip geometry, active alkali charge, concentration of effective alkali and liquor to wood ratio, sulfidity, and pulping time and temperature.

Suitable assumptions were made for the two mills and correspondingly a few figures were deduced from them, data for the section has been shown in Table 1.

BLEACHING SECTION

Conventional (CEHH) Plant

An estimate of the composition of the unbleached pulp blend available for bleaching processes is given in Table 2. The pulp blend for conventional bleach plant is estimated to have 1.9% lignin (kappa number =14.5) compared to 3.9% lignin (kappa number =30) for the pulp to be handled by the oxygen bleach plant.

Brightness of unbleached kraft pulp is only 20% ISO [11] and the color is primarily due to large number of phenolic groups of lignin present in both etherified and free forms which on oxidation are converted into quinone like substances that are known to absorb visible light.

A schematic of such a sequence is shown in the Figure1. Generally the washings from any stage is recirculated to the previous stage in order to conserve water and any make up fresh water is added in the last one or two stages. Bulk of residual lignin in the unbleached pulp is removed by chlorination -alkaline extraction treatments.

Chlorine is the most popular, economical, reliable and lignin specific bleach chemical. Chlorination is carried out at pH of 1-3 without too drastic action on the carbohydrate fraction of pulp and it undergoes substitution, addition as well as oxidation reactions to form chlorolignins. Nearly 90% of the lignin content of the pulp is degraded after the chlorine-alkaline extraction stage. Nearly one-half of the lignin is lost from the pulp during the chlorine stage and the rest of the degraded lignin goes into the liquor during the extraction stage [12].

Chlorolignins in the bleach plant effluent are non biodegradable and are not metabolized during conventional biological wastewater treatment processes and tend to escape into the receiving water bodies. They are potential carcinogens and have been linked to adverse health effects in both humans and animals.

During alkaline extraction stage, soda extracts the chlorinated lignin compounds at 50-70°C at 2-3% alkali dosage. The alkali displaces the chlorine and makes the lignin soluble by reactions such as [11].

$$\text{Lignin - Cl} + \text{NaOH} \rightarrow \text{Lignin -ONa} + \text{HCl}$$

Alkali also acts on the pulp carbohydrates through peeling reactions' leading to 2-3% yields loss due to loss on this account [13].

Hypochlorites are used as oxidative bleach chemicals and since they are not specific for lignin degradation, optimal physical conditions are chosen to enhance the attack on lignin compounds and minimize the cellulose degradation. Substantial savings in the chemicals and improved brightness are obtained by two stage bleaching with 70% of the total chemicals are added in the first stage [13]. Nearly 0.25% lignin is lost in this stage Carbohydrate losses have been divided thereby in the ratio of 70:10 of the total loss experienced in the stage yield.

An estimate of stagewise pulp characteristics and effluent quality obtainable during CEHH sequence is given in Table 3. The estimates show organic pollutant load equivalent to 182 kg BOD per ton of bleached pulp. (255 kg COD per ton of bleached pulp) to be handled by the effluent treatment plant together with the other process wastewater streams.

Oxygen Bleach Plant. [OD (EO pulp) D]

Pioneers in oxygen based technologies for pulp bleaching in North American and Scandinavian countries have adopted OCD EDED sequence [3] and various modifications with the dual objectives of achieving higher levels of pulp brightness (90+%ISO) and to close the loop of bleach plant towards zero discharge [15]. Bleach sequences like OC/D (EOP)D, CDEOHHD, (C/D) EOD, have been adoted by some Indian paper mills [5,16,17] and incorporated oxygen use in the bleach plant. The use of chlorine dioxide to achieve an ECF sequence and to benefit from the nearly two-third reduction in AOX generation [18] and the extent of delignification is comparable to C stage.

The sequence recommended adopts a short oxygen predelignification stage prior to the rest of the bleaching in order to minimize the chemical input in the bleaching section. A schematic of the sequence is shown in Figure 2 consisting of oxygen delignification chlorine dioxide Extraction + oxygen + peroxide - and chlorine dioxide [OD (EOP)D].

As recommended in many mill scale trials, oxygen - predelignification stage can yield more benefits with a high kappa number - 30-32 pulp [15]. Magnesium sulfate is added in this stage to protect the cellulosic groups from being oxidized . In this stage, nearly 50% delignification would occur and it is possible to recycle virtually all dissolved organics in the washer effluent to the recovery section [8]. Some of the major proven advantages of oxygen delignification process systems are listed below.

- Partial closure of the bleach plant by recycling the oxygen stage effluent to the chemical recovery system which enables a significant off-take of organic

TABLE 3.

STAGEWISE PULP CHARACTERISTICS AND EFFLUENT QUALITY DURING CONVENTIONAL BLEACH SEQUENCE (CEHH)

Parameters	Bleaching Stages				
	Unbleached pulp	C	E	H_1	H_2
A. Bleaching Conditions					
Time, h	-	1	1-2	2-4	2-4
Temperature ^0C	-	30	60	38-50	38-50
Consistency	-	3	8-10	8-10	8-10
pH	-	1.5	11	9	9
Chemical charged in %	-	3.0	2.5	2% as available chlorine	2% as available chlorine
B. Pulp Characteristics					
Cellulose, T	426.33	426.33	411.65	405.78	399.91
Hemicellulose, T	101.54	101.54	77.08	63.56	49.97
Lignin, T	10.17	5.59	1.017	0.76	0.577
Pulp yield, T (%)	538.04	533.46	489.76	470.1	450.47
Shrinkage	-	0.468	4.468	2.009	2.0
Lignin %	1.89	1.05	0.21	0.16	0.128
Kappa Number	14.54	8.07	1.6	1.25	0.98
Final Brightness	-	-	-	-	nearly 8% ISO
C. Effluent parameters					
Lignin COD, T		8.70	8.7	0.5	0.35
Carbohydrates COD, T		-	50	23.3	23.2

(Basis : 1 kg lignin = 1.9 kg COD, 1 kg Carbohydrate = 1.2 kg COD)

Total COD = 114.9 T/450T of pulp = 255kg/T of bleached pulp

Total BOD = 82 T/450 T of pulp = 182 kg/T of bleached pulp

pollutants load (BOD, COD) through combustion in the recovery boiler.

- ❑ An increase of 3-5% of organics in fuel supply to the recovery section [19].
- ❑ Pulp with comparable strength properties like conventional sequences.
- ❑ Less tendency for brightness reversion.

TABLE 4.

STAGEWISE PULP CHARACTERISTICS AND EFFLUENT QUALITY WITH OXYGEN INDELIGNIFICATION AND EXTRACTION STAGES [OD(EOP)D]

Parameters	Bleaching Stages				
	Unbleached pulp	O	D_1	EOP	D_2
A. Bleaching Conditions					
Time, min	-	60	120	75	120
Temperature °C		110	54	75	54
Pressure, kPa		550-720			
Consistency, %		10-15	10-12	10-12	10-12
pH		10-12	3.5-4	10.5-10.8	3.5-4.0
Chemical charged, kg/T		Mg = 0.5, O_2=20, NaOH-20	1.3	O_2=5.5, NaOH-0.7, H_2O_2-34	6.0
B. Pulp Characteristics					
Cellulose, T	399.51	394.11	394.11	387.36	387.36
Hemicellulose, T	93.42	80.82	80.82	65.07	65.07
Lignin, T	20.07	9.99	4.788	1.71	n.d.
Pulp yield, T (%)	513 (57)	484.92 (54.88)	479.72 (53.3)	454.14 (50.46)	452.43 (50.3)
Shrinkage		3.12	0.58	2.84	0.16
Lignin %		2.06	0.99	0.38	
Kappa Number		15.85	7.6	2.92	<1
Final Brightness					85-89%
C. Effluent parameters					
Lignin COD, T		19.2*	10	5.9	3.0
Carbohydrates COD, T	-	21.6*	-	27	-

*** Recycled to Chemical Recovery System**

(Basis : 1 kg lignin = 1.9 kg COD, 1 kg Carbohydrate = 1.2 kg COD)

Total COD = 45.9 T/450T of pulp = 101.6 kg/T of bleached pulp

Total BOD = 27 T/450 T of pulp = 50.7 kg/T of bleached pulp

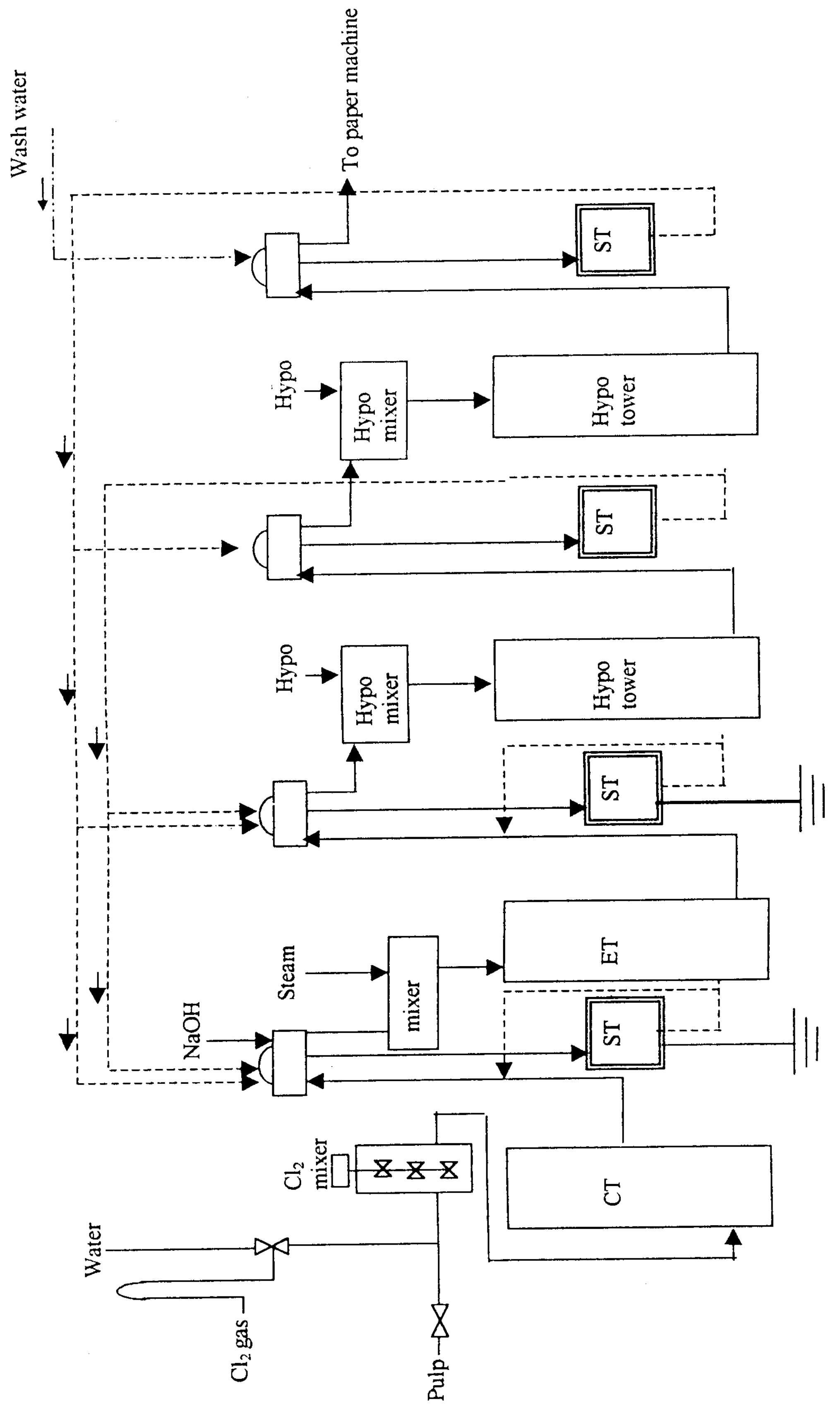

FIGURE 1. SCHEMATIC FOR CONVENTIONAL BLEACH PLANT (CEHH)

CT= Chlorination Tower; ET = Extraction Tower; ST= Seal Tank

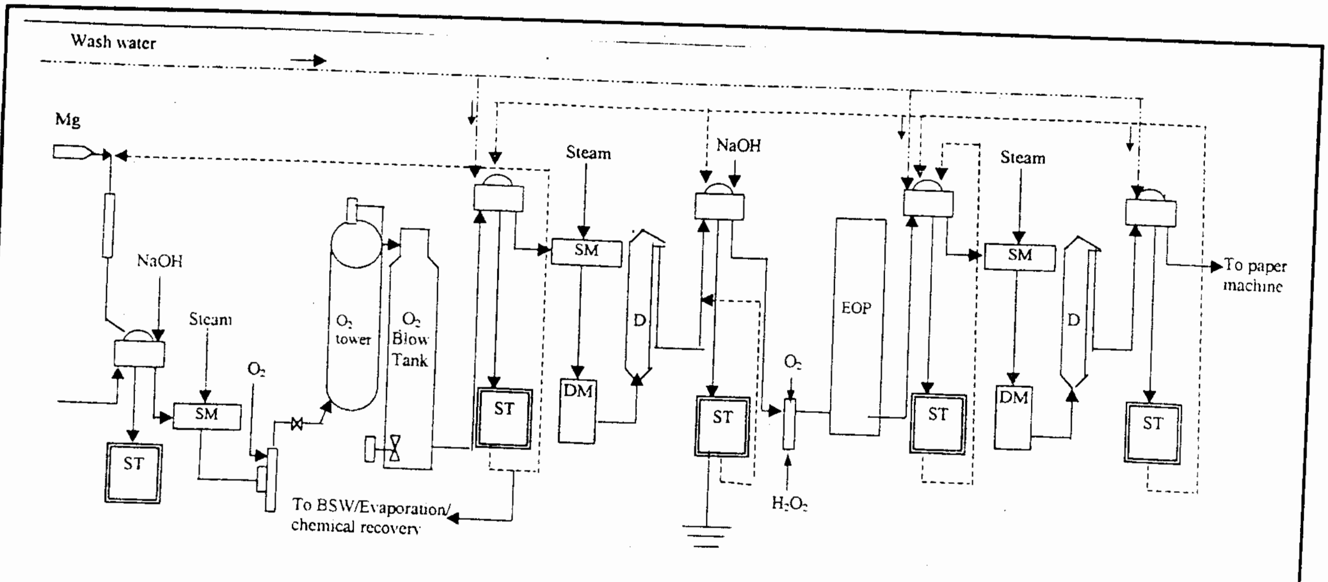

Figure 2. SCHEMATIC FOR ECF BLEACH PLANT [OD(EOP)D] SEQUENCE

ST= Seal Tank; SM= Steam mixer; DM= Chlorine Dioxide mixer; D= chlorine dioxide stage; EOP = Oxygen, peroxide enhanced extraction

- Cost savings for treatment of lesser volume of effluent discharged.

An alkaline extraction stage with oxygen (EO) has been found to be more effective and less degrading on the pulp properties [18]. In a mill survey a delignification of 82% was found after this stage [20]. Kappa number of nearly 3.0 is generally obtained after this stage [21]. Nearly 1% yield loss occurs due to degradation of carbohydrates in this stage. Pentosans in the liquor constitute 0.9% of the loss. Use of hydrogen peroxide along with alkali reduces color and chlorine demand during bleaching [4].

Oxidizing agents like peroxide specifically act on the chromophoric groups of lignin, without consuming the entire lignin and hence much of yield loss from the pulp.

An estimate of the stagewide performance indicating pulp characteristics and effluent quality with oxygen in delignification and extraction stages of the bleach plant configuration [OD (EOP)D] is presented in Table 4. The total BOD and COD loads released by this plant are 5 1.5 kg BOD and 102 kg COD per ton of pulp compared to bleach plant loads of 182 kg BOD and 255 kg COD per ton of pulp for the conventional CEHH plant. These represent a substantial reductions of pollution potential by 70% BOD and 60% COD by adopting the oxygen based processes. The latter also enables the recycling of organic pollutant load equivalent to 90 kg COD per ton of pulp through the recycle of oxygen delignification stage effluent to the chemical recovery system thereby preventing the release of such large quantum through the process wastewaters of the bleach plant.

SUMMARY

Several tangible benefits are highlighted by the comparative assessment of conventional and oxygen based bleach sequences in this study. Oxygen delignification has a potential to yield savings in fibrous raw material used and pulping chemical requirement with an increase in unbleached pulp yield. The recycle of process effluent from this stage to the recovery also prevents the release of organic pollutants equivalent to 100 kg COD per ton of pulp.

Downstream bleaching by [OD(EOP)D] sequence also demonstrated substantial reductions of pollution potential by 70% BOD and 60% COD compared to conventional CEHH sequence. The total oxygen requirement is estimated to be 11.5 TPD for a 450 TPD paper mill based on estimated demand of 20 and 5 kg per ton of pulp for the oxygen delignification and oxygen bleaching stages respectively.

REFERENCES

1. Chemical Week, 1998. New challenges in pulp and paper May 8, 36-38.

2. Carter, D.N., Mckenzie, D.G., Johnson, A.P. and

Idner, K., 1997. Performance parameters of oxygen delignification. *Tappi,* 80 (11), 111-117.

3. Tench, L. and Harper, 1987. Oxygen Bleaching Practices and benefits- An overview. *Tappi,* 70 (11) 55-61.

4. Gupta, H.K., Shivhare, P. Tripathi S. and Jain R., 2000. Energy saving and environment protection through improvement in bleaching *IPPTA,* 12 (2) 81-88.

5. Bokstorm, M. and Germgard, U., 1998. Wood and non-wood fibers- A modern approach. *IPPTA Convention Issue,* (12) 7-18.

6. Dubey, D.P. and Jindal, 2000. Adoption of energy and environmental Friendly technology - A case study at JK Paper mill, *IPPTA,* 12 (2) 117-121.

7. Boman R. and Simonson, O., 1989. Oxygen Delignification in Pulping of Annual Fibers. CHINA PAPER, Nov.- 9-14. Beijing, PRC.

8. Jain, N.K. and Boman, R., 1997. The Sunds Defibrator Non-wood fiber Technology. *IPPTA Convention issue.* 45-50.

9. Proceedings of the symposium on recovery of pulping chemicals, 1969. sponsored by IUPAC, EUCEPA (European Committee for Pulp and Paper). Organized by the Finnish Pulp and Paper Institute.

10. Kasiviswanathan, K.S., 1998. Utilization of bagasse for paper making *IPPTA.* 10 (3) 9-13.

11. Biermann, C.J., 1993. Essentials of pulping and papermaking. Academic Press, Oregon.

12. MacDonald, R.G. and Franklin, J.N., 1969. Pulp and Paper Manufacture. The pulping of wood. Vol. 1, ed II McGraw Hill Co. New York.

13. Rydholm, S.A., 1965. Pulping processes. Interscience publishers, New York.

14. Jamieson, A. and Smedman, L., 1974. Oxygen bleaching - A mill scale application of oxygen bleaching in Scandinavia. *Tappi,* 57 (5) 134-136.

15. Nasman, L. A decade of technological change in kraft pulping focusing on emissions, quality and operating costs. *Sunds Defibrator, Sweden.*

16. Personal communication with Center for Science and Environment, N. Delhi.

17. Boman R. and Jain, N.K., 2000. Technological changes in non-wood pulping focussing on emissions, quality and operating costs. *IPPTA* 12(1) 47-56.

18. Liebergott, N., B. van Lierop, T. Kovacs and A. Nolin, 1990. A comparison of the order of addition of chlorine and chlorine dioxide in the chlorination stage. *Tappi,* 74 (10) 207-213.

19. Enz, S.M. and Emmerling, F.A., 1987. North America's first fully integrated, medium-consistency oxygen delignification stage. *Tappi,* 70 (6) 105-111.

20. Pryke, D.C. and Reeve, D.W., 1997. A survey of ClO_2 delignification practices in Canada. *Tappi,* 80 (5) 153-161.

21. Ljunggren, S., Gidnert, E.B. and Sousa, F.P. 1998. Reduced AOX and biological effects by modification of a mill ClO_2 stage. *Tappi,* 81 (1) 267-273.