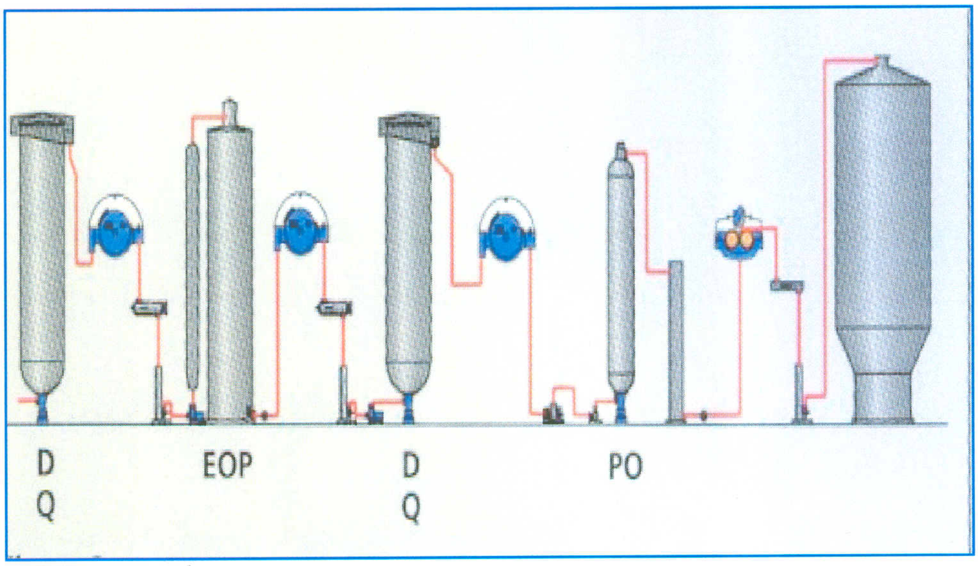
Report on

EFFICACY OF ECF AND TCF BLEACHING PROCESSES ON WHEAT STRAW, BAGASSE, BAMBOO AND EUCALYPTUS PULPS



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DEVELOPMENT COUNCIL

FOR

PULP,PAPER & ALLIED INDUSTRIES

Central Pulp and Paper Research Institute
Saharanpur-247001

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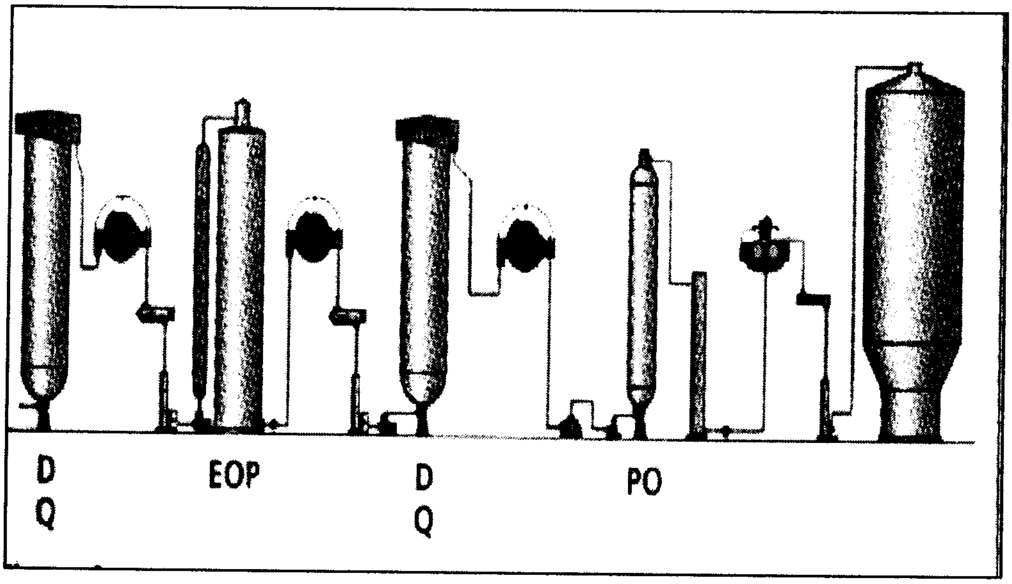

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ACKNOWLEDGEMENT

Physical Chemistry, Pulping and Bleaching Division is thankful to **Development Council for Pulp , Paper & Allied Industries** for awarding the project on "Efficacy Of ECF And TCF Bleaching Processes on Wheat Straw, Bagasse, Bamboo And Eucalyptus Pulps - Process Optimisation Studies."

We are thankful to Director, Central Pulp and Paper Research Institute, Saharanpur (U.P.) for providing guidelines for completion of this project. We are also thankful to supporting technical staff of Physical Chemistry and Pulping Bleaching Div., Stock Preparation Paper Making & Conversion Division and Engineering & Maintenance Division for their cooperation .

(Vimlesh Bist)

Scientist E-II

Head PCPB Div.

CPPRI Saharanpur

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1.0 PROPOSAL SUBMITTED TO DEVELOPMENT COUNCIL FOR PULP, PAPER & ALLIED INDUSTRIES

1.1 Project Title: Efficacy of ECF and TCF Bleaching Processes on Wheat Straw, Bagasse, Bamboo and Eucalyptus Pulps – Optimisation Studies.

1.2 Broad Area: Cleaner Production Technologies

1.3 Project Duration: 24 months

1.4 Institution/Organisation: Central Pulp & Paper Research Institute
Saharanpur – 247 001

1.5 Actual location where research project work will be carried out:
Central Pulp & Paper Research Institute, Saharanpur

1.6 Laboratory research at:
Central Pulp & Paper Research Institute, Saharanpur

1.7 Principal Investigator:

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1.8 Other Investigator (s):

i.

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Name:	Dr.Priti, S.Lal
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1.9 Name and address of persons/institutions interested in the outcome of the project:

Paper industry having bleach line operations.

1.10 Summary of the project: (Maximum 150 words)

Toxic compounds are generated to a very high level in the conventional bleaching of chemical pulps using elemental chlorine. The other bleaching chemicals like chlorine dioxide, hydrogen peroxide, oxygen, and ozone are the alternatives for the elemental chlorine, which generate significantly less or practically nil amounts of toxic compounds and hence are environmentally friendly processes. However, it is not well established about the efficacy of the ECF and TCF pulp bleaching processes on the unbleached chemical pulps of the most commonly used Indian fibrous raw materials viz. Wheat Straw, Bagasse, Bamboo and Eucalyptus. The project activities will be targeted to find suitability of ECF and TCF processes for the most commonly used Indian fibrous raw materials.

1.11 Objective:

Improvement in bleached pulp quality in terms of optical and strength properties and reduction/removal of elemental chlorine bleaching process for improved quality of liquid discharges.

1.12 Practical/Scientific Utility:

Product quality improvement along with cleaner production technology will give an edge in the global competitiveness.

1.13 Review of research conducted/being conducted on the subject in India and abroad:

Research work done and in progress abroad:

C.P.P.R.I. has carried out extensive work in the area of pulping and bleaching and has carried out technical survey of the mills in the big and medium sector using conventional forest based fibrous raw materials and agro based fibrous raw materials and analysed the current technological status of these mills. We are aware of the needs of these mills and could come up with some feasible solutions.

1.14 Technical Programme:

i. Literature survey in the area of ECF and TCF processes.
ii. Pulping of different raw materials to various residual lignin levels.
iii. Assessment of optimum kappa for conventional and agro based raw materials using batch and continuous digesters respectively.
iv. Trials of ECF and TCF processes on conventional agro based fiber pulps.
v. Recommendations and report preparation.

1.15 Facilities:

- Laboratory pulping digesters.
- Quantum Mixer
- Controlled water baths.
- UV-VIS Spectrophotometer
- Flame Photometer
- AA Spectrophotometer
- Light and Electron Microscopes
- Fiber Quality Analyser

Apart from the above mentioned equipment, the Institute is fully equipped with all the infrastructure facilities for testing and measurement of optical and strength properties and to conduct various pulping and bleaching trials.

1.16 Time schedule of activities giving milestone (time period – 24 months)

Literature survey in the area of ECF and TCF processes.	2 Month
Pulping of different raw materials to various residual lignin levels.	6 Month
Assessment of optimum kappa for conventional and agro based raw materials using batch and continuous digesters respectively.	15 Month
Trials of ECF and TCF processes on conventional agro based fiber pulps.	22 Month
Recommendations and report preparation.	24 Month

1.17 Total cost of the project: Rs. 35.00 Lacs

Recurring (Rs. in Lacs)

PARTICULARS	Rs. In Lacs
Manpower	6.00*
Consumables & Contingencies	5.00
Travel & Others	5.00
Total	10.00

* Manpower cost will be met from the CESS base level support

Nonrecurring (Rs. in Lacs)

PARTICULARS	Rs. In Lacs
Equipment	15.00

Budget Estimation (Rs. in Lacs)

Sl.No.	Particulars	Recurring	Nonrecurring	Total
1.	CPPRI	10.00	15.00	25.00

Total (Rs. in Lacs) : 25.00 (Rs. Twenty Five Lacs)
Grand Total (Rs. in Lacs) **i + ii** : 25.00 (Rs. Twenty Five Lacs)

2.0 LITERATURE SURVEY

A vast literature survey was conducted on the different techniques of ECF and TCF bleaching technology for bleaching of different raw materials. These techniques are mostly on raw materials used by US, Canada, and Scandinavian countries. Since these technology are widely used by these countries. Systematic studies on indigenous raw material pulp were carried out under the project.

The literature surveyed during the project work is given in **Annexure -I**

3.0 BACKGROUND

3.1 Reason for Adoption of ECF & TCF Bleaching of Pulp

Pulp is produced by several methods. These production techniques yield different products and by-products. Although it is possible to generally classify mills by their process technology, this results in an oversimplification of the nature and concentrations of the products and byproducts of the mills. The degree to which chemicals released from pulp and paper production will potentially have an impact on the receiving water is dependent on several factors. These are: the wood species used, the degree of spill control and pulping liquor recovery, the bleaching process (if any) and the degree to which mill effluent is treated before being released. Effluent treatment technology has changed rapidly. Potential environmental impacts may differ significantly over time and from one receiving environment to another as well. Thus, it is important to realize that effluents from pulp mills are not necessarily comparable from one mill to the other or over time at any particular location.

To reduce the bleach plant effluent load and look for closer of mill it is now mandatory to adopt the ECF and TCF bleaching technologies. The adoption of these technologies in order to step towards cleaner production is not the matter of choice but a mandatory option to reduce the effluent load and meet out the environment regulation norms on discharge of effluent.

Again the world divided in two categories over the issues of pulp bleaching, i.e. developed and developing. Most of the developed countries are using the ECF and TCF technologies for pulp bleaching, while few mills in developing countries are opting these techniques of pulp bleaching.

3.2 World Wide Production of ECF and TCF Bleached Pulp

Paper industries in developed countries , due to stricter environment norms has mostly switched over to ECF or TCF bleaching technologies. But the growing trend as indicated in fig. 1 clears that ECF technology has larger share than that of TCF bleaching technologies. The ECF sequence which is widely used DEpDED is generally applied for softwood or hardwood pulp bleaching, to achieve brightness level in the range of 88-90%ISO. The slow growth of TCF bleaching technologies is may be because of ozone treatment required during TCF bleaching and further due to its consequence on pulp strength, particularly drop in intrinsic strength of pulp. No significant growth in the market of TCF bleaching technique is observed after 1995, while the ECF bleaching technology is taken place constant growth in market share.

Contrary the conventional bleaching technique viz. CEpHH is declined continuously. Industry in Developing countries are half way on their adoption of ECF technology.

In India big mills are adopting ECF technology after installation of oxygen pretreatment system, while small mills are still following conventional bleaching sequence i.e CEpHH. In India there are two or three mills which has completely switched over to ECF bleaching technology. But many more are on their way to adopt ECF bleaching process.

ECF: Leading the Market

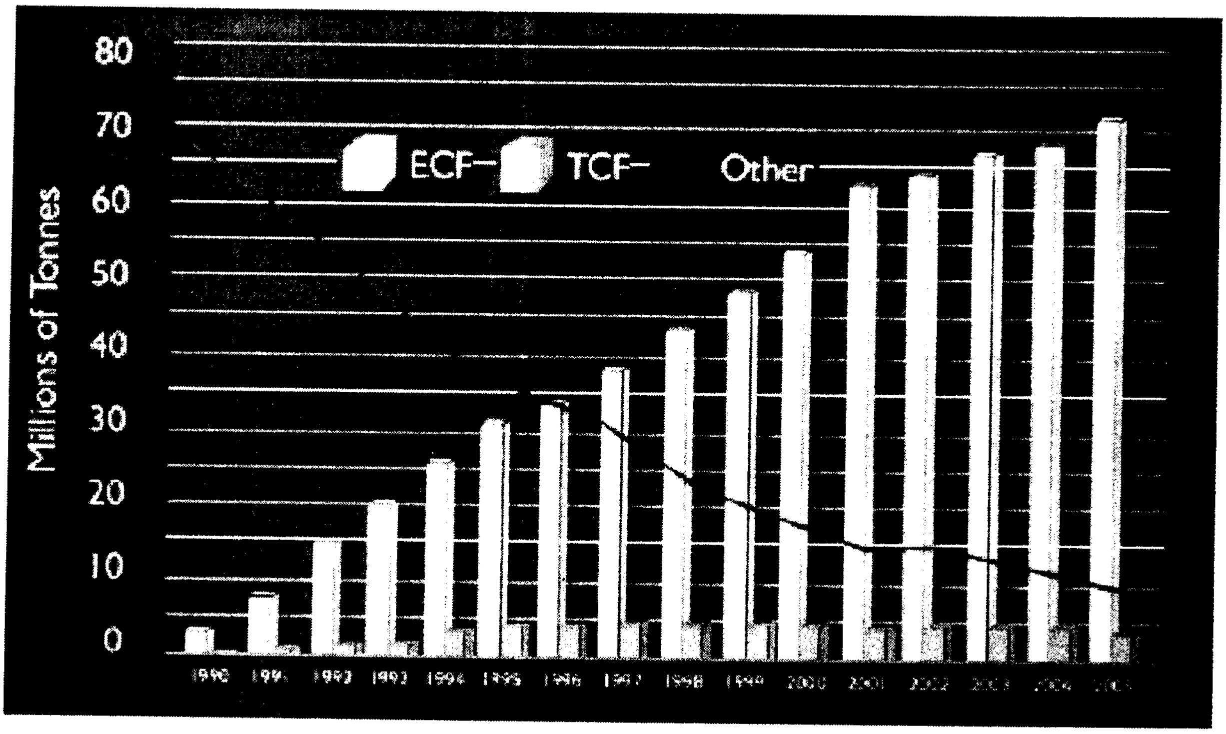

FIG. 1 WORLD WIDE TREND IN DIFFERENT BLEACHING TECHNOLOGY

3.3 Chlorine and Chlorine Dioxide Bleaching Chemistry

What makes the difference Actually?

To understand or appreciate the complex chemistry of bleaching with chlorine dioxide, it is necessary to set out some fundamental information about the various active chemical species involved. The oxidation level of the chlorine atom in chlorine dioxide (ClO_2) is +4, while in elemental chlorine (Cl_2) the oxidation level of the chlorine atom is +1. Based on reduction to chloride ion (Cl^-), which has a oxidation level of -1, there is a change of 5 oxidation levels for ClO_2 and 2 for Cl_2. Chlorine dioxide thus has 2.5 times the oxidation potential of elemental chlorine and is therefore more effective (on a weight basis) for removing lignin from pulp by oxidation.

Elemental chlorine (Cl_2), in addition to acting as an oxidizing agent, acts as a chlorinating agent. In the first stage of bleaching, about half the elemental chlorine applied to pulp combines with the lignin and the remainder oxidizes the lignin and is converted to chloride ion. Following alkaline extraction, about 90% of the original elemental chlorine applied to pulp has been converted to chloride ion, the rest remaining as solubilized chlorinated organic material. Chlorine dioxide reacts differently with lignin. Chlorine dioxide is reduced by lignin to chlorite ion and hypochlorous acid. It is the hypochlorous acid which reacts with organic material to form chlorinated organic compounds . The relative concentration of Cl_2, HOCl and OCl^- is sensitive to pH and careful control of the pH can reduce the formation of organochlorines.

A second difference between elemental chlorine and chlorine dioxide bleaching concerns the nature of the chlorinated products produced by the reaction of chlorine dioxide and elemental chlorine with lignin. Hypochlorous acid and elemental chlorine react differently with the chemical structures present in lignin . For example, hypochlorous acid (a byproduct of chloride dioxide oxidation of lignin) reacts with double bonds to produce chlorohydrins . Elemental chlorine, on the other hand, reacts with double bonds to produce dichlorinated products . Chlorine is eliminated from chlorohydrins during subsequent alkaline extraction more readily than from dichlorinated products. Therefore, as a result of the different kinds of products formed by reaction of hypochlorous acid and elemental chlorine, less chlorinated organic material ultimately results from chlorine dioxide.

A third factor which contributes to the different nature of the chlorinated organic products produced in chlorine dioxide bleaching is the difference in the lignin present at the time of reaction. Hypochlorous acid is generated as a secondary product only by reduction of chlorine dioxide as the lignin is oxidized. Therefore, the lignin that is available to react with hypochlorous acid is more oxidized and contains fewer aromatic structures than that which reacts with elemental chlorine as the primary oxidant . As a result, more of the hypochlorous acid is consumed by reaction with non-aromatic structures and thus less chlorinated aromatic material is formed.

The combination of the strong oxidizing capability of ClO_2 (thus requiring less material), the reduction in the extent of chlorination, and the changes in lignin result in an approximately five to ten-fold reduction in the formation of organochlorine compounds when ClO_2 is substituted for Cl_2. In addition, the nature of these organochlorine compounds is very different (i.e. less chlorine substitution, less aromaticity). These factors influence the potential environmental properties of ClO_2-derived organochlorines in terms of persistence, bioaccumulation potential, and toxicity.

3.4 Nature of the Compounds Produced

The chemical bleaching of pulp produces (in addition to bleached pulp) a complex mixture of degradation products of residual lignin and other components such as wood extractives. The degradation products vary greatly in properties such as molecular weight and chemical structure. Material which has a molecular weight >1000 is referred to as high molecular weight material (HMM) while that <1000 is referred to as low molecular weight material (LMM). About 50% of the organic material in the effluent from high substitution (100%) chlorine dioxide bleaching is HMM. This compares with 70 - 80% HMM reported for effluents from elemental chlorine bleaching . The structure of the HMM is not known precisely. This may be inconsequential since its general characteristics are known. A major difference between HMM from chlorine dioxide and elemental chlorine bleaching is the chlorine content. The HMM from chlorine dioxide bleaching contains about one chlorine atom for every one-hundred carbon atoms whereas that from elemental chlorine bleaching contains seven to ten chlorines for every one-hundred carbon atoms, i.e. a factor of about five to ten-fold different. The HMM is soluble in water by virtue of the presence of large numbers of hydrophilic functional groups, particularly carboxylic acid and alcohol groups and, it is largely non-aromatic .

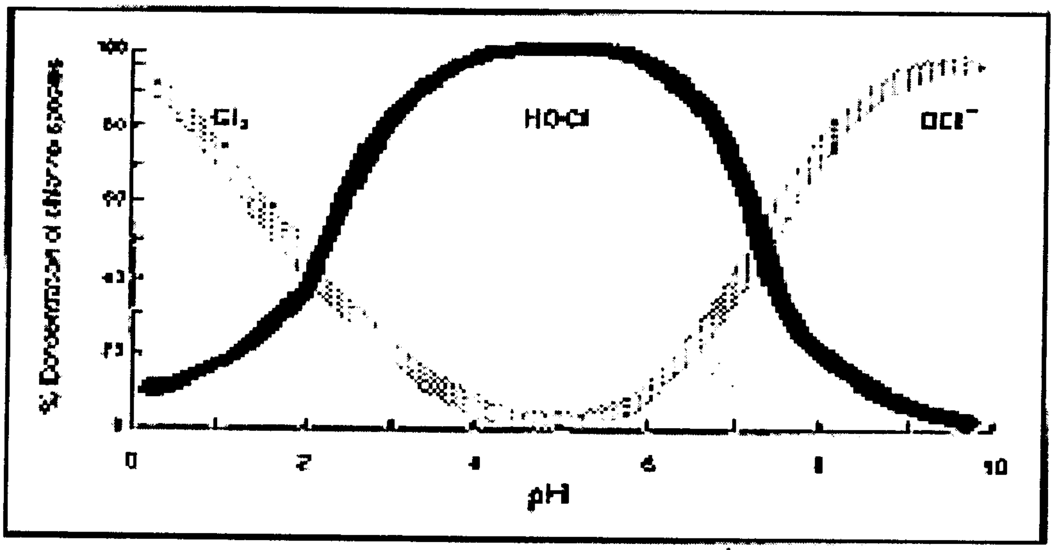

FIG 2-CONCENTRATION OF CHLORINE SPECIES AT VARIOUS pH

Hydrophobic compounds are of most concern because of their ability to bioconcentrate in organisms and, if persistent, their movement through the food chain. Highly chlorinated compounds, such as PCDDs (polychlorinated dibenzo-p-dioxins), PCDFs (polychlorinated dibenzofurans) and polychlorinated phenols, have a greater potential for bioaccumulation and are more persistent than their lesser chlorinated counterparts because these properties are enhanced by the presence of the additional chlorine atoms.

Chlorophenols have been studied in detail, probably because they were originally identified as contributing to the acute toxicity of effluent produced with elemental chlorine bleaching. Low substituted chlorophenols are classified as "non-hydrophobic" because they have low octanol-water partition coefficients (K_{ow}s of 2, as for monochlorocatechols). Only the more highly chlorinated species are considered hydrophobic and hence bioaccumulative (log K_{ow}s ranging from 4 for trichloroguaiacols to 5 for pentachlorophenol).

3.5 Bleaching Agents and Processes for Chemical Pulps

The whiteness of produced pulp has traditionally been regarded as an index of quality not only within the industry, but also by the consumer. The whiteness of pulp is measured by its ability to reflect monochromatic light in comparison to a known standard, usually of magnesium oxide. Unbleached pulps exhibit a wide range of brightness values. Kraft pulp is generally dark brown in colour while sulphite pulps are a light yellow-brown.

The principal aim of pulp bleaching is to increase the brightness of the pulp. The chromophoric (light absorbing) components in pulps are predominantly functional groups of degraded and altered residual lignin which is both darker and more tightly bound to the fibres than the original lignin component (McDonough 1992). This can either be converted and stabilised (lignin preserving bleaching) or removed (lignin removing bleaching). In the production of dissolving pulps, the bleaching stage is also regarded as part of the refining process, helping to produce a pure pulp with high alpha-cellulose content. In the less highly refined pulps, bleaching is regarded as removing wood extractives and bark specks, and conferring superior strength characteristics. Mechanical pulps are bleached using oxidative chemicals, predominantly hydrogen peroxide.

TABLE-1

BLEACHING CHEMICALS AND PROCESS SHORT HAND NOMENCLATURE

Stage	**Chemicals Used**	**Symbol**
Chlorine	Cl_2	C
Alkaline extraction	NaOH	E
Hypochlorite	NaOCl+NaOH	H
Chlorine Dioxide	ClO_2	D
Peroxide	Na_2O_2+NaOH	P or P/E
	H_2O_2+NaOH	P or P/E
Oxygen	O2+NaOH	O
Chlorine/ ClO_2	Cl_2/ClO_2	C_D
Sequential Bleach	ClO_2/ Cl_2	D/C
	Cl_2/NaOCl+NaOH	C/H
	ClO_2/NaOCl+NaOH	D/H
Mixed Bleach	Cl2+ClO2	C+D
Low level chlorine	Cl2	(C)
Gas phase bleaching	Cl2	C_g
	ClO2	D_g
Ozone	O_3	Z
Acid	CH_3CO_3H (example)	A

TABLE – 2

ESTABLISHED PULP BLEACH SEQUENCES SHOWING THE PREDOMINANT ROLE OF Cl2 AND ClO2 IN THE INDUSTRY

Pulp Type	**Sequence**
Sulphite and Bisulphite Pulp	
3-Stage	C-E-H
4-Stage	C-E-H-H
	C-E-H-D
	C-E-D-H
	C-C-E-H
	C-H-E-H
	H-C-E-H
	C-E-D-D/H
	C+D-E-H-D
	E-C-H-D
Five Stage	C-E-H-D-H
	C-C-E-H-H
Kraft Pulp	
Three stage semi-bleached	C-E-H
	D/C-O-D
Four stage part semi-bleached	C-E-H-D
	C-E-H-P
	C-E-H-H
	C-H-E-H
	C-D-E-D
	O-C-E-H
	O-C-E-D
	O-D-E-D
	O-D-O-D
Five Stages	C-E-H-P-D
	C-E-H-D-P

	C-E-H-E-H
	C-E-D-E-D
	C-E-D-P-D
	C-E-H-E-D
	C-H-D-E-D
	D-E-D-E-D
	C-C/H-E-H-H
Six Stages	C-H-E-D-E-D
	C-E-H-D-E-D
	C-E-H-E-H-D
	C-E-H-D-P-D
	C-E-H-E-D-P
	C+D-E-H-D-E-D
	O-C-E-D-E-D
	O-C+D-E-D-E-D
	O-D-E-D-E-D
	O-C-D-E-H-D
Seven Stages	C-H-H-D-D-D-P

TABLE- 3

PULP BLEACH SEQUENCES DESIGNED TO REDUCE OR ELIMINATE THE USE OF CHLORINE BASED COMPOUNDS AND CHLORINE

Application	**Bleach Sequence**
Reduced Chlorine	(C)-P-H
	(C)-P-D-H
	(C)-P-H-D-H
Peroxide replacement	P-D-P
	P-D-H
	P-H-H
	P-H-D
	D-P-D
	P-H-D-H
	P-D-P-D
Oxygen Bleaching	O-P
	O-D
	O-H
	O-P-D
	O-D-P
	O-C-P
	O-H-P
	O-C-P-D
	O-D-P-D
	O-C_g-E-D_g
	O-D_g-E-D_g
Ozone Bleaching	Z-E-P
	Z-E-Z
	Z-E-Z-P
Peracaetic acid	P-A-P
	A-E-A-E-A
Others	OQP
	OQPP
	OQPZP

The chemical pulps are generally bleached using a multistage process of three to six steps, depending upon the pulp characteristics. Hardwood pulps generally require less bleaching than softwood pulps content. Sulphite and bisulphite pulps are more easy to bleach than kraft pulps, and can be manufactured entirely without bleaching with chlorine or its compounds although chlorine bleaching is used. The following text, therefore, largely considers the bleaching of kraft pulps which is the dominant production process on a global basis.since they have a lower lignin.

Chlorine dioxide, despite handling difficulties, is largely replacing elemental chlorine in the initial bleaching stages. Its perceived advantages are: higher pulp brightness, improved fibre strength properties, lower chemical consumption and considerable reduction in the AOX of discharged effluents. Peroxide in combination with chlorine dioxide is often used in the later stages of bleaching chemical pulps.

Chlorine dioxide was first used on a large scale in the 1940's and was first used in Sweden in 1947. This led to the multi-stage CEDED bleaching sequence which allowed high brightness products from kraft pulp without the loss of strength. The evolution of bleaching techniques has followed pulping process developments to a very large extent. In particular, the chemicals applied have changed as the lignin content of the pulps entering the bleach sequence has been reduced.

A key factor was the development of oxygen bleaching in the process during the 1970's followed by use of oxygen in the alkaline extraction stages a decade or so later. Oxygen bleaching was inserted as a step after the digestion stage and allowed the lignin content of the pulp entering the bleach plant to be reduced from on average 5% to 2.5%. This effectively halved the potential problem from the bleach plant effluent. In addition, extended cooking time of the pulp in the digester also reduced the quantities of lignin entering the bleach plant and this was commercially demonstrated in the 1980s.

Substantial substitution of chlorine dioxide for chlorine has been known since the 1960's but became widely accepted during the 1980's as a result of growing concerns about the environmental impacts of organic chlorine compounds formed during chlorine bleaching. Complete substitution led to elemental chlorine free processes (ECF) becoming dominant first in Sweden and then in Canada and this is widely attributed to market pressures. Even so, cost considerations, particularly in the US appear to have inhibited the application of chlorine dioxide. Chlorine dioxide is relatively more expensive than chlorine with respect to the bleaching power per unit mass. Further development led to bleaching processes that did not use chlorine based chemicals (totally chlorine free or TCF).

Development of hydrogen peroxide and ozone bleaching technology was an essential prerequisite of the commercial feasibility of such methods.

Overall, various bleach sequences have been employed with varying degrees of chlorine substitution. Moreover, variation in the base technology means that a wide range of ECF processes in particular exist. This point is discussed further below.

3.6 Chlorine and Chlorine Dioxide Linkage

It has been suggested by Rappe and Wagemann that the explanation for chlorinated dioxins found in brownstock was due to the presence of elemental chlorine in the bleaching gas. Reeve *et al.* established that decreasing the pulp consistency, increasing the pH or reducing the chloride ion at low pH all tended to reduce AOX discharged with the effluent. The Swedish study Miljo$_{93}$) found chlorinated dioxins present in ECF effluents. These findings suggest that ECF is an incorrect term due to the inevitable presence of elemental chlorine. Hence ECF processes cannot correctly be described as chlorine free under existing definitions. For example, The Confederation of European Paper Industries (CEPI 1992) has published the following definition of ECF:

3.6.1 ECF (Elemental Chlorine Free) Refers To A Pulp Bleaching Process Which Does Not Use Chlorine Gas.

Elemental chlorine can be present in chlorine dioxide through two routes. Production of chlorine dioxide is accompanied by the co-production of elemental chlorine. All commercial processes are based upon the reaction of a reducing agent with sodium chlorate. This may be hydrogen chloride, sodium chloride, sulphur dioxide or methanol. The sulphur dioxide process (Mathieson process) produces less elemental chlorine than other reducing agents (Clapper 1978; McDonough 1992). A proportion of the elemental chlorine can be absorbed in the scrubbing tower used to prepare the bleaching solution. In systems using chloride as the reducing agent, the chlorine dioxide may have up to 15% by weight of chlorine. Where a sulphur dioxide based system is used, the produced chlorine dioxide can contain between 1 and 5% elemental chlorine Fredette, notes that where sodium chloride is used in the R2 process, it produces around 0.6t of chlorine per tonne of chlorine dioxide. Approximately 1g/l appears in the chlorine dioxide solution while the balance is used to manufacture hypochlorite. Virtually all R2 units were sold in the Southern United States. Subsequent R series and SVP series plants were designed to reduce waste acid output, but increased levels of 2g/l of chlorine were present in the chlorine dioxide solution. Eventually, hydrochloric acid based systems were developed. This could be made from the by produced chlorine. Even in plants using methanol, chlorine is not eliminated due to the need for chloride ion to be present in the reaction mixture. In the R8 process 0.1g/l of chlorine are present in a solution of 10g/l of chlorine dioxide. Hydrogen peroxide processes which can eliminate the chlorine by-production entirely are limited by the high cost of using peroxide in these processes. CEFIC also recognise the by-production of chlorine in chlorine dioxide generation. Reeve notes that with the R2 & R3/SVP producing a 10g/l chlorine dioxide solution, 10% of the oxidising equivalents are provided by chlorine.

Even if this problem of chlorine by-production is solved, free chlorine is also generated during bleaching with chlorine dioxide as noted by Rapson and Strumila and Reeve *et al.* Hypochlorous acid is generated as an intermediate. Chlorine dioxide reacts with the pulp to produce bleached pulp and chlorous acid. A pH dependent equilibrium then becomes established between the chlorous acid, chlorite ion and hydrogen ion. The concentration of chlorous acid becomes lower with increase in pH value. Chlorous acid is highly reactive towards lignin and in the course of the reaction is reduced to hypochlorous acid. In the presence of chloride ion, the hypochlorous acid enters into another pH dependent equilibrium with free chlorine being evolved. This free chlorine is available to produce chlorinated organic compounds measured as AOX. Hence,"elemental chlorine free", where this means "molecular chlorine free" is not true of any bleach sequence involving chlorine dioxide. Gaseous chlorine is inevitably evolved either in the production of chlorine dioxide or in the pulp mixture to which it is applied. Ultimately, therefore, it appears that only those commercial processes entirely free of chlorine chemicals as bleach agents merit the term of elemental chlorine free

3.7 Studies on ECF /TCF Bleaching Reported in literature

A study on ECF and TCF bleaching of different kappa number pulp is depicted in **Table -4.**

TABLE – 4

DATA FOR AVAILABLE OPTIONS

Case	A	B	C	D	E
Cooking					
Kappa number	25	25	15	25	15
Yield, % on wood	47	47	43	47	43
Oxygen Delign.					
Kappa number	-	12	8	10	8
Yield, % on pulp	-	94.7	97.5	92.6	97.5
Yield, % on wood	-	44.5	41.9	43.5	41.9
DEoDD Bleaching					
yield, % on pulp	92.6	95.5	97.4	-	-
yield, % on wood	43.5	42.5	40.8	-	-
ZEoZQP Bleaching					
yield, % on pulp	-	-	-	96.1	95.0
yield, % on wood	-	-	-	41.3	40.3
Wood, t/ADt	2.07	2.12	2.21	2.18	2.23
Recovery Solids					
Dry, t/ADt	1.52	1.63	1.76	1.81	1.91
Organic, t/ADt	1.06	1.13	1.21	1.24	1.29
Bleach Effluent					
Volume, m^3/ADt	18.4	6.2	5.9	5.8	5.8
Organic solids, kg/ADt	72.7	45.2	26.0	59.6	44.0
White Liquor*					
EA, kg/ADt	414	453	532	515	578
On Site Energy**					
kWh/ADt	620	650	660	830	835

* Part must be sulfide-free

** Gross energy demand at mill site

TABLE-5

TCF BLEACHING OF DIFFERENT KAPPA No. PULP WITH DIFFERENT SEQUENCE

Starting Pulp	**Unbld**	**Unbld**	**Unbld**	**Unbld**	**O2del**
Kappa no.	27.9	27.9	26.1	26.1	17.1
O_2 del	0	0	QOO	QOO	QO
Kappa no.	18.9	18.9	11.6	10	9.2
Brightness, %	34.7	34.7	45.3	49.8	52.7
Visc. dm^3 /kg	990	990	9000	880	820
Sequence	**QZPZP**	**QPZPZP**	**ZPZP**	**QZPZP**	**QZQPZP**
Chemical %	Z/.49	P/3	Z/.53	Z/.41	Z/.3
Final pH	2.6	10.3	2.5	2.6	2.6
Brightness, %	42.4	66.3	55.7	60.2	62.1
Visc. dm^3 /kg	860	900	740	790	760
Kappa no.	13.5	9.7	6.9	5.9	6.2
Chemical %	P/2.	Z/.5	P/2.	P/2.	P/2
Final pH	10.2	2.5	10.4	10.1	10.5
Brightness, %	69.9	70.1	77.9	80.1	79.2
Vis.dm^3/kg	810	760	650	710	740
Kappa No.	6.5	5.4	3.4	3	3.5
Chemical %	**Z/.2**	**P/2.**	**Z/.2**	**Z/.2**	**Z/.2**
Final pH	2.5	10.2	2.5	2.5	2.6
Brightness, %	71.4	83.4	78.8	82.3	82
Visc dm^3/kg	750	710	600	660	670
Kappa No.	4.7	2.7	2.2	1.8	2
Chemical %	**P/2**	**Z/.15**	**P/2.**	**P/2.**	**P/2.**
Final pH	10.4	2.5	10.4	10.5	10.5
Brightness, %	82.2	82.7	87.8	89.6	89.1
Vis, dm^3/kg	720	670	570	640	650
Kappa No.	2.9	1.7	1.3	1	1.1
Chemical charge/cons, %	--	**P/2**	--	--	--
Final pH	--	10.4	--	--	--
Brightness, %	--	89.6	--	--	--
Viscosity, dm^3/kg	--	650	--	--	--
Kappa No.	--	0.9	--	--	--
Total O_3 Consumption, %	0.57	0.49	0.55	0.44	0.38
Total H_2O_2 Consumption, %	2.07	2.79	2.28	1.54	1.25

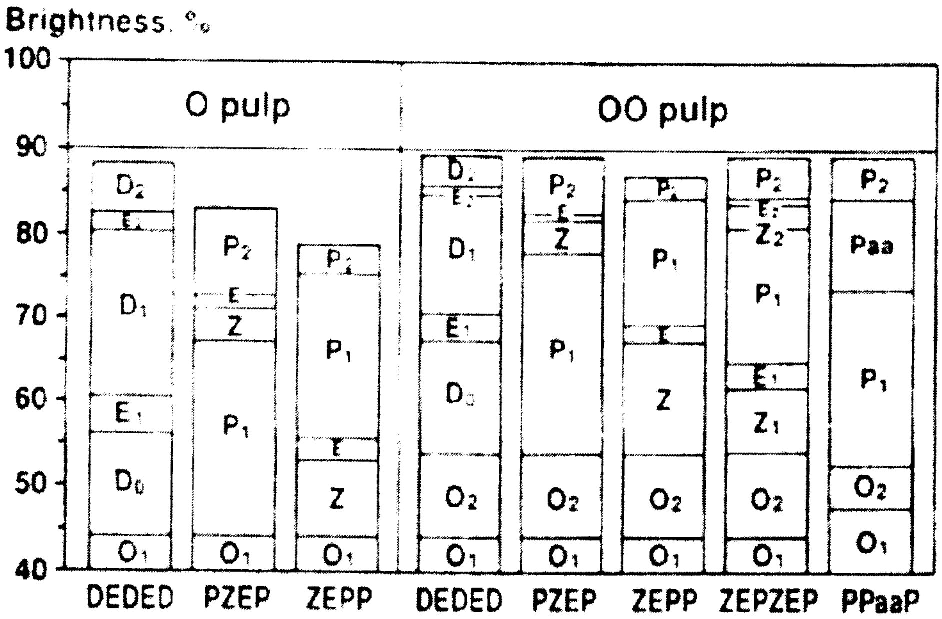

FIG. 3 EFFECT OF ECF AND TCF BLEACHING ON FINAL BRIGHTNESS

The effect of kappa number on final stage bleaching is shown in **Table 4 & 5. Fig.3** indicates the effect of bleaching sequence on final brightness

4.0 EXPERIMENTAL

4.1 Collection / Preparation of Raw Material

Air dried wheat straw , bagasse, bamboo and Eucalyptus used for the studies was stored in the polythene bag to attain uniform moisture level. The moisture content of representative sample was determined, before performing the experiments.

4.2 Pulping of Raw Material

Experiments were performed in a series digester consisting of six bombs each of 2.5-liter capacity, rotating in an electrically heated polyethylene glycol bath. At the end of the cooking time, the bombs were removed and quenched in the water tank to depressurize the bombs and the cooked mass from each bomb was taken for washing. Washing was carried out with hot water till the cooked mass was free from spent liquor. After thorough washing, the unscreened pulp yield was determined and the pulp was screened in laboratory 'Serla' screen by using mesh of 0.20 mm. slot width. Kappa number of the screened pulp was determined as per the Tappi standard procedure T-236-OS-76. The constant cooking conditions are given below:

Cooking Conditions

Raw material in each bomb, g	:	200
Bath ratio (Material : Liquor)	:	1:3
Cooking temp., °C	:	As required

Cooking Schedule

Time to raise temp. Ambient to 100°C , min.	:	30 minutes
Time to raise temp.100°C to 162 °C ,min	:	90 minutes
Time at temperature 162 °C ,min	:	120 minutes

4.3 Determination of Pulp Kappa Number/K Number , Brightness and Viscosity

Unbleached pulp samples were analyzed for yield, kappa number (Tappi T:236 OS 76), brightness (ISO 2470) and intrinsic viscosity (Scan C:3)

4.4 Oxygen Pre-Treatment of Pulp*

Oxygen treatment of pulp sample was carried out in quantum mixture. 250 gm. of pulp was taken for oxygen treatment in reactor vessel, at a time. After mixing the sodium hydroxide to the pulp, the pulp was pre heated in the microwave oven to 90 °C and pH of the pulp was determined. Volume of the reactor vessel is 3.5 liters and it is electrically heated, the temperature of the reactor vessel was maintained 90°C prior starting the experiment. The preheated pulp was placed in reactor vessel. The oxygen gas was injected in to the reactor vessel through the cylinder. Mix time/heat transfer time was given after every 15 minutes for 12 seconds. The oxygen treatment was given using following constant conditions.

Pulp consistency .%	:	10
Sodium hydroxide charged ,%	:	2.0
Oxygen pressure ,kg	:	5
Treatment temp, °C	:	90
Treatment time ,minutes	:	60

After oxygen treatment the pulp pH was determined. Kappa number, brightness, viscosity and yield were determined after thorough washing of the pulp.

* The procedure of oxygen treatment as described in manual of oxygen reactor supplied by Quantum Inc, Ohio, USA.

4.5 DEpD Bleaching of Chemical Grade Pulp

The chemical grade pulp of wheat straw of different kappa number was bleached by conventional CEpH and DEpD sequence to get optimum brightness

CONDITIONS FOR DIFFERENT STAGES OF BLEACHING

Parameter	Chlorination/Dioxide	Alkali Extraction	Chlorine Dioxide
Consistency, %	3.0	10.0	10.0
Reaction time (min)	60	90	360
Reaction temp (°C)	50	80	70
pH	2-2.5	10.5-11	3.5-4

5.0 RESULT AND DISCUSSION

The aim of the project is to assess the bleachability of different kappa number pulp of four raw materials. Study was planned to give three different treatment to unbleached pulp of four raw materials to get pulp kappa number in different range, followed by ECF DEpD bleaching and TCF Q- P1 P2 Bleaching of pulp.

5.1 Acid Pretreatment

The acid pretreatment of unbleached pulp is discussed in literature for the minimization of soda carryover and better bleaching point of view, but in some recent studies, the elimination of hexenuronic acid (HexA) by acid pretreatment and reduction of bleach chemical demand is discussed. The unsaturated sugars derived from hemicelluloses undergoes alkaline degradation during pulping and form glucuronic acids, also called hexenuronic acid,(HexA). These compounds readily consume bleaching reagents such as chlorine, chlorine dioxide, ozone, and hydrogen peroxide.

Analysis of hardwood data indicates that HexA contribute approximately 20-60% of total kappa number for the commercial hardwood kraft pulp **(4).**

It can be eliminated by acid pretreatment in certain conditions. And this can follow in bleach chemical requirement of unbleached pulp. ECF bleaching studies of birch kraft pulp suggested that an acid hydrolysis stage prior to Do stage could lead to a 50% reduction in bleaching cost **(5).**

The advantages of acid pretreatment are triple fold **(6-7).**

1. Elimination of hexanuronic acid by converting them into 2- Furoic acid and 5- carboxy-2- furaldehyde.
2. Removal of metal ions.
3. Removal of pitch content.

All three benefits finally results in low bleach chemical demand, better bleaching response and enhanced brightness ceiling effect.

5.2 EFFECT OF HEXENURONIC ACID ON PULP BLEACHABILITY

The determination of HexA in acid treated effluent of pulp of different raw material is shown in **Table - 6.** Normally the drop as reported in literature after acid treatment varies from 1-3 depending on the raw material, which is proportionate to raw value of HexA.

TABLE - 6

DETERMINATION OF HEXA IN DIFFERENT RAW MATERIAL

Raw material	Kappa before AALP	Kappa after AALP	HexA in mmol/kg
Bamboo	17	16.1 (0.89)	9.71
Bagasse	17	16 (1.0)	10.2
Wheat straw	15.2	14 (1.20)	13.1

5.3 EFFECT OF ACID TREATMENT ON METAL ION REMOVAL

The acid treatment of pulps also helps in removal of metal ion. As shown a in **Fig. 4** to **Fig. 6** it is clear that a substantial removal of metal ion viz, calcium, magnesium and iron is possible by acid treatment. The treatment with EDTA, a conventional way of metal ion removal by complex formation is compared with acid treatment. It is observed that the removal of metal ion by acid treatment is as much as by EDTA, except in case of bamboo, where it is slightly low than EDTA treatment. Since the metal ions specifically iron is responsible for poor bleachability can be removed by acid treatment effectively.

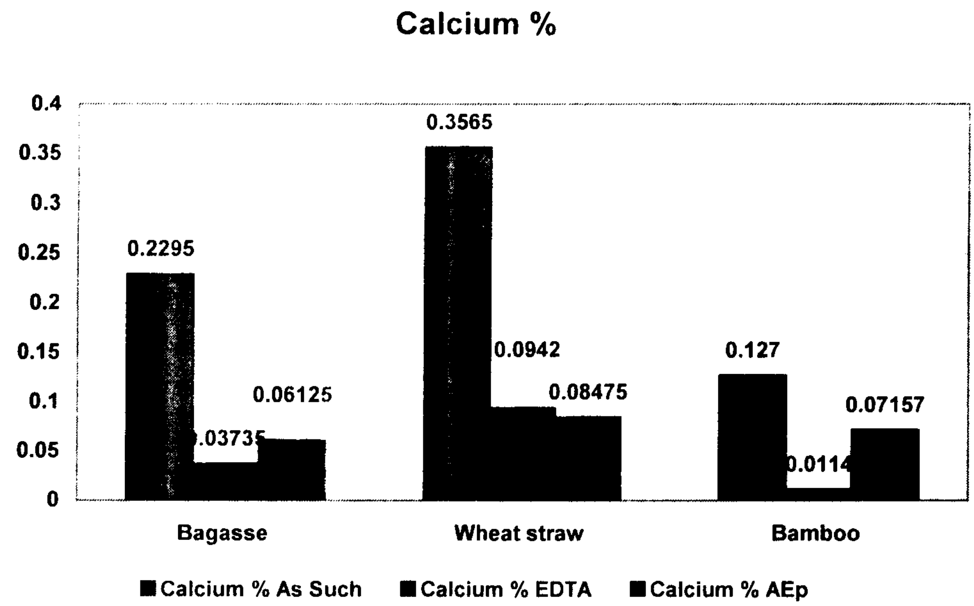

FIG 4- % REMOVAL OF CALCIUM BY EDTA & AEP TREATMENT

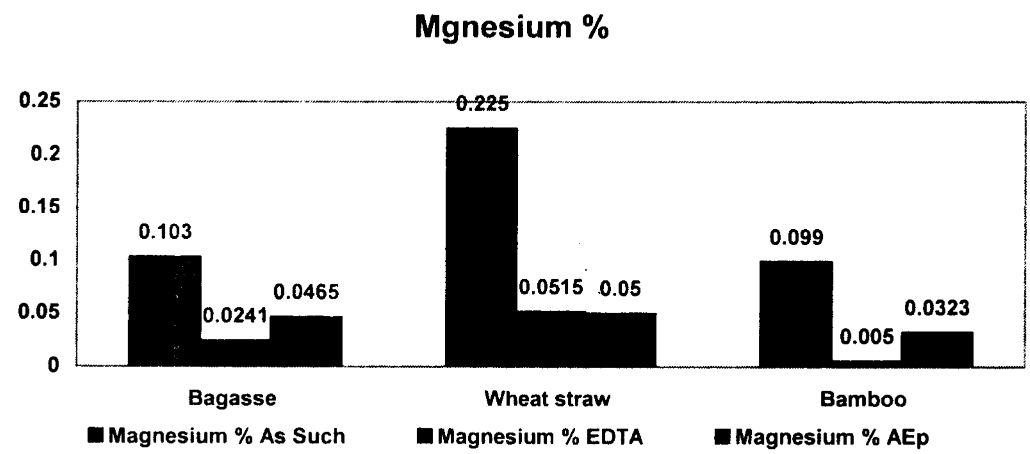

FIG 5- % REMOVAL OF MAGNESIUM BY EDTA & AEP TREATMENT

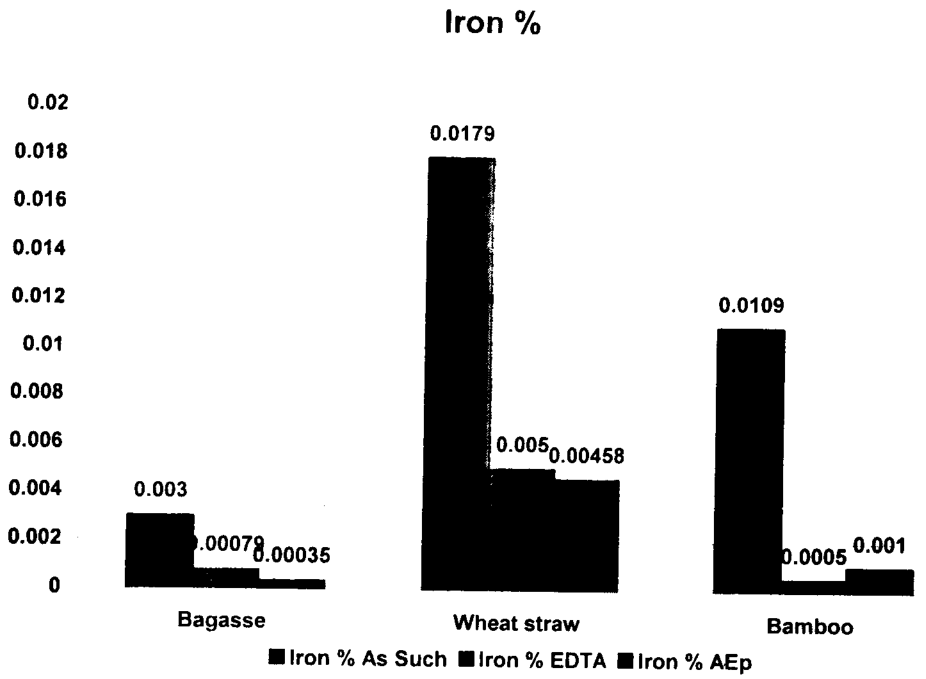

FIG 6- % REMOVAL OF IRON BY EDTA & AEP TREATMENT

5.4 Effect of Acid Treatment on Metal Ion Removal

Effect of acid treatment on ion removal in whaet straw ,Bagasse & Eucalyptus pulp was studied in the laboratory. Ion removal efficiency of acid treatment in these pulps is shown in **Table--7**

TABLE-7

EFFECT OF ACID TREATMENT ON METAL ION REMOVAL

Parameter	Drop in the concentration of the metal Ions In %					
		Bagasse	**Wheat straw**	**Eucalyptus**	**Bamboo**	**Mill D**
Calcium , %	**As Such**	0.2295	0.3565	0.147	0.127	0.242
	EDTA	0.03735	0.0942	0.122	0.0114	0.0975
	Drop %	**83.73**	**73.58**	**17.01**	**91.02**	**59.71**
	AEp	0.06125	0.08475	0.149	0.07157	0.04825
	Drop %	**73.31**	**76.23**	**-1.36**	**43.65**	**80.06**
Magnesium %	**As Such**	0.103	0.225	0.021	0.099	0.082
	EDTA	0.0241	0.0515	0.033	0.005	0.0517
	Drop %	**76.60**	**77.11**	**-57.14**	**94.95**	**36.95**
	AEp	0.0465	0.05	0.0419	0.0323	0.03725
	Drop %	**54.85**	**77.78**	**-99.52**	**67.37**	**54.57**
Iron ,%	**As Such**	0.00003	0.0179	0.00007	0.0109	0.0057
	EDTA	0.00079	0.005	0.0011	0.0005	0.00201
	Drop %	**-2,533.33**	**72.07**	**-1,471.43**	**95.41**	**64.74**
	AEp	0.00035	0.00458	0.0001	0.001	0.0026
	Drop %	**-1,066.67**	**74.41**	**-42.86**	**90.83**	**54.39**
Copper, %	**As Such**	0.00003	0.0006	0.00001	0.00036	0.00016
	EDTA	0.0001	0.0002	0.00006	0.00006	0.00012
	Drop %	**-233.33**	**66.67**	**-500.00**	**83.33**	**25.00**
	AEp	0.00003	0.00015	0.00001	0.00006	0.00014
	Drop %	**0.00**	**75.00**	**0.00**	**83.33**	**12.50**
Zinc, %	**As Such**	0.00026	0.0044	0.00002	0.0067	0.0005
	EDTA	0.00016	0.0005	0.00018	0.00012	0.00043
	Drop %	**38.46**	**88.64**	**-800.00**	**98.21**	**14.00**
	AEp	0.00013	0.00047	0.00003	0.0001	0.00029
	Drop %	**50.00**	**89.32**	**-50.00**	**98.51**	**42.00**

5.5 ECF and TCF Bleaching of Wheat Straw, Bagasse, Bamboo and Eucalyptus

5.5.1 ECF/TCF Bleaching of Wheat Straw

Wheat straw pulp of different kappa numbers i.e. 15.8, 10.1, 5.5 and 3.7 were subjected to DEpD bleaching. Results are summarized in **Table-8.** Wheat straw pulp of Kappa No. 11 & 14.75 were subjected to oxygen delignification followed by two stage peroxide bleaching. **Table-9** depict the results of TCF bleaching of wheat straw .

TABLE-8

ECF BLEACHING OF WHEAT STRAW

Parameters	**unbleached**	**O2 treated**	**OP treated**	**AEp treated**
Bleaching Sequence	**DEpD**	**ODEpD**	**OPDEpD**	**AEpDEpD**
Initial brightness ,%ISO	33.1	47.8	66.2	44.9
Viscosity cc/g	863	850	823	864
kappa	15.8	5.5	3.7	10.1
DEp stage				
Kappa factor	0.3	0.25	0.22	0.25
Dioxide as avl. Cl_2, %	4.8	1.4	0,8	2.5
Extraction stage (Eop)				
NaOH added, %	3	2,5	2,0	2.5
Peroxide added, %	0.5	0.5	0.5	0.5
Brightness,%ISO	65	79	81	80
Viscosity cc/g	815	805	753	807
Dioxide Stage				
DEpD brightness ,%ISO	83	85.4	86.4	85
DEpD viscosity cc/g	780	740	702	644
Total D applied ,%(as D)	2.6	1.12	0.852	1.75
Final yield,%	96	95.2	94	95

Observations

- The pulp of different kappa numbers i.e. 15.8, 10.1, 5.5 and 3.7 were subjected to DEpD bleaching.
- The brightness obtained by DEpD bleaching in respect of 15.8, 10.1, 5.5 and 3.7 kappa number pulp was 83, , 85.4 86.4 and 85% respectively
- It indicated that lower the bleaching plant entering kappa number, better is the brightness gain.
- Results showed that higher is the initial pulp viscosity , higher will be the end pulp viscosity.
- The consumption of dioxide was directly related to kappa number entering to bleach plant.

TABLE –9

PEROXIDE BLEACHING OPTIMIZATION OF OXYGEN TREATED WHEAT STRAW PULP

Parameters	**Low Kappa Pulp**			**High Kappa Pulp**		
Initial kappa number	11.03	11.03	11.03	14.75	14.75	14.75
Initial Brightness	39.4	39.4	39.4	36	36	36
Kappa after Oxygen treatment	4.8	4.8	4.8	7.0	7.0	7.0
Brightness	52	52	52	46.3	46.3	46.3
Intrinsic Viscosity, cm^3/g	932	932	932	900	900	900
DTPA added %	0.4	0.4	0.4	0.4	0.4	0.4
I stage peroxide H_2O_2 dose, %	4	6	10	4	6	12
Brightness obtained , %ISO	77.23	79.3	80.3	75.5	76	81
II stage peroxide H_2O_2 dose, %	4	2	--	4	4	--
Brightness obtained, %ISO	80.2	81.4	80.3	80.12	81	81
Intrinsic Viscosity, cm^3/g	816	752	884	786	805	871

Observation

- The Oxygen treated pulp of wheat straw having bleach plant introducing kappa number was 4.8 and 7.0 respectively.

- The two stage peroxide bleaching of pulp resulted in maximum brightness gain of 81.4 and 81.0% ISO brightness.

5.5.2 ECF/TCF Bleaching of Bagasse

Results of ECF & TCF bleaching of bagasse are given in **Table -10 & 11** Unbleached pulp of bagasse having 17 kappa number was separately treated by oxygen,Hydrogen Peroxide reinforced Oxygen and AEp. These pulps were further bleached by DEpD sequence (ECF) and two stage Hydrogen Peroxide (TCF)

TABLE-10
ECF BLEACHING OF DIFFERENT KAPPA NUMBER PULP OF BAGASSE

Parameters	Unbleached	O2 treated	AEp treated	OP treated
Bleaching Sequence	**DEpD**	**ODEpD**	**AEpDEpD**	**OPDEpD**
Initial kappa number	17	17	17	17
Initial Brightness	36	36	36	36
Intial viscosity , cm^3/g	1020	1020	1020	1020
Kappa after treatment	--	10.3	13.5	3.4
Brightness,%ISO	--	42	44	52
Intrinsic Viscosity, cm^3/g	--	916	936	965
Kappa factor	0.3	0.25	0.25	0.2
D1 stage, % applied as avl Cl2	5.0	2.5	3.3	0.7
Extraction stage, Alkali added,%	2.8	1.6	1.6	0.8
Brightness obtained %ISO	68	76	80	81
D2 stage, applied,%	0.8	0.5	0.5	0.5
Brightness obtained %ISO	84.0	85.3	86.1	86
Intrinsic Viscosity, cm^3/g	800	691	664	752

Observations

- The pulp of different kappa numbers as 17.0, 10.3, 13.5 and 3.4 were subjected to DEpD bleaching.
- The brightness obtained by DEpD bleaching for 17.0, 10.3, 13.5 and 3.4 kappa number pulp was 84, 85.3, 86.1 and 86.0% respectively
- It indicated that lower the bleaching plant entering kappa number, better was the brightness gain.
- Higher initial pulp viscosity resulted into higher end pulp viscosity.
- The consumption of dioxide was directly related to kappa number entering to bleach plant.

TABLE-11

TCF BLEACHING OF DIFFERENT KAPPA NUMBER PULP OF BAGASSE

Parameters	**O2 treated**	**AEp treated**	**OP treated**
Initial kappa number	17	17	17
Initial Brightness	36	36	36
Intial viscosity , cm^3/g	1020	1020	1020
Kappa after treatment	10.3	13.5	3.4
Brightness	42	44	52
Intrinsic Viscosity, cm^3/g	916	936	965
DTPA added %	0.4	0.4	0.4
I stage peroxide H_2O_2 dose, %	4	4	4
Brightness obtained %ISO	59	60	64
II stage peroxide H_2O_2 dose, %	2	2	2
Brightness obtained %ISO	65	65	75
Intrinsic Viscosity, cm^3/g	816	752	884

Observations

- The two stage peroxide bleaching of pulp resulted in brightness gain of maximum 65 , 65 and 75%iso brightness for oxygen treated , AEp treated and A-OP treated pulp.

5.5.3 ECF/TCF Bleaching of Bamboo Pulp

Bamboo unbleached pulp having kappa number 21 was also treated separately by oxygen, AEp and OP. These pulps were further treated by DEpD sequence (ECF) and two stage Hydrogen Peroxide (TCF). Results are summarized in **Table-12 & 13**

TABLE-12

ECF BLEACHING OF BAMBOO PULP

Parameters	**Unbleached**	**O2 treated**	**AEp treated**	**OP treated**
Bleaching Sequence	**DEpD**	**ODEpD**	**AEpDEpD**	**OPDEpD**
Initial kappa number	21	21	21	21
Initial Brightness	28.5	28.5	28.5	28.5
Intial viscosity , cm^3/g	953	953	953	953
Kappa after treatment	--	8.43	13.2	6.7
Brightness,%ISO	21	36.6	37.2	45.5
Intrinsic Viscosity, cm^3/g	953	756	927	734
D1 stage, % applied as avl Cl2	6.3	2.1	3.3	1.34
Extraction stage, Alkali added,%	3.5	3	3	3
P added	0.5	0.5	0.5	0.5
Brightness obtained %ISO	62	69.8	74.5	77.8
D2 stage, applied,%	0.1	0.5	0.5	0.5
Brightness obtained %ISO	83	86	88	88.5
Intrinsic Viscosity, cm^3/g	620	635	639	717

Observations

- The pulp of different kappa numbers i.e. 17.0, 8.4, 13.2 and 6.7 were subjected to DEpD bleaching.
- The brightness obtained by DEpD bleaching for 17.0, 8.4, 13.2 and 6.7 kappa number pulp was 83, 86, 88 and 88.5% respectively
- It indicated that lower the bleach plant entering kappa number, better was the brightness gain.
- High initial pulp viscosity resulted into high the end pulp viscosity

TABLE-13

TCF BLEACHING OF BAMBOO PULP

Parameters	**Unbleached**	**O2 treated**	**AEp treated**	**OP treated**
Initial kappa number	21	21	21	21
Initial Brightness	28.5	28.5	28.5	28.5
Intial viscosity , cm^3/g	953	953	953	953
Kappa after treatment	--	8.43	13.2	6.7
Brightness	--	69.8	74.5	77.8
Intrinsic Viscosity, cm^3/g	--	756	927	734
DTPA added %	0.4	0.4	0.4	0.4
I stage peroxide H_2O_2 dose, %	4	4	4	4
II stage peroxide H_2O_2 dose, %	2	2	2	2
Brightness obtained, %ISO	78	73	75	75

Observations

- The two stage peroxide bleaching of pulp resulted in maximum brightness gain of 78 , 73 and 75 and 75 %iso brightness for untreated, oxygen treated , AEp treated and A-OP treated pulp.
- The pulp could not be bleached to higher brightness due to high initial kappa number
- A combination of ozone and peroxide bleaching can lead to high brigtness gain in case of TCF bleaching.

5.5.4 ECF/TCF Bleaching of Different Kappa Number Pulp of Eucalyptus

ECF & TCF bleaching studies were also conducted on Eucalyptus unbleached pulp. Results obtained are given in **Table-14 & 15.**

TABLE-14

ECF BLEACHING OF DIFFERENT KAPPA NUMBER

Parameter	Unbleached	O2 treated	OP treated	AEp treated
Bleaching Sequence	**DEpD**	**ODEpD**	**OPDEpD**	**AEpDEpD**
Initial brightness ,%ISO	21.6	40.8	51.03	40
Viscosity cc/g	650	544	569	613
Kappa No.	18.2	9.6	7.8	13.5
Bleaching Sequence	**DEpD**	**ODEpD**	**OPDEpD**	**AEpDEpD**
Kappa factor	0.25	0.25	0.22	0.25
Dioxide as avl. Cl_2, %	4.55	2.40	1.72	3.38
NaOH added, %	3	2,5	2,0	2.5
Peroxide added, %	0.5	0.5	0.5	0.5
Brightness,%ISO	65	74.3	77	75
Viscosity cc/g		445	486	588
Dioxide Stage	**Dioxide Stage**	**Dioxide Stage**	**Dioxide Stage**	**Dioxide Stage**
DEpD brightness ,%ISO	DEpD brightness ,%ISO	DEpD brightness ,%ISO	DEpD brightness ,%ISO	DEpD brightness ,%ISO
DEpD viscosity cc/g	DEpD viscosity cc/g	DEpD viscosity cc/g	DEpD viscosity cc/g	DEpD viscosity cc/g
Total D applied ,%(as D)	Total D applied ,%(as D)	Total D applied ,%(as D)	Total D applied ,%(as D)	Total D applied ,%(as D)
Final yield,%	Final yield,%	Final yield,%	Final yield,%	Final yield,%

Observation

- The pulp of different kappa numbers i.e. 18.2, 9.6, 7.2 and 13.5 werre subjected to DEpD bleaching.
- The brightness obtained by DEpD bleaching for 18.2, 9.6, 7.2 and 13.5 kappa number pulp was 83, 83., 84.3 and 85.0% respectively
- It indicated that lower the bleaching plant entering kappa number, better was the brightness gain.
- High initial pulp viscosity resulted into high the end pulp viscosity

TABLE-15

TCF BLEACHING OF EUCALYPTUS PULP

Parameters	O2 treated	AEp treated	OP treated
Initial kappa number	17.5	17.5	17.5
Initial brightness	25.5	25.5	25.5
Intial viscosity , cm^3/g	581	581	581
Kappa after treatment	8.43	13.2	6.7
Brightness	43.0	42	45
Intrinsic Viscosity, cm^3/g	493	490	429
DTPA added %	0.4	0.4	0.4
I stage peroxide H_2O_2 dose, %	4	4	4
Brightness obtained %ISO	65.3	64.2	68
II stage peroxide H_2O_2 dose, %	2	2	2
Brightness obtained %ISO	73	72.5	78.0
Intrinsic Viscosity, cm^3/g	484	466	420

Observations

- Pulp of three different kappa number viz 8.43, 13.1 and 6.7 was subjected to two stage peroxide bleaching
- It was observed that pulp of lower kappa number (6.7)could be bleached to higher brightness (78%)

6.0 PAPER PUBLISHED ON ECF AND TCF BLEACHING OF PULP

A number of paper were published during the project period on ECF and TCF bleaching of different indigenous raw materials. The list of paper published is given in **Table-16** and abstract are enclosed as **Annexure –II**

TABLE-16

PAPER PUBLISHED ON ECF AND TCF BLEACHING

S.No	Title of paper	Name of journal
1	ECF bleaching of bamboo	paper published in the proceedings of International Pulp Bleaching Conference, Held at Stockholm in May 2005.
2	Prospects of ECF/TCF Bleaching of Nonwood Fibers- A fresh look	Indian Paper 2005, held at Coimbatore, Tamilnadu, India.
3.	Bleaching of bamboo pulp to high brightness	In IPBC (international Pulp Bleaching Conference held at Stockholm in May 2005
4.	Unbleached pulp kappa number reduction –Oxygen Pretreatment Vs Acid –Alkaline Peroxide Treatment (AALP)	5th International Non-wood Fibre Pulping and Paper making Conference (INWFPPC) and 3th International Symposium on Emerging Technologies of Pulping and Papermaking (ISETPP) scheduled held at China in November, 2006.
5.	Modified Oxygen Pretreatment of Unbleached Pulp of Indigenous Raw Material For Better Bleachability	Paper published in proceedings of IPPTA Annual Seminar, Feb. 2008

7.0 LIST OF SPONSORED PROJECTS CARRIED OUT DURING THE PROJECT

During project duration a number of sponsored projects were also carried out which are given in **Table-17**.

TABLE-17

LIST OF SPONSORED PROJECTS

S.No.	Name of the project	Sponsoring agency
1.	ECF bleaching of bamboo by DEpDED sequence	Cachar Paper Mills (A unit of HPC) , Panchgram (Assam)
2.	ECF bleaching of bamboo by DEpDED sequence	Nagaon Paper Mills (A unit of HPC) , (Assam)
3.	Evaluation of Bamboo Chips for Pulp quality	Cachar Paper Mills (A unit of HPC) , Panchgram (Assam)
4.	TCF bleaching of Turkmenistan wheat straw pulp	Hindustan Dorr Oliver Ltd.,Bombay.
5.	Pulping and bleaching of bamboo	J. K. Papers Ltd , Fort Songarh, Surat (Gujarat)
6.	Pulping of hardwood chips	J. K. Papers Ltd , Fort Songarh, Surat (Gujarat)
7.	Bleaching optimization of mill pulp	Naini Tissues Limited, Kashipur (Uttaranchal)
8.	Optimization study for ECF bleaching of non-wood fibers (Wheat straw, Bagasse and Sarkanda)	Ruchira Paper Mills Limited Kala Amb (HP).

8.0 RECOMMENDATIONS

8.1 FOR ECF

- In order to get the full efficacy of ECF bleaching technology, it is recommended to keep unbleached pulp kappa number as low as possible. (>10) without affecting the unbleached pulp strength.

- This is also economic as chlorine dioxide is the costlier bleaching agent .

- The kappa number can be reduced by different technology. Higher brightness can be achieved using oxygen and A-OP(technology developed by CPPRI)

- Acid pretreatment of pulp can be a better option for efficient removal of metal ions for better bleaching response.

8.2 FOR TCF

- The bleaching of pulp by TCF technology is a cleaner option for bleaching of pulp without use of chlorinated compounds
- Like ECF, the performance of TCF bleaching technique depends on initial kappa number.
- It is better to reduce kappa number >10 to get better brightness level.
- In order to achieve brightness above 80% use of Ozone which is cheaper than Chlorine Dioxide is required.
- A proposal on ozone bleaching is submitted before CESS Grant Authority, to study the ozone treatment of pulp of different raw materials.

ANNEXURE-I

ANNEXURE-I

LITERATURE SURVEYED

S.No.	TITLE	JOURNALS
01.	Enhanced Alkaline Peroxide Bleaching of Softwood Kraft Pulps Using a New Activator	Journal of Pulp and Paper Science: Vol. 27 No. 12 December 2001
02.	Changes with in the Modified Kraft Process Aiming to Improve TCF Bleachability	Journal of Pulp and Paper Science: Vol. 25 No. 5 May 1999
03.	Selective Hydrolysis of Hexenuronic Acid Group & its Application in ECF & TCF Bleaching of Kraft Pulps.	Journal of Pulp and Paper Science: Vol. 25 No. 5 May 1999
04.	Effect of ECF and TCF Bleaching Sequence on the Properties of Softwood Kraft Pulp	Journal of Pulp and Paper Science: Vol. 23 No. 10 October 1997.
05.	TCF Bleaching to High Brightness-Bleaching Sequence and Pulp Properties	Journal of Pulp and Paper Science: Vol. 23 No. 8 August 1996.
06.	A Comparison Between Acid Treatment and Chelation Prior to Hydrogen Peroxide Bleaching of Kraft Pulps.	Journal of Pulp and Paper Science: Vol. 21 No. 6 June 1995.
07.	Process Modification to Decrease Organochlorine Formation During Chlorine Dioxide Delignification	Journal of Pulp and Paper Science: Vol. 21 No. 6 June 1995.
08	Fundamentals of High-Pressure Oxygen and Low-Pressure Oxygen-Peroxide (Eop) Delignification of Softwood and Hardwood Kraft Pulps: A Comparison.	Journal of Pulp and Paper Science: Vol. 21 No. 6 June 1995.
09.	Chelation Prior to Hydrogen Peroxide Bleaching of Kraft Pulps: An Overview	Journal of Pulp and Paper Science: Vol. 21 No. 8 August 1995.
11.	A Comparison of Bleachability in TCF Sequence for Alkaline Sulphite and Kraft Pulps	Journal of Pulp and Paper Science: Vol. 22 No. 8 August 1996.
12.	A Comparison of Bleachability in TCF Sequence for Alkaline Sulphite and Kraft Pulps	Journal of Pulp and Paper Science: Vol. 22 No. 8 August 1996.
13.	Eucalyptus Kraft Pulp Bleaching with Chlorine Dioxide at High Temperature	Journal of Pulp and Paper Science: Vol. 29 No. 2 February 2003.
14.	A New Insight into the Bleachability of Kraft Pulps	Journal of Pulp and Paper Science: Vol. 29 No. 2 August 2003.

15.	Reduction of AOX Formation During Chlorine Dioxide Bleaching	Journal of Pulp and Paper Science: Vol. 44. January 2000.
16.	Low-Kappa Pulping without Capital Investment: Using Anthraquinone for Low-Kappa Pulping	Journal of Pulp and Paper Science: Vol. 77 No. 7 Tappi Journal 95
17.	Oxalic Acid Formation During ECF and TCF Bleaching of Kraft Pulp	Journal of Pulp and Paper Science: Vol. 83 No.2tappi Journal 73
18.	Influence of Kraft Pulping on the Kinetics of Oxygen Delignification	Journal of Pulp and Paper Science: Vol. 83 No.2tappi Journal 65
19.	Influence of Sulfur Compounds, Manganese, and Magnesium on Oxygen Bleaching of Kraft Pulp	Journal of Pulp and Paper Science: Vol. 80 No.10tappi Journal 263
20.	Oxidative Extraction of Hardwood & Softwood Kraft Pulps with Sodium Carbonate – Sodium Hydroxide Mixture or Oxidized White Liquor During Multistage Bleaching	Journal of Pulp and Paper Science: Vol. 80 No.10tappi Journal 253
21.	Xylanase- and Mannanase-Aided ECF and TCF Bleaching	Journal of Pulp and Paper Science: Vol. 79 No.7 Tappi Journal
22.	High Pressure Oxygen Delignification of Kraft Pulps	Journal of Pulp and Paper Science: Vol. 80 No.10tappi Journal 241
23.	A Novel Method to Measure Fiber Kappa Number	Journal of Pulp and Paper Science: Vol. 82 No.9 Tappi Journal 107
24.	TCF Bleaching of Eucalyptus Kraft Pulp: The Selection of the Sequence and the Best Conditions	Journal of Pulp and Paper Science: Vol. 23 No.11 November 1997
25.	Mechanism of Chlorate Formation During Bleaching of Kraft Pulp with Chlorine Dioxide.	Journal of Pulp and Paper Science: Vol. 19 No.1 January 1993
26.	Mechanism of Chlorate Formation During Bleaching of Kraft Pulp With Chlorine	Journal of Pulp and Paper Science: Vol. 19 No.1 January

	Dioxide	1993
27.	Shive and Knot Elimination with TCF and ECF Bleaching Sequences	Journal of Pulp and Paper Science: Vol. 81 No.6 Tappi Journal 163
28.	Enzymatic & Mechanical Treatment of Chemical Pulp	Journal of Pulp and Paper Science: Vol. 64, November 2000.
29.	Alkaline Peroxide Mechanical Pulping of Wheat Straw Part 1: Factors Influencing the Brightness Response in Impregnation	Journal of Pulp and Paper Science: Vol. 62 July 2000.
30.	Interaction Of Hydrogen Peroxide and Chlorine Dioxide Stages in ECF Bleaching	170 Tappi Journals, June 1998
31.	Oxygen Delignification of Soda & Soda-AQ Bagasse Pulps	184 Tappi Journals, December 1998
32.	Alkali – Oxygen Piulping of Rice Straw Two- Stages Pulping By Alkali Soaking and Oxygen Cooking	Vol. 77 No. 7 Tappi Journal 109
33.	Influence of Process Parameter in Pre-Bleaching Stages of "Dandrocalamus Strictus" Chemical Pulp on Bleach Plant Waste Water Quality.	Ippta Vol,- 10, No.-3, Sept. 1998
34.	Using On-Site-Produced Alkaline Peroxide for Pulp Bleaching	Ippta Vol,- 82, No.-3, Tappi Journals 157
35	Kraft Bleach Plant ECF Conversion: Comparison of Sequence Involving Enzymes, Chlorine Dioxide, Oxygen and Hydrogen Peoxide	Journals 1999.
36.	Emerging Pulping and Chlorine-Free Bleaching Technologies: In Search of The Ideal Pulp Mill.	06 July 1991 Tappi Journal
37.	Pulp Bleaching Without Chlorine – A Future Reality	Activity 4.1.6 Paper Asia, April'98
38.	Partial Closure in Modern Bleaching Sequences	136 Tappi Journal April 1998
39.	The Environmental Fate of Chlorophenoli Constituents Of Bleachery Effluents	March 1990 Tappi Journal 239
40.	Pulp Bleaching Without Chlorine – A Future Reality	Paper Asia, April 98.
41.	The Influence of Chlorine Ratio & Oxygen Bleaching on the Formation of PCDFS & Pcdds in Pulp Bleaching	June 1989 Tappi Journal 163
42.	Bleaching of eucalypt kraft pulp with peracids the effect on pulp characteristics	November 2002

43.	Is extended cooking nessessary for the closure of bleach plant? – a strategic shift in pulping and bleaching.	1997 Pulping Confrence 739
44.	The use of hydrogen peroxide in the bleaching of pulp	-
45.	Bleaching with new reductive chemicals: replacement of hydrosulphite	-
46.	High-Brightness Bleaching of Softwood Kraft Pulps with Oxygen, Ozone Asn Peroxide	Journal Of Pulp And Paper Science: Vol. 23 No. 9 September 1997
47.	Comaring Bleaching Sequence Configuration With Respect to Chemical Efficiency and Brightness Response.	-
48.	On the Potential to Improve Kraft Pulping And Pulp Strength Properties with a New Chipping Technique.	1997 Pulping Confrence 127
49.	Bleahing with New Reductive Chemicals: Replacement of Hydrosulphite	Pulp & Paper Canada T 72

ANNEXURE-II

ECF BLEACHING OF ASSAM BAMBOO PULP

(Paper published in IPPTA J. Conference proceedings, December 2004)

Priti S.Lal*, Sandeep Tripathi*, Arvind Sharma*, S.V.Subrahmanyam* and A.G.Kulkarni**

Abstract

The ECF/TCF bleaching is today's most concerned area in large paper mills of India. The demand of TCF and ECF bleached pulp has been growing rapidly during the last years, which is indicative of people's awareness towards cleanliness of environment. ECF and TCF bleaching sequences help in minimizing the bleach plant effluent load by minimizing the pollution parameters such as BOD, COD, AOX, and color that can eventually lead to totally effluent free production. Successful implementation of ECF and TCF sequence in a system demands low kappa number of unbleached pulp, as chlorine free bleaching agents are less efficient than elemental chlorine. ECF bleaching studies are reported for different Indian forest based raw material. Response of bamboo pulp in conventional bleaching sequences is very poor that has induced us to take up a study where-in the pulp could be bleached to reasonably higher brightness levels with out sacrificing the strength properties. A study on oxygen treatment of bamboo pulp of two different kappa numbers followed by ECF bleaching is conducted. The merits of ECF bleaching process are compared with conventional sequence and impact on strength viz viscosity and liquid discharge quality.

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Paper published in IPPTA J. Conference proceedings, December 2004

BLEACHING OF BAMBOO PULP TO HIGH BRIGHTNESS

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Abstract

Bamboo is nature's steel, used for variety of products of functional and commercial nature for many decades. This tree grass is one of the most primitive plant species that survive today and occurs in diverse conditions from perennially poor to perpetually rich soils from tropical jungles to high mountains. India is endowed with a large number of bamboo species and perhaps having the world's one of the largest resources of bamboo. Paper making properties of bamboo are well established. Use of bamboo as a main raw material is well reported in the beginning of history of papermaking in India.

In spite of being good cellulose fiber source bamboo handling for paper making process is not free from problem. Bleaching of bamboo pulp to high brightness is very difficult due to its lignin structure, using conventional CEH sequence. In the present communication bleaching response of bamboo pulp for high brightness using different sequences including oxygen pretreatment are discussed.

Paper published in Proceedings of IPBC (international Pulp Bleaching Conference held at Stockholm in May 2005

IMPROVEMENT IN BLEACHABILITY OF PULPS FROM NON-WOOD RAW MATERIALS USING ACID FOLLOWED BY ALKALINE PEROXIDE TREATMENT

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ABSTRACT

The technological developments of paper industry worldwide particularly in the areas of pulping and bleaching have been remarkable one. The kappa number of unbleached pulp entering the bleach plant was as high as 30 during 1970's which has now dropped to 10-15, and even lower. The trend is to retain less residual lignin in pulp so that bleaching step is accomplished in small stage. The environmental benefits arising out of low unbleached kappa number, such as - reduction in effluent load, color, BOD and chlorinated organic compounds are significant for a mill to comply with environmental norms, which are becoming stricter day by day. One such technology developed to reduce the kappa number was oxygen delignification technology which was driven mainly by environmental, economical and energy related issues.

In India, agro residues contribute a major raw material furnish in papermaking. The adoption of oxygen treatment technology for the size of the Indian mills is matter of economic viability. Due to its high capital cost, most of the small paper mills based on agro residue raw materials are unable to adopt oxygen treatment for reducing the kappa number. An alternate cost effective route for unbleached pulp kappa number reduction may be of great interest for such mills.

In present study, a combination of acid followed by alkali and peroxide treatment on unbleached pulps from wheat straw, bagasse and bamboo was carried out. It was observed that, when oxygen treatment was carried out on unbleached pulps from these raw materials, the drop in kappa number was as high as 45-55%. However, there was considerable loss in pulp strength, which varied between 10-20%. Such a loss in strength from agro residue pulps before the subsequent bleaching stages is not desirable. In contrast, when these pulps were treated with acid followed by alkali and peroxide, it was observed that the drop in kappa number of pulps was quite appreciable (30-42%). The maximum drop in kappa number was observed with bagasse (42%) followed by wheat straw (36%) and bamboo (30%) pulps. This was accompanied by simultaneous gain in brightness of up to 10 units. When compared with the oxygen treated pulps, the drop in the pulp strength was negligible. It was further observed that the bleaching response of such pulps was better than the oxygen treated pulps and it was possible to achieve higher end brightness. The removal of undesirable metal ions like

calcium, magnesium, iron, copper and zinc from the pulps was equally significant in acid leaching step. The above studies clearly indicated that the acid followed by alkali and peroxide treatment of pulps from wheat straw, bagasse and bamboo could be a viable route for reducing unbleached kappa number for small mills using these raw materials and achieving high end brightness and can be seen as substitute for oxygen delignification step.

** Director, * Scientists

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MODIFIED OXYGEN PRETREATMENT OF UNBLEACHED PULP OF INDIGENOUS RAW MATERIAL FOR BETTER BLEACHABILITY

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Abstract

The oxygen pretreatment of unbleached pulp of fibrous raw material used for papermaking is world wide well established technology for reduction of pulp kappa number. In context of Indian paper industry, the indigenous raw material like bagasse, wheat straw, eucalyptus and bamboo has responded well at laboratory scale. Though there are only few mills (based on hardwood, bamboo and bagasse) which has installed the oxygen pretreatment technology in their fiber line.

The kappa number reduction after oxygen pretreatment for pulp of different indigenous raw materials ranges between 40-60%, The reduction of unbleached pulp kappa number further lead to low bleach chemical demand and lower effluent generation during bleaching, depending on the quality of raw material and types of lignin. But it is observed that normally industrial oxygen treatment operate around 20% below their delignification potential i.e. compared to what can be obtained in laboratory experiments.

The efficiency of oxygen treatment technology is of great concern considering the scale of operation in Indian Paper Mills and high cost of technology. Literature reveals number of studies carried out to enhance the efficiency of oxygen treatment technology. It includes the treatment of oxygen along with some additional chemical, change in treatment conditions etc.

To meet out norms set by government for paper mill effluent discharge, Indian paper mills are looking for the modern technological options, which are cost effective and support their scale of operation. In the present study, the work is carried out on oxygen treatment and modified oxygen treatment (treatment along with peroxide) of pulp of Indian raw materials as bagasse, wheat straw, eucalyptus and bamboo. A comparison of characteristics of unbleached pulp, oxygen treated pulp and modified oxygen treated pulp followed by DEpD bleaching was carried out.

The study results in substantial drop in unbleached pulp kappa number after modified oxygen treatment, viz. 80, 76,62,63% compared to oxygen treatment viz.53,62, 47 and 55% respectively for bagasse, wheat straw, eucalyptus and bamboo. There was not any appreciable difference in pulp intrinsic strength after modified oxygen treatment and it has been preserved during the treatment (962, 823, 569 and 734 cc/g) compared to oxygen treated pulp (816, 863,544 and 750

cc/g) respectively for bagasse, wheat straw, eucalyptus and bamboo pulp. There is significant gain in brightness after modified oxygen treatment viz. 54, 66, 51 and 46 % ISO compared to oxygen treatment viz.38, 48, 41, 37 % ISO respectively for bagasse, wheat straw, eucalyptus and bamboo . The impact of better delignification and better initial brightness is also observed in DEpD bleached pulp brightness. There is 1-4 point gain in DEpD bleached pulp brightness for modified oxygen treated pulp as 88,87,85 and 86.5 % ISO compared to oxygen treated pulp 85, 85.4, 83 and 83.5 % ISO respectively for bagasse, wheat straw, eucalyptus and bamboo .

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