

**REPORT
ON
ECOLOGICAL & ENVIRONMENTAL FACTORS
IN PAPER INDUSTRY**

VOLUME-III

**TECHNOLOGICAL OVERVIEW IN INDIAN PAPER INDUSTRY
WITH SUGGESTIVE MEASURES FOR IMPROVED
ENVIRONMENT MANAGEMENT**

**PREPARED
FOR**

INDIAN PAPER MANUFACTURER'S ASSOCIATION

BY

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VOLUME III

TECHNOLOGICAL OVERVIEW, IN INDIAN PAPER INDUSTRY WITH SUGGESTIVE MEASURES FOR IMPROVED ENVIRONMENT MANAGEMENT

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I. INTRODUCTION:

With recent economic reforms in the country, the paper industry has been exposed to severe competition from the global players. With the globalisation of the economy, the Indian paper industry is now in pursuit of its modernisation and up gradation to improve quality, productivity & cost effectivity through value addition. There is need for inducting cost effective manufacturing process in Indian pulp and paper industry to make it competitive in the international market. Environmental issues have also emerged as a key theme during recent years. With the discovery of the dioxin and furans in pulp and paper mill effluent, there has been widespread concern over the adverse impact of AOX and during last decades much of the concern from the traditional parameters of BOD, TSS and colour over effluent emission has shifted to chlorinated organic compounds and AOX.

The Indian paper industry is posed to enter a new era, but the challenges that lie in hand are varied, multidimensional and complex. Indian paper industry needs to upgrade its technology to boost production with, cleaner technologies, more energy efficient processes, higher resource recovery and recycling and improved capital effectiveness to become globally competitive. The present chapter highlights the technological, trends prevailing in the industry and the necessary measures required to be taken for process & technological improvements in large, medium & small paper mills.

The volume briefs:

1. The present technological trends prevailing in Indian paper mills and the innovative measures for technological improvements.
2. Discharge characteristics, End-of-pipe treatment practices and Advanced treatment technologies for:
 - (i) Large paper mills - Forest & Agro based with Chemical Recovery
 - (ii) Medium & small paper mills - Agro based with no Chemical Recovery and Waste Paper Based Mills.

CHAPTER -1

I. TECHNOLOGICAL TRENDS & SUGGESTED MEASURES IN LARGE PAPER MILLS:

Pulp & Paper manufacturing is a complex process involving several unit operations & processes.

The main sections are:

- Raw material preparation & handling
- Cooking
- Washing & Screening
- Bleaching
- Chemical recovery
- Stock preparation & paper making
- Utilities (steam ,electricity, air & water)
- Effluent treatment

In order to become globally competitive, Indian paper industry must go in for the following steps:

- a) Cost reduction
- b) Quality improvement & competitiveness
- c) Increased productivity with export orientation and
- d) Energy efficient & Environment friendly technologies.

For achieving the above goal, some concrete steps are required to be taken.

The cleaner production options along with the salient pulp & paper manufacturing processes being practiced are discussed for individual sections:

1.0 Raw Material Preparation & Handling:

Both woods & non-woods are used for papermaking. The fibrous raw material based on agricultural raw materials differ from woody raw materials morphologically and chemical composition wise. These are seasonal, bulky with short fibre lengths, low lignin contents, high pentosans and high ash contents. The non-woods are considered to have more open structure. Materials like straws have the outer surface covered with impervious waxy material, while the volume occupied by the non fibrous components is high. Unless these characteristics are properly accounted and the raw materials properly prepared, the pulping and subsequent processes are likely to result in generation of large quantities of emission (liquid and gaseous), besides causing operational problems. The steps, which need to be looked into are:-

- wood debarking
- wood chipping, screening;
- Non wood storage and preservation;
- Non wood preparation (like depithing, dedusting, cutting);
- Improved mechanical handling of raw materials;
- Materials like straws can be treated in disc mills to significantly improve pulp characteristics;

1.1 Improved Raw Material Handling:

The fresh water consumption in wet debarking operations for wood is around $10 \text{ m}^3/\text{m}^3$ of wood ($50 \text{ m}^3/\text{t}$ pulp), which can be reduced to 10% values by closed systems with combination of dry and wet debarking.

In case of bagasse, both storage and depithing results in generation of waste waters. Bagasse storage results in $10\text{-}50 \text{ m}^3/\text{t}$ pulp with BOD of the order of $20\text{-}40 \text{ kg./t}$ pulp and COD of the order of $80\text{-}240 \text{ Kg./t}$ pulp. These values can be reduced by 30-50% by improved recycling practices.

Similarly, open depithing results in waste water generation of $30\text{-}60 \text{ m}^3/\text{t}$ bagasse with $60\text{-}120 \text{ Kg./t}$ COD and $10\text{-}30 \text{ Kg./t}$ BOD. In closed systems, these values can be brought down by 50-85%.

Washing of raw materials is extremely important particularly for non woods as it has direct bearing on the quantity of extraneous silica & other non-process elements like potassium & chlorides entering the system, which influences all the down stream processes.

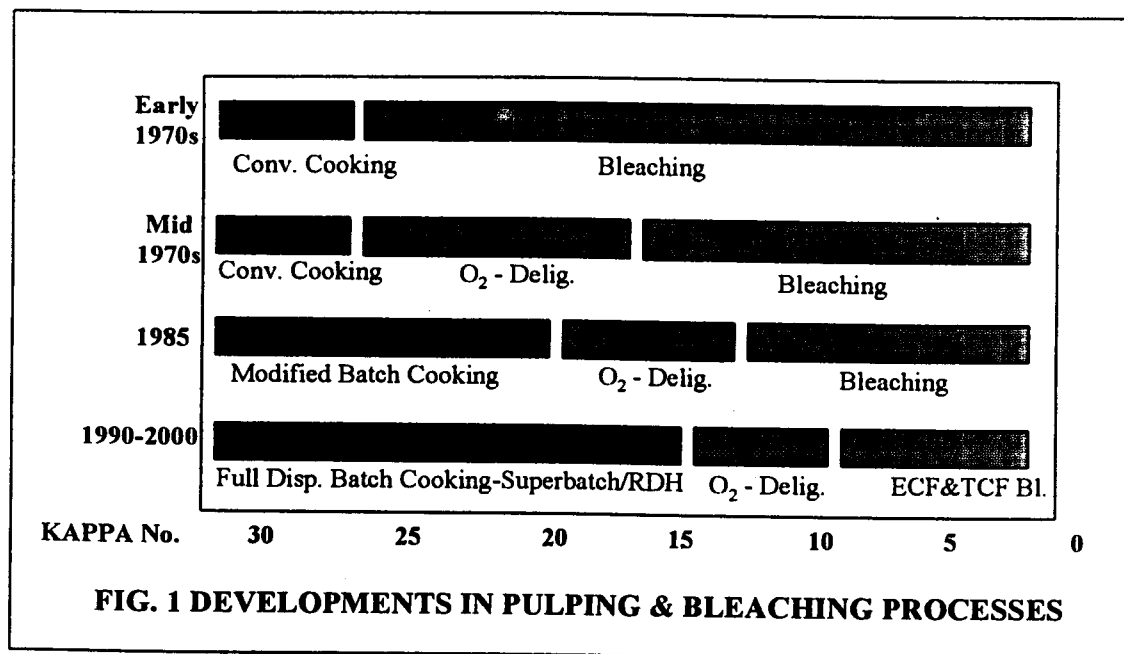
Similarly improved material handling practices can reduce the handling losses of raw materials (non-woods) from 4-9% level to 2-3% level.

2.0 Pulping & Bleaching:

In the recent years, environmental factors are forcing the paper industry to devise pulping & bleaching alternatives which are revolutionary in nature – since sulfur & chlorine compounds are harmful to environment and life cycle, efforts are being made to do away with these chemicals by using sulfur free pulping & Cl_2 free bleaching methods. In recent years, these are the following trends:

- Elimination and / or minimising the use of sulfur
- Elimination of use of Cl_2 in bleaching by elemental chlorine free bleaching (ECF) using ClO_2 & O_2 etc. and Total Chlorine free bleaching (TCF).
- Biotechnological applications- Biopulping & Biobleaching.
- T C F using O_2 , O_3 & H_2O_2 etc.
- Production of high yield pulps with acceptable optical & mechanical properties
- Energy & Environmental concern.

Fig.1- shows the changes in pulping concepts from 1970-2000 in developed countries, which shows extended cooking stage, while there is shrinkage of bleaching profile.



2.1 Trends in Pulping:

Soda and kraft processes are most common chemical cooking methods followed for non-wood and wood raw materials. Cooking is done in either Batch or Continuous Digesters with indirect or direct steaming. The cooking conditions adopted are governed by the raw materials used and type of end product to be made. The cooking operations are chemical intensive and energy intensive. There is need to look at these operations carefully to conserve energy, raw materials and chemicals. During cooking attempts are made to separate cellulose by dissolving lignin. The selectivity is a parameter which one would like to have at highest level by controlling the chemical profile and temperature profile and adding agents like AQ. The Yield and kappa number of the pulp are influenced by the H-factor. The energy consumption is dependent on how much energy is recovered.

The parameters which influence the operation are chip size, loading, bath ratio, time-temperature profile, alkali profile and heat recovery. The developments include modified cooking, RDH, super batch, cold blow and continuous cooking.

The normal out put from cooking process, besides pulp are spent black liquor, blow condensate, non condensable gases, clean condensate (in case of indirect steaming). Pulp and spent liquors are sent to washing department. The blow condensates are heavily polluted. In batch digesters, the blow condensates of 1-1.2 t/t pulp with 5-8

Kg. BOD/t pulp are generated. The condensate can be stripped and the volatiles can be destructed in a boiler or a lime kiln together with other noncondensibles.

2.2 Modified Cooking Process:

Due to high energy cost, high cost of chemicals and continuous pressure from environmental authorities to minimise impact, process technology suppliers are in continuous search of new technology for energy efficient and environmental friendly processes. This has led to the development of highly energy efficient batch cooking processes using various kinds of liquor displacement technology. In the displacement batch cooking process, the heat and residual chemicals in the black liquor at the end of cook are stored by displacing the spent black liquor into separate pressure accumulators from where it is used to heat chips and white liquor for the next cook and so on.

Following liquor displacement batch cooking technology are in use these days. The common feature of all these processes is that heat needed in cooking is transferred from one cook to another cook by displacement.

- a. **RDH Cooking System:** offered by Beloit, England/USA
Heat is recovered from hot black liquor at the end of cooking and reused in the subsequent cooks. The impregnation temperature is generally 100-130C
- b. **Superbatch Cooking System:** offered by Sunds Defibrator, Sweden.
The principle is the same as RDH. The impregnation temperature is around 70-90°C.

Advantages:

The following benefits have been reported:

- ➔ Energy saving and reduction of steam consumption by 60-70%
- ➔ Reduction of chemical consumption in cooking, washing and bleaching
- ➔ The tear strength is higher by 15 to 20% than conventional cook. Due to higher strength paper machine runnability improves.
- ➔ Pulp of low kappa no. can be produced without loss of strength. Strength of pulp is better than conventional cook.
- ➔ Pulp of higher Brightness can be produced
- ➔ Alkali losses in washing are minimised
- ➔ Viscosity of Black liquor is low. Hence firing in the recovery furnace can be done at 75-80% solids.
- ➔ Percentage solids in black liquor is higher than conventional cook which saves steam in subsequent evaporation plant.
- ➔ Due to higher yield percentage, considerable amount of costly and scarce raw material is saved
- ➔ Technology is environmental friendly with following benefits:
 - a. Reduction in BOD, COD, AOX, volume and color

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- b. No emission of obnoxious gases like Mercaptans, as shown in Table – 1
- c. Reduction in TRS emissions.

TABLE –1

GASEOUS EMISSIONS IN CONVENTIONAL AND MODIFIED BATCH COOKING PROCESS

Particulars	H₂S	MM	DMS	DMDS	Total
Conventional	0.04	0.9	0.11	0.03	1.08
Modified Batch	0.00	0.0	0.01	0.01	0.02

MM-Methyl mercaptan ; DMS- Dimethyl sulphide; DMDS- Dimethyl disulphide.

2.3 Options & Opportunities For Cleaner Pulping Techniques:

- (i) Only the mills where raw material variation is not much and restricted to one raw material can go for continuous digestion including rayon grade pulps. Agro based mills can go for Pandia digester .
- (ii) The mills which are already having battery of batch digestion systems can think of modified batch systems.
- (iii) With AQ, once available at competitive price can replace sulphur at least partially.

From environmental view point, the new trends in pulping should help in following areas:

- Minimisation of rejects by uniform cooking;
- Low kappa number pulps without yield reduction thus enhancing chemical energy recovery in recovery section and reducing the bleach chemical consumption.
- Elimination of malodorous air pollution problems.

3.0 Pulp Washing & Screening:

Washing operation serves to separate the pulp from spent liquor. A thorough washing leaves low residues of black liquor in washed pulp, which is decisive for the amount of polluting discharges from the screening and bleaching sections. The cleanliness of the washed pulp can be easily improved by using excess wash water, but this will result in dilute black liquor going to evaporation plant, where energy demands will increase. The crux of washing operation is to wash pulp to highest cleanliness with least dilution. The factors influencing the results of washing are:-

- ➡ Type of pulp to be washed;
- ➡ Type of washing equipment;

- ➡ Dimension of the washer;
- ➡ Number of washing units;
- ➡ Washing liquid (composition, amount and temperature);
- ➡ Vacuum level;

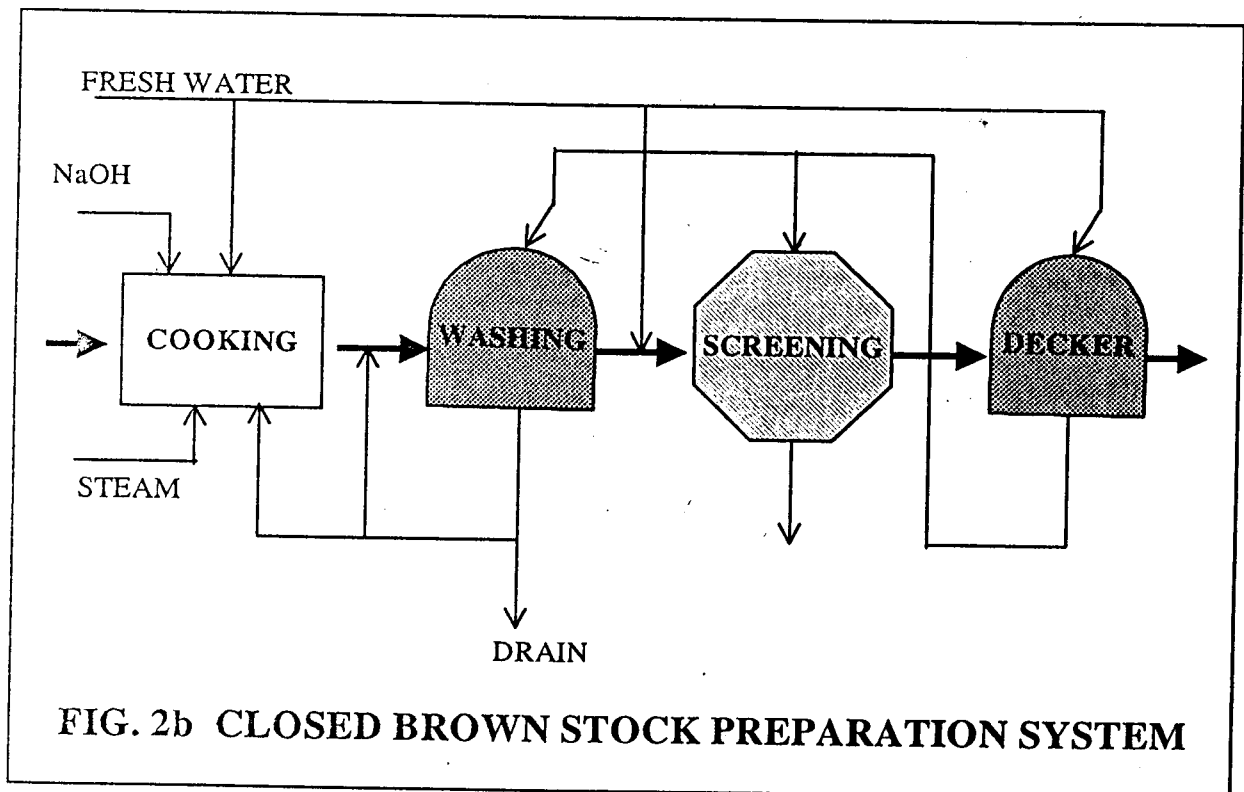
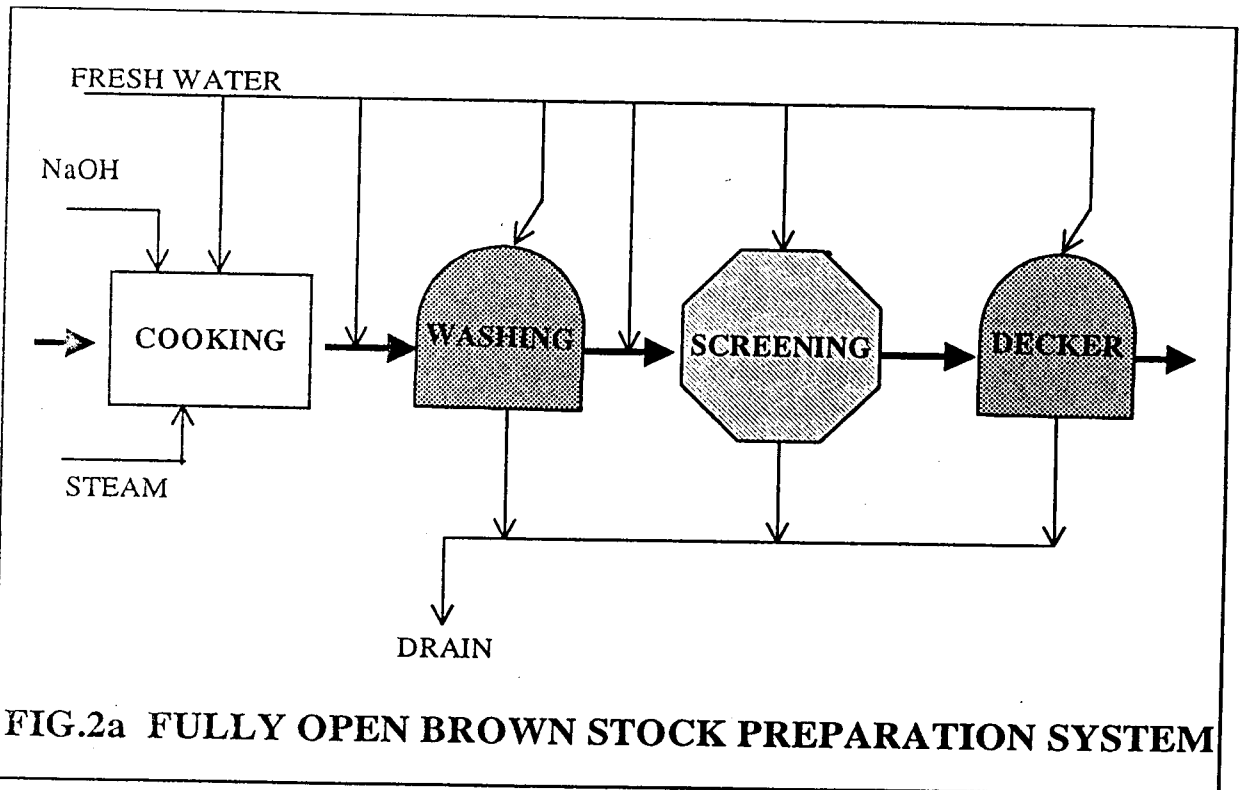
Non-wood pulps with slow drainage, need careful design of washing systems.

A lot of work has been done on improving the washing efficiencies, by installing highly efficient equipment. The following are the equipment used for this purpose:

- Pressure diffuser washer
- Horizontal belt washer
- Compact washer
- Drum displacer washer
- Screw pumps in combination with rotary drum washers.

In screening operation, knots, shives and other impurities are removed. Thus dewatering after screening has the function of final washing stage, when its filtrate is used as wash liquor in previous stages (counter current washing). This is known as "Closed Screening", and is now a common practice to reduce polluting discharges.

The process routing diagram of open & partially closed brown stock preparation is shown in Fig.2a &2b-



4.0 Pulp Bleaching:

With increasing environmental pressures, changing customers preferences, there is need to critically evaluate the bleaching techniques adopted by Indian Paper Industry. It has been well established that the high proportion of chlorinated organics in the effluent and also in the end products have adverse effect on ecological and human health. The developed countries recognised the consequences of toxic chemicals generated during bleaching, by employing elemental chlorine & over a period of time the mills in Scandinavian countries and Canada and the USA have slowly eliminated the elemental chlorine in the last two decades and slowly are moving towards the implementation of total chlorine free (TCF) bleaching techniques. The ECF & TCF techniques have proved, beyond doubt, the advantages in terms of cleaner environment and product quality but still economic aspects are not very clear. Indian Paper Industry which primarily utilises about 40% wood, 40% non-wood and about 20% of waste paper invariably bleach the pulp by chemicals with elemental chlorine, like- chlorine gas & Ca-hypochlorite which are producing high proportion of chlorinated phenolics, which are major forms of adsorbable organic halide (AOX). The quantity of elemental chlorine applied show a wide variation from 200 Kg. to 50 Kg. There is a need for critical evaluation of technology & bleaching practices.

4.1 Current Practices :

CEH is the traditional sequence used by mills to produce semi-bleached pulp particularly for supplementing newsprint furnish. The traditional market pulp sequence is CDEO DED. Use of chlorine is decreasing rapidly with oxygen, peroxide and chlorine dioxide providing more environmentally compatible bleaching

It is more probable that a wood based mill, designed with all of the dioxin reduction features, will be successful in producing an effluent with undetectable dioxin levels. It is also probable that producing a wood kraft pulp mill effluent with dioxin levels below the detection limit will be required by some regulatory authorities.

4.2 AOX Sources, Formation and Toxic Effects:

It has been well established that a series of chlorophenols are formed during bleaching process. The nature & extent of formation of AOX is determined primarily by the

residual lignin content in the pulp & the type of bleaching chemical employed. Among the chlorophenols the dioxins and dibenzofurans are a group of chlorophenols which have been found to have toxic effect. The prominent among the dioxins are 2,3,7,8 TCDD (Tetra Chloro dibenzo dioxin) & 2,3,7,8 TCDF (Tetra Chloro dibenzo furan). It is clear that out of 100% AOX the percentage of dioxin is less than 0.1% which is supposed to be highly lipophilic & bio-accumable compound.

The formation of AOX & other chlorinated polyphenols is largely dependent on the

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type of bleaching chemical besides residual lignin. The formation of chlorinated phenolics is strongly affected by the chlorine multiple. The AOX formed increases exponentially above a chlorine multiple of 0.05 which corresponds to about 10-15 kg of Cl_2 /t of pulp having kappa no. 20.

This is one reason why the AOX formation is more predominant in bleaching sequences involving the elemental chlorine like Cl_2 , $\text{Ca}(\text{OCl})_2$ etc.

4.3 Constraints & Limitations Prevailing in Indian Paper Industry:

One of the most important step for regulating the levels of AOX is to ensure that the pulp reaching the bleaching stages has a low Kappa No. & the carry over of the black liquor is minimum. Under the prevailing conditions & due to economic reasons it may be difficult to obtain pulp of low kappa no. however, the mills can certainly improve the washing efficiency thereby reducing the carryover of lignin to bleach plants.

Because of the limitations in the process equipments and due to the size constraints most of the medium & small size mills resort to either single stage or two stage bleaching with chlorine doses ranging from 70-100 kg/per tonne of pulp.

It is evident that one of the most effective steps to controlling AOX levels is partial or complete substitution of elemental Cl_2 & moving towards what is called as ECF. The following Table – 2 shows effect of bleaching sequence on AOX levels with different bleaching sequences.

TABLE-2

EFFECT OF PULP QUALITY & BLEACH SEQUENCES ON AOX LEVELS

Raw Material	Kappa No	Bleaching Sequence			
		CEH		OCEH	
		Cl_2 Demand kg/t pulp	AOX kg/t pulp	Chlorine Demand kg/t pulp	AOX, Kg/t pulp
Eucalyptus	19.2	60.0	4.18	30.0	1.27
Bamboo	18.2	80.0	4.63	30.0	1.32
Bagasse	14.6	45.0	17.0	0.86	

4.4 Modified Bleaching:

4.4.1 Total Chlorine Free Bleaching Process (TCF);

As indicated nearly 2 million tonnes of pulp is produced in the country & on an average it is estimated that 40,000 tonnes of chlorine is used for bleaching of pulps.

By & large the developed world has inducted ECF to contain the AOX levels. And most of these countries are planning for total elimination of chlorine compounds by switching over to TCF techniques. The main bleaching chemicals employed are molecular oxygen, hydrogen peroxide & ozone.

4.4.2 Oxygen Delignification:

The oxygen delignification which is often termed as extended delignification has been well established technology & many mills in other countries are practicing & recently some of the mills in India have started using oxygen in bleaching stage preferably called oxidative extraction stage, thereby partially substituting elemental chlorine. There are good prospects of inducing oxygen for delignification due to number of advantages from energy & environment view point. Extended delignification, oxygen delignification can substantially eliminate the chlorine based chemicals. However, the high capital inputs is one of the constraints influencing the adoption of the system to a raw material mix as well as smaller scale operation prevailing in Indian paper industry. There is a need for thorough techno-economic evaluation of prospects of introducing oxygen for delignification.

4.4.3 Hydrogen Peroxide:

Hydrogen peroxide is one of the effective bleaching reagent and has been very popular in bleaching of the mechanical pulps. Some of the newsprint mills in India have already adopted hydrogen peroxide bleaching of mechanical pulps. The following Table – 3 clearly shows the advantages of peroxide.

TABLE –3
EFFECT OF H₂O₂ ENHANCED PROCESS ON CHLORINATED ORGANICS

Parameters	No H₂O₂	With H₂O₂
2,3,7,8 – TCDD in pulp, pg/Odg	4.8	Not determined
2,3,7,8 – TCDF in pulp, pg/Odg	49.0	1.3
AOX in untreated effluent, Kg/t	4.2	3.1

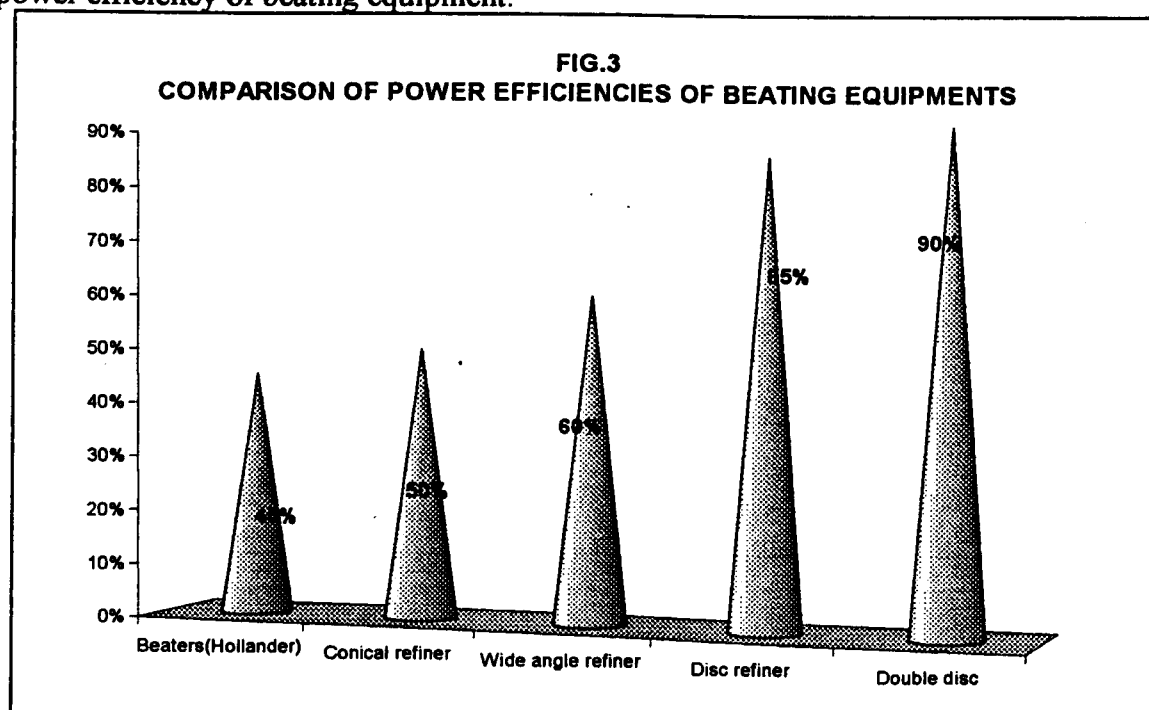
4.4.4 Ozone Bleaching:

Recently ozone has attracted the paper industry as one of the most effective bleaching agents which has already been applied on commercial scale but still the economics have not clearly emerged.

5.0 Stock Preparation & Paper Making:

5.1 Stock Preparation:

Stock preparation is a major power consuming area in paper making process. Electrical energy requirement is influenced by the fibre properties. Larger the fibre more will be the refining energy. The energy efficiency during refining is influenced by the type of refining equipment. Most of the mills, earlier using beaters, conical and/or wide angle refiners are switching over to energy efficient Disc refiners. Besides energy intensiveness, the old fashion mechanical equipments for beating required low consistency and thereby high water consumption. Fig.3- shows the comparison of power efficiency of beating equipment.



5.1.1 Dyes and Additives:

In some specific grades of paper production, toxic dyes like Rhodamine, Metanil yellow etc. are used in paper manufacture and normally the white water goes to the effluent whenever there is a change in the product. Today instruments and dye retention chemicals are available where the consumption of dyes can be substantially reduced.

5.1.2 Double Dilution System:

Approximately 80% of the water and as high as 40% of the fibres and fillers leaving the slice are drawn into the white water trays. A huge quantity of water and stock is forced through the centricleaners at a considerable head, resulting in a considerable energy consumption. We can reduce the energy consumption if by some system by

which the quantity of dilute stock fed to the cleaners is reduced. This can be done easily by by-passing a part of the already cleaned stock through the centricleaners. In this system the overflow from the machine head box, the secondary screen accepts and a part of the wire tray water, which have already cleaned, by-pass the centricleaner systems. Adoption of double dilution system would enable a mill to save 20-24% in power demand than that of a single dilution system.

5.2 High Consistency Web Formation:

The consistency of head box stock is normally 0.5-1% i.e. dilution of 100-200 times. This low consistency means that much energy is consumed in pumping stock and water in the paper machine's short circulation. In developed countries the energy consumed in short circulation pumping is about 10% of the paper industry's total electricity consumption. If the stock consistency in the short circulation is raised – say to 1.5 to 2.5%, the volume of water pumped round the short circulation would be reduced by 50-75%. The energy saving effect would thus be considerable. The smaller amount of water involved in high consistency paper making would also be beneficial in terms of the dewatering capacity of the wire section.

5.3 New Pressing Technologies:

Over 97% of the total water is removed in the forming section, about 2% in the press section and the remaining 0.5-1% in the dryer section. Yet the forming section is responsible for 10-14% of the total dewatering costs, while the press section accounts for 18-25% and the dryer section for the remaining 61-72%. So it is more economical to remove water in press section than dryer section. A typical 3-5% increase in dryness in the last press will provide a 10-15% reduction in steam consumption in dryer section. Today extended nips and hot pressing can be effectively used to save energy or to increase the dryness in press section. The amount of water removed in press section is directly proportional to applied nip pressure and width and inversely proportional to the viscosity of the water in the nip. In this process by increasing the temperature of web in press section, viscosity of water reduces considerable and high water removal takes place and resulting high off press dryness.

5.4 Alkaline Papermaking:

The alkaline papermaking is a recent development over the acid papermaking. The alkaline papermaking is carried out at pH of 7.0 – 9.0 while the acid papermaking is carried out at pH of 4.0 – 5.0 with rosin.

The acid papermaking suffer due to uncontrolled deposition of hydrophobes (rosin-alum-complex) on the cellulose leading to pitch problem in paper machine. Alkaline paper making is the current trend in USA and EUROPE. Today more than 75% of writing & printing manufactured is by alkaline paper making in these countries. However, the key factor affecting successful conversion to alkaline papermaking are:

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- Pulp quality and paper making
- Paper machine & configuration
- Press section
- Dryers
- Size press
- Quality of alkaline chemicals (namely sizing agents, retention aids, PCC aid biocides)
- Delivery system for new wet end additives
- Technical level of mill and operating personnel.

Alkaline papermaking is yet to come up for non-woody raw materials. Moreover, availability of high purity CaCO_3 is also a constraint for Indian Mills.

5.5 Paper Machine:

Mills abroad are using twin wire formers where as the mills in India use conventional fourdrinier system with few exceptions, where some of the mills are using twin wire formers for newsprint & writing and printing grades of paper. Some mills are also in a stage of going for twin wire formers. The advantages of twin wire formers are:

- Effective removal of water from the pulp stock coming out of head box reduces the load on the press & dryers and this helps in reducing the steam consumption.
- High productivity
- Less space
- Can take up the weaker pulps also.

6.0 Chemical Recovery:

The black liquor today constitutes 6th major fuel in the world behind natural fossil fuels like gasoline, coal, oil, natural gas, etc and notable advances have been made in improving the efficiency of evaporator & chemical recovery boiler with respect to pollution control & safety precautions.

Today, a modern chemical recovery has eliminated direct contact evaporator. **Ultra high solids** black liquor firing takes place at concentration beyond 75-80%. Thereby gaseous emissions are considerably reduced, which otherwise are controlled efficiently by using electrostatic precipitator & also by desulphurizing the flue gases to prevent SO_x and NO_x emissions. The earlier smoke Stack chemical recovery units can today be seen that almost no smoke is coming out of the stacks due to highly controlled operating techniques. Today a modern chemical recovery boiler is producing steam at

pressure more than 100 Kg./Cm². The lime sludge has been recycled completely and even the mills are generating bioenergy from the condensate rich in BOD & COD.

For good chemical recovery operation following factors are important:

- A relatively high concentration of free alkali in weak black liquor (8 gpl);
- A high initial weak black liquor composition;
- A short storage time for black liquor;
- As constant as possible temperature profile throughout the evaporation;
- A low fiber content of black liquor through installation of a fiber filter before evaporation;
- A good periodical cleaning of evaporators;
- Avoiding Direct Contact Evaporator Kraft Black Liquor;
- Proper design of recovery boiler, proper distribution of liquor droplets;
- Proper soot blowing;
- Effective ESP;
- Suitable Smelt Spout Design;
- Use of good quality lime in causticizing;

There are several improvements possible in this section like:-

- Desilication of black liquor for bamboo, straws & reed based mill,
- Thermal treatment of black liquor
- High solids evaporation,
- Use of free flow falling film evaporators and
- Improved recovery boiler design,
- Recycle of foul condensate after stripping.

All these are expected to reduce the pollution load from recovery section. New recovery systems like Gasification, Fluidized Bed Combustion and DARS need to be considered, where ever appropriate. Small pulp mills which do not have chemical recovery system must plan installation of the system either independently or in places where there are cluster of such mills can think of combined chemical recovery system.

6.1 Chemical Recovery- Issues in Indian Mills:

Chemical Recovery is a major step in chemical pulp mill to control discharges. The processing involves dilute black liquor concentration, combustion, causticization, lime mud reburning. The parameters, which influence the operation of this section include the initial weak black liquor concentration, black liquor composition, silica content, calorific value, combustion, characteristics, volatiles, foaming tendency, viscosity, residual active alkali level. Many Indian mills do not have lime mud reburning recovery section resulting in high solid waste disposal.

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Compared with wood pulping, the pulping of bamboo and agro residues results in:-

- high silica containing black liquor, besides agro black liquors show-
- low solids concentration of weak black liquor
- highly viscous black liquor

With exception of five of agro based mills equipped with chemical recovery system, rest of the 106 no. of mills are without recovery mainly due to

- high capital cost
- low scale of operation
- chemical recovery technology is not fully known.

As a result significant pollution load in terms of high COD is being discharged, which requires high cost towards end of pipe treatment and also results in huge resource drainage due to discharge of organics and chemicals.

It is therefore required that from the experience of agro based mills those equipped with chemical recovery system and based on conventional chemical recovery and fluidized bed reactor technology, (FBRT) the other mills should start thinking in similar direction as chemical recovery is the best option for black liquor handling.

The only drawback of FBRT is that it is not as energy efficient as conventional soda recovery boiler, the operation of the plant demands lower concentration of potassium & chlorides below 0.5%, since no steam is generated in FBR. This drawback is however compensated by way of savings in the capital cost, capability to handle silica rich black liquor.

Table-4 gives a comparative account of various chemical recovery technologies.

TABLE - 4

COMPARATIVE ACCOUNTS OF VARIOUS CHEMICAL RECOVERY TECHNOLOGIES

Particulars	Advantages	Limitations	Optimum Pulp Mill Capacity
Conventional Chemical Recovery System	<ul style="list-style-type: none"> -Higher thermal efficiency -High alkali recovery -Lesser support fuel-mainly during start ups -Wide & long experience for all raw materials -Indigenous know-how available 	<ul style="list-style-type: none"> -High capital investment -Complicated operation -Possibilities of smelt water explosions 	100 tpd
Modified Conventional Chemical Recovery System of ENMAS	<ul style="list-style-type: none"> -Reliable and adequate instrumentation for better process control, safety and high recovery efficiency -High boiler operating pressure and temperature for better reliability and co-generation -Insulation of lower furnace refractory for faster black liquor drying & free flow of smelt. -Variable frequency drive for ID fan for better energy efficiency. 	<ul style="list-style-type: none"> -The technology will be capital intensive when desilication and thermal treatment are incorporated 	80-100
Enders Process	<ul style="list-style-type: none"> -Low black liquor solids firing. -Safe operation as no smelt formation. -Low capital investment 	<ul style="list-style-type: none"> -Low alkali recovery -low heat recovery -normally generates hot water -less tolerable to Non-process Elements like chlorides and potassium 	60 tpd
Modified Conventional chemical Recovery Process (TMTL).	<ul style="list-style-type: none"> -Avoidance of Chemical deposits in boilers. -Autogenous combustion of black liquor at 54% of black liquor solids. 	<ul style="list-style-type: none"> -Same as conventional however no provision has been made for silica rich black liquors, specially from raw based. 	60 tpd.

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		-High Auxiliary Fuel Requirement.	
Epytek Process	-High thermal efficiency -Quick start-up shut down -Parallel or counter current running of black liquor in the different effects.	-Expensive evaporators & combustion furnace -No provision for desilication for silica rich black liquors	>80 tpd
DARS Process	-Low black liquor solids firing. -Safe operation as no smelt formation -Low capital investment -Autocausticization	Experience in equipment design & furnace lining to handle high density iron ore. Sustained availability of high quality iron ore	>50 tpd
MKCR Process	-Low black liquor solids concentration is sufficient -Rice husk as low cost renewable fuel -No smelt formation -Recovery of silica in marketable form -Possibilities of lime sludge reburning	-No commercial installation so far Large number of steps involved.	Proposed for 50 tpd & high
Black Liquor Gasification	-System operates at low black liquor solids concentration -Adaptable for silica rich black liquors	-No installation for agro based black liquor so far Complicated pulse combustion reactor.	Proposed for 50 tpd & high

6.2 Control of Gaseous Emissions:

Digester house operations viz. Liquor preparation, cooking and chemical recovery, involve discharge of particulates, boiler also releases particles. Air pollution control is generally exercised through provision of the following types of equipment.

- a) **Cyclones:** Cylindrically shaped collectors in which the particles collect at the bottom. The clean gas rises from the center and is released from the top. The cyclone collector is simple and reliable with a low initial cost and easy maintenance.
- b) **Dynamic Precipitators:** The centrifugal fan and a dust collector, in which the centrifugal force of the fan pushes the particles to the tips of the blades from where they are drawn off in a concentrated stream;
- c) **Electrostatic precipitators:** Operate on the basis of electrostatic attraction, and can be used for dry particulates or fumes, as well as mists; and

- d) **Fume Incineration:** Utilised for the collection and oxidation of blow gases and digester release gases. Direct flame incineration is used when the waste materials are capable of combustion on mixing with air. If the stream does not contain enough combustibles to support a flame, thermal incineration is utilised by using gas burners.

7.0 Utility:

The boilers are coal fired types. 11% of the total capacity has been installed during the past five years. These are mainly fluidised bed boilers. Prior to 1975, the capacity was 20 tph of steam generation at 20-30 kg/cm² pressure and 380°C to 400°C temperature and thermal efficiency was between 50% to 60%. After 1975, the steam generation capacity increased to 25-27 tph at 40 kg/cm² pressure and 400°C to 480°C temperature. The thermal efficiency has gone upto 70-80%.

The improvement in the steam generation capacity at higher pressure will reduce the burden on fossil fuels through fuels flexibility employing unconventional fuels like rice husk, pith, bark etc. in fluid bed boiler which will substantially reduce the solid waste pollution.

8.0 Machinery & Equipment:

Manufacture of paper, requires utilization of wide range of plant and equipment from raw material storage/transportation to packing and handling of the finished product apart from the actual process machinery for paper making. In addition various auxiliary items such as steam boilers, power generation equipment, effluent treatment equipment etc. are also required. India has now developed capability to manufacture and supply of almost entire range of equipment for paper industry including pulping plant, stock preparation, paper machine, steam and power generation equipment, chemical recovery equipment etc. The estimated share of equipment in a project is 60-70% and extent of indigenisation is about 70%. Almost all the manufactures have collaboration with reputed international firms.

CHAPTER - II

STATUS OF TECHNOLOGY IN MEDIUM & SMALL PAPER MILLS

I. Infrastructure of Small and Medium Sized Mills:

Most of the mills falling in this category came in existence by acquiring second hand machinery and equipments from other countries where the scale of operation was increased considerable. As a consequence, the machinery and the process followed in this sector of paper industry are not efficient and are not in position to produce quality papers for Competition in Global Market. The industry required modernisation in most of the sections and some mills have already started expansion programs to improve overall efficiency.

Manufacturing Process:

1.0 The Raw Material Collection & Preparation:

There is not much of the improvement in raw material collection & preparation practices especially with regards to cleanliness of the raw material. Due to lack of efficient equipments, significant proportions of extraneous material like sand, grit, metals, grains, husk etc. enter the pulping process. As a result, there is additional burden on cleaning systems which have to be operated at lower capacities.

2.0 Pulping:

The agro based mills use predominanatly spherical digesters of varying capacities in multiple numbers. Some of the mills use as many as 8-10 digesters. Number of mills have not taken to the insulation of the digesters & often the temperature, maintained are somewhere between 140-150°C, requiring longer cooking cycles of 6-10 hrs, thus consuming more steam and electrical energy.

Most of the units do not have the blowing, system, which ultimately results in spillage of black liquor in to open streams. The waste paper based mills normally use hydropulper for producing the pulp and lot of contrary, coming with the waste is also going along with the pulp which becomes major problem in screening operations. Since, no mill practices organised deinking method, so the pulp from the waste paper is not ideal for producing quality papers.

3.0 Washing System:

The washing of pulps in these category of mills is an obsolete technique, normally employing poacher followed by one or two drum washers. Often the drum washer do

not work at required efficiency levels for lack of required pulp mat formation thereby reducing the vacuums. So the mills in variably use high quantities of water up to 40-60 m³ in washing stage/ton of pulp for the purpose of extraction of the black liquor and mills producing unbleached varieties do not wash properly and carry over of the black liquor gets extended to the paper making process. Segregation of black liquor in the concentrated form before washing is an essential step, the mills have to follow up for proper management of pollution problems.

4.0 Screening & Cleaning Systems:

Due to low temperature & low chemical dosage, nearly 10-15% of the uncooked material enters as reject with lot of extraneous material coming with the pulp. Battery of cleaning systems are employed requiring huge amount of water. In the waste paper based mills, the screening & cleaning have often been a problem since contraries like plastic pieces, resins are difficult to get rid off and sometimes appear as transparent spots on paper.

5.0 Bleaching:

Only few mills are producing bleached varieties and bleaching is done in an unconventional way by using either elemental chlorine or calcium hypochlorite. Since, these mills do not have chemical recovery, the mills produce pulps of high kappa number and chlorine consumption figures are reported as high as 20-25% in some mills. Required temperature, consistency for effective utilization of bleaching chemicals are not maintained.

6.0 Stock Preparation & Paper Making:

These mills are using old machinery & equipments. The stock preparation equipments like conical refiners, wide angle refiners operating at low consistency require high energy inputs without giving the desired results. The paper machines are not ideally designed for straws and bagasse and as a result the required efficiency is not obtained.

Energy Status of Medium \Small Paper Mills:

In general, small and medium paper mills use energy in two forms namely electricity and steam. The entire power requirements are met from state grid power and steam from their own generation in boilers using primary fuel as coal and secondary fuels such as bagasse pith, rice husk etc. There are differences in specific energy consumption in forest based large mills and medium/small mills. It is mainly due to the differences in raw material usage, mill design, choice in selection of suitable process and process equipment, product mix and capacity utilization. The capacity utilization in these mills is only 50-60%, where as in large mills it is around 90%. The second hand imported machines being used by these mills are not only outdated but are

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designed for long fibred chemical pulps. These machines when operated on unconventional raw materials give lower production and hence the efficiency of the machines is much below their rated capacities. The Table – 1 shows the specific energy consumption in Indian mills:

TABLE – 1

SPECIFIC ENERGY CONSUMPTION IN LARGE AND SMALL PAPER MILLS

Particulars	Small Paper Mills		Large Paper Mills	
	Without Recovery		With Recovery	
	1	2	1	2
Production t/day	25	45	210	130
Power KWh/t	1208	1215	1500	1390
Steam tonne/tonne	7.0	8.0	12.0	11.0

There is no co-generation system in small mills due to high investment costs. On this account mills are loosing significantly on electricity. Further, they are more prone to power failures and cuts leading to reduced capacity utilization which in turn leads to increased specific energy consumption. **The various measure which can be taken by these mills are:** shown in the following Table – 2. The table summarises some of the In-plant control measures which results in improved fibre recovery, specific water consumption and reduced process consumption.

TABLE - 2

Sl. No.	Measures	Benefits
1.	Reuse of waste water in the process	Water consumption reduction by 60% (From 200m ₃ /T to 80m ₃ /T.)
2.	Replacing poacher washing by Screw Press for black liquor extraction.	<ul style="list-style-type: none"> - Reduction in water consumption from 80m₃/T. to 11m₃/t. - Opening up opportunities for black liquor utilisation by anaerobically/aerobic and / or chemical recovery (combined chemical recovery)
3.	Installation of squeezing crusher to take the black liquor from cooked hessian pulp	<ul style="list-style-type: none"> - Water consumption reduction by 15% - Beating time has been reduced from 3 hrs. to 30 minutes only. - Power consumption – reduced by 35% (From 330 units/T of hessian

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		pulp to 200 units/T of pulp).
4.	Floating washing instead of wire washing.	- Reduction in water consumption by 75%.
5.	Husk/coal dust fired boiler to be replaced by Bagasse fired boiler.	- Steam cost reduction by 50% - Electricity cost reduction by 30%. - Quantity of unburnt reduced considerably.
6.	Installation of Hailey's screen	- Fibre recovery of 5%.
7.	Modification in paper machine by Double Felting System.	- Reduced paper breakage and increased production capacity by 15-20%.
9.	Installation of high velocity hood in the paper machine drying section.	- Production increase by 10% and reduction in energy consumption
10.	Increase in wire mesh size in the depithier from 8 mm to 10 mm.	- Chemical cost in the digester reduced by 10% - Pith recovery goes up from 20% to 30% - Pith with high calorific value can be sold. - Net savings Rs. 3.25 lacs/annum for the unit.

II Utilization of Recycled Fibers:

Utilization of waste paper for papermaking is ecologically desirable in countries with a shortage of other fibre raw materials thus preventing over-cutting of forests.

1.0 Ecological Impact:

Replacing virgin pulp with waste paper also decreases the energy demand and total pollution load from these mills, as shown in Fig.-1-3. Although there is a great variation in literature references to what extent energy can be saved by the use of waste paper (10-80%).

Over the past few years, the environmental factor has become increasingly important and the paper industry has responded to this development by offering more recycled fibre based, so called environmentally friendly products.

The introduction of these issues into the paper industry and the enforcement of mandatory measures in developed countries are creating strong pressure to recover and utilise more waste paper, and thus ease the landfill problems.

At 50% waste paper composition, pollution load in terms of SS, BOD, and COD can be reduced by about 35-50%. Further about 25% reduction in steam generation. Air pollution is in significant as there is no other significant source of air emissions from the pulp and paper machine sections. It also reduces the problems of handling and disposal of solid waste generated from the pulp mill and also helps in preserving the land ecology with less water consumption.

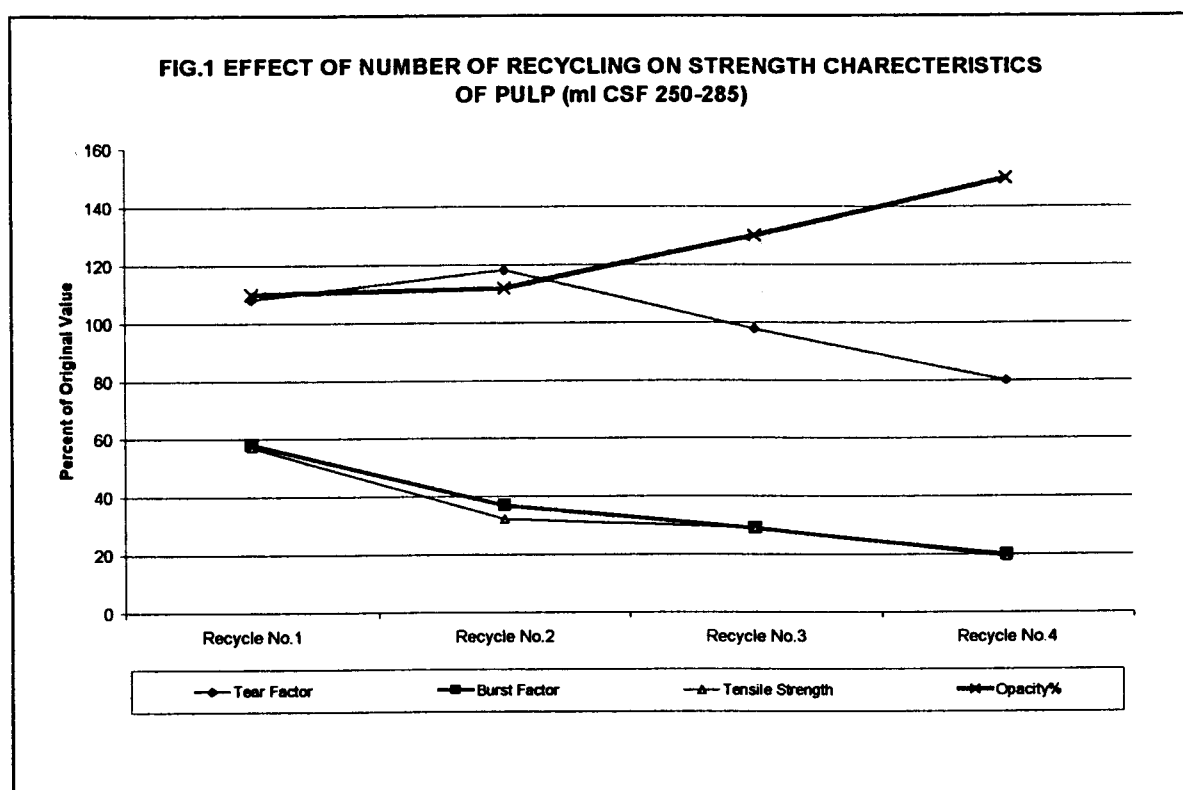


FIG. 2 REDUCTION IN INPUT MATERIALS & WASTE GENERATION

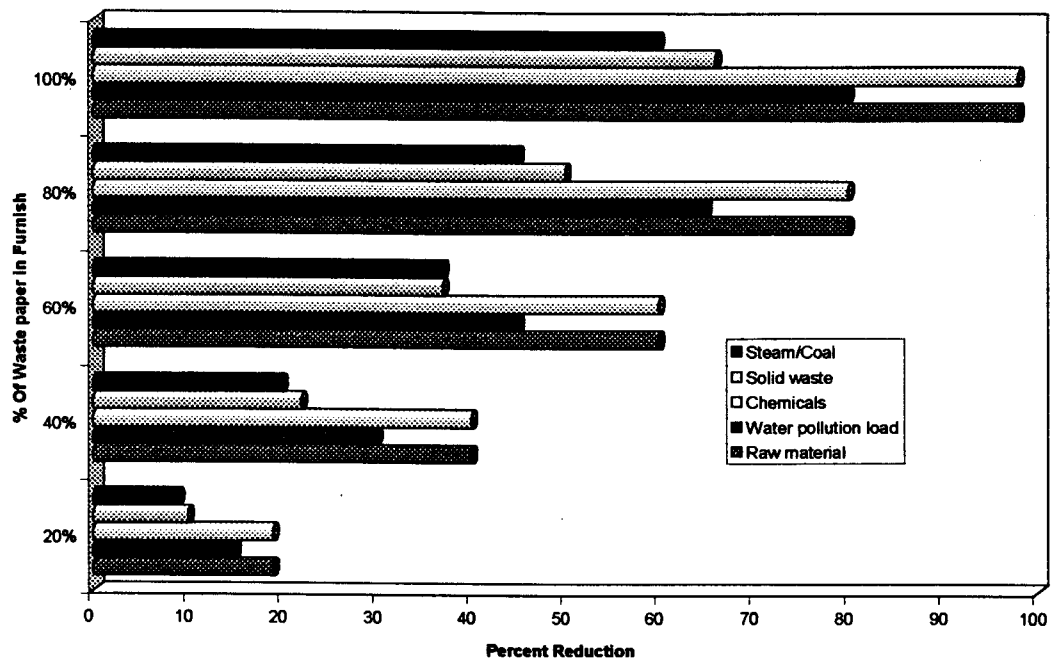
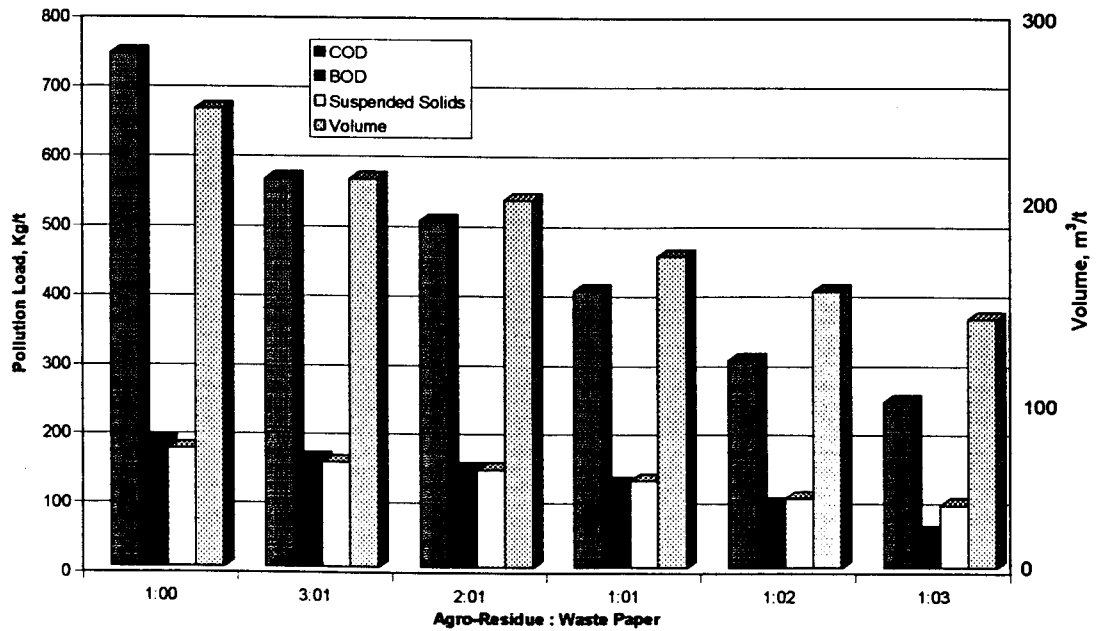


FIG. 3 REDUCTION IN POLLUTION LOAD WITH INCREASED USE OF WASTE PAPER



CHAPTER –III

DISCHARGE CHARACTERISTICS, MAGNITUDE OF POLLUTION AND IMPACT ON ECOLOGY & ENVIRONMENT

I. INTRODUCTION:

The Indian paper industry is in general an intensive industry. Its fibrous, power, water, steam & chemical demands are heavy than those of developed countries, therefore the final discharges to the environment are also considerable. The potential pollutants from a pulp and paper mill fall into three principal categories as under:

- (i) Water effluents
- (ii) Gases & particulates
- (iii) Solid Waste

II. MAGNITUDE OF POLLUTION FROM LARGE PAPER MILLS

A. Water Effluents:

- a) Suspended solids including bark particles, fibre, pigments, dirt and the like
- b) Dissolved colloidal organics like hemicelluloses, sugars, lignin, compounds, alcohols, turpentine, sizing agents, adhesives like starch and synthetics which create BOD load.
- c) Color bodies, primarily lignin compounds and dyes.
- d) Dissolved inorganic such as NaOH, Na₂SO₄, bleach chemicals etc.
- e) Thermal loads
- f) Micro-organisms such as coliform group.
- g) Toxic chemicals like chloro-organics and dyes having **acute** (short term) & **chronic** (long term) toxicity effects.

B. Gases & Particulates:

• Gases:

- a.) Malodorous sulphur gases such as mercaptans and H₂S released from various stages in kraft pulping and recovery processes
- b) Oxides of sulphur from power plants, kraft recovery furnace and lime

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- c) kiln
Steam since it can be hazardous when visibility is impaired / lime kilns containing particulate matters.

- **Particulates:**

- a.) Fly ash from coal fired power boilers
- b.) Chemical particles primarily Na and Ca based
- c.) Char from bark burners

C Solid Wastes:

- a) Sludges from primary and secondary treatment and causticization plant in recovery section
- b) Solids such as grit, bark and other mill wastes.
- c) Ash from coal fired boilers

D Environmental Impact:

Basic resources which are likely to be influenced due to pulp & paper manufacturing activities are:

Physical Component:

- Metrology, air quality surface water, hydrology, ground water, topography and geology, soil material.

Ecological Effects:

- An ecological effect is shown by the departure from an original equilibrium of the ecosystem, i.e. a disturbance of the equilibrium.

A Short-term effects are reversible within a period of up to a few weeks if the discharges cease.

- Substances with high acute toxicity
- Light absorbing Substances
- Substances causing avoidance reactions.
- pH – Changing substances
- Substances stimulating heterotrophic growth.

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B Intermediate effects are reversible with in a year.

C Long term effects are irreversible for up to a year or more.

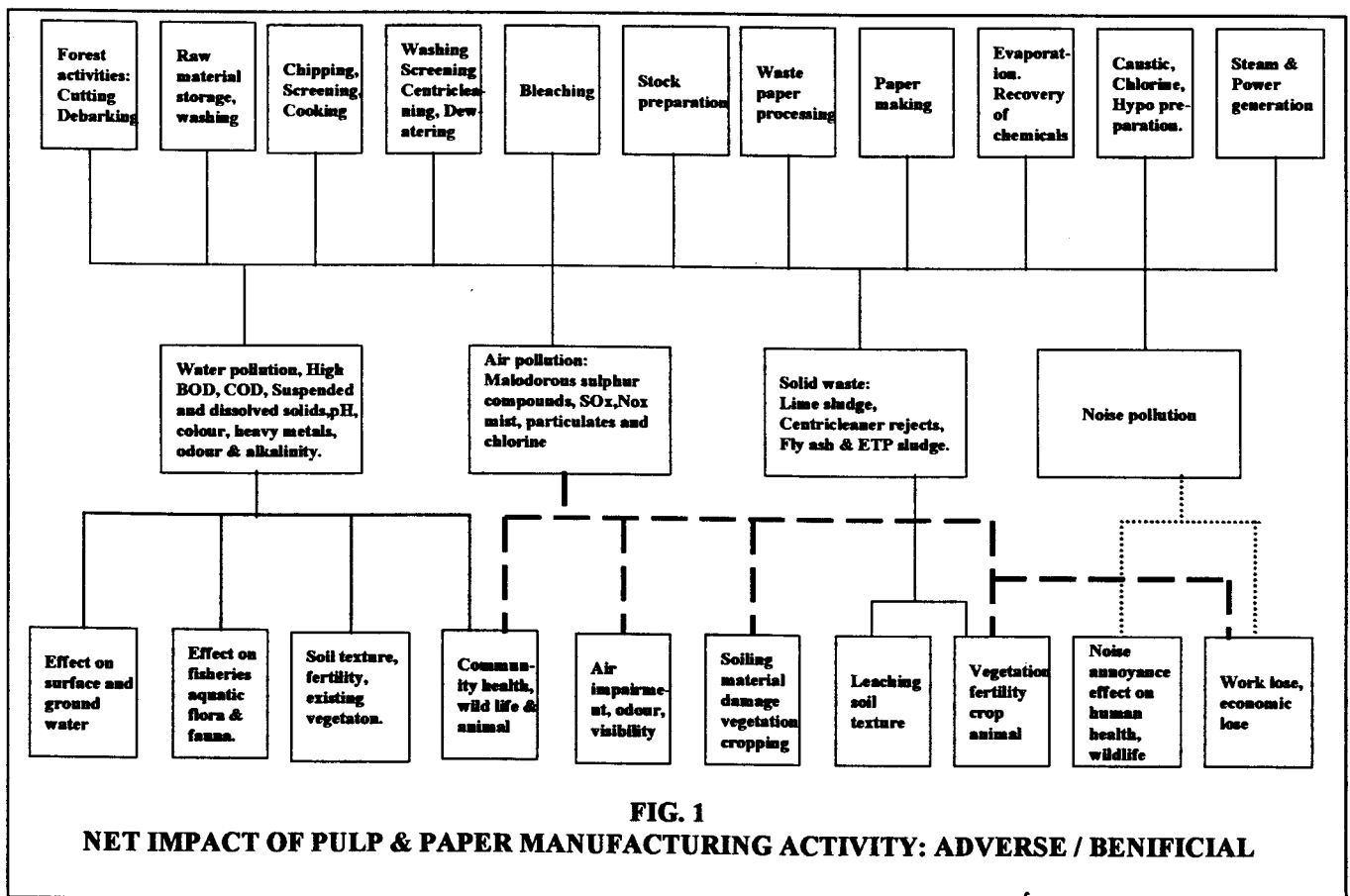
- Fibres and other settleable solids
- Substances which show a tendency to bioaccumulate in fish and other aquatic organisms
- Substances which through their accumulation may cause chronic toxicity or interfere with reproduction.
- Bad taste or odour
- Substances stimulating algal growth and thereby cause eutrophication
- Persistent substances which have genotoxic and/or other chroniczally toxic properties and thereby present risks to consumer of drinking water contaminated by these substances.

Human Use Values:

A. Land use, transportation, water supply, medical facilities, industries and other occupation, fisheries animal, husbandry fisheries, gross economic yield etc.

B. Impact on socio economic & cultural aspects, economic yield.

The net impact of pulp & paper manufacturing activities are shown in Fig.-1



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I. WATER EFFLUENTS:

The manufacture of paper requires a large volume of water, the bulk of which is released as waste water. The process water discharged from paper mills contains bark, wood debris, fibres and lignin and their decomposition products; clay, certain minerals, resins, phenolics, starch, etc.; unsaturated fatty terpenes, metal oxides and other suspended solids.

Apart from dissolved toxic pollutants which have an adverse effect on fish, aquatic fauna and flora, public health, a major problem associated with water pollution is the "Biochemical Oxygen Demand" or BOD. BOD is the amount of oxygen required to biologically oxidise the water contaminants to carbon dioxide and is thus a measure of the suspended, colloidal or dissolved organics. Related to the BOD and often measured instead, is the COD, or chemical oxygen demand, which is a measure of the amount of oxygen required to chemically oxidise the contaminants to carbon dioxide. The value of the COD is higher than that of the BOD, since use of strong oxidants is involved in forcing many substances to react, which do not react to biological micro-organisms. The COD value represents almost 100 percent of the total organics present.

The discharge of suspended solids (SS) has a deleterious effect on the receiving streams as anaerobic decomposition of these solids consumes dissolved oxygen in the over-laying water and thus adversely affects the aquatic life.

Effluents also impart colour and turbidity to the streams. Discharge of untreated waste water therefore creates serious water pollution problems resulting in damage to aquatic life, deterioration in water quality and increase in the cost of water treatment.

1.0 Sources of Discharge & Intensity of Pollution:

During the manufacture of pulp & paper the waste water is released from the following sections:

SOURCES		DISCHARGE	INTENSITY OF POLLUTION
a.	Fibrous raw material washing	Washing of raw materials	Small volume with least pollutants.
b.	Digester House	Leaks and spills of black liquor & gland cooling water	Small volume but high concentration of pollutants
c.	Pulp washing	The final wash often referred as brown stock wash or unbleached wash	Small volume and large quantity of pollutant
d.	Centricleaners	Rejects containing high concentration of fibres and girt or sand.	Small quantity but high suspended solids.

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e.	Pulp bleaching	Wastewater from chlorination stage having low pH and high chlorilignins, from caustic extraction stage with dark brown colour & high pH as well as chlorolignins from hypochlorite stage	Very large volume with high concentration of pollutants. About 60-65% of waste water is contributed from this section. The effluents is shown to contain toxic as chloroorganic compounds.
f.	Paper machine	Often referred to as white water.	Volume depending upon the extent of recycling. It contains maximum suspended solids like fibers, fines and small quantity of dissolved pollutants.
g.	Chemical Recovery	Spills of black liquor in the evaporators, foul condensates and washings of the causticiser.	Small volumes, but high pollutants.

2.0 Characteristics Of Combined Waste Water From Large Mills:

The combined waste water characteristics alongwith the various pollution load is given in Table-1 as under for large integrated paper mill & Newsprint mill.

TABLE-1

CHARACTERISTICS OF COMBINED WASTE WATER FROM LARGE MILLS:

Parameter	Large Paper Mills Range (Average)	Newsprint Mill Average
Flow, m ³ /t paper	167-281 (220)	-
PH	6.6 – 10	-
S.S., mg./l	620-1120 (764)	-
COD, mg/l	840-1660 (1118)	-
BOD ₅ , mg/l	240-380 (295)	-
Color, mg/l PCU	300-655	-
Sodium Absorption Ratio	2.0-5.3 (3.5)	-
Pollution Load, Kg/t paper		
Suspended solids	160	188
COD	213	313
BOD	87	150
AOX	1-3.0 (< 0.5- Rayon grade)	< 0.5

2.1 Pulp Bleaching & Toxicity of Effluents:

Bleach plant effluents are highly coloured due to the presence of chromophoric groups in the degraded chlorolignin products. The coloured compounds reduce light penetration into the water affecting photosynthesis which in turn reduces the primary productivity in the eco-system. Colour of the bleach plant effluent varies with its pH.

Total organically bound chlorine (TOCI) measurement is proposed for monitoring the pollution load, particularly chloro-organics. This test measures total organically bound chlorine, but does not measure the highly volatile chlorinated organics such as chloroform.

AOX, adsorbable organic halide has been accepted as a quantitative measure of organic chlorine compounds formed during bleaching process. Regulations to limit the discharge of AOX has been set in many countries. Total organic halides (TOX) and AOX for bleached kraft mill effluents are same. AOX is easy to analyse. Adsorption of the halides on active carbon directly from the water solution is done. The carbon is washed and carbon is burnt to detect HCl. AOX values are different from TOCI.

AOX = (1.2 to 2) times TOCI

The following empirical relationship exist between the charge of chlorine containing bleach chemicals, as active chlorine and AOX value for bleach plant effluent.

$$AOX = K \left(Cl_2 + \frac{ClO_2}{5} + \frac{Hypo}{2} \right)$$

K varies between 0.11 – 0.14 for kraft pulps.

2.1.1 Toxicity of Bleach Plant Effluents:

The toxicity of bleach plant effluents has been an area of extensive study. During chloro-bleaching of pulp the lignin micro molecules are degraded to non volatile smaller species which have harmful effects on the environment and human health. The toxicity, bioaccumulation potential and persistence of these non volatile low molecular weight chloro-organics discharged from bleached kraft pulp mill alter the quality of receiving water.

Mutagenicity is a measure of the ability of the effluent to induce genetic mutation and is commonly measured with Amestest.

Another aspect of water quality assessment is related to the aesthetic and social parameters of taste and odour. The chlorinated phenolics present in bleached kraft mill effluent (BKME) have often been implicated as taste and odour causing compounds in surface water and potable water.

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Approximately 300 low molar mass compounds have been identified in BKME, but these only account for about 10% of TOCl. The remainder are high molar mass compounds which are generally too large to pass through cell membrane and hence are probably biologically inactive.

The main generic types of chlorinated organic compounds are as shown in Table-2

TABLE – 2

CHLORINATED ORGANIC COMPOUNDS IN BLEACHED KRAFT MILL EFFLUENT

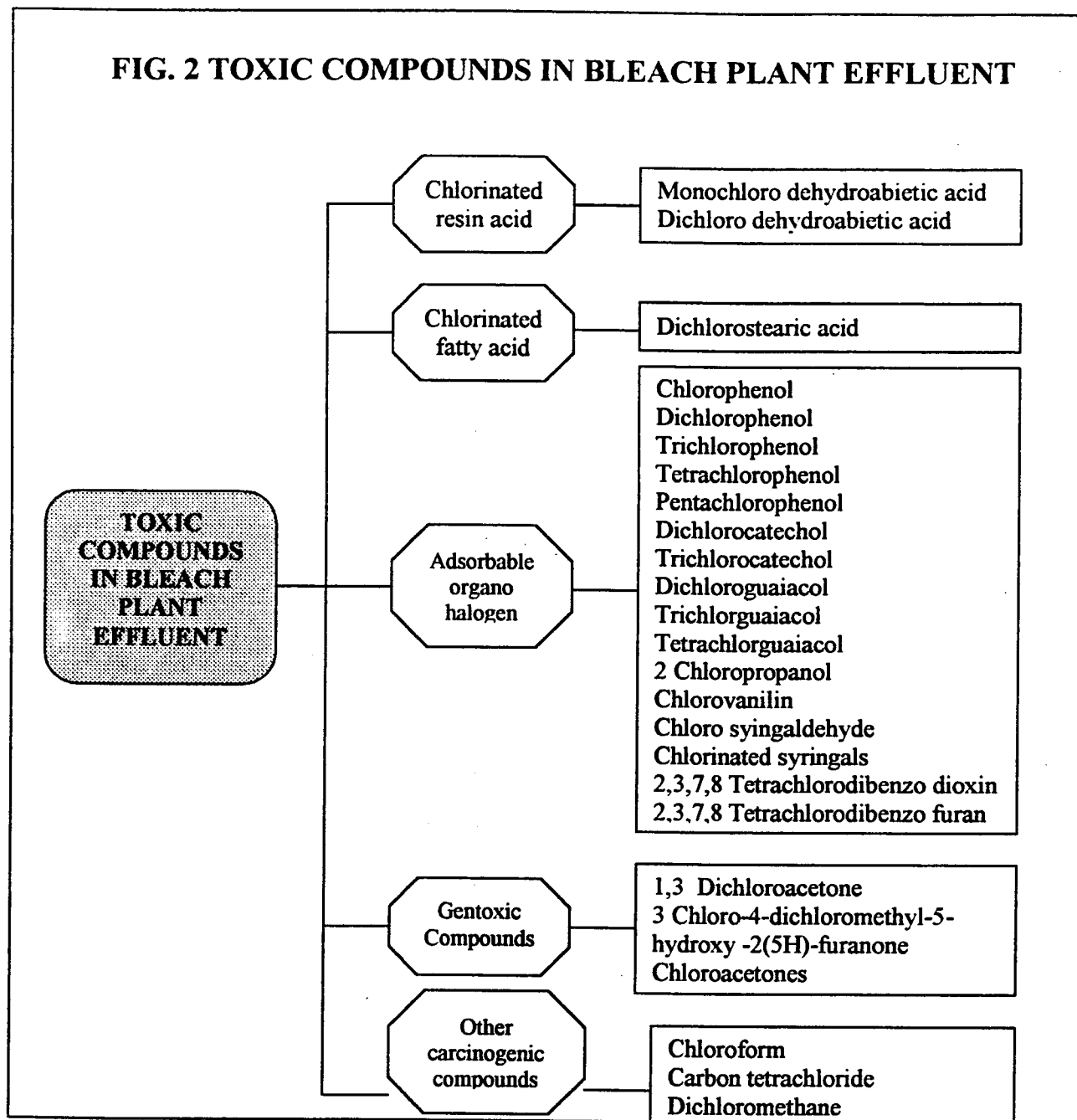
Type	No. of Varieties	Amounts
Chlorinated acids	40 types	Upto 50 g/t pulp
Chlorinated Phenolics	40 types	Upto 100 g/t pulp
Chlorinated Aldehydes and lactones	45 types	Upto 500 g/t pulp
Chlorinated Hydrocarbons	45 types	-
Chlorinated others	20 types	-
Chlorinated High molar mass Compounds	-	Upto 4 kg/t pulp

The compounds responsible for toxicity of C-stage effluents are mainly chlorophenols with catechols and quinones playing lesser role. **Fig.- 2** shows the list of toxic compounds in bleach plant effluents. About 90% of toxicity of E stage effluents is due to acids (mono and dichloro abietic acid and epoxy stearic acid). Non chlorinated acids such as resin and fatty acids also have toxic properties. Traditional bleach plant liquor was also found to be dependent on the residual lignin content of the pulp or the kappa number of the pulp.

Free chlorine in effluent is toxic to fish. Hypochlorite, chlorine and chlorate are also toxic compounds, but normally these are in low concentrations in bleach plant effluents. Chlorates can be transformed to chlorite in some organism such as algae or bacteria and can poison them.

Sublethal effects of bleach plant effluents are probably of more importance to environment than lethal effects. Sublethal effects show the longterm effects and lethal acculation of toxic substances in the organism. **Lethal concentrations** seldom occur when there is adequate dilution of the effluent. The concentration is above 0.1-0.2 of 96 hour LC 50 values. The lethal and sublethal effects are esseentially due to low molecular weight chloro lignin compounds and chlorinated resin and fatty acids.

FIG. 2 TOXIC COMPOUNDS IN BLEACH PLANT EFFLUENT



TOXICITY LEVELS OF DIOXIN : Besides 12 highly toxic chloro organic compounds

Agency/Country	Risk dose	Toxic/health effect
EPA	6.4×10^{-3} *	Cancer
Germany	1.0*	Cancer/reproductive
Netherlands	4.0*	Cancer
Switzerland	A**	
FDA	5.7×10^{-2}	Cancer

* Pico grams of 2,3,7,8 TCDD per Kg. Of body weight per day.

** (A) the studies have not established the safety levels.

2.1.2 Bio-degradation of Chlorinated Phenolic Compounds:

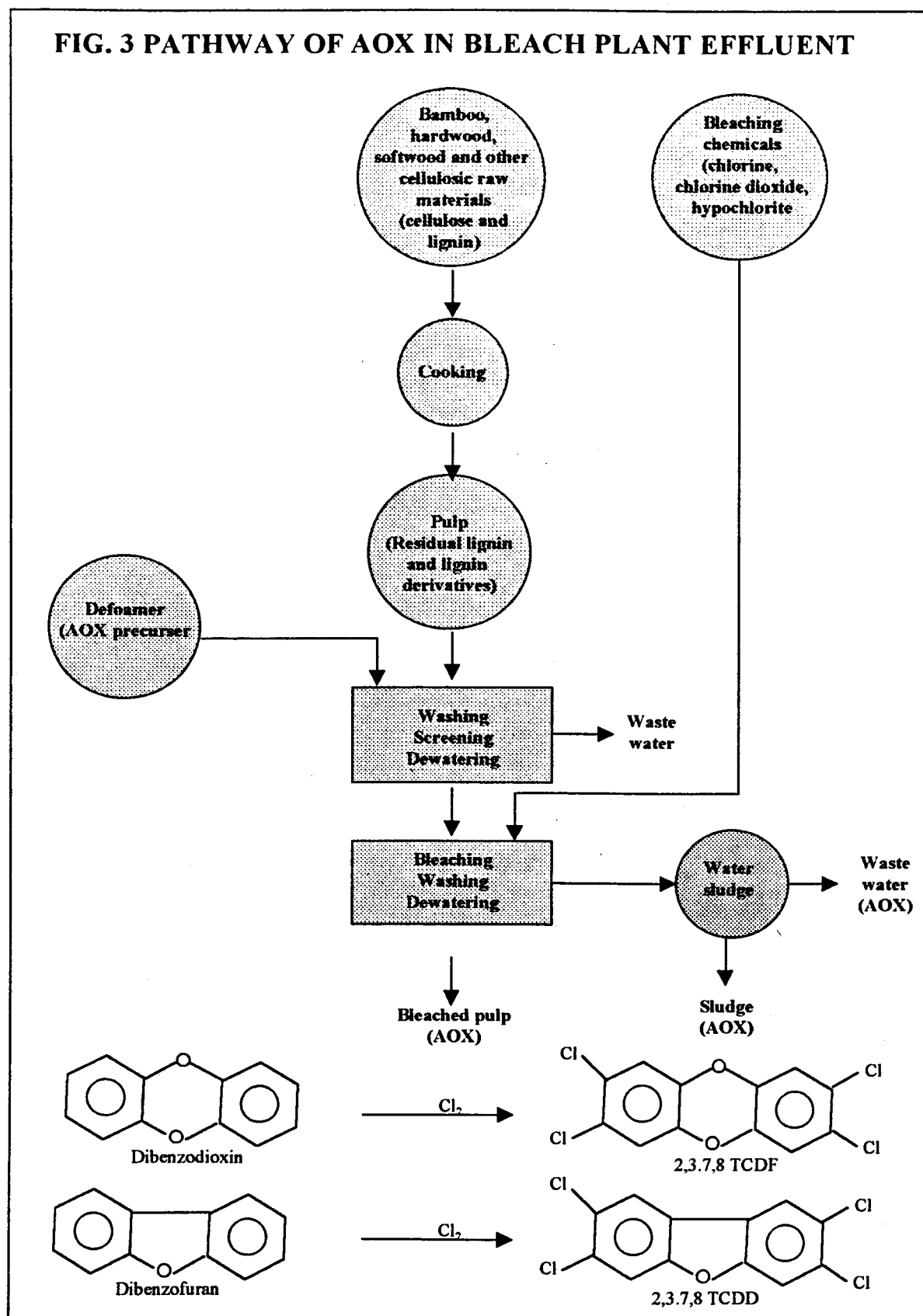
Chlorinated phenols are generally biologically degraded. Biodegradation rate decreases as the level of chlorine substitution rises. However, the more highly substituted chlorophenols are often unstable at high pH and in ultraviolet light.

Trichlorinated phenols are susceptible for bioaccumulation in fish at particular pH. It decreases with increasing pH. Mutagenicity is mainly due to chloro acetones, chlorinated furans and 2 chlorophenol. Most of mutagenic compounds are unstable at high pH and in sea water.

Chlorinated Dioxins and chlorinated furans are two particular forms of chlorinated organic compounds which are in public focus. Dioxins (more correctly – Dibenao – dioxin) are a group of organic compounds composed of two benzene rings connected by two carbon-oxygen-carbon bonds opposite one another. Furans (Dibenzo-furans) are composed of two benzene rings connected by carbon – carbon bond and carbon – oxygen-carbon bond.

The toxicity vary with concentration of Chlorinated phenolic compounds in the effluents. A small increase in the concentration of phenolic compounds can change the toxicity level from 0-100%. Chlorinated phenolic compounds are the most toxic compounds in bleach plant effluents. Fig.-3 Shows the pathway of AOX formulation in bleach plant effluent.

FIG. 3 PATHWAY OF AOX IN BLEACH PLANT EFFLUENT



3.0 Solid Waste:

Solid waste constitutes a complex problem in the industry due to the varying nature and enormity of the wastes generated. The main sources of solid wastes are:

- The raw material handling/preparation.
- The effluent sludge from the combined mills effluent treatment plant.
- Fly ash from coal fired boilers and fines in the coal.
- Coal cinders from coal fired boilers.
- Lime sludge from the chemical recovery plant.
- Hypo mud from the hypo plant.

Table -3 shows the quantity of solid waste from large paper mills with chemical recovery & based on forest & non-wood based mills.

Table-3**SOLID WASTE FROM LARGE PAPER MILLS.**

Organic Waste	Quantity
Raw material preparation (wood, bamboo dust)	0.1
Pulp Mill Rejects	0.01
Paper Machine Cleaner rejects	0.1
ETP sludge	0.2
Inorganic Waste (t/t of paper)	
Ash (under + fly ash) From boilers	0.8
Lime sludge & guts Recovery + black liquor preparation)	0.7*
Total	1.91

* In mills with lime kiln, the lime sludge quantity varies from 0.07- 0.28, depending on the quantity of silica.

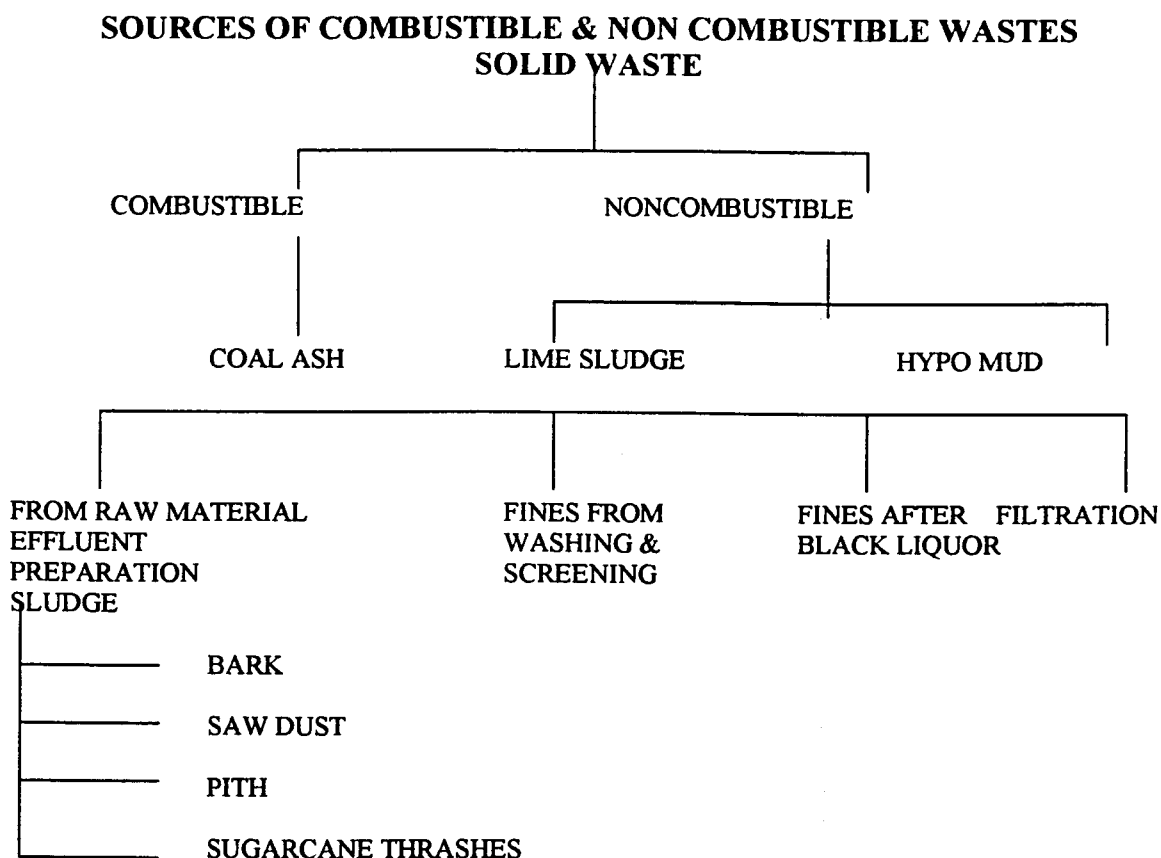
3.1 Types of Solid Wastes:

It is estimated that the magnitude of solid waste generation in totality is almost closer to the total paper produced in the country. The entire solid waste can be broadly categorised as:

- (i) Combustible
- (ii) Non-combustible waste

The source of solid waste is illustrated in Fig .4 ,which shows the details of combustible & non-combustible solid waste.

FIG.-4



Only few mills recycle the combustible waste as fuel and majority of the mills do not recycle and dispose it as land fill. The magnitude of non-combustible waste is primarily due to fly ash from the boiler and lime sludge in mills which are not reburning the lime sludge due to silica problems.

3.2 The Effect of Lime Sludge on Ground Water Contamination:

The lime sludge disposed carry significant proportion of Na which gets leached during rainy season and gets contaminated with the ground water & subsequently increases the salinity of the surrounding soil.

4.0 Air Pollution:

The major sources of air emissions are through discharge of gaseous and particulate emissions. The large paper mills based on kraft process are major source of gaseous

pollution causing obnoxious odor problem, because of the presence of Reduced Sulphur Compounds.

Table-4 shows the main emission of reduced sulphur compounds from sulphate pulping process, which are the major sources of odor problem.

TABLE – 4.0
MAIN EMISSIONS OF REDUCED SULPHUR COMPOUNDS FROM
SULPHATE PULPING PROCESS

Emission Source	H ₂ S	Emission rate, kgs/t 90		
		MM* CH ₃ SH	DMS* CH ₃ SCH ₃	DMDS CH ₃ SSCH ₃
Digester, batch	0-0.15	0-1.3	0.05-3.3	0.05-2.0
Digester, continuous washing	0-0.1	0.5-1	0.05-0.5	0.05-0.4
Evaporation	0.05-1.5	0.05-0.8	0.05-1.0	0.05-1.0
Recovery furnace (with DCE)	0-2.5	0-2	0-1	0.03
Smelt dissolving tank	0-1.0	0-0.08	0-0.5	0.03

- MM-Methyl mercaptan. DMS – Dimethyl sulphide. DMDS – Dimethyl Disulphide.

Source : UNEP, Pulp & paper , 1981.

The gaseous stack emission & fugitive gas emission is shown in Table-5.0 & 6.0

TABLE-5
STATUS OF STACK EMISSION FROM PULP AND PAPER INDUSTRY:

Sl. No	Particulars	Particulate matter, mg/Nm ³	Sulfur Dioxide, mg/Nm ³	Nitrogen oxides mg/nm ³	Hydrogen sulfide mg/Nm ³
1.	Coal fired boilers	100-1500	50-300	2-50	-
2.	Oil fired boilers	120-160	0.5-10	0.5-15	
2.	Recovery boilers	50-300	10-225	0.5-10	0.5-125.0
3.	Lime kiln stack	30-150	10-25	125-300	

Limits:

1. SPM = 150 mg/Nm³
2. H₂S = 10 mg/Nm³

ECOLOGICAL & ENVIRONMENTAL FACTORS IN PAPER INDUSTRY**TABLE-6****FUGITIVE EMISSIONS AND AMBIENT AIR QUALITY IN INDIAN PULP AND PAPER MILLS**

Sl. No.	Particulars	Suspended Particulate Matter, $\mu\text{g}/\text{m}^3$	Sulfur Dioxide, $\mu\text{g}/\text{m}^3$	Nitrogen oxides $\mu\text{g}/\text{m}^3$	Hydrogen Sulfide $\mu\text{g}/\text{m}^3$	Chlorine $\mu\text{g}/\text{m}^3$
1.	Chipping/depithing operations	500-1800	0-30	0-75	-	-
2.	Coal yard	800-1500	15-110	2.5-25	-	-
3.	Boiler house, coal fired boiler (shop Floor)	1000-2500	0.5-110	0-125	-	-
4.	Boiler house, recovery boiler (shop floor)	300-3000	5-75	0-75	0.5-75	-
5.	Causticizing plant (Shop floor)	1500-3300	0-5	0-0.5	25-35	-
6.	Bleach liquor preparation (Shop floor)	135-235	0-2.5	0-0.5	25-35	-
7.	Bleach washers pulp (Shop Floor)	125-15	0.5-5.5	0-2	-	0.25-75.3
8.	Upwind	80-300	0.5-35	0-10	0-0.05	-
9.	Downwind	100-400	0.5-40	0-10	0.01-0.5	-

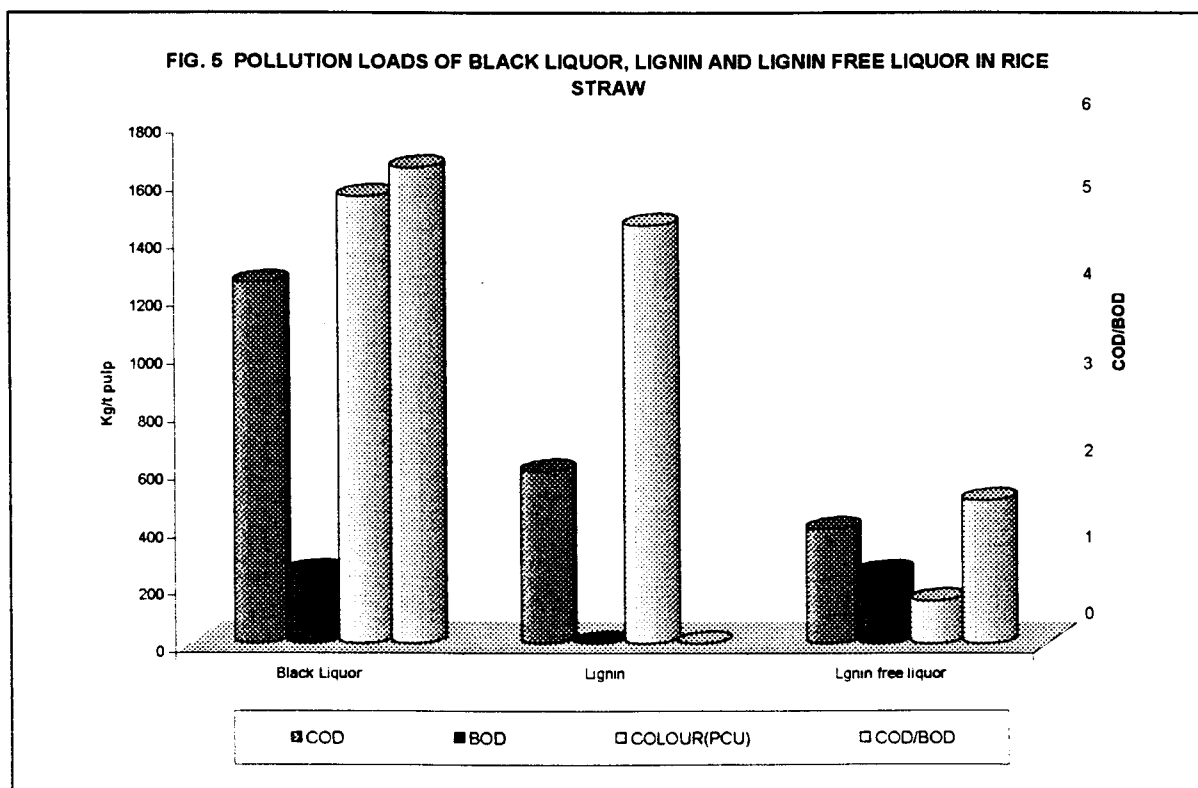
LIMITS: **SPM** = **500/200/100** **(Industrial/Mixed use/Sensitive)**
 SO₂ = **120/80/30**
 NO_x = **120/80/30**

III. MAGNITUDE OF POLLUTION & DISCHARGE CHARACTERISTICS IN MEDIUM & SMALL PAPER MILLS

1. Water Pollution:

This chapter describes the pollution load of agro based paper mills without chemical recovery and small waste paper based mills. In absence of chemical recovery systems in small and most of medium sized paper mills based on agricultural waste, huge amount of energy and chemical rich biomass are discharged as waste products, aggravating the normal pollution loads already caused by paper mills. The pollution from a agro based mill is almost 3 times more than a mill integrated with chemical recovery as shown in Table-. However, the waste paper based mills are not significant contributor of pollution.

The primary reason for heavy pollution in small agro based mills is discharge of spent pulping liquors carrying high proportion of organic matter. Fig-5.. indicates the different loads in black liquor, lignin and lignin free effluent in straw black liquors. The lignin present in the black liquor is almost non-biodegradable. There is a wide variation in the volume and composition of waste waters generated in different mills, even through making same varieties of paper employing similar raw materials and process.





MAGNITUDE OF POLLUTION FROM CHEMICAL PULP MILL WITH & WITHOUT RECOVERY

Particulars	Mill chemical recovery with	Mill chemical recovery without	Waste paper based mill
COD,Kg/t	480	1100	70
BOD, Kg/t	90	225	20
Color, Kg/t as PCU	150	1200	White
Suspended solids,Kg/t	100	900	150
Flow.m3/t	220	252	107
AOX, Kg/t pulp	3.0-5.0		-

2. Air Pollution:

These mills may not have serious air pollution problems, since they do not use sulphur compounds in pulping. Further these mills only generate steam for the process and do not have captive power. However, certain amount of malodorous organic compounds are released into the atmosphere during pulping. At times, chlorine leakage from plants affects the life of the workers. The nature and extent of pollution created by these mills have not yet been investigated.

However, most of these mills are equipped with package boilers without adequate control systems as a result the fuel – air mixture is not controlled properly and consequently gaseous emissions also carry carbon mono oxide and carbon dioxide levels more than the levels per tonne of steam. The particulate emissions are also on higher side with excessive use of air and no intermediate equipments to control the particulate emissions.

3. Solid Waste Pollution

Although, the paper industry generates large amount of solid waste, but in case of small mills the magnitude is much lesser than integrated mills. The magnitude of solid wastes in these mills is shown in Table – 8.

TABLE – 8

SOLID WASTE GENERATION IN PAPER MILLS

Waste Sources	Kg. Dry Solid/Tonne Paper	
	Medium/Small Paper Mills	
Raw material handling	210	Straws
Preparation	550	Bagasse
Power plant/boiler ash*	1300	
Waste Water Treatment Plant		
Primary sludge	116	-
Secondary sludge**	105	-
Total	1731	(2071)
% organic solids	25	(35)
% Inorganic solids	275	(65)

Status of Compliance of Regulatory Standards in Medium & Small Paper Mills:

Although Central & State Pollution Control Boards have laid regulatory standards for discharge of various pollutants. But as far as these medium & small mills are concerned, which have low level of technology, it seems to be rather difficult task to accomplish the specified norms with the available infrastructure of the mills.

CHAPTER-IV

POLLUTION CONTROL PRACTICES IN INDIAN PAPER MILLS & ADVANCED END-OF-PIPE TREATMENT TECHNIQUES

1.0 Techniques for Improved Environment Management:

Besides internal measures to reduce the pollution load, various external treatments are required for reduced discharge emission of water, air & land pollutants in to the eco-system. The common methods employed by the paper industry world wide & those being practiced in Indian mills for water treatment are shown in Table-9.

TABLE – 9.
VARIOUS BIOLOGICAL WASTE WATER TREATMENT PRACTICES

Treatment Method	Area requirement	Load range kg/m³	H.R.T.*	BOD₅ Reduction
Stabilization	Very Large	0.055-0.01	10 days	50-80%
Aerated lagoon	Large	0.04-0.2	5-10 days	50-90%
Activated Sludge	Small	1-5 BOD ₅ /m ³ /d	-	40-75%
Anaerobic	Small	10-20Kg COD/m ³ /d	4-12	70-80%
Land disposal	Large area	200 lb/acre/day 225 kg/ha/day	-	90-95%

* Hydraulic Retention Time

1.1 Pre-Treatment:

Coarse solids such as pieces of wood, stones, sand, etc., are generally removed by screening as a part of pre-treatment; excessive acid or alkaline content can also be neutralized at this stage by suitable treatment since pH adjustment (6 to 9) is an integral part of the system.

1.2 Primary Treatment

The most common method used by the paper industry to separate suspended matter is sedimentation by settling ponds or clarifies. Clarifies are basins to which the effluent is discharged, where the solids settle due to gravity at the bottom, while the water rises to the surface and is withdrawn. Rakes or scrapers are employed to remove the settled sludge. Only the BOD related to organic and fibrous material is removed during primary treatment.

1.3 Secondary Treatment:

The main purpose of treatment is to remove soluble BOD using biological water treatment process. This generally consists of the following stages:

- (i) **Lagoons** – which is the most common method of treating pulp and paper effluents. These may be simple oxidation ponds utilizing micro-organisms and sedimentation, anaerobic lagoons utilizing methane bacteria stabilizing the organic matter, or aerated lagoons having a mechanical aeration device to increase the supply of oxygen to the bacteria for achieving stabilization, and
- (ii) **Activated Sludge Ponds** – the activated sludge process utilizes flocculent micro-organisms for treatment of organic matter which can be separated by physical means. It employs an aeration tank in which waste water and micro-organisms are aerated and the resultant mixed liquor flows into a clarifier, where the biological mass (referred to as the activated sludge) is separated.

Generally, a combination of one or more stages of these methods are employed, before the waste waters are discharged into rivers.

Present waste water treatment practices employing biological method is given in **Table 9** below. Each process has its own advantages and disadvantages. These biological treatment processes are capable of reducing BOD, COD, foaming tendency and dispersed turbidity. However only slight reduction in TOC and color is achieved. It is therefore, essential to provide other suitable methods for treatment of bleach plant effluents.

1.4 Tertiary Treatment:

This is primarily meant to recycle water through methods such as filtration, chemical oxidation, ultrafiltration, electrodialysis and reverse osmosis, and is generally not employed by Indian Paper Mills.

All the standard operations used for waste water treatment can be successfully adopted for treating paper mill waste waters, and technology for suspended solids and BOD is available. Removal of color constitutes a more difficult problem as special methods involving high cost are called for.

It is generally recognised that more attention has to be paid to internal preventive measures applied to the manufacturing process in the mill itself, reducing the pollutant load to be handled. One of the important measures of internal control is to reduce the amount of raw water used in the manufacturing process by recycling, so that the volume of effluent is lowered substantially, with consequent saving in investment on external treatment plants, and reduction in the quantity of pollutants discharged. Utilisation of waste water for irrigation has also been found feasible, after removal of settleable solids.

Some units such as Seshasayee Pulp & Paper and Tamil Nadu Newsprint, both use the waste water for irrigation of nearby areas.

1.5 Optimum Requirements for Effluent Treatment Practices:

- ❖ The methods should provide sufficient treatment efficiency towards the removal of various categories of pollutants
- ❖ Stability of the system for interruptions in power supply, peak loads, feed interruptions and/or for toxic pollutants should be high.
- ❖ The flexibility of the process should be high, with respect to the scale at which it is applied, possibilities for future expansions, possibilities to improve the efficiency.
- ❖ The system should be simple in operation, maintenance and control, so that a good performance does not depend on the presence of highly skilled operators and engineers continuously.
- ❖ The land requirement should be low specially when little land is available and/or the price of land is high.
- ❖ The number of required (different) process steps should be as low as possible.
- ❖ The life time of the system should be long.
- ❖ The application of the system should not suffer from any serious sludge disposal problems.
- ❖ The application of the system should not be accompanied with malodour nuisance problem etc.
- ❖ The system should offer good possibilities to come to recovery of useful by-products to irrigation and fertilization.

1.6 Advanced Effluent Treatment Technologies:

Most of the larger mills have sufficient Primary & Secondary Treatment Systems operating. However, certain modifications in Secondary Treatment Methods are as described.

1.6.1 Pure Oxygen Systems – Activated Treatment Plants:

Recently pure oxygen has been used in the activated sludge process as a substitute for air. This method is especially suitable when treating high strength wastes. By using oxygen instead of air higher dissolved oxygen levels can be maintained in the waste water and a highly aerobic biological mass that flocculates well will be produced.

A pure oxygen system can be highly loaded and is less susceptible to organic shock loads often associated with the treatment of high strength wastes.

Different pure oxygen systems exist. The most common of these is the UNOX system. In this system the waste water is treated in three or four tanks in series. The tanks are

covered and the flow of waste water and oxygen gas proceeds in the same direction. The sludge is separated in conventional gravity clarifier.

Observations:

Pure oxygen activated sludge system is generally attractive only when the pulp mill has a process oxygen demand such as oxygen delignification and oxygen bleaching.

Plastic media tricking filters, rotating biological contactors, and aerobic contact filters are other biological systems gaining attention.

1.6.2 Anaerobic Method of Treatment:

Methods generally used by mills for treatment of effluents is conventional aerobic treatment, mostly activated sludge process. However, the investment and operational cost are quite high, which makes it difficult for the mills to maintain such system. In this regard, anaerobic treatment has several economic advantages over aerobic systems.

The advantages are:

Lower production of biosolids per unit of organics (i.e. BOD₅, COD, TOC) removed. Typically 1/3 to 1/5 that of aerobic treatment of similar substrates.

- ❖ Lower requirements of nutrients (Nitrogen & phosphorous) as a consequence of less biosolids produced. (1: 2-5:0.5) (BOD:N:P)
- ❖ No aeration is required, significantly reducing over-all treatment system power requirements.
- ❖ The methane produced is recoverable as a by-product fuel source, typically 0.35 m³/Kg COD removed.
- ❖ Anaerobic system can be left dormant without feed for long periods of time (12 to 18 months) without severe deterioration in biomass properties and can be brought back into operation at normal treatment efficiency within very short periods of time (typically 1 to 3 days).
- ❖ Very high active biomass densities (1% to 3% and higher) can be achieved under favourable conditions in anaerobic reactors.
- ❖ Increased resistance to organic shock loads.
- ❖ Less capital investment.
- ❖ Less land requirement.

1.6.2.1 Different Configurations of Anaerobic System:

Following configurations of anaerobic systems are under operation and their market share is as under:

➤ UASB process	61%
➤ Contact process	12%
➤ Anaerobic filter	6%
➤ Hybrid reactor	4%
➤ Expanded granular sludge bed reactor	3%
➤ Fluidized bed reactor	2%
➤ Fixed film reactor	2%
➤ Anaerobic lagoon	7%
➤ Others	3%

1.6.2.2 Suitability Of Anaerobic Systems in Large Mills:

In context to larger mills, the system finds its application in effluent streams from raw material pretreatments, prehydrolysate of rayon grade pulps and condensates. The system works perfectly for treating non inhibitory pulp and paper mill waste water rich in readily biodegradable organic matter (carbohydrate & organic acids) such as paper recycling waste waters, mechanical & thermo-mechanical pulping effluents.

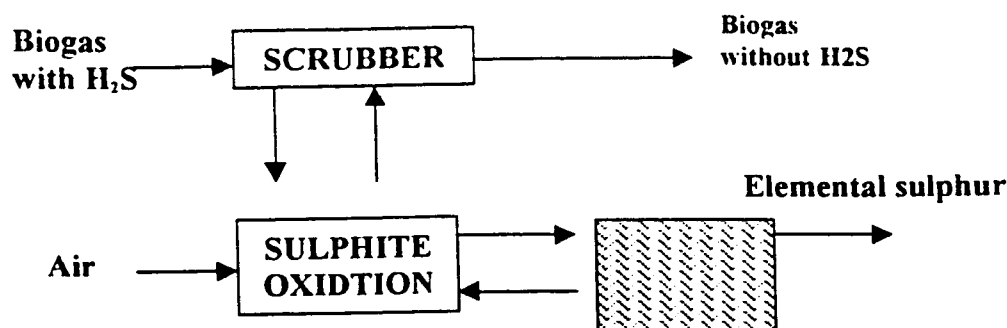
1.6.2.3 New Emerging Technology for Anaerobic Waste Water System in Presence of Sulphur:

The major energy sources for the methane producing bacteria are acetic acid and hydrogen, which are produced by acid-forming bacteria and acetogenic bacteria. Sulphate reducing bacteria use the same energy sources and thus compete with the methane producing bacteria, although several other organic compounds can be used as well, sulphate reducing bacteria are however from energy view point. The toxic effect of sulphurous compounds increases in the following order:

Sulphate < thiosulphate < sulphite < sulphide.

Biological Scrubbing of H₂S: The biological scrubbing of H₂S from biogas Is a revolutionary invention for purification of biogas containing H₂S. The process is known as Thio Scrubber process, which is based on biological oxidation of sulfide into elementary sulfur. The process is even more distinguishing since the sulfur is not formed in the scrubber itself but outside the scrubber. The removal efficiency of H₂S in thioscrubbing process is more than 99% and process and process increase the operational safety (particularly no risk of blockage), - a clear advantage compared to conventional methods. Fig. 7

ECOLOGICAL & ENVIRONMENTAL FACTORS IN PAPER INDUSTRY



1.6.2.4 High Rate Biomethanation For The Mills Having Capacity Below 50 Tpd:

Anaerobic system has shown to be successfully working in agro based mills with their effluents rich in black liquor. In absence of chemical recovery, one of the alternative could be to treat the black liquor in an anaerobic digestion system. In the last two decades, the anaerobic system has become popular primarily due to its ability to handle effluents with high concentration of COD & generation of methane as a source of energy. For the small pulp and paper mills (below 50 tpd), either waste paper based or agro based, the system is excellent as it biodegrades the organic mass and at the same time generates energy which can be used in the pulp & paper mill for power generation. Another alternative is, the mills which have very small capacity (5 to 10 tpd), if located at the close proximity of each other can have a combined effluent treatment plant based on high rate biomethanation, where the effluent after the primary clarification at the mill site can be brought to the common treatment plant.

The performance of the biomethanation plant in one of the agro based mill in India is shown as under.

Parameters	Designed	Achieved
No. of Bioreactors	Two	-
Volume of each reactor, m ³	2623	-
Volumetric loading rate kg COD/m ³ /d	10.0	12.0
COD recudtion, %	55-60	45-50
BOD re	70-75	80-82
duction, %		
Biogas production, m ³ /d	8500	11000-11500
Equivalent rice husk, t/d	17-18	22-24

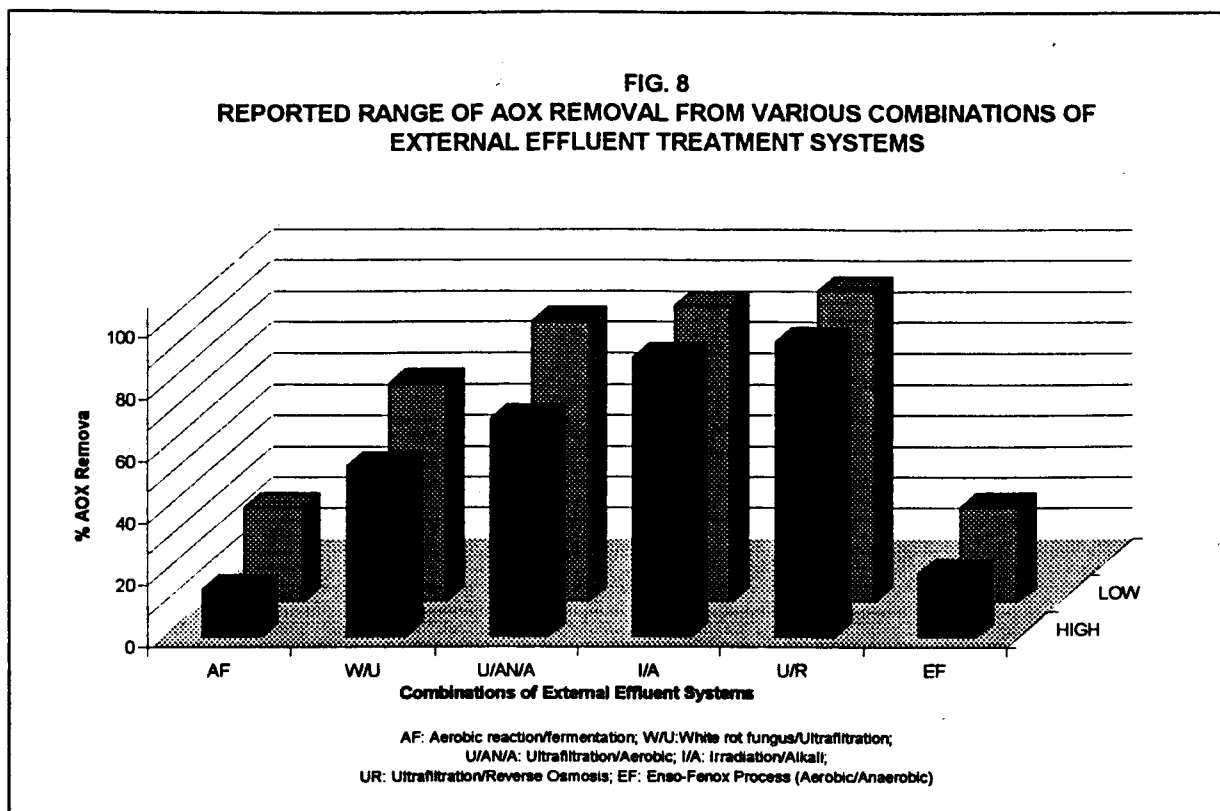
1.7 Waste Water Treatment Containing Deinking Effluents:

The PACT system – developed by Zimpro and Dupont Co. and marketed world-wide by Zimpro- combines biological treatment and physical adsorption in a single process step. Powdered activated carbon, much finer than carbon granules and having much

greater adsorptive capacity, is added to conventional biological treatment. The biological micro-organisms break down the biodegradable contaminants, while the non-biodegradable (toxic in particular) are adsorbed by the carbon.

1.8 Detoxification of Bleach Plant Effluents

Fig- 8 shows the reported range of AOX removal from various combinations of External effluent treatment system.



2.0 Solid Waste Handling:

Environmental & economic characteristics have led to reexamination of traditional solid waste management practices. Now solid waste is generally recognised as both a major problem and an underutilized resource for material & energy. Soon the standard legislations are expected for discharge of solid waste. The incineration technique has been adopted to utilise the combustible waste generated from effluent treatment sludges, raw material preparation plant & other organic waste by few of the mills in their fluidised bed boilers.

Non-combustible waste like fly ash is being used for brick making in few of the mills and work on utilisation of lime sludge in the cement manufacture is being carried out at CPPRI in association with National Council of Cement & Building Materials, Ballabgarh.

2.1 Utilization Of Solid Waste:

2.1.1 Organic Waste:

After looking into the characterisation data, the following possible utilization of organic wastes can be considered. However, a mill can adopt any of the suggested options after considering all factors like location, process, economic conditions, land availability, disposal suitability and other possible modes like those needed for agricultural use, etc. rather than following a particular way of utilisation of organic solid waste:

1. As a source of fuel.
2. As a soil conditioner for land application
3. Other utilization like conversion to
 - fodder
 - particle board
 - biogas generation
 - alcohol & industrial important chemicals by biotechnology applications.

2.1.2 Inorganic Solid Waste:

Boiler ash: Utilization of fly ash in production of different building materials.

Lime Sludge: Lime sludge containing high silica is not considered to be an economical option for lime sludge reburning. Therefore, following approaches may be considered.

- Burning to get low grade lime
- In the cement industry for partial substitute of lime stone
- As a conditioner for soil especially active one.
- Burning after desilication.

3.0 Control of Air Pollution:

3.1 Control of Particulates & Gaseous Emissions:

Gases and dust are emitted from pulp & paper mills, SO_2 , H_2S and other malodorous compounds are emitted from sulfate mills and SO_2 from sulfite mills. Small amounts of Cl_2 and ClO_2 are also emitted from bleach plants, which need to be considered with new environmental restrictions. The solid material – the particulates can be controlled by installation of electrostatic precipitators along with flue gas scrubber.

The kraft mills are highly polluting due to the presence of non condensable gases which are emitted from the digester and evaporator departments. The odorous gases from the evaporation plant are chiefly hydrogen, sulfide, methyl mercaptan and organic

sulphides (dimethyl disulfide, in addition to gases like methanol, etc.). These sulphur compounds are dissolved in the black liquor and to some extent they flash to the condensates or to the vents during evaporation.

3.2 Collection & Combustion of Non-Condensable Gases:

The collection and combustion of offensive smelt sulphur contaminants and methanol is necessary in today's pulp mill. The system is not only protective to the environment, it is also a tool to control chemical balance. Sulphur compounds are recovered in reduced form in white liquor and via SO₂ scrubbing of flue gases. Combustion occurs most effectively in a separate incinerator, developed for rapid oxidation. Condensed methanol is used to advantage as support fuel.