TRAINING PROGRAMME

ON

"PULPING, BLEACHING & PULP QUALITY"

2nd – 5th DECEMBER, 2002

ORGANISED BY

CENTRAL PULP & PAPER RESEARCH INSTITUTE
SAHARANPUR – 247001 (U.P) INDIA

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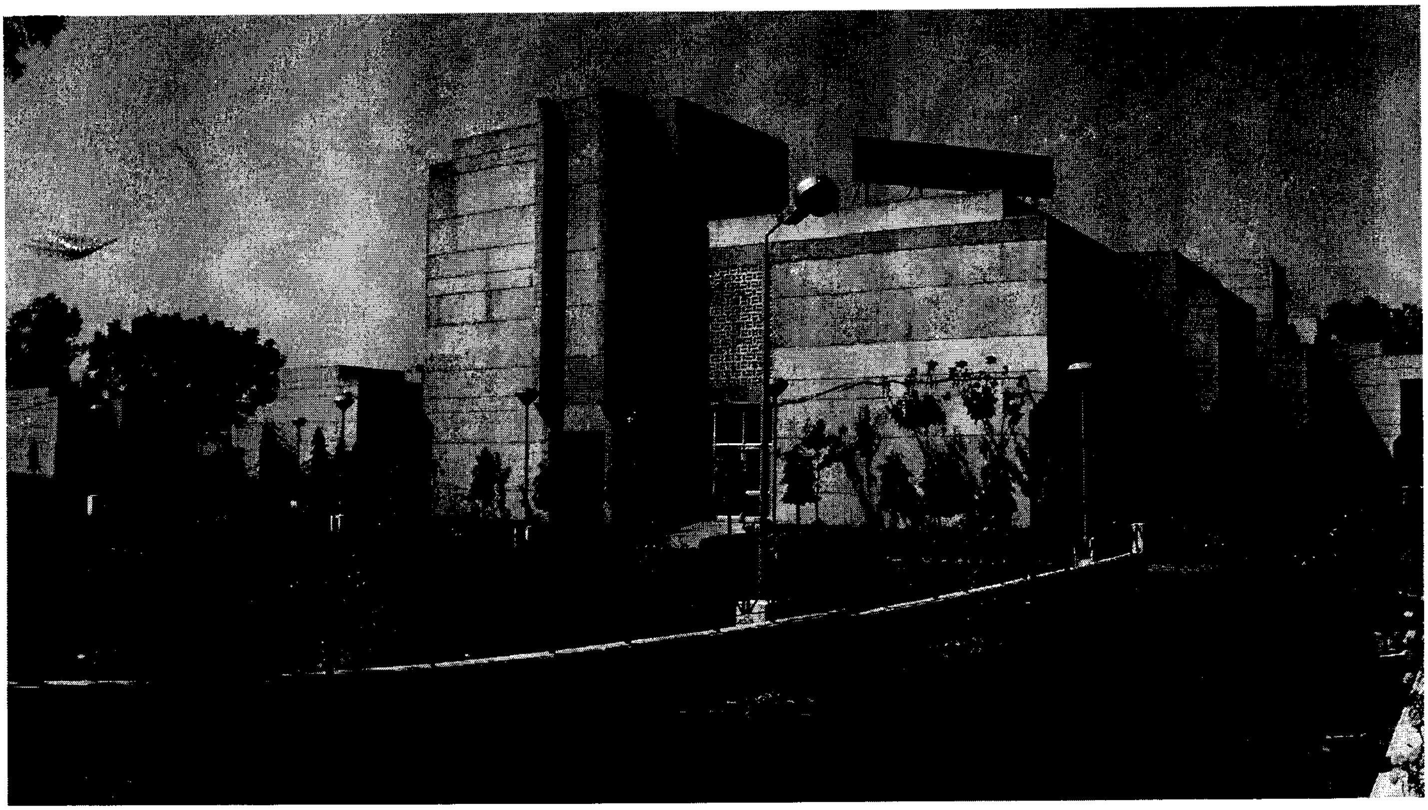

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CENTRAL PULP & PAPER RESEARCH INSTITUTE
SAHARANPUR – 247001 (U.P) INDIA

S. JAGADEESAN
Joint Secretary

Phone : 3012750
Fax : 3013655

वाणिज्य एवं उद्योग मंत्रालय
(औद्योगिक नीति और संवर्धन विभाग)
उद्योग भवन, नई दिल्ली–११००११
Ministry of Commerce & Industry
(Deptt. of Industrial Policy and Promotion)
Udyog Bhawan, New Delhi-110011

FOREWORD

The growing Indian Paper industry needs a competent task force to meet the challenges of globalisation. The historical background of the industry indicates that little attention has been paid to the manpower developments and training. The capital, raw material and energy intensive paper industry is manpower intensive too. The average usage of manpower in Indian paper industry is around 78 per 1,000 tonnes per annum. Largest segment of this manpower is in production related functions and above 75% of this manpower have only high school and lower qualifications. About 20-40% of the manpower is either casual or contract labour. In agro mill sector, about 30 man days of human resource is needed per tonne of product with a large proportion in raw material handling. The technical degree and diploma holders are around 8.0% and 6.0% respectively.

The industry has become conscious of the need for improving productivity through removal of obsolescence, modernization and expansion. Increased use of non-wood & secondary fibres, use of high yield pulping processes, energy and environment consciousnes, introduction of microprocessor and computer based control systems are common today in the industry. In order to meet these challenges and complex tasks, the technical skills of manpower has to go up. The maintenance systems are changing from centralized sector and are likely to be integrated to production functions. The demand of pulp & paper specialists is increasing, so will be the demand on professionals and technical personnel in the field of environment and quality management. Besides qualified and skilled personnel, it is also important for this manpower to update its knowledge on day-to-day developments in process technology & engineering fields. Training programs, which facilitate the one-to-one discussion are tools for updating the knowledge of skilled manpower.

I am glad to note that CPPRI has made a good beginning in this direction which is well indicated through the concerted efforts the Institute has made in last five years. The forthcoming training program on **Pulping Bleaching & Pulp Quality from 2nd to 5th December, 2002** will help technical personnel from paper mills in updating their scientific knowledge and understanding the new horizons of technological developments in the area of pulping, bleaching and pulp quality. I am glad to know the overwhelming response from the industry for this training program.

I wish this training program a success and hope that the eminent faculty will act as a driving force in catalyzing and fulfilling the training requirements of the manpower of the Indian paper Industry.

(S. Jagadeesan)

केन्द्रीय लुग्दी एवं कागज अनुसंधान संस्थान

Central Pulp & Paper Research Institute

An autonomous organisation registered under societies Act Under the administrative
control of the Ministry of Industry (Govt. of India)
POST BOX NO.174, PAPER MILLS ROAD, HIMMAT NAGAR, SAHARANPUR -247001 (U.P.) INDIA
Tel. EPABX (0132) 725317, 722756, Direct 727227, 726834, 726794
Cable: CEPPRI, Saharanpur Fax (0132) 727387, 721367 website:www.cppri.org. e.mail director @ cppri.org.

PREFACE

Learning is a continuous process and it is very important for the technical personnel workingin the industrial sectors to update their knowledge. Short term training courses(STC) are efficient tools in updating the knowledge of the technical personnel though one-to-one discussions.keeping in view of the importance of such training programmes, a decision was taken by the Cess Committee to have the ***"Continuing Education Programmes"*** *for pulp and paper technical personnel, in the different areas of* ***Pulp And Paper Science & Technology*** *through these short term training courses.*

"Pulping, Bleaching And Product Quality" *is first such training programme being organized at Central Pulp & Paper Research Institute(CPPRI), Saharanpur (Uttar Pradesh) from December 2-5, 2002. The topic chosen for this training programme is very relevant looking intothe remarkable developments which have taken place during the last two decades. It is important for the mill's personnel to know about these developments, and how these developments can be adapted in their mills for improving the productivity, product quality and also the cost effectiveness.Institute has the privilege of having senior faculty members drawn from the industry & academic institutions, who will share their wide experience along with the recent developments which have been adopted in the different pulp & paper mills in the country. Faculty members drawn from the Institute will share their experience in the area of pulping, bleaching, chemical aspects of pulping & bleaching, pulp quality & environmental aspects.*

A team of dedicated young Scientists of the Institute have worked hard to make this training progrramme useful & meaningful through selective ***"Lectures & Demonstrations"****. The training* ***MANUAL*** *covering the articles by various faculty members from the Department of Paper Technology(IIT,* ***Roorkee****), CPPRI and Industry is a comprehensive one and should be an useful Manual for the participants. The over-whelming response by the industry has been inspiring one for the training organizers.*
I must thank management of the various Pulp and Paper Mills for responding to our request by nominating their representatives. I also thank all the faculty members, who have responded to the request to be a resource persons.
I must also record my sincere thanks to ***Shri S. Jagadeesan,IAS, Joint Secretary (DOIPP) & Chairman, Cess Committee, Govt. Of India,*** *and all the honourable members of Cess Committee for supporting this training programme, which will go a long way in imparting knowledge to the technical personnel from the Pulp and Paper Industry.*

I wish the training programme a success.

(Dr. A G Kulkarni)
Director, CPPRI

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PRESENT STATUS OF THE PAPER INDUSTY

Dr. A.G. Kulkarni,
Director, CPPRI

About The Author

Dr. A.G. Kulkarni, Director Central Pulp & Paper Research Institute (CPPRI) Saharanpur, Uttar Pradesh, India has been with the CPPRI since its inception. He holds a Master degree in Chemistry & Doctorate in Black Liquor and Lignin Chemistry.

Dr. Kulkarni has pioneered the research work on Desilication of black liquor with eventual development of mill scale plant, installed at Hindustan Newsprint Ltd., Kerala and High Rate Bio methanation of black liquor rich effluent and a mill scale unit is successfully operating at Satia Paper Mills is another achievement of Dr. Kulkarni. His contribution in the area of physico chemical & thermal properties of agro - residue non-wood black liquors has now made it possible to process this liquor in chemical recovery boilers. He has published more than 300 scientific papers in Indian and International journals. He is widely traveled in Europe, S. E. Asia, and Australia and has been on several foreign missions as UNDP/UNIDO Consultant.

His areas of specialization include pulping and bleaching, black liquor-its chemistry & processing, environment and energy management. Dr. Kulkarni holds several patents-important ones being on desilication of black liquor, thermal treatment of black liquors and Direct Alkali Recovery System etc. He is a member of several National and International Scientific & Technical organizations and also on board of Directors of Paper Mills & Research organizations

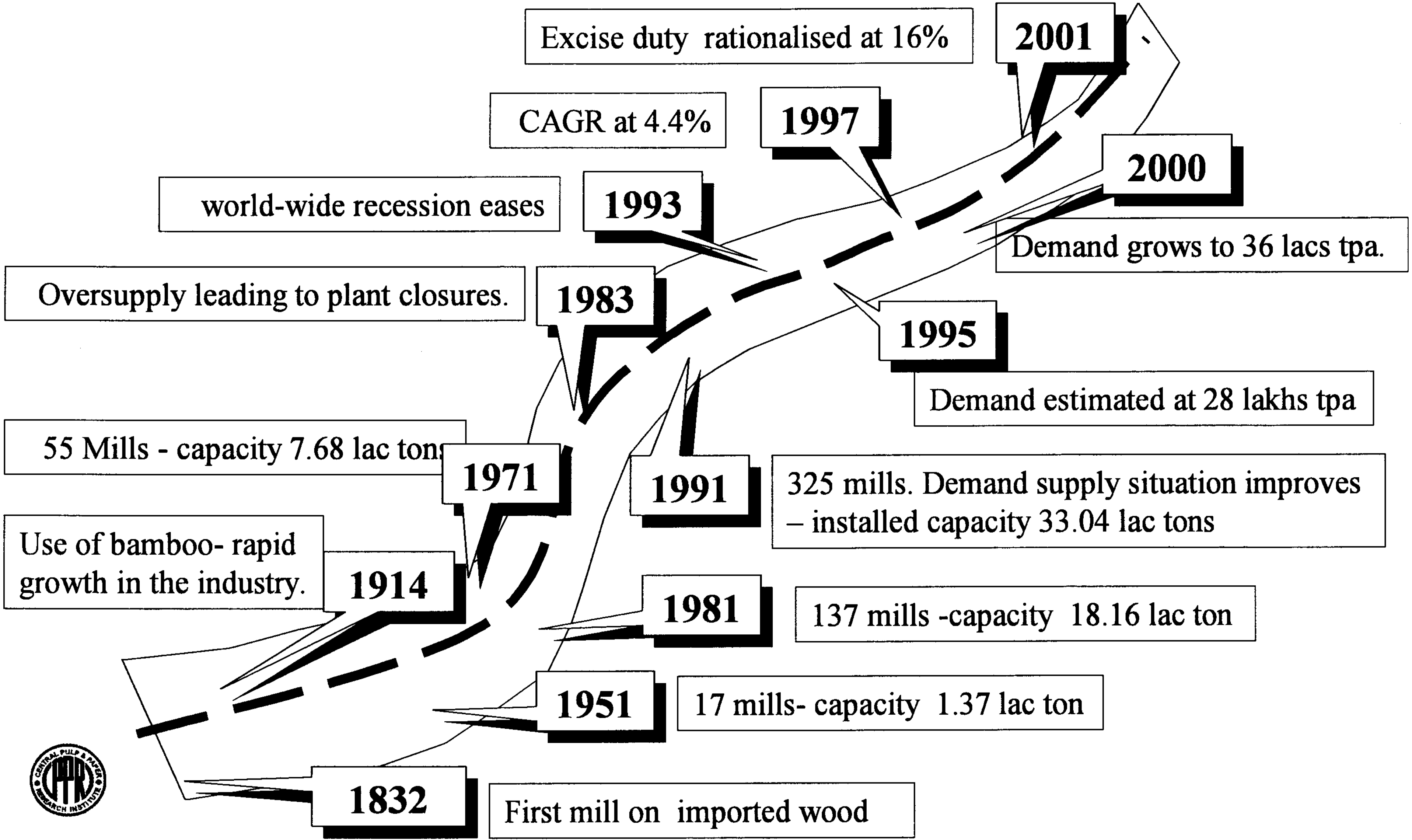
PRESENT STATUS OF THE PAPER INDUSTY

A G Kulkarni*

The article discussing the chronological developments in Indian Paper Industry in terms of its growth, production level and levels of capacity utilization. The information also provides the technological status of our industry in terms of trends available on raw material and basic input requirement along with there costing. The technological development in pulping and bleaching and requires addressing the energy and environment are well focused in various categories of the mills. Further, the emerging issues and challenges found be the Indian Paper Industry is making it internationally addressed.

*** Director,. CPPRI, Saharanpur, UP-247001**

Indian Paper Industry : The Road Map from 1832 to 2001



1832 First mill on imported wood

1914 Use of bamboo- rapid growth in the industry.

1951 17 mills- capacity 1.37 lac ton

1971 55 Mills - capacity 7.68 lac ton

1981 137 mills -capacity 18.16 lac ton

1983 Oversupply leading to plant closures.

1991 325 mills. Demand supply situation improves – installed capacity 33.04 lac tons

1993 world-wide recession eases

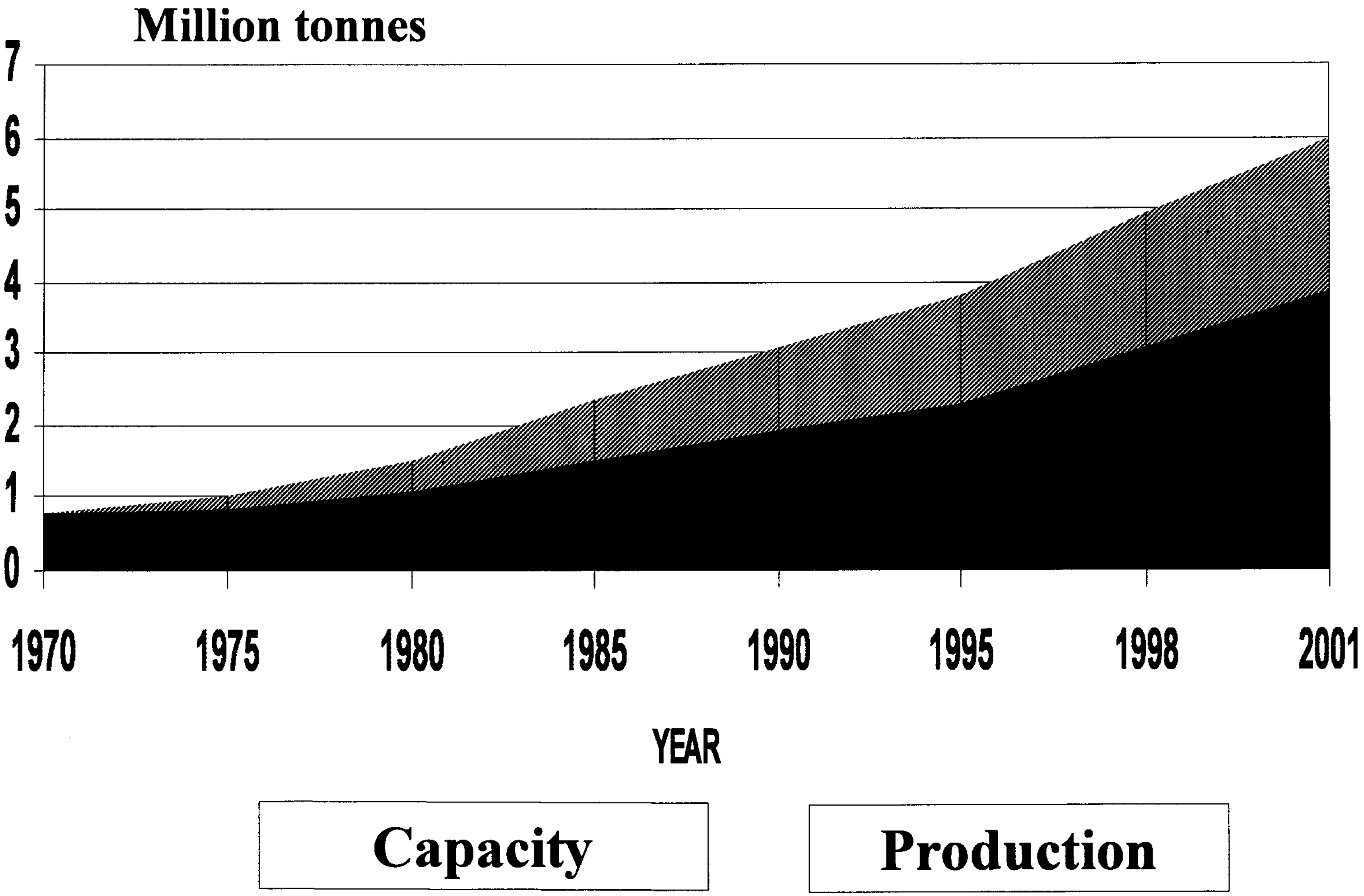
1995 Demand estimated at 28 lakhs tpa

1997 CAGR at 4.4%

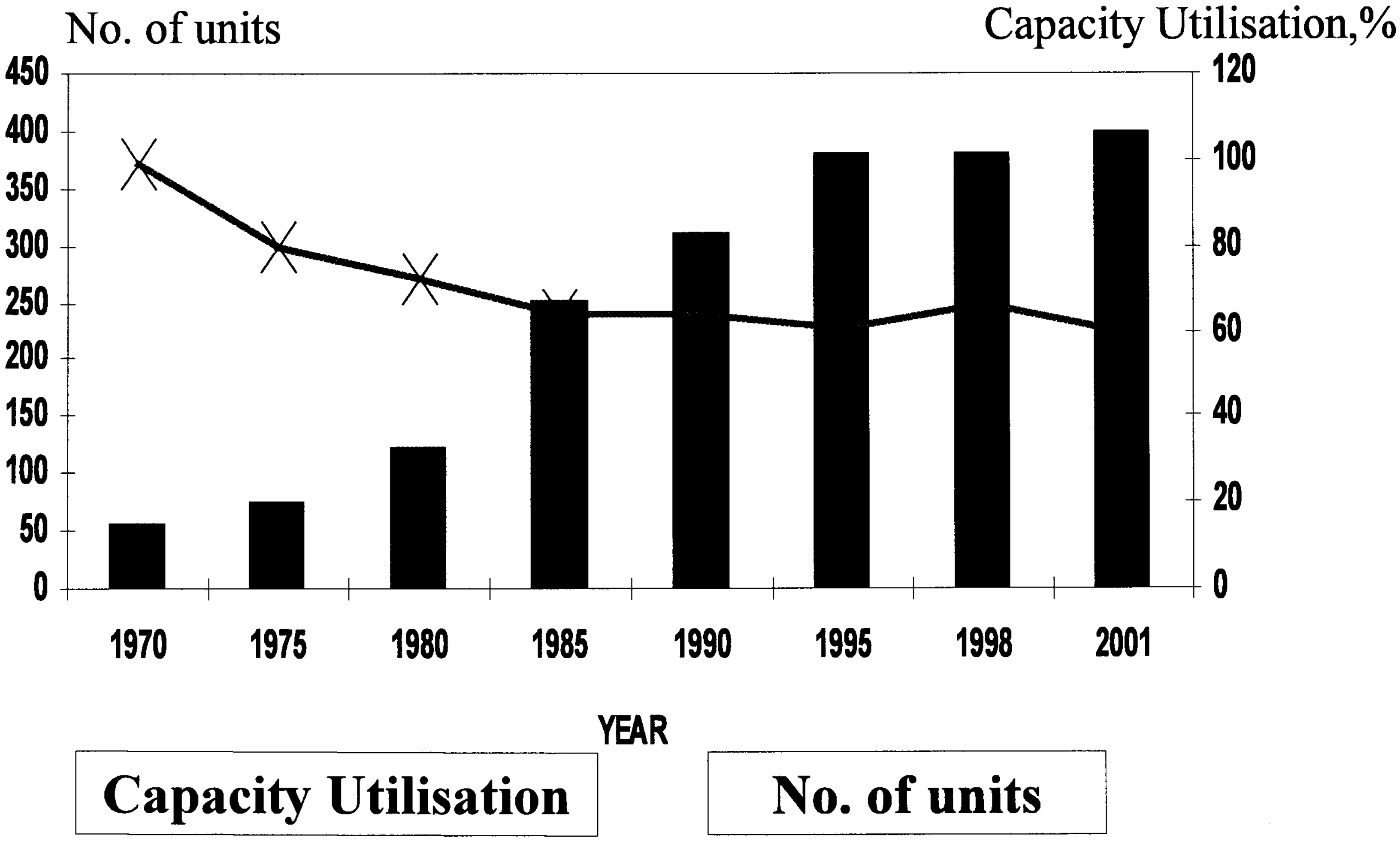
2000 Demand grows to 36 lacs tpa.

2001 Excise duty rationalised at 16%

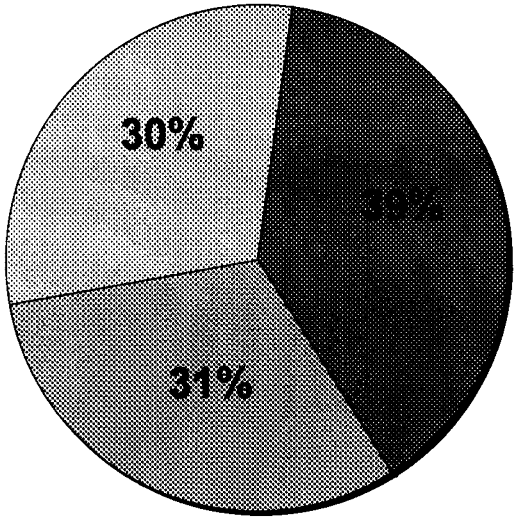
Growth of Indian Paper Industry
Installed Capacity & Production



GROWTH OF PAPER INDUSTRY - CAPACITY UTILIZATION & NUMBER OF UNITS

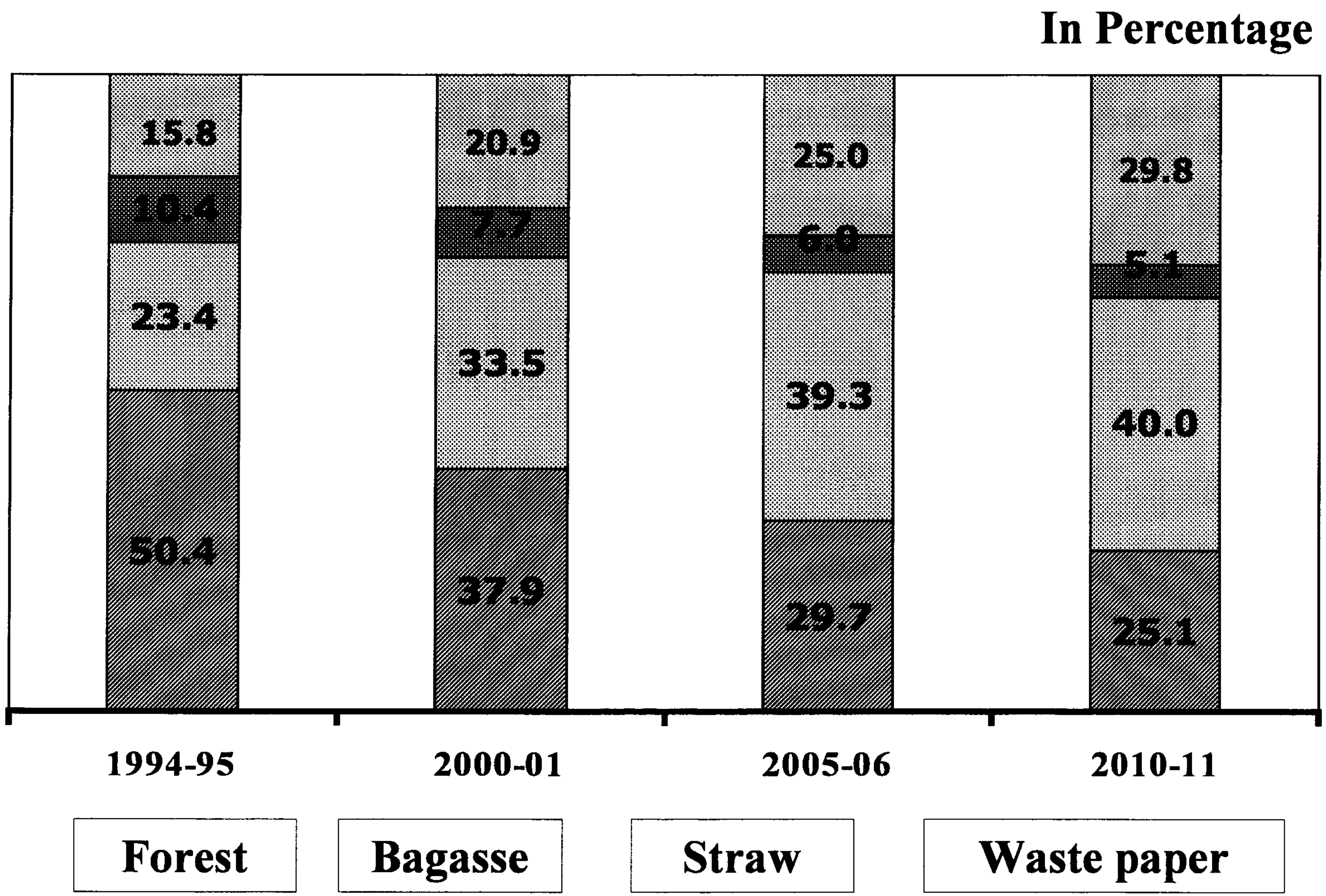


Indian Paper Industry : It's Structure

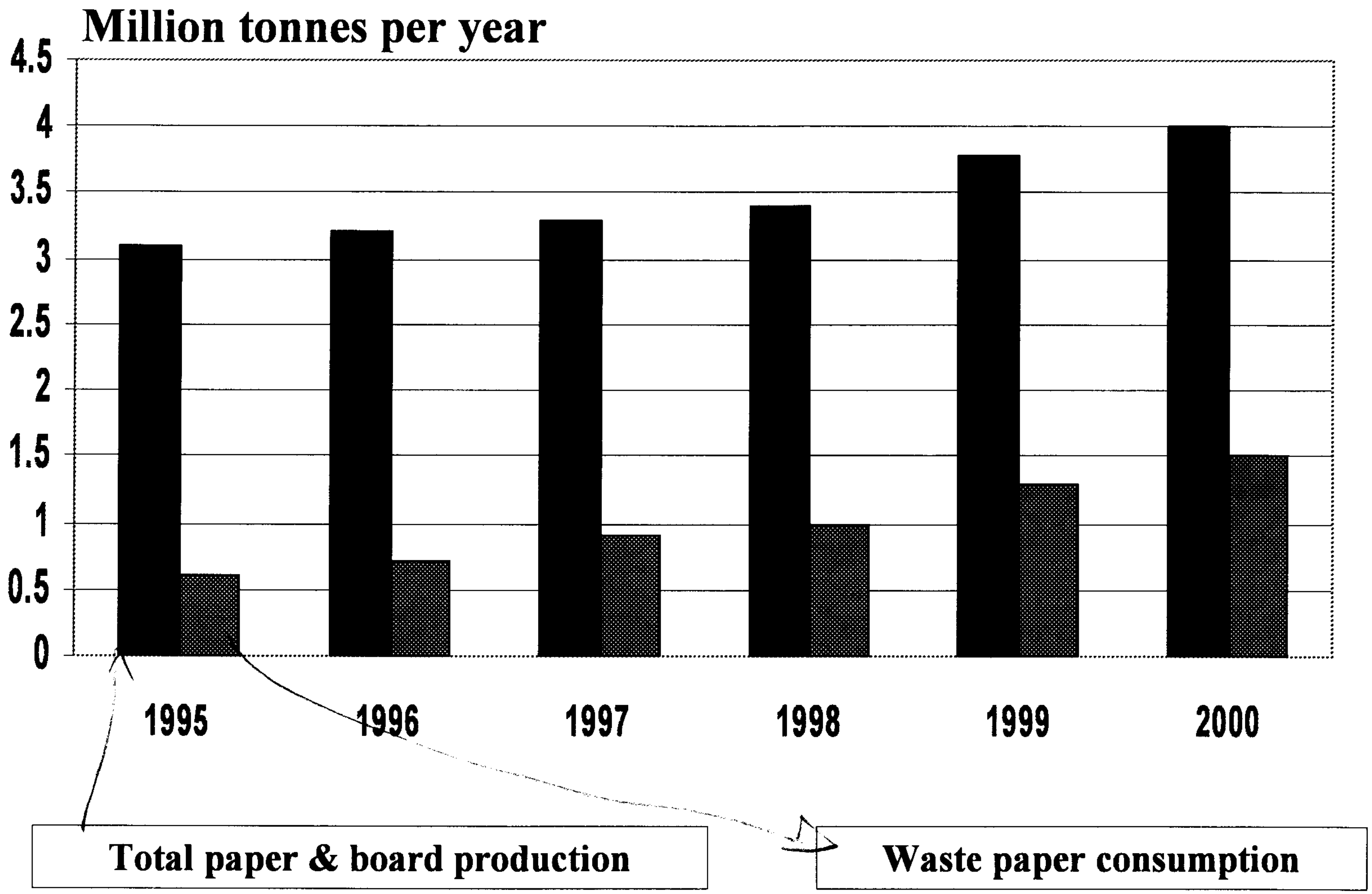


Data	Sector			Total
	Forest based	Agro Based	Recovered Paper	
No.of Mills	28	131	241	400
Installed, Capacity Mn tons/yr.	2.4	2.1	1.9	6.4

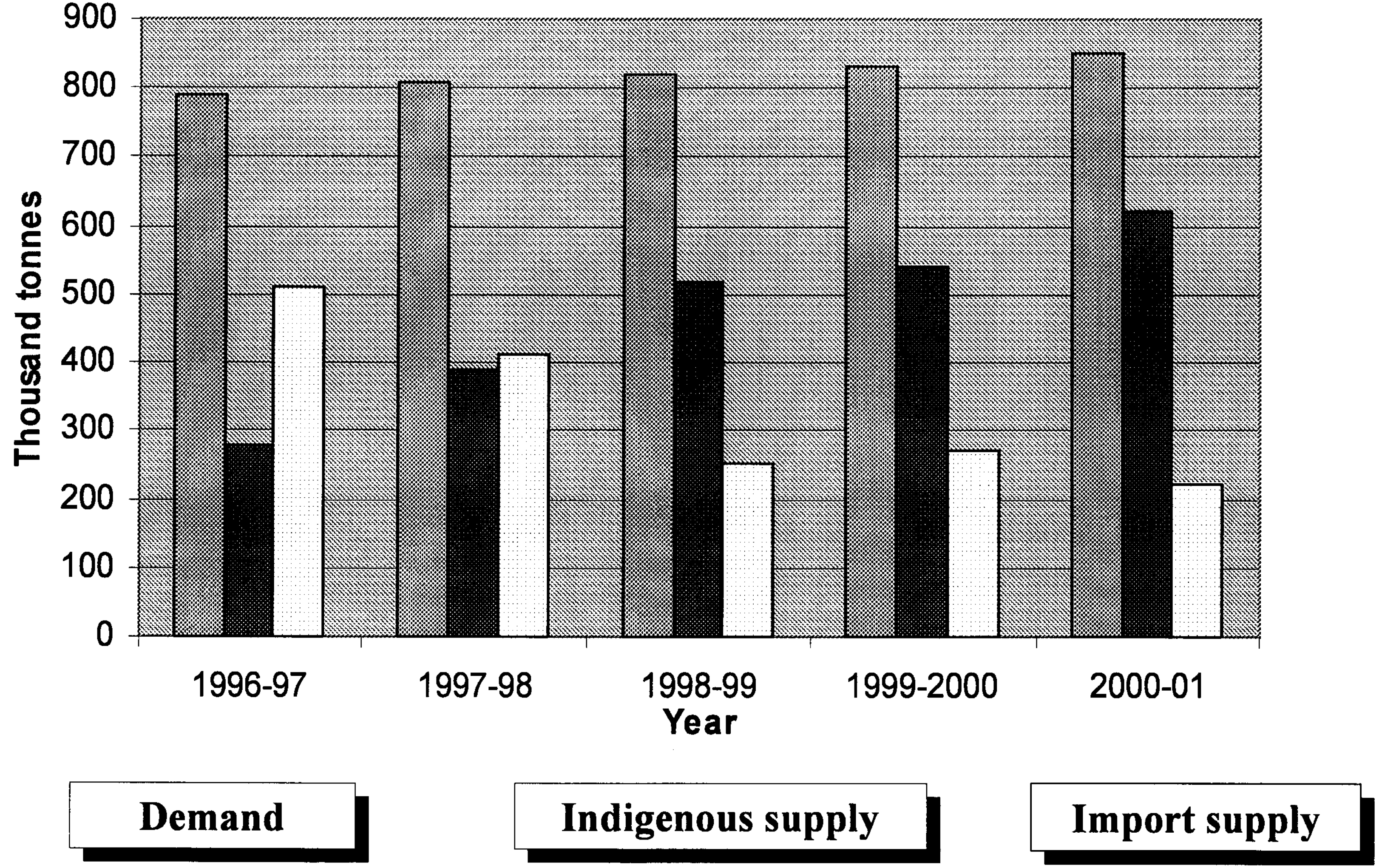
Paper Production from Fibrous Raw Materials



Share of Waste Paper in Total P & B Production (1995 - 2000)

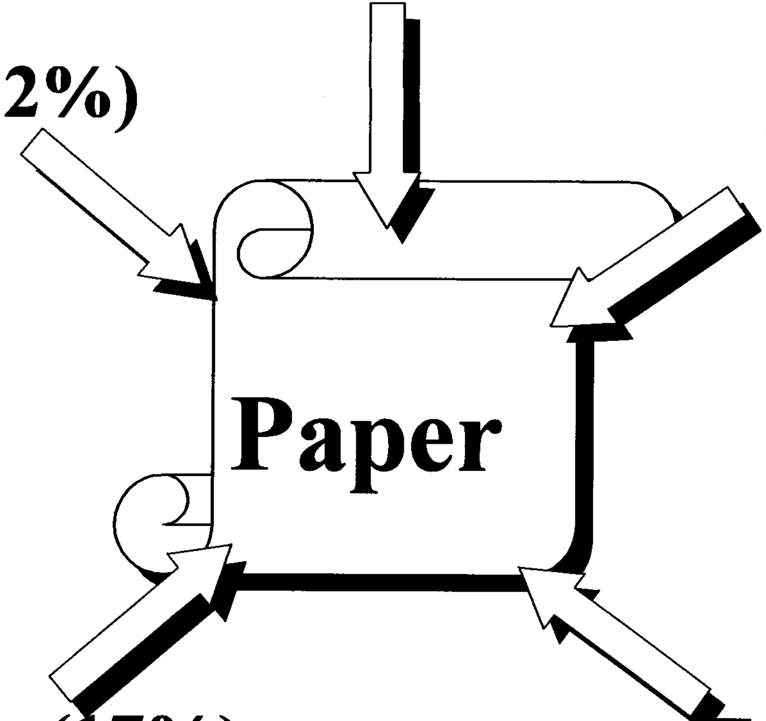


Newsprint Demand & Supply



BASIC INPUTS:
COSTS & COMPARISON

Basic Inputs



Water &
Utilities (4%)

Labour(22%)

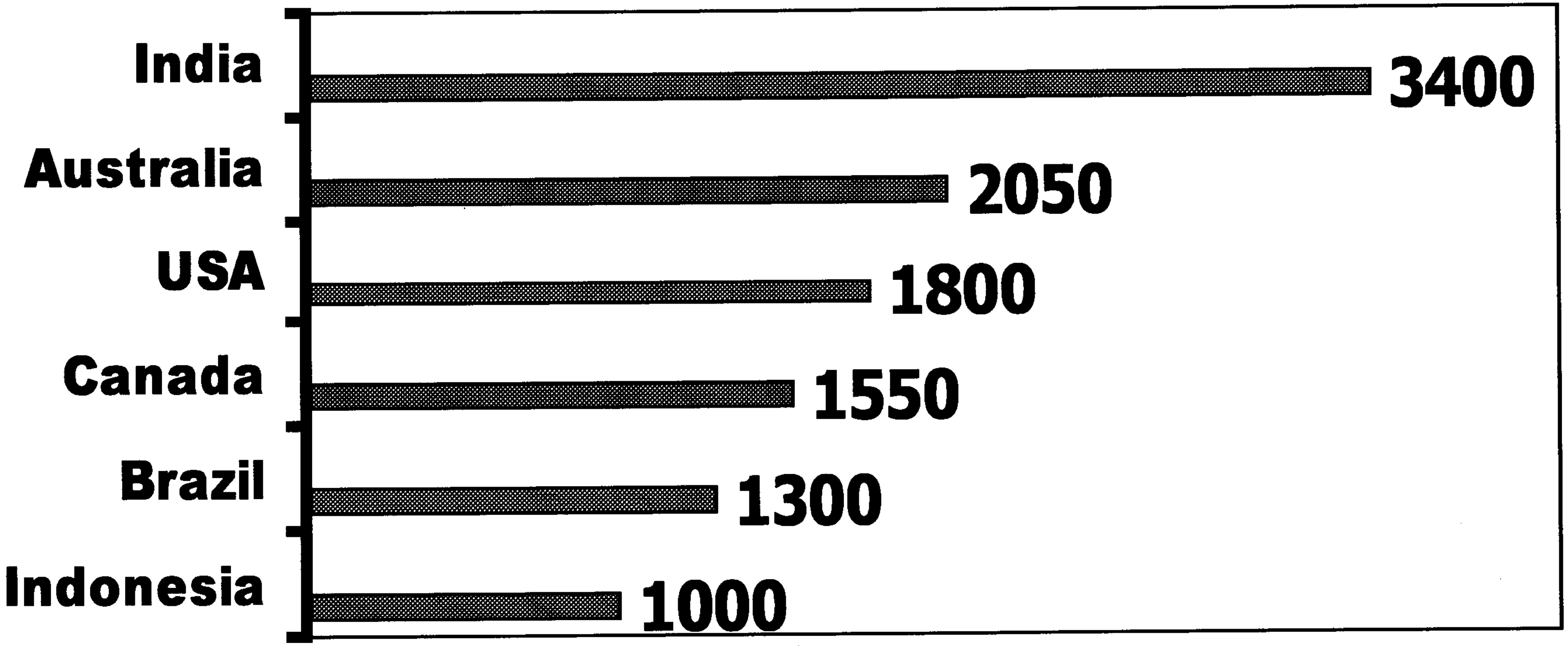
Raw Material
(27%)

Paper

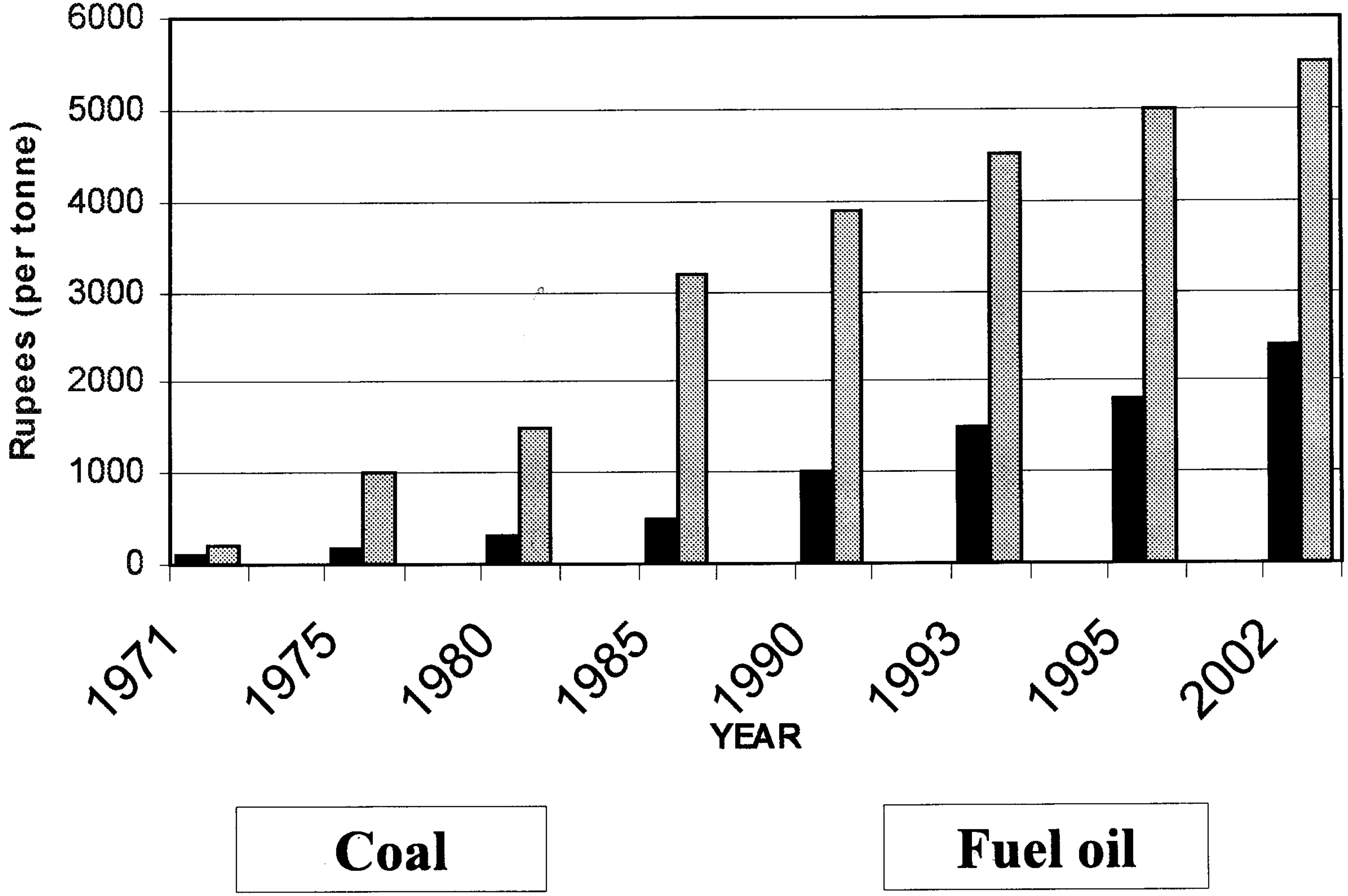
Chemicals (17%)

Energy (30%)

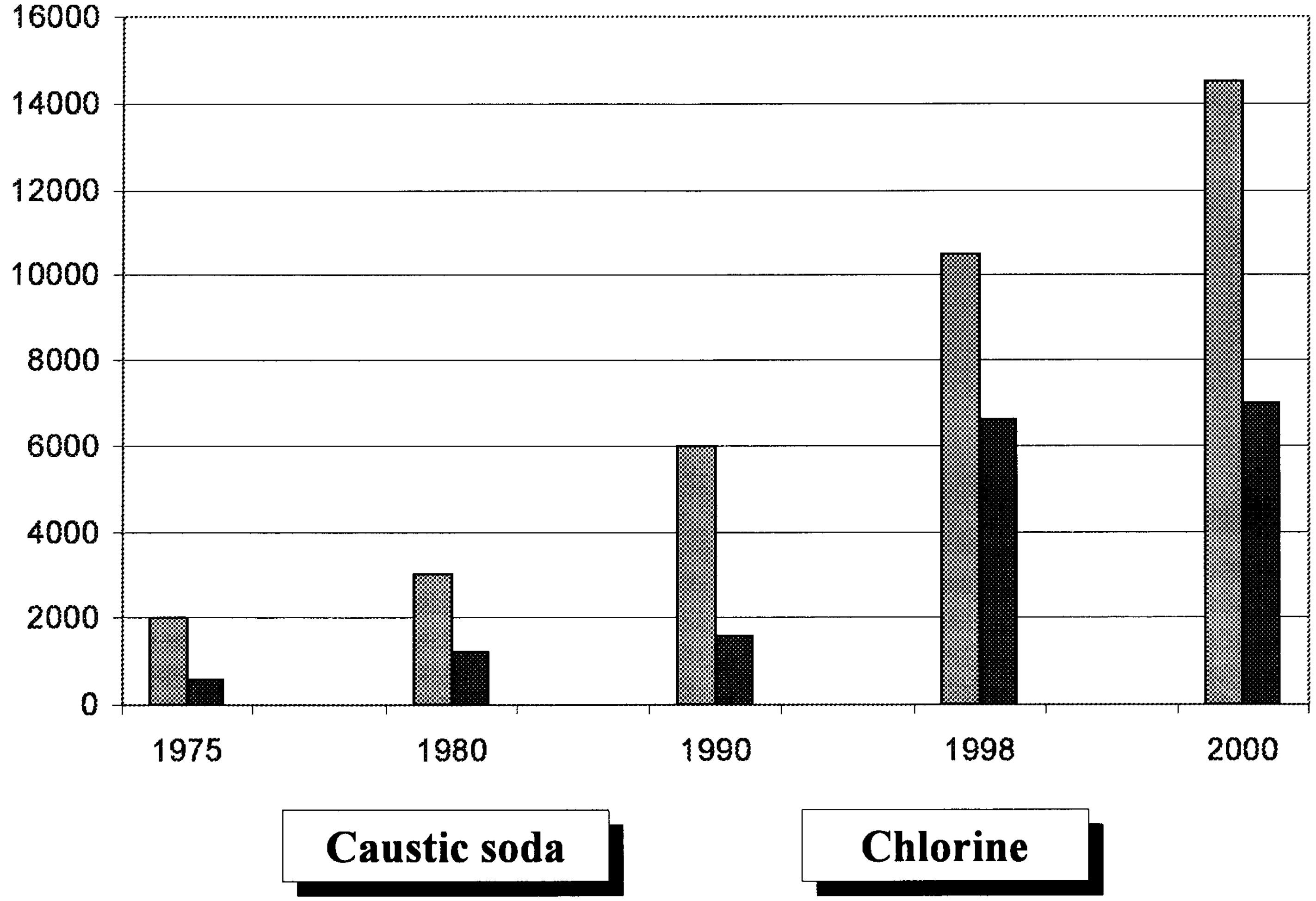
Raw Material Cost (Rs per Ton)



COSTS TRENDS OF COAL & FUEL OIL



TREND IN RISE IN COST OF CAUSTIC SODA & CHLORINE

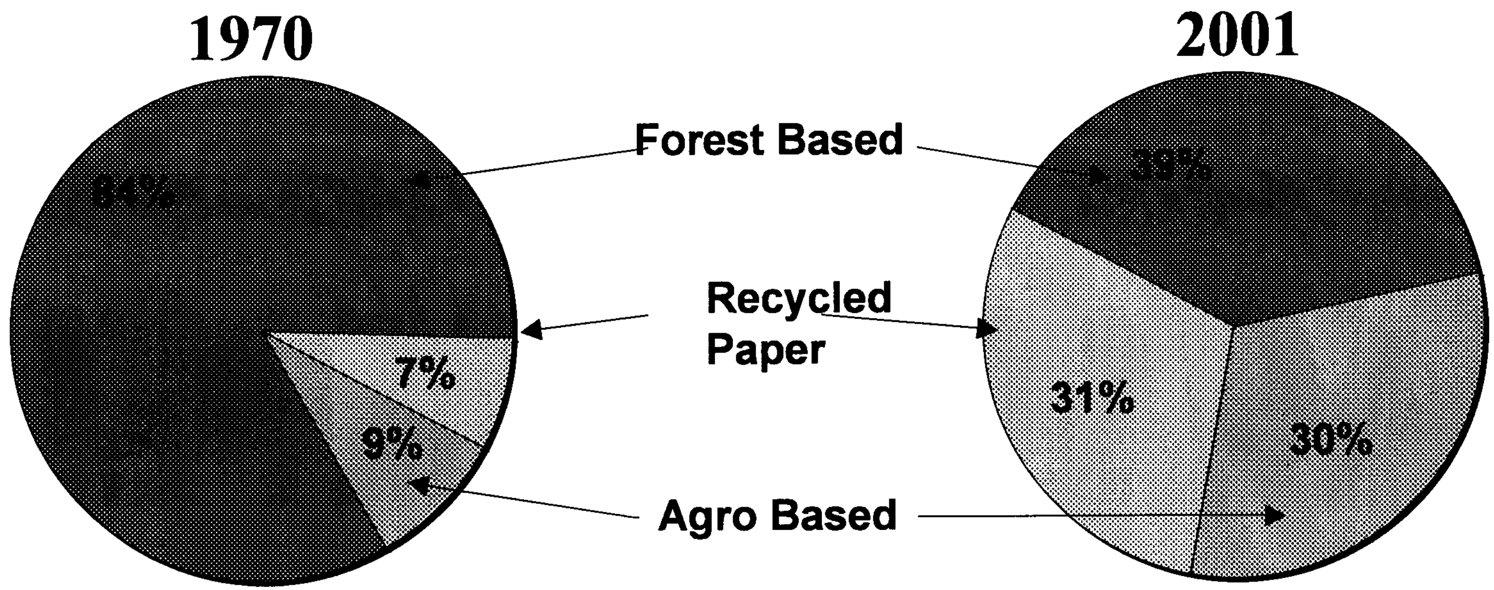


TECHNOLOGICAL TRENDS

Technological Issues

- Sustained raw material availability.
- Inadequate infrastructure.
- Uneconomic scale of operation.
- Obsolesence of technology in most cases.
- High cost of basic inputs.
- Eco friendly state of art processing technologies.

Raw Material : Change in Trends

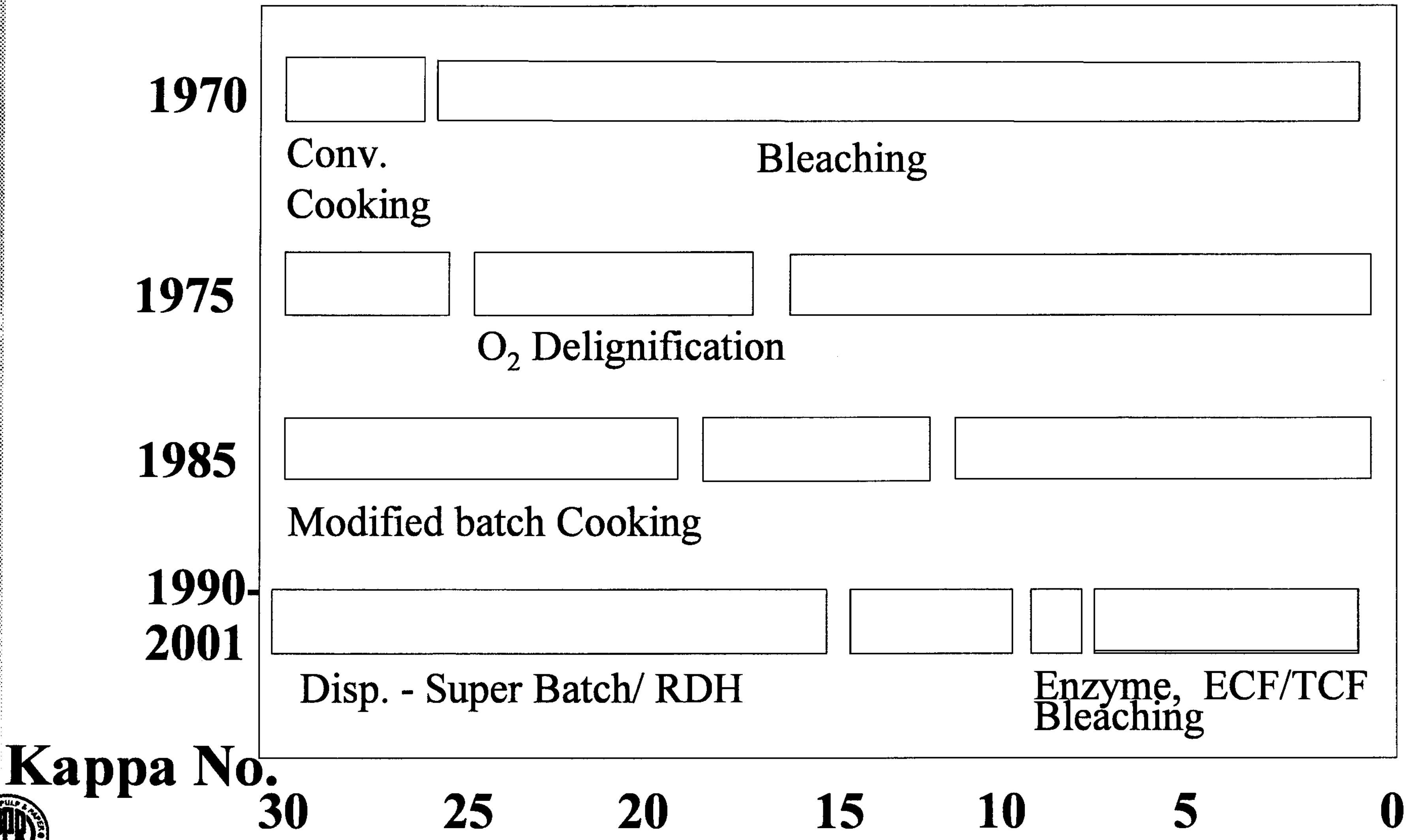


Data	Year	
	1970	2001
Registered Units	57	400
Production, Million tons/yr.	0.77	3.85

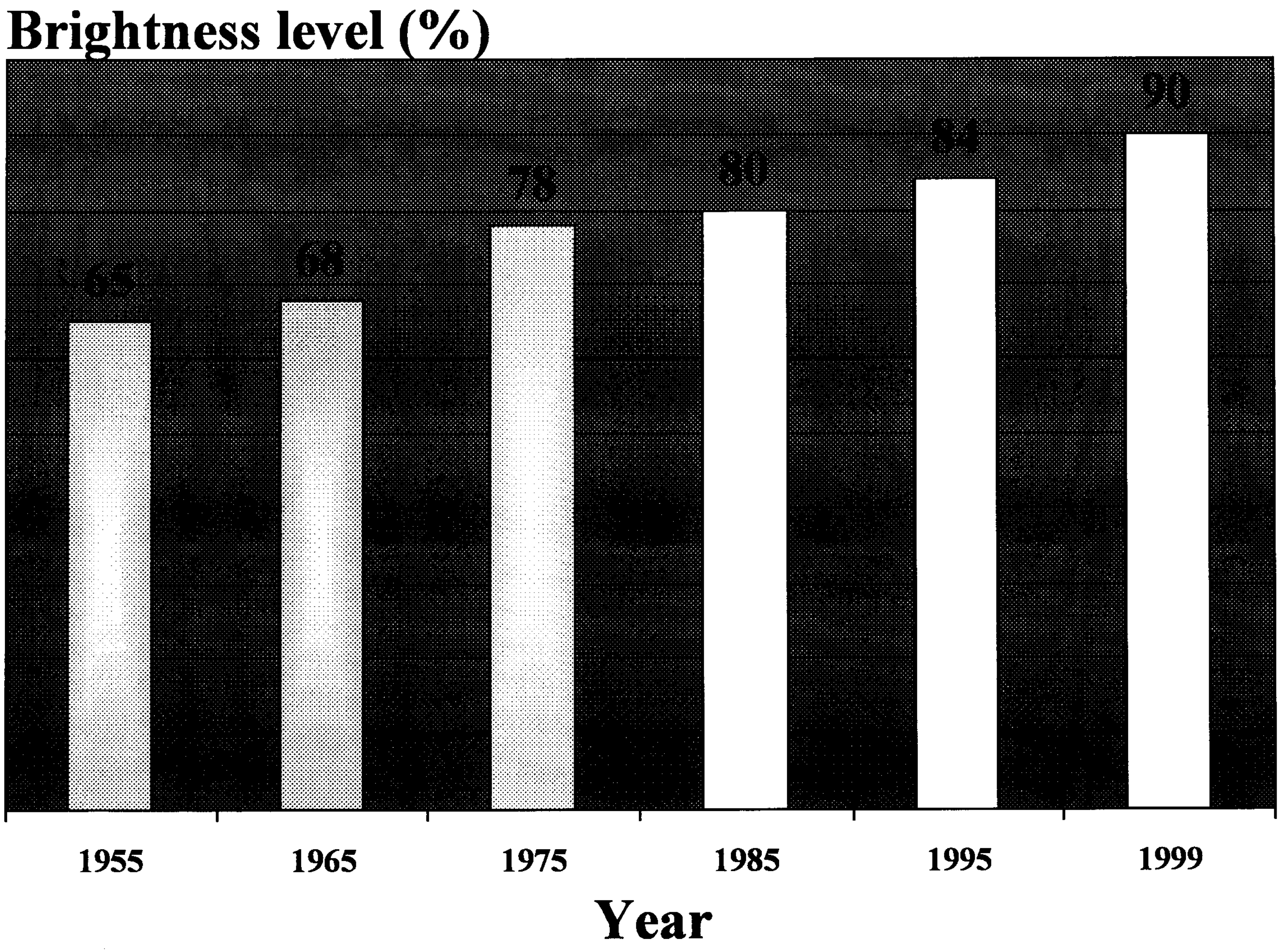
Development in Technology

- Improved Raw Material Handling & Cleaning.
- Continuous/ Modified Batch Digesters.
- State of Art Washing Systems.
- Elemental Chlorine Free Bleaching.
- Omission of Direct Contact Evaporators.
- Lime Sludge Reburning System.
- Improved Solid- Liquid Separation Techniques.
- Energy efficient Effluent Treatment practices.

Pulping & Bleaching Scenario
(1970-2001)



Brightness Level of Paper



ENERGY AND ENVIRONMENTAL ISSUES

Energy & Environmental Issues in different sectors of paper industry

Large Paper Mills

- Higher energy consumption, water usage and discharge of colored effluent
- Discharge of Toxic chlorinated organic compounds (AOX).
- Solid waste generation – Lime sludge & Fly ash.

Medium & Small Paper Mills

- Higher AOX generation.
- Lack of chemical recovery leading to energy & chemical losses.
- Inefficient equipments leading to high utilities.

AOX DISCHARGE LEVELS : SEGMENT WISE

TYPE OF MILL	AOX LEVEL kg/T PAPER
RAYON GRADE PULP	<0.5
NEWSPRINT PULP	<0.5
LARGE PAPER MILL	1.0 – 2.5
MEDIUM & SMALL MILLS	4.0 – 6.5

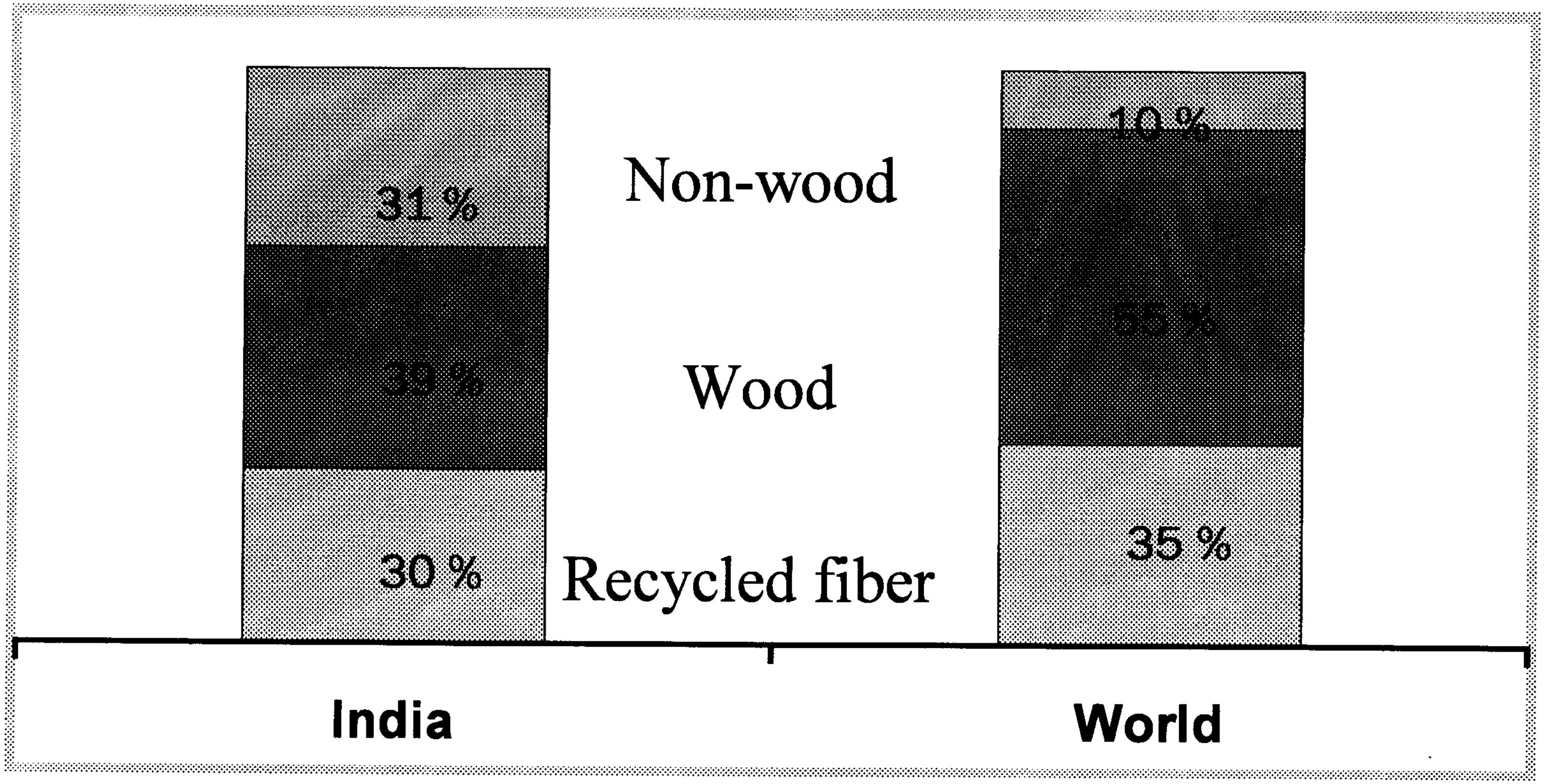
GLOBAL COMPETITIVENESS OF INDIAN PAPER INDUSTRY

ISSUES AND CHALLENGES

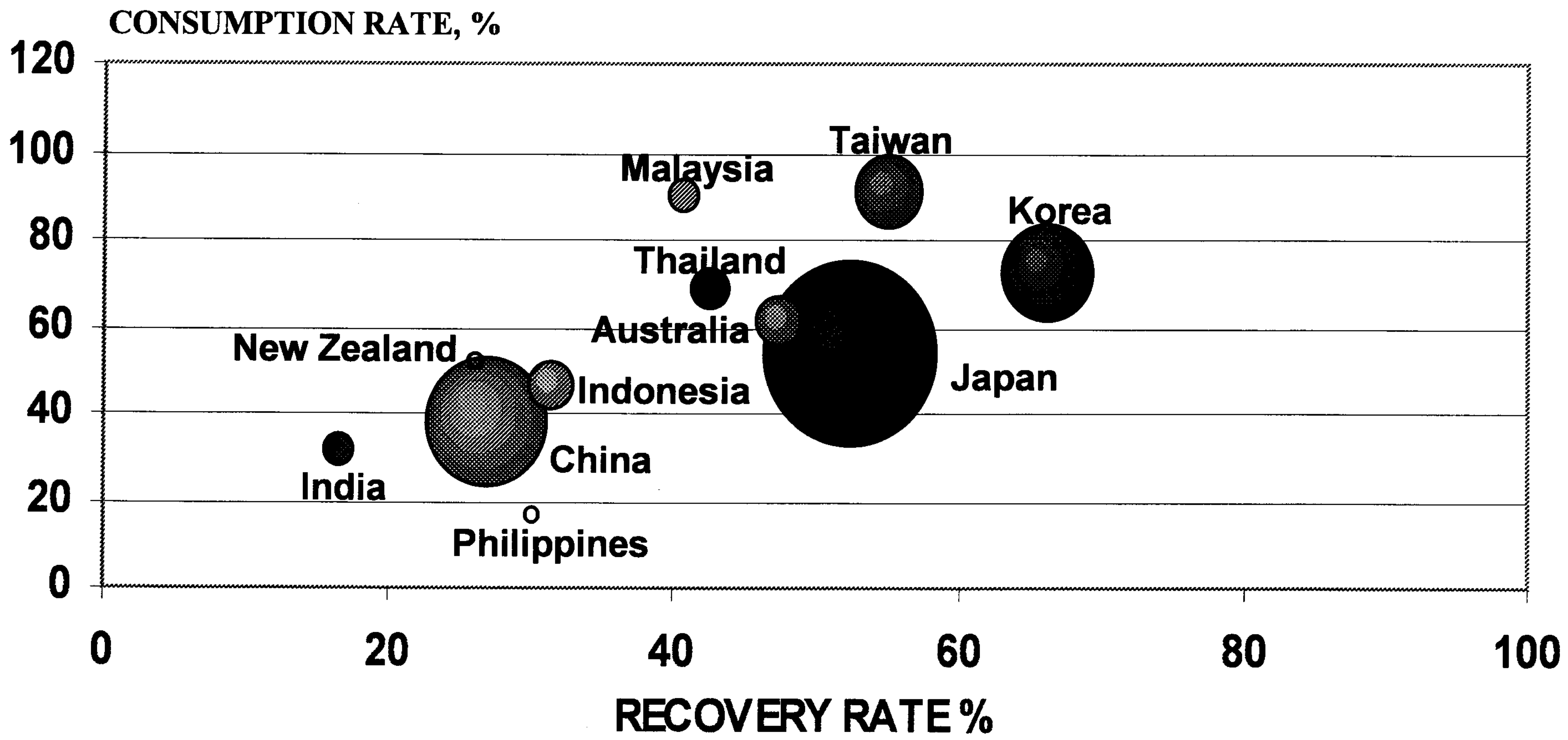
India Vs World : An Overview (2000)

Parameter	**India**	**World**
Installed Capacity, Million tons/yr.	5.4	364
Average size, tons/yr.	13,300	41,000
Production, Million tons/yr.	3.9 (1.2%)	323
Production Growth Rate,%	4.6	2.6
Per Capita Consumption, kgs	4.0	54.0
Consumption Growth Rate,%	3.5	2.9

Raw Material



Waste Paper Consumption & Recovery

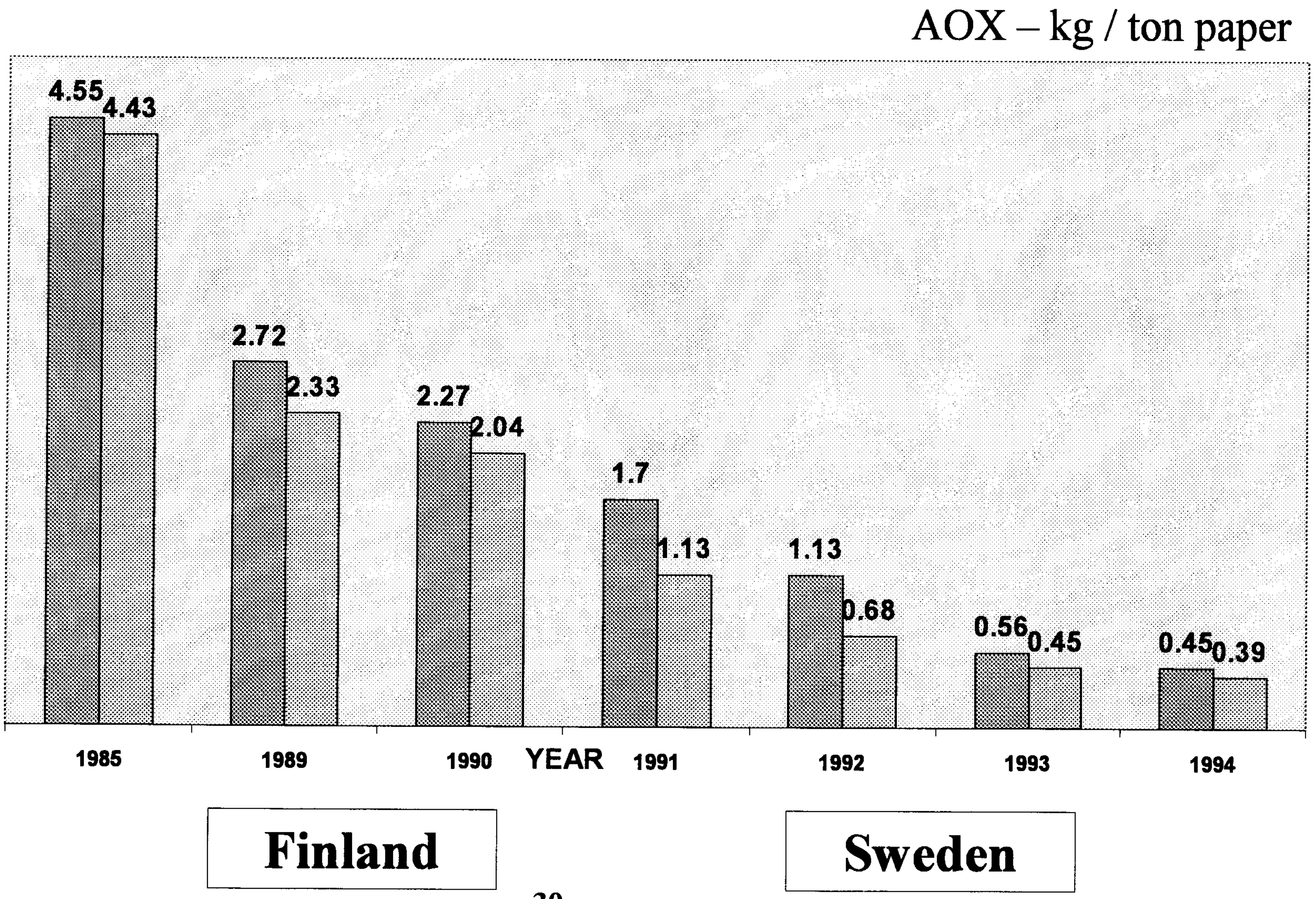


Bubble size is a function of w aste paper recovery in tonnes

Consumption of Basic Inputs

Input Norms (per ton basis)	**Mills in India**	**Mills Abroad**
Raw material, tons	2.0- 2.4	1.8-2.0
Energy, GJ	23-37	18-22
Water, m^3	120-150	50-100
Chemical Recovery,%	88-94	95-98
Manpower,nos.	14-20	5-7
Technical manpower, no.	2	4

DEVELOPMENT OF AOX DISCHARGES FROM PULP AND PAPER INDUSTRY



Global Competitiveness of Indian Paper Industry : Constraints

High cost of transportation and power

Low scale of operation

Low capacity utilisation

High capital costs

Issues & Challenges

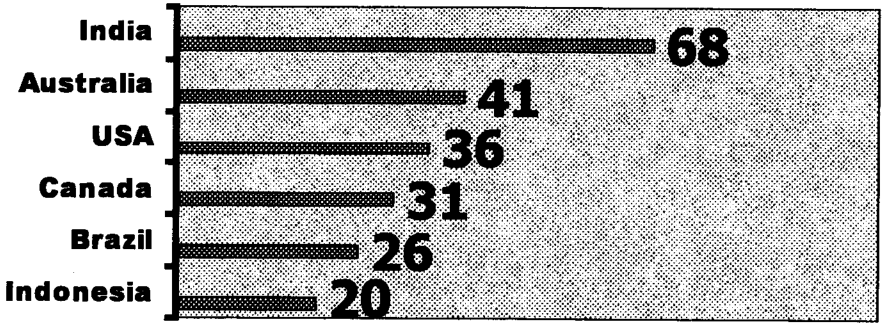
Inferior pulp & paper quality

State of art equipment & machineries

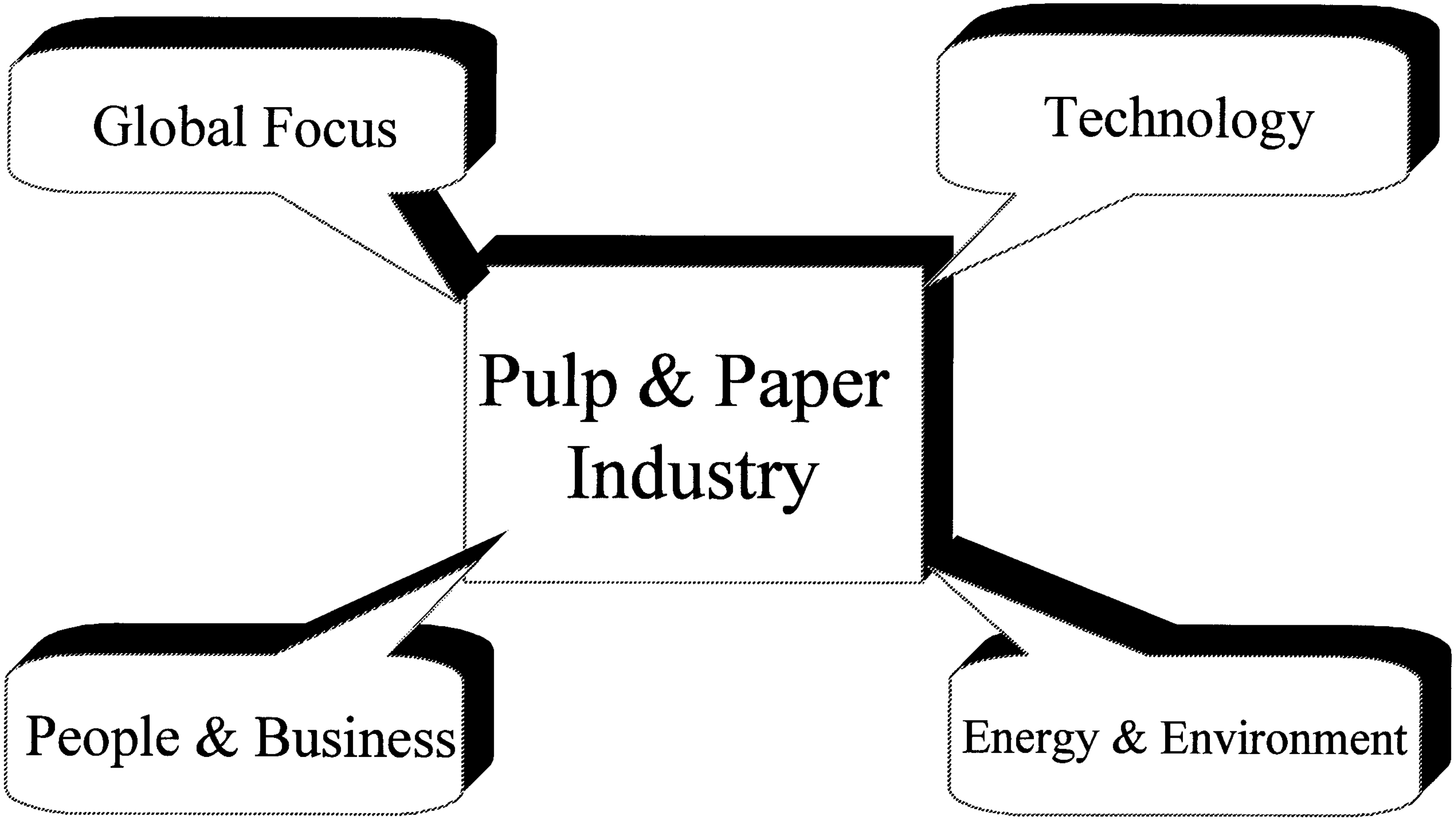
High costs of raw materials

Only 20% of the total used paper is recycled in India compared to a global recycling average of 40%

Raw material cost (USD per Ton)



Key factors that will affect growth of Indian Paper Industry



Global Focus

Technology

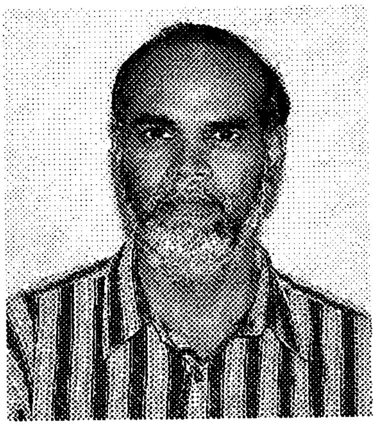
Pulp & Paper Industry

People & Business

Energy & Environment

FIBER MORPHOLOGY

STRUCTURAL VARIATIONS IN FIBER SOURCES AND THEIR INFLUENCE ON FIBERLINE OPERATIONS



Dr. S.V. Subrahmanyam
Scientist E - I

About The Author

Dr. Subrahmanyam has a Masters degree in Botany with specialization in Wood Science and obtained his Doctoral degree in Botany from Sardar Patel University, Gujarat.

He joined Hindustan Paper Corporation in 1981 in their R & D group in the Kerala unit and worked in the area of biotechnological application in Pulp & Paper industry and evaluation of various fibrous raw materials for their suitability in Paper industry.

Subsequently in 1990, he joined Central Pulp & Paper Research Institute, Saharanpur as a Scientist. He has worked in the areas of refining of wood and non-wood fibers. He has obtained training in the area of fiber morphology and quality control from PAPRO, New Zealand. He is currently working in area of Pulping & Bleaching.

STRUCTURAL VARIATIONS IN FIBER SOURCES AND THEIR INFLUENCE ON FIBERLINE OPERATIONS

S.V.Subrahmanyam*, R.D. Godiyal*, Priti S. Lal*, A.K.Sharma* & S. Tripathi*

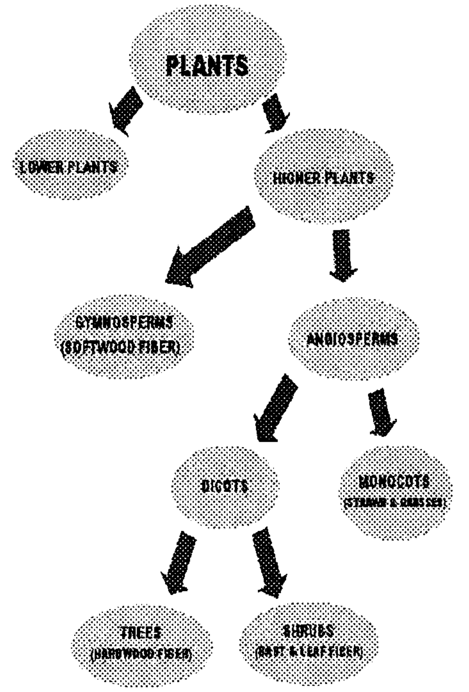
1. Vegetable Fibers

Pulp fibers are manufactured by chemical digestion of the lignin from the raw material that keep the fibrous tissue together to form the original structure of raw material. The aim is liberate the fibers with least possible damage. These fibrous tissues are called fiber tracheids in softwoods, libriform fibers in hardwoods and fibers in annual / seasonal plants.

2. Morphology and Fiber Processing

Fibers from any plant source can be used for making paper. Fiber morphology, pulp composition and economics will ultimately determine the utility of a raw material for pulp and papermaking.

3.



Plants based on their evolutionary status are grouped and sub grouped. The raw material for paper industry is derived from gymnosperms (softwoods), dicot trees (hardwoods), dicot shrubs (mostly bast fiber) and monocots (grasses straws and bagasse). Depending on the evolutionary status, the tissue components vary in their morphology, quantity determining the quality of the pulp that it yields. Eg. Monocots have very high non-fibrous tissue and finer fibers

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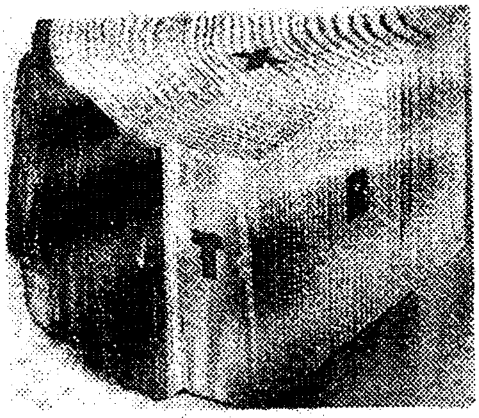
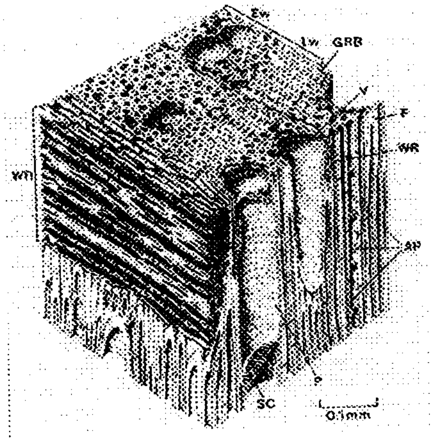
** Scientists, PCPB Div. CPPRI, Saharanpur, UP-247001*

4.



The wood structure is studied in three different planes ie. Cross sectional plane, Radial plane and Tangential plane. This will give the complete information about different tissues in wood.

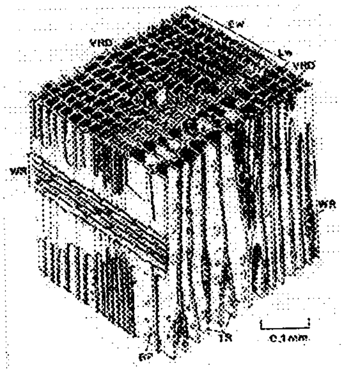
5.



Schematic section of hardwood : AP – axial parenchyma; F – wood fiber; Ew – early wood; Lw – late wood; GRB –growth ring boundary; p – pit; WR – wood ray; Sc – scalari-form plate.

The hardwoods are porous. The size and distribution of pores is an inherent character of each species. The pores are normally visible to the naked eye. The pores help in free flow of liquids.

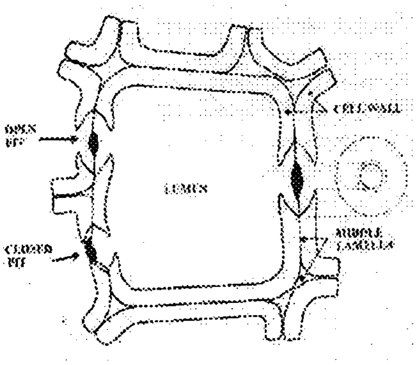
6.



Schematic section of softwood (pine): BP – bordered pit; Ew – early wood; Lw – late wood; TR – tracheids; VRD – vertical resin duct; WR – wood ray; Sc – scalariform plate.

The softwoods have only fiber tracheids (fibers) and parenchyma. The fibers have a radial width of 30 to 40 □m. The liquid flow happens through pits of these fibers only.

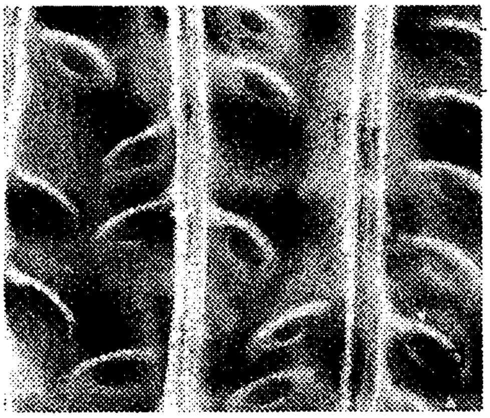
7.



Cross section of one tracheid showing bordered pits.

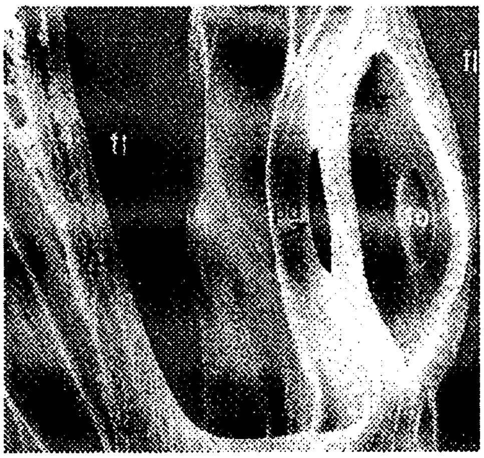
Penetration/flow of liquids or vapour primarily takes place through these pits only in softwoods

8.



Softwood fibers (tracheids) have prominent pores, known as pits along their walls. Based on the pattern, orientation and morphology, it is possible to identify the species.

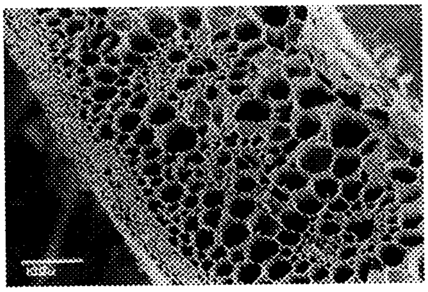
9.



Pa – pit aperture; to - torus

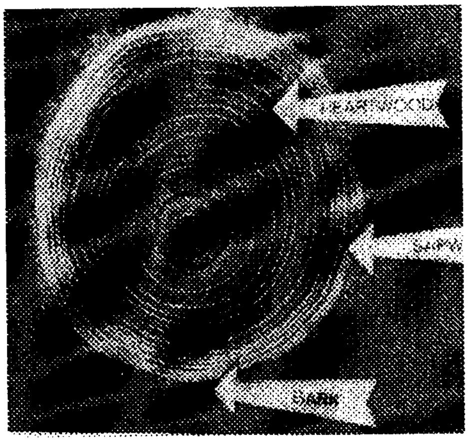
The softwood pits are cup shaped with an aperture in the center. A pit pair connects two adjacent tracheids and facilitates the liquid flow in the wood.

10.



Fibers are located differently in grasses and woods. Fibers in grasses (eg. Wheat straw) are located i) in the sub-epidermal zone of 5 to 15 layers and ii) in the strands of vascular bundles suspended in the ground parenchyma tissue. Fibers in woods are located in the woody portion of the stem below the bark.

11.



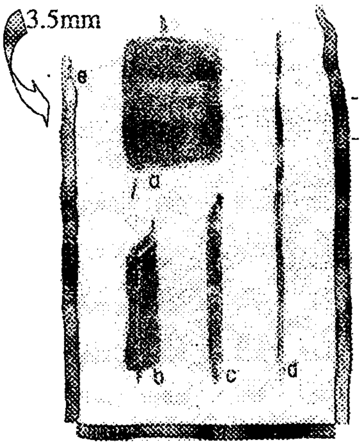
Cross section of wood trunk may reveal two distinct zones. Dark colored heartwood in the core and light colored sapwood in the periphery. Heartwood has higher extractive content.

12.

The magnified view of growth rings in cross sectional view.

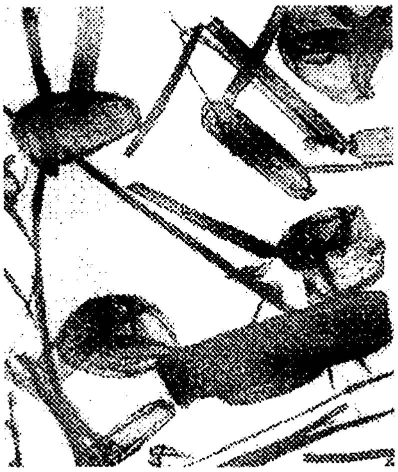
Fibers formed in spring/summer/have wide fiber lumen and thin walls, known as spring/summer/early–wood fibers. Fibers formed in winter have thick walls and known as winter/late-wood fibers. The papermaking properties of these types of fibers are entirely different.

13.



All pulps irrespective of the sources have fibers and parenchyma. Parenchyma tissue constitutes the primary fines in any pulp. Primary fines content may vary from species to species. Fibers of softwoods, also known as tracheids, are the longest and widest wood fibers available. The tracheids are normally 2-3 times wider and 3-4 times longer than those of hardwood fibers.

14.



The non-wood pulps have high proportion of non-fibrous tissue namely, parenchyma, epidermal cells, spiral vessel thickenings in addition to fibers. The quantity of non-fibrous tissue in a pulp ranges from 35 to 45%. The non-fibrous tissue has very high specific surface area resulting in very low freeness of the pulp.

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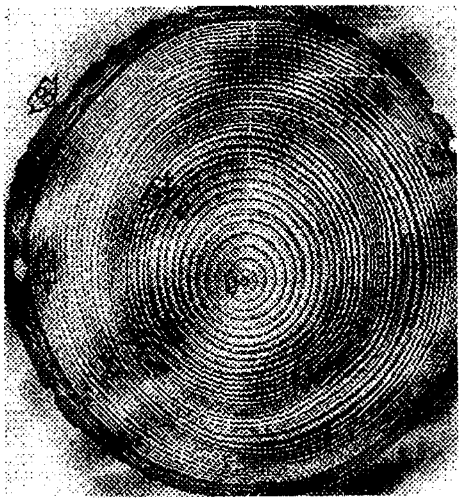
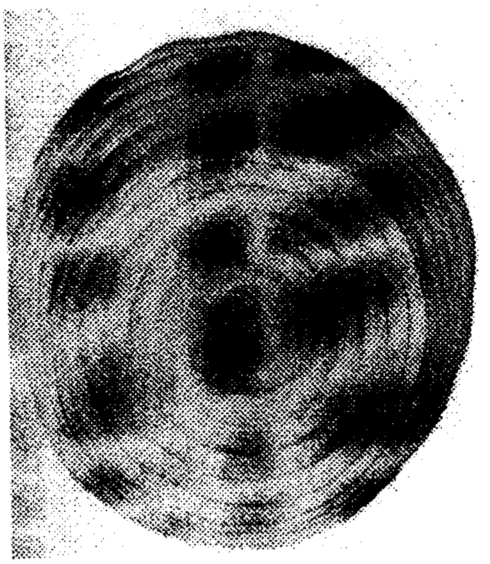


Cross-section of tree trunk showing concentric rings. One dark (latewood) and one gray (earlywood) ring constitute one growth ring, which is added to the trunk every year. The fiber dimensions vary with tree maturity.

Radiata pine kraft pulp fibers

	Length mm	Width □m	Diameter □m
Slab wood	3.1	6.2	38.6
Core wood	2.9	5.5	
Thinnings	2.2	4.2	36.7

16.

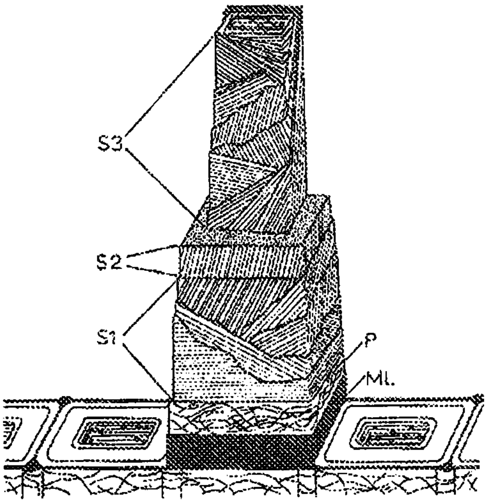


Reaction wood and quality variations:

Reaction wood is formed as compression wood, which is rich in lignin, in the lower sided of slanting trunk in softwoods.

Reaction wood is formed as tension wood, which is rich in cellulose, in the upper side of slanting trunk in hardwoods.

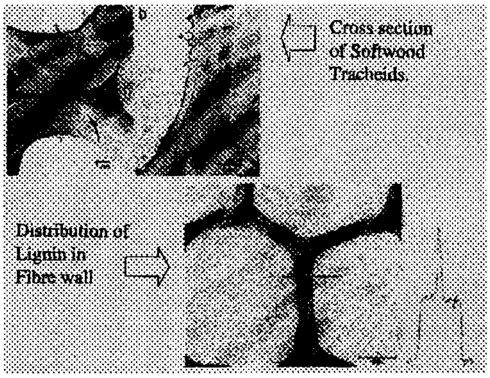
17.



The cell wall of fibers is structured in layers. The outer most amorphous and lignin rich layer, known as middle lamella (ML) cements fibers together. The cell wall is divided into two layers ie. Thin primary wall (P) with random network of micro fibrils embedded in amorphous material and the thick secondary wall (S). The secondary wall is subdivided into three layers S_1, S_2 and S_3. The orientation of micro fibrils with respect to the fiber axis is an inherent factor. This fibril angle is responsible for the varying degree of fiber extensibility and tensile strength, and fibril angle has inverse relation with fiber wall thickness.

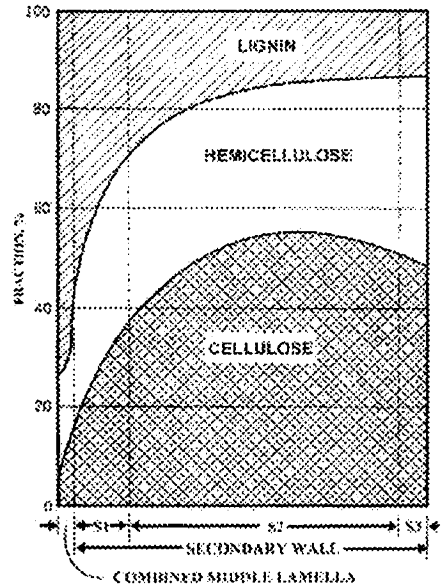
Fiber	Fibril angle	Tensile 100kg/mm^2 / wall thickness	Source
Spruce	10° 30°	100 50	DH Page
Slash pine	30° 5°	5□m 10□m	Hiller

18.



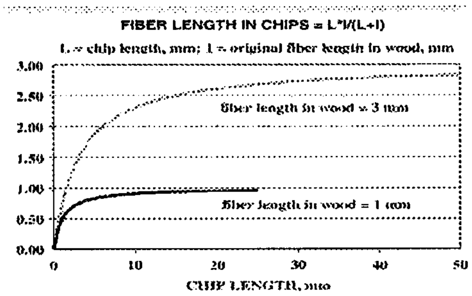
The middle lamella is rich in lignin, which can be made out from the concentration profile of lignin content across two cells.

19.



The chemical composition of fiber wall varies across the cross section. The major components are lignin, cellulose and hemi-cellulose. Lignin concentration is highest in middle lamella and lowest in S_2 and S_3 layers of secondary wall. However, due to the proportion of wall area in S_2 layer is maximum (≃ 80%) the total lignin content is more in S_2 layer.

20.



Chip length is dictated by fiber length for a given type of fiber source. Fibers are shortened during chipping. Hardwoods can be chipped to a length of 10 mm without much damage to fiber length, whereas softwoods can not be chipped to lengths lower than 20 mm.

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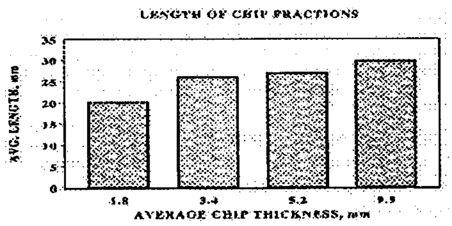


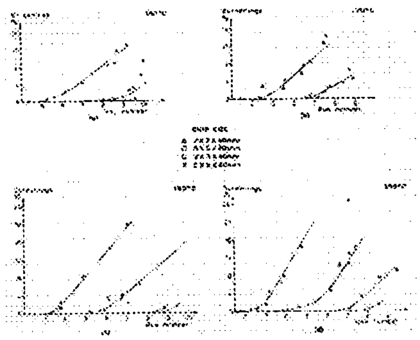
Chips thickness is dependent on chip length.

22.

Chip length (mm)	2	2-4	4-6	6-8	8-10	Total
Fraction as % wood	2.0	26.6	40.1	21.6	9.6	-
% rejects of fraction	1.5	0.5	1.1	3.1	6.8	-
% rejects on wood	0.03	0.13	0.44	0.67	0.65	1.92

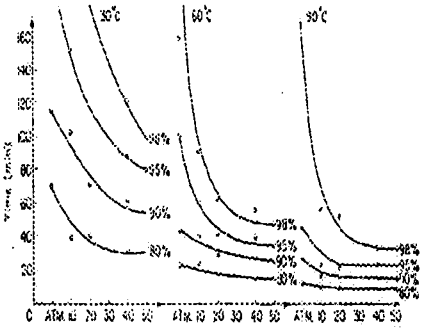
Reject levels across the chip fractions: Average values for white spruce, Douglas fir and western red cedar)

23.



Rejects percent and concurrent Roe number is influenced by chip (pinewood) thickness and cooking temperature. Roe number indicates the lignin content in pulp.

24.



Impregnation: Chips are saturated with liquor in this phase. This has to be achieved in shortest possible time to optimal level. To achieve, the air has to be expelled. Steaming helps in heating of chips that would cause the air in chips to expand and about 25% of air will be expelled. The chip moisture is converted to vapour by the steam heat, will help in expulsion of further air. Diffusion of steam inward and air outward will further reduce air content. Important variables in this process are temperature, time and steam pressure.

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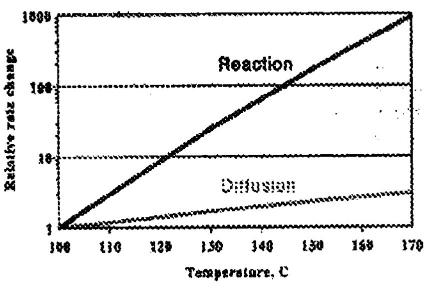

Reaction rates are much more temperature dependant than rates of diffusion. The delignification non-uniformities are bound to develop where the rate of diffusion is the controlling factor. Such situations are probable with poor impregnation, low liquor concentrations and thick chips.

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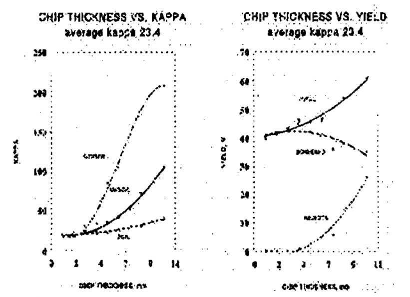
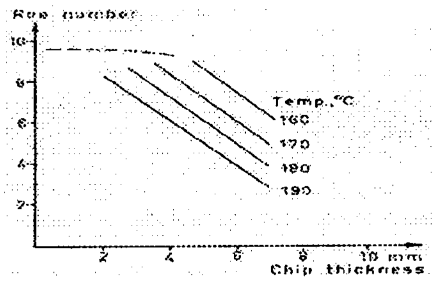


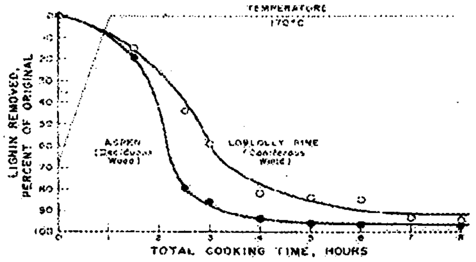
As cooking proceeds, reactive ions must diffuse into chips. If the diffusion distance is too long and rate of diffusion too slow, the chemicals are consumed before they can reach chip center, resulting in non-uniform delignification. These are critical balance between rate of ion transport, chip thickness and rate of chemical reaction. Delignification non-uniformity increases with the structure, quality and thickness of chips.

27.



Thick chips generate more screen rejects compared to thin chips, which is aggravated by higher cooking temperature. The higher the cooking temperature, the higher is the rate of difference between delignification and diffusion., Cooking uniformity can be improved by improved chip uniformity, good impregnation, lowest possible (optimum) cooking temperature.

28.



Delignification	% of removal	Location
Initial	20	S_2
Bulk	90	S_2 to ML
Residual	>90	S_2 to ML

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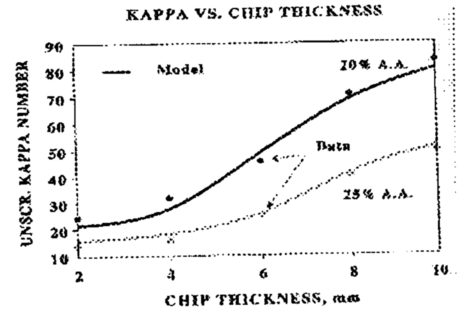
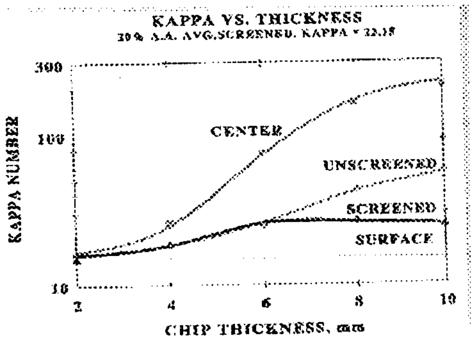


Chips of varying thickness layered in the same digester. Diffusion of new alkali into thick chips is too slow to compensate for consumption. Higher initial alkali helps in improving the situation to some extent, but the limitation could be the handling of black liquor with higher inorganics.

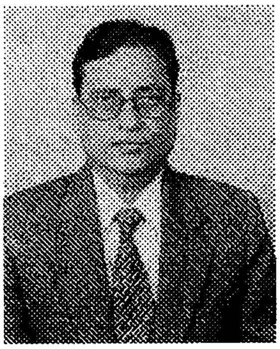
30.



Chip thickness over 4 mm shows distinct delignification gradients. But chips of thickness over 8 mm are not delignified in the center. Application of any physical forces to convert the rejects to accept portion will have serious consequences in bleaching area.

PULPING

CHEMICAL ASPECTS OF PULPING & BLEACHING



Dr. A.G. Kulkarni,
Director, CPPRI

About The Author

Dr. A.G. Kulkarni, Director Central Pulp & Paper Research Institute (CPPRI) Saharanpur, Uttar Pradesh, India has been with the CPPRI since its inception. He holds a Master degree in Chemistry & Doctorate in Black Liquor and Lignin Chemistry.

Dr. Kulkarni has pioneered the research work on Desilication of black liquor with eventual development of mill scale plant, installed at Hindustan Newsprint Ltd., Kerala and High Rate Bio methanation of black liquor rich effluent and a mill scale unit is successfully operating at Satia Paper Mills is another achievement of Dr. Kulkarni. His contribution in the area of physico chemical & thermal properties of agro - residue non-wood black liquors has now made it possible to process this liquor in chemical recovery boilers. He has published more than 300 scientific papers in Indian and International journals. He is widely traveled in Europe, S. E. Asia, and Australia and has been on several foreign missions as UNDP/UNIDO Consultant.

His areas of specialization include pulping and bleaching, black liquor-its chemistry & processing, environment and energy management. Dr. Kulkarni holds several patents-important ones being on desilication of black liquor, thermal treatment of black liquors and Direct Alkali Recovery System etc. He is a member of several National and International Scientific & Technical organizations and also on board of Directors of Paper Mills & Research organizations

CHEMICAL ASPECTS OF PULPING AND BLEACHING

A G Kulkarni*

1. Introduction

1.1 Pulping Of Wood

The wood is composed of cellulose, lignin and extractives. The main aim of the pulping is to separate the cellulosic fibers from other components of the wood. Different kinds of pulping processes like **chemical, semi-chemical and mechanical pulping processes** are employed depending on the type and end-use of the pulp to be produced. Only in chemical pulping process almost all lignin and extractives are dissolved leaving behind cellulosic fibers. For writing, printing and other fine grades of paper, chemical pulps are used. Different chemical methods like – Soda process involving cooking with sodium hydroxide, Sulfite process with calcium or sodium bi-sulfite and Kraft process with the mixture of sodium hydroxide & sodium sulfide, are available. Kraft process is the predominating one among all chemical pulping processes. The pulping treatment involves heating of wood chips in an aqueous solution of sodium hydroxide and sodium sulfide at cooking temperature of about 170°C for a period of one or two hours. During this treatment lignin is extensively degraded and degradation products are solubilized. Carbohydrates, in particular, hemi-celluloses, undergo partial degradation and dissolution. Extractives are, to a large extent, removed. Major reasons for the success of Kraft process are – simplicity and rapidity of pulping, ability to pulp almost all types of wood, higher pulp yields and high quality of resultant pulp. Due to these reasons although the process was introduced in 1879 only limited changes have been made in the practical performance of the process[6]. The process is also known as Sulfate process as sodium sulfate is used as the make-up chemical during chemical recovery operation. Almost all big mills in India are employing Kraft process for production of chemical grade pulp.

2. Extraction In Alkaline Pulping

When looked into the anatomy of the wood it is evidenced that cellulose fibers are cemented by polymeric lignin in middle lamella portion (Fig1&2). The basic principle of chemical pulping is to solubilize this lignin thereby separating cellulose fibers.

*** Director, CPPRI, Saharanpur, UP-247001**

This process is called delignification. Delignification involving lignin degradation is accompanied, to a varying extent, by degradation of carbohydrate constituents, i.e. cellulose and hemicelloses. Thus the quality of pulp and also the composition of spent pulping liquors are influenced by type and extent of lignin and carbohydrate degradation reactions.

2.1 Lignin Reactions

Lignins are broadly classified into two groups – "Guaiacyl" lignins and "Guaiacyl-Syringal" lignins[7]. Former type is present in softwoods, while the latter type in hardwoods. The basic difference in guaiacyl and guaicyl-syringal moities is that the former contains one methoxyl group per arylpropane unit and the latter two-methoxyl groups per unit[8]. However the elementary building blocks of all lignins are phenyl propane units inter-connected by C-O and/or C-C bonds[9]. Reactions of lignin during kraft pulping can be divided into two categories – degradation reactions which lead to liberation of lignin fragments and ultimately to their dissolution and the second type is condensation reactions which increase the molecular size of the lignin fragments and may result in their precipitation[10]. Extensive studies, during the past few decades, have been carried out using model compounds to elucidate the mechanism of these reactions[11, 12]. The main types of linkage in lignin and estimated values of their frequencies are given in (Fig.3). During pulping most of the carbon-carbon bonds are stable whereas carbon-oxygen bonds are cleaved to varying extent. Two main types of ether linkages in lignin phenolic aryl propane units exist i.e. – α -aryl ether bonds (types A and B) and β -aryl ether bonds (type C). Due to high frequencies of α -aryl ether linkages the alkali promoted and sulfide-lytic cleavage reactions play the dominating role in fragmentation of lignin during kraft pulping process. Only minor contributions are from β -aryl ether linkages in non-phenolic units.

2.1.1 Degradation Reactions

α -aryl ether bonds (types A & B Fig.3) are readily cleaved by the reaction involving an alkali promoted rearrangement of phenolate structure (I) into corresponding quinone methide structure (II) with the elimination of α - aroxy substituent[14, 15]. The rate is independent of hydroxide ion concentration provided the phenolic hydroxyl group in the substrate is completely ionized[16]. The degradation reactions are illustrated in (Fig 4&5) Phenolic units containing β -aryl ether bonds (type C in Fig. 3) undergo some initial transformation into intermediates of quinone-methide type by alkali promoted elimination of α -hydroxy or aroxyl groups.

In kraft pulping the presence of hydrosulfide and sulfide ions (SH^-, S^-) as species in sulfate cooking liquor has to be taken into account. These ions are weaker bases but stronger nucleophiles than hydroxyl ions. So quinone methide (III) formation (Fig.5) is followed by reversible addition of hydrosulfide ions giving benzyl mercaptide structure (IV). The mercaptide anion then intramolecularly attacks the β -carbon atom forming thiirane intermediates (V) with the elimination of the β -aroxy substituent (β -aryl ether cleavage) [17]. The thiirane structures eliminate elemental sulfur affording the corresponding p-hydroxy styrene structures (VI). Delignification is faster in sulfate (kraft) process as compared to soda process due to the fact that intermediates react with stronger nucleophiles (SH^-, S^-) rather than stronger base (OH^-).

Thus the main reactions responsible for lignin fragmentation are cleavage of α -aryl ether bonds in phenolic units via quinonemethide intermediate and cleavage of β -aryl ether bonds in phenolic units via quinone methide & episulfide intermediates. When all the phenolic units of the α and β -aryl ether types have reacted further lignin degradation requires drastic conditions in which β -aryl ether linkages in non-phenolic units are cleaved in bulk phase of delignification[18]. In the last phase i.e. residual phase possible cleavage of carbon-carbon bonds takes place via alkali promoted retrograde aldol type reactions[19]. Thus the initial phase comprises of the pulping treatment upto a temperature of about 150°C and results in dissolution of 20-25% of the total amount of lignin content. The bulk phase at 150-170°C results in dissolution of about 60% lignin and finally the residual phase at 170°C results in dissolution of 10-15% lignin.

The other type of cleavage is that of methyl aryl ether bonds occurring in almost every aryl propane unit. These are cleaved to an appreciable extent by action of sulfur containing nucleophiles (HS^- and $CH_3S^{-\ \text{ions}}$) present in pulping liquor. These reactions do not contribute to lignin fragmentation. The reaction affords methyl mercaptan and dimethyl sulfide, the main compounds responsible for malodor developed in kraft pulping.

Recently, the development of Anthraquinone(AQ) additive pulping has added more knowledge to the mechanism of delignifications. In AQ – additive pulping AQ acts as catalyst. The reaction involving AQ with AQ/AHQ – redox system is analogous to redox system of kraft process sulfur/hydro-sulfide ion. AQ/AHQ system has more pronounced effect on cleavage of β -aryl ether bonds facilitating the faster delignification rate (Fig 9&11).

2.1.2 Condensation Reactions

During all three phases of sulfate pulping (initial, bulk and residual delignification) lignin degradation and lignin condensation proceed concomitantly. Extent of degradation and condensation can be interpreted in terms of competition between nucleophiles supplied by cooking liquor (SH^- , S^- and OH^-), and carbonions from other phenolic units for quinone methide intermediates[20]. One type of primary condensation reaction is nucleophilic addition of carbanions formed from other phenolic units to yield cyclohexadienione intermediate (VII) which stabilize by elimination of a proton or a side chain giving rise to 1, 1-diaryl-propane (VIII) structures[15] (Fig 6).

Thus the ratio of degradation to condensation should be determined by the reaction conditions (sulfidity, alkalinity and concentration of dissolved lignin fragments). The dissolved portion of lignin should contain products rendered soluble by fragmentation. Analysis of kraft spent liquor revealed the presence of monomeric, dimeric compounds in addition to high molecular weight fraction[21].

2.1.3 Delignification Process

Lignin reactions in kraft pulping can be divided into three distinct phases: **initial delignification, bulk delignification and residual delignification**

(a) Initial Delignification Process

Lignin reactions in kraft pulping can be divided into three distinct phases: **initial delignification, bulk delignification and residual delignification.** Initial delignification takes place mainly in the inpregnation phase, well before final cooking temperature has been reached (i.e.<140°C). Very little lignin is dissolved here (20%-25% of total). Hydrosulfide sorption in the initial delignification phase will perform two important tasks: it will improve penetration and be in place to speed up bulk-phase reactions, simultaneously protecting cellulose from degrading and dissolved lignin from recondensing. Lignin does not readily decompose in this phase. Only those lignin fragments that are small enough to dissolve are extracted from the S2 cell wall.

(b) Bulk Delignification

The rate of delignification increases dramatically when the cooking temperature is elevated above 140°C, and 70%-80% of all lignin dissolves during this phase. The dissolution begins in the S2 layer of the cell wall and progresses into the middle lamella. The bulk delignification phase strongly depends on the OH^- ion and HS^- ion concentration and on temperature. The rates increase the higher these concentrations are. The rate of delignification slows down as the concentration of dissolved lignin increases. The overall rate is also slower in thick chips, since the rate is diffusion controlled. This means that thick chips will be left with a higher average lignin content than thin chips.

(c) Residual delignification

The bulk delignification phase will continue until about 90% of all lignin has been dissolved. The residual delignification phase which follows is considerably slower in which the three different rate phases for a softwood and hardwood are shown as a function of H-factor(a variable which combines time and temperature).

Alkali depletion in any phase of the delignification process will lead to recondensation of lignin polymers, and further dissolution will stop. This means that there must be some free alkali concentration("residual alkali") left after delignification has been completed. (5-15 g/L is considered normal).

2.1.4 Rate of Delignification

It is evident that the complexity of reactions occurring in phase boundaries between of wood surfaces and pulping liquor means that no pulping process can be treated as a homogeneous reaction system. It is however, possible to consider cooking as a first-order reaction mechanism.

The relation between time and temperature can be expressed as an Arrhenius type of rate equation Vroom[32] defined the term H-factor to account for the relative rate of delignification versus temperature (Fig 8). The H-factor is defined as 1 for a pulping effect of 1 h at 100°C, it increases with temperature as determined by the activation energy typical for delignfication. As a rough rule of thumb, one can assume that the rate of reaction in kraft pulping doubles with every 10°C increase in temperature. Examples of the effect of H-factor on yield and residual lignin content (Fig 10&12).

The effect of alkali charge or concentration on pulping rate is also a dominating factor, which shows the effect on delignification rate of various alkaline solutions when cooking spruce at 160°C. The increase in rate when changing the solvent from water to an alcohol is explained by easier penetration and reaction with organic solvents. Delignification time can be reduced by half when increasing sulfidity from 0% to 31% at 170°C.

The initial concentration of cooking reagents is set by the liquor-to-wood ratio applied and the charge of active chemicals. All reactions with the wood material take place in the liquor phase, which means that a prerequisite for homogeneous cooking is that the chips are submerged in liquid. This requirement limits the minimum liquor-to-wood ratio in a batch cook to about 4-5 t/t_{wood} depending on the degree of chip compaction and chip density. In continuous-flow cooking liquid and chips can move through the process at different velocities allowing much lower initial liquor-to-wood ratios ($2\text{-}3t/t_{wood}$) while still meeting the requirement of complete chip immersion. The possibility of changing chemical concentrations applied in cooking is limited by white liquor concentration and process selection.

2.2 Carbohydrates Reactions

Carbohydrates in wood are broadly grouped into cellulose and hemicelluloses. Cellulose is a linear chain polymer with β-D-glucopyranose units joined by 1 to 4 linkages. The amorphous polymeric carbohydrates that are associated with cellulosic portion are termed as hemicellulose. Hardwoods contain more hemicellulose than softwoods and consist mainly of pentose sugar-xylose, while in softwoods, it consists mainly of hexose sugar i.e. mannose[22]. During kraft/soda pulping process two types of reactions are mainly responsible for degradation of wood carbohydrates namely; the peeling reaction which may start at temperatures of about 100°C and the other type of reaction – the alkaline hydrolysis of glycosidic bonds at elevated temperatures. Typical end wise degradation of cellulose chain is given in (Fig.7).

The degradation involving cleavage of glycosidic bonds in reducing and groups involving rearrangement to enolate anions with the elimination of the adjacent sugar unit is a key step of peeling reactions and is called β-elimination and is analogous to aroxy sustituent in β-aryl ether linkages in lignin[24]. Glucoisosaccharinic and xyloisosaccharinic acids are the main components of the polysaccharide degradation products. Significant proportion of other aliphatic acids, like lactic and acetic acids are also formed due to degradation of xylan portion of carbohydrate. It has been reported that more than 20 different carboxylic acids are present in the spent liquor and amount to over 90% of the total acid fraction[25] (Fig 13).

Substantial amounts of carbohydrates will dissolve during alkaline coking, despite the fact that delignification is the prime goal of pulping. This is especially true during the initial delignification phase. Galactoglucamannan for example, will dissolve already almost completely below 130°C. About 75% of all the carbohydrates dissolved in range 100-130°C is glucomannan. Xylan will dissolve at higher temperatures, i.e. >140°C will slow down during the bulk delignification phase. Dissolution of carbohydrates, mainly hemicelluloses, will slow down during the bulk delignification phase and speed up again – relative to delignification – during the residual delignficiation phase.

The degradation of hemicelluloses generates acid groups which consume alkali. Most of the alkali is consumed during the initial and early bulk phases of kraft cooking for neutralization of the acidic compounds formed. The difference is selectivity of different delignification phases is well demonstrated by ploting carbohydrate yield against lignin yield.

Cellulose will also dissolve to some extent (10%-15%) during alkaline cooking. Cellulose degradation is especially strong during the residual delignification phase. This measured as a greater pulp yield loss late in delignification and as reduction in the degree of polymerization of the polysaccharides. Continuing the residual delignficiation phase in a standard cook will lead to weak fibers at low yield. The lower yield of softwood kraft pulp is due to its higher initial lignin content (and hence the greater relative amount of lignin removal) and particularly the high dissolution of glucomannan.

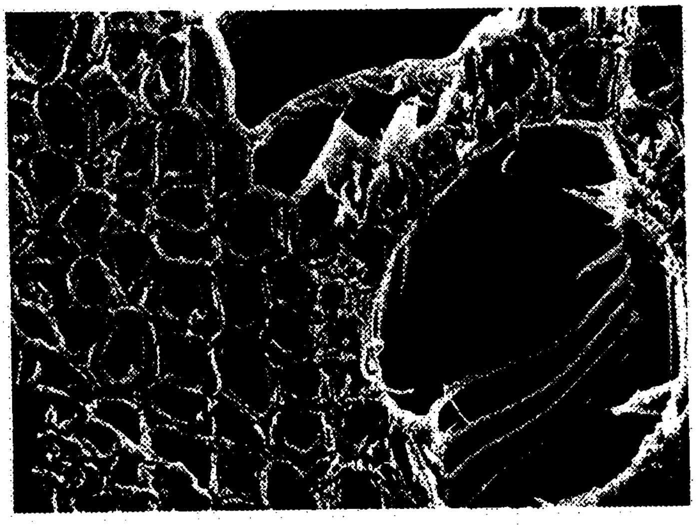


Fig 1 Transverse plane of a hardwood *(Betula verrucosa)* showing the cross-cut fibres and a vessel with a ladder-like perforation. SEM micrograph.

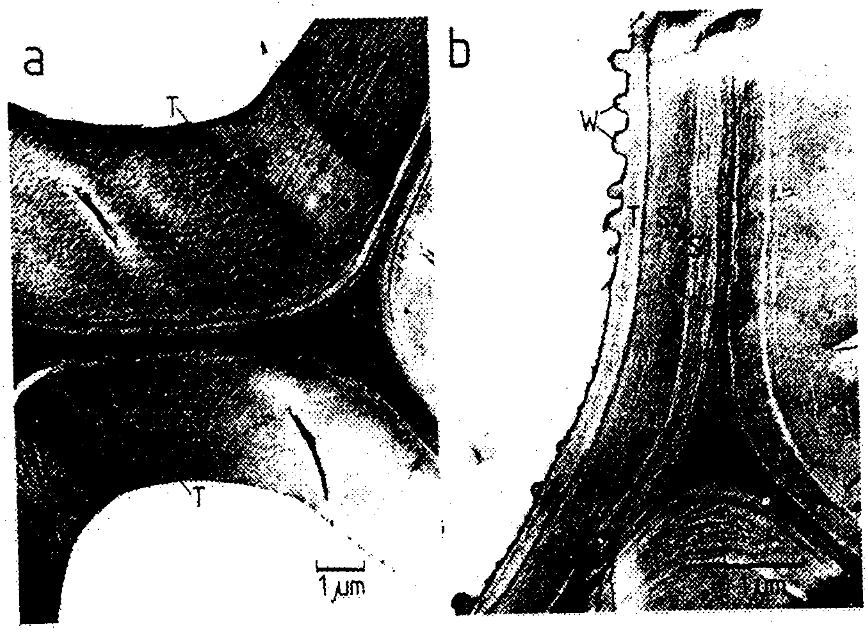
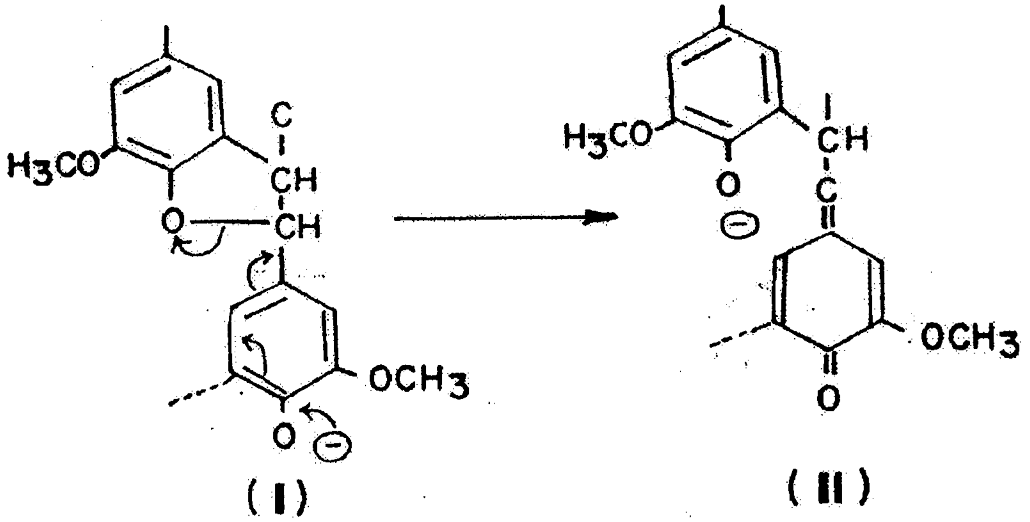
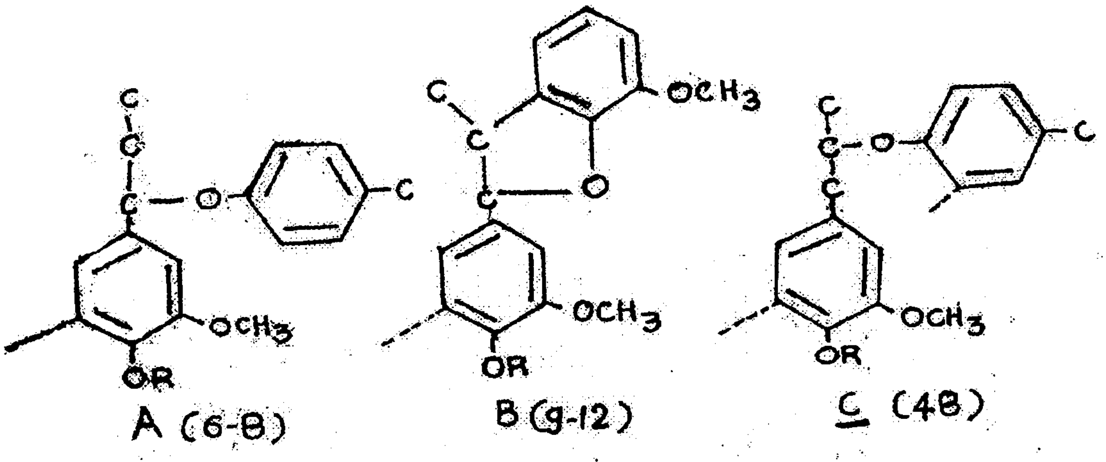


Fig 2 Ultrathin sections of the walls of softwood tracheids (a) *(Picea abies)* and of a hardwood vessel (b) *(Fagus sylvatica)*, which show the various wall layers: ML = middle lamella, M = compound middle lamella, P = primary wall, S 1 = secondary wall 1, S 2 = secondary wall 2, T = tertiary wall, W = warts. TEM micrographs.



Alkaline Cleavage Of α - Aryl Ether Bonds

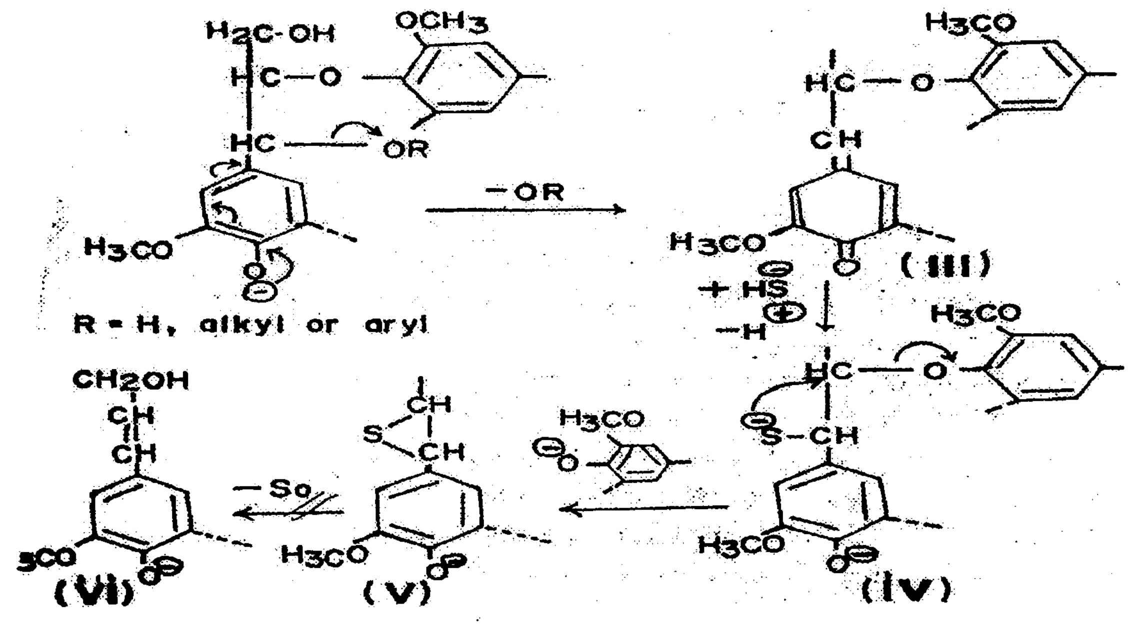
Fig 3



(DOTTED LINE INDICATE POSSIBLE LINKAGES TO ADJACENT UNITS)

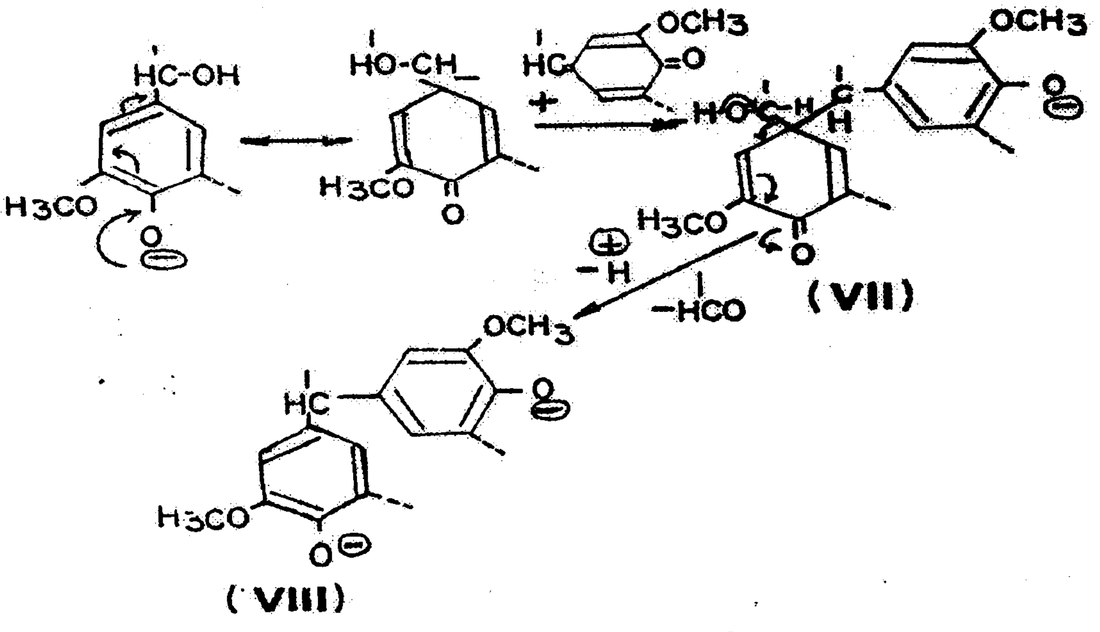
Type Of Bonds Interconnecting Aryl Propane Units Of Lignin

Fig 4



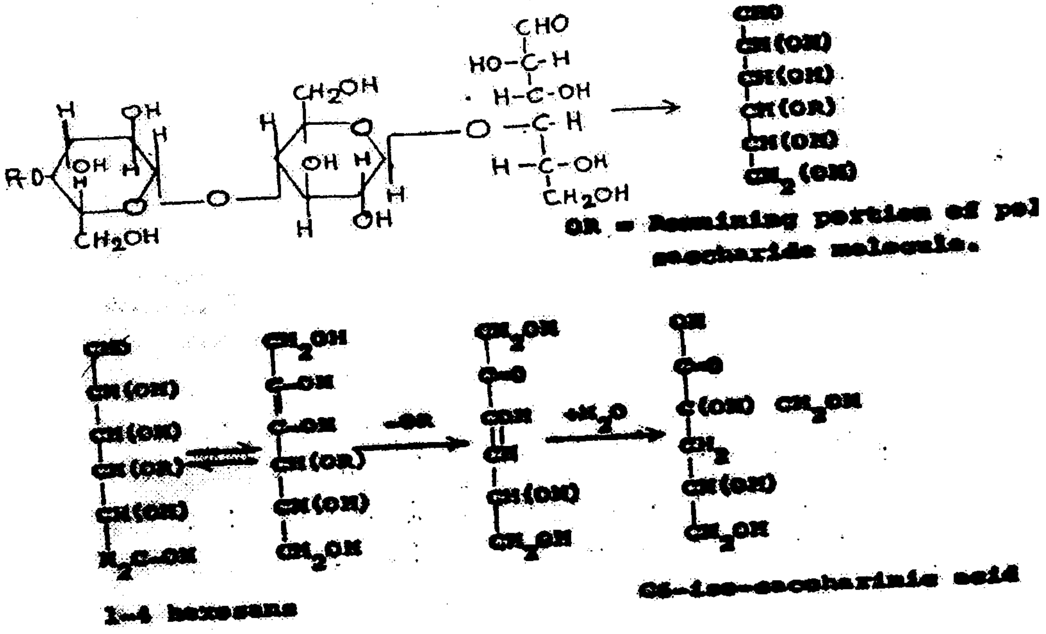
Sulfidolytic Cleavage Of β - Aryl Ether Bonds

Fig 5



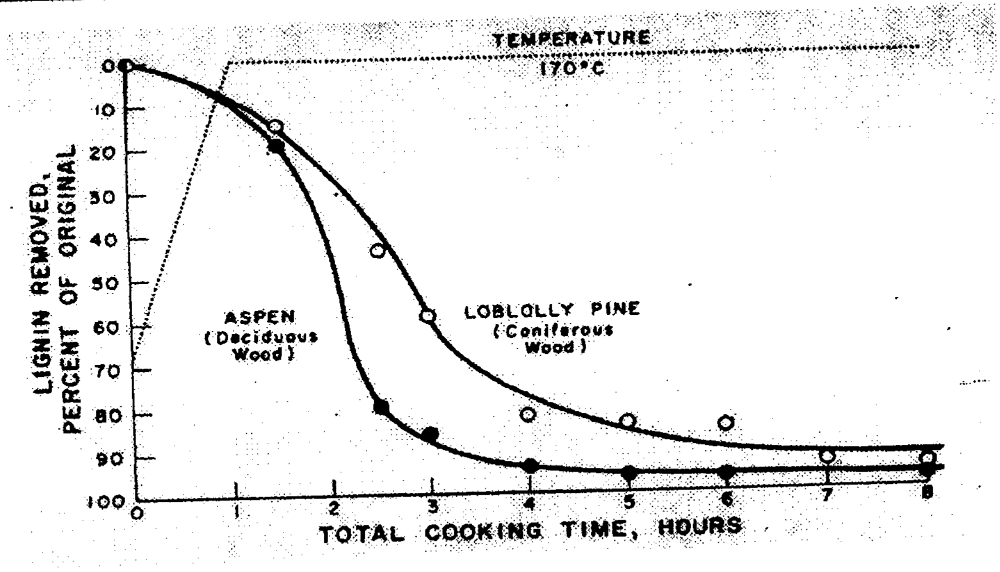
Primary Condensation Reaction

Fig 6



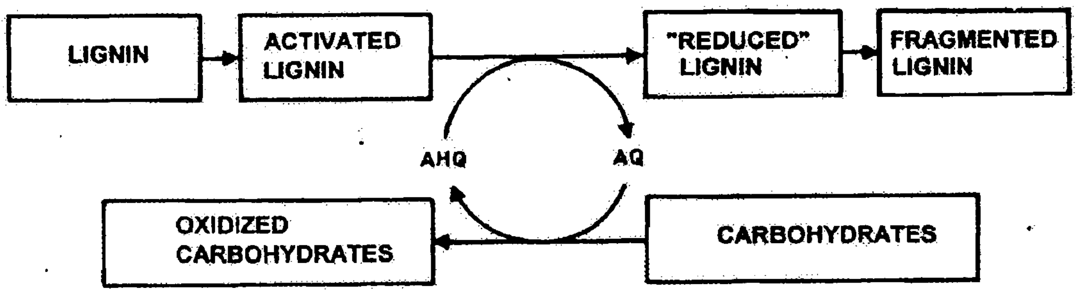
End-Wise Degradation Of Cellulose Chain

Fig 7



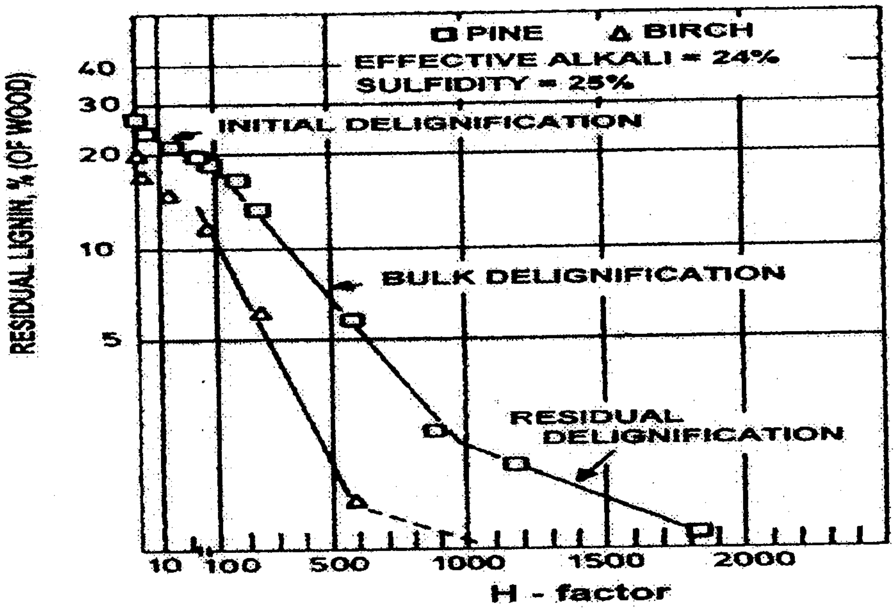
Rate Of Dissolution Of Pine And Birch Lignin As A Function Of H-Factor

Fig 8



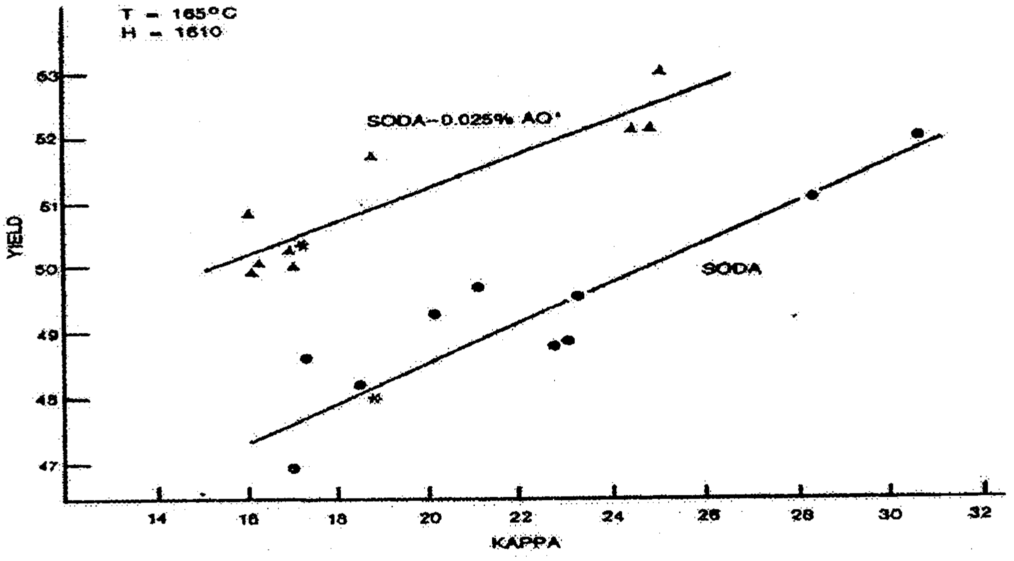
The Oxidation And Reduction Cycle In Anthraquinone- Enhanced Kraft Pulping

Fig 9



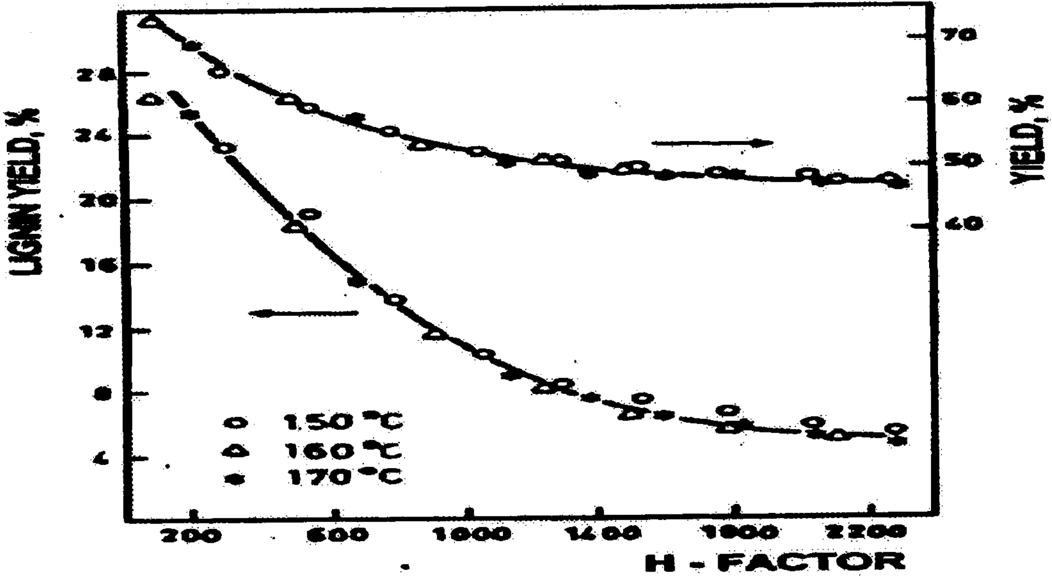
Rate Of Dissolution Of Pine And Birch Lignin As A Function Of H-Factor

Fig 10



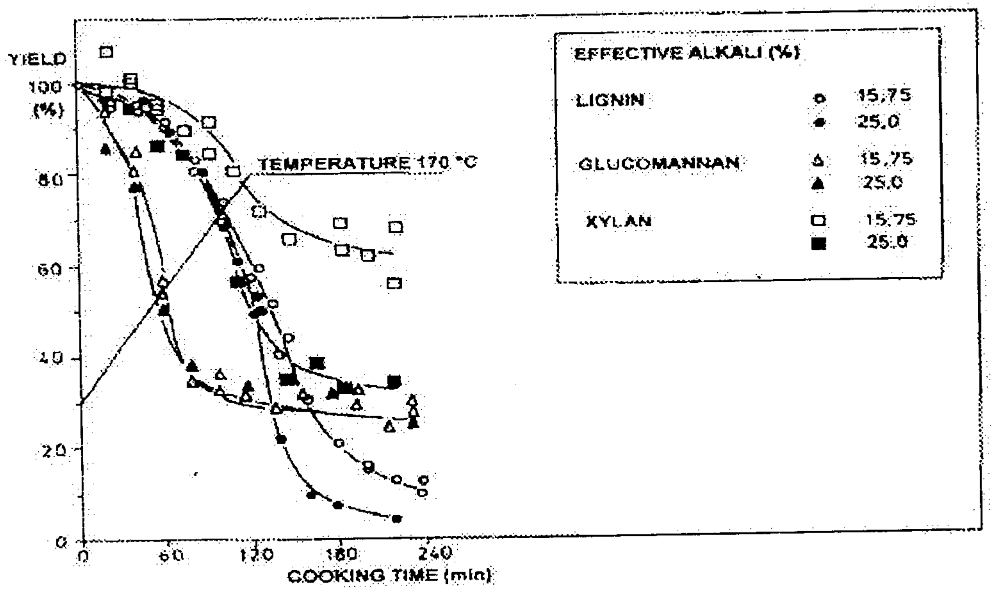
Effect Of Anthraquinone On Mixed Southern Hardwood Soda Pulping

Fig 11



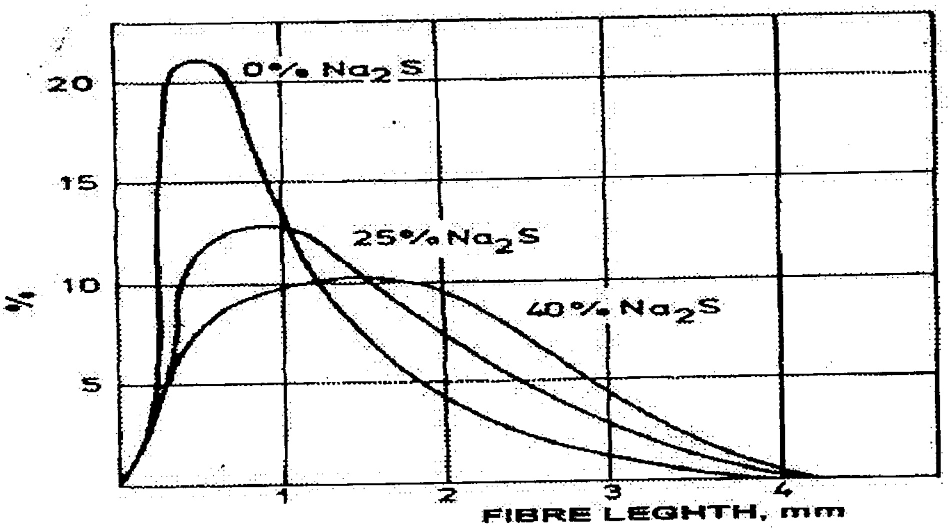
The Effect Of White Liquor Sulfidity On Fiber Length Of Beaten Pulp

Fig 12



Dissolution Of Lignin, Glucomannan And Xylan In Kraft Cooking Of Pine

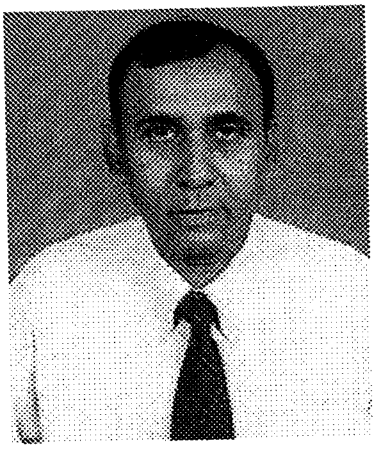
Fig 13



The Effect Of White Liquor Sulfidity On Fiber Length Of Beaten Pulp

Fig 14

AN OVERVIEW OF BIOPULPING OF FIBROUS RAW MATERIALS



Dr. R.M.Mathur,
Scientist E-II & Head,
Chemical Recovery, Energy Management, Effluent Treatment and Biotechnology Division.

About The Author

Dr. R.M. Mathur, is presently working as Scientist E-II and Head, Chemical Recovery, Energy Management, Effluent Treatment and Biotechnology Division.

After completing his D. Phil in Pulp Chemistry, joined CPPRI, in 1978. He has more than 100 publications to his credit. Area of specialization includes Black liquor properties, Lignin byproducts, Energy Conservation in Paper Industry and Biotechnological applications.

He has widely traveled abroad as UNIDO fellow to Canada, France, Germany, Australia & Japan and been to Turkey & Thailand for Demonstration of Desilication Technology developed by CPPRI. He has four patents to his credit

AN OVERVIEW OF BIOPULPING OF FIBROUS RAW MATERIALS

R. M. Mathur*, Vasanta V Thakur *, R.K. Jain * & Abha Gupta*

1. Introduction

The pulp & Paper Industry utilizes mechanical or chemical pulping methods, or a combination of the two to produce pulps of desired characteristics. Continuous pressure from environmental management authorities is forcing the industry to devise pulping technologies, which are ecofriendly in nature, since sulfur and chlorine compounds are harmful to life, efforts are being made to do away with these chemicals by using sulfur free pulping and extended delignification. Mechanical pulping accounts for about 25% of the wood pulp production in the world today. Mechanical Pulping, with its high yield, is viewed as a way to extend these resources. However, mechanical pulping is electrical energy intensive and yields paper with less strength compared to the chemical pulping process. These disadvantages limit the use of mechanical pulps in many grades of paper. Chemical pulping accounts for about 75% of the wood pulp production in the world. This process produces paper with very high strength. However, the process has the disadvantages of being capital and energy intensive, giving low yields, producing troublesome waste products, and producing byproducts that are of relatively low value.

Biotechnology derived technologies have been implemented in pulp and paper production in recent years. Energy savings and strength improvements in refiner mechanical pulping have been successfully demonstrated for the use of white rot fungi in the pretreatment of wood chips (Akthar et.al.,1992;1995;Leatham et.al.,1990). Biopulping is an environmentally friendly technology that substantially increases mill through put or reduces electrical energy consumption at the same throughput in conjunction with mechanical pulping. Electrical energy is the major cost of conventional mechanical pulping. By producing stronger pulp with longer fibers and increased fibrillation, biomechanical pulping may reduce the amount of Kraft pulp required to increase pulp strength.

Biopulping, defined as the treatment of lignocellulosic materials with lignin degrading fungi prior to pulping, has the potential to ameliorate some of these problems associated with conventional pulping.The concept of biopulping is based on the ability of some White rot fungi to colonise and degrade selectively the lignin in wood, there by leaving the cellulose relatively intact. In the case of mechanical pulping, the aim of biopulping is to reduce the energy requirement and to improve paper strength.

*** *Scientists, CR & Biotechnology Div. CPPRI, Saharanpur, U.P – 247 001***

For chemical pulping, Biopulping should help to reduce the charge of cooking chemicals, to increase the cooking capacity or to enable extended delignification resulting in reduced consumption of bleaching chemicals. Biopulping may prove to be environmental friendly technology with higher pulp yield, better quality of the pulp in respect to strength & optical properties with less emanation of pollutants with savings in chemical/ energy during pulping process.

2. Biological Delignification Of Raw Materials (Biopulping)

The objective of the biopulping process is to optimize enzymatic/microbial treatments for delignification of raw materials in order to provide a biotechnological solution, increasing productivity and decreasing lignin in effluents and to reduce simultaneously the costs of energy and chemicals used in pulp manufacture that will be combined with biological means. This interdisciplinary approach will include the following tasks.

- Testing and improving strains of selected species of ligninolytic fungi for preferential degradation of lignin
- Identification and production of the fungal enzymes that could contribute to lignin removal
- Enzymatic treatment of the raw materials by the individual enzymes and by enzyme mixtures
- Evaluation of the efficiency of the fungal/enzymatic treatments in terms of the modifications of lignin composition
- Testing pulping properties of the enzyme treated raw materials in combination with other pulping treatments and with special emphasis on the reductions in energy and chemicals and the decrease in the amount of lignin-derived products in effluents.

3. Microbiology, Physiology & Enzymology Of Microbial Degradation Of Lignin

Biotechnological processes are intrinsically friendly to the environment and dezincification is a biochemical process, basic to the earth's carbon cycle. Although many microorganisms are involved in the decomposition of wood, fungi are the dominant decomposers in terrestrial systems. Some of the most important organisms used in biotechnology are fungi. Fresh wood chips destined and stored for pulp production are rapidly colonised by a variety of microorganisms including many species of fungi. These organisms compete vigorously till easily assimilable food stuffs lasts and thereafter their populations decreases. They are replaced by fungi that are able to degrade and gain nourishment from polymers of the cell wall structure: cellulose, hemicelluloses and lignin. White rot fungi are the only micro-organisms known to be able to mineralise lignin. These last colonisers, mostly white rot fungi selectively degrade the lignin component thereby partly accomplishing the process of chemical pulping. The colour and texture of the resulting wood is often used to categorise different forms of decay i.e. white rot, brown rot and soft rot. The emphasis is on their characteristics of ligninolytic enzymes which are useful for biopulping. A number of species of white rot fungi have found their way in to industry or are being studied for their potential industrial application. White rot fungi are of prime interest for use in various industrial processes utilizing lignocellulose because of their ability to degrade lignin. Most white rot fungi degrade cellulose and hemicellulose in addition to lignin (Blanchette, 1991; Eriksson et.al.,1990).

3.1 Wood Deteriorating Fungi

1. Soft rot fungi -Polysaccharides
2. Brown rot fungi -Polysaccharides, +/- Lignin
3. White rot fungi --Lignin & Polysaccharides.

The technology has focussed mainly on white rot fungi, like *Phaenorochaete chrysosporium, Fomes lignosus, Pleurotus sps.* which have complex extracellular lignolytic enzyme systems that can selectively remove or alter lignin and allow to produce cellulose fibres with less chemical/ energy during pulping process. Lignin degrading fungi or their enzymes also have the ability to degrade highly toxic organic compounds such as dioxins and PCB's and could have an important role to play in the remediation of contaminated soils and the disposal of chemical wastes.

3.2 Wood Decay Pattern By White Rot Fungi

Simultaneous decay -- --Removal of cellulose, Hemicellulose &Lignin.
Delignification -- -- Removal of lignin & Hemicellulose & Low molecular wt. cellulose.

White Rot Fungi

1. Phanerochaete chrysosporium
2. Coriolus (Tremetes) versicolor
3. Ceriporiopsis subvermispora
4. Ganoderma applanatum
5. Pleurotus Ostreatus
6. Pycnoporous cinnabarinus
7. Phlebia radiata

3.3 Mechanism Of Biopulping Process

White rot fungi produce a very powerful delignifying enzyme system

Ligninolytic Enzyme Complex

- H_2O_2 producing enzymes
- Phenol oxidases (Laccases)
- Lignin - peroxidases(LiP)
- Manganese peroxidase (MnP)

Major Three Components Of Lignin Oxidising System

MnP	Molecular weight of about 50-60 kDa. In presence of peroxide, MnP oxidises Mn^{2+} to Mn^{3+} which can oxidise phenolic units in lignin. The system composed of MnP, Mn^{2+} , H_2O_2 & unsaturated lipids, however, also oxidise non-phenolic units and depolymerise lignin.
LiP	Molecular wt. of 40 kDa, glycosylated protein, oxidised by H_2O_2 to 2-electron deficient intermediate compound (compound - I) which returns to its resting state by performing two 1-electron oxidation of donor substrates known as compound-II, which is high oxidant than that of H_2O_2. In the presence of H_2O_2 oxidise both phenolic & non-phenolic units in lignin & also depolymerise the lignin polymer.
Laccases	Molecular wt. of 60-80 kDa, acidic pH & pI optima. Breaks the aryl-Ca Cleavage. Oxidises phenolic units in lignin in presence of O_2.

3.4 Physiology Of Lignin Biodegradation

- Requirement of a co-substrate (Carbon source)
- Produced even in the absence of lignin.
- Triggered by carbon, nitrogen limitation
- Sensitive to trace metals
- Relatively narrow pH optimum (4.0-5.0)
- Affected by O_2 concentration.
- Mycelial mat rather than pellet culture

3.5 Obstacles To Lignin Degradation

- The complex Polymeric nature of lignin.
- Its presence in close association with other polysaccharides.
- A few microorganisms being capable of utilising it selectively.
- An unclear mechanism of its enzymatic degradation

3.6 Industrial Microbial Process

To increase the effectiveness and efficiency of biopulping and decrease its cost through optimisation of variables, It is essential to study the following variables.
Many variables can affect biopulping .

1. Selection of a suitable fungus
2. Chip surface decontamination
3. Inoculum
4. Engineering and scale – up challenges

3.7 Commercialisation Of Biopulping

Several engineering challenges have to be answered in order to bring biopulping to commercialization. Most challenges involve a successful laboratory procedure and redesigning it to be practical on a larger scale. An overview of laboratory biopulping process is shown in fig.1 in which some steps in the process are not practical on a larger scale. The difficulties are mainly in two areas.

1. Preparing and inoculating the chips.
2. Maintaining the proper growth conditions for the fungus during incubation.

Current efforts are focused on bringing the successful laboratory scale procedures up to the industrial level.

3.8 Objective Of Biopulping

- To reduce the requirement of chemicals, during pulping & bleaching and saving energy during production of mechanical pulps
- Improved pulp quality
- Reduced pollution load

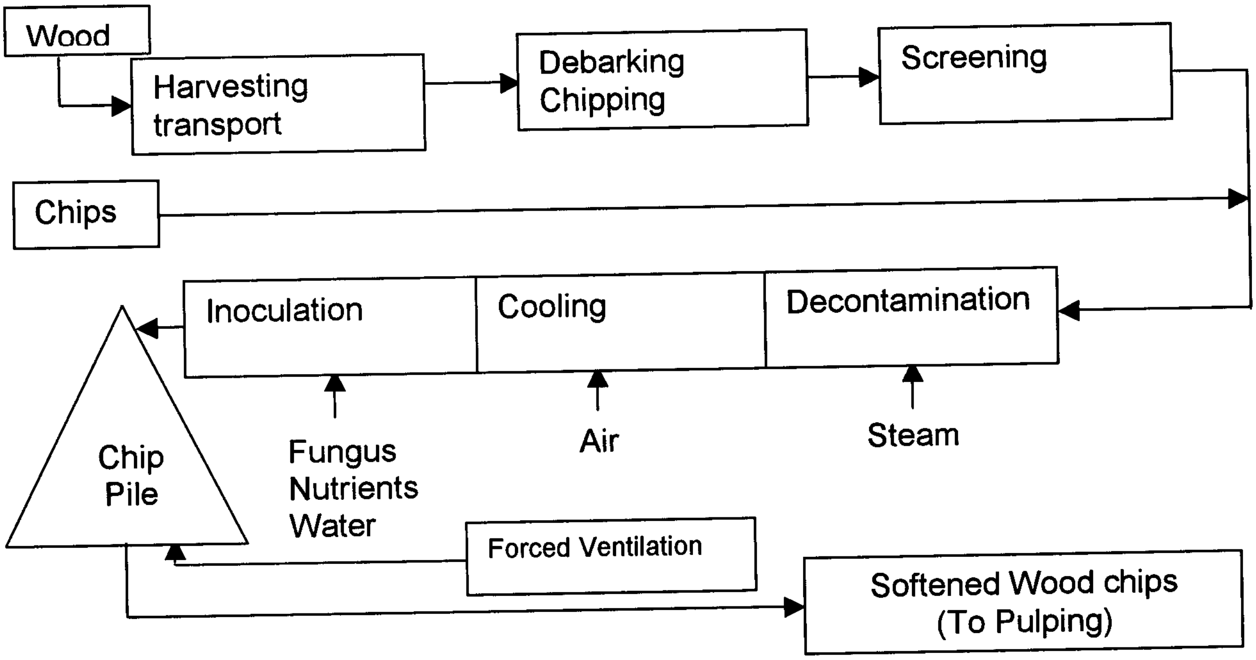


Fig.1 Overview Of Biopulping Process

4. Status Of Biopulping

Preliminary research on biopulping was conducted at the Forest Products Laboratory (FPL) in the 1970s. In 1987, a biopulping consortium was launched in USA and the overall goal was to evaluate the technical feasibility of fungal pre-treatment to save energy/chemicals and have less environmental impact than chemical pretreatments. The consortium research was conducted by team of scientists engaged in fungal, pulp & paper, enzyme, molecular genetics, engineering scale-up and information research teams (Kirk.et.al.,1993).

Research on the development of cellulase less mutant of white rot fungi & their use as microbial delignification was pioneered at STFI in Stockholm. One major problem with fungal treatment is that the time required is a matter of weeks. Some of the work Carried out at biotechnology research laboratory, Japan on mechanical pulping using white rot fungi IZU-154 have been shown in table-1 (Kashino et.al.,1993). The results clearly indicated that with the pre-treatment of spruce and pine with fungal strain IZU-154, there is remarkable decrease in the requirement of refining energy to approximately 35% and the pulp properties also improved in respect of tensile, tear strength and burst index.

Table-1

Refining Energy And Strength Properties Of Soft Wood Before & After Treatment With Fungus Izu-154

Particulars	Spruce		Pine	
	Control	Treated	Control	Treated
Incubation time, days	--	10	--	14
Refining, KWh/ton	2627	1700	2073	1367
Energy %	100	64.7	100	65.9
Tensile Index, N.mg	33.3	38.8	17.3	23.5
Burst Index, kpa. m/g	2.77	2.76	1.26	7.71
Tear index, mN.m/g	8.54	8.22	1.55	7.32

5. Biomechanical Pulping Of Wood

Early workers recognized the potential of using fungal treatment prior to mechanical pulping (biomechanical pulping) to save energy and/or improve paper strength, and conducted limited research which verified that potential. However, researchers encounter difficulties in attempting to scale up the process. The subsequent effort to research and develop biomechanical pulping at the USDA Forest Service Forest Products Laboratory (FPL) has been a unique collaboration among a diverse group of government bodies, research institutions, and private companies. Beginning in April 1987,a consortium was formed, including the FPL, the Universities of Wisconsin and Minnesota, and several pulp and paper and related companies. The overall goal of the consortium research was to evaluate the commercial and economic feasibility of biomechanical pulping. Because the fungal pretreatment is a natural process, environmental impact is expected to be minimal. The outcome of their research has now been scaled up to near industrial level, and the overall conclusion is that biomechanical pulping works. Through the use of the proper lignin-degrading fungus, at least 30% electrical energy can be saved in mechanical pulping, paper strength properties are improved, and pitch content is reduced.

6. Biochemical Pulping Of Wood

Unlike biomechanical pulping, in-depth information on biochemical pulping (fungal pretreatment prior to chemical pulping) is not available. However, published information indicates the potential of fungal pretreatment for sulfite pulping, dissolving pulp production organosolvent pulping and kraft pulping.

Studies indicate that fungal pretreatment causes swelling and loosening of cell wall structures, which increases the porosity of wood chips. Also, these fungi remove or modify lignin in wood cell walls that might be easily removed during kraft pulping. There is a hypothesis that these fungus-induced physico-chemical changes in cell walls will improve chemical penetration and subsequently aid the kraft pulping processes. If so, this will reduce chemical load, cooking temperature, cooking time, emissions, and effluent load during pulping.

A Collaborative study of Forest products laboratory, USA and Thapar group, India on biokraft pulping of eucalyptus chips demonstrated some of the benefits of fungal treatment. The fungal pretreatment reduces the cooking time from 90 to 30 minutes without affecting the quality of the final product. This means that kraft pulp mills could increase throughput and thus get more pulp production from the existing capital investment.

7. Biopulping Of Non-Woody Plants

The preservation of forests and increasing environmental awareness have focused research on exploration of agro based resources for paper making. Forest products laboratory, USA determined the efficacy of the biopulping fungus, C.subvermispora ,on different non-woody plant materials utilizing different pulping methods. Six different materials were investigated, Kenaf, bagasse, corn stalk, wheat straw, rice straw, and flax and got promising results. Current research is focused on process optimization, engineering/scale up and process economics.

8. Status Of Bio Pulping In Indian Paper Industry

As far as the implementation of biopulping in Indian paper industry is concerned, the work is in the primitive stages. However efforts are going on seriously to bring it to the pilot scale followed by the commercial scale implementation. Major raw materials used for paper production in India are wood, bamboo, bagasse; waste paper etc. 37% of current paper production in India is from forest based raw materials. The agro residue based paper production totalled to 31% and the balance 32% is contributed by waste paper based units. The expenditure on raw materials is greater than that of energy in the manufacture of paper.

Pulping section is the single largest polluting section in a paper mill, accounting for about 80% of the total pollution load. Thaper Research Group, Patiyala in collaboration with FPL,USA has done some work on biokraft pulping of eucalyptus and showed some encouraging results as shown in table-2 (Akhtar, 2001).

Table-2

Bio-Kraft Pulping Of Eucalyptus Chips With *Ceriporiopsis Subvermispora* (2-Week Treatment)*

Parameters	**Control**	**Treated Pulp**
	Cooking time 90 minutes	**Cooking time 30 minutes**
Pulp Yield, %	46	46
Brightness,%	88.6	90.5
Burst Index, kN/g	4.6	4.8
Tear index, mNm^2/g	7.8	8.0
Tensile Index, Nm/g	68.9	70.5
Breaking length (m)	7026	7193

*17% active alkali; 23% Sulfidity. Time,90 min

9. Work Done At CPPRI In The Area Of Biopulping

Studies carried out at the institute mainly stressed upon the screening of various identified white rot fungal strains like *Phanerochaete chrysosporium, Pleurotus ostreatus, Ceriporiopsis subvermispora* collected form reputed culture banks in India and abroad and two white rot fungal strains isolated from Indian paper mills renamed as CPPRI-1 (ST-2) CPPRI-2 (ST-4) for their ability to delignify eucalyptus and bagasse, the major fibrous raw material for Indian paper industry .The preliminary studies indicated that these strains have different de lignifying efficiency. The fungal strain CPPRI-ST -2 could be screened as better delignifying fungus having efficiency at par with any imported strain. The result of pre-treated raw material of eucalyptus chips with various fungal strains are shown in Tables-3. These results show that the pre-treatment of the fibrous raw material with lignin specific strain of white rot fungi could raise the possibility for biopulping which could prove to be energy efficient and cleaner production technology.

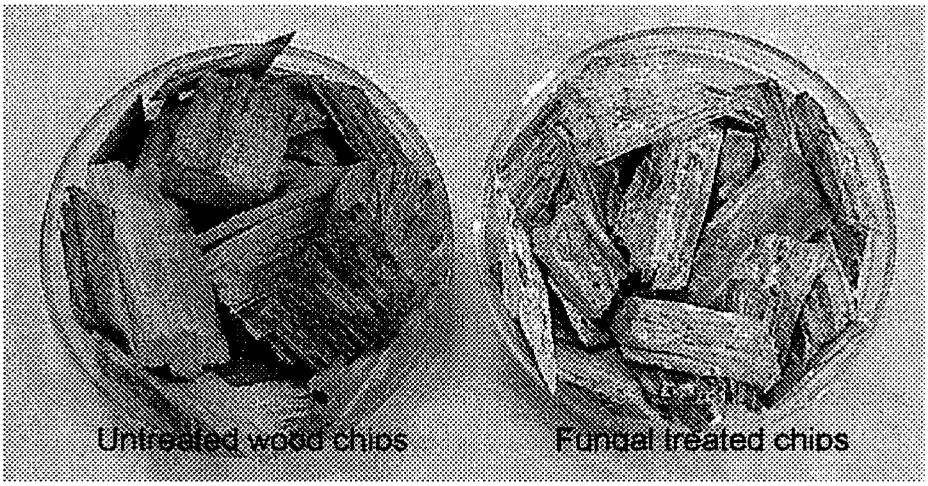


Fig.2 Wood Chips Before And After Treatment With White Rot Fungus

Table-3

Chemical Composition Of Fungal Treated (30 Days) & Untreated Chips Using Different White Rot Fungi

Parameters	Untreated	S2 treated	S4 treated	*Ceriporiopsis subvermispora* treated
Weight loss, %	0	3.84	3.81	1.86
Klasson Lignin, %	32.64	30.7	31.21	32.27
K-Lignin loss, %	0	5.94	4.38	1.13
Holocellulose, %	66.9	63.85	64.06	65.93
Cellulose, %	67.38	70.67	70.66	71.49
Pentosans, %	16.2	12.6	12.31	16.07
H/L Ratio	2.05	2.07	2.05	2.04

However, scale up to the industrial process requirements presents challenges that are difficult to simulate in pilot scale or commercial tests. Inoculation, aeration and heat dissipation are key parameters for maintaining fungal activity. It may be possible to monitor and maintain consistent treatments through a programme of wood chip pile management. Overcoming these challenges will determine, if biopulping becomes a reality.

10. Conclusion

Considering the area of pulping, biopulping offers a potential technique in delignification process. Therefore, the aim is to critically evaluate the general applicability of biopulping in Indian Paper Industry, these studies are in very primitive stages. On a pilot scale level, engineering and economic analyses indicate that the biopulping process is technologically feasible and economically attractive. Based on the electrical energy savings alone, the process appears to be economically feasible. The additional benefits of biopulping –better quality pulp, greater through put and environmental improvements – enhance the economic picture for this technology. Large-scale trials in conjunction with pulp and paper mills are needed to further confirm the economic feasibility of biopulping.

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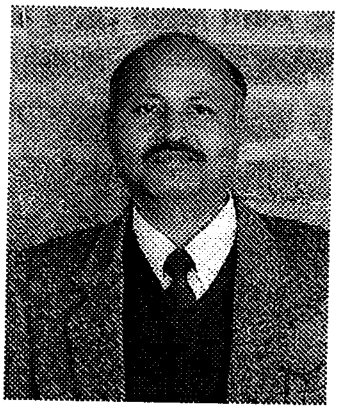
WASHING

BROWN STOCK WASHING



Dr. S. P. Singh
Associate Professor
Deptt. of Paper Technology
Indian Institute of Technology
Roorkee ,Saharanpur Campus

About The Author

Dr. S.P.Singh, Associate Professor, holds Masters degree in Chemical Engineering and Ph.D degree in Paper Technology in the field of "Characterization of Surfaces of Printing Paper" is now working as Associate Professor at Dept. of Paper Technology under IIT, Rorkee. Prior to joining this Institute in year Feb, 1982, he was working as a lecturer at BITS, Pilani since March 1979. Dr. Singh has worked at STFI during his Ph.D course. The major field of his excellences is Process Engineering and Printability. He has delivered several lectures at different mill sites namely, BILT, HPC,HNC, Orient Paper Mills, SPB etc. he has total 12 numbers of publications in different journals.

BROWN STOCK WASHING

S. P. Singh*

1. Introduction

The washing operation serves to separate pulp fibers from spent cooking liquor that contains inorganic cooking chemicals and the organic substances dissolved from the fibrous raw material. An efficient washing operation is essential for the following reasons.

a. Process economy has a great bearing on recovery of inorganic cooking chemicals and thermal energy of the organic materials.
b. Carryover of black liquor to bleaching plant consumes more bleaching chemicals and adds to the bleaching costs.
c. Carryover of organic substance to bleaching will result in increased discharge of chlorinated organic compounds, which are slowly degradable in the recipient of the discharge and may be toxic.

2. Washing Loss (Washing Efficiency)

The washing loss is the quantity of dissolved washable substance that is not removed from the pulp in the washing operation. It is defined in a number of ways:

- As inorganic substance expressed as kg Na_2SO_4 per ton pulp.
- As organic dissolved substance expressed as kg COD per ton pulp. Other measures of dissolved organics are chlorine demand, iodine demand, and permanganate demand.
- As total dissolved substance expressed as kg TDS per ton pulp.

Originally, the washing loss was commonly expressed in terms of equivalent make-up of sodium sulphate, as the loss of cooking chemical was of great economic importance. Nowadays, the washing loss has increasingly become a measure of environmental problems and bleach chemical consumption. For addressing these issues, a method capable of determining oxidizable organic material would be helpful in improving and controlling washing relative to the bleach plant. The two types of measures are different since the ratio of inorganic to organic dissolved substances in black liquor is not a constant. It largely depends on the pulping variables rather than on those of washing.

***Associate Professor, Department Of Paper Technology, IIT, Roorkee**

Washing loss in terms of percent solids (total dissolved solids) takes into account both inorganic and organic components. Nevertheless, it would be a poor choice for a routine method because of the difficulty of accurately measuring the solids concentration in dilute filtrates. COD is used but it also is time consuming. One test takes about two hours and a spectrophotometer is required. Permanganate test is recommended because the chemicals used are the same as used in k-number or kappa number testing. The test is fast as it takes about 10 minutes to complete.

3. Dilution Factor

The cleanliness of the washed pulp can be rather easily improved by using an excess amount of wash water. However, this excess water consumes a substantial amount of energy to evaporate in the recovery cycle besides its own cost. Therefore, it is desired to wash the pulp clean with the low dilution.

By definition the dilution factor is equal to the mass of liquor going to the recovery section minus the mass of the original liquor, expressed in kg per kg of dry pulp. Dilution factor is also equal to the total wash water added minus that leaving the washing equipment with the pulp.

4. Basic Washing Methods

Various washing equipment have different ways of operation. They combine several unit operations such as dilution, mixing, dewatering, displacement, diffusion etc. Quite often, more than one unit operation is involved concomitantly in an industrial washing process. The basic washing methods can be divided into the following types:

1- Dilution-agitation-extraction washing
2- Displacement washing
3- Combination of dilution-extraction-displacement washing

4.1 Dilution-Agitation-Extraction Washing

In this method the unwashed pulp stock is diluted with wash water and agitated to promote and accelerate diffusion between the stronger and the weaker liquors. The liquor is then extracted from the pulp.

An early approach was to use a series of open cylinder thickeners, where the unwashed pulp was diluted to about 1% consistency in an agitated zone and then thickened and discharged at about 5% consistency. Nearly complete equilibrium (uniform concentration of dissolved solids in the liquid phase) was easily reached at that low consistency, but the degree of extraction was poor. It took five or more countercurrent stages to reach an acceptable degree of washing. This system has become obsolete.

The screw press provides an excellent means of dewatering pulp to a high consistency of 30 to 35%. However, the maximum dilution possible in these presses is about 11% consistency. At such a high consistency, it was not possible to approach sufficient equilibrium between the strong liquor coming with the pulp and the weaker dilution liquor. This system is also not practised these days. There are, however, presses available now that can be fed at 4% consistency and still reach 30 to 35% discharge consistencies. The presses are arranged in a series with an agitated tank between the presses. At the 4% consistency with agitation for about five minutes, sufficient equilibrium is achieved to obtain satisfactory washing efficiency in three stages.

4.2 Displacement Washing

In displacement washing, the liquor present in the unwashed pulp is displaced by the clean water. In the classical approach, the unwashed pulp is taken into vessels with perforated bottoms. The top of the pulp mass is flooded with wash water and continuously drained from the bottom. The wash water moves through the pulp like a piston driving away the concentrated liquid ahead of it. Originally, the method was used in sulphite mills. Since the chemicals used in this process were relatively inexpensive, the washing pits were drained to the sewer until an acceptable cleanliness of pulp was achieved.

The pressurised diffuser is a displacement type of washer. The washing is carried out in a series of vessels shaped like a batch digester with perforated bottoms and arranged in a ring. These vessels are emptied and filled with pulp consecutively, each vessel receiving the content of one batch digester at a time. Wash water is introduced under pressure in the oldest filled vessel and circulated countercurrently through the preceding vessels. The word "diffuser" for this method is a misnomer as the process is one of displacement. True diffusion, by definition, does not take place in all types of washing, and the rate of diffusion in all cases determines the degree of dissolved solids removal that can be obtained by any particular method.

Continuous in-digester washing is another displacement method. As practised today, weak liquor is introduced in the base of the downflow unit in excess of that blown with the pulp, passes upward, and is extracted along with the mother liquor. Steam is recovered in flash tanks; the liquor then goes to the evaporators.

The continuous "ring diffuser" is also a displacement method. It incorporates a series of concentric rings of perforated strainers which move upward with the same velocity as the advancing pulp mass in an upflow tower. At the point of maximum advance, the direction of advancement of strainers is abruptly reversed, and the strainers are rapidly brought back to their starting position. The wash water is introduced by travelling nozzles rotating at the midpoint between the concentric strainer rings.

Washing on a fourdrinier machine is also displacement washing. The pulp mat formed on the wire is washed countercurrently as it moves from the headbox to the couch roll. The wash water is added in the final shower ahead of the couch roll and is drained through the mat and is transferred consecutively to the other showers. Extraction occurs after each shower treatment by means of flat suction boxes. A similar type of washing is obtained on double wire press and belt washer.

4.3 Dilution-Displacement-Extraction Washing

A countercurrent washing system using vacuum or pressure rotary drum filters incorporates both the type of washing previously discussed. The pulp from about 10% consistency is diluted to approximately 1% consistency before entering the washer vat. It is extracted to approximately 6% consistency in the filtration zone. The wash liquor is showered onto the pulp mat formed on the drum to displace its liquor. The pulp is re-extracted and discharged at about 10-15% consistency depending upon the type of equipment used. A number of such filters are arranged in a countercurrent fashion to increase washing efficiency. The fresh wash water is applied in the showers at the final stage. The filtrate of this stage is used to dilute the pulp from the preceding stage and the excess is used in the showers of the preceding stage.

5. Washing In Stages

The washing operation is usually carried out in stages for efficient washing of pulp with minimum amount of wash water used. Two types of pulp and liquor flow arrangements in multistage washing are commonly discussed. In cross flow washing the clean water is used in each stage. This requires large quantities of wash water. Moreover, the liquors obtained after washing from different stages have different concentrations and it will be a bad practice to mix very dilute liquor from the last stage with the concentrated liquor extracted from the first stage. This arrangement is not used for pulp washing.

In countercurrent washing, the wash liquor and the pulp flow in opposite directions. The cleanest wash water is used to wash the cleanest pulp in the final washing stage. The filtrate from any one stage is then used as wash liquor in the preceding stage. This is the most commonly employed flow arrangement in the pulp washing systems.

6. Displacement Ratio

The performance of a single stage in the washing system is often expressed as displacement ratio, which is the ratio between the actual displacement and the theoretically achievable displacement when all the incoming liquor is displaced by wash liquor.

The displacement ratio attains values between zero and one. In the ideal displacement, the concentration of dissolved solids in the liquor with outgoing pulp is the same as the concentration in the wash liquor. In rotary drum filter washing systems, the displacement ratio however, does not account for the actual washing that takes place due to dilution and extraction stages. There will be some washing even if the displacement ratio values were zero. The practical range of DR appears to be between 0.5 and 0.8 for most washing systems.

The displacement ratio largely depends on the type of washing equipment. It varies, however, slightly with the following conditions:

- Dilution,
- Pulp properties
- Production load
- Presence of air (foam) in pulp,
- Spray nozzle arrangement on a filter,

- General condition of the filter.

The value of displacement ratio has traditionally been used from experience or concentration measurements in practical operations.

7. Factors Affecting Washing Efficiency

The important factors affecting the washing results will be briefly discussed in the following:

- Type of pulp (raw material)
- Type of washing apparatus (filters, presses etc.)
- Number of washing stages
- Amount of washing liquor (dilution)
- Operational control strategy

7.1 Type Of Pulp

The type of pulp has a profound influence on the washing result. The two most significant properties are drainage resistance and the diffusivity of the liquor. These are mainly dependent on fiber liquor characteristics given by the raw material. Softwood pulps have low dewatering resistance and thus give a high capacity and washing efficiency. Hardwood pulps are more difficult to dewater. Agri-residue pulps such as straw and bagasse are even more difficult to dewater. Consequently, they give a lower capacity and washing effectiveness. Typical loading capacity of drum filter washer for these raw materials are:

• Wood pulp	5 to 8 tons/m^2 24 hr
• Bagasse pulp	≈ 3 "
• Wheat straw pulp	1 to 5 "
• Rice straw pulp	Still lower

7.2 Type Of Washing Equipment

The rotary vacuum filter (or drum) washer is by far the most widely used piece of equipment for brown stock washing. However, the vacuum filter washers have many severe limitations.

1. Dilution between washing stages makes this type of washer less efficient than the more recent equipment; the low consistency after dilution results in high volume of wash water used.
2. The spray type shower allows substantial air contact with the stock and liquor and liquor foaming is a problem in almost all these washing plants.

3. When required to increase production capacity more than the original design capacity, low washing efficiency, low discharge consistency, and high dilution factor result.

Over the last several years major machinery suppliers to the industry have brought out new methods of brown stock washing. The main thrust of these methods have been on the following:

1. Displacement has become the main operation.
2. Higher discharge consistency (15-50%).
3. Higher feed consistency.
4. High capacity.
5. Less space requirement.
6. Low power demand.
7. Reduced foaming problems by eliminating pulp liquor to air contact.
8. Multistage displacement without sheet reformation.

7.3 Operational Control Strategy

A good operational strategy and reliable control of the chosen operational parameters are necessary tools to achieve a good washing result and low polluting discharges. One must, however, be aware of the difficulties encountered in most existing filter and diffuser washer plants with their counter current washing system and long time lag due to large buffer volumes. Equipment like belt washers and wash presses, that allow a shorter time lag in the system are off course better in this respect.

The best possible control of pulp and liquor flow as well as the concentration of dissolved substance in various liquors is very essential. The pulp flow and the dilution factor should be kept as constant as possible. Consequently, the washing plant should never be allowed to serve as a buffer between the cooking and the bleaching department (or the paper mill)

7.4 Closed/Open Screening System

The entire system of washing, screening and thickening must be considered when seeking to improve the removal of organics.

In older mills, screening of pulps was performed after the washing. The water used for dilution in the screens was discharged to sewer together with fiber losses and dissolved substance. In the modern mills the screening, or at least part of it, is often integrated with the washing. This means that the last washing stage lies after the screening and a substantial part of the dilution water needed in the screens is used as washing liquor. By this integration most of the screening discharge has been eliminated.

With the increasing attention on environmental concerns, the option of closing the screen room or keeping it open must be considered carefully at each mill. A disadvantage with closed screening is that the carry over of dissolved organic substance to the bleach plant or to the paper mill is increased, unless the washing efficiency can be improved correspondingly. During the last few year the need to eliminate the occurrence of toxic chlorinated compounds in the dissolved organic substance, has led to alternatives, which mean a partly reversion to some type of open screening .In these case the very last washing stage is made with warm water that is directly sewered or led to an aerated lagoon.

An important consequence of closed screening is that the temperature will be higher than that is usual in open screening. This requires a special design of the equipment, as an increased concentration of dissolved substance in the circulating liquor is likely to increase the risk of foaming. The apparatus may have to be furnished with hoods and ventilators.

8. Some Considerations In Rotary Vacuum Filter Washer

8.1 Air, Foam & Soap Considerations

Air enters the system through the pulp cake on the washer face. The amount of air entering the cake must be adequate for driving out the water or liquor, but at the same time it must be minimised to avoid foaming which can create operating problems. The air that comes down the washer drop leg is separated from the liquor in the filtrate tank. The air separation is important because entrained air will interfere with formation and drainage of the mat in the subsequent stages. Higher drainage gives better washing efficiency and increases effective washer capacity.

Foam generated from entrained air collects on top of the liquor in the filtrate tanks. The filtrate tanks are vented to a foam tank. Moving foam through the system requires a considerable amount of energy. Pressures that are developed in the filtrate tanks to deliver form to the foam tank naturally take away from the vacuum and the capacity of the washer or filter. Foam lines are generally quite large, however, build-up can occur in foam lines over long operating periods. Foam build-up can be related to many things, including ray cells and fiber fines from the pulp, as well as soap and resinous materials. Foam Build-up is difficult to clean out and usually requires cutting hole in the line and using a high-pressure water hose.

8.2 Press Rolls

The function of press rolls is to squeeze air out of the pulp mat. A press roll on the first stage washer is most effective since it can remove air from the pulp mat leaving this washer and by doing so raise the displacement ratio on the second stage, typically the lowest. Additional press rolls on succeeding stages will be decreasingly beneficial. The proper utilisation of press rolls is hindered somewhat by poor operator acceptance. To be useful, a press roll must be closely observed to ensure that it is being operated at the design or optimum loading and not merely turning with the drum.

8.3 Shower Bars And Washing Showers

Significant washing improvement can be accomplished by having the correct number and type of shower bars. If too much water is forced through too few shower bars, the force of the water disturbs the mat formation, which reduces efficiency. If too many shower bars are used to provide the desired shower flow rate, uneven washing can occur, because shower water may come out only from one side of the bars – particularly when the water feeding the bars is delivered from one side only. Air breakthrough can occur on the side where insufficient water is being supplied and reduce vacuum and efficiency of the washer. Shower bars should be uniformly distributed over a long washing zone.

The number of shower pipes is limited somewhat by the diameter of the filter. Generally, five showers are considered adequate. The shower nozzle should be designed to distribute the water uniformly on the mat. The nozzle must be cleanable without shutting down. While simple, the spoon nozzle best satisfies these requirements. The size of the nozzle should be so selected that the velocity forms a "fan". Excess velocity disrupts the sheet and may cause foam. Insufficient velocity causes localised application and poor distribution.

8.4 Vat Consistency

Maintaining low vat consistency (≈ 1%) improves mat formation and promotes more ,uniform washing. However, increasing vat consistency allows a higher washer capacity. Washer capacity is roughly proportional to square root of vat consistency.

8.5 Drum Speed

Washer capacity can be increased by increasing the drum speed. Doubling the drum speed, from 2 to 4 rpm, will accomplish a 42% increase in the washing rate.

8.6 Wash Water Temperature

Low-viscosity wash liquor gives better diffusion into the sheet and therefore better washing. For hardwood stock, the temperature range should be 50 to 80 °C, with 68 °C being the optimum.

8.7 Drop Leg Design & Configuration

The dropleg (barometric leg) is to siphon the water or liquor out of the washer vat through the face of the filter. The liquor is drawn into the drum, lifted up, and extracted through the trunion and down the drop leg. A vacuum is created as the liquid falls down the drop leg and a vacuum will register in the trunion outlet from the washer. It is also possible to allow some amount of air to flow with the liquid in the drop leg as long as this air is totally dispersed so that it does not separate out. This air is always in the form of foam and does not move as rapidly as free air. The presence of air reduces the mass of moving material by as much as 25%, and the vacuum will drop depending upon the amount of air. Maximum vacuum can be obtained by making the dropleg longer or by reducing the amount of air in the leg. In general, vacuum will run about 175 mm of Hg on the first stage, 225 mm on the second and 300 mm on the third stage.

8.8 Drop Leg Diameter

The dropleg should be sized to handle the amount of water that is going through it to ensure proper vacuum. If the loads on washers have increased, new droplegs may be required. The diameter is based upon washer types, foaming tendency of the filtrate, and normal filtrate volume. The filtrate volume is calculated from the feed to the washer at the vat consistency plus the shower water flow minus the filtrate leaving with the cake. The filtrate volume has to be considered together with the presence of air, and the air volume is determined from experience on various washers and washing systems. The type of washer has a bearing on the amount of air present in the washer system. The foaming tendency of the filtrate has a substantial effect on the diameter also. As the liquor is extracted from the cake, it flows through the drainage channels and out the end of the machine into the dropleg itself. The result of this action is an air-liquor emulsion.

Velocity in drop leg for a pipe type filter are in the range of 3 to 4 m/s, and for filters having liquor trapping are in the range of 3.5 to 4.5 m/s.

8.9 Drop Leg Height

Drop leg height depends upon the amount of air drawn into it. The more the air drawn, the lower is the specific gravity of the air-liquor emulsion in the leg, therefore longer the leg must be to compensate. Dropleg height for a pipe type filter is shown 10 to 12m. Allowing 3m for level in the filtrate tank would put the washer operating floor level at 13 to 15 metres. A low air-volume washer may be installed about 10 m high.

8.10 Drop Leg Configuration

In designing drop legs, it is crucial to consider that the air liquid emulsion must exist. If there is separation, vacuum will be lost with resulting drop in consistency and in drainage and possibly loss of the sheet from the washer.

An ideal drop leg would be perfectly vertical for its full required drop into the seal tank. If it is necessary to provide horizontals offsets, it should be taken as low as possible in the vertical distance, after at least a 5 metre drop. In this case, the important consideration is to keep horizontal runs truly horizontal and vertical drops truly vertical. An angle run or a slope in the drop leg allows air to separate out of the filtrate, and thus air begins to flow back up the leg. Horizontal runs are probably best installed on a slight upward slope. If air does separate, it will be carried into the filtrate tank instead of back up the leg.

8.11 Seal Chamber

The bottom of the drop leg is routed to a seal pot or seal chamber. The drop leg does not have to be sealed to operate but is normally sealed to prevent more air from being drawn into the liquid. A recommended seal chamber is one that centrifugally separates the air from the filtrate discharged from the drop leg. The diameter of the seal chamber should be three to four times the diameter of the drop leg.

The drop leg enters the centre portion of the seal chamber tangentially to create vortex or swirling action, which tends to separate the air from the liquor. The liquor passes down and comes out through slots in the bottom of the inner chamber into the outer chamber. The circular motion is stopped in the outer chamber and the liquor rises gradually and spills into the filtrate tank proper. The discharged liquor has very small bubbles in it, and the retention time in the filtrate tank is utilised in further air removal.

8.12 Filtrate Tank

The seal chamber is always placed as far from the pump suction as possible to maximise the retention time with the tank itself. The vent area to the foam tank is at the maximum distance from the seal chamber for maximum foam retention. It is generally not recommended to put foam breakers directly on the filtrate tanks. Generally, it is desirable to place the foam removal outlet at a maximum distance from the liquor inlet so that the foam is given maximum time for breakdown.

8.13 Vacuum Pumps

Early in washer installations it was thought that vacuum pumps were required to operate washers, but after the siphon effect was identified it was found that vacuum pumps were not required. Vacuum pumps are generally high energy users and should be avoided if possible. Another disadvantage is that liquor carried in the foam stream will enter the liquid seal water and could be lost to the sewer.

9. Washer Control

There are two basic controls in the washer system: a) the speed control of the drum and b) the flow control of stock into the system.

A washer system is operated at a constant flow of pulp with varying consistencies and therefore varying volumes of stock. Vat level can be maintained by leaving the washer speed at one point and regulating the flow of stock by changing the consistency. The other control method is drum speed control, where stock flows are kept constant and the vat level is maintained by speeding up or slowing the drum. Speed control is found mostly in bleach plant washers, with dilution control more common in brown stock washers. The wash water flow and temperature are controlled. The filtrate flow through the system to the preceding washer is on level control.

10 Process Modifications

10.1 Improvement Of Pulp Washing By Addition Of Carbon Dioxide (1, 2)

Several European mills are using carbon dioxide in washing. In those mills, the CO_2 is applied with different objectives: to reduce maintenance costs, increase production, reduce carry-over, reduce effluent load or to decrease wash water consumption. The charge of CO_2 has to be optimised for each system, as a too high charge will result in lignin and extractives precipitation. The gas is easily dissolved in the alkaline liquors, which means that a simple dissolving equipment can be used. It is, however, important to have a good regulation of the CO_2 charge to avoid the negative effects.

Addition of CO_2 to the wash system gives:
- Locally reduced pH at the addition point
- Increased content of carbonate in the wash system

$$CO_2 + 2\ OH^- \dashrightarrow CO_3^{2-} + H_2O$$

$$\text{Ca-soaps (s)} + CO_3^{2-} = \text{soluble soap} + CaCO_3\text{ (s)}$$

Reduced pH in the washing leads to improved removal of inorganic substances as an effect of ion exchange and reduced swelling of the fibers. The deswelling of the fibers also increases the dewatering ability of the pulp. This improves the runnability of the washing machines, and gives higher dry content of the pulp leaving the wash stage. However, the pH reduction must be controlled such that the main part of the washing should be kept at high pH. A high pH enhances the leaching of substances from the fibers into the surrounding liquor.

Added carbonate reduces the amount of precipitated calcium soaps in the pulp and on the surfaces of the equipment. Some of these soaps become soluble and act as detergents in the system by contributing to reduced surface tension of the liquor and to improved solubilization and dispersing of the dissolved organics. This prevents redeposition on surfaces and reduces the foaming tendency of the liquor.

The added carbonate is insignificant compared to the original carbonate content of the weak liquor leaving the wash plant. Thus, no influence on the deposits in the chemical recovery system has been found.

With a directed pH reduction to the proper site and a modified surface chemistry of the system, negative consequences of the pH reduction can be reduced. There is an optimum in the charge of CO_2 to reach these benefits. A too high charge of carbon dioxide or improper site for application of CO_2 in the wash plant can give adverse results such as lignin precipitation etc.

10.2 Mill Scale Results Of Carbon Dioxide Use (1)

A summary of the main achievements in some mills using CO_2 in washing is given below.

I. Swedish mill producing bleached kraft pulp in a swing line (softwood and hardwood), with oxygen delignification. The washing after the oxygen stage is performed in two stages, with two wash presses. 3 kg CO_2/t is applied to the last wash press. About 10% increase in production capacity, especially in hardwood kraft pulp line has been achieved. There is some improvement in the COD carry-over also.

II. Swedish mill producing bleached softwood kraft pulp with oxygen delignification and with two wash presses in series as washing after the oxygen stage. The carbon dioxide is charged to both wash presses, with a total amount of 4 kg/t. Main achievements have been a significant reduction of deposits on the machine surfaces, and an improvement of the runnability. Total productivity increase is estimated to be about 5 %.

III. Swedish mill producing bleached softwood kraft pulp with oxygen delignification. Carbon dioxide is applied to the post oxygen stage washing, and the charge is divided between the stages, which consists of a diffuser washer and a wash press. Total amount applied is 3 kg/t. The COD carry over has been considerably reduced, and the runnability has improved leading to a higher production capacity.

IV. Swedish mill producing bleached hardwood kraft pulp. The pulp washing is ended with a wash press where the CO_2 is applied.

A considerable reduction of pitch deposits in the system has been achieved.

V. Swedish mill producing bleached kraft pulp, with washing after the oxygen stage consisting of a belt washer. Carbon dioxide, 3 kg/t, is applied after oxygen delignification. Reduced COD carry-over and reduced pitch deposits are achieved.

VI. Finnish mill producing bleached kraft pulp, both hardwood and softwood with oxygen delignification. The washing plant consists of two Pro-Feed lines and one DD-washer line. Carbon dioxide is applied to all wash lines. Carbon dioxide charge is 4 kg/t. Achievements with CO, are improved runnability, decreased wash loss (COD and Na^+) by about 30% in the Pro-feed lines and about 6% COD and 2% Na^+ in the DD washer line, increased dry content of liquor to the evaporation, and reduced dilution factor.

VII. Finnish mill producing bleached kraft pulp without oxygen delignification. In the hardwood line, the CO_2 is applied to the last filter washer at a rate of 3 kg/t. The main achievements are decreased COD carry-over by 20-30%, improved runnability of the drum, stabilised wash loss, increased dry content of pulp after the drum, and increased dry content of liquor to evaporation. In the softwood line, 4-4.5 kg/t CO_2 is applied to four-stage drum wash plant. Carry-over of COD and Na^+ has decreased considerably, giving a very clean pulp, at the same time as the production rate has been increased by about 8%.

VIII. Finnish mill producing unbleached softwood kraft pulp. Carbon dioxide is applied to the last drum washer at a rate of 4 kg/t. Achievements are decreased wash loss of about 20% as Na^+, decreased consumption of wash water by about 18%, and a stabilised runnability.

IX. Finnish mill producing unbleached softwood kraft pulp. With a charge of 3 kg CO_2 /t, production capacity increased by 10-20% and wash losses as COD and Na^+ decreased by about 10%. Other achievements are increased dry content of pulp and reduced need of maintenance as the system is cleaner.

X. Austrian mill producing bleached softwood kraft pulp, with oxygen delignification. Carbon dioxide, 3 kg/t, is applied to the last wash press after oxygen delignification. A significant improvement of the runnability of the system and some reductions in carry-overs is observed.

10.3 Use Of Acidic Shower Water (3)

A acidic water in the shower on the last stage of pulp washing increases chemical recovery in the Kraft process. The lowered pH causes sodium ions to desorb from the pulp fibers and thus become available for removal through washing. However, the results of an experimental study indicate that acidic showers also increase the retention of bound organic materials with the pulp. Although the total amount of lignin leaving with the pulp is not changed, a greater proportion of lignin is bound to the fibers as they leave the last washing stage. The increased bound organic materials may increase bleach plant chemical demand and the load on a mill's effluent treatment system. The bound organic materials will affect the economics of the process. Thus, the behavior of organic materials must be accounted for when considering using an acidic shower system.

However, the effects of the acidic shower on the washing of organic materials are largely unknown. There are grounds for believing that an acidic shower would adversely affect the washing efficiency of organic materials (lignin). Since these organic materials are a source of aqueous pollutants, use of acidic shower streams may increase the need for wastewater treatment in a typical Kraft mill.

10.4 Use Of Washing Aids (4)

Wash aids are offered to give improved washing, lower organic and inorganic carryover, increased mat consistency, and lower shower flows. These benefits have been demonstrated in brown stock and bleach plant vacuum drum washers and chemi washers. Mill objectives, such as reduction of mill bottlenecks, decreased organic deposition, lower bleach chemical cost, increased production, and improved effluent quality, can be realized using wash aids. The chemicals used should be environmentally friendly. Examples of this trend are oil-free defoamers and alkyl phenol ethoxylate-free (ape) surfactants.

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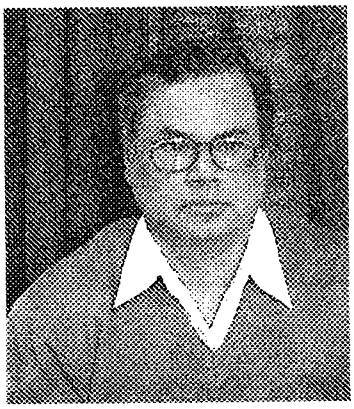

Dr. A. K. Ray
Professor,
Department of Paper Technology,
Indian Institute of Technology ,
Roorkee

About The Author

Dr. A.K. Ray Professor, holds a Bsc. (Honors) in Chemistry, B-Tech in chemical Engineering & Technology, Masters & PhD in Chemical Engineering , Post Doctoral research in University of Quebec on Explosion pulping of Indian Bamboo, Bagasse & rice straw is now working as professor at the Dept. of Paper Technology under IIT, Roorkee. Prior to joining this Institute in year Feb 1982, he was the faculty of National Sugar Institute, Kanpur in the Dept. of Chemical Engineering . Professor Ray was the head of the Institute during 1994-97 & acted as Director from time to time during 1980-91. Prof Ray has been credited with140 research publications out of which 52 published in International journals.

Professor Ray has been credited with number of awards including NOEIDEER gold medal from STAI, Silver medal & Sugar Industry cup from sugar tech. Association of Indian Institute of Chemical Engineers (CHEMCON), distinguished participant certificate from cellulose 91 and American chemical society New ORLEANS, USA. Her has been invited foreign university of America, Canada and China.

Prof. Ray has offered 5 PhD students in the area of modeling & stimulation of pulp and paper making process. His special lies in the area of chemical engineering application to pulp and paper technology, sugar and alcohol technology, mathematical modeling and stimulation and mathematical statistical and their application.

CONTROL SYSTEM FOR WASHING

A.K.RAY*

1. Introduction

1.1 Brief Description Of The Design Aspects Of Rotary Vacuum Washer

For any kind of paper manufacture (writing, printing, NSSC, corrugating medium, board, tissues, sack etc.) brown stock pulp needs to be washed efficiently.

Pulp washing is an essential key unit operation during pulp manufacture and plays a pivotal role in recovery of energy and spent chemicals on one hand, and reducing bleach chemicals vis a vis cost of bleaching and degradation of environment (especially, effluent treatment cost) on the other. The main goals are: with minimum amount of water addition, one can

(a) Clean the outgoing pulp produced from digester operation as practicable as possible through cleaner water so that it does not carry any black liquor solids (sodium based and lignin based) to the bleach plant

(b) Extract all the solutes (organic and inorganic) present in pulp and put in to the black liquor stream.

1.1.1 Principles Of Pulp Washing (1-8)

Regardless of the type of washer used, the separation of black liquor from pulp in the real washing process is accomplished with a combination of displacement and dispersion / diffusion processes, hence departing from a plug flow of wash liquor as expected in an ideal displacement washing. Sorption and diffusion are also important mass transfer phenomena.

In a rotary vacuum washer pulp-washing operation can be divided in to several steps. Pulp enters a washing stage at medium consistency (~12%) and is diluted by recirculated filtrate/weak wash liquor to low consistency (~1%) before entering the vat. A rotating vacuum drum picks up pulp from the vat, and a mat is formed and partially dewatered. Shower water is applied to displace dissolved solids, and further dewatering takes place before the pulp is removed from the drum. The filtrate is deaerated in a filtrate tank, and is recirculated as dilution water for pulp entering the stage or as shower water on the previous washer. The various zones present in a single stage washing consists of cake formation (cake build-up), first

Professor, Department Of Paper Technology, IIT, Roorkee

dewatering, washing, second dewatering, cake discharge zone and the dead zone. This is shown in Fig. 1. Vacuum is applied to all the zones except the last two though the quantum of vacuum in cake formation zone and the washing zone must be different to get better solute extraction.

The solute present in an unwashed pulp can be categorized based on their habitats. Some of the solute will be contained in stagnant areas between fibers, in the fiber lumen, and within the fibre walls. This material must diffuse out of the stagnant areas before it can become available for displacement.

Viscous fingering, axial dispersion and even diffusion from stagnant areas between fibers all occur on a relatively short time scale and must be controlled using washer variables: shower water application method and volume (proportional to dilution factor), vat consistency, machine speed etc.

Diffusion of inorganics, degraded lignin, and other pulping byproducts out of the fiber lumen and walls occurs on a longer time scale and is less dependent on machine variables.

1.1.2 Washing Equipment

Hosts of equipments offer to accomplish the above objectives. These are as follows

- Gravity Decker/potcher washer
- Rotary Vacuum Filter
- Rotary Disc Filter
- Twin Wire Press (belt filter press)
- Screw Press
- Pressure washer
- Wash press
- Horizontal Belt washer (Chemi-Washer/Flex-S-Washer/Delkor)
- Fiberfuge (continuous centrifuge washer)
- In-built indigester washer (counter current Hi heat washer etc.)
- Diffusers (atmospheric and pressure induced).
- DD washer
- Submersed washer

Some of the more important washers are shown in Fig. 2

The above equipments either alone or with combination are generally employed to wash the pulp obtained from various sources like virgin pulp or recycled secondary fibres. The design considerations are also different depending on the fibre type (Softwood, Hardwood, Rice straw/ Wheat straw, Bagasse, Kenaf, hemp, Jute etc.). Washing of pulp made from secondary fibres such as pulp from cotton linters, gunney waste etc needs slusher along with the washer.

The overview description of all the washers is presented by many authors without nurturing the equipment design details and the analysis pertaining to it. It gives a snapshot view of the equipment configurations. It is also difficult in the sense that most of the details lie in the hand of the manufacturers and are also shrouded with secrecy.

Rotary vacuum multistage washer containing 3-5 stages is a widely preferred piece of equipment around the globe because of its simplicity in design and flexibility in operation. Description of a rotary vacuum drum filter is well known and is not discussed here.

1.1.2.1Horizontal Belt Washer

The machine contains a split block, which represents the formation zonewhere the pulp is drained from the initial feed consistency of between 2%and 3% to the displacement washing consistency of around 10%. This is then followed by a number of washing stages working in a countercurrent manner. The inter-stage flows and consistencies can not be measured directly and have to be determined by material balances using the discharge consistency, feed flow, consistency and filtrate flows.

The inherent capability of this washer includes a large number of stages, in a single unit, allows for high chemical recovery with low water use. The results show COD removal efficiencies between 98.3% and 99.9% at dilution factor between 0.2 and 1.3. Even it works with negative dilution factor and also with highly efficient displacement plug flow type wash. The lower dilution factor results in considerable savings in steam costs in the evaporation plant while at the same time the capacity goes up. It results higher black liquor solids with low maintenance costs inspite of multi-stage washing in a single piece of machine, eliminates large interstage dilution liquor pumps causing lower power consumption, provides simple and flexible operation. Generally three-stage washing is the most economical.

Modeling is more important for horizontal belt washers as there are multiple stages in one machine. As a result, not all parameters can be measured between stages. The simplest studies would treat the unit as a " black box " and measure inlet and exit conditions. This will indicate how the machine is performed, but does not provide the information necessary for improving performance or to improve washer efficiency. This demands predictive modeling and iterative calculations for interstage material balance. For the above it needs DCS control and GEMS tool for modeling.

1.1.2.2 Belt Filter Presses

Belt filter presses, applicable satisfactorily with slow draining pulps, use one tenth of the energy as compared to rotary vacuum washer, permit much higher loading without lateral movement of the cake, and do not need elaborate civil construction. It comprises a continuous belt of filter fabric traveling horizontally over a bed of rollers, pressure being applied to the suspension gradually increasing by an opposing belt of impervious material or porous filter fabric, moving in the same direction. The fiber suspension is introduced at the top of the press belt. It can also work for very thin suspension and even for gelatinous system. Higher degree of dryness can be achieved by increasing greater degree of shear or higher pressure or by extending to a fourth stage press. Modern machine includes a pre-thickening stage. The filter belts woven from polyester monofilament with wide range of weave pattern come together initially in the form of an longer elongated wedge provided with foils. In the shear zones the belts roll around rollers of decreasing diameter considerably lengthening belt path and providing much longer pressing time.

The pulp is dewatered before washing, expelling strong black liquor. Washing is done at the first roller, which is perforated, and the water is fed in by a rotameter on the inner side of the roller. Subsequently the pulp is squeezed to remove the weak black liquor, by the shear zone of the press. Pulp at 20% Cy is obtained. Higher consistency can be obtained if required. The advantages claimed are: Simple and versatile operation, low maintenance, energy, space and time requirements with lesser capital investment, ease of installation, no heavy two-storey building and heavy foundation requirements.

1.1.3 Design And Process Parameters Affecting Performance And Efficiency (1-2)

For classical design most of the designers consider two important parameters: Specific loading factor and fiber production rate in order to evaluate the area of the drum. The design consideration of a washer system for varying fiber production rate however consists of rotary vacuum filter design specifying the parameters, which affect the performance. These parameters can be classified as

1.1.3.1Design Parameters

- Radius of the drum or area of the drum
- Drum mesh size (perforations) and layout
- Length of each zone (selected by each designer)
- Number of suction pipes and their sizes

1.1.3.2Operational Parameters

- Cake thickness
- Consistency (inlet and outlet)
- Velocity and amount of wash liquor
- RPM (total time of washing operation)
- Pressure Drops
- Degree of submergence (slurry level)
- Filtrate flow rate
- Fiber variables (specific surface area, specific volume)
- Fiber mat variables (specific resistance of cake, permeability constant, compressibility constants and porosity)
- Wash water variables (concentration of dissolved solids, nature of solutes, pH etc.)

The design equations for some of the parameters are given in Table 1

Table 1

Design Parameters For Wood Pulp

Parameters	Equations/models	Typical values
ε_t,Total Porosity	$\rho_f(1-C_y)/ [\rho_l C_y+\rho_f(1-C_y)]=1-6.8*10^{-4}*C_y \rho_l/(1-C_y)$	$C_y=0.1$, $\varepsilon_{t=0.93}$
K,Permeability cons.,m^2	$\varepsilon_t^3/5.55 S_v^2(1-\varepsilon_t)^2;[3.5S_v^2(1-\varepsilon)^{1.5}\{1+57(1-\varepsilon)^3\}]^{-1}$	$1.708*10^{-11}$; $789*10^{-11}$;
α, Drainage resistance, m/kg	$\alpha =k(1-\varepsilon) S_v^2/\varepsilon^3\rho_f =1/K\rho_f(1-\varepsilon)$	$6.254*10^8;13.54*10^8$
FPR, Fiber flow rate, kg/s	$(1-\varepsilon_t)NAL\rho_f$	N=1.5;FPR=2.975
W, loading Factor, kg/m^2s	FBR/A	$249.09=5.978t/m^2d$
A, Area of filter, m^2	$V/t_c[c\alpha_o\mu t_c/2(-\Delta P)^{1-s}g_c f]^{0.5}$	43
L, Cake Thickness, m	$[2K\rho_l\cdot C_{yi}*f (-\Delta P)/\mu*\{(1-c*C_{yi})(1-\varepsilon_t)*\rho_f\}*N/60=(1/N)FPR/(1-\varepsilon_t)\rho_f*A$	0.028-0.0296
f, Frac. Submergence	$(1/\pi)Cos^{-1}\{R''+(R-N_2)/R\}$	0.34
u, Speed in cake mm/s	$K (-\Delta P)/\mu\varepsilon_t L$	8.0
T_w, Total Wash Time, s	$A_c*(1/N)/2\pi RL=l_w/2\pi RN$	5.543
V_w, Wash flow rate, m^3/s	$u\varepsilon_d NAT_w$	0.025
V_d, Filtrate flow in dewatering zone, m^3/s	$NAL\varepsilon_t(1-S_s)$	-

The other considerations, which are common to all fibre types, are

- Number of stages
- Piping design
- Vacuum system design (sizing of siphons)
- Seal tank design (Air and filtrate separation)
- Shape of drop leg
- Intermediate repulper design

From process design considerations, the important factors are

- Uniformity of pulp feed by hydro dynamically splitting with tees to distribute the pulp across the face of the washer
- Feed dilution
- Proper foam handling

1.2 Design Alteration For Non-Wood Fibres & Recycled Pulp Washing (5)

For non-wood fibre washing design alterations are essential as both the operational and the design parameters will change. Some of the variables as indicated are especially applicable to rotary vacuum washers. Variables like filtrate flow rate, fibre variables, wash water variables etc are common to all the cases. Most of the non-wood fibres induct slow drainage problems causing low production efficiency, & poor pulp quality. This requires in-depth study of the basic drainage properties of non-wood fibers. The drainage properties include specific surface area (describing the fibre shape), specific resistance of mat, permeability of cake, and Schopper-Riegler values. This in turn depends on particle size, particle size distribution, shape of fibres, surface properties (describing the structure of fibre wall) like compressibility parameter, specific volume, and the structure of the fibre wall. For example, wheat straw pulp is more difficult to be compressed than expected beforehand as the compressibility of wheat straw is affected by inner hydraulic pressure inside the pulp mat during compression. Though it has the same specific volume as that of wood pulp, has more specific surface area due to fines formation and smaller in dimensions causing poor drainability. A set of comparative values is shown in Table 2.

Table 2

Comparative Values Of Some Fiber Parameters Of Wheat Straw Pulp

Variables	Wheat Straw	Softwood	Hardwood
Arth.Fib.length, mm	0.26	1.03	0.57
Length weighted	0.63	2.18	2.09
Weight weighted	1.09	2.83	3.02
Specific volume, m^3/kg	0.00244	0.00236	0.00220
Specific surface, m^2/m^3	$1.8*10^6$	$0.426*10^6$	$0.581*10^6$
Square load, kg/m^2	1.96	4.86	4.87
Drainage velocity, mm/s	1.1	7.4	5.2
Drainage resistance, m/kg	$79.3*10^9$	$4.8*10^9$	$6.7*10^9$

The capacity of the equipment for washing can be evaluated only when the above-mentioned properties are estimated accurately either experimentally or through modeling technique.

The steady state process modeling starts with the following algorithm

- Estimate compressibility parameters M, and N from Eq.: $c=Mp^N$ using linear regression
- Calculate specific cake resistance using Kozeny Carman Eq.:$\alpha = kS_w{}^2c/\varepsilon^3 = AP/\mu w_f u; S_w = S_v v_{sp}$
- Replace the porosity value,ε by ε_{av}: $\varepsilon_{av}=1-(1-N/2)^2 v_{sp} Mp^N$
- Estimate Kozeny Constant, k according to Davies: $k=3.5\varepsilon^3/(1-\varepsilon)^{0.5}[1+57(1-\varepsilon)^3]$
- Calculate the area requirement, A
- Estimate thickness of the cake, L
- Calculate Fiber production rate, FBR and the Loading Factor W, slurry feed rate
- Estimate the fractional submergence, f in case drum and disc/leaf filters

1.3 Equipment-Operation & Subsystem Descriptions For Recycled Pulp Washing

The washing efficiency of secondary fibre processing is usually expressed in terms of theoretical washing efficiency (TWE). TWE of contaminants in a single stage washing can be calculated from the inlet and outlet consistencies, assuming the same concentration of contaminants in the inlet, outlet and filtrate streams with no fibre loss.

TWE(%)=$100*(C_o-C_i)/C_o(1-C_i)$; C_i=Pulp inlet consistency, C_o=Pulp outlet consistency.

With multistage washing systems, the theoretical removal efficiency of contaminants can be calculated using the theoretical removal efficiency of each individual washing stage as

TWE(%)=$[1-[(1-E_n)(1-E_{n-1})....(1-E_1)]]*100$; n=number of washing stages, E_i=Theoretical washing efficiency of stage i(i=1 to n)

The experimental washing efficiency of subsystems (each washing stage) is calculated for dissolved solids, ash content and ink particles. The efficiency for each washing stage is calculated through the following equation involving concentration of contaminants in the inlet and outlet pulps as well as pulp flows

EWE (%)=$100*(P_1X_1-P_2X_2)/P_1X_1$;P_i=pulp flow(fibres +ash) (1=feed,2=outlet); X_i = contaminant concentration

It is well known that many variables influence the performance and efficiency of washing systems in deinking mills. These are given as under:

(a) Nature of Contaminants and liquid media characteristics
Dissolved Solids

- Physico-chemical effects (adsorption, electrostatic charges, colloid chemistry, ionic bonding, bridging...)

(b) Suspended Solids

- Size and shape
- Physico-chemical effects (adsorption, electrostatic charges, colloid chemistry, ionic bonding, bridging...)

(c) Washing Equipment Design and Operating Conditions

- Mechanism of slurry dewatering (filtration, settling, pressing...)
- Wire mesh/Screen Size
- Production Rate
- Feed and Discharge Consistency

1.4 Recycling And Deinking Process Conditions And Variables

1.4.1 Successive Washing / Thickening Stages (2 To 3 Stages)

- Decker/ Screw Press

- Screw Extractor/Screw Press
- Disc Filter/Screw Press
- Decker/Decker/Decker
- Screw Extractor/Decker/Decker

1.5 Washing Equipment Location

- Prior to first-stage floatation
- End of Process, prior to and post bleaching
- End of Alkaline and Acid loops

1.6 Quality And Amount Of Water Used

The following Tables indicate the variables for four waste paper processing units, equipment employed, and the washing efficiencies. The configuration are shown in fig. 3

Table-3
Suspended Solid Profile Through Each Washing Sub- System

Stages	Mill A ONP/OMG (90:10)	Mill B ONP/OMG (70:30)	Mill C ONP/OMG (60:40)	Mill D MOW/Ledger
First Stage	Decker	Disc Filter	Slusher	Decker
Inlet (%)	0.58	0.59	0.78	0.88
Outlet (%)	3.33	7.19	5.23	6.83
Filtrate(%)	0.05	0.07	0.08	0.23
Second Stage	Screw Press	Twin Wire Press	Screw Press	Decker
Inlet (%)	3.33	3.31	3.68	1.03
Outlet (%)	27.5	31.97	36.5	10.2
Filtrate(%)	0.59	0.07	0.62	0.15

Table-4
Theoretical Washing Efficiency Of Each Washing Sub-System

Stages	Mill A	Mill B	Mill C	Mill D
First Stage	83.1 Decker	92.3 Disc Filter	85.8 Slusher	87.9 Decker
Second Stage	90.9 Screw Press	92.7 Twin WirePress	93.4 Screw Press	90.0 Decker
Global System (Theoretical)	98.5	99.4	99.1	98.8
Dissolved Solids	97.7	89.6	89.9	82.9
Ash	85.5	78.3	72.3	90.4

Ink Particles	65.8	10	60	70.9

2. Performance Parameters Of A Washer System (1-8)

The parameters used to describe the performance of pulp washers can be divided in to three categories

- Wash liquor usage parameters
- Solute removal Parameters
- Efficiency Parameters

2.1 Wash Liquor Usage Parameters

These parameters describe the amount of wash water used in pulp washing operation and measure the evaporation load. Dilution Factor (DF), Wash liquor Ratio, Weight Liquor Ratio, Filter Entrainment are some of the commonly used parameters.

2.2 Solute Removal Parameters

These parameters describe the amount of solids removed during a washing stage or washing operation and can be used to predict the amount of bleach chemical consumption. Displacement Ratio (DR), Equivalent Displacement Ratio (EDR), Solid Reduction Ratio (SR), Wash Yield (Y), and Thickening Factor (TF) are some of the typical parameters.

2.3 Efficiency Parameters

The efficiency of a washer is directly proportional to the amount of solids removed during the washing operation. Some examples are: Soda loss, Salt Cake loss, COD loss, Percent efficiency, Norden's efficiency Factor, Modified Norden's efficiency factor, Total System Efficiency, Wash Yield etc.

Different kinds of washers are compared for their performance in terms of the above parameters. The definitions of some widely used terms, their symbolic representations and some typical values (1,2) are shown in Table-3. Table 4 represents a comparison of different kinds of washers and their working conditions.

Table 5

Definition Of Some Performance Parameters

Parameters	Model Equations	Typical Values
DF, Dilution Factor	$L_s-L_d=1+(V_w\rho_l/FPR)-(100/C_{yd})$	2.28
WR, Wash Ratio	$V_w\rho_l C_{yd}/[FPR\ (100-C_{yd})]$	1.32
DR, Displacement Ratio	$[(C_i/\rho_l)-(C_d/\rho_d)]/[(C_i/\rho_i)-(C_s/\rho_s)]$	0.807
EDR, Equivalent Displacement Ratio	$(1-EDR)=(1-DR)(DCF)(ICF)$; $DCF=L_d/7.33$;$ICF=[99(L_i+DF)]/[L_i(99+DF)-L_d(99-L_i(99-L_i)(1-DR)]$;$L_i=(100-C_i)/C_i$; $L_d(100-C_d)/C_d$	-
E, Norden Eff.	$Log[\{L_i(x_i-x_f)\}/\{L_d(x_d-x_s)\}]/log(L_s/L_d)$	-
E_{st}, Mod. Norden Eff.	$Log[\{L_i(x_i-x_f)\}/\{L_d(x_d-x_s)\}]/log(1+(DF/L_{st})$;$L_{st}=(100-C_{st})/C_{st}$	
W, Weight Liq. Ratio	L_f/L_i; $L_f=L_i+DF$	-
% Efficiency	$[1-\{(C_d.C_s)(100-C_{yd})\rho_i/\{(C_i-C_s)(100-C_{yi})\rho_s\}]*100=[1-(1-DR)\{(100-C_{yd})/(100-C_{yi})\}*100$	82.82
Y,Wash Yield	$L_fx_f/L_ix_i=(L_i+DF)x_f/FPR/C_{yi}$	0.9988
Y*, Theoretical yield	$TWE=[(C_{yd}-C_{yi})/\{C_{yd}(100-C_{yi})\}]*100$	0.918
System Efficiency	$[1-(1-DR_1)(1-Dr_2)(1-DR_3)....(1-DR_n)]*100$	95.05%
FE, Filter Entrainment	$L_d(1-DR)m$	-
TF, Thickening Factor	$(Lp-Ld)/L_p$; L_p, liquor in stock entering	-
SR, Solid reduction Ratio	x_d/x_p	-
%E,	$[TF+(1-TF)\ DR]*100$	-

Table 6

Typical Operating Conditions And Correction Factors For Different Kind Of Washers

Washer Type	C_{yi},%	C_{yd},%	DR	DF	EDR
Vac. Drum Washer	**1.5**	**11.0**	**0.786**	**3.0**	**0.758**
Press Drum Filter	**4.0**	**13.0**	**0.769**	**3.0**	**0.758**
Twin Roll Press	**...**	**35.0**	**0.0**	**3.0**	**0.758**
Washer	**10.0**	**10.0**	**0.866**	**3.0**	**0.758**

From the above data it is possible to speculate the effectiveness of different kinds of washers used in Industry.

3. Process Design Using The Factors Affecting Rate Of Solute Removal-The Alkaline Leaching

Out of the many ingredients present in black liquor, which are essential, to remove, the lowering pulp lignin levels before bleaching becomes more important aspects as far as bleaching of pulp vis a vis environmental load is concerned in today's scenario. Current industry alternatives include oxygen delignification, modified cooking operation (extended cooking-RDH, Super batch etc.), modified cooking processes or their combinations. But all the processes require a significant capital investment. It is a serious questions now how to assess the feasibility of modifying the brown stock washing unit operation to maximize the leaching of freeable lignin? The only answer is to understand the behavior of lignin in mill brown stock washing situations and to determine the process conditions (the most controlling parameters) that have the greatest effect on lignin removal. These parameters are controlling parameters. Analysis of the washing variables therefore suggests the most feasible ways through configurational changes in an existing mill wash line.

The parameters influencing the solute removal (lignin) rate are: retention time, wash liquor pH, temperature, electrolyte concentration and initial kappa number.

The rate of leaching increases dramatically with increasing pH and increases linearly with temperature in the range of 20°C to 90°C. Electrolytes in solution are found no effect on leaching (as against the earlier findings of inhibiting effect on lignin removal and fiber swelling) when using wash liquors of elevated pH. The kappa number of pulps, in the range of initial kappa number 30-18 could be reduced 25% by leaching 24h with 0.1 N NaOH. Typical design alternatives are shown in Figure 5a and 5b.

As regards sodium removal it is observed that at low liquor concentration the sorbed sodium decreases rapidly towards zero. At high liquor concentration the sorbed sodium approaches an asymptotic value. The sorption behaviour of both lignin and sodium can be well described by Langmuir adsorption equation as $S=Abc/(1+Bc)$

3.1 Benefits From Improved Process Design Consideration

Moderate process modifications would allow a reduction in kappa number of 10% over that achieved with the current washing system if the pH in storage were raised to 13 and the temperature were maintained at 70°C. The optimum retention time is probably in the range of 4 to 8 hours.

4. Process Optimization

Process optimization (2) can be initiated with the consideration of the following aspects:

- Steady state modeling of the washers in terms of material balance of all the stages, their interconnecting appliances and the constitutive equations of the respective zones of a drum washer
- Steady state modeling of multi - zone washer in a single stage washer (horizontal belt washer (Chemi-washer)/Pressure washer
- Defining and objective function based on minimum annual total cost
- Identifying a return function
- Defining various cost contributing factors including power cost
- Inter-relating other operations such as multi-stage bleaching operations, effluent treatment plant, multiple effect evaporator operation and chemical recovery operation.

The cost includes evaporator steam and condenser water cost, fuel value of the black liquor, secondary treatment cost, bleaching chemical cost, sulfur value, neutralization cost in the bleach plant , fixed charges, etc.

The steady state modeling of a multistage washer should be done taking the adsorption of solutes on pulp fibers in to account. For a single stage with filter area A and any arbitrary mat thickness L in any location of the filtration zone, the microscopic material balance can be written as

$$AL\rho_f(1-\varepsilon_t)+AL\rho_f(1--\varepsilon_t)Abc/(1+Bc)=(V+\varepsilon_t AL)\rho X_i+AL\rho_f(1-\varepsilon_t)^*Abc/(1+Bc)$$

For macroscopic material balance the usual procedure for liquor balance, solid balance, fibre balance and water balance should be followed.

4.1 Optimization-Simulation Of Filter Washer Operation & Control

The first step of control system design is to develop static and dynamic modeling of the system and then seeking for the optimal parameter followed by controlling the plant.

Many attempts have been made to control brown stock washers automatically to the optimal operating point. However, few attempts were successful due to the lack of understanding of the fundamental dynamic characteristic of brown stock washers. The process is very difficult to control due to its countercurrent nature. The main dynamic characteristics of the system are the long response time and the large interactions between the seal tank levels when subjected to a disturbance.

4.1.1 Dynamic Modeling

One such dynamic model is presented here. $D_L\delta^2C/\delta z^2=u\delta C/\delta z+\delta C/\delta t+(1-\varepsilon_t)/\varepsilon_t\ \delta n/\delta t$

To solve this dynamic model one has to know initial and boundary conditions, and the adsorption isotherm equations of linear/non-linear, finite rate type. As an example, for a finite rate type: $\delta n/\delta t=k_1c-k_2c$. Details are found elsewhere (1,3,8). The equation has been solved in terms of Peclet Number,where $Pe=D_L/uL$.

By using this microscopic model, black liquor concentration of different streams can be found, which can be used to measure the performance of brown stock washing system as a whole or can be used for control and simulation purposes.

Another widely used equation for optimization and control for filter washer is reproduced here
$\varepsilon L\ (dS/dt)=q_i-k_rk(\Delta P/\mu L);\ k_r=f(S)$

4.2 Dynamic Simulation Of The Multistage Washer And Its Implementation At The Pulp Mill Using Cause- Effect Relationships)

For testing and evaluating a control configuration it is necessary to know the dynamic response of a washing system as a whole to process disturbances and changes in operating variables. For modern washing system the dynamic simulation has been developed by many mills and the response of the system to changes in the concentration of dissolved solids in the feed stream, pulp production rate, shower water flow rate, and to several washers in series was analyzed.

4.3 Description Of Control Strategy

The primary aspect of washer control strategy is to lower operating costs by using shower water more effectively and to control the foam and soap formation.

The control strategy depends on the type of paper to be produced. For linerboard manufacture, the goals are:

- Reduce process variations, improving the paper machine runnability

- Optimize the shower flow to reduce carryover of black liquor solids and improve paper strength
- Optimize the relationship between the shower flow and soda loss
- Develop an operational online control model (computer

based/microprocessor based/automatic) for the brown stock washers. The above strategy will be altered if a mill intends to produce writing and printing paper.

4.3.1 Control Loop Design & Architecture

As already indicated the purpose of automatically controlling a brown stock washing system is to minimize the effect of process disturbance on the removal of dissolved solids from the pulp. The benefits include a reduction in production costs and environmental loading, and possible improvements in product quality and mill capacity. Most washing plants are still controlled manually, however due in part to a lack of sensors to monitor the process continuously.

Automatic control of brown stock drum washers has been limited to low-level control loops. The drum rotation speed is adjusted to keep a constant vat level, and the flow rate of shower water is manipulated to stabilize the liquor level in the filtrate tanks. A few mills keep the dilution factor constant on each washer by monitoring pulp production rate as a function of feed consistency and flow rate, and by manipulating the shower water flow rate. However more sophisticated control strategies have been possible using a conductivity probe to monitor the concentration of dissolved inorganic in a process stream.

Control systems have been proposed by many designers using negative feedback, feed forward, and the combination of feed forward and feedback loops. The strategy of the control loop configurations are shown in Figure 6 and 7 development of the strategy used considerable modeling and stimulation work.

A control strategy must include Seal tank level control, feedback conductivity control feed forward control on pulp production and vat level control with drum rotational speed. This strategy needs measurement of pulp washing quality, decoupling level, anti-windup, bumpless transfer, operating modes etc. In order to evaluate the control strategy the brown stock washing system has to be simulated for which the dynamic models for vat, seal tank and the main washers need to be developed. These are now available. Advanced methods are also possible in washing control. Reports are available using a predictive control and Kalman filter, the predictive controls calculates the black liquor solids (fig. 8). A new control system using Neural Network to control the brown stock washer is now known. Neural Network has use as soft sensor to measure mat consistency, mat density and soda loss to control dilution factor. Fig. 9 shows the target is to stabilize the black liquor solids. Results show a 25% reduction in the standard deviation of the black liquor solids using an 8-day trial. The controller also maintained large disturbance in an automatic mode for the input variables.

4.4 Sensor Selection

The washing department in a mill is a multi-variable system, and the effect of a single variable is often difficult to analyze.

Sensors should be selected based on the properties of two main streams – brown stock pulp in different consistencies of black liquor. The most important properties of the streams are described below:

- **Liquor Conductivity**

  Mat liquor conductivity is highly correlated with soda loss and total dissolved solids loss. There also exists a good correlation between the later two. Proper mat liquor conductivity can sometimes be measured with conventional conductivity meters but in many cases it is necessary to measure the liquor conductivity while the pulp is still on the washer. A mat liquor conductivity probe can serve these requirements. There is sufficient amount of free liquor to give a good, but somewhat noisy, conductivity signal and the action of the pulp keeps the probe clean.

- **Baume / Density Gauge**

  Measurement of solids content in the first stage as determined by a hydrometer, together with soda loss tests after the last stage can be a simple method but it is operator dependent. This does not optimize the wash flow and can be costly.

- **Nuclear Back Scattering Gauge (NDC Gamma)**

  The NDC gamma backscatter gauge allows one to measure the total mass on the cylinder. It is a mass-measuring device that operates on the principle of soft gamma backscattering.

- **Measurement Of Water Content Of The Mat By Means Of A Capacitance Gauge Or Microwave Gauge, And The Total Mass Of The Mat With A Nuclear Gauge.**

  This allows a measure of the consistency and the mass of the pulp in the mat and the process is then controlled to run to the optimum (highest) consistency and the optimum wash rate based on the dilution factor.

- **Refractometer Measurements**

  The amount of dissolved solids in the filtrate leaving the first washing stage is measured by using an on-line refractometer. This instrument transmits a beam of light through a portion of the weak black liquor, and the density of liquor is measured by the degree of refraction, or bending of the light. This on-line measurement of dissolved solids removed by the washers is used in adjusting the shower water.

5. Trouble Shooting Measures(Foam Control, Deaeration Aspects Etc.)

Entrained air impedes drainage because the air bubbles attach themselves to the fibers, making it more difficult for water to flow freely from the furnish. Great benefits are achieved with deaeration by improved drainage, higher washing efficiency as well as other improvements in the washing plant.

The development to full-scale operation of a deaeration system by physical, chemical and mechanical means are now available. Chemically a defoaming agent is used to reduce the amount of entrained air in the stock, which is measured with an entrained air tester. A large body of literature is available reporting the fundamentals of foam stability, foam drainage, bubble rupture, interfacial viscosity, marangoni stabilization etc. and the defoamer types, their action and mechanisms. From the process control point of view the controlling of amount of defoamer by the use of variable- speed pumps is found the most important by the mills.

The measurement of entrained air, which creates foam, can be done by

- Density methods
- Ultrasonic methods
- Direct methods (compressibility or by gravimetric techniques)
- Volumetric measurement of air content

A control strategy has been developed as already shown in Fig.6. Typically, the 4-20 mA output from the microprocessor is sent to a process controller with proportional and reset capability.

6. Techno-Economic Factor Considerations

Washing plants differ with respect to equipment and layout. Therefore, the economics will vary from mill to mill and with the quality of pulp to be processed.

The elements to be considered in the design of a washing system in general including the design of recycled mills are:

- Pulp Quality Considerations
- Capital Cost (Equipment Sequence, Auxiliaries required, Layout consideration)
- Water Consumption
- Recirculation Strategy
- Production Cost

-Electrical Energy Considerations
-Heat Requirements
-Equipment Design/Operating Conditions
-Maintenance
-Operating Personnel Required
-Effluent Treatment
-Solid Waste Disposal

- **Control System**

Computer control offer possibilities to use good control strategies, which can decrease the production cost, improve product quality, increase production capacity, and decreased environmental load. A successful control installation has achieved in many mills. The cost reduction, originating from decreased steam demand at evaporation plant, is the most easily calculated benefit from the control system. In one such a mill the percentages of unnecessarily low and too high washing losses have been reduced by about 50% and the benefit from the decreased dilution factor is about 5 lac US dollars per year, other benefits are not included. This corresponds to a payback time of just about 5 months. The goal of soda loss was to 8.0 kg Na_2SO_4 /t with small variations. The details of reduction in production cost through decreased dilution factor are as follows:

- Dilution factor down: 0.5m^3/adt
- Steam consumption down: 0.1 t/adt
- Production cost down: 1.4 US dollars /adt

The layout of this specific washing plant was as follows:

The fibres pass a countercurrent digester with four hours Hi-Heat washing, a continuous diffuser washer, a blow –tank that is also a pulp buffer, a screen-room and finally a filter-washer. The net flow of the washing liquor is moving in the opposite direction, passing three liquor tanks.

Before starting the development of control strategies, extensive measurements were made and the data were collected. The data were also used for developing a dynamic model, by which different control strategies were examined through simulations.

7. References

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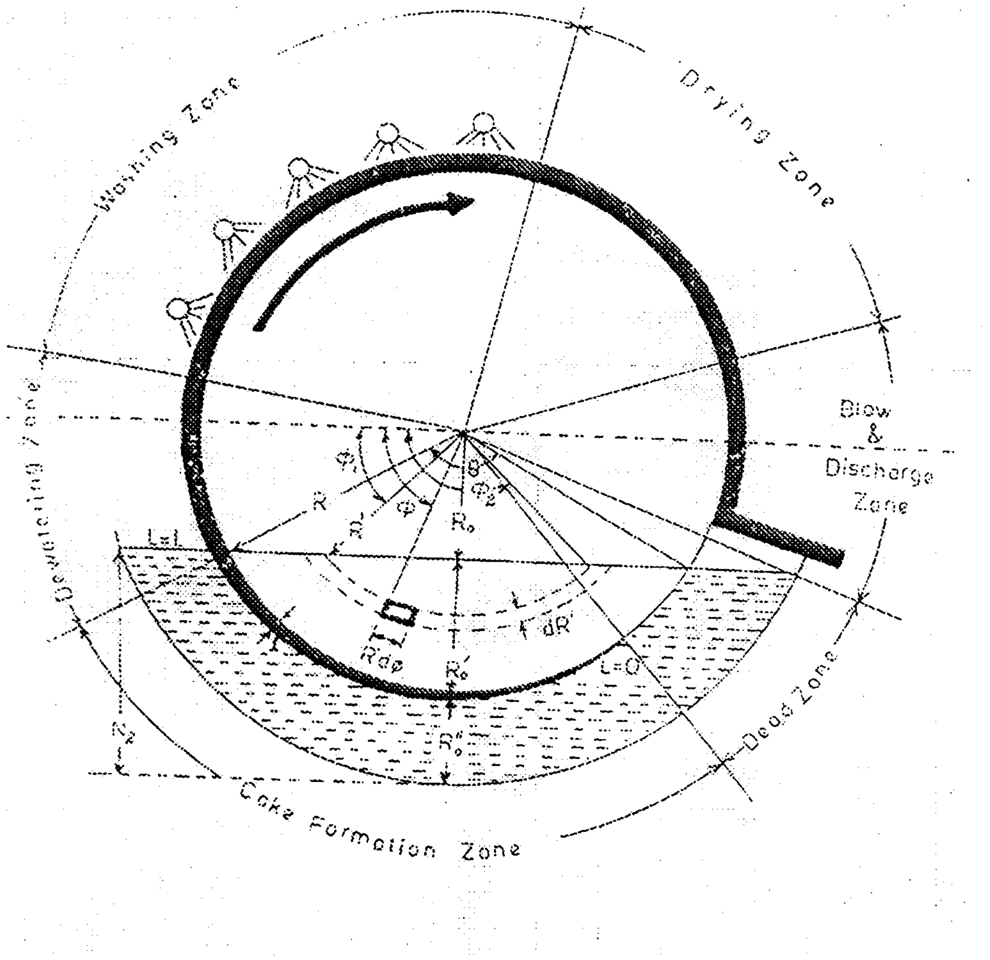


Fig 1 Different zones of rotary drum filters

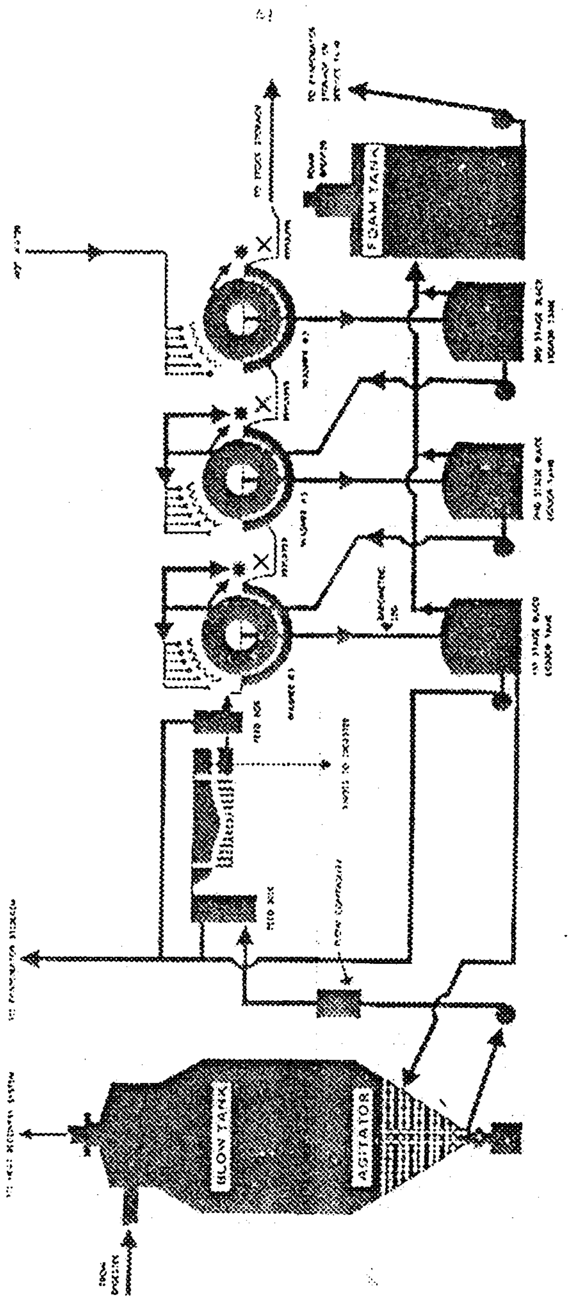
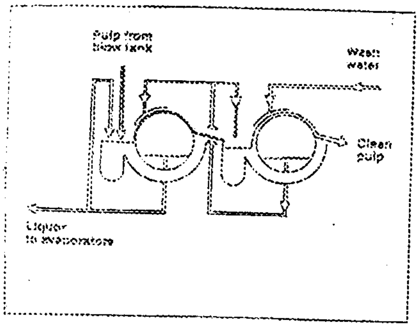
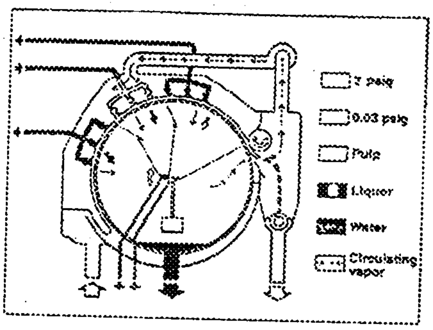


Fig. 1.4 Schematic Diagram of Three Stage BSW.

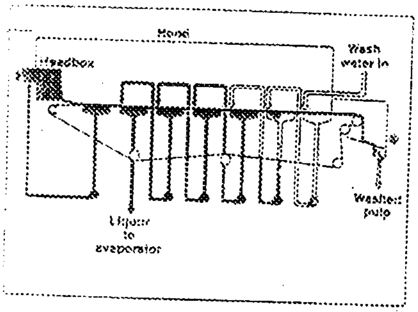
2 a, Two vacuum washers in series



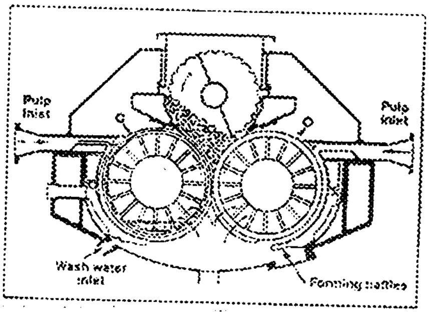
2 b, Rauma-Repola pressure washer



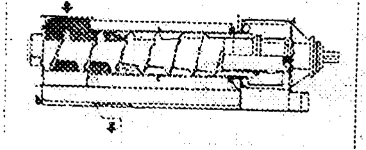
2 c, Black-Clawson belt washer



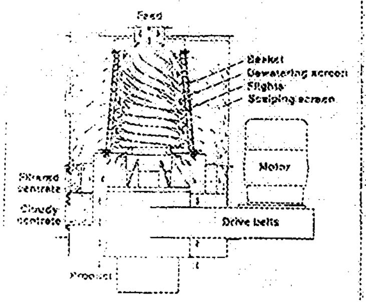
2 d, Ingersoll-Rand twin-roll washing press



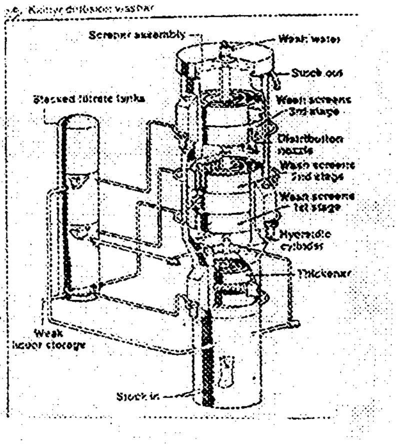
2 g, Thune screw-type washing press



2 f, Centrifuge washer



2 e, Kamyr diffusion washer



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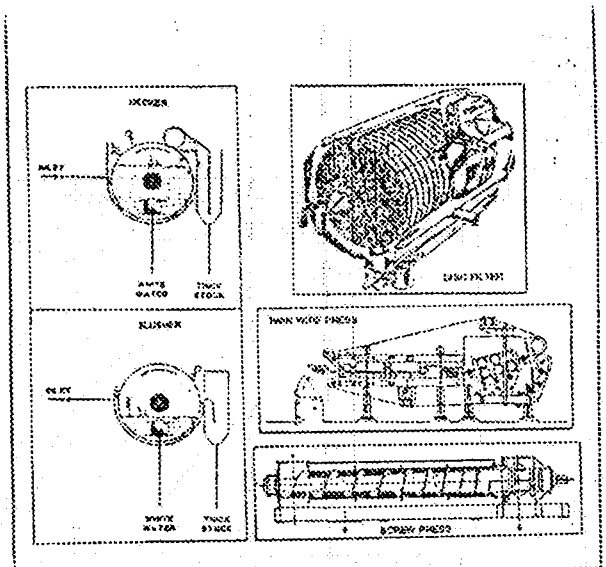


FIG. 2: SCHEMATIC OPERATION DIAGRAMS OF A DECKER, SLUSHER, DISC FILTER, TWIN WIRE PRESS AND SCREW PRESS

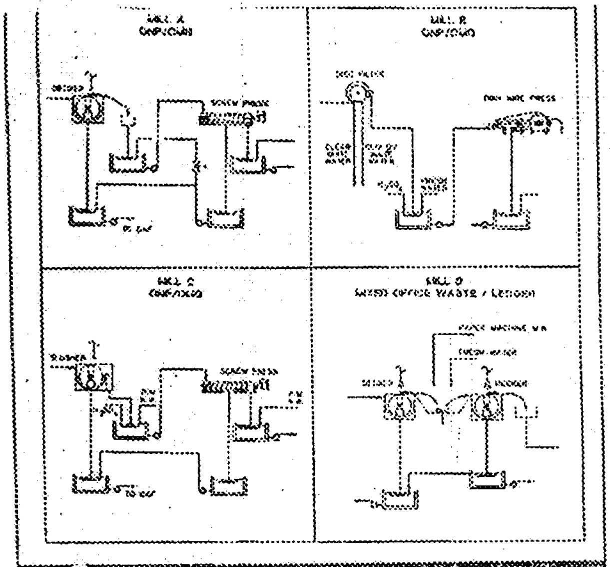


FIG. 3: PROCESS DIAGRAM OF THE FOUR WASHING SUB-SYSTEMS EVALUATED.

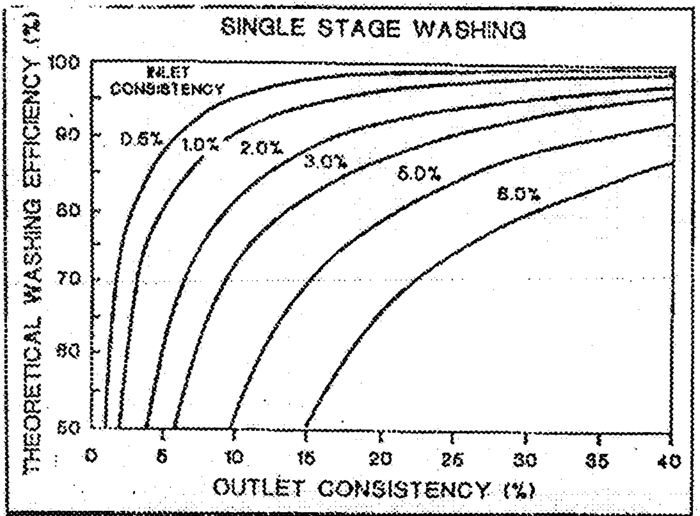


FIG. 4A. THEORETICAL WASHING EFFICIENCY FOR WASHING DEVICES USED IN SINGLE-STAGE.

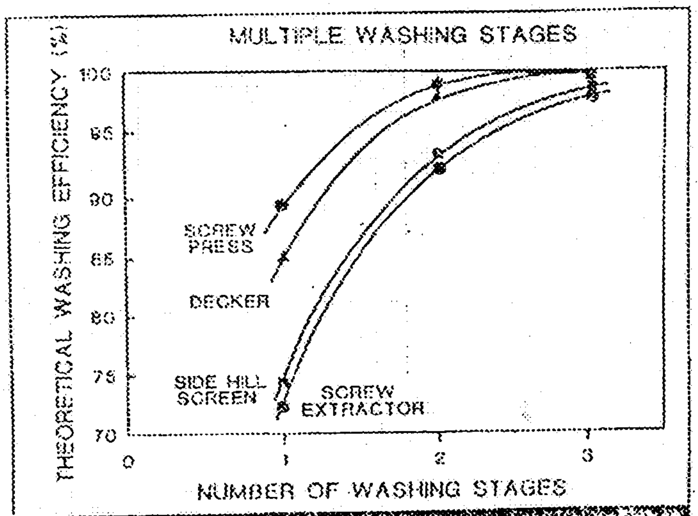
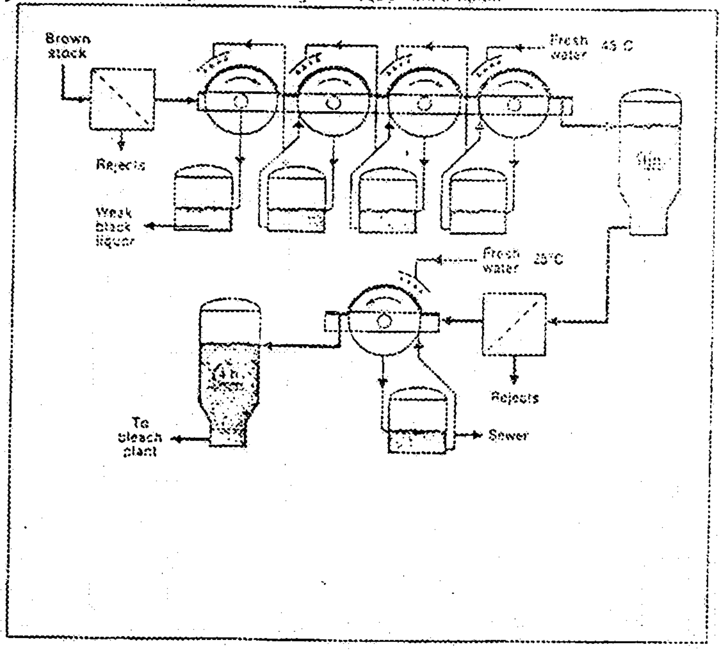
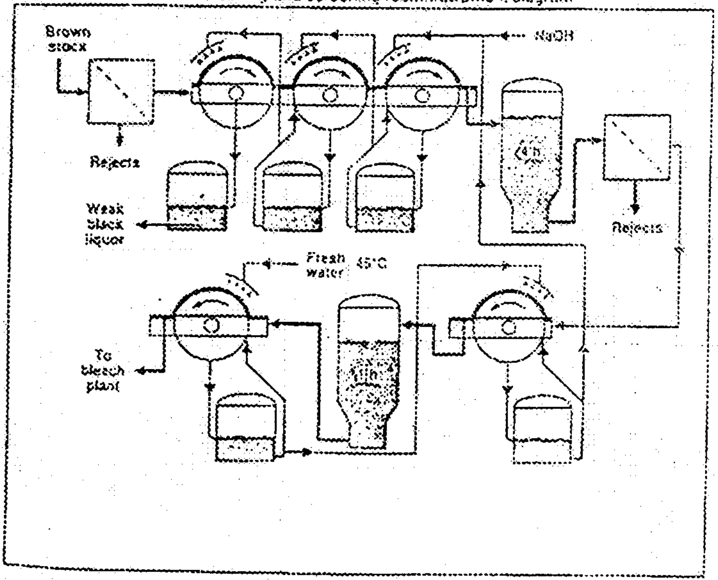


FIG. 4B. THEORETICAL WASHING EFFICIENCY FOR MULTI-STAGE WASHING SYSTEMS WITH DIFFERENT WASHING DEVICES

5a. Brownstock washing and screening room equipment diagram



5b. Modified brownstock washing and screening room equipment diagram



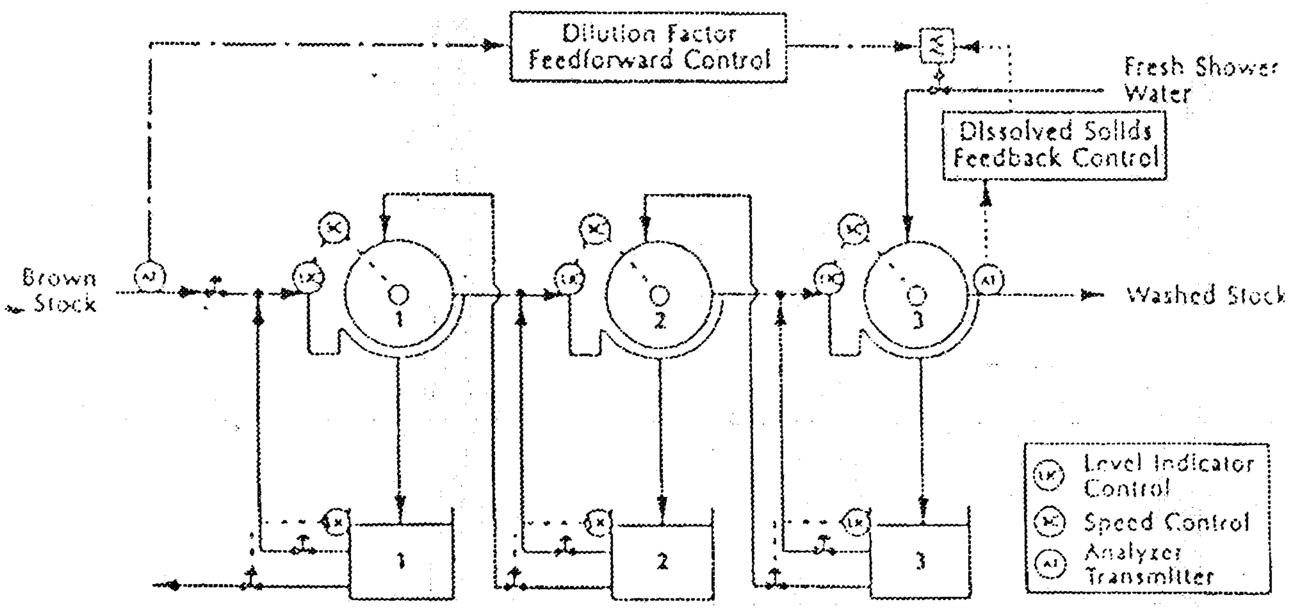


Fig. 6 - Control Strategy for Brown Stock Washer System.

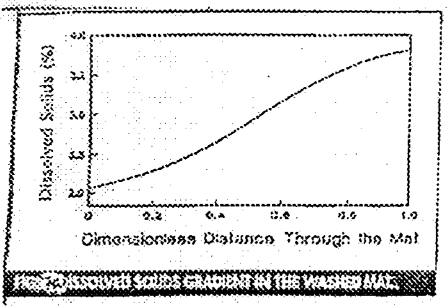


FIG. [illegible] DISSOLVED SOLIDS GRADIENT IN THE WASHED MAT.

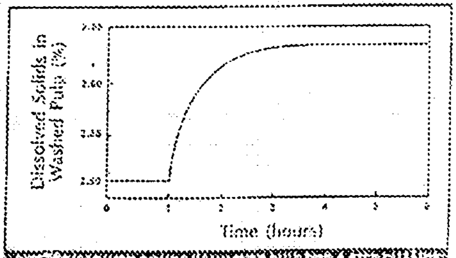


FIG. [illegible] DISSOLVED SOLIDS IN WASHED PULP FOR A STEP CHANGE IN FEED CONCENTRATION.

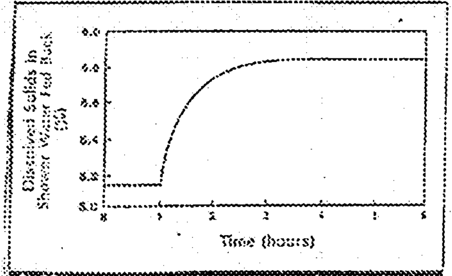


FIG. [illegible] DISSOLVED SOLIDS IN SHOWER WATER TO PREVIOUS WASHER FOLLOWING A STEP CHANGE IN FEED CONCENTRATION.

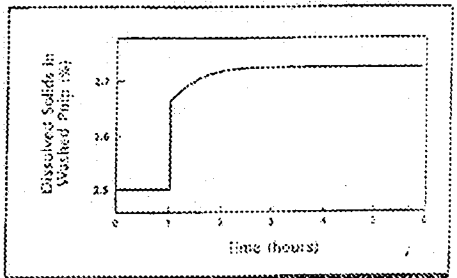


FIG. [illegible] DISSOLVED SOLIDS IN WASHED PULP FOR A STEP CHANGE IN PRODUCTION RATE.

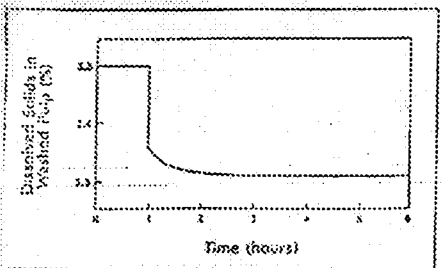


FIG. [illegible] DISSOLVED SOLIDS IN WASHED PULP FOR A STEP CHANGE IN SHOWER WATER FLOW RATE.

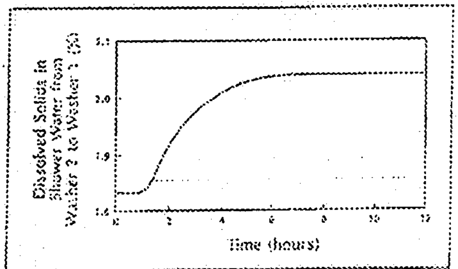


FIG. [illegible] DISSOLVED SOLIDS IN SHOWER WATER FROM WASHER 2 TO WASHER 1.

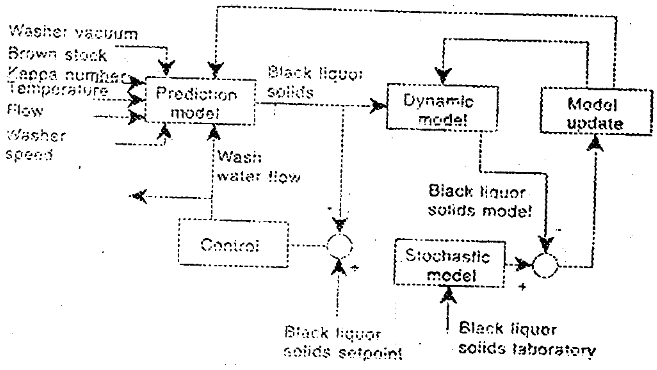


Figure 8. Washing control using the prediction of black liquor solids

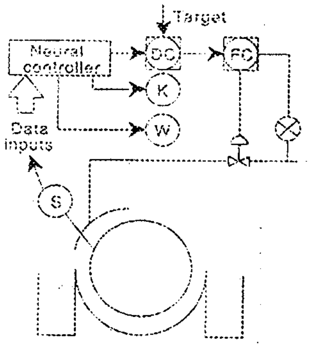


Figure 9. Neural network based control strategy

APPLICATION OF DOUBLE WIRE BELT WASHER CONCEPT FOR EFFICIENT WASHING OF AGRICULTURE RESIDUE PULP

Mr. V.K. Mohindru
Scientist - F &
Head. E.E & Pilot Plant

About The Author

Mr. Vijay Kumar Mohindru, Scientist-F, Central pulp & Paper Research institute (CPPRI) Saharanpur is a Chemical Engineer from Banaras Hindu University(BHU), Banaras. He always stood first right from metric to final year engineering.

He has 11 years of Industrial experience out of which 2 years in Orissa Cement Ltd. as Chemical-cum-Mechanical Engineer and Deputy Production Manager and 11 years in Titagarh Paper Mill as Incharge Pulp Mill and Laboratories. He has 2 years of teaching experience of teaching final year engineering students of BE Pulp & Paper and Post Graduate Diploma in Pulp & Paper of IPT, Rorkee University. He has 22 years of Research and Development (R&D) experience in CPPRI and is presently working as Scientific -F and Head, Consultancy and International Cooperation Division and Environmental Engineering Division. In connection with research has visited Germany, Austria, Finland, Swedan, Denmark, Nethrland, Myanmar and Bangladesh and has got number of research papers to his credit.

APPLICATION OF DOUBLE WIRE BELT WASHER CONCEPT FOR EFFICIENT WASHING OF AGRICULTURE RESIDUE PULP

V.K. Mohindru*

1. Introduction

In Indian paper industry, 40% of paper production is made by small paper mills using agriculture residue as major raw material. The conventional equipment used in paper industry for washing e.g. Rotary drums vacuum washer have been designed on the basis of data available with conventional raw material like bamboo and hard wood. It is observed that agricultural residues differs widely from the forest based raw material in the morphological and physical characteristics. Referring to Table No.1, particularly to the freeness value and fiber classification, it is evident that the agriculture residue, straw pulp is a difficult material to wash in the conventional Rotary drum vacuum washer. Of the total fiber, 50% represent bast and scleranshyma, 30% Parenchyma, 15% epidermal cells and 5% vessels, as reported by Reydohlm. The fiber classification results or straw pulp is in the following order : Long fiber – 30.9%, short fiber 46.5% & lines 22.6%.

Approximate dimensions of straw pulp fibers range between 0.5 -1.5 mm length and the diameter of fiber ranges between 7-27 microns. Although fiber length to diameter ratio is excellent from papermaking consideration, its wide variance in lengths and diameters creates a very closely woven mat on the brown stock washers, and the washing efficiency is greatly retarded due to poor filterability.

Aside from the physical properties of straw pulp, its chemical properties are also contributing factors in creating difficulties in washing such as high pentosan content, swelling of cell walls and tendency for easy hydration. These specific properties of straw pulp are major differences compared to hardwood pulp, and therefore demand special attention in washing operation. Bagasse, which forms about 70% of the sugarcane, consists of 50% moisture and 50% fibre along with pith cells. The fiber content of this bagasse is around 65% and pith around 30% and solubles around 5%. The bagasse has a higher degree of hydration as compared to bamboo or wood.The disadvantages faced during processing the agriculture residue pulp in a Rotary vacuum washer can be summarized as follows:

a) Specific loading of agriculture residue pulp is less.
b) Frequency of break and pick up over the washer surface is more due to less vacuum created in a drop leg system

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*** Scientist, Environment & Engineering Div. CPPRI, Saharanpur, UP-247001**

c) Difficult to wash due to low drainage characteristics of low porosity of the pulp mat.
d) High dilution factor, low conc. Of black liquor to soda recovery resulting increased energy demand.
e) Frequent cleaning of the filtering surface, due to presence of some non-fibrous cells, fines and mineral matters (silicate), resulting in decrease in productivity.
f) Low outlet consistency and low washing efficiency.

1.1 Drainage Characteristic

The drainage characteristic of pulp made from rice straw, wheat straw and bagasse were studied using PIRA Drainage Tester (Table-1).

It can be seen that drainability rate of rice straw pulp is quite less in comparison to wheat straw and bagasse. The permeability/sp. Surface area was calculated for various pulp made from agricultural residue. Among these, Specific surface area of straw pulp is maximum and for bagasse it is minimum. Therefore permeability of rice straw is minimum. Considering the disadvantages of washing of agriculture residue pulp in a rotary drum washer and with the emphasis on chemical recovery, it is essential to generate the black liquor at maximum concentration. With the stringent pollution laws, it has become most imperative that efficient washing of this agriculture residue pulps is done. The common ways of reaching a better washing are either applying an increased wash water dilution or installation of one additional washing stage. Increasing the wash water dilution is normally an expensive way due to the rapidly increasing evaporation cost. The concept of double wire can thus be adopted by small and big mills using agricultural raw materials as well as woody raw materials and offers maximum advantages.

1.2 Development Of Brown Stock Washing Equipment

Considerable success has been achieved for washing of different kinds of pulp in advanced countries by suitable designing and sizing the equipment to achieve improved washing.

1.2.1 Displacement Press

The displacement press is now in operation in a number of brown stock washing application. It combines high washing efficiency with limited building requirements and greatly reduced liquor tank volumes (Fig-1).

1.2.2 Ultrawasher

The latest development for brown stock washing is the ultra washer. The ultrawasher, which is utilizing the so called fourdrinier principles makes it possible to do the complete brown stock washing on one singe machine (Fig-2).

As can be seen the so called fourdrinier principles is used to dewater and wash the pulp. The pulp suspension of about 3% Cy. is dewatered to a pulp mat (8 to 9% Cy.) on a wire and is transported on the same wire through the machine where wash liquor is added counter-currently in a number of stages. In this way the liquor flow in the machine is strictly countercurrent from wash stage to wash stage all the way up to the main liquor tank (Fig-3).

1.2.3 Pressure-Washer (Rauma-Ropola)

A pressure washer depicted in Fig-4 is similar to a rotary vacuum washer in many ways. A pulp mat is made on the surface of the cylinder and dewatered with the aid of pressure applied inside the washer hood (outside the cylinder). On the upper part of the cylinder, where the pulp mat is not immersed in the vat, wash water is applied with showers. The washer can be operated with two or three displacement stages by subdividing the effluent draining in to the rotating cylinder. The cleanest effluent, collected under the last set of showers, is led back to the previous set of showers on the same washer. Thus in addition to the dilution/extraction washing, as many as three distinct displacement washing stages can be employed.

1.2.4 Twin-Roll Washing Press (Ingersoll-Rand)

A wash press (Fig-5) is dilution/extraction washer and is used frequently for pulp that is difficult to permeate. The high efficiency of these devices is derived from the high consistency of the discharged pulp, which is typically 30-40%, depending on the design of the washer. Some wash presses also have a displacement stage, but these are not effective for pulp that is difficult to permeate.

1.2.5 Fiber Fuge Washer

An interesting new development which is also particularly useful for washing pulps that are difficult to dewater is the fiber fuge continuous pulp centrifuges (Fig-6). A pulp slurry at 3-4% consistency is fed into a rotating basket fitted with a dewatering screen. Helical flights rotate in the same direction as the basket but a slower speed, sweeping the dewatered pulp from the screen. A subsequent scalping screen further clarifies the large portion of the concentrate. The product consistency is typically 20-30%.

1.2.6 ANDRITZ Double Wire Belt Washer

The ANDRITIZ double wire belt washer (Fig-7) has three main functions – dewatering, displacement and pressing. Due to high efficiency of double wire washer, it is notable that washing efficiency is high even at low wash water dilution.

The belt washer consists of two converging wires, forming a wedge section, which results in purely mechanical dewatering due to gravity as well as due to the wire tension applied at the S-Roll. In the Wedge zone, the wires containing the pulp are deflected at the S-Roll, before entering into wash shoe, this increases the dryness to about 15 to 17% O.D.

The washing module is mounted after the wedge-shaped dewatering zone; the wash water is fed to the washing module at definite pressure at the No.3 compartment and there is a countercurrent washing at compartment No.2 and 1. This design permits proper displacement washing in countercurrent. In order to remove the remaining chemicals the water runs through holes in the face of the washing modules and is pressed through the press cake between the wires.

Immediately, after the washing module the stock cake is pressed approximately 25-40% OD in 3 press nips.

The ascending wire arrangement allows the water drainage channels to be mounted in front of the individual pressing points and the water pressed through the top wire can be carried off before it can be reabsorbed by the stock web. This method contributes considerably towards eliminating re-absorption

Take off removes web and scraps off any remaining stock from the wires.

2. Result And Discussion

2.1 Productivity

There are various washers, where pulp washing is applied to meet the required production. There are drum washer (vacuum or pressure), cylinder thickener horizontal belt washer and double wire washer. Every type of washer has a special property, which satisfy to some kind of pulps. The productivity of rotary vacuum washer can vary in a wide range for different kinds of pulps, which are listed in Table-3.

The productivity is influenced by the characteristic and the operating condition of the pulp washer. In the double wire washer the mechanical dewatering takes place due to the tension of two wires at the wedge zone. Therefore different type of pulp can very easily be processed without much difficulties to a consistency of 15 to 16% and it is further washed at the wash shoe without any disturbances of the pulp sheet and finally pressed to 31 to 32% Cy. (approx.) – Table-5.

The total active filtration area of the pilot machine was 2.3 m^2. The basis wt. Of rice and wheat straw and bagasse was found to be 650 gsm, 750 gsm and 900 gsm respectively.

Therefore output in double wire belt washer for agriculture residue is considerably more in respect to a drum washer and is continuous as shown in Table-3.

Washing Efficiency

The washing efficiency of double wire belt washer is superior to any conventional three stage washing system for rice and wheat straw and bagasse. Results shown in Table-4 clearly indicate that washing efficiency of more than 93%, 94% and 95% are obtained respectively at a dilution factor of 2 to 2.5 (Fig-8).

The percentage reduction of solids at different zones is shown in Table-5. About 85% of the total dissolved solids is removed from the pulp at the wedge zone and the remaining 8-10% is washed out at the washing zone and press zone.

From the above, it is interesting to note that washing efficiency up to 90% can be achieved even without addition of wash water which occurs because of dewatering as well as pressing action at wedge and press zone respectively (Table-4).

It is, therefore, concluded that the final dry content of the washed out pulp is mainly responsible for achieving higher washing efficiency and the later increases if former rises. It is further added that the machine speed has considerable influence on washing efficiency as lower machine speed results in higher washing efficiency.

Displacement washing: Table-4 shows that the wash water quantity used hardly influenced the displacement ratio. Though D.R. increases with the increase of dilution factors (Fig-9) and are in the range of 0.2 to 0.5 with all the three raw materials. On careful examination of the results shown in Table-4, Fig-9, it is found that bagasse pulp showed highest D.R., whereas D.R. is lowest in case of rice straw. This behaviour may be explained because morphological characteristics of these pulps. From the Fig-10, it is also observed that the D.R. is affected by the density of the formed pulp mat and that the nominal basis weight 650 gm/m^2 gives a better DR than a density weight of 850 gm/m^2 in case of rice straw. The same seems to apply in wheat straw and bagasse also.

Pressing

Pressing do, however, have a place in the washing picture as it removes the loose liquor which is close to the fiber and contains most of the remained solids after washing. The results on the effect of pressing in D.W. belt washer is shown in Table-5. Fig-11 showing TDS reduction in wheat straw/rice straw bagasse pulp which are to the tune of 3.07/3.63/3.29 with a stock processed at inlet consistency of 15-16% (approx.) and was squeezed out up to 34% consistencies. Though there is a tendency of higher reduction of TDS at higher consistencies but beyond a consistency of 34% (wheat straw) the TDS reduction is not proportionate to increase in consistency as explained by Stone, J.E., et. al[5] that the fiber wall contain sub-micropores, which are smaller than the biggest dissolved carbohydrates or lignin molecules but significantly large to contain water. Thus this water sometimes called 'Non-solvent water' is inaccessible for dilution the macromolecule. Upon intense compaction the 'Non-solvent water' is partially squeezed out of the pulp and is then able to dilute the surrounding liquor.

Chemical Carryover

Soda losses of rice straw, wheat straw and bagasse around to be 37.5, 31.6 and 26.1 Kg/MT of pulp when no wash water is added to the system, i.e. because of dewatering and pressing only which decrease as DF increases. For each particular DF, there is substantial decrease of chemical carryover with all the three types of pulps up to a dilution factor of 2 (2.5 in case of wheat straw) beyond which the trend became an asymptotic (Fig-12) indicating the sue of said DFs to be economical while considering other important factor such as evaporator capacity and the cost of evaporation, etc.

From Fig-12, it is, however observed that soda carryover in case of rice straw is highest and lowest for bagasse (23 Kg/MT pulp) which attributes the morphological behaviour of the different fibres and are in accordance with the studies of et.al[6].

3. Experimental

Pilot Plant Trials: The pilot plant trials were conducted at Saharanpur pilot plant unit of CPPRI. The flow sheet of pilot plant pulping and washing unit is shown in Fig-13. The raw material was charged to a stainless steel tumbling digester of 11 m^3 capacity. Cooking liquor from liquor preparation tank was sprayed from the top of digester. After cooking the pulp along with liquor was blown into 30 m^3 blow tank.

Then the pulp was diluted to about 3% consistency and taken to pulp chest for finding its yield, freeness and total dissolved solids. Pulp was processed to ANDRITZ belt washer at a uniform rate to the head box, to wedge section, washing section and press section. The speed of the belt washer was regulated to achieve the required basis weight and wash water added at the washing shoe to maintain dilution factor. Black liquor samples at wedge section, washing section and press section were collected to determine the 'total dissolved solids' at different stages. Pulp sample was collected from the outlet of the washer to find out the TDS in pulp, rate of production, dryness % and washing efficiency.

Spent Liquor Analysis

The analysis was carried out according to procedure described in Tappi Standard Method T-625—15-64.

Pulp Analysis

The kappa number of the pulp was determined according to Tappi method T-236-05-76. Basis wt. Of the sheet and freeness of pulp was determined according to Tappi method T-220-05-71 and (T-227-05-58) and sodium content of wet pulp according to SCAN-C30:73.

Physical Layout Of Pilot Plant

D.W. Washer

1. Physical Layout:	
Length	8100 mm, 319 inches
Width	1700 mm, 67 inches
Height	3300 mm, 130 inches
Types of fabric	Synthetic
Filtering	0.25 meters width
Area	2.3 square meter
2. Application	
Inlet cons.	0.5-6% (Depending upon the types of raw materials)
Discharge	15-35% (Depending upon the types of raw materials)
Specific production	25-40 O.D. TPD per one meter working width (Depending on kind of pulp)
3. Electrical	
Power	440 V, 50 HZ, 3 phase
Supply	60 Amps.
Motor	20 HPDC TEFC 1760 RPM Std. Theramosrale.
Reducer	Sew Eurodrive Right angel (Helical-Beval) Reducer.
4.Air (filtered Mill air)	
85 PSI	6 CFM

5. Press:
3 NIP Presses
Line pressure of 300 N/cm of roll width (max.)
6. Wire tension:
Maximum 80 N/cm wire width (max.) using a pneumatic-mechanical device
7. Wire guide:
Pneumatic-Mechanical

4.0 Advantages And Economics Of Use Of Double Wire Belt Washer Over The Conventional Drum Washers Taking A Plant Of 30 Tpd Capacity

a. Single Machine For The Whole Brown Stock Washing

The double wire washer is a single compact unit where in case of conventional washing system we require two or three rotary drum washer with their accessories each having individual operation

b. **Small Building Required**

The drum washer have drop legs of more than 10 m height so they need a building of approximately 16 m height. For drum washer plant 10 m width and 20 m length is required, whereas for belt washer 6.5 m height, 10 m length and 4 m width is required.

c. **Small Filtrate Tanks Required**

The drum washer require big volume filtrate tanks having volume of approximately 40 m3 each whereas for belt washer the filtrate tanks of size 1-2 m^3 are sufficient and they can be placed just below the belt washer if it is placed on raised foundation.

d. It can be housed on ground floor and being on one floor the operation is easier.

e. The pulp produced is of higher consistency so the material handling cost decreases and the less volume of storage chest is required and one can go for higher consistency bleaching.

f. It is versatile for different types of pulps. It can process pulp produced from agricultural residues as easily as produced from conventional raw materials. If the drum washer is to be used for agricultural residues, the vacuum pumps have to be added and size has to be increased for same production.

g. Higher concentration of black liquor going to recovery so there is saving in steam energy in evaporators. By reusing the filtrate in cooking liquor preparation and digester, the concentration of black liquor going to recovery can be slightly less than that in blow tank.

h. **Low Consumption Of Electrical Energy**

The electrical consumption in case of belt washer is almost one-third as compared to drum washer because of less heat required to lift filtrate and pulp, single drive motor for whole of the unit and less volume of liquor to be handled.

i. **Less Manpower Required**

The whole of unit can be handled by a single man whereas in three-stage drum washer, four men are required, so there is saving in man power.

j. Less Maintenance

Due to compact single unit, the maintenance required is less.

k. Less Amount Of Fresh Water Requirement

Less amount of fresh water is required as dilution factor is less and the output consistency being high, the liquor carry over by the pulp is less.

5.0 Economics Of Belt Washer

The comparison of economics of belt washer and drum washer is given below on the basis of 30 TPD plant.

Table-1

Capital Investment

S. No.	Particulars	Belt washer	**Drum washer**
1	**Building cost @ Rs.450/ft**	Rs.3.25 lacs (12m x 6m x 6.5m ht)	Rs.23.0 lacs (20m x 10m x 16m ht)
2.	**Filtrate tank**	Rs.20,000 for 3 tank of 1m, 1m^3 & 2 m^3	Rs.6.0 lacs for three seal tank of 45m^3 each
3.	**Equipment cost**	Rs.20.0 lacs (for 1m deckle width)	Rs.24.0 lacs (Rs.8.0 lac for each)
4.	**Piping cost**	Rs.7000 (40m)	Rs.25,000 (135 m 4" MS pipe@ Rs.120/m)
	Total	**Rs.23.51 lacs**	**Rs.53.25 lacs**
	Saving Per Year	**Rs.29.74 Lacs**	

This excludes electrical cables and fitting of pipes.

Table-2

Saving In Steam Energy

Basis: 30 TPD pulp plant per day basis

Dilution factor of belt washer	:	0.5
Dilution factor of drum filter	:	3
Liquor with pulp at 5% bath ratio	:	150 m^3
Total solid	:	31.55 MT
Washing efficiency of belt washer	:	95%
Washing efficiency of drum washer	:	90%
Liquor going to recovery in case of drum washer (for same TS as belt washer	:	150 + 90 = 240 m^3
Liquor going to recovery in case of belt washer	:	150 + 15 = 165 m^3
Saving in liquor going to recovery	:	75 m^3
Saving in steam per day (75/3.2)	:	23.43 MT
Saving of steam per year (23.43 x 330)	:	7732 MT
Saving in Rupees (7732 x 400) app.	:	Rs.30.92 lacs

Table-3

Saving In Electrical Energy

Particulars	Belt washer	Drum washer
KWH per ton of pulp	40 KWH	120 KWH
KWH/day	1200 KWH	3600 KWH
Power cost per year	Rs.15.84 lacs (1200x330x4.0)	Rs.47.52 lacs (3600x330x4.0)
Saving in power	**Rs.31.68 lacs**	

Saving In Man Power

For 30 TPD plant for belt washer 1 man per shift is required, whereas in drum washer 4 men per shift are required., so saving is 3 men per shift.

So, saving in man power per year = 3 x 3 x 360 = **3240 man days**

So, saving in rupees (3240 x 100) app. = **Rs.3.24 lacs**

Table-4

Processing Cost

Particulars	Belt washer	Drum washer
Power cost per day	Rs.4800/-	Rs.14,400/-
Man power cost	Rs.300/-	Rs.1200/-
Cost of water	Rs.450/-	Rs.900/-
Total	Rs.5550/-	Rs.16,500/-
Saving per day	**10,950/-**	
Saving per year	**Rs.36,13,500/-** (10,950 x 330)	

Saving in capital investment	-	Rs.29.74 Lacs
Saving in operating cost	-	Rs.67.33 lacs
Electrical energy saving	-	Rs.31.68 lacs
Steam energy saving	-	Rs.30.92 lacs
Saving in manpower	**-**	**Rs.3.24 lacs**
Saving in water	-	Rs.1.49 lacs
Total Savingwithout chemical recovery	**-**	**Rs.36.0 lacs**

6.0. Conclusion

6.1 The extended inlet wedge zone, allows for a higher throughput and renders the washer more flexible with regard to fluctuations of the inlet consistency and dewatering of the fibrous stock.

6.2 The double wire washer shows that total dissolved solids in wedge zone filtrate very close to dissolved solid in the liquor from the blow tank.

6.3 Low Dilution factor, reducing load on evaporators, consuming less steam.

6.4 Washing efficiency up to 90 percent can be achieved without addition of wash water and this because of the high consistency dewatering at the press zone.

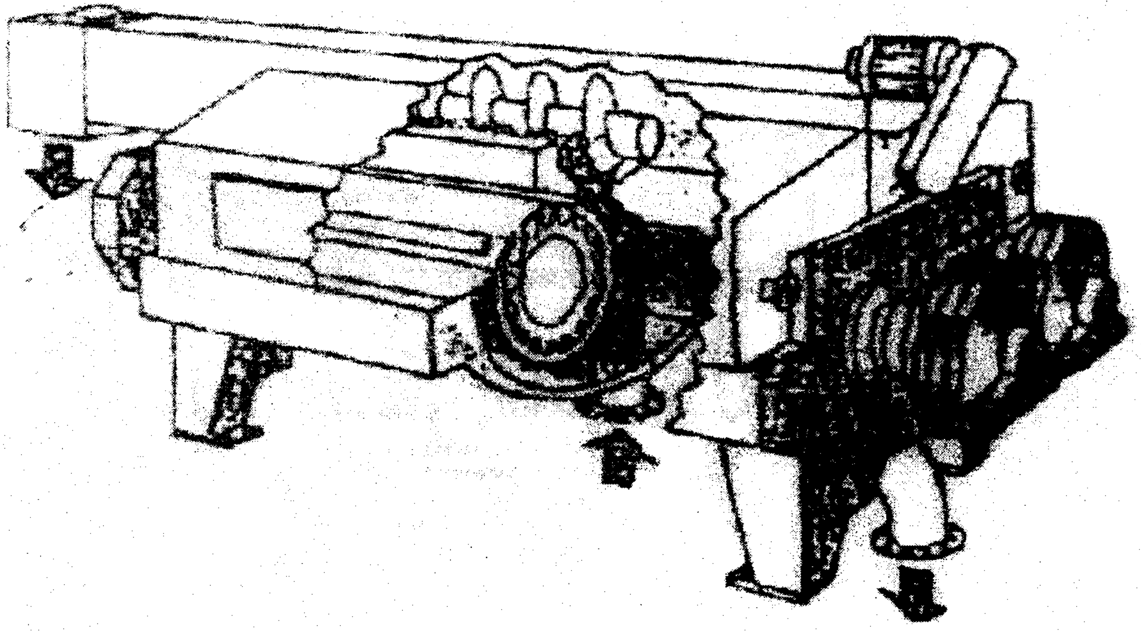
6.5 Displacement washing in bagasse pulp is superior among the three followed by wheat and rice straw, because of the permeability characteristic of the fiber.

6.6 Pressing action removes further, the loss liquor which is close to the fiber and contains most of the solids after washing. However, the TDS reduction is not proportional to increase in consistency of the pulp.

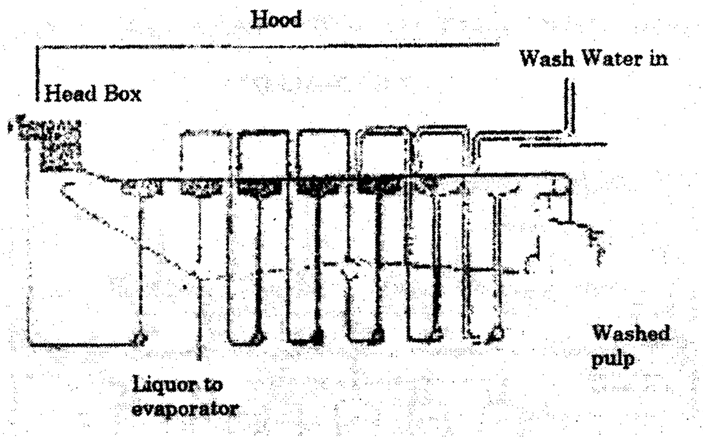
6.7 Soda loss in Double wire washer is comparatively lower than a conventional drum washer, resulting higher percentage of TDS in black liquor going to Recovery. Chemical carryover in rice straw is comparatively higher than wheat straw and bagasse pulp due to the higher surface specific area of rice straw fiber in comparison to wheat straw and bagasse.

6.8 It is suggested that there is sufficient scope for the Indian paper industry to utilize the double wire washer for small mill as well as big mill for energy conservation, with less capital investment, higher output and less chemical loses. Further investigation is being carried on with different agriculture residue pulp with emphasis on a viable chemical recovery plant for small paper mills.

Sunds Defibrator Dewatering Press
Fig-1

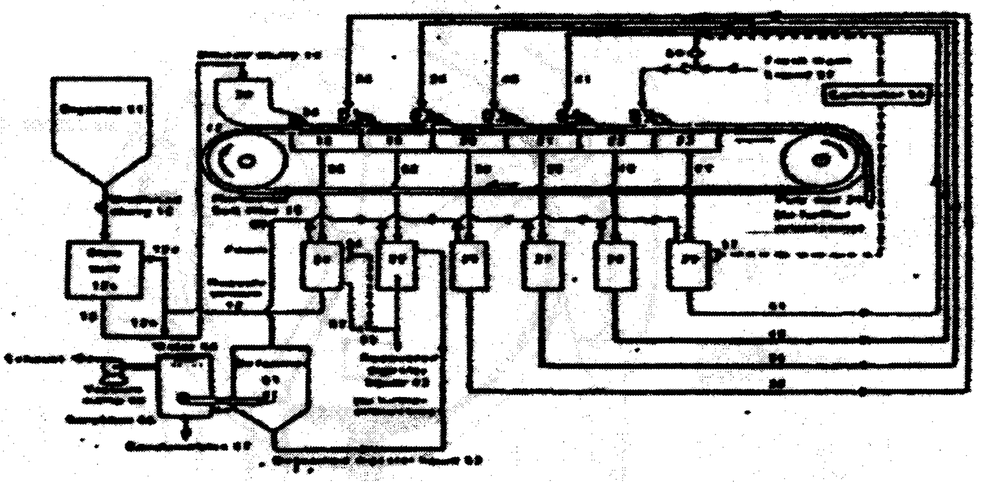


ULTRA WASHER
FIGURE NO 2



FLOW DIAGRAM OF A ULTRA WASHER

FIGURE NO. 3



PRESSURE WASHER

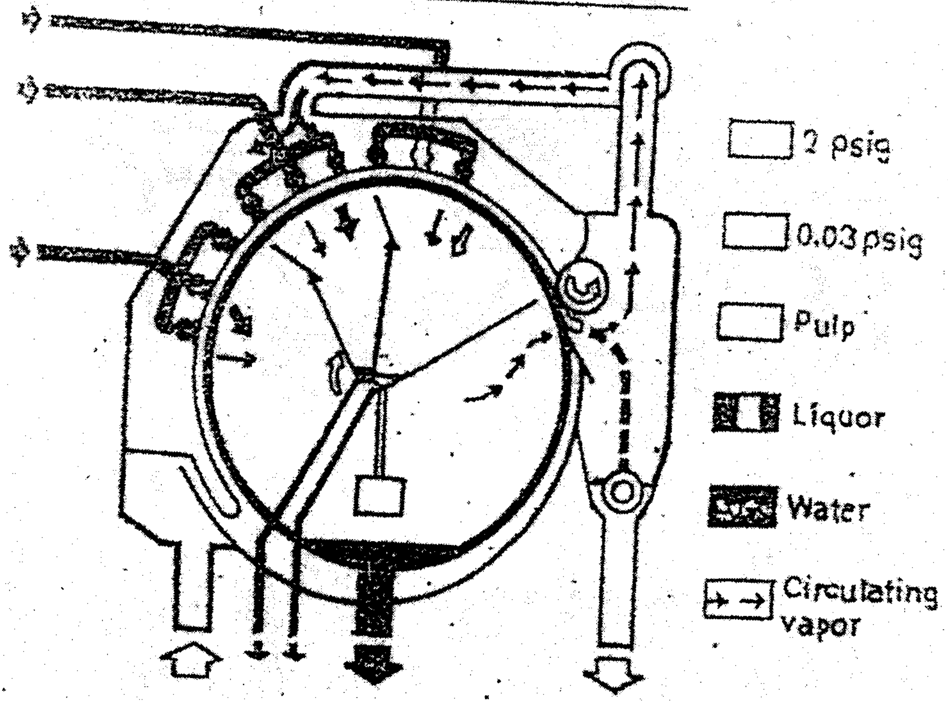
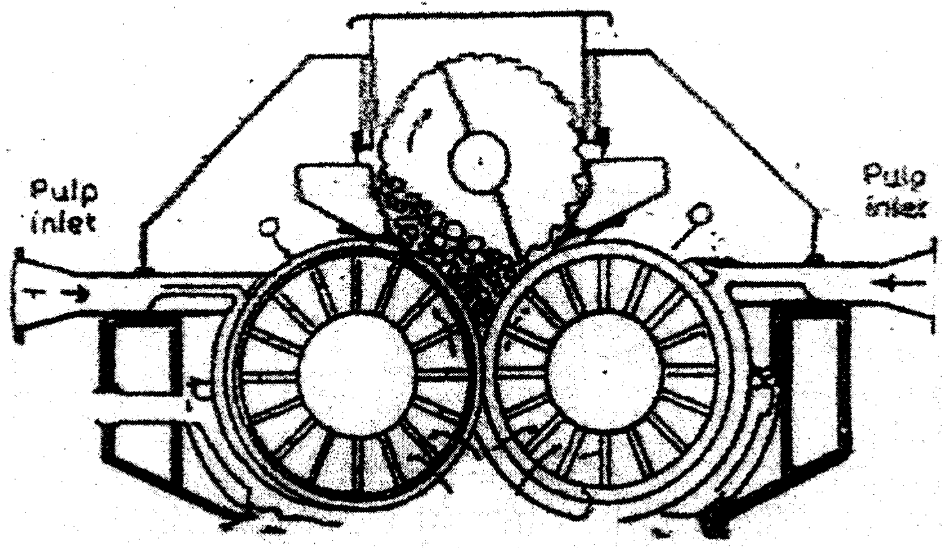


FIGURE NO. 4

TWIN - ROLL WASHING PRESS

FIGURE NO.5



FIBERFUGE WASHER

FIG. 6

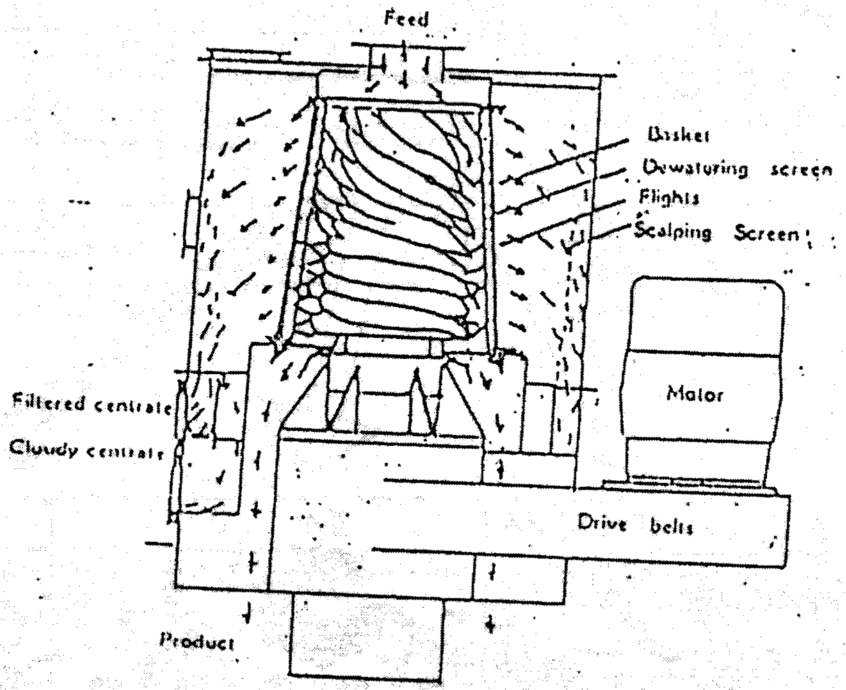
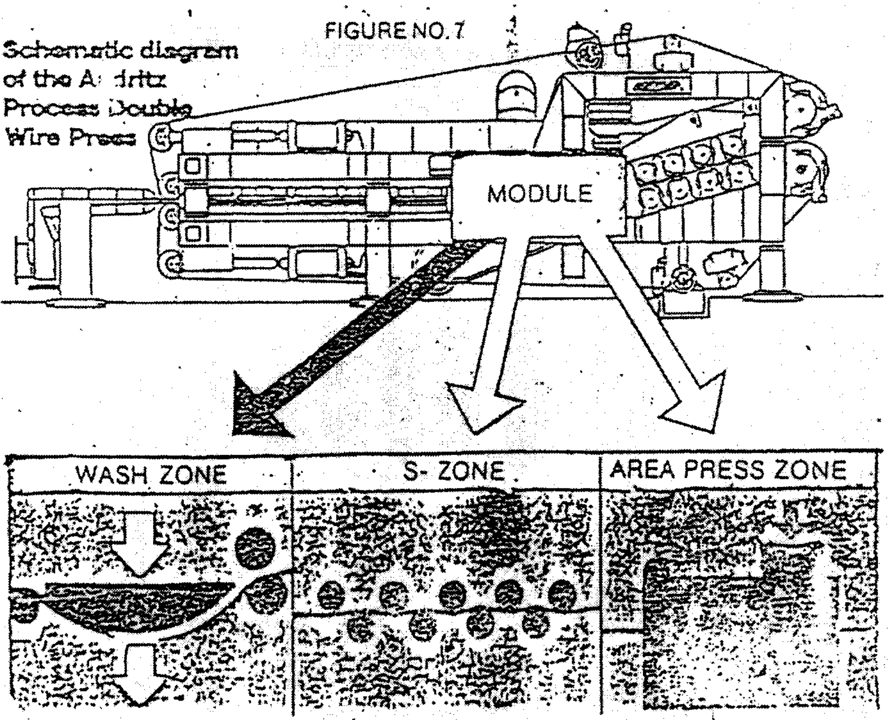


FIGURE NO.7

Schematic diagram of the Andritz Process Double Wire Press



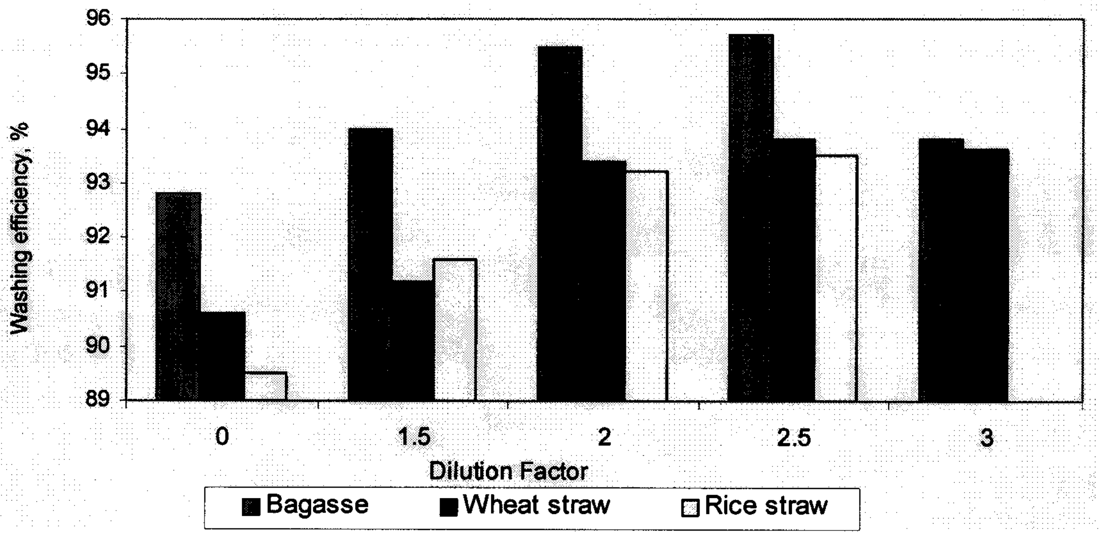


Fig 8 :- Washing Efficiency Vs Dilution Factor

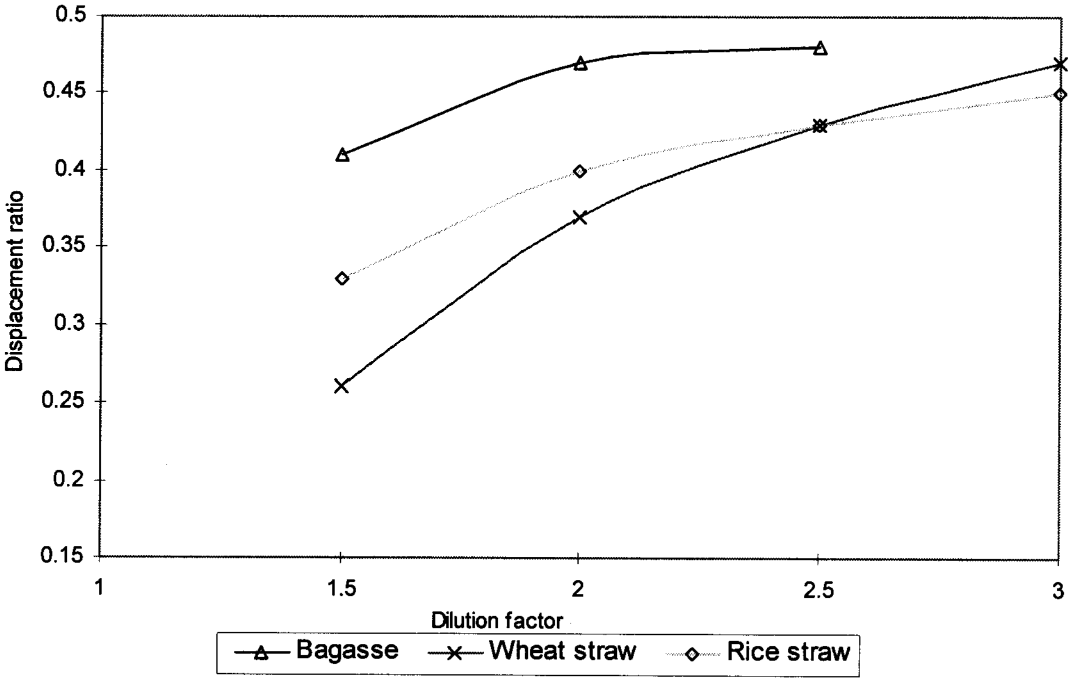


Fig 9 : Displacement Ratio Vs Dilution Factor

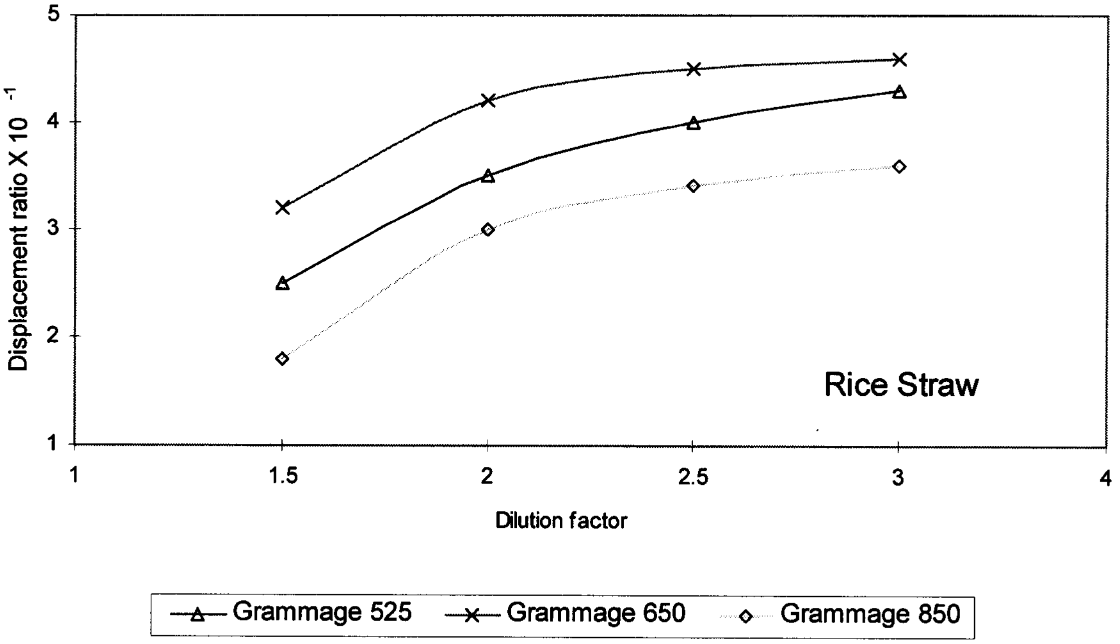


Fig 10 : Displacement Ratio Vs Dilution Factor

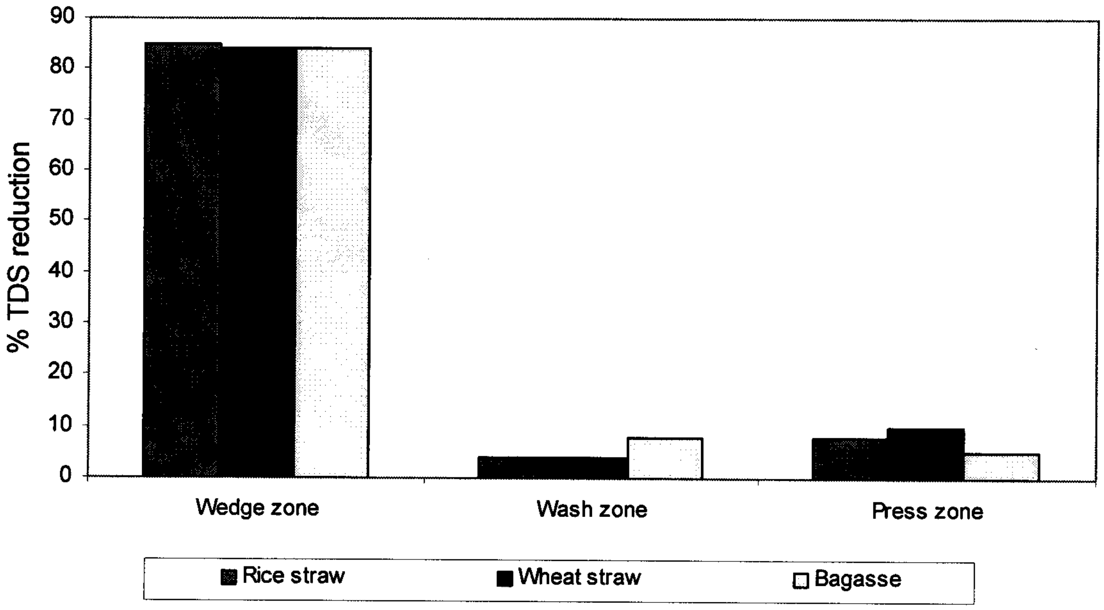


Fig 11: % TDS Reduction at Different Zones

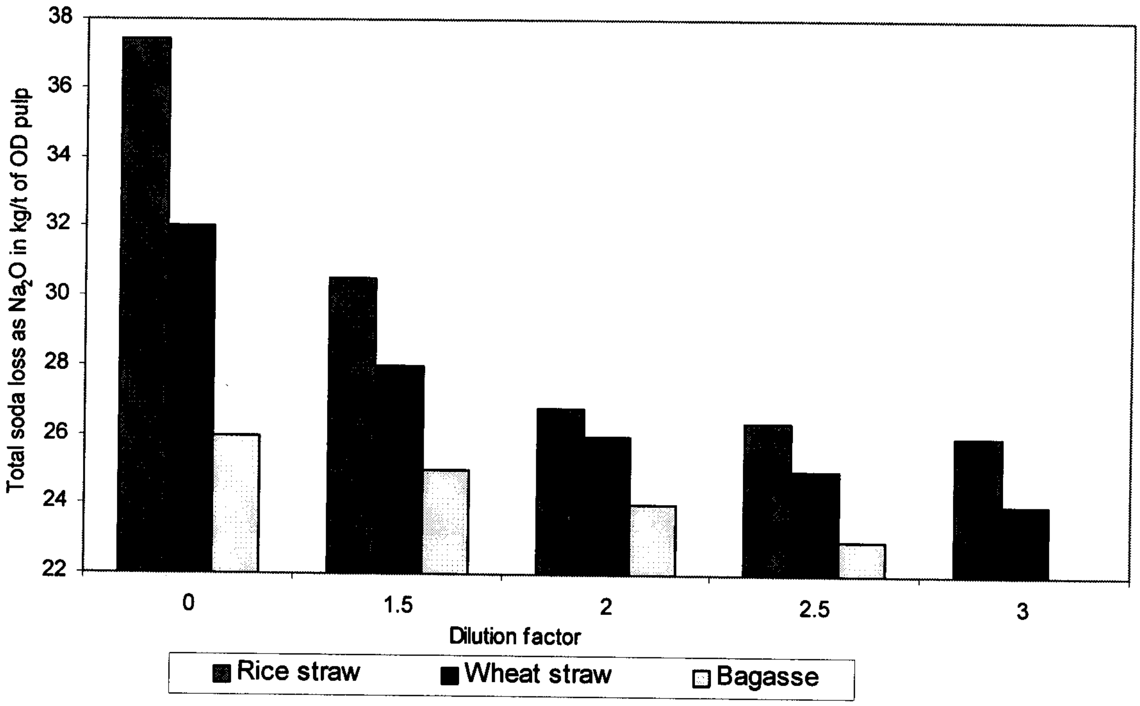
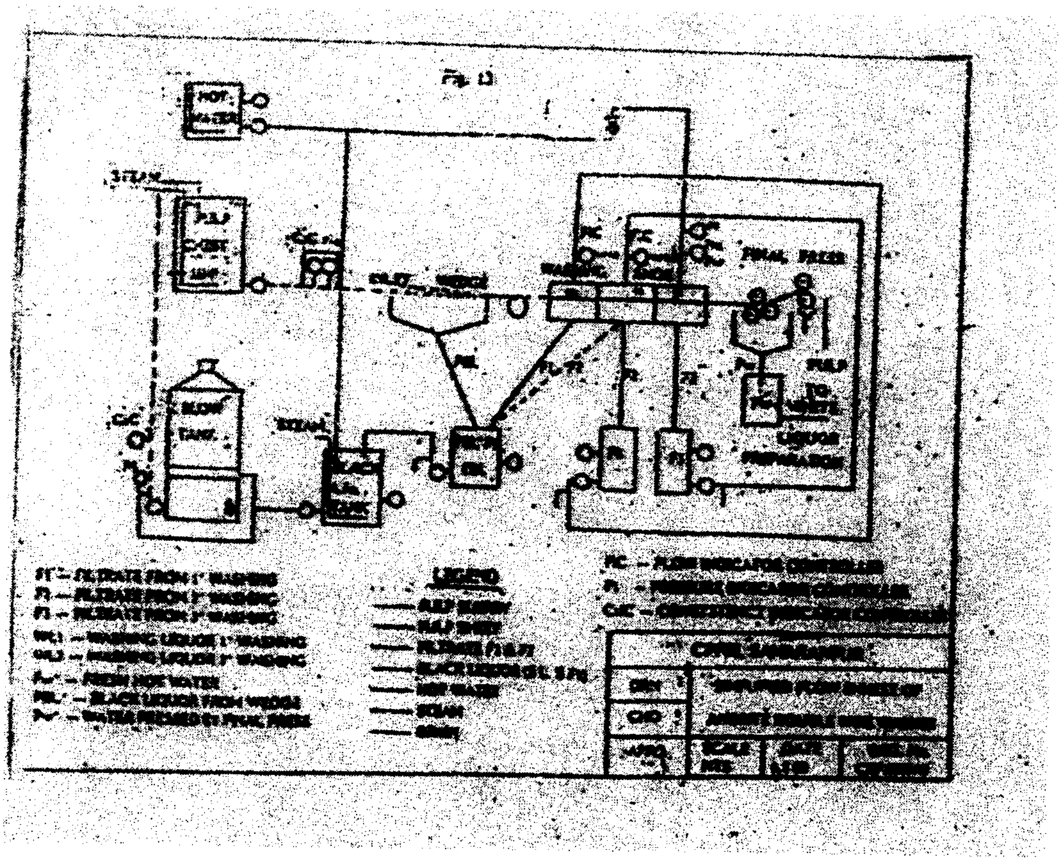
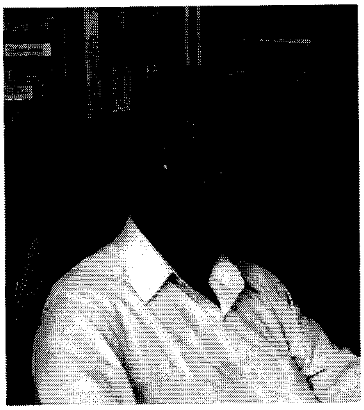


Fig 12 : Total Soda Loss Dilution Factor



BLEACHING

PULPING & BLEACHING PRACTICES IN INDIAN PAPER INDUSTRY



Dr. A.G. Kulkarni,
Director, CPPRI

About The Author

Dr. A.G. Kulkarni, Director Central Pulp & Paper Research Institute (CPPRI) Saharanpur, Uttar Pradesh, India has been with the CPPRI since its inception. He holds a Master degree in Chemistry & Doctorate in Black Liquor and Lignin Chemistry.

Dr. Kulkarni has pioneered the research work on Desilication of black liquor with eventual development of mill scale plant, installed at Hindustan Newsprint Ltd., Kerala and High Rate Bio methanation of black liquor rich effluent and a mill scale unit is successfully operating at Satia Paper Mills is another achievement of Dr. Kulkarni. His contribution in the area of physico chemical & thermal properties of agro - residue non-wood black liquors has now made it possible to process this liquor in chemical recovery boilers. He has published more than 300 scientific papers in Indian and International journals. He is widely traveled in Europe, S. E. Asia, and Australia and has been on several foreign missions as UNDP/UNIDO Consultant.

His areas of specialization include pulping and bleaching, black liquor-its chemistry & processing, environment and energy management. Dr. Kulkarni holds several patents-important ones being on desilication of black liquor, thermal treatment of black liquors and Direct Alkali Recovery System etc. He is a member of several National and International Scientific & Technical organizations and also on board of Directors of Paper Mills & Research organizations

PULPING AND BLEACHING PRACTICES IN INDIAN PAPER INDUSTRY.

A G Kulkarni, Director*

1. Introduction

Indian Paper Industry uses wide range of fibrous raw materials, and generally employ the Kraft or Soda pulping processes. The medium size mills which do not have the chemical recovery system invariably employ the Soda pulping process, whereas the integrated big mills employ the Kraft pulping process. Wide range of fibrous raw materials such as bamboo, hardwoods, cereal, straws, bagasse & annual plants makes it difficult for the industry to adapt uniform pulping & bleaching processes. Some time when there is mixed raw materials furnish, mills intend to use the mixed pulping processes, as it is capital intensive to have different streets of puling and washing streams. It is also generally been observed that in case of big mills the Kappa Nos. varies from almost 15-30 depending on the products and raw materials used. It has been often observed that the intrinsic strength of the cellulosic fiber is lost significantly because of the non-uniform and non-controlled pulping & bleaching operations.

Medium size mills which are operating pulp mills without chemical recovery system generally have a tendency to use the minimum cooking chemicals during pulping operation purely from the economic point of view and subsequently removal of the residual lignin is accomplished in bleaching stage. As a consequence these mills are also producing bleached pulps which have very low strength properties. It has also been further observed that in the mills which are using straws & bagasse the cooking chemical is not mixed properly with the raw materials due to equipment constraints leading to non uniform cooking. With few exceptions generally it is observed that considerable intrinsic strength of the fiber is lost and pulps thus produced have poor run ability on the paper machine.

2. Pulping Operations

The pulping is one of the most important steps in the paper manufacturing process and during the pulping process the lignin is slowly dissolve by degradation with alkaline chemicals at elevated temperatures, and only a small portion of the lignin is retained which is subsequently removed in the bleaching operation.

*** Director,. CPPRI, Saharanpur, UP-247001**

One of the important steps in pulping operation is to ensure that the pulp is not degraded. In order to protect the carbohydrate fractions generally Sulfate pulping process involving the mixture of sodium hydroxide and sodium sulfide is employed and sodium sulfide facilitates in the faster dissolution of lignin through degradation reactions, and that is one of the reasons why generally the kraft pulps are stronger compared to soda pulps. The sulfidity level depends on the lignin contents in the raw materials. For instance; the **Scandinavian** countries which are using soft woods containing more than 30% lignin generally employ high percentage of sulfidity ranging from 30-35%. Most of the Indian paper mills; the sulfidity levels are in the range of 20-25%. During the pulping operation a care will have also to be taken to keep the minimum free alkali level, so that subsequent processing of spent liquor is smooth.

Due to less lignin contents in the cereal straws & bagasse, generally it has been observed that the Sulfate process does not have much advantages. Further, keeping in view of the odor and corrosion problems, the medium size mills without chemical recovery system commonly practice the Soda pulping process. With cost of the anthraquinone coming down, now the number of paper mills are using anthraquinone as a pulping additive during the Soda pulping process. Anthraquinone to a large extent prevent the degradation of cellulosic fibers while improving the de-lignification.

3. Pulping Equipments

Most of the large paper mills which are using Sulfate pulping process, generally employ the **Vertical Stationery Digesters (VSD)** having capacity ranging from 60–120 m^3·Most of these Digesters have the indirect heating arrangements using pre-heaters(**Fig.1**). Depending on the pulp mill capacity, mills are using blow heat recovery arrangements where the cooked material is blown to achieve the de-fiberisation while recovering the waste heat. Only few mills are having facilities for continuous cooking. The continuous Digesters are working efficiently for wood, and generally they are not efficient in case of continuous pulping of bamboo.

Most of the medium and small mills generally are using the **Spherical Digesters** of varying capacity are in the range of 40-80 m^3. After the demonstration of **Vapour Phase Pulping (VPP)** process by CPPRI, some of the medium size mills started pre-impregnation of the chemicals to achieve the uniform cooking (**Fig.2**). Most of these mills do not have the arrangements for the recovery of the blow heat.

4. Washing Of The Pulp

The pulp washing is one of the key steps which determines the concentration of black liquor (BL) and the undesirable carry-over of COD to the leaching operation. Most of the commonly used equipment and process for washing of the pulp for the counter-current **Vacuum Washing System (VWS)** where the hot fresh water is added on the various washing stages and washing are circulated continuously. The principle of washing is shown in **Fig.3 & 4**. The advantages of the counter-current washing system is the high solids concentration in the weak black liquor and efficient washing. The washing efficiency depends on the fiber properties and generally the bagasse and straw requires more washing area compared to the soft wood, bamboo and hardwoods. With the limitations of the conventional **Brown Stock Washing System** in the last two decades tremendous developments were taken place in the pulp washing technology and today, we have new generation of washing system like; **Trim Roll Press, Double Wire Washer, Ultra Washing and Screw Press(Fig.5)**. These new generation washing systems ensure lowest dilution of the water and high concentration of black liquor solids. Further, it is also observed that the COD carry-over using these modern washing systems has reduced the carry-over to a level less than 5 Kgms of COD. Most of the Indian Pulp and Paper Mills use nearly 80%(**Integrated Big Mills**) employ conventional Brown Stock Washing System, and only recently some of the mills have the modern washing system. The Hindustan newsprint Limited (HNL), Kerala has got "Twin Trim Roll Press", and AP Paper Mills Limited (AP), has got "Ultra Washer System".

In the medium and small mills most of the mills adapt obsolete poacher washing system followed by 1 or 2 stage Vacuum Drum Washing System. As these mills does not have any chemical recovery system, they would like to manage washing with the high volumes of fresh waster using 1 or 2 stage washing system. Generally the carry-over of COD in these mills is very high and the bleached chemicals demand in terms of chlorine is sometimes as high as 200 Kg. It is very important for any mills to have a efficient pulp washing system both from the environmental view point and also from the bleaching operations. The typical advantages of good washing system are shown in the **Table Nos 1 & 2.**

5. Bleaching operation

Bleaching of the unbleached pulp is to accomplished in order to achieve two objectives namely; (1) to remove the residual lignin; & (2) to brighten unbleached pulp to the brightness level depending end products. If we see the trends on the quality of the bleached pulps in the Indian paper industry, there has been a remarkable change in the last 50 years. In the early 50's, the final brightness used to be some where around 68-70%, which has now increased to almost close to 90%. Today, there is a demand for brighter paper products in the global market. Further with the requirements of massive quantities of Reprographic papers there is a tendency of the Customer to ask for brighter Photo-copier papers.

5.1 Bleaching Chemicals

Major portion of production of the Indian paper industry still continues to depend on the chlorine and chlorine based bleaching chemicals primarily because of the economic reasons and also inability of the majority of the paper mills to afford for advanced Chlorine dioxide & Oxygen bleaching techniques.

5.2 Chlorine Based Belaching Chemicals

Generally, chlorine gas during chlorination stage and calcium hypo chlorite during the bleaching stage are employed. Chlorine is essentially a delignification agent and the chlorine substitution reactions lead to the formation of chloro-lignin, which is subsequently dissolved in the alkali extraction stage. The calcium hypo chlorite helps in improving the brightness of the pulp by producing active bleaching intermediate controlled hypo chlorous acid. Hypochlorite always produce the major proportion of the undesirable chloro-phenols. Hypochlorite while improving the brightness of the pulp also intends the decrease the intrinsic strength fiber by degradation cellulosic polymers.

5.3 Chlorine Dioxide Bleaching

Chlorine dioxide bleaching became popular in the year 1980's and in the last 20 years chlorine dioxide has gained popularity because of its ability to increase brightness level to the level upto 90% while preventing major degradation of the cellulosic fibers. Further chlorine dioxide does not generate as much AOX as in the case of hypo chlorite bleaching. However, the chlorine dioxide generation cost and process controlled systems makes it prohibitive for small scale operations. It is encouraging to note that more than 10 Pulp and Paper Mills in India have gone for chlorine dioxide bleaching and some more mills are planning to go for.

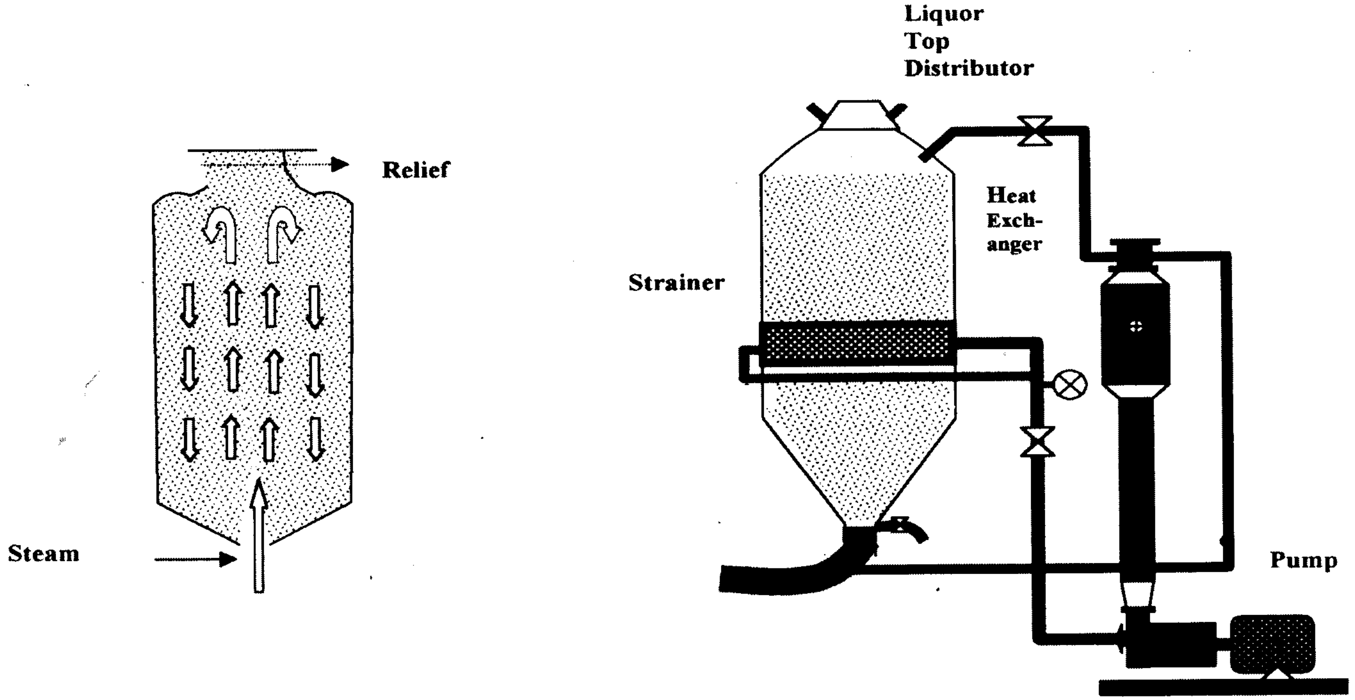
6. Bleaching Practices In Small And Medium Size Paper Mills

Number of small and medium size paper mills do produce bleached pulps either for the Newsprint manufacture, or for the manufacture of writing & printing papers, and generally it is observed that in such mills they cook to higher Kappa No., and subsequent delignification is usually done by employing a very high dosage of chlorine and chlorine based chemicals. Some of the mills, to avoid the problems in handling of chlorine gas, generally tend to bleach the pulps only using calcium hypo chlorite and it has been observed that mills use calcium hypo chlorite to the extent as high as, and as a consequence the pulp degradation takes place invariably resulting poor quality of the products. In most of these small and some of the medium size paper mills it has also been observed that proper equipments for mixing of bleached chemicals with the pulp do not exit and bleached chemicals are some time mixed in conventional **LAUNDER,** which result in the carry-over of free chlorine, which is responsible for the generation of a very level of AOX.

7. Conclusions

Keeping in view of the environmental aspects, pulp quality and the product quality it is very important for every paper mill to have optimum pulping and bleaching configurations, so that the intrinsic strength of the fiber is retained while protecting the environment & quality improvements.

BATCH DIGESTERS



Direct Heating System

Indirect Heating System

Fig.1

ILLUSTRATION OF CONVENTIONAL (A) & MODIFIED DIGESTERS(B) WITH CHEMICAL PREMIXING ARRANGEMENT

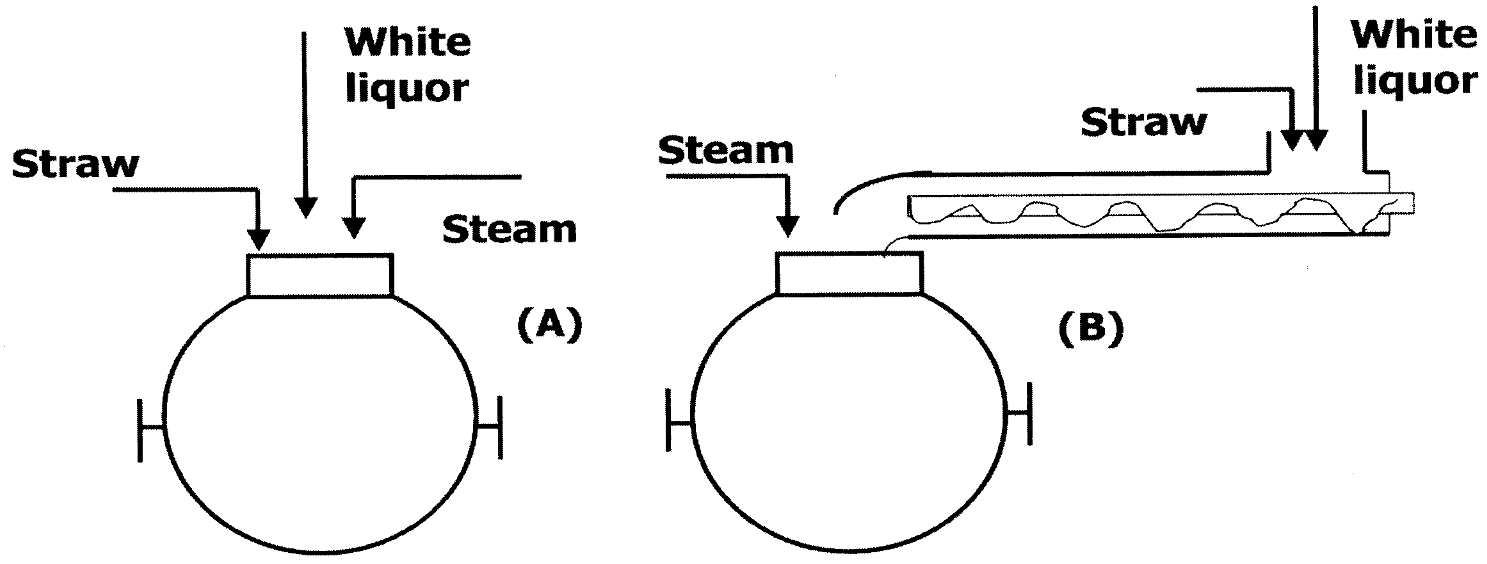


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Fig.2

DISPLACEMENT WASHING

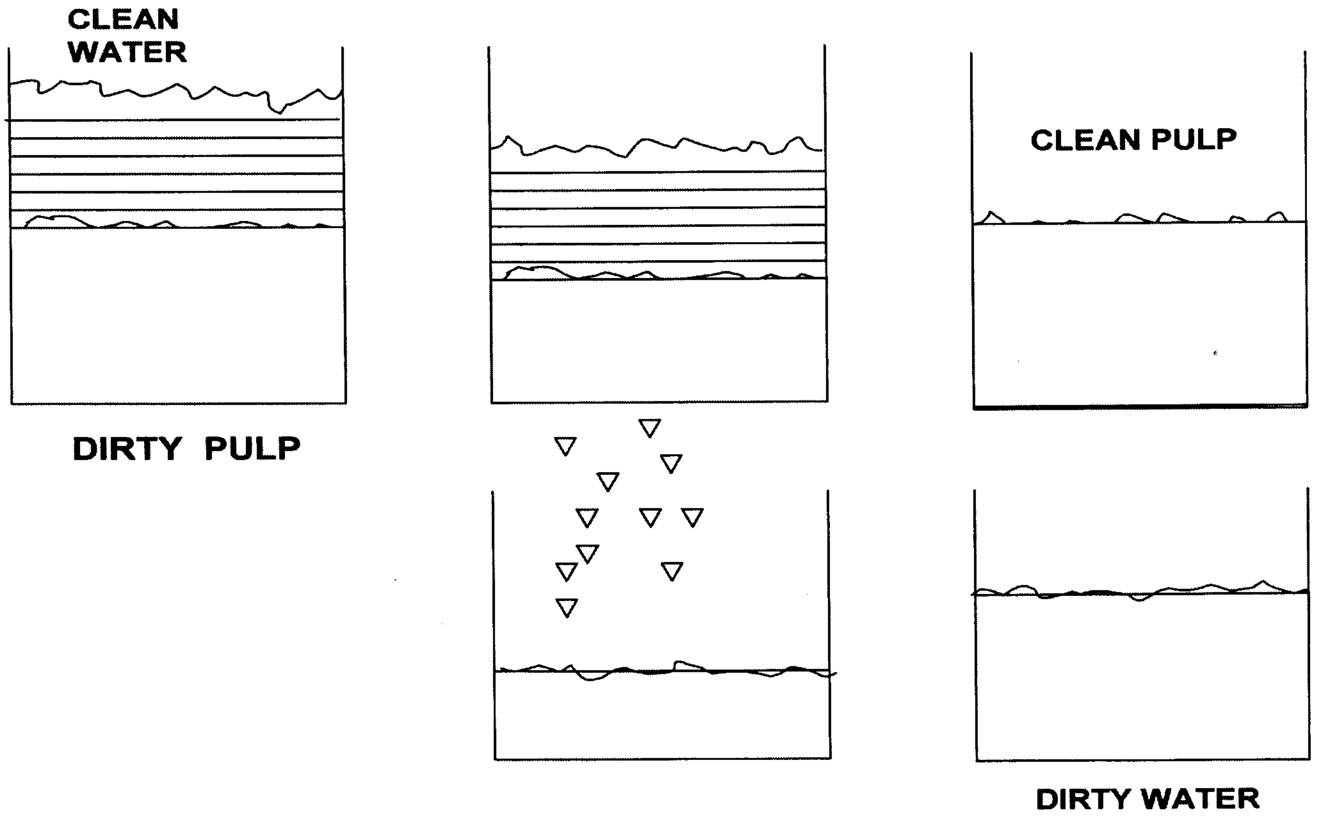

Fig.3

DILUTION WASHING

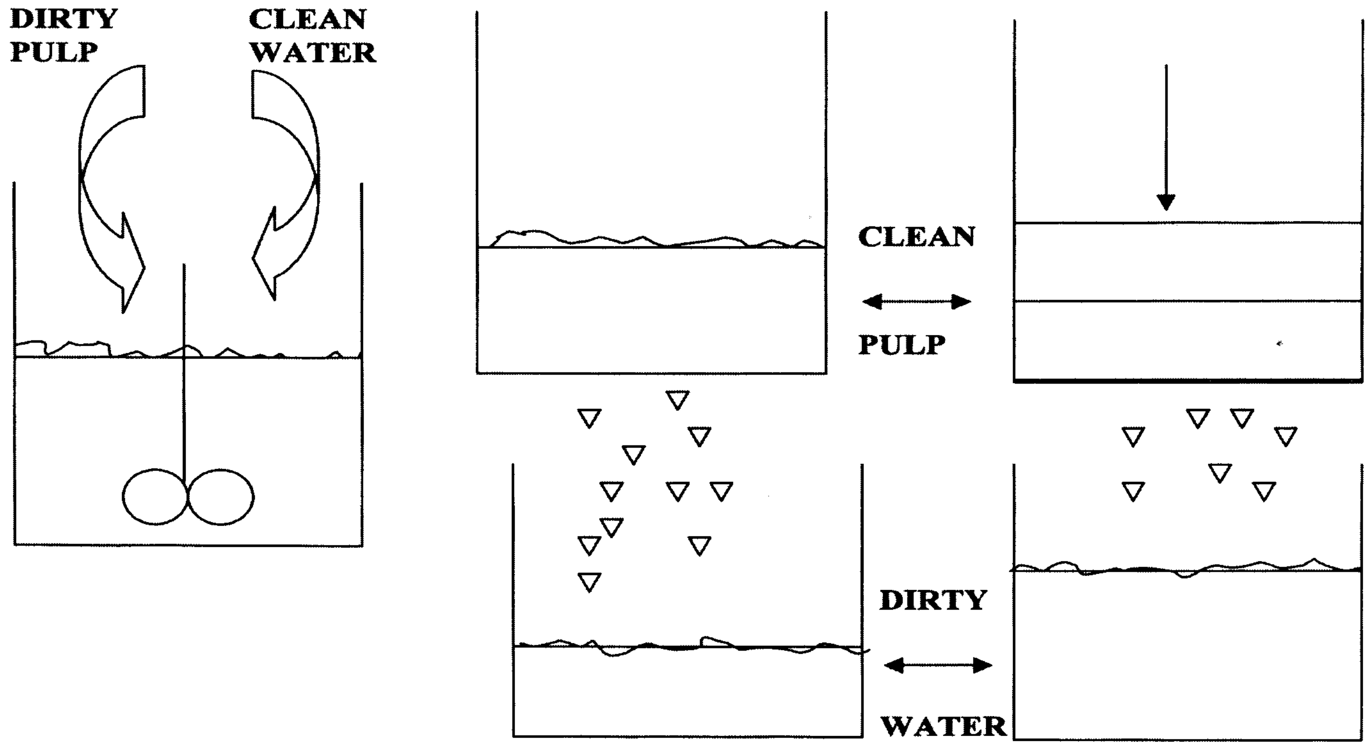

Fig.4

MECHANICAL DEWATERING DEVICES-RELATIVE USES IN PULP AND PAPER INDUSTRY

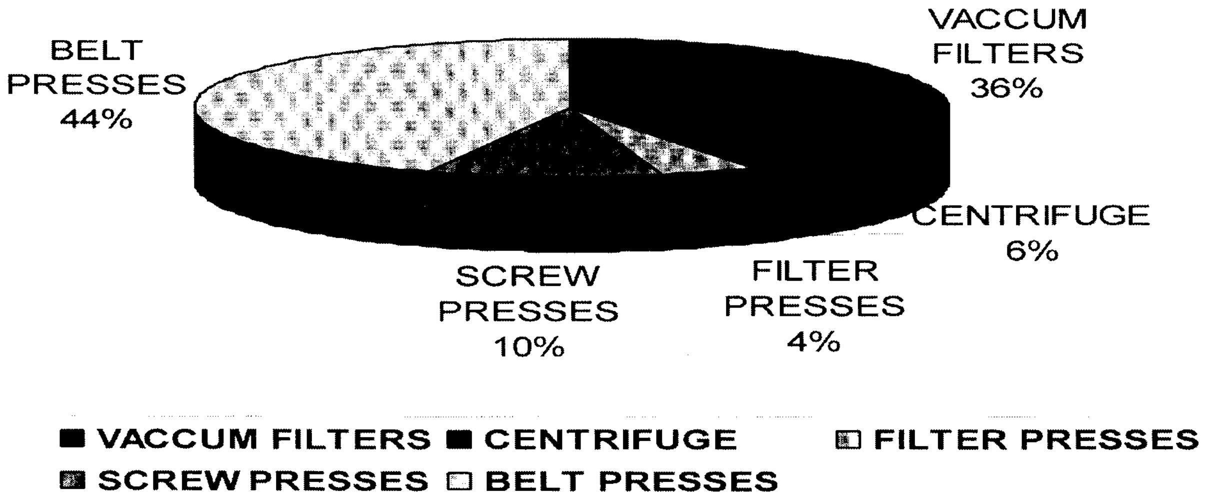

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Fig.5

Table-1

BENEFIT OF IMPROVED WASHING SYSTEM

Raw material Processed	Saving in Chlorine consumption, kg/t	Steam saving in evaporation to achieve 50% conc. T/t PULP
Straw/ bagasse	75-100	(Raising conc. From 6-10%)
Bamboo	40	(Raising conc. From 13-16%)
Wood	30	(Raising conc. From 15-18%)

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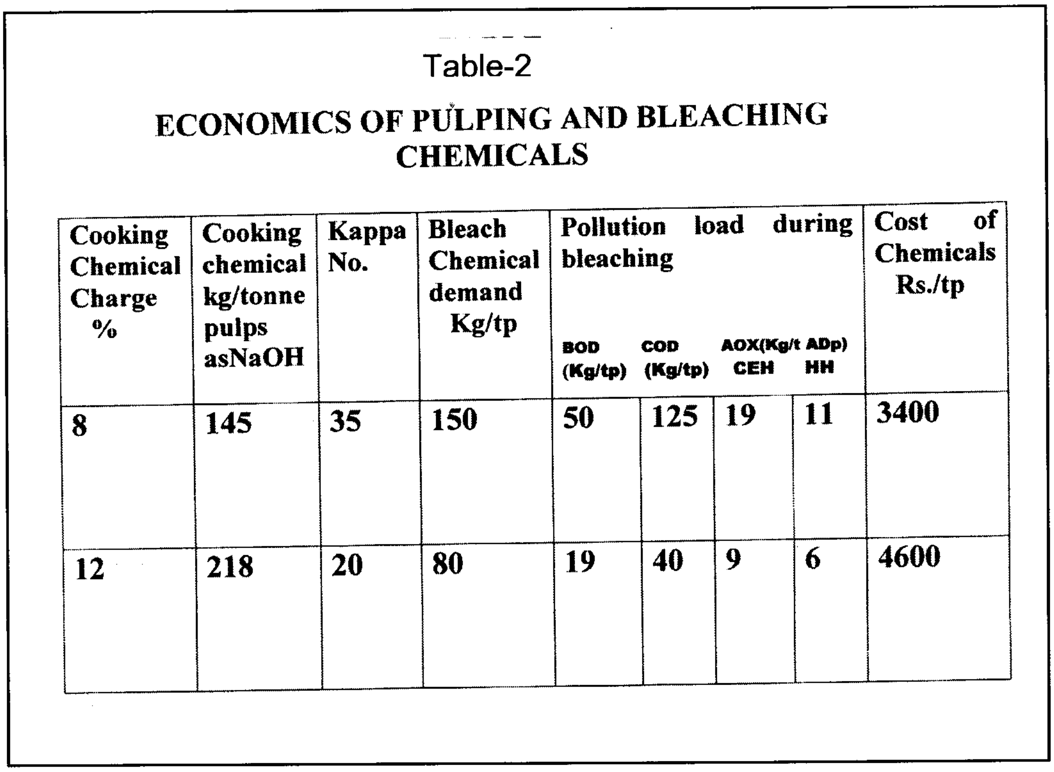

Table-2

ECONOMICS OF PULPING AND BLEACHING CHEMICALS

Cooking Chemical Charge %	Cooking chemical kg/tonne pulps asNaOH	Kappa No.	Bleach Chemical demand Kg/tp	Pollution load during bleaching				Cost of Chemicals Rs./tp
				BOD (Kg/tp)	COD (Kg/tp)	AOX(Kg/t ADp) CEH	HH	
8	145	35	150	50	125	19	11	3400
12	218	20	80	19	40	9	6	4600

ENZYMATIC PREBLEACHING OF PULPS IN INDIAN PAPER INDUSTRY - LABORATORY & MILL EXPERIENCES

Dr. R.M.Mathur,
Scientist E-II & Head,
Chemical Recovery, Energy Management, Effluent Treatment and Biotechnology Division.

About The Author

Dr. R.M. Mathur, is presently working as Scientist E-II and Head, Chemical Recovery, Energy Management, Effluent Treatment and Biotechnology Division.

After completing his D. Phil in Pulp Chemistry, joined CPPRI, in 1978. He has more than 100 publications to his credit Area of specialization includes Black liquor properties, Lignin byproducts, Energy Conservation in Paper Industry and Biotechnological applications.

He has widely traveled abroad as UNIDO fellow to Canada, France, Germany, Australia & Japan and been to Turkey & Thailand for Demonstration of Desilication Technology developed by CPPRI. He has four patents to his credit

ENZYMATIC PREBLEACHING OF PULPS IN INDIAN PAPER INDUSTRY – LABORATORY & MILL EXPERIENCES

R. M. Mathur*, Vasanta V Thakur*, R.K. Jain* & Abha Gupta*

1. Introduction

Environmental concern and the strict legislation regarding imposition of the discharged norms for adsorbable organic hallides (AOX) in Indian paper industry has prompted the mills to develop and look for alternative technologies with low AOX levels in the effluents discharged. The pulp processing industries are operated in large-scale, which are also considered as the major polluting industries. Conventionally, after digesting the wood with alkali or acid, bleaching is done with chlorine based chemicals, which emits chlorinated phenolics into the environment. These pollutants are carcinogenic and hence harmful to human health and aquatic beings. The large scale pollution generated by the excessive use of molecular chlorine in the bleaching process by the paper industries have forced researchers to seek alternative eco-friendly technologies. The use of chemical pulp paper for the manufacture of baby diapers and food packaging is also of concern since it is sometimes associated with chlorinated compounds including the animal carcinogen dioxin (2,3,7,8-tetrachlorodibenzo-p-dioxin) (Shoham *et al.*, 1992).

2. Changing Trends In Bleaching Technology

The growing public concern regarding environmental impact of pollutants from paper and pulp industry was the strong driving force behind the endeavours leading to novel bleaching techniques. Conventional bleaching of Kraft pulp has evolved over the years but there has been particular pressure for change to bleaching sequence like Elemental Chlorine free Bleaching & Total Chlorine Free Bleaching (ECF & TCF) in Europe & Scandinavian countries. A similar situation also exist in Asian countries particularly in India where in the Pulp & Paper mills started switching over to partial ECF bleaching. With the current trends changing to employing 'Clean Development Mechanisms', xylanases have come into sharp focus for their potential application in reducing the environmental load exerted by the Paper Pulp Industry.

The options open to pulp mills considering a change to elemental chlorine free bleaching are substitution by chlorine dioxide, oxygen delignification & extended delignification to reduce Kappa No. before bleaching, substitution by hydrogen peroxide and ozone to replace chlorine based chemicals. However, all the processes suffers with disadvantages like

- High capital cost
- Risk of loss in pulp viscosity and strength and
- High cost of bleaching chemicals.

This change of climate has provided an opportunity for enzymes as pre-bleaching agents with a basic aim of

- Reduction in use of chlorine & chlorinated bleach chemicals
- Reduction in discharge of AOX in bleach effluents
- Gain in final brightness & improved pulp properties

The bleaching of pulp is done in multistage and uses a large amount of Cl_2 & Cl_2 compounds. By products from using these chemicals are chlorinated organic substances some of which are toxic, mutagenic, persistent, bio accumulating & create harmful disturbances in biological systems. Mills have the option to consider a chlorine free bleaching by including any of the following options like:

3. Enzymes In Pulp & Paper

During the last years the number of new applications of enzymes in pulp and paper manufacture has grown staidly. These include enzyme aided bleaching with xylanases, direct delignification with oxidative enzymes, energy saving , refining with cellulases pitch removal with lipases, freeness enhancement with cellulases and hemicellulases as well as enzymatic slime control of the paper machine. A number of enzymes are being envisaged to have an impact on pulp processing. These are at various stages of development and are yet to become commercialized. eg. Cellulases and xylanases in deinking, laccases and peroxidases in lignin removal, proteases and lipases in removal of protein deposits and pith on paper machines.

Xylanases are of great importance to pulp and paper industries as the hydrolysis of xylan facilitates release of lignin from paper pulp and reduces the level of usage of chlorine as the bleaching agent (Shoham *et al.*, 1992). Viikari *et al.* (1986) were the first to demonstrate that xylanases could be useful in paper and pulp industry effecting delignification in bleaching process. Recently, xylanases attracted attention for application in food, feed and pulp industries. To avoid the pollution, alternative

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*** Scientists, CR & Biotechnology Div, CPPRI, Saharanpur, U.P – 247 001**

strategies are being developed the use of hemicellulases has been suggested. Among them, xylanases play a major role in minimizing the consumption of chlorine.

4. Worldwide Status Of Biobleaching Technology

In the developed western countries where public awareness coupled with stringent regulations have stimulated the paper mills to adopt newer and greener technologies such as pre- bleaching of the paper pulp with xylanases. The long-term use of enzymes on regular production scale has been reported by a number of paper mills. This has been possible due to the availability of reasonably prized commercial enzyme preparations coupled with low investment and ease of process operations, compatible with the existing processes.

4.1 List Of Pulp And Paper Mills Employing Plant Scale Trials For Enzymatic Pre-Bleaching Of Pulps

Name of The Mill	Bleached Pulp Production / Raw material	Reduction In Chlorine Demand, (Reported)
Canfors international Mill, British Columbia (Canada)	Softwood & Hardwood	15% Cl_2
Tasman Pulp & paper Company ltd. N. Zealand.	500 tpd From Pinus Radiata	20% Cl_2 as ClO_2
Morrum Pulp Mills, Sweden	Softwood	18% as ClO_2
Bukoza Pulp Mills, Vranov	220 tpd Softwood	30% as Chlorine
Metsa - Sellu Mill, Aanekoksi Finland	Softwood & Hardwood	12% as Chlorine
Enso Gutzeit Oy, Finland	Softwood	25% as Chlorine
Donohue St. Felicien Mill, Quebec	Softwood	25% as chlorine
Intercontinental Mill, Prince George, British,, Columbia Canada	Softwood	15% as chlorine dioxide
Huelva Pulp mill, Spain	Hardwood, 1000 tpd	10% as chlorine dioxide

* Mill claimed to use enzyme in their ECF bleaching sequence (XDEOPD) on continuous commercial basis for last more than 5 years.

5. Current Status of Bio - Bleaching Technology in India

In view of the stringent regulation abroad limiting the use of toxic chlorine compounds in paper Industry, it will soon become obligatory that paper manufactured in India will also necessitate minimizing the use of chlorine compounds.

The application of xylanases in pre-bleaching of wood pulp in India is yet to reach a commercial stage due to several factors. Moreover, in-depth studies need to be carried out with indigenous substrates as the xylanases being used in the western world are more suited to softwood pulps which have a different composition to that of tropical hard woods. Totally chlorine free technology in the pulp and paper industries has become a reality in many of the European countries and in Canada. However, the impact of their development is yet to percolate to the developing countries. In the absence of stringent environmental regulations, use of conventional hazardous chemicals is still being widely used in the paper mills and tanneries in India. Switch over to chlorine-free paper manufacture may soon become obligatory when environmental regulations abroad enforce restrictions even on food products exported to the developed world using paper products based on chlorine bleaching for wrapping. In view of the diversity of substrates employed for paper manufacture in our country, more than one xylanase suited to individual substrates may need to be developed. Besides, there is also a need to carry out studies on the application of other enzymes in pulp biotechnology. A closer interaction and linkage must be established immediately between the paper industry and biotechnologists and perhaps a national consortium established to make an in-depth analysis of the problem in perspective and find meaningful solution to establish a viable biotechnological approach to paper industry in our country.

Bio-bleaching technology is in the developmental stage as far as Indian paper industry is concerned. Xylanase enzyme have been developed and available in the market but these enzyme preparations are highly sensitive to pH and temperature which varies a lot from mill to mill depending upon the fibrous raw materials employed in Indian Paper Mills and also the equipments. Under the conditions prevalent in the Indian Industry, it is required to develop tailor made indigenous enzyme which could tolerate the extreme conditions existing in the mills so that enzymes could work effectively.

The future growing public concerns regarding the environmental effects of these chlorinated organic compounds have driven Indian pulp mills to seek new bleaching technologies that reduce or eliminate the use of elemental chlorine in pulp bleaching. Chlorine dioxide, ozone and oxygen delignification have been adopted as alternatives or partial substitutes for chlorine, however, these alternatives due to their high capital cost, seem to have more viable at capacities more than 300 tpd.

The use of xylanase enzyme for bleaching Kraft pulp has generated a great deal of interest because it seems to offer a more cost effective solution in this direction.

6. Enzyme Aided Bleaching

The enzymes used commercially in pulp bleaching are hemicellulases, which selectively affect the accessible hemicellulose fraction of the pulps. Among various available hemicellulases, xylanases have been found to be more effective as pre-bleaching agents.

The use of hemicellulolytic enzymes particularly the xylan attacking enzymes - Xylanases as prebleaching agents are now available and currently in use in commercial bleaching sequence for production of bleached pulp from soft wood and certain species of hardwoods in the developed countries. wherein it has been possible to reduce chlorine demand to a level of 15-20% during bleaching with corresponding reduction in AOX level (20%) and improved pulp brightness to a level of 2-3% ISO. Since the effectiveness of a particular xylanase enzyme may vary in respect of its

- Activity
- Purity particularly in terms of cellulase freeness
- Enzyme pretreatment conditions and the type of pulps

Some of the primary reasons for mills to consider the use of bleaching enzymes are:

- Environmental (eg. reduction in Cl_2, ClO_2 & hypochlorite and ultimately reduced discharge of AOX)
- Economic (decreased ClO_2 and / or peroxide requirement)
- Improved pulp quality (higher brightness ceiling)
- Improved mill flexibility

The non-availability of cellulase -free xylanases was a serious drawback in the commercial application of this concept as the associated cellulase in xylanase preparations caused weakening of the cellulose pulp and lowered its quality.

The benefits obtained by using enzymes are dependent on the chemical bleaching sequences used as well as the residual lignin content of the pulp (Viikari, *et al.*1994). Enzymatic pretreatment has been reported to result in a higher final brightness and a reduction in the consumption of bleach chemicals with a concomitant reduction of AOX (Adsorbable organic halogens) in effluents (Koponen, 1991, Tolan *et al.*1996). An average reduction of 25% in active chlorine consumption in pre-bleaching or a reduction of 15% in total chlorine consumption has been reported with softwood kraft pulps (Koponen, 1991). In the TCF bleaching process the brightness gained obtained by enzymatic pretreatment is of significance.

7. Raw Materials / Substrates

The efficacy of enzymatic pre-bleaching is largely dependent on the type of biomass, the pulping operations and the nature of the xylans. A large variety of ligno-cellulosic substrates are used by the paper industries. The composition and distribution of xylan in these substrates play an important role in the bio-bleaching process. The xylan content of hard wood, straw and bagasse is very different to that of soft woods. The xylan content in hard wood and non-woody tissue ranges between 20 - 35 % while the xylan content is 7-12% in soft wood and is characterized by a higher propotion of 4-O-methyl-D-glucuronic acid. In contrast, soft wood contains a higher content of mannans. The xylans from hard wood are devoid of arabinose residues, while xylans from softwood as well as grasses contain substantial quantities of arabinose. Moreover, soft wood is often preferred over hard wood as the cellulosic fibers obtained from soft woods are longer and devoid of vessels which often interfere in pulping operations. In India bagasse is one of the raw materials used in pulping operations. There are no detailed studies on the exact mechanism of action of xylanases on non-wood species such as bagasse, straw etc. These studies are essential to optimize xylanase treatment and develop tailor - made enzymes suited to indigenous substrates for the soft woods may not be compatible with our raw materials for paper making (Timell, 1964, Joseleau *et al.* 1992).

Extensive modification of hemicelluloses takes place during pulping processes. During the initial heating period in Kraft pulping, when the alkali concentration is comparatively high, the xylan is partially depolymerized and stripped of substituents such as acetyl and arabinosyl groups. As pulping proceeds, the alkali concentration decreases and degraded, short-chain xylans precipitate in a more or less crystalline form on the surface of cellulose microfibrils. Overall, xylan constitutes over 90% of the hemicelluloses in hardwood Kraft pulp and 50% in softwood pulp. Because of the reprecipitation, hemicelluloses are concentrated on the fiber surfaces of microfibrils although a part remains at its original location in the fibers.

8. Production Of Xylanases As Pre-Bleaching Agents

Xylanases are produced by a large number of bacteria, actinomycetes and fungi. Several reviews have appeared in the literature regarding microbial xylanase production (Wong *et al.* 1988, Bastawde, 1992). Although filamentous fungi such as *Trichoderma, Penicillium,* and *Aspergillus* are known to produce high levels of xylanases, they normally also co-secrete cellulases.

Several criteria are essential for choosing microorganisms to produce xylanases. In addition to give the desired biobleaching effect, the enzyme must be produced in sufficiently huge quantity & should be completely free of cellulase activity. Any cellulase activity will have serious economic implication in terms of cellulose loss, degraded pulp quality & increased effluent treatment cost.

Studies with fungal xylanases have resulted in the reduction of chlorine consumption; however, use of cellulase-free xylanases selectively remove hemicellulose components with minimal damage to cellulose (Srinivasan and Rele, 1995) and hydrolysis of reprecipitated and reabsorbed xylan or xylan-lignin complex. As a result the pulp becomes more accessible to bleaching chemicals.

The two main enzymes which depolymerise the hemicellulose backbone are endo-1, 4 - β -D - xylanase and endo-1, 4 - β -D - mannanase, referred to generally as xylanases and mannanases, respectively. Xylanases and mannanases are produced by many species of bacteria and fungi. Xylanases, the enzymes applied in commercial bleaching, are available from several different sources.

9. Desirable Enzyme Characteristics

Several features determine which xylanases are effective for bleaching . Following features are necessary for effective enzyme activity. It is desirable to have a low molecular weight xylanase that is able to penetrate the fiber. An enzyme must have access to the substrate if it is going to release chromophoric groups and lignin. It must have an appropriate pH optimum . Kraft pulps are alkaline and the enzyme must be able to function at the ambient pH.The enzyme should have an alkaline pH in order to bind to negatively -charged fiber surfaces.The enzyme must be thermal stable at the temperature prevailing in the pulp stock. It should possess appropriate substrate specificity. The objective is to release chromophores and extract residual lignin and not to remove the bulk xylan.

10. Influence Of External Factors On Enzyme Activity

Because of the nature of the enzyme/pulp interaction, several factors are important to be taken into account in order to use enzymes effectively in a mill. Although all of the commercial enzymes act primarily on xylan, the conditions for mill usage are quite different. In addition, to get best value from enzyme usage, the conditions chosen for any one enzyme should be tailored to each mill, based upon careful laboratory testing. The key factors are for better enzyme response are pH, Temperature , Enzyme dispersion , Reaction time, Enzyme dose , Washing of the pulps.

11. Proposed Mechanism Of Enzyme Action

The exact mechanism of the action of xylanases is not known till yet. However, the literature survey reveals that some theories proposed, which explain the possible mechanism of the enzyme, are described below.

- One of the predominating hypotheses for the mechanism of xylanase activity in bleaching is that these enzymes catalyze the hydrolysis of reprecipitated xylan on the surface of the pulp fibers making the lignin fragments in and on the fiber easier to remove in the following bleaching and alkaline extraction stages. This hypothesis is not supported by the results of experiments in which pulp was delignified under high alkalinity conditions which precluded xylan deposition. In that situation, xylanase treatment lead to a reduction in the amount of chemical required to reach a final brightness equivalent to that obtained for a conventional pulp in which the xylan was reprecipitated on the pulp surface But it has been found that removal of redeposited xylan with DMSO does not improve the bleachability of pulp xylanases specifically attack a small fraction of xylan in the pulp that is different from the DMSO - extractable xylan.

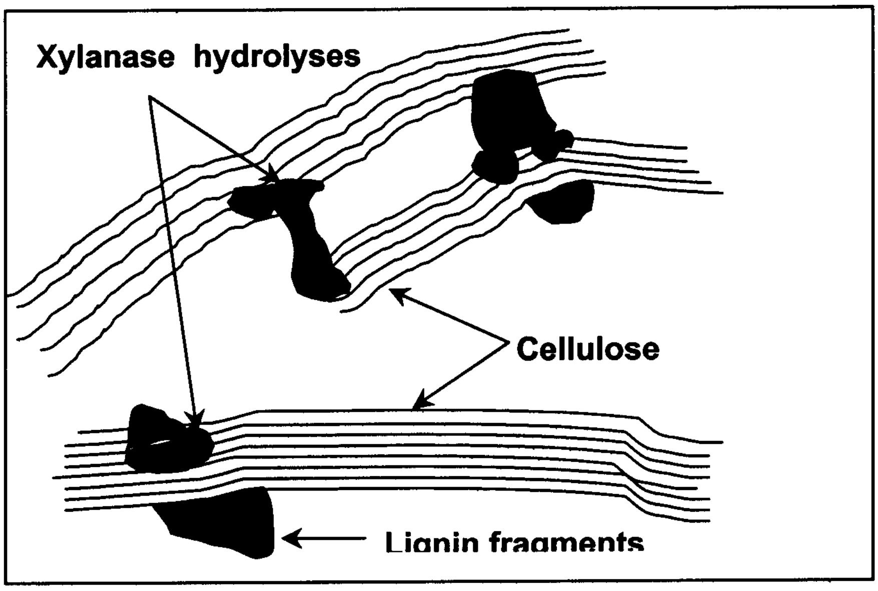

FIG : 1 PROPOSED MECHANISM OF XYLANASE ACTION ON PULP FIBRES

- The enzymatic treatment causes a physical loosening of the fiber wall due to partial depolymerization of hemicellulose chains. Literature survey reveals a significant decrease in xylan DP and removal of only a small amount of xylan during xylanase prebleaching. The decreased chain length of xylan or its removal results in increased freedom for lignin to diffuse from hemicellulose - lignin matrix.

- The disruption of xylan chain by xylanases cleaves lignin - carbohydrate bonds, and thus improves the accessibility of bleaching chemicals to the fiber & facilitates the removal of solubilized lignin in bleaching.

12. Performance Of Hemicellulase Enzymes During Bleaching

When a mill wants either to reduce its conventional bleaching costs or to improve the economy of TCF bleaching, it is faced with the need for using existing processing equipment. Introduction of enzymatic treatment prior to first step of bleaching is the most obvious choice. To achieve a good effect of enzymatic pre-bleaching, mixing of pulp with chemicals must be sufficient, both after pH adjustment and after enzyme addition. As the amounts of chemicals used are small, the equipment needed for mixing of these chemicals is also minimal.

13. CPPRI – R & D Activities In The Area Of Biobleaching

Although studies have been carried out using various hemicellulases and xylanase enzyme for prebleaching of kraft pulps from soft wood and hard wood in the developed countries but very little work has been done on enzymatic prebleaching of pulps produced from hardwoods , non -wood fibers like bamboo , grasses employed by Indian paper industry. The work on enzymatic prebleaching of pulps from various raw materials especially being employed by Indian paper industry -bamboo, hardwoods and other non woody raw materials is primarily aimed to assess the suitability of bleaching enzymes produced indigenously and the imported ones in terms of their suitability with pulps produced from various raw materials in Indian paper industry in respect of improvement in pulp quality and improved environmental situation particularly the reduction in requirement of Cl_2-based chemicals and reduction in toxicity in the final discharged effluents without loss in pulp quality.

Detailed laboratory work has been carried out to adapt the enzymatic treatment to existing mill conditions. Response of various xylanases on different kinds of raw materials & pulps employed in Paper Industry were evaluated with conventional bleach sequences, CEH, CE(p)H , CEH D/ ,CE(p)HD, C/DE(O)HD. The Institute has extensively evaluated various enzymes on various kinds of pulps like hardwood pulp, Bagasse, Bamboo and mixed pulps both in laboratory and at the mill and got very encouraging results in terms of brightness gain 2-3%, 15-20% reduction in chlorine demand, 20-25% AOX reduction. (Jain et.al , 2001)

13.1 Increase In Pulp Brightness

Due to globalisation, paper mills in India are facing continuous pressure to produce paper with higher brightness levels. Chlorine Dioxide and

Oxygen/ Ozone bleaching processes are highly capital intensive. Enzyme bleaching technique offers a cost effective route for these mills to achieve higher brightness levels with out loosing strength properties.

The results achieved in various laboratory and bench scale trials has shown that it is feasible for the mills to enhance the final brightness of the bleached pulps by 1.5 to 3.0 point, thus enabling them to cope with growing market demand for higher sheet brightness.

13.2 Environmental Impact Of Enzyme Treatment: Reduction In AOX Level /BOD:COD/Color

There is a new 'environmental' thrust in India to reduce the level of AOX (Absorbable Organic Halide) discharged by the paper mills. The classical approach of substituting gaseous chlorine with Chlorine Dioxide is found to be highly capital intensive. By using Xylanase enzymes, prior to chlorination stage, mills can now easily achieve reduction in gaseous chlorine consumption to the extent of 20%-25%, thereby realizing consequent reduction in AOX levels. There was an indirect improvement in terms of colour in the bleach effluent after enzyme treatment was reduced and the biodegradability of effluent was also improved as reflected from COD:BOD ratios.

13.3 Reduction In Bleach Chemical Consumption

Mills which have high environmental loads in terms of AOX in bleach effluents and have no necessity or incentive to increase brightness, can use the enzyme prior to conventional bleaching stages to cut down chlorine and hypo consumption up to 15-20%, thus resulting in reduced pollution levels with little increased pulp strength.

14 Comparative Account Of Results Of Xylanase Enzymatic Prebleaching Technology

Enzyme	% Reduction in Cl_2 demand	% Brightness gain	% Reduction in AOX
XYL - A	15	2.3	30
XYL - B	13	3.2	20
XYL - C	9.3	3.0	18-20
XYL - D	12	2.6	ND
XYL - E	12	4.0	17 - 20
XYL - F	14	2.2	20-25
XYL - G	15	3.0	20-30
XYL - H	15	1.9	ND
XYL - I	15	1.9	ND

15 Conclusion

Based on the studies, it was found that these enzymes have different pH & temperature optima. The effectivity of the enzymes also varied from sample to sample enzyme to enzyme. In view of the above and because of this specific requirement of Industry, the enzyme prebleaching technology, employing these globally available enzymes could not make a break through as far as its adoption is concerned. No major modifications need to be implemented for full scale runs. The only requirement is the addition of pH adjustment facilities which will not be required in the case of alkaline xylanases. The information on an ideal xylanase enzyme for pulp & paper industry will motivate the enzyme manufacturers for the production of an efficient xylanase enzyme.

The data generated by the Institute on enzyme prebleaching will provide new opportunities to pulp and paper industry to adopt eco-friendly bleaching technology and to reduce AOX generation with improved optical properties of the pulp. The adoption of enzyme based technology in pulp and paper industry reduces the pollution loads created by the conventional pulping and bleaching processes. The experiences of CPPRI in the area of enzymatic prebleaching in some mills which could help the mills in conducting commercial trials on Enzyme prebleaching. There is a need to demonstrate enzymatic-prebleaching techniques to the mills through commercial scale of operations, utilizing state of the art pH control systems, enzyme mixers, and temperature controllers to obtain full potential of this technique in Indian Paper Industry.

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ENZYMATIC PRE BLEACHING OF PULP

Scientist E-I &
Office Incharge, CPPRI
Base Office, New Delhi

About The Author

Dr. R. K. Jain holds M.Sc. and D. Phil. in Chemistry with specialization in Lignin Chemistry. He has the experience of more than 20 years of Research and Development working in Chemical recovery, Energy and Environment and Biotechnology areas in Pulp and Paper Industry. Dr. Jain has more than 50 research papers published in National and International journals and more than 25 research reports and 2 patents at his credit.

He has visited China and Sweden under UNIDO fellowship training programme in the areas of Chemical recovery and Environment management.

He is presently working as Scientist & Office Incharge, CPPRI Base Office, New Delhi and looking after Industrial Coordination and Business Development activities.

ENZYMATIC PRE BLEACHING OF PULP

Dr.R.K.Jain*, Dr. R.M. Mathur*, Dr. Abha Gupta*, Dr. Vasanta* & Dr. A.G.Kulkarni**

1. Introduction

The pulp and paper industry plays an important role in a country's economic growth because of its highly intensive nature. It is intensive in terms of raw material consumption, chemical consumption, energy consumption, water consumption, capital requirements besides generation heavy pollution loads. The industry continually tries to improve its processes and products. However, due to economical and technical constraints, new approaches to pulp and paper manufacture are rare. Biotechnology can however, give rise to new possibilities with its diverse array of activities. The attractiveness of biotechnology lies in its potential to provide processes/products where non-biological processes are impractical.

Biotechnology implies the technical exploitation of biological processes. With in the past few years, biotechnologists have sought specific applications for microorganisms/enzymes in the pulp and paper industry. The biotechnological approaches for use in the pulp and paper industry are in different stages of development i.e. some are in laboratory scale, some attained pilot scale level, some applications like Hemicellulases for pulp bleaching have found their way in to the mill.

The primary goal of chemical pulp bleaching is to reduce the residual lignin of pulp without effecting the carbohydrate and! or the physical properties of the pulps. Two different enzyme approaches have been generally in use for achieving the goal, which include.

a. Use of helnicellulases (specifically xylanases) enzymes as prebleaching agents (bleach booster) for enhancing the chemical removal of lignin in multistage bleaching sequence.

b. Another alternative approach is direct delignification of the unbleached pulps using enzymes called ligninases or laccases, which acts directly on the residual lignin in the pulp (1).

The first approach, which is the use of xylanase enzyme as prebleaching agents for chemical pulps has been successfully, applied in pulp and

Scientists, ** Director Central Pulp & Paper Research Institute, Saharanpur / New Delhi

paper mills worldwide using various xylanases preparations of different origins.

But the technology still is in nascent stage as far as Indian Paper Industry is concerned.

The biggest success story in the use of enzymes in the pulp and paper industry is hemicellulases (mainly xylanases) as aids in pulp bleaching ("enzymatic pre-bleaching. The pulp bleaching technologies entered a new era in late 80s due to growing concern about the formation and release of chlorinated compounds in the recipient. In this context, the hemicellulase-aided bleaching, first introduced in 1985, offered an alternative environmentally safe approach.

Xylanase enzymes used in bleaching of chemical pulps are being developed by Companies which claim their products suitable as prebleaching agents for the pulps produced in the paper industries. However, these enzymes, which are marketed by several suppliers are found to be highly sensitive to the conditions like temperature, pH & doses of the enzymes (2,3). Therefore it becomes difficult for the pulp and paper mills to decide which particular enzyme should suit to the specific requirement of their industry in order to achieve desired effect.

In view of the above, Central Pulp & Paper Research Institute (CPPRI) has been engaged for the last many years in conducting studies on evaluation of various xylanase enzyme preparations which are available globally and also being developed indigenously by several reputed biotechnological laboratories to study their response on the type of pulps produced in Indian paper mills.

The present paper highlights the studies carried out at the Institute in which several xylanase enzymes have been evaluated for their bleach response on Kraft wood and Kraft bagasse pulps, in order to explore potential for commercial application of the enzyme prebleaching technology in Indian paper industry.

2. Mechanisms Of Enzymatic Bleaching

The effect of hemicellulases enzyme (xylanases) in bleaching of pulps is based on the modification of pulp hemicelluloses, enhancing the removal of lignin in chemical bleaching. It has been proposed that the action of xylanases is due to the partial hydrolysis of reprecipitated xylan or removal of xylan from the lignin-carbohydrate (LC) complexes. Figure shows the proposed mechanism of xylanase enzyme on kraft pulps. However, these hypotheses are not mutually exclusive, i.e. relocated xylans may contain LC complexes and both mechanisms would allow the enhanced diffusion of entrapped lignin from the fibre wall. Limited removal of pulp xylan is known to increase the leachability of residual lignin from kraft pulps and thus also to increase the pulp bleachability during subsequent bleaching stages. Figure-3 shows how xylanase enzymes act of kraft pulp. In addition, it has been suggested that the hemicellulase treatment removes chromophoric groups from the pulp. Figure-2 shows the suggested mechanisms as well as their consequences during xylanase treatment of kraft pulp.

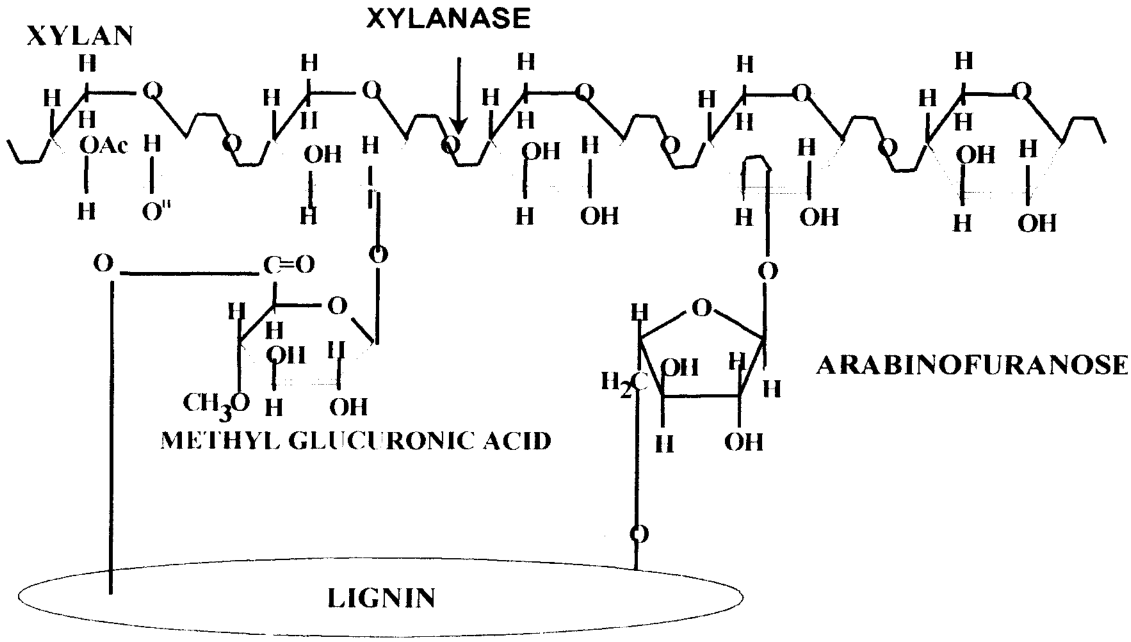


FIG-1 Enzymes For Pulp Bleaching- Xylanase

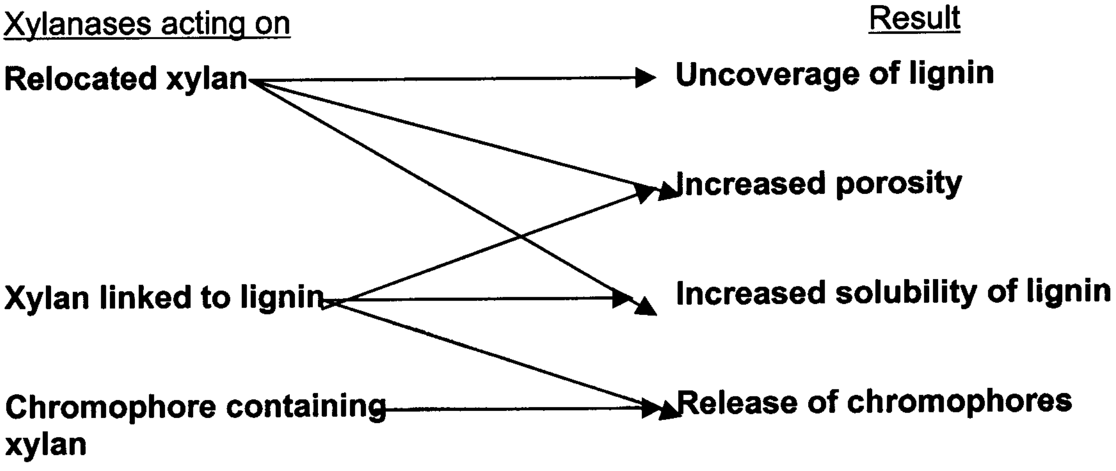


FIG-2 Suggested Mechanisms As Well As Their Consequences During Xylanase Treatment Of Kraft Pulp

2.1 How Xylanase Act On Kraft Pulp

2.1.1 Extraction Of Relocated Xylan

Both xylan and lignin are dissolved and partially reabsorbed on the fibres during the pulping rather high content of lignin has been observed both in the primary fines and in the surface material of fine kraft fibres. It can be expected that removal of xylan from kraft pulp by treatment of xylanase treatment improves the extraction of lignin by exposing lignin surfaces. As dissolved xylan molecules can penetrate most of the pores in cellulose fibers. It can be postulated that xylan active on all available surfaces, enhance the removal of lignin in hole fibre. The figure-3 depicts how xylanase enzyme hydrolyses redeposited xylanase on the fibre making the extraction of lignin easy from the fibres.

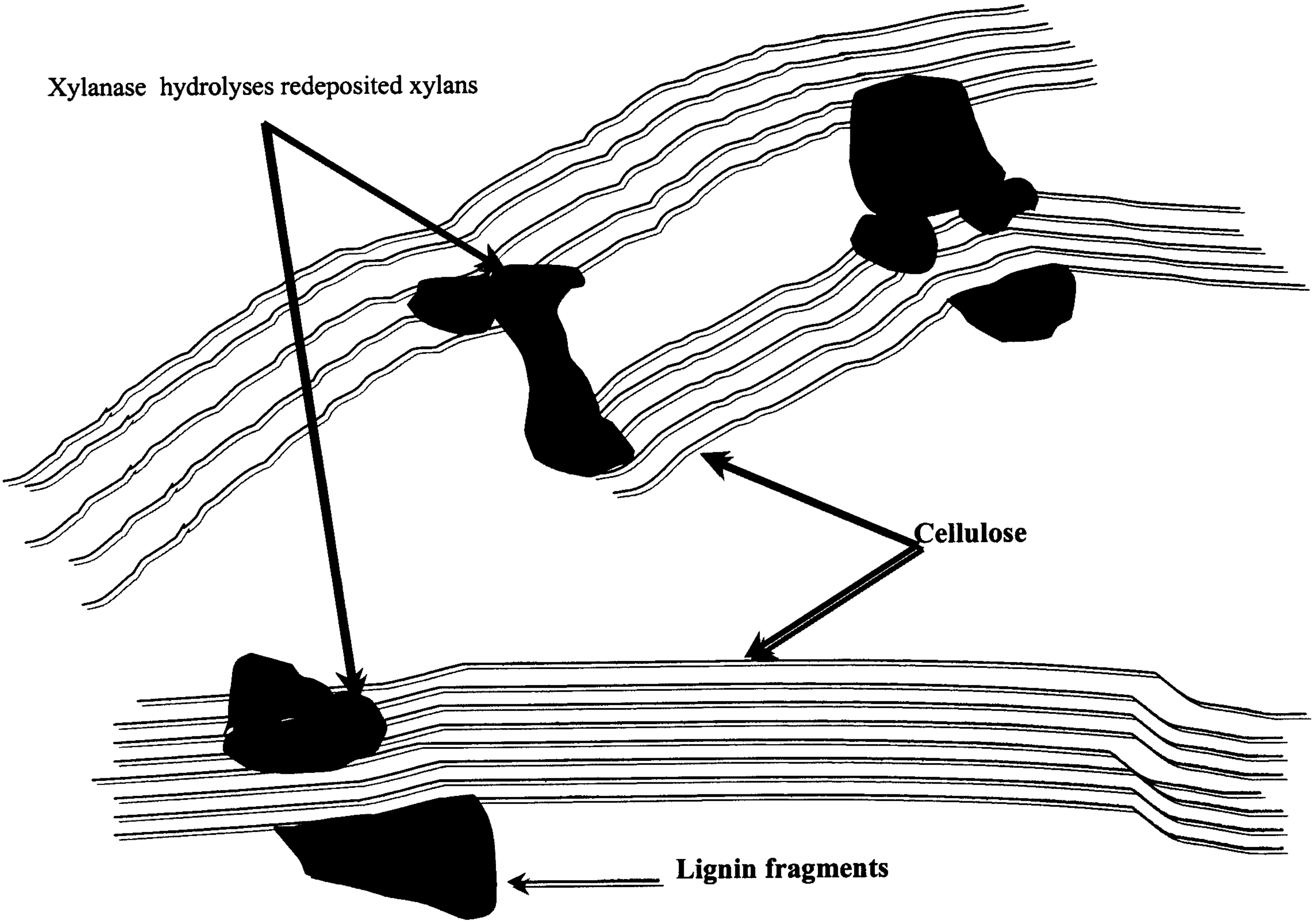


Figure 3 How Xylanase Act On Kraft Pulp

2.1.2 Lignin Carbohydrate Complexes

Both softwood and hardwood kraft pulps have been reported to contain LC-complex in which carbohydrates and lignin may be connected to each other by ether or glicosidic linkages. Increased solubilization of xylan-lignin complexes both from model pulps and from kraft pulps has been observed by xylanase treatment.

2.1.3 Chromophores.

It has frequently been observed that xylanase treatment has a slight decreasing effect on the kappa number. This has been explained to be due to removal of lignin fragments or chromophoric structures from pulp. However, the reduction in the kappa number as measured by permanganate oxidation may be partially due to an artefact. The recently discovered hexenuronic acid, containing a double bond, may give rise to the consumption of permanganate. increasing the apparent kappa number. Thus, enzymatic removal of xylan containing hexenuronic acid groups can lead to a lower kappa number.

3. Required Xylanases Enzyme Characteristics

Effective Xylanases Should Have Several Properties.

- They should be stable on kraft pulps. Some xylanase preparations non-specifically absorb to pulp fibers and are inactivated by degradation products from kraft pulping.
- They should have a neutral to alkaline pH optimum. Residual alkali leaks out of the pulp during enzyme treatment, and the pH of even well washed pulp stocks can shift upwards dramatically.
- They should have good thermal stability. The pulp is hot (75^{0}C) when it first comes out of the stock washers, and heat-tolerant enzymes generally have higher turnover numbers.
- Factor affecting the interaction of the enzymes with the pulps are important. These include the effective molecular weight, net ionic properties, and specific action pattern.
- They should not be contaminated with cellulases. If cellulases are present, pulp viscosities decrease. Without cellulase, xylanase treatment increases viscosity, because some lower molecular weight xylans are removed. Even so, excess xylan removal can reduce burst strength and long span tensile strength by reducing inter fibre bonding even though it does not weaken the fibres themselves.

4. External Factors Influencing Enzyme Activity

The key factors influencing the success of the enzyme prebleaching technology in a pulp mill are:

	Factors	Mill Conditions
1.	pH at 25 °C	7- 9
2.	Temperature	45 - 55
3.	Enzyme dispersion	-
4.	Reaction time	-
5.	Enzyme dosage	-

5. Results Of Enzymatic Pre-Bleaching

While optimising the dosages of enzymes during enzyme treatment of woof Kraft and bagasse Kraft pulps, it was observed that excess dosages of xylanase enzymes for a longer time has resulted in decreased pulp yield and strength properties of the pulps. This could probably be due to loss of hemicelluloses by the action of enzyme. However under optimised dosages of enzymes i.e. 5-7 IU/gm of pulps and optimised treatment conditions, no significant loss in pulp yield could be observed except with enzyme preparation E where even the treatment of the pulp at optimised conditions of time and temperature could result in 1.5% pulp yield loss along with drop in viscosity which was reduced from 560 to 510 cm3/g of the pulp leading to loss in strength properties (Table-1). Reasons for the same could be attributed to contamination of xylanase with cellulase activity, which could be ascertained by determination of the cellulase activity in the xylanase enzyme by filter paper activity. Therefore this enzyme named as E was found to be unsuitable for its application in bleaching of pulps.

Table – 1

Characterization Of Unbleached Pulp For Yield & Other Parameters Of Wood Kraft Pulp Before & After Enzyme Treatment

		Pulp treated with enzymes				
Parameters	**Control**	**A**	**B**	**C**	**D**	**E**
Pulp Yield, ,%	99.89	99.82	99.62	99.80	99.74	98.10
Kappa number of pulp	18.0	16.5	16.7	16.6	17.0	16.0
Brightness, %ISO	27.5	28.5	29.0	28.4	28.0	29.0
CED Viscosity, cm^3/g	560	620	590	557	604	510

5.1 Effect Of Xylanase Treatment On Bleach Chemical Requirement

Bleaching of the xylanase enzyme treated Kraft pulps, both wood and bagasse have been found to respond in different manner than untreated pulps while bleaching with conventional CEH bleach sequence. Based on optimisation studies of the chlorine dosages during chlorination stage, it was observed that significantly less chlorine is required to bleach Kraft wood and Kraft bagasse pulps while bleaching to similar targeted brightness level.

Table - 2 shows the effect of various xylanase preparations on the bleach chemical requirement during conventional CEH bleach sequence of wood Kraft pulps with a targeted brightness level of 80% ISO. From the results shown it is clearly seen that there is a reduction of nearly 14 - 15% of chlorine demand with all the enzymes preparations in case of wood Kraft pulps except enzyme preparation D, where chlorine saving of only 9.3% could be noticed. Further the enzyme treated pulps could be bleached to higher brightness with a gain in brightness level of 2-3% ISO in all the cases while using similar chlorine dosages as in case of control pulp sample.

Table- 2

Effect Of Enzyme Pretreatment On Bleach Chemical Requirement Using Various Xylanase Preparations On Kraft Wood Pulp

		A		B		C		D		E	
Parameters	Control	ET1	ET2	ET1	ET2	ET1	ET2	ET1	ET2	ET1	ET2
Savings in elemental chlorine	-	-	15	-	15	-	14	-	9.3	-	-
% Reduction in Kappa No. after X stage	-	8.0		7.2		7.3		5.5		11.1	
% reduction in Kappa No. After XCE stage	-	28.0	-	25.9	14.5	26.0	16.0	27.0	23.0	-	-
Final brightness of the pulp, % ISO	80.0	82.5	80.0	82.5	81.3	83.0	80.2	82.0	80.0	83.0	80.0

X - Enzyme treatment
XCE - Enzyme, Chlorination & Extraction
ETI - Enzyme treated Pulp treated with similar chlorine dose
ET2 - Enzyme treated Pulp treated with optimised less chlorine dose

Reduction in chlorine requirement or improved pulp brightness in case of enzyme treated pulps was reflected from the reduction in Kappa number of the unbleached pulps after enzyme treatment and further after the alkali extraction stage. The reduction in kappa number by 7-8% after enzyme treatment and further reduction of kappa number by more than 25% after alkali extraction was achieved in enzyme treated pulps.

Similar observation were made in case of Kraft bagasse pulps where nearly 18% reduction in chlorine demand could be observed in enzyme treated pulps with targeted brightness level of 83.0% wherein brightness gain of 2.0% ISO could be achieved when the enzyme treated pulp was bleached with similar chlorine dose of 5.1% as in case of control pulp. Results are shown in Table-3. This reduction in chlorine demand and gain in pulp brightness is also reflected from reduction in kappa number of the enzyme treated pulp where 20% reduction in kappa number after alkali extraction stage could be noticed.

Table-3

Xylanase Pretreatment Of Kraft Bagasse Pulps & Strength & Optical Properties

Bleaching of Pulp using Conventional CEH Sequence Before & After Enzyme Treatment

Particulars	**Control**	**ET-1**	**ET-2**
Chlorination			
% Chlorine Applied	5.1	5.1	4.2
% Chlorine Consumed			
%, chlorine savings	-	-	17.6
Alkali Extraction			
% NaOH Applied	2.0	2.0	2.0
% NaOH Consumed	74.2	61.2	73.8
Final Ph	10.24	11.55	10.25
Kappa no.	5.07	4.04	4.30
Hypo Stage			
% Hypo Applied	2.0	2.0	2.0
% Hypo Consumed	80.0	80.0	74.0
Final Brightness of pulp % ISO	83.0	85.0	84.0
Strength and optical properties			
Parameters	**Control**	**Enzyme B**	**Enzyme D**
Revolution PFI	500	500	500
Freeness CSF	335	350	355
Apparent density, .g/m^3	0.66	0.74	0.72
Burst Index Kpa.m2/g	2.60	3.05	2.55
Tensile Index , Kpa.m^2/g	45.5	56.0	45.0
Tear Index, Mn m^2/g	4.05	4.40	4.20
Optical properties			
Brightness of pupls, % ISO	83.0	85.0	84.0
Yellowness, %	13.5	9.2	9.6

. ET1 -- Pulp treated with similar chlorine dose
. ET2 -- Pulp treated with less optimized Chlorine dose

5.2 Effect Of Enzyme Treatment On Unbleached Pulp Yield And Physical Properties Of Wood Kraft And Bagasse Kraft Pulps

Table-4 shows the bleach chemical demand, Strength & Optical properties of Kraft wood pulp treated with identified xylanase enzyme preparations B & D against control. From the results shown in Table-4, it is clearly evident that with a savings of nearly 15% chlorine demand employing enzyme preparation B, no loss in strength properties like burst, tensile & tear could be noticed, however the tear index was improved significantly from 5.3 Mn m^2/g to 6.0 Mn m^2/g whereas in case of enzyme D treated pulps, the strength properties, though were at par with control pulp but the chlorine savings were lower i.e 9.3% only. With regards to the optical properties of the enzyme treated pulps, there is an improvement in the yellowness of the pulp both with enzyme preparations B & D, since the yellowness of the enzyme treated pulps were decreased from 14.94 %to 9.79% & 10.65% respectively.

Table-4

Enzymatic Prebleaching Of Kraft Wood Pulp Using Xylanase

Bleaching of Pulp using Conventional CEH Sequence Before & After Enzyme Treatment			
Particulars	**Control**	**Enzyme B**	**Enzyme D**
Chlorination			
% Chlorine Applied	3.9	3.3	3.54
% Chlorine Consumed	94	99	96
%, chlorine savings	-	15	9.23
Alkali Extraction			
% NaOH Applied	1.30	1.30	1.5
% NaOH Consumed	61.1	63.2	58.3
Final Ph	10.88	10.76	11.21
Kappa no.	3.51	2.99	3.2
Hypo Stage			
% Hypo Applied	1.8	1.8	1.8
% Hypo Consumed	71.0	75.0	68.0
Brightness, % ISO	80.0	82.05	82.0
Brightness Gain, %	-	2.5	2.0
Strength and optical properties of the wood Kraft pulps before & after enzyme treatment using two identified xylanase enzymes B & D			
Parameters	**Control**	**Enzyme B**	**Enzyme D**
Revolution PFI	4000	4000	4000
Freeness CSF	220	250	250
Apparent density, g/m^3	0.79	0.76	0.75
Burst index Kpa.m2/g	4.43	4.49	4.51
Tensile Index, $Kpa.m^2/g$	64.4	64.3	64.4
Tear Index, Mn m^2/g	5.3	6.0	5.3
Optical properties			
Opacity, %	92.2	91.2	91.0
Yellowness, %	14.94	9.79	10.65

Similar observations could be made in case of Kraft bagasse pulps. Treatment of the Kraft bagasse pulp with xylanase enzyme B preparation showed no loss in pulp yield or pulp viscosity (Table- 5). Bleach chemical demand of both enzyme treated and untreated pulps & the results of strength properties were shown in table-3. From the results it is clearly evident that strength properties of the enzyme treated pulps like Burst, Tear and Tensile could be maintained at par with control pulps with improvement in optical properties particularly in respect of yellowness which was dropped from 13.5 to 9.2 - 9.6%.

Table -5

Yield & Other Characteristics Of Unbleached Kraft Bagasse Pulp Before & After Enzyme Treatment Using Mentified Xylanase (B) Enzyme

Parameters	Pulp treated with enzymes	
	control	Enzyme treated
Pulp yield, %	99.20	99.02
Kappa number of unbleached Pulp	26.2	25.5
Kappa No. of CE Stage	5.07	4.04
Brightness, % ISO	30.3	3.08
CED Viscosity	535	520

5.3 Impact Of Enzyme Treatment On Environment

Characterisation of the resultant bleach effluent from wood Kraft pulps and Kraft bagasse pulps before and after enzyme treatment indicated that effluent properties namely AOX (Adosorbable Organic Halides) & COD are improved indirectly through the use of xylanase treatment which helps in release of lignin and other chromophore bearing compounds and allowing the use of lesser quantities of elemental chlorine or other chlorine based compounds in subsequent bleach sequence. Results of characterisation of enzyme treated wood Kraft pulp and Kraft bagasse pulps against control pulps are shown in Table-6. From the table it is clearly indicated that AOX level was reduced to 0.69 kg/tp in case of hard wood Kraft & 1.0 kg/tP in Kraft bagasse pulps compared with control pulps where AOX was reduced from 2.29 kg/tp to 1.6 kg/tp and from 4.13 kg/tp to 3.13 kg/tp respectively. Further decreased ratio of COD to BOD from 7.7 to 3.9 and from 4.12 to 3.33 in bleach effluent from Kraft wood and Kraft bagasse after enzyme treatment is an indication of improved biological treatability of the bleach effluent.

Table-6

Characteristics Of Bleach Effluents Of Kraft Wood & Kraft Bagasse Pulps Before & After Enzyme Treatment Using Xylanase Enzyme B

	Wood Kraft Pulp		**Bagasse Kraft Pulp**	
Parameters	**Control**	**Enzyme treated**	**Control**	**Enzyme Treated**
AOX, Kg/tp	2.29	1.60	4.13	3.13
COD, Kg/tp	23.3	28.5	34.6	50.7
BOD, Kg/tp	3.02	7.31	8.5	15.0
COD: BOD ratio	7.7:1	3.9:1	4.1:1	3.3:1

6. CONCLUSION

6.1 Enzymatic prebleaching of chemical pulps using xylanase enzyme could prove to be an effective technology in reducing the chlorine demand to the tune of 15% & 18% with gain in bleached pulp brightness of 2-3 % ISO while reducing the AOX level in bleach effluent to more than 25% in case of wood Kraft and Kraft bagasse pulps.

6.2 Xylanase enzyme respond better on wood Kraft pulps than non-woody raw materials due to the nature of the hemicelluloses wherein it has been observed that hard wood hemicelluloses are more responsive to xylanase enzyme action than those in Pulps from Kraft bagasse mills, due to the nature of the hemicelluloses. It has been observed that hard wood hemicelluloses are more responsive to xylanase enzyme action than those in pulps from aglo residue raw materials.

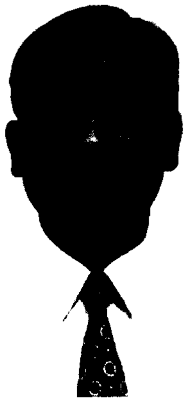
6.3 Studies indicated that before selection of a particular xylanase enzyme preparation it is important to evaluate the enzymes for their activity and cellulase contamination, since excess dose of xylanase enzyme and cellulase contamination results in loss of pulp yield and strength properties of the pulp as in case of enzyme preparation E.

6.4 Before introducing enzyme-prebleaching technology in any mill it is important to evaluate particular enzyme preparation for its response towards pulp being produced in the mill for various parameters as discussed in the paper.

6.5 Enzyme being sensitive and specific in nature, it is very important to optimise the temperature, pH, dosages and proper dispersion or mixing of the enzyme with the pulp in order to achieve the targeted response.

6.6 The technology is relatively new as far as Indian paper industry is concerned. Efforts are required by researchers, technologists and enzyme manufacturers to isolate new xylanase enzymes suitable for pulps being produced in Indian paper industry from wood and non wood based raw materials and also to investigate the effect of other hemicellulases and lignolytic enzymes like laccase and lignin peroxidases on pulp bleaching to further reduce requirement of chlorine based chemicals.

ENVIRONMENTAL IMPACT OF TOXIC CHLORINATED PHENOLIC COMPOUNDS RELEASED IN PULP & PAPER INDUSTRY & ITS CONTROL MEASURES



Dr. Suresh Panwar
Scientist E-I
CPPRI, Saharanpur

About The Author

Dr .S. Panwar is a senior scientist working in Effluent Treatment Div of CPPRI for the last twenty years. He has Masters Degree in Chemistry and has Doctoral degree in Pulp & Paper Chemistry.

He has a rich and wide experience in the area of pulping & bleaching, environmental management including bioenergy recovery from wastes, performance evaluation and trouble shooting of effluent treatment plants, environmental auditing etc. He has been responsible for commissioning of full-scale biomethanation plant for recovery of bioenergy from black liquor. He has been actively associated with the projects completed on behalf of CPCB like "Development of Standards of AOX for Large and Small Scale Pulp & Paper Mills" & "Standardization of Methods for Determination of AOX in Environmental Samples".

He has undergone an advanced training at Finland and Sweden on microbial aspects and application of biomethanation technology in pulp and paper industry. He has also been actively associated with prestigious projects sponsored by UNDP, MNES, and mill associations like IARPMA, IPMA etc. He has represented CPPRI at various national & International Conferences and Seminars. He has around 30 publications to his credit and has been author/ co-author of a number of R& D reports, training and course manuals.

ENVIRONMENTAL IMPACT OF TOXIC CHLORINATED PHENOLIC COMPOUNDS RELEASED IN PULP & PAPER INDUSTRY & ITS CONTROL MEASURES

Suresh Panwar*

1. Introduction

The release of toxic chlorinated phenolic compounds during bleaching of pulp with chlorine became an environmental issue in seventies when high level of these toxic compounds were detected in fish, (particularly of streams which received bleach plant effluent). Moreover the cause of acute and chronic toxicity in these aquatic organisms was also attributed to the chlorinated phenolic compounds. It has been reported that the use of chlorine based bleaching chemicals generate number of phenolic compounds which contain varying number of chlorine atoms attached to benzene ring. The toxicity of chlorinated phenolic compounds increases with the increase of chlorine atoms in the ring. For e.g. 2,3,7,8 tetrachloro di benzo dioxin is reported to be extremely toxic and has tendency to persist in environment for long time. The major part of chlorine is associated with high molar mass which constitute about 70% of total organic chlorine associated with organic fractions. Later on the detection of dioxins and furans in product, sediments, ETP sludge have received extensive media attention.

The imposition of strict environmental regulations, public awareness to the adverse effect of chlorinated phenolic compounds have initiated R&D organisations, pulp mills to develop the technologies to control the release of these toxic compounds in mill effluents. In the same perspective, efforts were made to develop the technologies to reduce the residual lignin content to the lowest possible extent in the unbleached pulp before bleaching process and find alternatives of elemental chlorine and hypochlorite to minimise the formation of these toxic, mutagenic and carcinogenic chlorinated compounds. This resulted in adoption of new fibre line (including modified pulping and bleaching technologies) by almost all the pulp mills in developed countries.

With growing environmental awareness & public perception & availability of eco friendly high brightness imported paper, stricter environmental legislations and judicial activism, the Indian pulp & paper mills are facing serious environmental challenges for their sustainability as well as ability to compete even in domestic market.

* *Scientist, ET Div, CPPRI, Saharanpur, U.P – 247 001*

In Indian scenario almost all mills are employing conventional pulping processes and are still persisting with high dosages of chlorine based bleaching chemicals to attain high brightness paper due to economic reasons which results in release of high level of toxic chlorinated phenolic compounds. Moreover, the scale of operation and use of mixed fibrous raw materials are among the major limitations of the Indian pulp & paper mills to adopt the new ecofriendly technologies.

The present paper highlights the technological level, status of adsorbable organic halides **(AOX)**, their environmental impact and the integrated approach to control the release of the toxic chlorinated phenolic compounds in Indian pulp & paper mills.

2. Pulping & Bleaching Technologies Practiced In India & Abroad

With the increase in awareness about the adverse environmental impact of AOX & dioxin, most of the pulp mills in developed countries have adopted new pulping and bleaching techniques to reduce the discharge of chlorinated phenolic compounds in mill effluents, some of these are:

- Extended delignification
- Improved pulp washing
- Oxygen delignification
- Elemental chlorine free (ECF) & Total Chlorine Free (TCF) bleaching
- Oxidative alkali extraction bleaching

The use of elemental chlorine (which contributes 70 - 80% of total AOX) has gradually phased out in most of the developed countries. Some of the pulp mills have adopted even Total Chlorine Free **(TCF)** bleaching process. However the majority of pulp mills still continue to use chlorine dioxide for bleaching of pulp to achieve high and stable brightness. In contrast Indian paper mills have continued with the use of elemental chlorine for production of bleached grades of papers due to economic reasons and moreover the measurement of the chlorinated organic compounds was not felt necessary till recent past. Till now techno-economic consideration have restricted the adoption of modern methods of pulping like extended pulping & oxygen delignification by the large integrated mills and major part of lignin is still removed in bleaching stage. The conventional CEH or CEHH bleaching sequences are commonly used by Indian mills to bleach the pulp to the desired brightness level. The consumption of chlorine in large mills varies from 35-60 kg/t of pulp. The small scale agro based mills in the absence of chemical recovery produce normally pulp of high kappa number and major part of lignin is still removed in subsequent bleaching process.

Use of chlorine dioxide, hydrogen peroxide & oxygen reinforced alkali extraction is limited to very few large mills which are producing rayon grade pulp & high brightness quality papers. An estimate indicates that approximately 2.5 million tonnes of chemical pulp is produced in India, 60% of this is high brightness bleached pulp mostly bleached by chlorine & chlorine based chemicals.

3. Formation Of Chlorophenolic Compounds

The nature & extent of formation of chlorophenolic compounds is determined primarily by the residual lignin content in the pulp and type of bleaching chemicals employed. The bleaching of pulp with chlorine-based chemicals generates various chlorinated phenolics **(Table- 1 & Fig- 1)** which include chlorinated resin acids, fatty acids, chlorinated phenolics, dioxins & furans. The identification and characterisation of bleach plant effluents for individual chlorinated compounds are exceedingly complex, so a generic measurement is used normally to indicate the level of these compounds in environmental samples like **Adsorbable Organic Halides (AOX), Extractable Organic Halides (EOX) & Purgable Organic Halides (POX)**. The distribution of various AOX related compounds released during bleaching of pulp in general is illustrated in **Fig-2**. As indicated about 80% of chlorine is associated with high molecular weight lignin material (MW>1000D) commonly referred as chloro-lignin. The main environmental concern is the generation of the low molecular weight chlorinated organic material (MW<1000D) as this fraction is considered to contain compounds which are toxic due to their ability to penetrate the bacterial cell membranes and has tendency to bioaccumulate in the fats of higher organism. The nature of chlorophenolic compounds depend on type of raw material used and bleaching sequence employed.

Among the chlorinated phenolics, the dioxins and dibenzofurnas are a group of chlorophenolics which have been found to have toxic effects. The prominent among the dioxins are 2,3,7,8 tetra chloro dibenzodioxin (TCDD) and 2,3,7,8 tetra chloro dibenzofuran (TCDF) **(Fig-3).** The major source of chlorinated dioxins has been found to be the Chlorination Stage and its formation is mainly dependent upon:

- Kappa number of brown stock
- Active chlorine multiple
- Mixing conditions during chlorination
- Carryover of COD alongwith washed unbleached pulp and
- Wash water quality.

4. Environmental Impact Of Chlorinated Phenolics

As discussed earlier, the discharge of chlorinated phenolic compounds formed during bleaching of pulp with elemental chlorine using conventional bleaching became an environmental concern when high level of these compounds were detected in fish of streams receiving bleach plant effluent. Earlier the high molar chlorinated, compounds was thought to contribute little or no toxicity to the aquatic organisms due to its large size of molecule. But later on, the studies conducted revealed that high molecular weight chlorolignin accumulated in sediments & over a period of time, these compounds further break down into more biologically active lower molar mass which can cause toxicity to the aquatic life.

5. Chorinated Phenolic Compounds

Low molecular weight chlorinated phenolic are reported to cause acute toxicity and mutagenicity due to their ability to penetrate living cell membrane. The chlorinated organic compounds present in alkali extraction stage (E) effluent are found more toxic and contributes more than 90% of acute toxicity. The major examples of such compounds are trichlorophenol, tri & tetra chloroguaicol which have tendency to accumulate in fish and are responsible for acute toxicity. The formation of these compounds is directly proportional to the consumption of chlorine and a sharp increase in the formation of tri & tetra chloroguaiacols has been observed when active chlorine multiple was increased from 0.15 to 0.20 **(Fig - 4)**.

6. Carcinogenic & Mutagenic Compounds

Some of the chlorinated phenolic compounds like chloro catechols formed in chlorination stage have been identified as strong mutagens.Chloroform & carbon tetra chloride produced during bleaching of pulp have also been classified as carcinogenic. The use of hypochlorite in bleaching has been reported to be the major source of these compounds. Studies conducted in developed countries revealed that the fish exposed to chlorinated phenolics discharged by bleached pulp mills demonstrated impaired function of lever, enzyme system, metabolic cycle as well as increase in the incidence of spinal deformities and reduced gonad development in both laboratory and field studies.

7. Polychlorinated Dioxins & Furans

Dioxins have received extensive media attention after Stockholm declaration of dirty dozen persistent toxic pollutants **(POP)** where in dioxins and furans have been put under the category of unintended industrial by products as these chlorinated dioxins have not any known use. The list of POP (commonly called as dirty dozen) is given in Table–2. Some other interesting facts about dioxins are summarised below:

- There is no known use for dioxins
- Dioxin is slow to break down and can last for long period.
- Animals consume dioxin contaminated water and plants and then it accumulates in their fat.
- People are exposed to dioxin through eating food high in fat, like dairy products and beef.
- Dioxin can be transmitted from mother to child during pregnancy and nursing.

The preliminary studies conducted on toxicity of dioxins on humans yielded contradictory findings. However, recently it has been accepted that dioxins even in trace amounts may cause a wide range of other adverse effects on human health. Some of them are listed below

- **Low-Exposure Effects**
    1. Altered immune function.
    2. Increased susceptibility to infections, and
    3. Thyroid and liver function abnormalities.
- **Higher Levels Of Dioxin Exposure**
    1. Birth defects,.
    2. Child growth retardation,
    3. Reduced levels of male reproductive hormones,
    4. Diabetes, and cancer
- **Human Carcinogen**

    Dioxins are classified by the International Agency for Research on Cancer as a known human carcinogen.

Though the level of dioxins is less than 0.1% (of total AOX) but these compounds are reported to be highly lypophyllic and bioaccumulable compunds. As such there is no safe level of dioxins. Such compounds are formed when unchlorinated dibenzodioxin (DBD) and dibenzofuran (DBF) present in unbleached pulp are chlorinated with elemental in chlorination stage. The oil based pulp mill additives particularly brown stock defoamer have been identified as potential sources of such compounds. Laboratory studies indicate a sharp increase in quantity of PCDD & PCDF when elemental chlorine consumption increased beyond 10-15 kg /t pulp.

8. Legislation To Control AOX Discharge

In the 1960's,when environmental consciousness was made related to the discharge of pollutants in mill effluents, the biological treatment plants were introduced in many of pulp & paper industry to reduce the pollution loads especially from bleach plant effluents which is the major source of pollution in large integrated pulp and paper mills.

The main emphasis was given for characterization & identification of hazardous chloro-organics present in bleach effluents when analytical methods & instruments became available. The new analytical methods and studies conducted created a basis for development of legislation for regulation of the level of chlorophenolics in discharge of pulp mills.

In the convention held in Paris for the prevention of pollution from land based sources & rivers, the AOX limit in general was set at 1.0 kg/t effective from 1995 for all types of bleached chemical pulp mills. The proposed AOX limit in general has been accepted by Belgium, Denmark, France, Germany, Ireland, Luxemburg, The Netherlands, Norway, Portugal, Spain, Sweden and U.K. Government agencies around the world have responded by imposing standard for emissions of Total Organic Chlorides **(TOCl)**, AOX or dioxins in mill effluents and in some cases, limiting the levels of these compounds found in paper products. Most countries have specified the maximum discharge limit for AOX or TOCl in mill effluent. A typical example is the Swedish TOCl standard of 0.10 kg/t by the year 2010.

The U.S. Environmental Protection Agency (EPA) on the other hand has issued a guideline to regulate the discharge of AOX & chlorinated compounds under so called **cluster rules** for several categories of pulp mills **(Table-3)**.

Based on studies conducted by CPPRI on Assessment of AOX level in Indian Pulp and Paper Industry, Central Pollution Control Board (CPCB) has finalised to impose the limit for discharge of AOX in mill effluents. The regulation for discharge of AOX in various countries are given in **Table-4**.

9. Status Of AOX Level In Indian Pulp & Paper Mills

In contrast to Internatioanl scenario, the Indian pulp and paper industry is characterised by low operational capacity, obsolescence in technology, high use of chlorine based bleaching chemicals, high water consumption and poor environmental performance. A comparative picture of technological status and level of AOX in Indian mills and those of developed countries is given in Table-5 Due to economic reasons the general trend in our country is to make pulp with high kappa no. using mild chemicals. Further delignification is achieved in bleaching stage which is mostly chlorine based resulting in high consumption of chlorine and leading to high level of AOX generation.

10. Large Paper Mills

The generation of AOX in general is higher in mill producing writing and printing paper and vary from 4.0 to 5.0 kg. AOX/t paper (due to use of chlorine based chemicals for bleaching) while in newsprint and rayon grade mills it is less than 1.0kg.AOX/t paper. The recent trend inmost of the large mills is to use oxidative alkali extraction employing peroxide. Only a few writing and printing paper mills which have switched over to chlorine dioxide bleaching or employed oxygen delignification have low level of AOX in their mill effluents.

11. Small Paper Mills

Further the problem of AOX is more severe in small agro based mills producing writing and printing paper. Since most of these mills are not having chemical recovery, they produce pulp of higher kappa no. and subsequently use higher chlorine dosage in bleaching stage to achieve desired brightness level. Moreover due to inherent poor drainage properties of agro residues coupled with poor washing efficiency of the washers (which leads to higher COD carry over along with the pulp to bleaching process) and low bleaching response of agro residues, the consumption of chlorine in these varies from 150 to 260 kg/t of pulp. This results in a high level of AOX generation between 6- 10 kg/t pulp. A comparative picture of status of AOX in Indian mills is indicated in Table –6.

12. Measures For Reduction/Control Of AOX

In response to environmental concerns, governmental regulations on emission of chlorinated organic matter and to also market demand, the pulp and paper industry has acted worldwide since the mid-1970's by developing & introducing a number of new processes & process modification in order to minimize the discharge of chlorinated phenolics.

The main strategy behind the development of internal process changes has been to remove as much lignin as possible before the pulp enters to bleach plant and also to replace elemental chlorine in bleaching process by other bleaching agents. As a result most of paper industry in developed countries have adopted modified processes & techniques to reduce kappa number , improved pulp washing system and bleaching techniques etc. and some of paper mills have achieved even lower value of AOX below 0.5kg/t pulp.

However, as discussed earlier, Indian paper mills still uses elemental chlorine which is considered major contributor of AOX. However some of paper mills in India have already started the use of chlorine dioxide, oxidative alkali extraction. J.K. Paper Mill is the only mill to introduce successfully RDH pulping, oxygen delignification, and chlorine dioxide bleaching in order to improve the quality of product & bleach plant effluent. In last two decades the major efforts worldwide have been to adopt & modify the inplant measures rather than at the end of pipe treatment in order to reduce the formation of chlorinated phenolic compounds. The inplant measures include extended delignification, efficient pulp washing, oxygen delignification enzyme pretreatment ECF, TCF bleaching, oxidative alkali, extraction etc. Some of these measures as well as those which can be implemented without any major modification in existing processes to control the discharge of AOX in Indian mills are discussed below:

12.1 Adoption Of New Technologies :

12.1.1 Oxygen Delignification

The process is used to treat the washed unbleached pulp to reduce the kappa number before bleaching stage. One of the requirements of the process is a special pressure vessel to maintain the desired treatment conditions. Almost all the pulp mills in developed countries are now using oxygen delignification process due to its inherent advantages. Some mills in these countries are even going / planning for two stage delignification process to further reduces the kappa number below 10. The main limitations for adoption of the process by Indian pulp and paper mills is again the low scale of operation and high capital investment. The scale of operation in most of Indian pulp mills varies from 100 to 275 t / day which restricts the adoption of oxygen delignification by these mills. Though J.K Paper Mill which is producing 300 tpd pulp is employing oxygen delignification process but the kappa number reduction efficiency is lower and varies between 30-35% one reason of which is use of mixed fibrous raw materials.

12.1.2 ClO_2 Substitution

The use of chlorine dioxide in bleaching not only reduces the formation of toxic and harmful, chlorinated dioxins but also improves the quality of pulp. Most of the pulp mills abroad have switched over to the use of chlorine dioxide bleaching in view of its advantages related to substantial reduction in formation of dioxins, furans and AOX related compounds. Few Indian mills have started the use of chlorine dioxide in chlorination stage along with elemental chlorine and also in the final stage of bleaching, to get a stable and high brightness level. One of the main requirements for induction of chlorine dioxide stage is to completely changeover to special grades of alloyed stainless steel (SS) system to prevent corrosion. This calls for heavy investments and scrapping the entire existing system in bleaching for induction of chlorine dioxide to substitute the elemental chlorine.

An extensive R & D studies were carried out at CPPRI related to the characterisation of bleached effluents generated in laboratory, generation of AOX in different raw materials using modified bleaching sequences. The result of AOX measured is given in **Table 7 & 8.** The chlorine consumption depends primarily on initial kappa number & bleaching response of pulp produced from different fibrous raw materials. **Table – 7** indicates that the requirement of total chlorine is higher for pulp produced from bamboo & eucalyptus. As indicated in the **Table -7& 8,** the chlorine requirement reduced drastically from 50-65%, when the unbleached pulp produced from same raw materials were subjected to oxygen delignification followed by conventional CEH bleaching sequences. As a result the level of AOX was also reduced from 60-70%.

The modified bleaching sequences like OC/DEOD, ODEOD were also used to bleach the pulp in order to evaluate the level of AOX. **Table- 8** clearly indicates that with the use of modified bleaching process the level of AOX can be reduced below 1.0 kg per ton of product.

12.2 Upgradation/ Retrofication In Existing Process / Technologies:

12.2.1 Controlled Pulp Mill Operation

The kappa no. of unbleached pulp is the main factor which governs the bleach chemical demand and ultimately responsible for AOX generation. Under the controlled and uniform cooking process, the kappa no. of pulp produced from wood may be attained between 18-20 without having any degradation in fibre quality. The mills must operate their pulp mill under controlled & optimum conditions to reduce the kappa number of pulp below 20.

12.2.2 Improved Pulp Washing

The carryover of organic matter along with pulp due to inefficient washing increases the consumption of bleach chemicals resulting in higher generation of AOX. Washing of pulp is an important step and can help in minimizing the carryover of organic matter to bleach plant. The existing washing system needs to be modified / upgraded to minimize the carryover of COD along with pulp between 15-20 kg/t. pulp.

12.2.3 Enzymatic Prebleaching Of Pulp

The enzymatic treatment of brown stock washed unbleached pulp increases the destruction and solubility of lignin present in pulp in the form of lignin carbohydrate complex. Most of the pulp mills in developed countries have already been using enzymatic prebleaching to reduce the overall bleach demand. The studies conducted at CPPRI reveal that enzymatic prebleaching of pulp produced from wood and agro residues reduces the total chlorine requirement by about 10-15% with additional gain of 2-3 units in brightness level. Some of the Indian pulp and paper mills have now started the use of enzyme for treatment of brown stock washed pulp to reduce the demand of elemental chlorine.

12.2.4 Oxidation Alkali Extraction Bleaching

The addition of small amount of oxygen or peroxide in alkali extraction stage improves the quality of bleach plant effluent by reducing colour & AOX. Most of the large paper mills have already started the use of hydrogen peroxide in alkali extraction stage. However the mills should also increase the use of oxygen in the alkali extraction stage due to the advantage of higher delignification and consequently less AOX generation.

12.2.5 Improved Chemical Mixing.

Improved mixing of chemicals in bleach plant is an important step. If the bleaching chemicals are not rapidly & uniformly distributed through the pulp, there is chance of a portion of pulp being over bleached.

12.3 External Measures:

12.3.1 Recycling Of Bleach Plant Effluent (C & E Stage)

In Indian mills C & E stage are the major contributors in generation of AOX. Reduction in their discharge by reuse/ recycle in the process can help to reduce the level of AOX to a greater extent. C stage effluent is acidic in nature while E stage effluent is the most polluted stream which limits possibility for their reuse in the process as it leads to adverse impact on product quality and as well as corrosion problem in system infrastructure. However, in mills employing oxidative extraction (E-stage) bleaching, the major part of E- stage filtrate is being reused in bleach plant. Detoxification of the bleach plant effluent by physico - chemical treatment methods can help in addressing to the above limitations to a greater extent. This requires removal of inorganic / recalcitrant and toxic compounds by physical / chemical treatment methods like membrane filtration, electroflocculation, chemical precipitation etc. CPPRI has been actively working in this area and the preliminary results obtained are encouraging and are summarized in **Table- 9,10 and 11.** Further work on assessing the techno-economics of the treatment methods & disposal of chemically precipitated sludge is under progress.

12.3.2 Effective Operation Of ETP

In the study conducted by CPPRI it has been found that AOX reduction by 45-70% is achievable by conventional effluent treatment practices. However the extent of reduction depends upon the operating conditions of ETP. Over the years most of the Indian paper mills have increased their pulp mill capacity without simultaneous expansion of their ETP's effluent handling capacity. This has resulted in poor performance efficiency of these ETP. The mills are required to operate their ETP under optimum conditions to achieve the maximum efficiency to reduce AOX & other oxygen consuming pollutants.

12.4 Other Measures :

12.4.1 Increased Use Of Recycled Fibre

The mills particularly small agro base mills must reduce/limit the production of chemical pulp and should use maximum proportion of recycled fiber to supplement the fiber furnish for production of bleached variety of paper grades. Such supplementary recycled fiber must be bleached with hydrogen peroxide.

12.4.2 Environmental Auditing

The regular environmental auditing is necessary which help to assess and also to improve the performance of process & the ETP. Due to increased environmental pressure and market competitiveness, the most of the mills are now going for ISO. Some mills are even accredited with ISO 14000, where regular environment auditing of the mill is mandatory.

13. Conclusions

Today the environmental issues particularly control of AOX is the major environmental challenge before the Indian pulp and paper industry for its sustainability and environment compatibility. The environmental challenges related to AOX generation have already been over come by pulp and paper mills in developed countries by adoption of new fiber line incorporating modern pulping and bleaching technologies. However Indian pulp & paper industry is still at cross roads due to its inability to adopt these modern technologies due to low scale of operation, use of mixed raw materials, and high capital investment. With the concept of eco-labeling and life cycle assessment of the product already introduced in international market, Indian pulp and paper industry should timely gear up to become cost competitive and environmental compatible to compete/ survive in this era of open market economy.

The ultimate solution to control the release of toxic compounds is adoption of modern fiber line to start with, the Indian pulp and paper industry must face the challenge in a phased manner by adopting short term & long term strategies to develop and employ new technologies in order to make pulp and paper industry more cost competitive and environmentally compatible. As most of new technologies are of imported origin and highly capital intensive, the performance of these new technologies are some times not up to the mark and need modifications to process the mixed fibrous raw materials available to Indian pulp & paper industry.

In view of increased global competitiveness, environmental awareness and imposition of stringent environmental standards, the Indian pulp & paper industry should come forward with short and long-term strategies to reduce the demand of chlorine based chemicals particularly elemental chlorine. As long-term strategies, the efforts are also required to strengthen the indigenous capability to develop the technologies suitable to our scale of operation and type of fibrous raw material available so as to make Indian pulp & paper industry cost competitive and environment friendly.

Table-1

Chlorinated Phenolic Compounds Generated During Bleaching Of Pulp With Chlorine Based Chemicals

Type	No. of Species,	Amounts
Chlorinated acids	40	Upto 500g/t pulp
Chlorinated phenolics	40	Upto 100g/t pulp
Chlorinated aldehydes, Ketone and lactones	45	----
Chlorinated hydrocarbons	45	----
Chlorinated others	20	----
High molecular weight Materials	--	Upto 4kg.Cl/t pulp

Table-2

List Of Dirty Dozen Persistent Toxic Pollutants (Pop) (Stockholm Convention)

S. No.	Compounds	Source
1.	Aldrin	Pesticide
2.	Chlordane	Pesticide
3.	DDT	Pesticide
4.	Dieldrin	Pesticide
5.	Endrin	Pesticide
6.	Heptachlor	Pesticide
7.	HCB	Pesticide
8.	Mirex	Pesticide
9.	Toxaphene	Pesticide
10.	PCBs	Industrial
11.	**Dioxins**	**By-product**
12.	**Furans**	**By-Product**

Table – 3

Polychlorinated Phenolic Compounds Proposed For Regulation By The U.S.E.P.A.

Polychlorinated phenols	**Minimum level, ppb (μg/L)***
Pentachlorophenol	5.0
2,3,4,6 - Tetrachlorophenol	2.5
2,4,5 - Trichlorophenol	2.5
2,4,6 - Trichlorophenol	2.5
3,4,5 - Trichloroguaiacol	2.5
3,4,6 - Trichloroguaiacol	2.5
4,5,6 - Trichloroguaiacol	2.5
3,4,5 - Trichlosyringal	2.5
3,4,5,6 - Tetrachlorocatechol	5.0
3,4,6 - Trichlorocatechol	5.0
3,4,5 - Tetrachlorocatechol	5.0
3,4,5, 6 - Tetrachloroguaiacol	5.0

The minimum level is defined as the concentration at which the analytical system gives recognizable mass spectra (corrected for background) and acceptable calibration points, using EPA method 1653

Table –4

Regulations For Discharge Of Aox (Kg/T)

Country	**1994**	**1995-2000**	**2000-2005**
Australia	1.0	-	-
Austria	0.76- 1.5	0.5-1.0	-
Canada	1.5	-	1.0
Germany	1.0	-	-
India	2.0	2.0	1.0*
Japan	1.5	-	-
Norway	1.0-2.0	-	-
Sweden	1.2 – 1.5	0.3 – 1.0	0.3- 0.50
USA	-	0.62	-

- Proposed limit

Table- 5

Status Of Aox In Indian Pulp And Paper Mills

Type of product	Kappa No.	COD Carry over during washing Kg.COD/t. pulp	Consumption of Cl_2 Kg./t. pulp	AOX Level Kg./t. Paper GEN-FINAL Discharge
Rayon grade Pulp	12 - 16	--	25 - 28	0.7-1.0 < 0.50
News print chemical pulp	20 - 22	--	20 - 25	0.50-0.60<0.50
Writing & Printing Paper:				
Large Mills	15 - 26	20 – 25	35 - 110	2.0 – 4.5 1.0 - 2.5
Small Mills (Agro-based)	30 - 32	30 – 40	140 - 160	6.0-10.0 4.0 - 6.5

Table –6

Technological Status In Large Integrated Pulp & Paper Mills

S. No.	Particulars	India	International
1.	Installed capacity, t/d*	250	1500
2.	Capacity utilisation, %*	70	100
3.	Raw materials used	Bamboo, eucalyptus , mixed hardwoods, bagasse	Soft wood & hard wood
4.	Pulping process	Sulphate	Sulphate
5.	Modified Pulping Process (RDH)	Not Employed**	Employed
6.	Oxygen Delignification	Not Employed**	Employed
7.	Bleaching Process	Conventional**	ECF & TCF
8.	AOX in final discharge, kg/t paper	2.0-2.5	0.5-1.0

* Average capacity under which most of the mills fall.

**Except J.K. Paper Mills Ltd., Orissa

Table-7

Level Of Aox In Different Pulps Bleached In Laboratory

Raw Material	**Kappa No.**	**CEH Bleaching**			**OCEH Bleaching**		
		Cl2 Demand kg/t pulp	**AOX kg/t pulp**	**AOX After Sec.treat kg/t**	**Cl2 demand kg/t pulp**	**AOX kg/t pulp**	**AOX after sec.treatment kg/t**
Eucalyptus	19	60.0	4.18	2.10	30.0	1.27	0.72
Bamboo	18	80.0	4.63	2.54	30.0	1.32	0.84
Bagasse	15	45.0	2.93	1.84	17.0	0.86	0.50

Table-8

Level Of Aox In Different Pulps Bleached In Laboratory.

Raw Material	Kappa No.	**AOX kg/t pulp**			
		CEH	**OCEH**	**OC/DEOD**	**ODEOD**
Eucalyptus	19	4.18(2.1)*	1.27(0.72)	0.83(0.46)	0.40(0.23)
Bamboo	18	4.63(2.54)	1.32(0.84)	0.90(0.63)	0.44(0.26)
Bagasse	15	2.93(1.85)	0.86(0.5)	0.6(0.30)	0.31(0.10)

* ( ) indicates values after secondary treatment

Table-9

Chemical Treatment Of Bleach Plant Effluent (Agro Based Mill)

Parameters	C-stage effluent	E-stage effluent	Combined bleach plant effluent
(A) Effluent Characteristics			
pH	1.8	7.1	6.6
COD mg/l	3528	2307	2883
AOX mg/l	48.2	125.3	50.02
colour, PCU	3372	6778	3689
(B) Chemical Dosages			
Alum : COD	1:1	0.5:1	1:1
Lime : COD	1.0 : 1	0.5:1	1:1
PAA, ml/l (1% solution)	1:1	2.0	2.0
(C) Treated Effluent Characteristics			
pH	5.5	5.6	5.0
COD mg/l	1033	438	542
AOX mg/l	23.82	62.2	21.06
colour, PCU	145	246	156
(D) Removal Efficiency, %			
COD	71	81	81
AOX	51	50	57
Colour	95	96	96

Table-10

Chemical Treatment Of Bleach Plant Effluent (Wood Based Mill)

Parameters	C-stage effluent	E-stage effluent	Combined bleach plant effluent
(A) Effluent Characteristics			
pH	2.0	9.0	6.4
COD mg/l	851	3048	612
AOX mg/l	46.16	134.0	37.8
colour, PCU	392	11320	1048
(B) Chemical Dosages			
Alum: COD	1:1	0.5:1	1:1
Lime: COD	0.75 : 1	0.5:1	1:1
PAA, ml/l (1% solution)	1.0	10.0	2.0
(C) Treated Effluent Characteristics			
pH	5.5	5.5	5.5
COD mg/l	240	596	306
AOX mg/l	18.14	25.43	13.23
colour, PCU	67.0	363	61.0
(D) Removal Efficiency, %			
COD	72	80	50
AOX	61	81	65
Colour	83	97	94

Table-11

Treatment Of Bleach Plant Effluent Through Electrofloculation (Wood Based Mills)

Particulars	Untreated Eop effluent	Treated Eop effluent 2 Lit. volume	% Reduction	Treated Eop effluent 5 Lit. volume	% Reduction
pH	11.7	9.3	-	8.5	-
COD, mg/l	1159	395	66	458	61
BOD, mg/l	178	69	61	105	41
AOX, mg/l	42.8	10.5	76	14	67
Colour, PCU	1133	60	95	135	88
Power consumption Watt h. / l	-	21	-	11.6	-

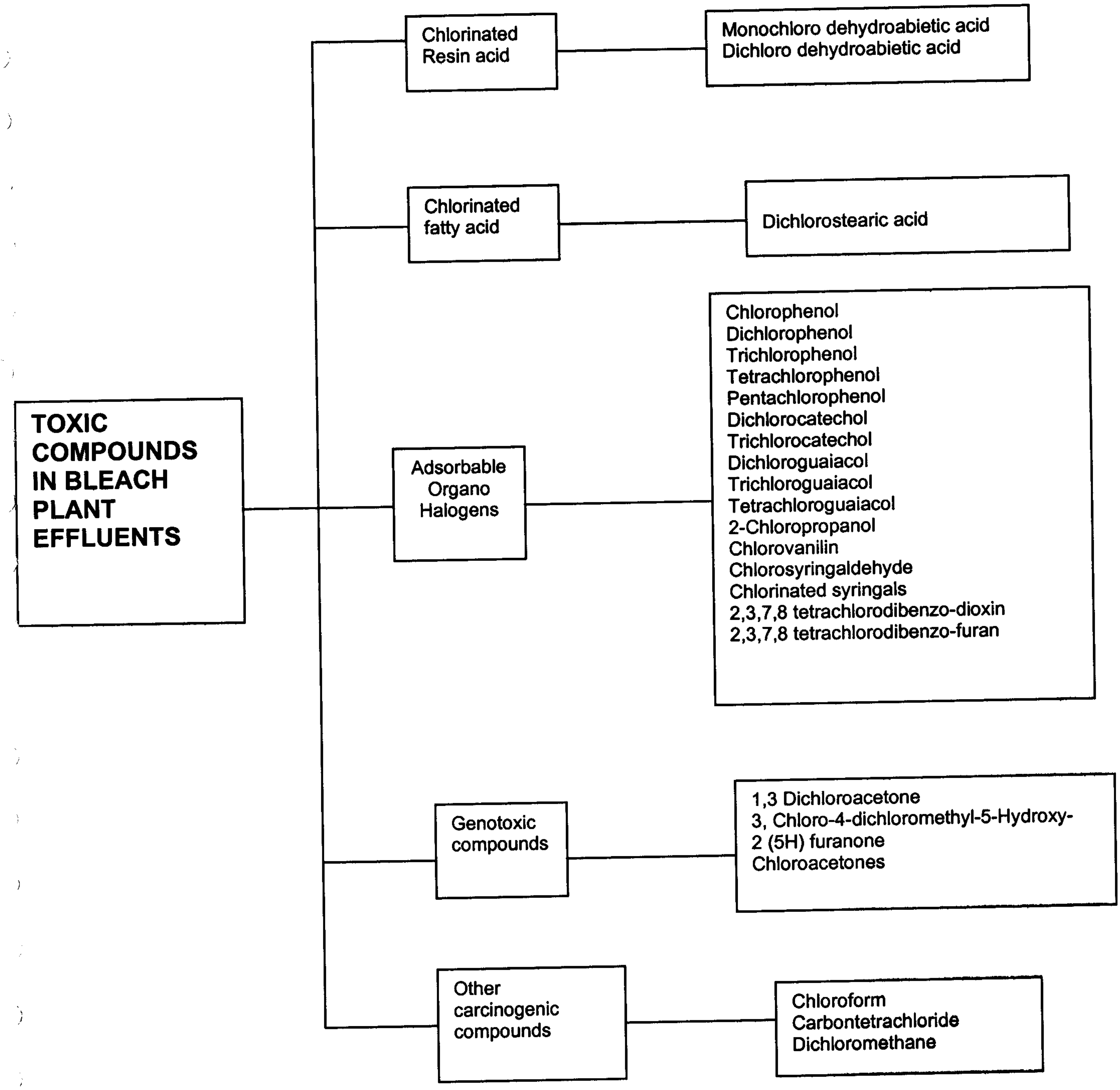
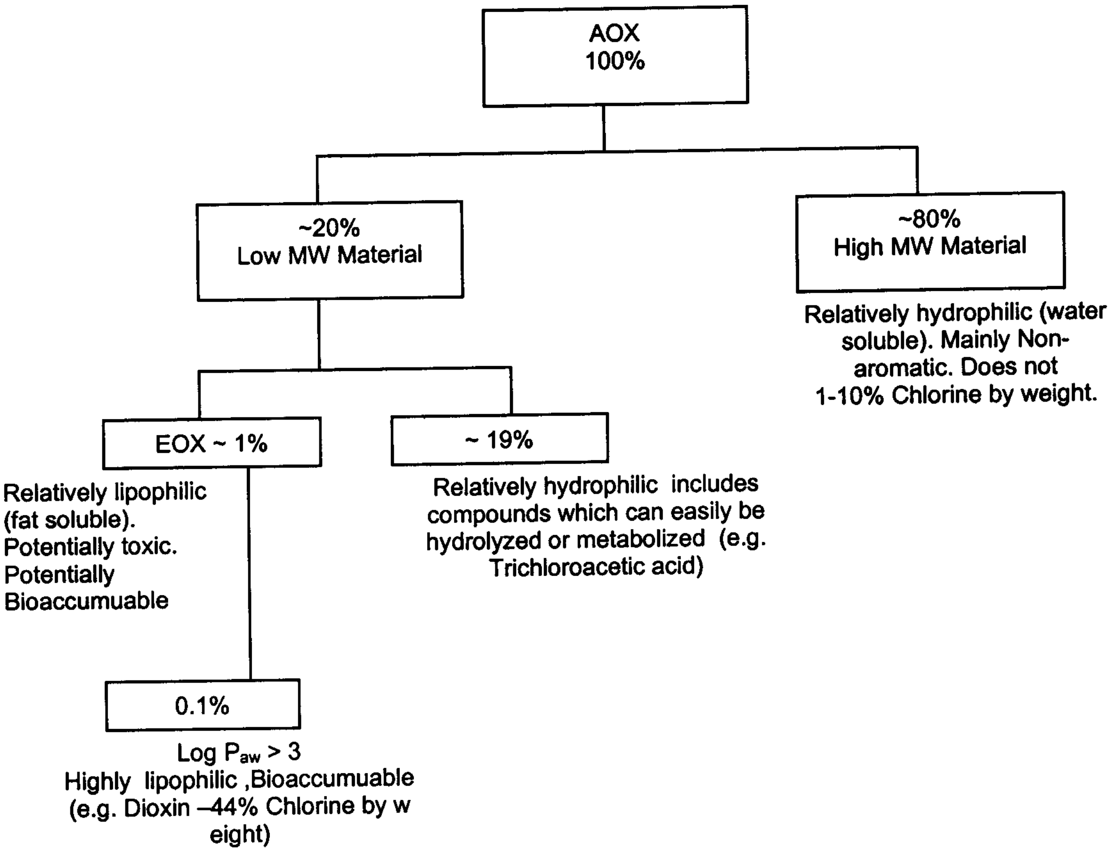
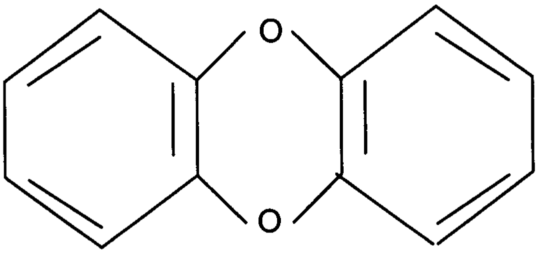


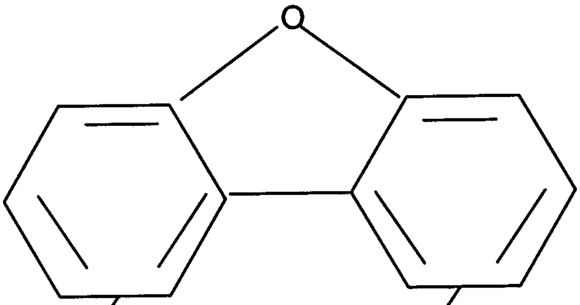
Fig.-1 Toxic Compounds In Bleach Plant Effluents



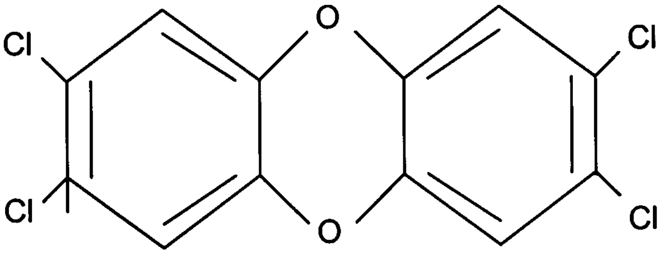
Fia- 2: DISTRIBUTION OF CHLORO PHENOLIC



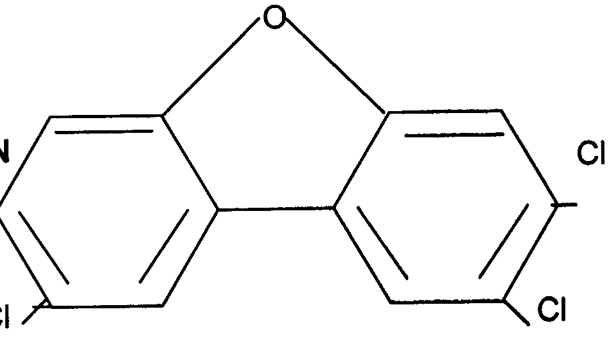
DIBENZO-P-DIOXIN(DPD)



DIBENZOFURAN(DPF)



2,3,7,8-TETRACHLORO-DIBENZO-P-DIOXIN
(2,3,7,8-TCDD)



2,3,7,8-TETRACHLORO-DIBENZOFURAN
(2,3,7,8-TCDF)

Fig.- 3 Structures Of Chlorinated Dibenzo-P-Dioxins & Dibenzofurans

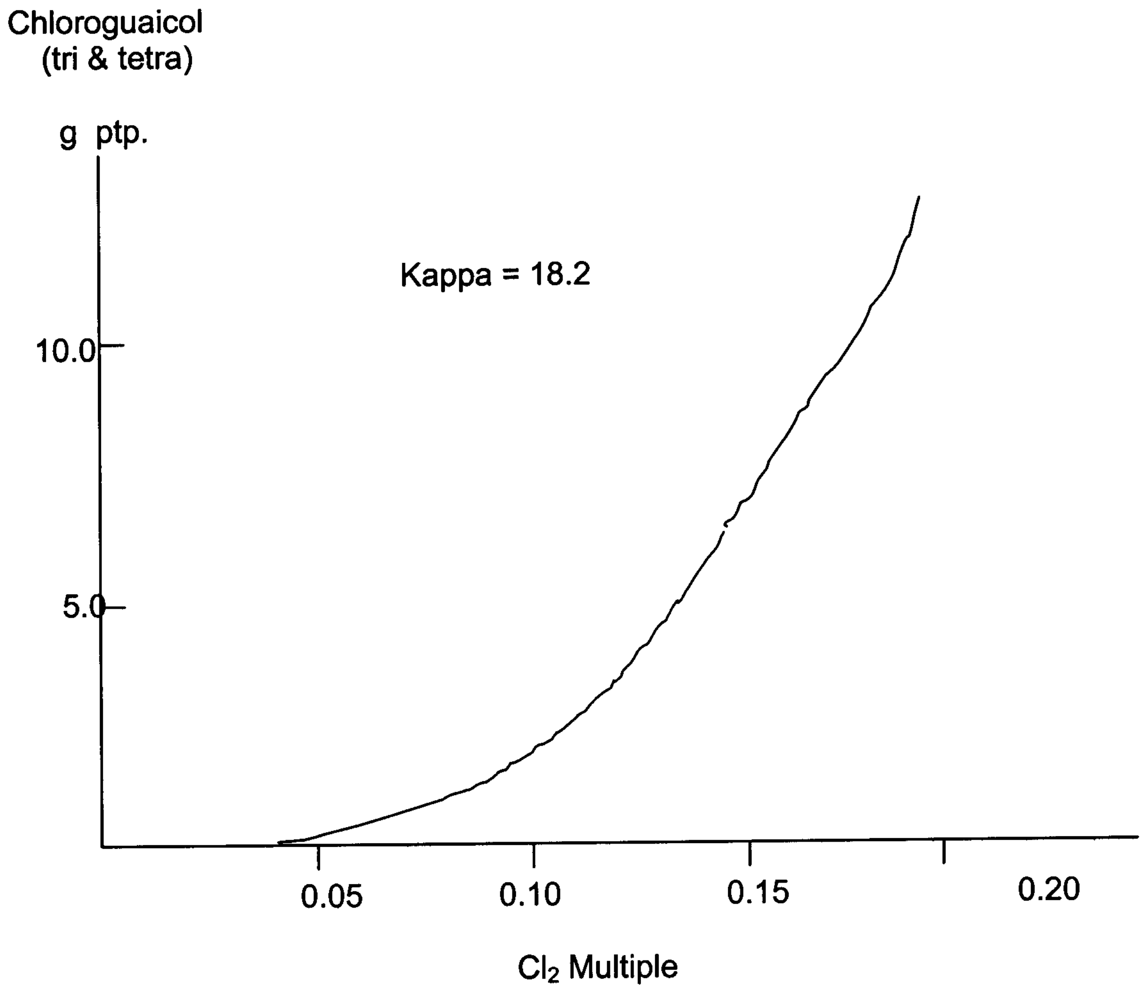
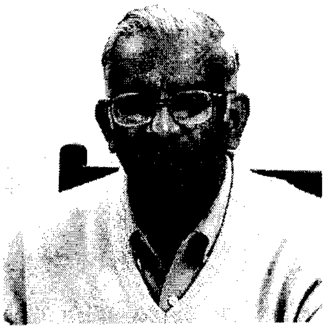


Fig.-4 The Formation Of Tri & Tetrachloroguaiacols Vs Chlorine Multiple In Chlorination Stage

ENVIRONMENTAL IMPACT AND BLEACH PLANT OPERATION

Dr. N.J.Rao
Professor,
Department of Paper Technology,
Indian Institute of Technology ,
Roorkee



About The Author

Dr. N.J. Rao Graduated from IIT , Kharagpur in Chemical Engineering (B.Tech. Honours) in the year 1965. In 1967 obtained M.Tech in Chemical Engineering also from IIT , Kharagpur. Is a Ph.D in fluid particle mechanics (fluidization) from Roorkee University . He joined Chemical Engineering Department of University of Roorkee in 1969 as lecturer . Before joining University of Roorkee he was with DCM ,Delhi for two years as a Chemical Engineer.

Since 1981 is a Professor with Institute of Paper Technology, Saharanpur now well known as Department of Paper Technology, IIT Roorkee Campus, Saharanpur and was the Director of IPT for a long time. He was also the Director of CPPRI in the year 1996-97. He is widely traveled abroad in association with activities of NIEM pertaining to Environmental Management in Pulp & Paper. Had been to China, Indonesia, Thailand, Vietnam, U.K., France, Canada, Germany and Scandinavia. He has more than 150 publications in national & international journals and warded 7 best paper awards. Also awarded GTZ equipment gift from Germany. He guided 6 Ph. D students and 12 M.Tech .

He has remained actively associated with CPCB, Delhi ,several State Pollution Control Boards, NPC, Paper mills associations . Also with Centre for Science &Technology, N.Delhi as one of the experts in Green rating project in paper and caustic -chlorine sector . Was on the Board of Directors of HNL, Kerala.

ENVIRONMENTAL IMPACT AND BLEACH PLANT OPERATION

N.J.Rao

1. Introduction

Environmental issues are and will remain a major topic in pulp and paper industry world wide and this trend will be followed in India Environmental compliable has become important globally and the cost of non compliance has increased. As a result of increasing environmental concerns from enforcement/regulatory agencies, public and NGO's the mills have been forced to look at their operation to improve environmental the market forces have been strong enough to prompt the start of a new era in pulping and paper making technology. The demand is on cleaner technology adoption, and manufacture of cleaner, environmentally friendly products. The need of the times is to look at processes responsible for greater environmental impacts and modify them suitably to meet the demand.

Environmental issues are today the major driving force for process and product changes. The manufacture of bleached kraftlsoda pulps have been a subject of continuous and intense development. The driving forces have been operating economy, new products, new bleaching chemicals, energy conservation with environmental, market and legislative issues on forefront.

The bleach plants have traditionally been the major contributors to polluting discharges. The environmental issues have involved from measuring environmental impact as salt cake loss BOD or COD, AOX or debate on dioxins. In the last 2-3 decades environmental issues have been the dominant driving force for development of both pulping /washing and bleaching processes. The present paper mill look at the bleaching process and the related developments. .

2. What Is Bleaching ?

A simple definition of pulp bleaching is chemical treatment of cellulose fibres to increase brightness. Brightness increase is achieved by lignin removal or by lignin decolourising. Lignin, one of the main constituent of cellulose raw materials is coloured. It darkens with age and cause deterioration of strength of the paper. Brightening by lignin removal not only increases brightness level, but also leads to brightness stability. One of the principal function of chemical bleaching of pulps is to clean the pulp by bleaching shives and dirt particles. Shives are bundles of fibres which have not been separated by the pulping process. Bleaching Can also be a purification process for hemi cellulose or extractives removal.

The important objectives of operating a bleach plant are production rate and pulp brightness. Capital and operating costs rank next. Pulp cleanliness and strength presence become next targets. However environmental protection has become most important target. The properties of pulp are the results of the principle components of pulp i.e. Cellulose, hemi cellulose and lignin and extractives.

2.1 Cellulose

Cellulose is a carbohydrate, a linear polymer of anhydroglucose. Because of large number of glucose units in a single molecule and the stability of cellulose, it is not soluble in water. However by acid hydrolysis or oxidation and alkaline hydrolysis, the bonds in cellulose chain are broken. Strength of paper is due to hydrogen bonds formed between adjacent cellulose molecules. If degradation of cellulose is sufficiently severe, the strength of pulp is decreased, yield of pulp is lowered. Cellulose is naturally white and so does not need bleaching. The extent of degradation of pulp is measured by knowing the average length of cellulose chain or pulp viscosity. Degradation of cellulose is a potential harmful effect of bleaching.

2.2 Lignin

Lignin is a random, three dimensional macromolecule of phenyl propane building blocks, different from cellulose. Some of the bonds in wood lignin can be hydrolysed so that the molecular weight is decreased and fragments of lignin are dissolved. This is what happens in kraft pulping. However not all lignin is not removed by hydrolysis. Residual lignin must be fragmented by oxidation for its dissolution. Lignin is coloured because of the conjugated structure which are some times formed in phenyl propane macromolecule. In high yield pulps, bleaching of lignin is achieved by decolouring, either with an oxidizing agent or a reducing agent.

Lignin content is not measured either in pulping or bleaching. The bleachability is measured by K number or p number (permanganate Number) or Kappanumber. Approximately K number = 0.66 (Kappanumber). Lignin content {weight %) = 0.15 (Kappa number)

2.3 Hemiculluloses

Hemiculluloses are carbohydrate polymers with considerable variety in their structure. These are 5 and 6 carbon sugars of lower molecular weights and hence easily dissolved and contribute less to the strength of paper Hemicullulose is white and relatively stable and need not be removed during bleaching. However hemicellulose does interfere with processing of dissolving grade pulps and so during bleaching of dissolving pulp, hemicellulose is removed by severe caustic extraction.

2.4 Extractives

Extractives are minor components of unbleached pulp. Extractives are those removed by extraction with neutral solvents like benzene or ethanol. They contain resin or rosin, tall oil, soap and most of these are removed in pulping. They call appear in form of 'Pitch' in bleach plants and cause processing problems.

3. Bleaching Chemicals

All the coloured material present in unbleached pulp cannot be eliminated by ally single chemical in any Single step so bleaching is a multi-step procedure. Two types of chemicals are used:

(i) Oxidants are used to degrade and decolurize lignin. These are chlorine (Cl). Oxygen (O), Hypochlorite (H). Chlorine dioxide (D), Hydrogen Peroxide (P) and ozone (Z). The Only reductant.used in hydrosulfite.

(ii) Alkali is used to degrade lignin by hydrolysis and to aid in its dissolution. The only alkali used is sodium hydroxide.

Bleaching has two-unit operation: delignification and brightening. Conventionally, chlorine is used virtually for delignification in all bleach plants treating chemical pulp. Chlorine is invariably followed by extraction to hydrolyze and dissolve chloro-ligning. Due to high capital cost of oxygen delignification equipment, use of oxygen for delignification has not been followed in countries like India so far. However, oxygen is now widely used in the first extraction stage called the E stage. Both chlorine and oxygen cannot be used for more extensive treatment because their poor selectivity results in cellulose degradation.

The brightening operation involves further oxidation of the pulp for removal of the remaining lignin. Chlorine dioxide, hypochlorite and peroxide can be used for this purpose in the later stages of bleaching because of their greater selectivity. Due to their higher cost, they should be used under the most efficient conditions. Besides the final brightness, bleaching chemicals are now a days selected on the bas-is of their environmental impact. For instance, increased concern about chlorinated organic compounds has led to elimination of many hypochlorite stages, which produce significant quantities of chloroform, and to increasing substitution of chlorine dioxide for chlorine.

The process conditions in each bleaching stage are a vital factor in achieving optimal performance from chemicals and equipment. The process conditions are the rate of application of chemical, temperature, time, oxidant concentration, consistencyd and pH. Most bleaching problems involve finding the proper balance among these factors which will do the desired degree of bleaching with the least degree of damage to the cellulose fibre. Progress in deliglIification is monitored by the Kappa number or permanganate measurement. The different bleaching chemicals used; their function, advantages and disadvantages are shown in table -1

4. CHEMICAL REACTIONS IN BLEACHING

The reactions between bleaching chemicals and pulp are complex. The bleaching chemicals react with all of the components of pulp (lignin, carbohydrates, basrk, shives etc.) simultaneously. The important factors in reactions between pulp and chemicals are summarized in Table -2.

The most important reactions are between the chemical and lignin. In the first part of bleaching, one wishes to delignify and so the Kappa No. decrease is a measure of the reaction. In the later stages of bleaching, the desire is to achieve an increase in brightness. This may be measured directly as such or in terms of a decrease in absorption coefficient.

The reaction between bleaching chemicals and cellulose is undesirable because it causes enough damage to the cellulose resulting in a decrease of pulp strength. The relative rate of reaction between bleaching chemical and lignin, compared to that between bleaching chemical and cellulose, determines the selectivity of bleaching chemical under particular conditions.

Table 1
Bleaching Chemicals

Chemical	Form	Function	Advantages	Disadvantages
Oxidants				
Chlorine	Gas	Oxidises and chlorinates lignin	Effective, economical, delignification, good particle removal	Can cause loss of pulp strength if used improperly organochlorine formation
Hypochlorite	Ca or Na Hypo soln 40 gpl as Cl2	Oxide, brighten and solubilize lignin	Easy to make and use	Can cause loss of pulp strength if used improperly chloroform formation
Chlorine dioxide	7-10 gpl ClO_2 in water	i) oxidizes, rightens lignin ii) In small amounts with Cl2 protects against degradation of pulp.	Achieves high brightness without degradation. Good particle removal	Must be made at site. Expensive. Some organo chlorine formation
Oxygen	Gas used with NaOH	Oxidises and solubilises lignin	Low chemical cost. Provides Cl2 free effluent recovery.	Used in large amounts, requires expensive equipment. Can cause loss of pulp strength.
Hydrogen peroxide	2-5% soln.	Oxidises and brightens lignin in chemical and high yield pulps.	Easy to use low capital cost particle bleaching	Expensive. Poor
Ozone	Gas in low conc.	Oxidises, brightens and solubilises lignin in oxygen	Effective, provides chloride free effluent for	Expensive, degrades pulp poor particle bleaching

			recovery	
Reductants				
Hydro-sulphite (for mechanical pulps only)	Solution of Na_2SO_4 yield pulp made on site from NaBH3 plus SO_2	Reduce and decolourise lignin in high	Easy touse. Low capital cost	Decomposes readily. Limited brightness gain
Alkali				
Sodium hydroxide	5-10% NaOH solution	Hydrolise, chlorination and solubilise lignin	Effective and economical	Darkens pulp

Table 2
IMPORTANT FACTORS IN REACTIONS BETWEEN BLEACHING CHEMICALS AND PULP CONSTITUENTS.

Chemical	Measure of Reaction	Stiochiometry	Kinetics
Lignin	Kappa or K.No. decrease	Chemical required per unit of Kappa decrease	Sometime limiting factor in extent of delignification
	Brightness increase [absorption coefficient (k) decrease]	Chemical required per unit of brightness increase (or chemical required per unit of K decrease)	Sometimes limiting
Cellulose	Viscosity decrease (DP decrease)	Not important	Selectivity determined by rate of reaction compared to rate of reaction compared to rate with lignin
Particles	% particles remaining, particle concentration	Not important	Cleanliness determined by rate of reaction compared to rate with lignin
Dissolved matter carried over	Extra chemical consumption	Extra chemical per unit of dissolved substance	Limits brightening

Particles do not consume a great deal of bleaching chemical, but the rate at which they are eliminated as compared to the rate of chemical-lignin reactions of fibres is important in determining the cleanliness of the bleached pulp.
Finally, dissolved organic matter carried over from washing of unbleached pulp or from one bleaching stage to another may consume extra chemical. Consequently this results in greater pollution load generation.

4.1 Lignin Reactions

a) Delignification

Delignification in bleaching is achieved by oxidation and alkaline extraction in combination. The oxidants react very rapidly with lignin resulting in changes in structure and in fragmentation of the macromolecules of lignin in the unbleached pulp. Oxidation of the lignin not only breaks bonds in the lignin macromolecule and so creates smaller, more soluble fragments, it also creates new functional groups, such as carboxylic acids and phenols. These functional groups increase the ionic character of lignin, particularly in alkali, and make it more soluble ill water.
Chlorine and chlorine dioxide are used under acidic conditions. Following the acidic oxidation step, the pulp is washed and treated with sodium hydroxide to ionise the phenolic and carboxylic acid groups introduced into the lignin. Further, chlorolignin is hydrolysed by sodium hydroxide to form phenols which immediately ionize and the solubility of lignin is further increased.
Sodium hypochlorite, oxygen, and hydrogen peroxide are all used under alkaline conditions. As a result, the carboxylic acid and phenolic groups introduced into the lignin structure are immediately ionized

Delignification takes place by

-fragmentation by oxidation.
-introduction of oxidized functional groups into the lignin structure.
-ionization of the oxidized groups in alkali
-dissolution of fragments which are small enough and sufficiently ionic.

Lignin reactions proceed very rapidly at first and then increasingly more slowly. It appears that there are two types of lignin -that which is easily removed, and that which is difficult to remove. An important consequence of this is that as more and more chemical is applied in an attempt to remove more and more lignin, the process becomes less and less efficient. As more chemical is applied to remove more resistant lignin, reaction of the chemicals with carbohydrates increases and degradation of pulp can reslut.
As more chemical is applied, delignification proceeds asymptotically toward a lower limit. The lower limit is significantly lower for unbleached pulps

containing higher concentrations of lignin. This makes it impossible to remove all the lignin in a single stage. Fortunately, treatment with alkali increases the reactivity of the remaining lignin to further oxidation. It is most economical to use oxidizing chemical to achieve the initial easy removal of lignin and then to stop and extract as the efficiency levels off

b) Brightening

In brightening reactions, pulp is treated with bleaching chemcials and decolourized Chlorine dioxide, sodium hypochlorites, and hydrogen peroxide are commonly used Some brightening takes place by fragmentation and dissolution of the lignin. In addition, bleaching chemicals may decolourize some chromophoric structures by oxidation mld the residual chromophoric structure may remain in the pulp.

Brightening also reaches a limit asylmptotically. This figure shows that, when chlorine dioxide is first added to pulp, the brightness increase per unit of chlorine dioxide is high, but as more chlorine dioxide is added the brightness gain per unit of chlorine dioxide steadily decreases. Fortunately, the bleachabilily of pulp is restored by an alkaline extraction stage so that pulp treated to its brightness limit in the D1 stage may be extracted al1d then raised to even higher brightness limit in the following D2. stage. As with delignification, there is a very rapid initial rate of brightness which quickly falls off to a much slower rate. The stoichiometry of brightening is Identical for both hypochlorite and chlorine dioxide bleaching.

4.2 Carbohydrate Degradation

Cellulose is the major component in bleached pulp and therefore is principally responsible for the strength of the pulp. Reactions of chemicals with hemicelluloses may result in loss of yield but may not be as important as far as loss of strength is concerned.

Cellulose reacts with oxidants in several ways. Chlorine and hypochlorite will oxidize the hydroxyl groups in the cellulose chain to carbonyl groups which sensitize the cellulose chain to hydrolysis. Hydrolysis decreases the DP of cellulose chain in alkali and may result in loss of pulp strength., Cellulose is also attacked by free radicals generated by bleaching chemicals, particularly chlorine, oxygen and ozone. These free radicals randomly attack the cellulose chain, decreasing the DP and thus loss in pulp strength. In oxygen bleaching, magnesium ion is added to protect the pulp against free radical attack and in chlorination, chlorine dioxide is added. These free radicals are also known to react very rapidly with lignin so that lignin not yet removed from the pulp also acts to protect cellulose from free radicals.

In alkali, cellulose will depolymerze from the reducing end of the cellulose molecule. End groups spontaneously rearrange and the bond linking them to the main chain is broken. This is called the "peeling reaction" and results in loss of pulp yield. Another rearrangement fortunately results in stabilization of the end group and this is called the "stopping reaction". Another important factor is that carbohydrates are more soluble in alkali. In bleaching in the alkali stages (alkaline extraction or hypochlorite oxygen or peroxide stage), shorter chain fragments of cellulose and shorter chain hemicellulose dissolve., resulting in decreased pulp yield.

Unlike reactions between bleaching chemicals and lignin, the efficiency of reaction between bleaching chemicals and cellulose does not decrease as more bleaching chemical is added. Cellulose is steadily degraded as more bleaching chemical is added. It is difficult to assess the stoichiometry of carbohydrate degradation during de lignification because the bleaching chemicals are consumed by both lignin and carbohydrate.

In treatment of pulp with bleaching chemicals, it appears that as long as there is sufficient lignin unreacted, the bleaching chemical will be consumed by it and the carbohydrate will be protected This is due to the reason that delignification in reactions are presumably much faster than the cellulose degradation reactions. Thus, the bleaching chemical is rapidly consumed and the driving force for reaction with the carbohydrates is diminished. What is most important in the treatment of pulp with bleaching chemicals is the relative rate of cellulose degradation compared to the rate of delignification or brightening. The objective is to decrease the relative rate of degradation alld thereby improve the selectivity. As the hypochlolrite stage progresses, an asymptotic limit of brighflless is achieved but carbohydrate degradation still proceeds. It is clear that the selectivity of chlorine dioxide is superior to that of hypochlorite.

4.3 Particle Bleaching

All particles contaminating pulp (bark, shives, stone cell aggregates etc.) are not bleachable and therefore efforts should be made to maximize their removal by mechanical means such as by screening and cleaning. The kinetics of particle removal are different from delignification and brightening.. Shives disappear relatively more .slowly and more steadily than do chromophores. It is important to maintain a residual throughout the whole available retention time. It is also known that higher concentration of bleaching chemical favours removal of shives compared to removal of chromophores i.e. increasing brightness. Cleanliness, as affected by the relative rates of particle removal versus de lignification or brightening, can also be significantly influenced by choice of bleaching chemical. It can be seen that chlorine dioxide offers the best particle removal compared to Kappa number reduction.

4.4 Reactions with Dissolved Organic Matter

Oxidants used to bleach pulp will react with dissolved lignin present in the carry over of black liquor from brown stock washing or from carry over from one of the bleach plant washers. Carry over can be estimated by the measurement of a filtrate "K number". The rule of thumb is that 1 kg of chlorine is consumed by 1 kg of black liquor measured as sodium sulfate. Other have found that the consumption of chlorine equals approximately 2 kg per kg of carry over as lignin. the general industry estimate is that in chlorination stages as much as 10 kg of chlorine per ton of pulp might be consumed by black liquor carry over from brown stock washing. Studies have shown that the rate of reaction of bleaching chemicals with black liquor is greater than with pulp or shives.

5. PROCESS VARIABLES

5.1 Chlorination

a) Chlorine Application Rate

The chemical consumed during chlorination is the most important variable. The optimum amount of chlorine to be applied to the pulp should be sufficient to dissolve as much lignin as possible in the subsequent extraction stage with minimum carbohydrate degradation. Frequently, the % chlorine on pulp will be set by a factor times the unbleached Kappa number (e.g. % Cl_2 on pulp = 0.2 x Kappa Number). the actual chlorine consumption based on the pulp varies from about 4 to 8% for the kraft pulps. In practice, about 65 to 70% of the total chlorine demand of the pulp is applied in chlorination stage. More frequently, however, sufficient Cl_2. is added to give a preselected residual concentration of chlorine at the end of the retention period.

It should be noted that the extent of delignification is usually measured after subsequent extraction as CE Kappa Number. The C and CE kappa number decreases with increased chlorine consumption in the chlorination stage. A higher chlorine application rate has been recommended for minimizing overall bleaching costs but lower application rate has been recommended to minimize environmental impact of effluents.

b) Time and Temperature

The time required in chlorination is related to the extent of delignification desired, the incoming kappa number, the temperature, the residual, and the quality of mixing. Chlorination towers must commonly have a retention time of 30-60 min. As discussed earlier, the rate of delignification is very high at first and then progressively decreases. The chlorination temperature is usually governed by the prevailing temperature of the mill water supply as it is not economically feasible to cool or heat the large quantity of water required. The temperature may be in the range of 25-65 o C. the efficiency of the de lignification is not affected by the temperature. There has been a controversy about chlorination at high temperature. The rate of reaction is significantly increased by increased temperature and it is necessary to control the extent of reaction in order to prevent over chlorination. If the extent of reaction is controlled so that the desired E Kappa number is achieved i.e. over chlorination is avoided, then there is no damage to the pulp. It is not the temperature but the extent of chlorination that affects pulp viscosity.

c) Consistency

Pulp is usually chlorinated at a consistency of2.5-4.0 % mainly because of the low solubility of chlorine in water. At this consistency, mixing and pulping operation are also facilitated. However, 10% consistency has been used in commercial installations.

d) pH :

Normally, no effort is made to regulate the pH of the chlorination system, which assumes a value dictated by the concentration of chlorine initially present and by the hydrochloric acid produced by the reaction. The chlorination stage pH is normally in the range of 1.6-2.2. The reaction of chlorine with lignin produces hydrochloric acid as a by-product which decreases the pH. Chlorination filtrate recycling causes accumulation of HCl and so the pH is still lower. It has been found that serious pulp degradation can result during chlorination if the end pH is greater than 2.0

5.2 Alkaline Extraction

In alkaline extraction those coloured components, which have been made potentially soluble in dilute warm alkali solutions by the action of the chemicals used in partial bleaching, are solubilized. Following are the main objectives of alkaline extraction :

- To remove chlorinated and oxidized lignins formed in the chlorination stage.
- To remove resins and fatty acids.
- To obtain stronger, brighter pulp, good cleanliness, easier bleachability in subsequent stages.
- To purify alpha-cellulose (remove hemicelluloses} for further use as a chemical pulp.

The process conditions of alkaline extraction depend on the ultimate product and may be from moderate (e.g. for paper grade pulps) to vigorous (e.g. hot alkaline purification process to enrich alpha-cellulose content of pulp). Typical process conditions are given below:

NaOH applied- Usually 60% of chlorine applied in the first stage (25-50 kglt pulp)
PH- A final pH of 10.8-11.2 is best to obtain properly extracted pulp for paper grades.
Consistency- Conventional level 10-12 %. This has no effect on kappa reduction.
Time - 60-120 min.
Temperature- 55-80 o C. With proper control, high temperature will not affect pulp strength but may increase effluent loading, requires steam and cause shrinkage.

In alkaline extraction stage, sufficient NaOH is applied to achieve a high-end pH. This ensures ionisation of phenolic groups in lignin which greatly increases lignin solubility. Most of the NaOH added is consumed in neutralization of organic acids, HCl (or chloride ion hydrolyzed from lignin) and carbon dioxide. A more NaOH is applied E kappa number decreases to an asymptotic limit which is lower if more chlorine has been applied in the chlorination stage. This figure also shows that the optimal addition rate of NaOH lies approximately at the point on the curve where less and less benefit is achieved.

Extraction temperature varies from 55-80°C with towers commonly providing

Chemical	1 to 2% hypochlorite as available Cl2 on pulp
applied	9-16%
Consistency	30-45 °C(30-80 °C)
Temperature	2-3 hours
Time	10.5-11 (8-10.5)

End pH 60-120 min. retention time. Increased extraction occurs with increased time and temperature. It may be noted that most of the caustic extraction takes place in the first few minutes and certainly by the end of 60 minutes, almost all the extraction has been completed.

5.3 Hypochlorite Stage

Calcium and sodium hypochlorite have been used for pulp bleaching for years due to their relatively low cost and the controlled degradation Hypochlorite was used

alone in early applications but recent practice has been to use it after chlorination and alkaline extraction. When hypochlorite is used with chlorine dioxide for peroxide, it is normally used early in the bleaching sequence to reduce the amount of higher cost chemcial used in the final critical bleaching stages. The ranges of process conditions used in hypochlorite are given below

a) Hypochlorite Charge :

The amount of hypochlorite charge depends on the kappa number of pulp coming from the extraction stage. As more and more hypochlorite is added, pulp brightness increases less and less per unit of chemical. As more and more hypochlorite is added, the concentration of lignin with which the hypochlorite reacts decreases and hypochlorite reacts more and more with the cellulose and pulp viscosity decreases.

b) pH

Hypochlorite bleaching process is optimized not only to maximize brightness improvement but also to maximize particle bleaching and minimize carbohydrate degradation. pH is the most important control parameter in this stage. The brightening reaction rate increases rapidly at pH below JO, but the reaction rate with carbohydrates increases even more rapidly than brightening reactions. It means selectivity drops at pH below 10.

The attack of hypochlorite on cellulose is less severe in the early stages of bleaching when appreciable amounts of lignin are present than in later stages when only the cellulose remains to be attacked. Therefore, high pH is most important in final hypochlorite stage.

As hypochlorite bleaching proceeds, organic acids are formed Therefore, NaOH is added to maintain the end pH of 10-10.5. As pH drops below 10, the viscosity starts to decrease sharply. If pH is too high, (> 11), the brightening reaction is retarded Low pH is used in calcium hypochlorite bleaching to minimize scaling.

c) Time, Temperature and Concentration

Brightening rate increases sharply with temperature, doubling about every 10 °C. It may be noted that maximum brightness is achieved in about 10 min at 70°C whereas a full 120 min are required at 35°C. The rate of consumption of hypochlorite follows a similar trend, Kinetic studies indicate that the rate of degradation increases much more rapidly with temperature than does the rate of brightening. Therefore selectivity is lower at higher temperature.

5.4 Chlorine Diaxide Stage

The rapid adoption of chlorine dioxide for pulp bleaching can be attributed to its high selectivity in destroying lignin with out degrading the cellulose or hemicellulose thus preserving pulp strength and resulting in high brightness. Typical process conditiol1S are given below :

Chemical charge	0.5 to 1.5% onpufp as ClO_2.
Time	3-5 hours.
Temperature	60-75°C
pH	3.5-4.5
Consistency	10-12%

As more and more chemical is added; the increase in pulp brightness per unit of chemical becomes less and less. The charge of ClO_2 is dependent on the incoming CE kappa number al1d is a function of residual lignin in the pulp and the target brightness of that stage. E extraction permits a sharp increase in brightness on addition of a small amount of ClO_2.in the following D2 stage. This figure also illustrates the higher brightness ceiling which can be achieved with a lower incoming kappa number (achieved in this case by enrichment of the extraction stage with oxygen).

The effectiveness of ClO is a function of pH. When ClO is added to pulp (particularly if the ClO solution has a significant amount n of Cl in it), the HCl acid and organic acids formed in bleaching reactions will cause the pH to drop to less than 3. NaOH is added to neutralize the acids formed. As the end pH in the D stage increases, brightness reaches a maximum in the range of 3.5-4. If too much caustic is added, the brightness will fall. Higher pH also has a negative effect on shives.

Time, temperature and ClO_2 concentration affect chlorine dioxide bleaching. The rate of bleaching reaction doubles for every 10°C increase in temperature. The rete of reaction is initially very fast but diminishes rapidly with time. It may be noted that more extensive treatment before ClO_2 brightening results in higher brightness ceiling.

6. Multi Stage Bleaching

Originally, bleaching of pulp was carried out in a single stage but since the introduction of hard bleaching pulps, multistage bleaching has been widely practiced Single stage bleaching is still practiced on easy bleaching, moderate brightness pulp but most chemical pulps are now bleached by multistage processes involving chlorination, hypochlorite, alkali extractions, chlorine dioxide, oxygen, peroxide and in some cases ozone. The desirable sequences and the number of stages are determined by the nature of the fibre to be bleached, the pulping process, and the use for which the fibre is designated. Thus, over the years, basic processes have been developed which are appropriate for the pulps which result from the different fibrous raw materials (such as agricultural residues, grasses and woods), for the fibres obtained by the various pulping processes (acid; neutral and alkaline cooking, mechanical, TMP, CTMP,and CMP, and for the type of end use (such as printing and tissue grade papers or dissolving pulps.

Kraft pulps are more difficult to bleach because the residual lignin present in the unbleached pulp and even after the initial stages of bleaching is hydrophobic in nature. Kraft pulps accordingly require more stages and chemicals for a given final brightness than do sulphite pulps. The modern trend is toward stepwise solubilization and removal of coloured materials, followed by oxidation of the remaining traces of colouring matter to colourless or soluble products. The bleaching sequences used for the pulp which is not intended for fully bleached market pulp are CEH, CEHH, CED, CEHD, CEDD and so on. The bleachjng sequellces which yield fully bleached market pulps having brightlless level of about 90 are CEDED, CEHDED, C/DEDED, D/CEDED etc. Other sequellces which result ill significant reduction in bleach plant effluents make use of oxygen and peroxide either as separate stage or in the extraction stages. Such sequences are ODED, CEHDP, OCEDED, C E HD, C E DED etc.

7. Bleaching Practices For Different Types Pulp

Based on the basic principles discussed earlier and the practice of bleaching pulp over several years, some standard practices have been evolved. These practices mainly depend on the nature of the fibre used for pulping, pulp process, and the end use for which the pulp is intended. Besides, there are factors such as availability and cost of water, steam, electric power, and bleaching chemicals as well as effluent treatment and disposal, climatic conditions, building and equipment costs. The cost of building bleach plant in a developing country is much more than the cost of the same type of mill in developed countries due to non-availability of facilities like cheap electricity, bleaching chemicals, size of the plant, mechanical workshop service and materials of construction for such components as washers, towers and mixers.

There are standard bleaching sequences for softwood and hardwood pulps depending upon the use for which these pulps are intended. It is possible to bleach these pulps to a brightness level of over 90. There are standard bleaching sequences as discussed in previous section. In addition to the requirement of high brightness and better quality pulp, the bleaching practices will mainly be dictated by the environmental considerations.

Pulps made from most of the non wood plant fibres are amenable to easy bleaching with the exception of pulp made .from certain varieties of bamboo. Although bamboo has been classified as a non wood pulping material, its morphology and texture are close to pulpwood characteristics. Many non wood pulps are produced in a low Kappa no. range and respond well to bleaching action. Although in some cases a correlation could be established between the chlorine requirement for bleaching and the lignin content in unbleached pulp, it is offset due to the presence of colouring maters, dirt, shives and other non-cellulosic constituents. It is essential that agricultural wastes be well cleaned and upgraded prior to pulping. The unbleached pulps should be well screened and centrifugally cleaned before the bleaching operation.

The bleaching practices in use for some of the raw materials are given below :

7.1 Bamboo

Bamboo pulp requires a conventional bleaching sequence similar to hardwood pulp bleaching. The CEHH bleaching sequence is the most common in India. The total chlorine consumption to bleach a pulp of Kappa number of 18-20 is 10-12% while for a kappa number range of 28-30, it is 14-16%. Approximately 45-60% of the chlorine is consumed in the chlorination stage, about 30% in the first hypochlorite tower, and the remaining 10% in the last hypochlorite tower. Caustic consumption for alkali extraction is 2-3% for low kappa number pulps and 3-4% for high kappa number pulps. The brighf11ess level attained is between 76 and 80%. The high brightness bleached bamboo pulp can be produced by employing CEHED and CEHEDH, sequences. Application of sulfamic acid in the chlorination controls viscosity and improves bleached yield.

7.2 Bagasse

Well-depithed bagasse requires a minimum of pulping and bleaching chemicals. If bagasse is pulped to a reasonably low permanganate number of 9-12, a brightness of 85% GE can be achieved with a simple three-stage CEH sequence using only 5-6% chlorine. With the addition of less then 0.5% chlorine dioxide in a CEHD sequence, the brightness can be raised to 90 + % GE.

7.3 Cereal Straws

Single stage hypochlorite bleaching is practised in many straw pulp mills to produce pulp of medium brightness (68-70%GE). In pulp mills of medium and large capacity, cereal straws are bleached in a three-stage CEH bleaching sequence. Bleachable grade pulp of kappa number 12-14 can be bleached with 8-10% total chlorine to a brightness of 82% GE or above. Bleached straw pulp beyond 84% brightness is susceptible to colour reversion. A SO_2 treatment following CEH sequence improves brightness stability and, at the same time, acts as an antichlor. Chlorine dioxide is used following the CEH sequence to increase the brightness level to 86-87% GE or more in large mills which can justify the bleaching expense.

7.4 Kenaf

Kenaf is readily pulped by the kraft and soda processes. Whole kenaf pulps bleach readily and have good papermaking properties. Bleaching can be carried out employing the CEH sequence or the CED sequence to produce bleached pulp exceeding 80 and 85 GE brightness respectively.

7.5 Sabai Grass

Sabai grass is used in mills as a supplementary raw material and its low tonnage cannot justify the economics of multistage bleaching. The sabai grass pulp is normally bleached with calcium hypochlorite in a single stage which gives a brightness of approximately 70%. A somewhat higher brightness can be obtained in double-stage hypochlorite treatment which is carried out in special towers by recirculating the pulp with hypochlorite on a semi-continuous basis.

7.6 Reeds

Any common bleaching sequence can be used to obtain a reasonable brightness. With a standard CEH process followed by SO_2 treatment, the kraft pulp can be bleached to a brightness of 77-79% GE with colour reversion of 4-7%. Higher and more stable brightness can be achieved by additional treatment with chlorine dioxide, and the pulp increases in strength by eliminating the hypochlorite treatment.

8. Bleach Plant Effluent Characteristics

The fibrous raw materials essentially consist of cellulose, lignin and other extraneous substances. During pulping mostly 80% of the lignin and other extraneous substances are dissolved in cooking liquor (as black liquor). the aim of the pulping process is to remove all lignin selectively without affecting the cellulose. The residual lignin imparts brownish colour to pulp which can be removed by bleaching with chlorine or some other chemicals. Chlorine is the most widely used bleaching chemical in Indian pulp and paper mills. The conventional bleaching sequence is CEH and CEHH in most Indian mills. The effluents from bleach plant are characterised by their BOD, COD, colour, pH, TOCl (AOX), mutagenicity, acute and chronic toxicity. Easily bio degradable compounds measured as BOD include low molecular weight hemicelluloses, methanol, acetic acid, formic acid, sugars etc. Release of these compounds to receiving waters leads to depletion of dissolved oxygen level.

Slowly biodegradable components measured as (COD-BOD), are high molecular weight lignins, chlorolignins and carbohydrates. The lower the BOD/COD ratio, the higher is the slowly biodegradable components.

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 photo synthesis which is turn reduces the primary productivity in the ecosystem. Colour of the bleach plant effluent varies with its pH.

Normal quantities of water discharges -BOD, colour and suspended solids from a bleached softwood sulphate pulp mill without a recovery system for spent cooking liquor are shown in Table-3. The corresponding pollution load from a pulp mill of the same type with a recovery system but without any special environmental measures taken is shown in Table -4. Condensates (digester, evaporator) and bleach plant effluent contribute with about equal amounts to the BOD discharge while the main part of the colour comes from the bleach plant. Most of the suspended solids is found in the effluents from the cooking liquor recovery and the bleach plant (fibres passing filter wires and screening rejects). Accidental spills may also be responsible for a substantial discharge of suspended solids mainly due to fibre losses.

Table – 3

Discharges to Water from Sulphate Pulping and Bleaching without Recovery

Source	BOD Kg/adtp	Colour Pt-units/adtp	SS Kg/adtp
Debarking*	10-20	25-50	10-20
Digester Condensate	5-10	-	-
Washing Screening	250-350	1000-2000	5-30
Bleaching	15-20	100-200	2-5
Total	280-400	1100-2300	17-55

*Coarse screening of effluent only.

Table 4
Discharges to water from Sulphate Pulping and Bleaching with Recovery

(No special Environment Measures Taken)

Source	**BOD Kg/adtp**	**Colour Pt-units/adtp**	**SS Kg/adtp**
Digester Condensate	5	-	-
Washing Screening	10	20	6
Spills	15	50	6
Evaporator Condensates	8	-	-
Bleaching	15	175	3
Total	53	245	15

Total organically bound chlorine (TOCl) 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. This is a laboratory procedure which is difficult to be followed in mill control.

AOX, adsorb able organic halide (chlorine in this case) 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 TOCl.

AOX = (1.2-2) times TOCl

Under chlorination will increase the difference. The following empirical relationship exists between the charges of chlorine containing bleach chemicals, as active chlorine and AOX value for bleach plant effluent.

$$AOX = K [Cl_2 + ClO_2 /5 + Hypo/2]$$

K = 0.11- 0.14 for kraft pulps.

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

Toxicity is defined m an adverse effect caused by the effluent to a test organism, typically fish or invertebrates over a specific period of time and at a particular concentration of the effluent. Acute toxicity is defined m the effect occurring with in a short period of time (such as 24 hours to 96 hours). Chronic toxicity characteristics are the long term effects of exposure to the effluent and examines the growth, metabolism and reproductive ability.

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.

Typical data of bleach plant effluents from different types of raw materials are presented in Table -5

Table -5
Bleaching Effluents from Different Raw Material

Raw Material	Pulping Process	Kappa Number	BOD (Kg/t Pulp)	COD Kg/t Pulp	Color Kg/t Pulp	TOCI Kg/t Pulp
Bamboo	Sulphate	-	17	90	-	-
Starw	Soda	12	16	60	70	1-2
Eucalyptus	Sulphate	20	14	60	70	2.5
Birch (Hardwood)	Sulphate	20	14	60	70	2.5
Scots Pine	Sulphate	33	15	80	160	3

9. 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 macromolecules 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-orgnics discharged from bleached kraft pulp mi/ls alter the quality of receiving water.

Approximately 300 low molar mass compounds have been identified in BKME, but these only accounts for about 10% of TOCI .The remainder are high molar mass compounds which are generally too large to pass through cell membranes and hence are probably biologically inactive. The main generic types of chlorinated organic compounds are shown in Table 6.

Table 6

Chlorinated Organic Compounds in BKME.

Type	No. of Variables	*Amounts*
Chlorinated Acids	40 types	Upto 50g/t pulp
Chlorinated Phenolics	40 types	Upto 100g/t pulp
Chlorinated aldehydes, ketones & Lactones	45 types	Upto 500g/t pulp
Chlorinated Hydrocarbons	45 types	-
Chlorinated others	20 types	-
Highmolar mass	-	Upto 4kg/t pulp

Chlorophenols and fatty acids are toxic constituents of BKME. The main chlorophenolics found in BKME and listed below in table -7

The compounds responsible for toxicity of C-stage effluents are mainly chlorophenols with catechols and quinones playing lesser role. About 90% of toxicity of E stage effluent is due to 3,4,5, -trichloroguaiacol, tetra chloroguaiacol and several fatty acids (mono and dichloro abietic acid and epoxystearic acid).

Table -7

Range of Concentrations (µg/l) of Main Chlorophenols in Raw and Biologically Treated BKME

Chlorophenol	Toxicity* µg/l	Raw Effluent µg/l	Treated Effluent µg/l
Dichloro catechol	500-1000	12-90	1-120
Dichloro Guaiacol	2300	22-100	12-60
2,4 Dichloro Phenol	2800	9-15	2-51
Tetra Chloro Catechol	400-1500	22-420	2-240
Tertra Chloro Guaiaco	200-1700	<10-620	<1-220
3,4,5, Trichloro Catechol	1000-1500	120-270	2-280
Trichloro Guaiacol	700-1000	<10-340	<1-220
2,4,6, Trichlorophenol	450-2600	<1-51	<1-16

*96 h LC50 value for aquatic organism.

Non chlorinated acids such as resin and fatty acids also have toxic properties. Resin acids appears with pine. The acids include dichloro stearic, epoxy stearic, linoleic. linoleric and oleic.

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

Trichlorinated phenols are susceptible for bioaccumulation in fish at particular pH. It decreases with increasing pH. Mutagenicity is mainly due to chloroacetones, chlorinated furanone and 2-chloropropenol. 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. Both "Dioxin" and "Furans" are generic terms. Dioxins (more correctly Dibenzo-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.

Chlorinated Dioxins and furans have extreme toxic properties which vary depending on mainly the degree of chlorine substitution. There are many possible forms of chlorination, but two of the greatest interest environmentally are:

2,3,7,8, -Tetra-Chloro Dibenzo-p-dioxine (TCD)
2,3,7,8, -Tetra Chloro Dibenzo furan (TCDF)

When the term Dioxin is used it to polychlorinated Dioxins (PCDD) or TCDD and polychlorinated furan (PCDF) or TCDF. These compounds are identified in BKME and mill sludge.

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 compound are the most toxic compounds in bleach plant effluents. The toxicity level of the effluent will depend on the residual lignin content of the pulp or the kappa number of the pulp.

Resin acids and fatty acids are the toxic compounds present in kraft pulping liquor. The amount of resin acids in natural and chlorinated form that ends up in bleach plant effluents depends on the wood species and on the degree of washing of the unbleached pulp.

Traditional bleach plant liquor has also been found to be mutagenic to bacteria based on Ames test. The main chemical contributors are thought to be chloroacetones, chlorinated furanone and 2- chloropropenol.

Most mutagenic compounds are extremely unstable in sea water which rapidly decomposes them.

Free chlorine in effluent is toxic to fish. Hypochlorite, chlorine and chlorate are also toxic compounds but normally these are in low concentration 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 long term effects and lethal accumulation of toxic substances in the organism. Lethal concentrations seldom occur when there is adequate dilution of the effluent. The sublethal effects are seen like biochemical changes when the concentration is above 0.1-0.2 of 96 hour LC50 values. The lethal and sublethal effects are essentially due to low molecular weight chlorolignin compounds aIJd chlorinated resin and fatty acids.

10. Some Comments On Bleach Plant Effluents From Indian Mills

For many Indian mills using hardwood, bamboo and agricultural residues with CEH pulping sequence, the bleach plant AOX levels are far higher than permitted.

Quantity of chlorophenolic compounds present in bleach plant effluents increase with inlet kappa number of unbleached pulp. Chlorocatechols are predominant in C stage while chloroguaiacols are predominant in E stage. Di- and Tri-chlorophenolics are major fraction of identified chlorophenolics. The concentration level of most of identified chlorophenic compounds are below the reported 96 LC50 values except 2,4,6-Trichlorophenol, dichlorocatechol, Pentachlorophenol. The untreated bleach plant effluent from C and E stages is toxic. In generate with regard to chlorophenolics release, non-woods like bagasse, wheat straw and kahi are better than bamboo and hardwood.

The concentration of fatty acids (saturated and unsaturated) is higher them the concentration of resin acids in both C and E stages effluents. Concentration of saturated fatty acids in bleach plant effluents is higher than unsaturated fatty acids. On the other hand, the concentration of chlorinated resin acids is much higher than the concentration of chlorinated chlorofatty acids. The nonwood bleach plant effluents have lower levels of resin and fatty acids than in wood based bleach plant effluents. The concentration of various resin and fatty acids are in general below the respective 96 hours LC50 values except for isopimaric and O-methyl podocarpic acids chlorodehydroabietic acid Levopimaric acid and palustric acids. In general nonwood plants generate lower toxicity effluents from bleach plants with regard to resin and fatty acids than wood and bamboo based mills.

11. Steps To Reduce Bleach Plant Effluents

The steps essentially to reduce generation of toxic effluents from bleach plants in Indian mills can be indicated as under.

- The raw material must be properly prepared and pulped with aim to get high selectivity and low kappa number. Newer mills must plan for modified cooking and oxygen delignification .
- Maximum attempt should be made to clean and wash the pulp so ensure minimum carry over of dissolved organics to bleaching. Particle carry over should be avoided by good screening.
- The use of chlorine multiple in first stage bleaching should be kept low (below 0.15) to reduce generation of chlororganics. The attempt to replace chlorine by chlorine dioxide completely is a step in the right direction.

- -Oxidative extraction (Eo, Ep, Eop) step is superior to direct extraction.

- -Reduce/eliminate use of hypochlorite bleaching.
- -Attempt to close bleach plant effluents by recyclingfiltrates concepts of jump stage and split stage should be tried to reduce discharge levels.
- -Ensure proper operation of ETP {aerobic treatment}
- -Evaluate TCF bleaching where feasible.

Indian Industry can make the pulp bleaching environmentally sound by modified cooking, oxygen delignification, good washing and with ECF bleaching. There is enormous scope to improve existing mill operations by careful control of process parameters.

12. Suggested Reading Material

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CESS TRAINING PROGRAMME ON "PULPING BLEACHING & PULP QUALITY" 2nd – 5th DECEMBER, 2002

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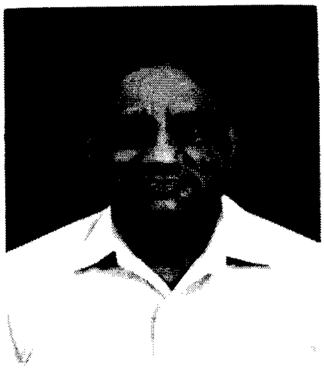
CENTRAL PULP & PAPER RESEARCH INSTITUTE

EVALUATION OF PULPS FOR PHYSICAL AND STRENGTH CHARACTERISTICS



Dr. Y.V.Sood
Scientist E-II, SPPMC Division
CPPRI, Saharanpur

About The Author

Dr. Yasho Vardhan Sood is B.Sc.(Hons.), M.Sc.(Hons.) in Physical Chemistry and D.Phil in Chemistry. He has got advanced training in Paper making, Printing and Sophisticated modern paper testing instruments handling at PIRA (U.K.), IGT (Holland), APPI Monash University Australia and L&W Sweden. He has about 28 years experience in Applied Research in different areas of Paper making in mill and Central Pulp & Paper Research Institute (CPPRI). He is presently a senior Scientist in CPPRI. He had published 80 Research Papers and Technical reports in National and International Journals.

Evaluation Of Pulps For Physical And Strength Characteristics

Y.V. Sood*

1. Introduction

To control the quality of any industrial process it is important to evaluate the raw material, end products and intermediate manufacturing processes. To do so an efficient, accurate and relevant testing is needed and its importance has increased now a days due to global competition and the processes becoming sophisticated with tighter tolerance variation. For any paper grade, pulp quality is the major contributing factor. So it become necessary that the pulps are evaluated for various characteristics according to standard procedures. The importance of such evaluation becomes more when a paper mill is using purchased pulp and paying substantial amount for it. Basically there are two broad objectives for pulp evaluation:

- Testing the quality parameters of specific pulp.
- Comparing the paper making potential of different pulps.

2. Pulp Evaluation Methods

Pulp evaluation methods have been formulated by different organizations like ISO, SCAN, TAPPI, and APPITA. The list is given in Table I. All these standards are similar in their main principles but differ in some details. One of the main differences amongst them is the atmospheric conditions used during testing. Different standard atmospheric conditions have been prescribed in different standards (Table II).

2.1 Sampling Of Pulp For Testing

For proper testing, representative sampling of pulp is important. The selection of sampling method and actual sampling must be carefully done keeping in view that pulp itself is heterogeneous in nature due to variation in wood quality, which is changing from time to time in the process. The sample should be stored properly and it depends on pulp type. Mechanical pulp slurry starts to deteriorate at room temperature in matter of days. Even in cold room conditions, the storage time has limitations. Chemical pulps can be stored for longer time especially if it is bleached. For longer storage one possibility is freezing, but properties of chemical pulp change in the freezing and defrosting process (1,2). With mechanical pulp, freezing changes are minimum.

*** Scientists, SPPMC Div. CPPRI, Saharanpur, U.P – 247 001***

The storage time can also be extended using biocides. Small dosage of formaldehyde may be used to prevent degradation. Pulp dried to 90% of solid can be stored for long period at room temperature.

Table 1

Different Standards For The Evaluation Of Pulps

Parameter	ISO	SCAN C chemical pulp M Mechanical pulp	TAPPI	APPITA
Sampling for Testing	7213			
Dry matter content	638	C 3	T 412	
Stock concentration	4119	C 17, M 1	T 240	
Standard water for physical testing	14487	CM 58		
Laboratory wet disintegration	5263	C 18, M 2	T 205	
Hot-disintegration of mechanical pulp		M 10	T 262	
Fibre length by classification (McNett)		M 6	T 233	
Fibre furnish analysis	9184	G 3, G 4	T 401	
PFI-mill beating	5264-2	C 24	T 248	
Valley-beating	5264-1	C 25	T 200	P 209-TS 75
Jakro-mill beating	5264-3			
Canadian Standard Freeness	5267-2	C 21, M4	T 227	
Schopper-Riegler	5267-1	C19, M 3		
Sheet forming ➢ Conventional method ➢ Rapid Kothen method ➢ Sheets for diffuse blue Reflectance factor (ISO brightness)	5269-1 5269-2 3688	C26, M5 CM 11	T 205 T 218	P 203-M 75
Measurement of diffuse blue reflectance factor (ISO brightness)	2470	P 3	T 452 T 525	
Standard atmosphere for conditioning and testing	187	P 2	T 402	
Laboratory sheets ➢ Determination of physical properties	5270	28, M 8	T 220	P 208-M 75

ISO- International Organization for Standardization
SCAN- Scandinavian Pulp, Paper and Board Organization
TAPPI- Technical Association of the Pulp and Paper Industry (USA)

APPITA- Australian Pulp and Paper Industry Technical Association

Table 2

Atmospheric Conditions Prescribed In Different Standards For Paper Testing

Country	Standard method	Relative humidity (%)	Temperature °C
Australia	APPITA P 415 m-73	65±2	20±1.7
Britain	BPBMA P T3 Sm-1951	65±2	20±1.7
Canada	CPPA A, 4; June 1973	50±2	23±2
France	AFNOR NF Q03-010, March 1958	65±2	20±2
Germany	DIN 50014, Dec. 1959	65±2	20±1
Holland	HCNN N 1108, May 1951	65±2	20±5
India	BIS 1060 (Part I)	65±2	27±2
Scandinavian countries	SCAN P 2:61	65±2 50±2	20±1 23±1
U.S.A.	TAPPI T 402 OS-70	50±2	23±2
USSR	SSSR GOST 7497-55	65±2	20±5
International	ISO 187-1961	50±2	23±1
	or	65±2	27±1
	or	65±2	20±1

2.2 Disintegration Of Pulp

Proper disintegration of pulp is important for the correct evaluation of its characteristics. Dried pulp requires soaking before disintegration. The soaking time depends on the dry matter contents in the pulp. Higher dry content necessiates longer soaking time. Different disintegration conditions have been prescribed in ISO 5263-1995 (E) standard for different pulps (Table III). Mechanical pulps often require hot disintegration to remove latency. Hot disintegration at temperature approximately 85°C is used for mechanical pulps.

Table 3

Conditions To Be Used In Standard Pulp Wet Disintegration Apparatus For Pulp Evaluation As Per ISO 5263-1995 (E) Method

Kind of pulp	Dry matter content	Pulp weight OD (g)	Minimum soaking time	Disintegration volume	Number of revolutions
	<20	30	-	2000	10000
Chemical	20 to 60	30	30 min	2000	30000
	>60	30	4 h	2000	30000
	<20	60	-	2700	10000
Mechanical	20 to 60	60	30 min	2700	30000
	>60	60	4 h	2700	30000

2.3 Different Types Of Laboratory Beaters Available

The common laboratory beaters used in pulp evaluation are

- PFI mill
- Valley beater
- Jokro mill

Some of the features of these beaters are

2.3.1 PFI Mill

In PFI mill beating occur between a bar roll and a smooth beater housing both rotating in the same direction but with different speed. The beating consistency is 10% compared with normal low consistency refining of about 2 to 5% in paper mills. The advantage with PFI mill is that single beating uses small amount of pulp i.e. 30 g. So it is possible to evaluate small quantity of pulp.

2.3.2 Valley Beater

Valley beater has a beater roll and bed plate with loaded lever arm, which controls the beating. Pulp consistency in the beater is about 1.5 %. The benefit of the valley beater is that the large amount of pulp in beating (360 g OD) which allows sampling from the beater at selected time interval to provide a complete beating using a single beating.

2.3.3 Jokro mill

The Jokro mill is similar to PFI mill by having no counter bars in the beater housing. Beating occurs between bar surfaces and smooth housing. Pulp consistency is 6%. Jokro mill has six beating chambers each taking 16 g OD pulp.

2.4 Beating Action In Different Laboratory Beaters

The beating action is different in all these three beaters. The main differences are listed in table IV.

Table 4
Difference In Beating Action In Pfi Mill, Valley Beater And Jokro Mill

Action	Valley beater	PFI mill	Jokro mill
Removal of primary walls/outer layer	Main	Less intense	Less intense
Internal and external fibrillation	Little	More	More
Fibre breakage	Significant	Less	Less

In many cases the PFI mill and valley beater classify pulp in the same order, but in some cases the results differ (3,4,5).

2.5 Preparation And Evaluation Of The Hand Sheets

The handsheets can be prepared and evaluated by any standard test method like ISO, TAPPI, APPITA or SCAN. Depending on the model of sheet former round or squared sheets are formed. In some places Rapid Kothen Sheet former is used. The properties achieved with a Rapid Kothen paper former differ to some extent from the results with the conventional method (10). When comparing the pulp evaluation results with paper from paper machine one should remember that there is clear difference between handsheets and paper from paper machine due to forming step. The orientation of fibre in handsheets is isotropic whereas in case of paper on paper machine it increases from upper side to wire side. The fines content in the wire side of handsheets is more whereas it is reverse in the case of paper made on paper machine. To get proper test results for handsheets it is important that the number of replications for each test is sufficient. ISO standard has prescribed the minimum number of replication for each test, which is given in Table V. To get these the prachce of cutting handsheets being followed in CPPRI is given in Fig 1. The different properties should be expressed as indicated in ISO:5270-1998 (E) Standard (Table VI). Some of the typical characteristics of different pulps evaluated at CPPRI are given in Table VII for reference.

Table 5

Minimum Number Of Sheet Piece To Be Tested For Different Characteristics

Property	**Standard method**	**Target grammage**	**Test piece diamension (mm)**		**Minimum number of test piece**
			Length	**Width**	
Tensile Index	ISO 1924-2	60 or 75	100±2 between clamps	15+0.2 -0.1	8 from at least 4 sheets
Tear Index	ISO 1974	60 or 75	According to apparatus		$2^{(1)}$ from at least 4 sheets
Burst Index	ISO 2758	60 or 75	Wide enough to securely clamped		8 from at least 4 sheets
Folding endurance	ISO 5626	60 or 75	According to apparatus 15±0.1		
Resistance to beating	ISO 2493	(2)	≥70	38±0.2	6 from at least 2 sheets
Flat crush resistance	ISO 7263	(2)	≥150	12.7±0.1	10 from at least 2 sheets
Compresion-Ring	ISO 12192	(2)	150 to 152.5	12.7±0.1	10 from at least 2 sheets

(1) One test piece consists of four cut from at least two trimmed sheets

(2) Unspecified

Table 6

Formula To Calculate Different Properties As Per Iso 5270-1998 (E) Method And Their Expression

S. No.	Property	Formula	Units of Expression	Report to nearest
1	Apparent Density	grammage thickness (micron)	g/cm^3	Two significant figures
2	Tensile Index	Tensile (N) Width of sheet (m) x grammage	N.m/g	0.5
3	Tear Index	Scale Reading (mN) x pendulam factor grammage	$mN.m^2/g$	0.1
4	Burst Index	Bursting strength (kPa) Grammage	$KPa.m^2/g$	0.1
5	Air permeance Gurley	127 t (s/100)	Micrometer Pascal second	Two significant figure
6	Folding endurance	Log (Fold number)	-	Two significant figure
7	Bending resistance index	Bending resistance (mN) x 10^6 $(\text{Grammage})^3$	Nm^6/kg^3	Three significant figure
8	Flat crush resistance index	Flat crush (N) Grammage	$N.m^2/g$	Three significant figure
9	Ring crush resistance index	Ring crush (N) Length (m) x grammage	N.m/g	Three significant figure

Table 7

Characteristics Of Some Paper Making Bleached Pulps At 350±50csf

Raw material	**Tensile Index (N.m/g)**	**Burst Index (kPa.m^2/g)**	**Tear Index (mN.m^2/g)**	**Sp. Scat. Coff. (m/kg)**
Mixed hard wood	48-64	2.8-4.3	8.1-9.0	34.2-36.3
Eucalyptus	60-78	3.2-4.9	7.0-10.0	36.0-42.0
Bamboo	52-60	3.0-3.9	15.5-17.0	27.0-29.2
Softwood Imported	70-80	4.9-6.0	11.5-15.0	20.7-22.1
Wheat straw	42-48	2.6-3.0	5.2-5.4	26.0-28.0
Rice straw	40-47	2.5-2.7	4.8-5.0	42.0-44.1
Bagasse	45-54	2.9-3.2	5.4-5.6	20.6-22.8

2.6 Interpretation Of Pulp Evaluation Results

To get more information from the pulp evaluation results it is important that comparison is made properly. The practice of comparing the strength properties of pulp at constant freeness has been criticized for many years. The shortcomings of freeness test have been summarized by Clark (6). He has proposed the use of sheet density as a more useful basis for comparison. The reason for this choice has been summarized in reference (7). Rydholm (8) has suggested that the relationship between tensile and tear is also a satisfactory indication of pulp strength and usefulness has been further demonstrated by Mcleod (9).

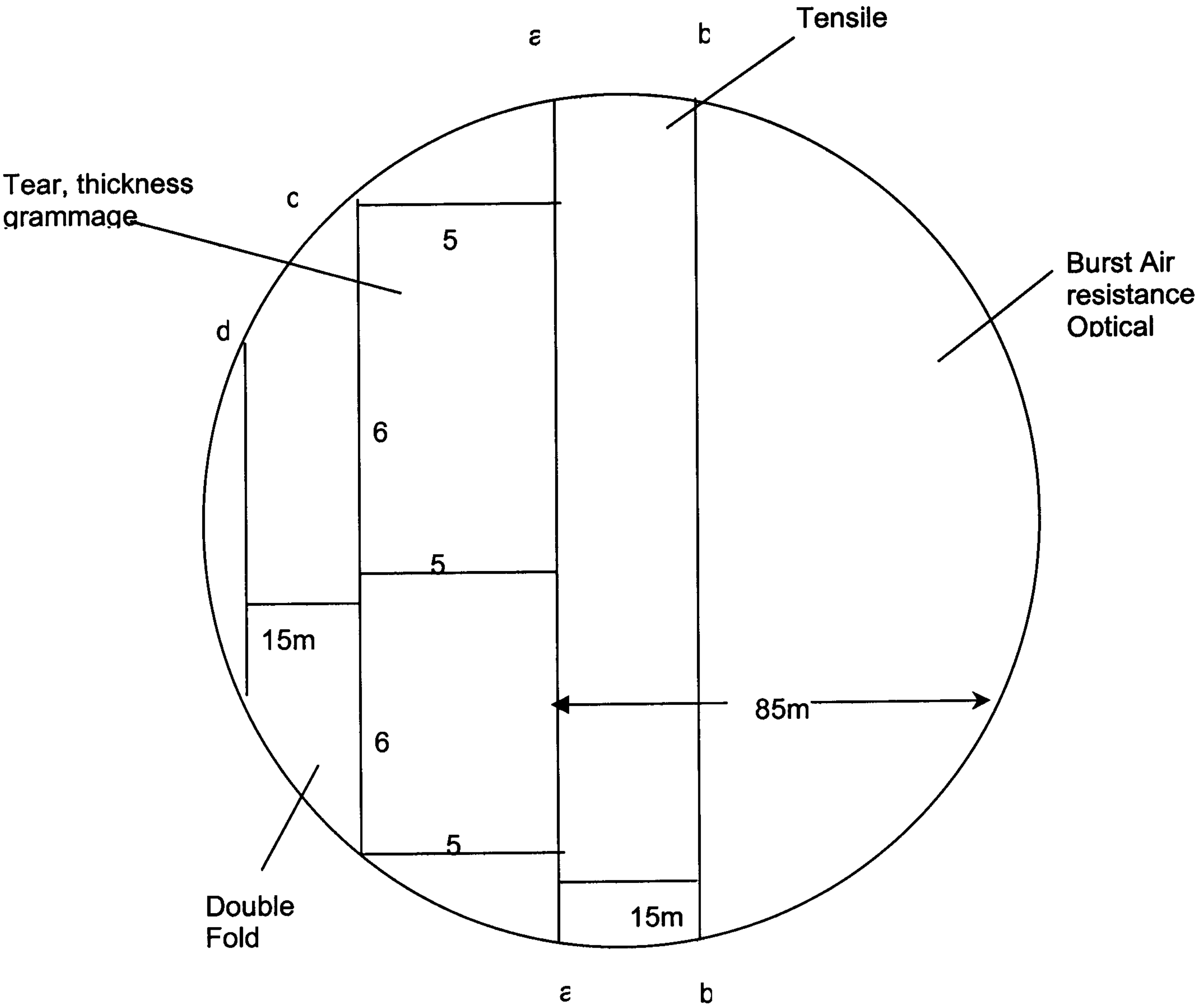


Fig 1 Cutting Of Hand Sheets For Testing

(a) First cut at 85 mm
(b) Second cut
(c) Third cut (15 mm)
(d) Fourth cur (15 mm)

As we know that the main purpose of beating is to improve the wet conformability of the paper making fibres. At the same time, specific bond strength, fines contents, fibre strength and stretch properties may be altered. Whether this alternation is desirable or otherwise depends on the end use of the paper. The effect of processing conditions e.g. pulping, beaching, refining on the fibre and pulp properties or their inter relationship can be estimated from the results of a normal pulp evaluation. The ways of obtaining such information are

- The three parameters which are not affected by intrafibre bonding (apparent density, air resistance and freeness) are all primarily controlled by wet fibre conformability the property level being modified by the fines content. As wet fibre conformability increases, the fibre mat is more readily compacted, both by drainage forces and by wet pressing. This leads to an increase in sheet density and to a reduction in effective pore diameter. As the flow of fluids through porous media is much more influenced by pore diameter than by pore length, the overall effect of reducing sheet thickness and pore diameter is to reduce the permeance of the fibre mat, both to air and to water. The presence of fines in the pulp produces significant changes in all these properties. The voids in the sheet are filled by small particles, giving an increase in sheet density and reduction in effective pore diameter. Keeping this in view by plotting a graph between log (air resistance) against sheet density the relative rates of development of conformability and fines production in pulp can be assessed. The way, in which the relationship is changed, either by changes in pulping or bleaching conditions or by modification to the beating process can be seen from such graph. For example in Fig 2. for treatment A there is greater fines production for a given degree of development of wet fibre conformabilities than treatment B.

- By plotting graph between tensile index and sheet density the changes in the specific bond strength of the pulp can studied. Most of the mechanical strength properties of paper like tensile index, tear index, burst index, stretch, folding endurance are largely dependent on inter fibre bonding although modified by other factors such as fibre length, fibre strength etc. Fibre coarseness is also important but it is not affected much by process conditions. The effect of inter fibre bonding is related to the inter fibre contact area and to the specific bond strength. When comparing the pulp with fibres of approximately in same dimensions one may assure that the area of inter fibre contact can be related to fibre conformability and hence to sheet density. Therefore, change in specific bond strength will lead to a change in tensile strength and sheet density. The effect of fibre strength on the paper strength/sheet density relationship becomes more evident as inter fibre bonding increases. In a well bonded sheet, failure may occur as a result of fibres breaking than through the breaking of inter fibre bonds. If the fibres have been weakened, the probability of fibres breaking is higher. In these circumstances the strength of a well bonded sheet will be lower than it would be. Inter fibre bond breaking was the sole factor controlling strength.

Consider Fig 3, which shows the relationship between tensile index and sheet density for three pulps A, B, C. The tensile index in case of B and C is higher which shows better bond strength than in pulp A. From the difference in slopes it is possible to get information that whether improvement in bond strength will help to improve the bonding properties or not. If the difference in slope is less then initial bond strength is already higher which indicates less improvement is possible.

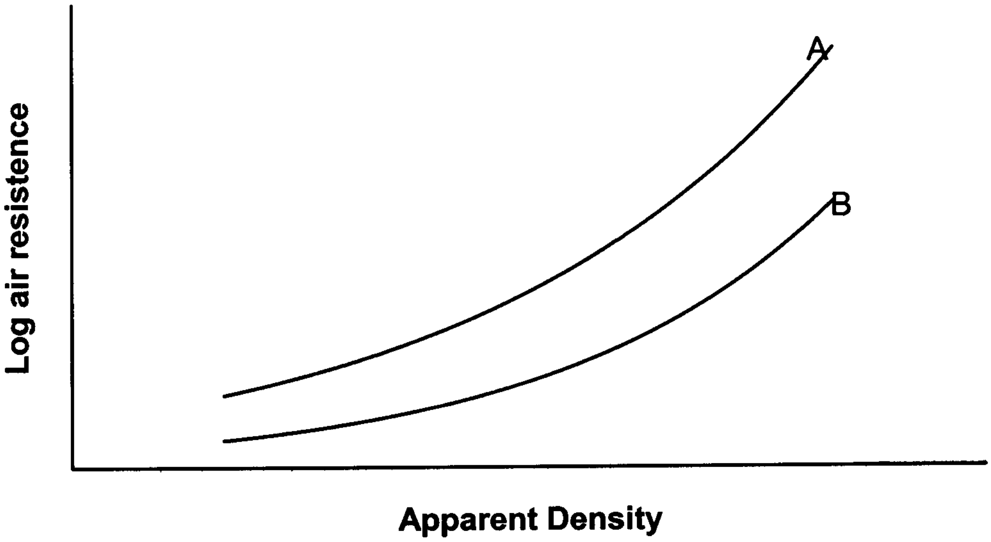


Fig 2: Graph Between Log Air Resistance And Apparent Density For Pulp A And B

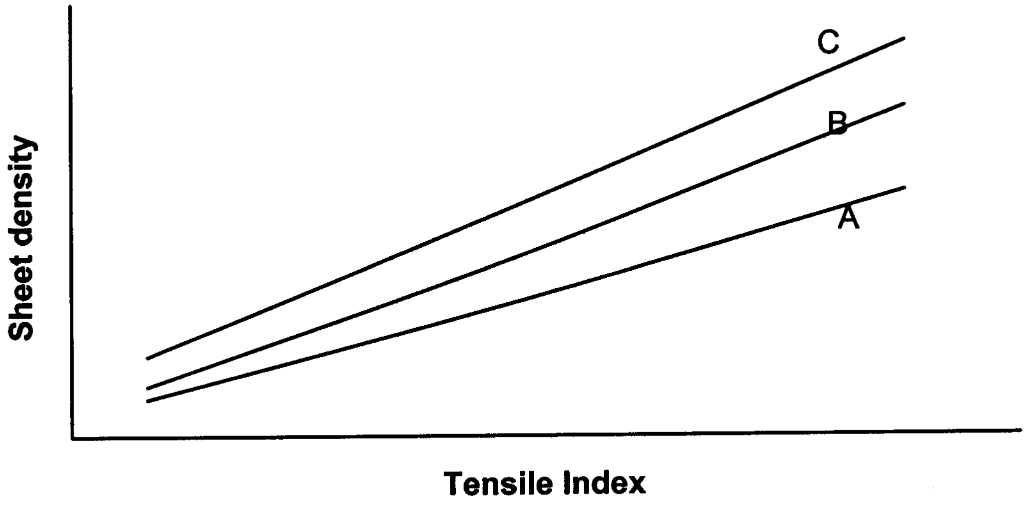


Fig 3 Graph Between Tensile Index And Sheet Density For Pulps A, B And C

The relationship between tensile/tear index provides a very sensitive indication of fibre damage especially in long fibre pulps. The damage may be brought about by pulping or bleaching or by refining. Fig 4 illustrate that pulp B is better than A.

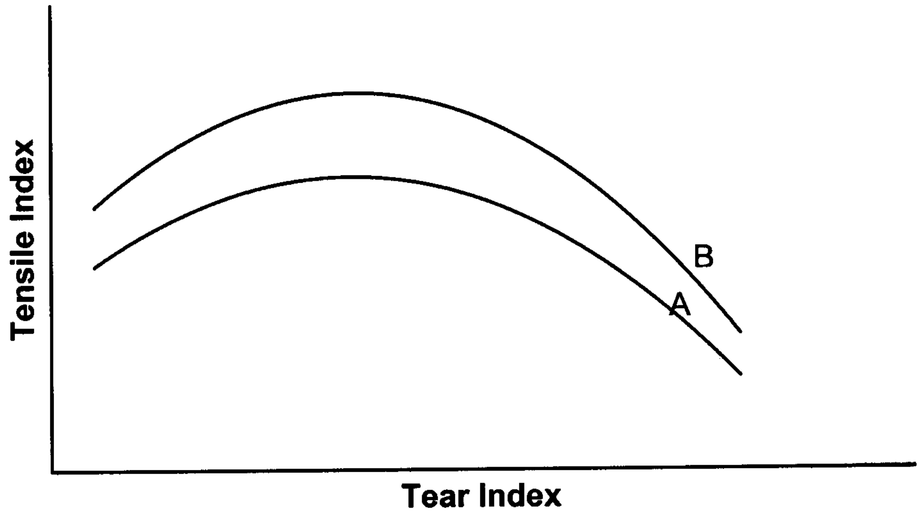


Fig 4 Graph Between Tensile Index And Tear Index For Pulp A And B

By plotting stretch against tensile index it is possible to detect the effect of processing on the development of stretch by mechanism other than a simple increase in inter fibre bonding. Papers such as bag and sack krafts and kraft wrapping are often required to have high tensile energy absorption-a combination of tensile strength and stretch. The stretch is largely controlled by inter fibre bonding. An examination of tensile index/stretch relationship will identify those pulps likely to give a superior product because of better stretch characteristics at a given level of inter fibre bonding. Pulp B is better than pulp A. The advantage of using the tensile index/stretch relationship for purpose of comparison is that the basic effect of increasing inter fibre bonding on stretch may not mark its effect on other factors which influence stretch properties.

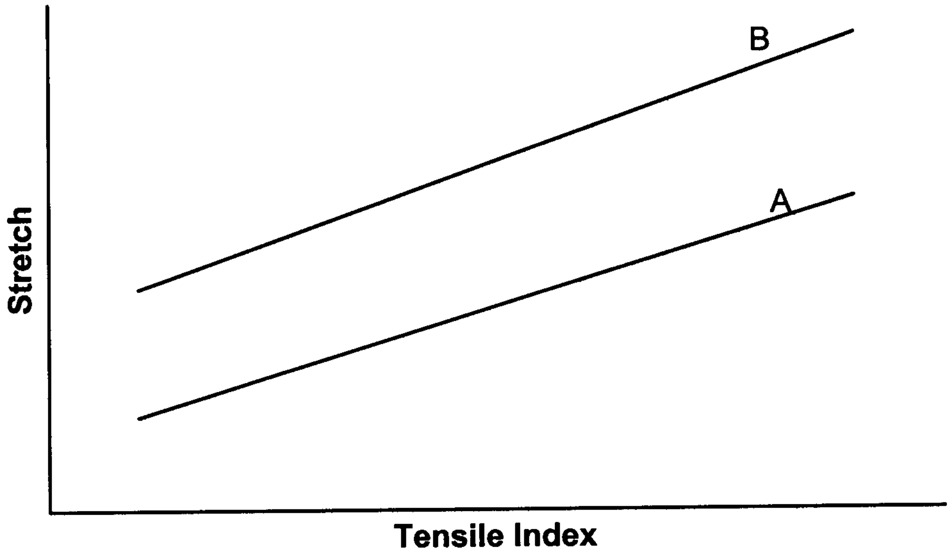


Fig.5 Graph Between Stretch And Tensile Index For Pulp A And B

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SIGNIFICANCE OF OPTICAL PROPERTIES OF PULP AND THEIR MEASUREMENT

Dr. S.K. Kapoor
Sc. - F & Head, SPPMC Div.
CPPRI, Saharanpur

About The Author

Attended advanced international training programme in paper technology in Sweden (1987). Was awarded FAO fellowship in 1976 and got training in Finish Pulp & Paper Research Institute, Bratislava. Have been associated with various UNDP funded projects since then as group leader and National Project Coordinator. Visited several times R&D Institutes and Mills in European and Scandinavian countries. Was UNIDO expert - Environment & Industrial Pollution Management Project, DPRK (North Korea), Member CSIR delegation to Iran technology upgradation in Food Processing, Leather, Pulp and Paper.

Has wide experience related to paper and newsprint development and quality related problems. The research team headed by him won the best research paper award for the studies on Newsprint in an international seminar organized by CSIR.

His contribution has been significant in the Evaluation of pulps, papers and chemical additives for mills, bulk users of paper and various State and Central Govt. agencies, review of IS standards related to paper and it's products, fresh paper saving programme in few mills etc.
Presently head of the stock prepration paper making & conversion division, cppri. (Joined in May 1976)

Publications & Report - 84, Supervised and degree awarded to 2 M.E./ M. Tech. Candidates & 2 D. Phil Candidates

Significance Of The Optical Properties Of Pulp And Their Measurement

Dr. S. K. Kapoor*

1. Introduction

The optical properties of paper/board/newsprint are very important as they give the first visual impression of their quality. The important factors which influence or determine the optical properties of the finished paper/board/newsprint include.

- Type of pulp used
- Presence of fillers
- Surface coatings
- Presence of dyes or colored pigment
- Method of stock preparation
- Method of sheet formation
- Presence of minor ingredients such as rosin and starch and
- Finishing operations that alter the surface of the sheet.

Since the main component of paper/board/newsprint is the pulp apart from fillers and other additives, therefore the optical properties of pulp are very important and greatly influence the visual appearance of the finished products whether it is paper, board or newsprint.

Obtaining the requisite optical properties of pulp is the main aim of bleaching operations in the pulp mill. Primarily the Diffuse reflectance is the basis for the assessment of optical properties of pulps and papers i.e. brightness, scattering & absorption which will be discussed here and few salient features of their measurement methods. A brief introduction of the nature of light i.e. photons/ electromagnetic radiations will make the subject more interesting and simple to understand.

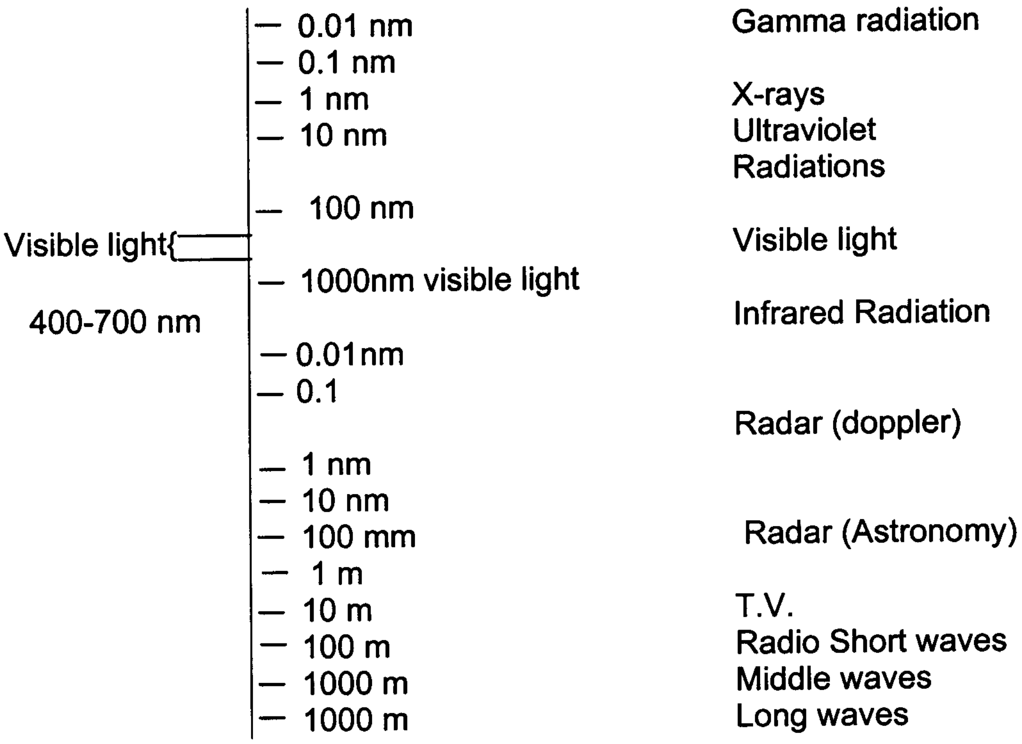
2. Light Is Photons & Electromagnetic Radiation With A Wavelength Of 400-700 Nm-

Physically, light can be described either as small energy particles (photons) which move at a speed of 300000 km/s or as electromagnetic wave which propagate at the same high velocity.

The speed at which the waves oscillate per second is called the frequency and the wavelength is the length of a wave.

***Scientist 'F' SPPMC Div. CPPRI, Saharanpur-247001 (U.P)**

Since the rate of wave propagation is constant, frequency and wavelength are inversely proportional to each other RADIATION WITH A HIGH FREQUENCY THUS HAS A SHORT WAVELENGTH WHEREAS RADIATION WITH A LOW FREQUENCY HAS A LONG WAVELENGTH. The INTENSITY in the radiation is determined by the AMPLITUDE of the oscillation. Man is exposed to electromagnetic radiation of many different kinds from short wavelength high frequency X-ray radiation to relatively low frequency radio waves with wavelength longer than 1 km **(Fig-1).** When the wavelength lies within the narrow interval from 400x 10^9 to 700 x 10^9 m (400-700 nm), the radiation can be perceived as visible light. The radiation comes mostly from the sun. From an intensity viewpoint, 80% of solar radiation is visible light.



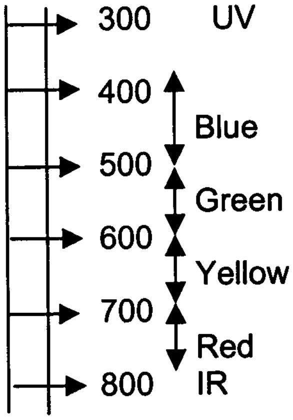
(approximate values)

Fig. 1

The colour spectrum stretches from the blue regions to red with approximate wavelength as-

Violet	-	400 to 450 nm
Blue	-	450 to 500 nm
Green	-	500 to 570 nm
Orange	-	590 to 610 nm
Red	-	610 to 700 nm

When the wavelength is shorter than 400 nm it is called ultraviolet radiation (UV) where as greater than 700 nm is called infrared (IR) Fig. 2.



(approximate values)
Fig.2

Although the UV radiation is invisible, it is important for the optical properties of the pulp and paper. It can cause photo-oxidation of the lignin so that paper tends to yellowing, and at the same time it increases the whiteness impression of products which contain a fluorescent whitening agent since this additive transforms the uv radiation to visible blue light (fluorescence).

At wavelengths above 800 nm, light gives way to infrared radiation (IR) which can also cause colour changes in paper & pulp.

3. Refractive Index

The refractive index determines how the light changes direction and is reflected. The velocity of light is maximum in vacuum 2.999 x 10^{10} cm/sc and decreases in any other medium i.e. water, glass, cellulose etc. The refractive index of a material RI is-

RI of a material = Speed of light in vacuum divided by Speed of light in material

THE VELOCITY DECREASE LEADS TO A CHANGE IN THE DIRECTION OF PROPAGATION OF THE LIGHT

The refractive index of the material also determines how large a part of the light is reflected.

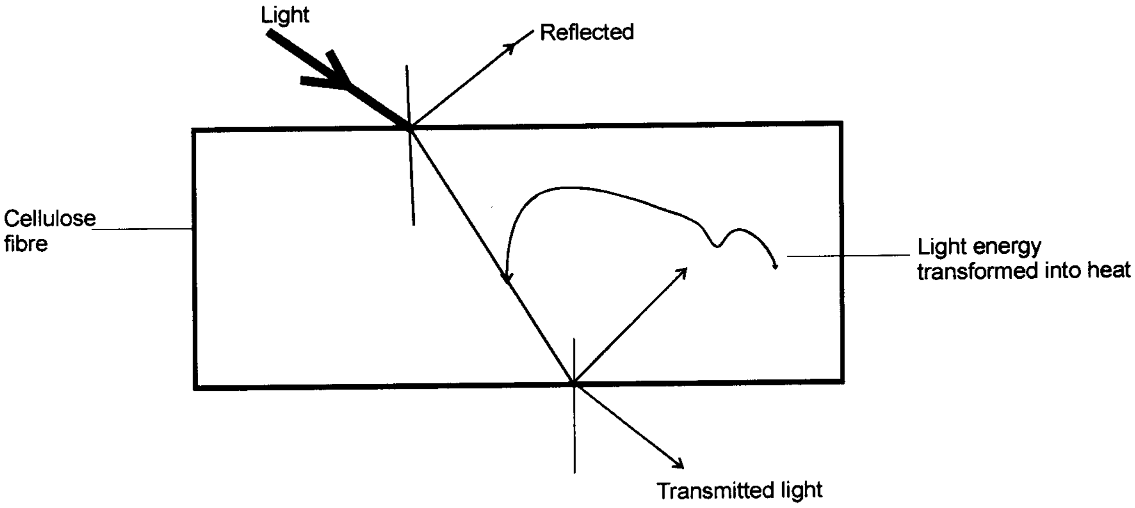


Fig.3

THE REFRACTIVE INDEX IS THUS A BASIC OPTICAL PROPERTY WHICH DETERMINES HOW THE LIGHT IS REFLECTED AND HOW IT CHANGES DIRECTION (IS REFRACTED) WHEN IT PENETRATES INTO A MATERIAL.

When light meets a cellulose fibre, it is reflected from the surface, but most of the light is refracted and penetrates into the cellulose where part of the light energy is transformed into heat. The rest passes through the material, is reflected and refracted at the second surface and leaves the fibre as transmitted light **(Fig.3)**

4. Diffuse Reflection, Refraction, Diffraction And Absorption

A pulp sheet or paper is a complex structure consisting mainly of a fibre network, filler pigment particles and air. Light is reflected at fibre and pigment surfaces in the surface layer and inside the paper structure. The light also penetrates into the cellulose fibres and pigments, and changes directions. Some light is absorbed, but the remainder passes into the air and is reflected and refracted again by new fibres and pigments. After a number of reflections and refractions, a certain proportion of the light reaches the sheet/paper surface again and is reflected at all possible angle from the surface. We do not perceive all the reflections and refractions which take place inside the paper but we perceive that the sheet/paper has a matt white surface i.e. we perceive a DIFFUSE SURFACE REFLECTION. **(Fig 4.)**

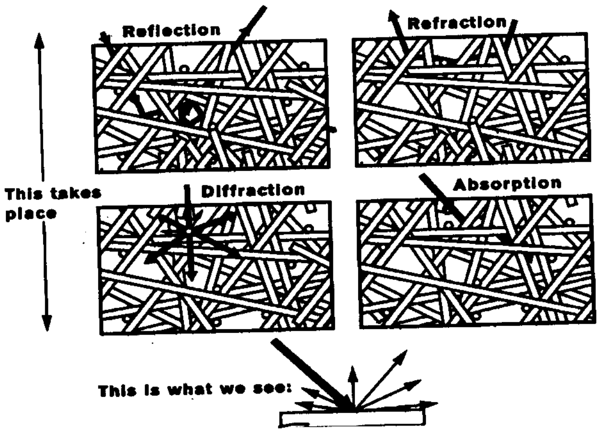


Fig. 4.

When light strikes a paper, a number of different optical phenomenon occur. We perceive all this as a diffuse surface reflection.

Some of the incident light exits at the back of the paper as transmitted light, and the remainder absorbed by the cellulose and the pigments. Besides reflection, refraction and absorption, there is a fourth effect called diffraction.

In other contexts, diffraction is usually the same thing as light scattering, but within the field of paper technology, diffraction is only one aspect of the light scattering phenomenon. Diffraction occurs when the light meets particles or pores which are as large as or smaller than the wavelength of the light, i.e. particles which are smaller than one micrometer. These small elements oscillate with the light oscillation and thus function as sites for new light sources. When the particles or pores are smaller than half the wavelength of the light, the diffraction decrease. It can be said that the light passes around the particles without being affected.

Reflection, refraction & diffraction are together summarized in one concept namely light scattering, which is an important property within the field of paper technology.

5. Light Scattering & Light Absorption

Light scattering occurs in many contexts. A good example is snow. The refractive index i.e. the relationship between the speed of light in ice and in vacuum is 1.3. This leads to the light being reflected and refracted in the many ice crystals. The result becomes a strong light scattering which makes the snow appear white. When the snow melts, the light scattering surfaces disappear, the material becomes transparent and the white impression disappears.

THE LIGHT SCATTERING IS THUS DEPENDENT ON THE REFRACTIVE INDEX AND ON HOW LARGE THE INTERNAL SURFACE OF A MATERIAL IS

The LIGHT ABSORPTION is a measure of how large a portion of the light is absorbed. It is directly related to MOLECULAR GROUPS which give colour, and the higher the light absorption the darker the material appears. When the absorption is different at different light wavelengths, we perceive the material to be coloured.

The Interaction Between Light Scattering And Light Absorption Determines The Magnitude Of The Diffuse Reflection.

For paper sheets the light scattering and absorption coefficient could be determined using Kubelka-Munk theory (details given in ISO:9416:1998 (E).

6. Brightness Of Pulp/Paper

True brightness refers to the lightness or overall reflectivity (i.e visual efficiency) of the pulp/paper. This is a function of the following-

- The illuminant
- The viewing conditions &
- The characteristics of the viewer

While visual efficiency is a function of the reflectance over the visible spectrum, PAPER MARKER'S BRIGHTNESS is based on a measurement of the reflectance of light from white or near white pulp/paper at a single wavelength in the blue region of the spectrum i.e. the light that has a dominant wavelength of 457 nm. The method for brightness was developed at the Institute of Paper Chemistry to provide a method for evaluating the degree of bleaching of pulp. The 457 nm was chosen as the one most sensitive to the change in colour that occurs when pulp is bleached.

6.1 Measurement Of Brightness

All the instruments developed for the measurement of brightness measure the reflectivity at 457 nm. However, they differ in the geometry of the instruments and the method of measurement of the reflectivity. Accordingly they measure either DIRECTIONAL BRIGHTNESS OR DIFFUSE BRIGHTNESS.

6.1.1 Directional Brightness Tappi T 452 ($45^0/0^0$) Ge Brightness Or Ipc Brightness.

The instrument most commonly used in USA was the one developed at IPC & manufactured by the General Electric Company. It was adopted as a TAPPI method in 1941 and is known as TAPPI brightness, IPC brightness or GE brightness. The method was standardized as TAPPI method (T 452) in 1945.

The TAPPI standard directional instrument uses parallel beams of white light and illuminate the paper at an angle of 45^0. The reflectance is measured normal to the paper (i.e 0^0 from the normal to the paper).

The advantages of $45^0/0^0$ geometry are

- it eliminates the influence of gloss
- it gives more stable illumination condition in the measurement of fluorescence because the fluorescent emission from the sample is not mixed with the illumination

The disadvantages are

- the measurement is dependent on the fibre orientation, and different values are obtained along and across the fibre direction.
- The surface roughness also affects the brightness values. (Fig-5)

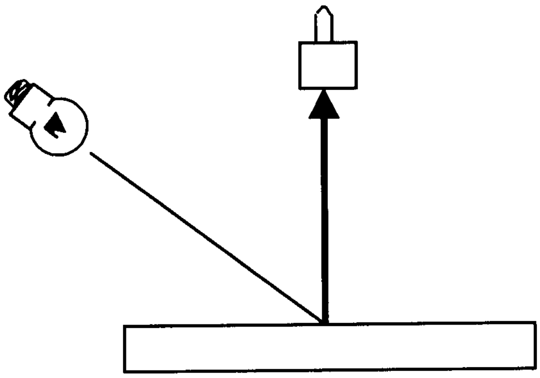


Fig. 5. 45/0^0 Means Illumination At 45 Degrees And A Measurement Made Perpendicular To The Sample.

6.1.2 Diffuse Brightness, Iso 2470(D/0^0) Elrepho Brightness, Iso Brightness, Cppa Brightness.

The diffuse brightness measuring instruments have d/0^0 geometry. The sample surface is illuminated by not a parallel beam of light but the diffuse light striking the sample from multiple angles and the reflected light is measured along the normal to the sample surface. The d/0 geometry as per ISO 2470 is created with a sphere which is coated on the inside with white barium sulphate pigment. The sample is placed against an opening in the sphere, and the sensor is placed perpendicular to the sample. The illumination is screened so that neither the sensor nor the sample are illuminated directly by the lamp i.e. only the light reflected diffusely from the inside of the sphere strikes the sample. Fig.6

The instruments like Elrepho, Datacolour etc have the d/0^0 geometry.

No direct method of transforming values from 45^0/0^0 to d/0^0 is possible.

The standard ISO 2470:1999(E) gives the details for paper, board and pulps- Measurement of diffuse reflectance factor (ISO Brightness) where as TAPPI T452 om-98 gives the details-Brightness of pulp, paper and paper board (directional reflectance at 457 nm)

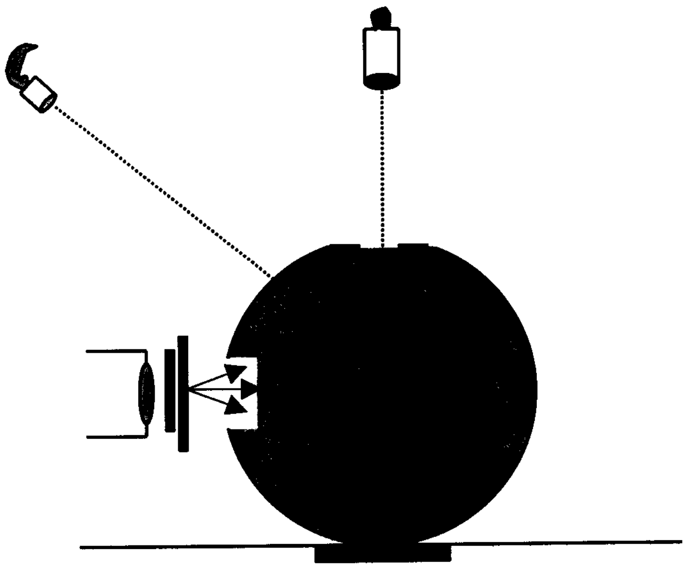


Fig.6. D/0^0 Means That The Illumination Is Diffuse And That The Measurement Is Made Perpendicular To The Sample.

7. Influence Of Different Pulping And Paper Making Processes On The Optical Properties

7.1 Bleaching

Bleaching of pulp can drastically change the appearance of the paper from the brown of unbleached Kraft pulp to the extremely light of highly bleached pulp.

Unbleached pulp has a high light absorption in the blue part of the spectrum. In bleaching, the light absorption decreases and, to reach the highest brightness values, the light absorption must be pressed down to very low values, Fig 7

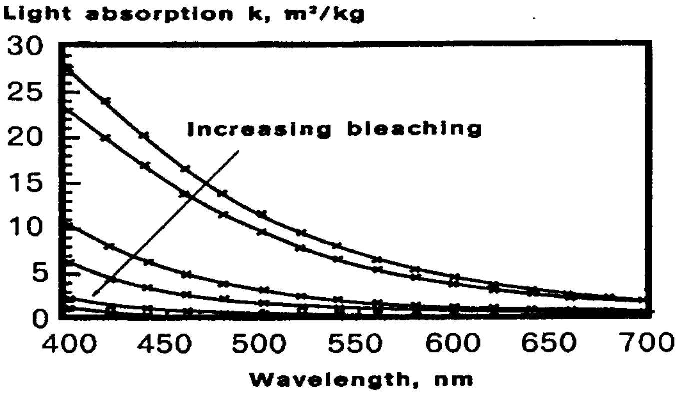


Fig 7 The Absorption For Sulfate Pulp At Different States Of Bleaching. The Pulp With The Lowest Absorption Had A Brightness Of 85 %

Unbleached sulphite pulp and mechanical pulp are relatively light compared with the brown unbleached sulphate pulp. The difference in colour is clearly visible in the light absorption values measured with an R457-function **Table 1**. The light absorption coefficient, which indicates that there are coloured substances in the pulp, is a good measure of the degree of bleaching.

Table 1

Light Absorption And Brightness For Different Types Of Pulp

Pulp type	**K(R_{457}) m²/kg**	**Brightness R_{457} %**
Unbleached sulphate	20-70	33-15
Unbleached sulphite	2-15	70-40
Ground wood pulp	5-12	67-55
Aspen CTMP	5-12	55-45
Bleached aspen CTMP	0.1-2	90-70
Bleached sulphate	0.1-2	90-70

7.2 Beating Of Chemical Pulps

In beating, the fibre bonds increase, and consequently the free fibre surface decreases. The result is that the tensile strength increases while the light scattering decreases. The light scattering ability of different pulps should therefore be compared at the same tensile index. Fig. 8 shows that the long-fibre spruce sulphite and pine sulphite pulps have a lower light scattering at a given tensile index than the hardwood pulps. One of the reasons why eucalyptus pulp has had so great a success is that it gives the highest light scattering at a given tensile strength of the chemical pulps.

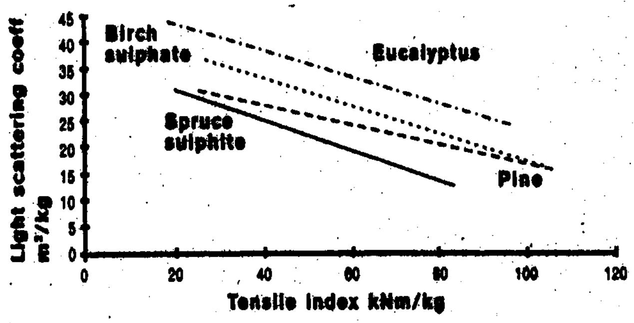


Fig 8 The beating always reduces the light scattering for chemical pulp, but differently for different pulps if the comparison is made at the same tensile strength

The explanation for the difference between different types of wood can be found in the structure of the fibre. Important properties are the number of fibres per gram and the surface area / weight ratio. For slender and thin-walled fibres, the surface area / weight ratio is greater than for broad and thick fibres. This gives more surface both for binding and for light scattering see **Table 2**.

Table 2

Comparison Between Fibre Dimensions And Light Scattering Ability For Different Types Of Wood

	Pine	Birch	Eucalyptus
Length mm	3.0	1.1	0.9
Width µm	38	18-22	12-16
Wall Thickness µm	8	3	2-3
Number of fibres per µ g of pulp	2	8	16
s at a tensile index of 50 kNm/kg	29	34	41

For printing paper, this is important since an in decrease in light scattering gives higher opacity. Hardwood therefore gives more opaque paper than softwood.

8. The Dependence Of Light Scattering On The Specific Surface Area

The specific surface area is the sum of all the small surfaces of fibres, fibrils, lumen etc., which are not bonded to each other. The specific surface can be determined by measuring how much nitrogen in a unimolceular layer can be adsorbed by the material. The value of the specific surface is expressed in m^2/g.

As shown in Fig. 9 there is often a linear relation- ship between the light scattering and the specific surface area of the sheet. The light scattering follows the changes in the specific surface of the sheet in beating and wet-pressing of the sheet, but the relationship is not generally valid since slightly different relationships are obtained for different types of fibres. One explanation is that the shape of the fibre can be important. This has been shown by studying model fibres which are triangular, circular, rectangular etc., Fig. 10.

The different fibre shapes thus give rise to changes in light scattering which do not correspond to the same change in the specific surface area of the material

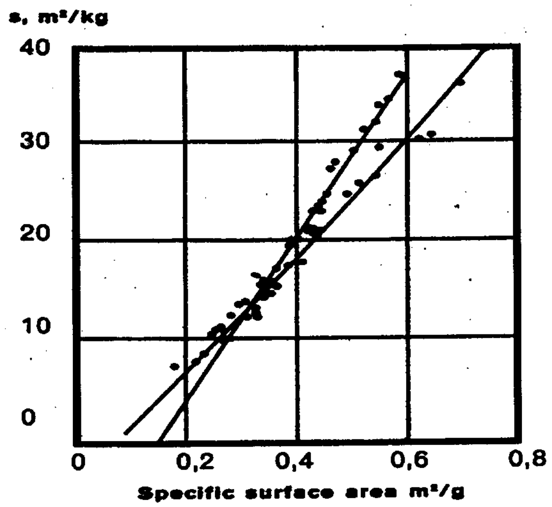


Fig. 9 The Relationship Between Light Scattering And Specific Surface Of Laboratory Sheets Manufactured From Different Types Of Fibres. The Point Indicate Different Wet-Pressing And Beating Conditions.

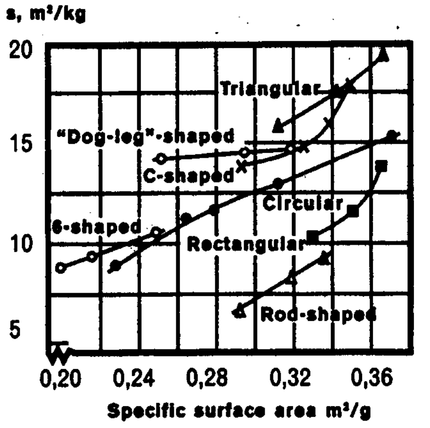


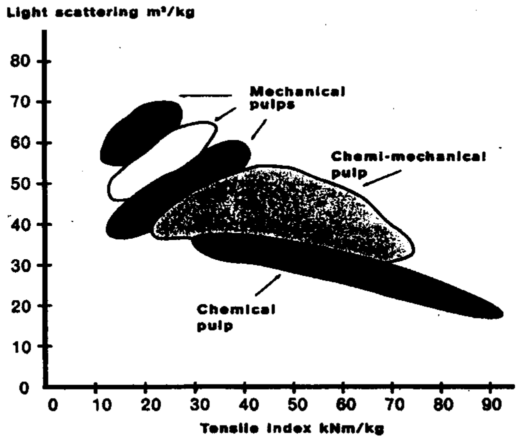
Fig.10 The Relationship Between Light Scattering And Specific Surface Is Influenced By The Shape Of The Fibres. The Figure Shows The Relationship For Model Fibres Of Rayon.

9. Comparison Between Chemical And Mechanical Pulps

The high light scattering associated with mechanical pulps is a consequence of a high content of fines/fine material. The fine material {crushed fibre fragments) also contributes to the bonding strength. This means that the light scattering can actually increase with increasing tensile strength in the case of mechanical pulps, as shown in Fig. 11.

The difference between chemical and mechanical pulp can be explained by the fact that different types of fines are formed when chemical pulp is beaten and when mechanical pulp is ground and refined. The fines in chemical pulp consist of fibrils and delignified fibres and these are strongly swollen by water. In the drying, these fines are attracted towards the fibre surfaces and contribute to the strength of the sheet. The result is a smaller free surface area and thereby lower light scattering

The higher light scattering of mechanical pulp means that it is suitable for printing papers with low grarnmages, such as newsprint and LWC. Since the light absorption coefficient is also high, an opacity increase is obtained when mechanical pulps are mixed into a paper, see Fig.12



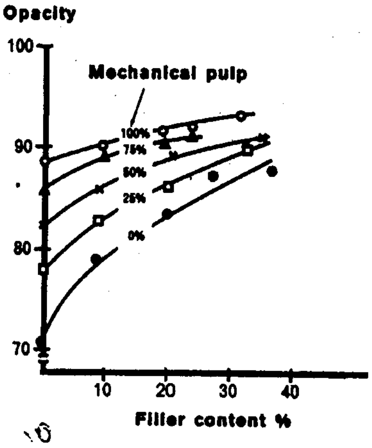


Fig.11 Mechanical Pulps Gave Higher Scattering Than Chemical Pulp

Fig.12 Mechanical Pulp Gives Higher Opacity

10. Filler

When paper contains filler, there are several different factors, which influence the optical properties of the sheet.

The most important are the refractive index of the pigment, the interaction of the pigment with the fibre, the specific surface of the sheet structure, the pore structure and the light absorption coefficient of the pigment.

10.1 The Influence Of Refractive Index

The refractive index of the pigments should be high since the light scattering arises in the interface between materials with different refractive indices. As shown in tableIII, there are two pigments which have a special position, titanium dioxide, TiO2, and zinc oxide, ZnO. These also give high light scattering values and are used as opacity-increasing additives.

TiO2 is a very effective pigment. The addition of 1% gives the same opacity-increasing effect as is obtained with the addition of 10-20% of conventional pigments such as clay and calcium carbonate CaCO3, see Fig.13 and table IV

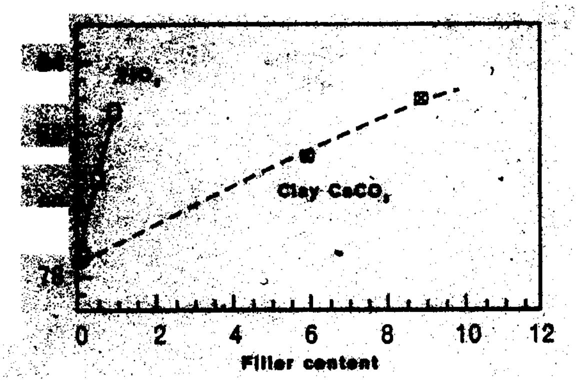


Fig.13. TiO_2 Is An Effective Pigment Which Gives Opacity Even With Small Quantities.

TiO_2 is an extremely effective filler due to its high refractive index which gives the pigment good light scattering properties. The pigment also has a low light absorption in the visible range. It thus gives high opacity and high brightness when it is used as filler and as coating pigment.

Table 3

Refractive Indices Of Different Materials

Material	Refractive index
Air	1.0
Cellulose	1.53
Clay	1.57
$CaCO_3$	1.61
Calcined clay	1.6
TiO_2	2.6
ZnO	2.0

Table 4

APPARENT S VALUE

Filler	s, m^2/kg
TiO_2	Ca
Clay and natural Calcium carbonate pigment (CaCO3)	130-150

TiO_2 has a disadvantage, however. It absorbs the UV-radiation very efficiently. Since fluorescent whitening agents are activated by UV-radiation, they function very poorly together with TiO2. **Fig.14**

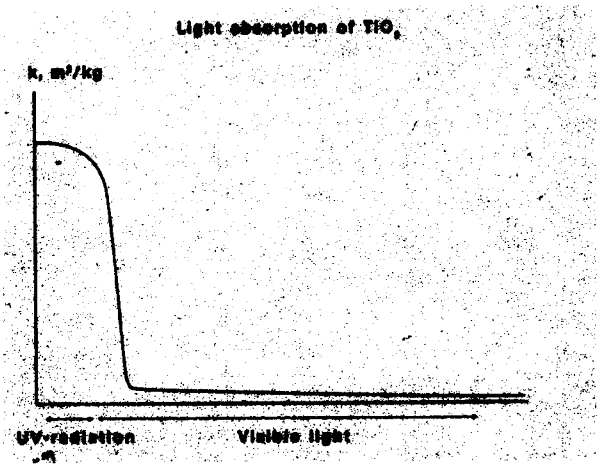


Fig.14. The High Light Absorption In Uv Range Means That Fluorescent Whitening Agents (Fwa) Function Poorly Together With TiO_2.

10.2 The Interaction Between The Fibre And The Filler

The most common pigments, such as clay and $CaCO_3$, have approximately the same refractive index as cellulose, and for these it is primarily the interfaces towards air which are important. Small pigment particles which are well scattered on the fibre surfaces give high light scattering.

The papermaker must therefore find retention agents which give good filler retention without the fillers aggregating together too much, see Fig.15 . It is not only the pigments which contribute to the light scattering of pigment filled papers, however. The fibre itself makes a contribution, which depends on how large a part of the fibre surface is free, i.e. does not participate in bonds

The addition of pigment means that fibre bonds are broken, so that the internal surface area associated with the fibres increases.

This explains part of the light scattering effect. This so-called debonding effect can in certain cases be the dominant contribution to the light scattering of pigment-filled sheets, but the light scattering gain takes place at the price of a reduction in the strength of the sheet.

The different contributions to the light scattering can be determined by an extensive analysis which includes measurements on sheets where the pulp has been beaten to different degrees, where the sheets have been pressed to different densities, and where the fillers have been dissolved out of the sheets (e.g. $CaCO_3$ by acids)

The light scattering of pigment-filled sheets can be divided into three different components

Light scattering from non bonded fibers

Light scattering from pigment particles

Light scattering from fines and fibrils which in the presence of pigments does not collapse on the surface

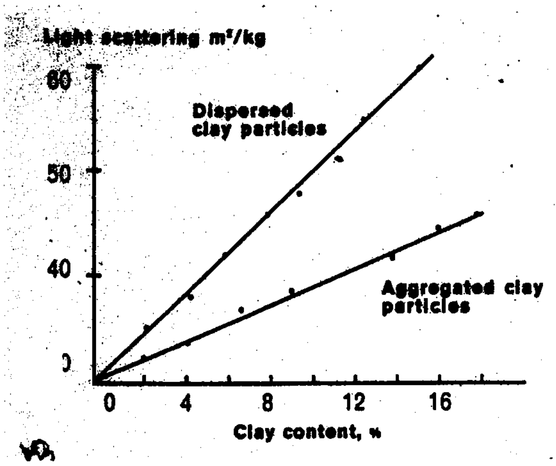


Fig.15. Light Scattering For Laboratory Sheets (Bleached Unbeaten Kraft Pulp) With Dispersed (Finely Distributed) And Aggregated Clay Particles.

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LITERATURE

Effect Of Steam Pressure During Blowing On The Pulp Strength In Jute Pulping

S.V.Subrahmanyam* , R.D.Godiyal* and A.G.Kulkarni**

*** Scientist ** Director**

Central Pulp & Paper Research Institute, P.O.Box 174, Saharanpur – 247001 (U.P.)

ABSTRACT

The cooked mass from the batch digesters in India is normally discharged at elevated pressures. The advantages of discharge of the cooked mass at high pressure are easy removal of pulp from the digester, liberation of individual fibers from the cooked chips and easy handling of liberated fibers in the later stages of fiberline operations. It was noticed in the late eighties of last century that the pulp mass left behind in the digester during the normal discharge has improved strength properties. The differences experienced between two such pulps have lead to the analysis of the reasons for such behavior. Similar experiments were conducted in CPPRI pilot plant on jute pulping. The results indicated that variations in discharge pressures have significant influence on the morphology of the jute fibers and on the strength of fibers as indicated by the intrinsic viscosity. The scanning electron microscopic observations on the individual fibers of high-pressure blow pulps have revealed severe physical damage.

INTRODUCTION:

Pulp fibers are liberated by chemically dissolving the non-cellulose components (mainly lignin) from the raw material, which cements the fibers together. The aim of the chemical pulping is to liberate the fibers with minimum possible damage so that the degree of polymerization of the cellulose component is retained to its maximum possible extent. Kraft process normally removes the lignin more selectively from the raw material and the kraft fibers are the strongest ones in the chemical pulping processes. The unbleached kraft fibers are flexible and dark in color.

The chips come apart into individual fibers by shear forces when the delignification process reaches its optimal level, which happens during the discharging process of the pulp from the digester either by pressure or by pumping. A series of experiments based on 'hanging bucket' method in the late 1980s have shown that the fibers in chip mass retained inside the batch digester at the completion of the cook are more stronger than the fibers blown from the digester. It indicates that the discharge conditions like pressure drop, heat, velocity, frictional forces and steam flashing are responsible for the loss of pulp strength. The experiments of Cyre et al (1989) on cold blow methods involving the addition of dilution liquor and pumping out the pulp mass from cooled and depressurized the digester at regulated flow have yielded a pulp with significantly higher pulp strengths. The adoption of cold blowing techniques has helped in improving the quality of pulp. Based on this background, the institute has carried out experiments in its pilot plant to investigate the role of blow pressure on the strength and quality of jute pulp.

EXPERIMENTAL:

The retted jute bast fiber was procured from West Bengal. The pulping optimisation was carried out in the laboratory using Kraft-Aq. The jute bast fiber was charged with Kraft liquor at 12% active alkali (as Na_2O) and added 0.05% anthraquinone and cooked in the 11 m^3 digester in the pilot plant. The cooked mass was discharged from the digester at three different blow pressures viz 3.5, 4.0, 6.0 and 7.0 kg/cm^2. These pulps were then washed in the laboratory, screened using ‘Serla’ screen. The screened pulp was used to estimate the intrinsic viscosity using CED based on Scan - C15: 62 method. Small quantities of the pulps were dehydrated in alcohol series and transferred to pure xylene. The fibers in the pure xylene were freeze dried to obtain free fibers. These free fibers were spread on the stubs using double sided adhesive tape and coated with gold using sputter coater. Observations were made on these fibers in Hitachi S-2300 Scanning Electron Microscope and some of the images were collected on photomicrographs.

RESULTS AND DISCUSSION:

The pulp strength estimated by the intrinsic viscosity indicates that the jute pulps prepared in the pilot plant and blown at 3.5 kg/cm^2 pressure have maximum strength ie 1100 cm^3/g viscosity compared to the jute pulps blown at higher blow pressures (Table 1). The pulps blown at 4.0 kg/cm^2 pressure have experienced minimum damage ie 1010 cm^3/g viscosity whereas viscosity of the jute pulp blown at 6.0 kg/cm^2 pressure dropped to 690 cm^3/g . The jute pulp blown at 7.0 kg/cm^2 pressure was severely damaged and the intrinsic viscosity of the pulp was dropped to 610-cm^3/g. Similar viscosity loss (from 24 to 36 mPa.s) was noticed in the basket experiments on the softwood kraft pulps by MacLeod and Pelletier (1987), and the strength properties of the mill blown pulps are lower by ~25% in tear-tensile strength compared to pulp obtained in 'hanging basket'.

Table 1. Effect of blow pressure on pulp strength

Sl.No.	Blow Pressure (kg/cm^2)	Intrinsic Viscosity of Pulp (cm^3/g)
1	7.0	610
2	6.0	690
3	4.0	1010
4	3.5	1100

The scanning electron microscopic observations on the jute bast cross sections (Fig. 1) show that the fibers are grouped in to bundles and the fibers are thick walled with a narrow lumen (Fig. 2). The scanning electron microscopic observations indicate that the pulps blown from pilot digester at low blow pressures have yielded the intact fibers (Figs. 3, 5). The observations on the jute pulps made in the pilot plant and blown at different pressures have revealed different degrees of physical damage to the fibers. The visual damage was clearly noticed in the pulp fibers blown at 6.0 kg/cm^2 pressure (Fig. 6). The fibers are completely split open along the length of the fiber in damaged fibers and the fiber wall is shattered in to fibrils (Figs. 6,7, 8). As the morphology of the softwood fibers (fiber tracheids) and the fibers from other sources like hardwoods, bast fibers and straws (libriform fibers) are compared the softwood fibers have wide lumen and porous whereas the libriform fibers from other fiber sources have fibers with narrow to very narrow lumen with either rudimentary pores or sometimes nonporous.

The photomicroscope observations of various softwood kraft pulps from mills by MacLeod and Pelletier (1987) indicated that mill blown pulp fibers exhibit collapse and damage of cell wall and such dislocations in the fibers could easily become failure points in paper webs as suggested by Forgacs (1960). During the discharge of pulps from batch digesters at higher pressures, the damage to softwood fibers will be relatively lower as the pressure within the tubular fiber can be released through the bigger pores connecting the lumen with outside. As the libriform fibers from bast pulp or hardwood pulp have minute or no pores, the pressure gradient will be very high between the fiber lumen and outside environment and such a closed tubular cylinder is bound to shatter. That is the reason why the jute bast fibers are severely damaged in higher blow pressures.

CONCLUSIONS:

- High pressure during the discharge of pulp from pulp severely affects the pulp viscosity.
- The fiber structure is severely damaged at high steam pressure blowing.

ACKNOWLEDGEMENTS:

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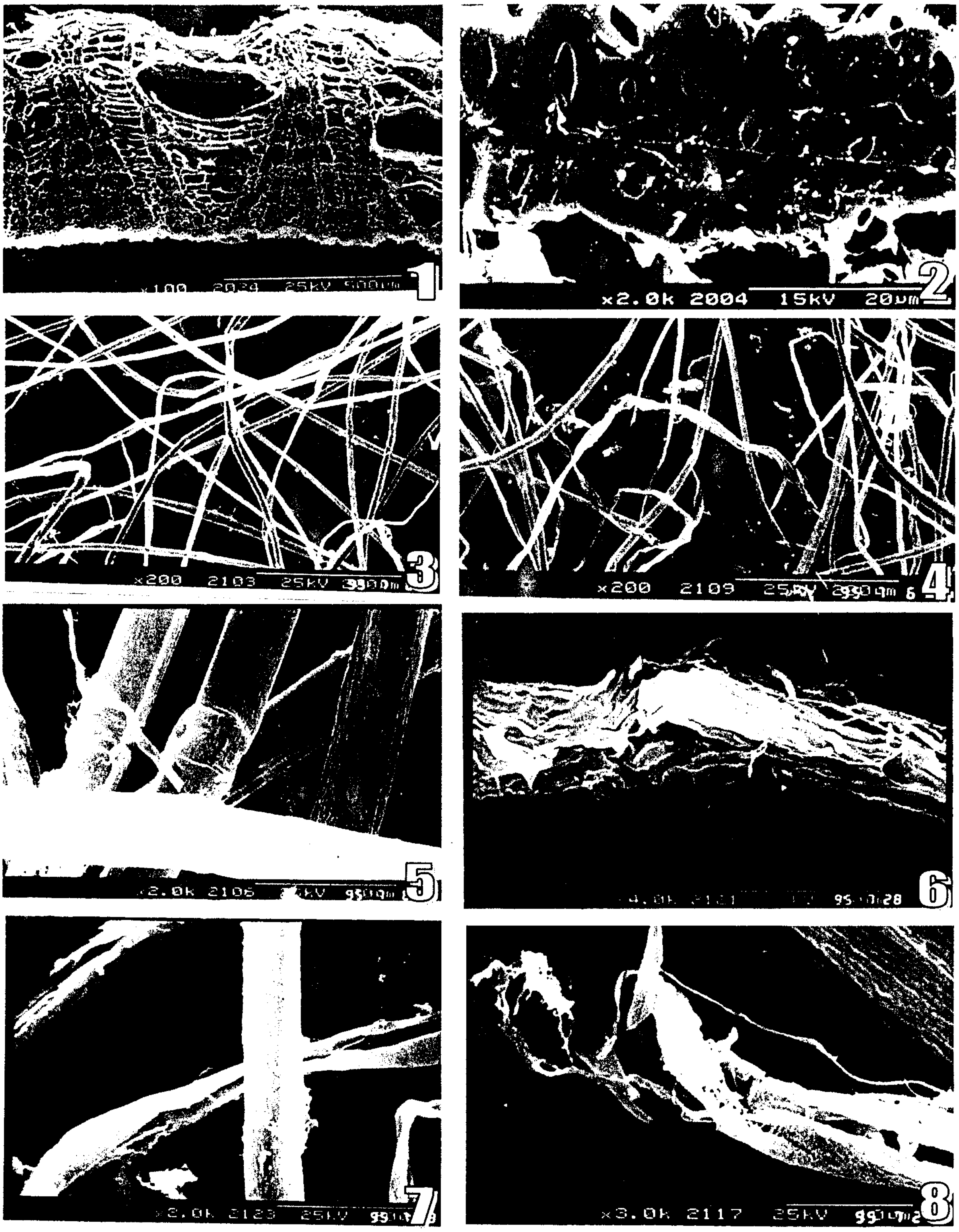

Figures 1 – 9 Jute bast fibers: 1. Cross section of Jute bast; 2. Cross section of a bundle of Jute bast fibers; 3. Jute bast pulp fibers blown at 3.5 kg/ cm^2 pressure; 4. Jute bast pulp fibers blown at 6.0 kg/ cm^2 pressure; 5. Jute bast pulp fibers blown at 3.5 kg/ cm^2 pressure – Note the intact fibers; 6. Jute bast pulp fibers blown at 6 kg/ cm^2 pressure – Note the cracking up of fiber along the length; 7, 8. Jute bast pulp fibers blown at 7.0 kg/ cm^2 pressure – Note the fibers completely split along the length of the fiber and generation of cell wall debris.

A MODEL FOR PREDICTING YIELD IN OXYGEN DELIGNIFICATION OF SOFTWOOD KRAFT PULPS

Thomas J. McDonough
Professor
Institute of Paper Science and Technology
Atlanta, GA 30318

J. Thomas Burton
Senior Research Chemist
PCI Chemicals Canada Inc.
2101 Hadwen Road
Canada L5K 2L3

Andrew E. Yethon
425 Goodram Dr.
Burlington, ON
Canada

ABSTRACT

A predictive model has been obtained for yield in the high consistency oxygen delignification of softwood kraft pulps. The model is based on a large collection of experimental data and is generally applicable to southern and western North American softwood pulps, as shown by its ability to predict effects of time, temperature, degree of delignification and unbleached kappa number for the entire set of 15 diverse softwood kraft pulps evaluated. It was also shown to accurately predict the absolute yield level for 13 of the 15 pulps. The model predicts that, at constant degree of delignification, increasing the temperature will decrease yield, but only at temperatures above 120°C. It also predicts that increasing time will have no effect at high degrees of delignification, but will decrease yield at low degrees of delignification. When kappa number reduction is maintained constant at 40%, very little additional yield loss is predicted when the unbleached kappa number is increased from 30 to 50. High kappa pulps become increasingly vulnerable as the extent of delignification is increased. At low and moderate degrees of delignification, specific shrinkage is sharply lower for high kappa pulps, but this advantage disappears as the extent of delignification is increased. Neither oxygen pressure nor substitution of oxidized white liquor for caustic was observed to affect yield. Comparison with literature data suggests that the model will also be applicable to medium consistency oxygen delignification.

INTRODUCTION

There has been considerable recent interest in the possibility of increasing bleached kraft pulp yields by terminating the kraft cook at a relatively high kappa number and extensively delignifying the resulting pulps with oxygen and alkali [1,2, 3]. In spite of this interest, the literature contains little detailed information on the yield of the oxygen delignification stage and how it depends on important operating variables such as unbleached kappa number. An understanding of these relationships may be expected to enable further yield gains by optimizing the system for maximum oxygen stage yield selectivity.

Proposals for extended oxygen delignification of high kappa pulps have generally involved the use of two-stage medium consistency oxygen delignification systems. This is dictated by the difficulty of obtaining high degrees of delignification in one medium consistency stage. High consistency systems, on the other hand, are known to be capable of higher degrees of delignification. In the present study, we have analyzed a large body of high consistency oxygen delignification data to develop a quantitative relationship between yield and the following independent variables: unbleached pulp kappa number, degree of delignification, time, and temperature. Under given conditions of time and temperature, the degree of delignification was varied by varying the alkali charge.

EXPERIMENTAL

Fifteen different softwood kraft pulps were delignified with oxygen and alkali at high consistency, each under a variety of conditions of time, temperature and alkali charge. Five of the pulps were from southern U.S. mills, while the remaining ten were from northwestern mills. Their kappa numbers ranged from 29 to 75.

For oxygen delignification, the pulp was first pressed to 40% consistency before crumbing. The requisite quantities of sodium hydroxide (or oxidized white liquor) and dilution water were added slowly to the pulp along with Epsom salt, $MgSO_4{\cdot}7H_2O$, (0.1% as Mg^{+2} on O.D. pulp) in a Hobart mixer to reach a final consistency of 27.0%. The pulp was fluffed and placed in the oxygen reactor where oxygen was applied at the desired pressure and temperature adjusted. At the end of the required reaction time the pulp was diluted to 4.0% consistency and thickened.

A total of 169 samples were oxygen delignified, and the yield of each was measured in triplicate by washing, drying and weighing the entire pulp sample, after removing a small portion for determination of kappa number. The resulting data were subjected to robust regression analysis for identification of "outliers," data points that were shown not to be part of the same population as the remaining points, presumably because of an error in handling or characterizing the sample. Ten points were objectively discarded on the basis of their having been assigned zero weight by the robust regression technique. The remaining 159 points were then subjected to conventional multiple regression analysis. Variable selection was begun by allowing the regression program to choose, in stepwise fashion, from among a set of variables consisting of the original variables, together with their squares and pairwise cross products. The resulting variable set, augmented by variables narrowly rejected and some suggested by plotting and inspection of the data, was then used for calculation of all possible regressions. The final variable selection was the one that contained only terms justified by a significance test (t-test at the 95% confidence level) while at the same time giving the highest value of the multiple correlation coefficient (R^2).

RESULTS AND DISCUSSION

The five southern pulps gave the results in Table I, while those for the Northwestern pulps are shown in Table II. The discarded points are shown with yield figures in brackets. Figure 1 is a plot of all 159 remaining yield determinations versus degree of delignification expressed as percentage reduction in kappa number. As shown in the figure and confirmed by the subsequent regression analysis, much of the variation in yield at a given degree of delignification is attributable to unbleached kappa number. As the unbleached kappa number increases, the yield is necessarily lower because more lignin must be removed to achieve the same degree of delignification.

Table I. Experimental data for southern U.S. pulps

Unbl. Pulp Sample	Unbl. Kappa Number	Expt. No.	Temp., °C	Time, min	Pressure, psig	Alkali Source (0=NaOH, 1=OWL)	NaOH, % o.d.p.	Final Kappa No.	Kappa No. Reduction, %	Yield, %
A	31.4	3	120	30	90	0	1.0	21.6	31.2	[98.3]
		4	120	30	90	0	2.0	14.4	54.1	[98.1]
		5	120	30	90	0	3.0	11.9	62.1	[97.4]
		6	120	30	90	0	4.0	10.9	65.3	[96.9]
		7	130	20	90	0	1.5	15.8	49.7	97.0
		8	130	20	90	0	2.0	13.1	58.3	96.7
		9	130	20	90	0	2.5	11.7	62.7	95.9
		10	130	20	90	0	3.0	11.1	64.6	95.1
		11	110	30	90	0	2.5	15.1	51.9	96.9
		12	110	30	90	0	3.0	13.9	55.7	96.8
		13	110	30	90	0	3.5	12.9	58.9	96.5
		14	110	30	90	0	4.0	12.4	60.5	95.7
B	30.2	15	110	30	90	0	1.5	19.7	34.8	97.7
		16	110	30	90	0	2.0	17.7	41.4	96.9
		17	110	30	90	0	2.5	16.6	45.0	97.0
		18	110	30	90	0	3.0	15.4	49.0	96.5
		19	130	15	90	0	1.5	19.0	37.1	96.7
		20	130	15	90	0	2.0	16.3	46.0	96.4
		21	130	15	90	0	2.5	15.2	49.7	95.9
		22	130	15	90	0	3.0	13.7	54.6	95.1
		23	110	20	90	0	1.5	20.4	32.5	98.4
		24	110	20	90	0	2.0	18.1	40.1	97.8
		25	110	20	90	0	2.5	16.7	44.7	97.5
		26	110	20	90	0	3.0	15.8	47.7	97.2

Table I. Experimental data for southern U.S. pulps (cont'd.)

Unbl. Pulp Sample	Unbl. Kappa Number	Expt. No.	Temp., °C	Time, min	Pressure, psig	Alkali Source (0=NaOH, 1=OWL)	NaOH, % o.d.p.	Final Kappa No.	Kappa No. Reduction, %	Yield, %
C	48.2	27	120	30	90	0	2.0	28.5	40.9	96.5
		28	120	30	90	0	3.0	22.4	53.5	95.1
		29	120	30	90	0	3.5	20.3	57.9	[96.0]
		30	120	30	90	0	4.0	20.6	57.3	94.1
		31	110	30	90	0	3.0	24.0	50.2	[97.2]
		32	110	30	90	0	3.5	22.7	52.9	95.1
		33	110	30	90	0	4.0	20.7	57.1	94.6
		34	110	30	90	0	4.5	20.2	58.1	94.3
		35	130	20	90	0	3.0	23.1	52.1	95.0
		36	130	20	90	0	3.5	21.3	55.8	94.2
		37	130	20	90	0	4.0	20.2	58.1	93.9
		38	130	20	90	0	4.5	19.1	60.4	92.4
D	33.8	39	110	30	90	1	2.0	17.9	47.0	97.1
		40	110	30	90	1	2.5	15.8	53.3	96.6
		41	110	30	90	1	3.0	14.6	56.8	95.7
		42	110	30	90	1	3.5	14.2	58.0	94.9
		43	130	10	90	1	2.0	17.6	47.9	96.4
		44	130	10	90	1	2.5	16.1	52.4	95.7
		45	130	10	90	1	3.0	14.9	55.9	95.5
		46	130	10	90	1	3.5	14.4	57.4	94.4
		47	130	10	90	1	2.0	17.6	47.9	96.8
		48	130	10	90	1	2.5	16.4	51.5	96.2
		49	130	10	90	1	3.0	15.4	54.4	95.7
		50	130	10	90	1	3.5	14.7	56.5	95.5
E	32.9	51	110	30	80	1	2.0	17.4	47.1	97.9
		52	110	30	80	1	2.5	15.6	52.6	97.5
		53	110	30	80	1	3.0	14.1	57.1	97.0
		54	110	30	80	1	3.5	13.4	59.3	96.7
		55	110	30	80	1	2.0	17.4	47.1	98.0
		56	110	30	80	1	2.5	15.6	52.6	96.6
		57	110	30	80	1	3.0	14.1	57.1	96.9
		58	110	30	80	1	3.5	13.5	59.0	96.5
		59	130	10	80	1	2.0	17.3	47.4	97.1
		60	130	10	80	1	2.5	15.6	52.6	97.0
		61	130	10	80	1	3.0	14.3	56.5	96.9
		62	130	10	80	1	3.5	13.6	58.7	[97.3]
		63	110	30	80	1	2.5	16.2	50.8	97.6
		64	110	30	80	1	2.5	17.2	47.7	98.5
		65	110	30	80	0	2.0	18.5	43.8	96.8
		66	110	30	80	0	2.5	17.0	48.3	97.3
		67	110	30	80	0	3.0	15.1	54.1	96.7
		68	110	30	80	0	3.5	14.1	57.1	97.2
		69	110	30	80	1	2.0	18.1	45.0	97.3
		70	110	30	80	1	2.5	16.2	50.8	97.1
		71	110	30	80	1	3.0	14.4	56.2	96.7
		72	110	30	80	1	3.5	13.8	58.1	97.1
		73	110	30	80	1	2.0	18.2	44.7	98.0
		74	110	30	80	1	2.5	16.2	50.8	97.1
		75	110	30	80	1	3.0	14.8	55.0	97.0
		76	110	30	80	1	3.5	15.7	52.3	97.0

Table II. Experimental data for northwestern pulps

Unbl. Pulp Sample	Unbl. Kappa No.	Expt. No.	Temp., °C	Time, min	Pressure, psig	Alkali Source (0=NaOH, 1=OWL)	NaOH, % o.d.p.	Final Kappa No.	Kappa No. Reduction, %	Yield, %
F	29.1	77	120	30	80	0	1.5	16.2	44.3	96.7
		78	120	30	80	0	2.0	14.3	50.9	97.0
		79	120	30	80	0	2.5	13.0	55.3	97.2
G	37.9	80	120	30	80	0	1.0	29.6	21.9	98.5
		81	120	30	80	0	1.7	23.0	39.3	97.1
		82	120	30	80	0	2.0	19.9	47.5	96.6
		83	120	30	80	0	2.5	18.0	52.5	95.9
		84	120	30	80	0	3.0	14.3	62.3	95.6
		85	120	30	80	0	4.0	13.3	64.9	94.6
		86	110	30	80	0	2.0	22.4	40.9	97.4
		87	110	30	80	0	2.5	19.8	47.8	96.8
		88	110	30	80	0	3.0	17.3	54.4	96.1
		89	110	30	80	0	3.5	15.3	59.6	95.5
		90	130	15	80	0	1.5	24.6	35.1	97.9
		91	130	15	80	0	2.0	20.8	45.1	96.9
		92	130	15	80	0	2.5	18.5	51.2	96.1
		93	130	15	80	0	3.0	16.8	55.7	95.5
H	36.2	94	110	15	90	0	1.0	29.9	17.4	99.9
		95	110	15	90	0	1.5	25.4	29.8	98.7
		96	110	15	90	0	2.0	21.7	40.1	98.0
		97	110	30	90	0	1.0	27.6	23.8	98.6
		98	110	30	90	0	1.5	22.2	38.7	97.7
		99	110	30	90	0	2.0	18.4	49.2	97.2
		100	110	30	90	0	2.5	16.6	54.1	97.2
		101	130	15	90	0	1.0	27.9	22.9	98.6
		102	130	15	90	0	1.5	21.8	39.8	96.6
		103	130	15	90	0	2.0	18.6	48.6	95.6
		104	130	15	90	0	2.5	15.3	57.7	94.5
I	44.1	105	110	30	90	0	1.5	29.1	34.0	97.7
		106	110	30	90	0	2.0	24.4	44.7	96.6
		107	110	30	90	0	2.5	21.6	51.0	96.2
		108	110	30	90	0	3.0	19.5	55.8	95.4
		109	130	10	90	0	1.5	28.8	34.7	97.6
		110	130	10	90	0	2.0	25.4	42.4	96.9
		111	130	10	90	0	2.5	20.6	53.3	96.0
		112	130	10	90	0	3.0	19.1	56.7	95.4
J	66.0	113	120	30	90	1	5.8	24.2	63.3	90.7
		114	120	30	90	1	6.2	23.0	65.2	89.7
		115	120	30	90	1	6.8	21.2	67.9	89.1
		116	110	45	90	1	5.5	24.8	62.4	90.2
		117	110	45	90	1	5.9	24.0	63.6	90.2
		118	110	45	90	1	6.9	20.6	68.8	88.9
		119	110	45	90	0	5.7	26.7	59.5	91.2
		120	110	45	90	0	6.0	25.1	62.0	90.5
		121	110	45	90	0	6.7	22.8	65.5	90.0
		122	100	45	90	1	5.9	29.6	55.2	91.9
		123	100	45	90	1	6.5	27.6	58.2	91.4
		124	100	45	90	1	7.2	25.1	62.0	90.6

Table II. Experimental data for northwestern pulps (cont'd.)

Unbl. Pulp Sample	Unbl. Kappa No.	Expt. No.,	Temp., °C	Time, min	Pressure, psig	Alkali Source (0=NaOH, 1=OWL)	NaOH, % o.d.p.	Final Kappa No.	Kappa No. Reduction, %	Yield, %
K	71.3	125	110	45	90	1	5.0	32.2	54.8	91.3
		126	110	45	90	1	5.4	31.5	55.8	91.8
		127	110	45	90	1	5.8	28.7	59.7	89.9
		128	110	45	90	1	5.5	31.5	55.8	91.1
		129	110	45	90	1	6.6	25.3	64.5	89.9
L	75.0	130	110	45	90	1	6.3	24.4	67.5	88.9
		131	110	45	90	1	7.0	21.0	72.0	87.6
M	67.6	132	110	45	90	1	6.6	22.5	66.7	[91.1]
		133	110	45	90	1	7.3	21.0	68.9	90.5
		134	110	45	90	1	7.8	20.6	69.5	90.1
N	69.7	135	130	20	60	1	5.8	35.5	49.1	92.9
		136	130	20	60	1	6.1	33.8	51.5	92.2
		137	130	20	60	1	6.3	33.8	51.5	91.7
		138	130	20	60	1	7.0	34.8	50.1	91.6
		139	130	20	90	1	8.7	32.2	53.8	[89.6]
		140	130	20	90	1	9.8	30.2	56.7	[86.8]
		141	120	30	90	1	6.1	30.6	56.1	90.9
		142	120	30	90	1	6.8	28.9	58.5	90.3
		143	120	45	90	1	8.0	26.7	61.7	90.8
		144	120	45	90	1	9.4	24.9	64.3	89.9
		145	120	45	90	1	9.6	25.0	64.1	89.1
		146	120	30	90	0	5.6	28.4	59.3	91.6
		147	120	30	90	0	7.0	26.4	62.1	89.4
		148	120	30	90	0	8.9	23.9	65.7	88.4
		149	110	45	90	1	6.4	30.2	56.7	91.3
		150	110	45	90	1	6.8	27.1	61.1	90.8
		151	110	45	90	1	7.4	26.4	62.1	90.7
		152	110	45	90	1	10.2	24.8	64.4	89.3
		153	110	45	90	0	8.7	27.9	60.0	91.1
		154	110	45	90	0	9.6	25.2	63.8	90.3
		155	120	30	90	1	5.8	26.6	61.8	90.8
		156	120	30	90	1	8.2	25.2	63.8	89.8
		157	120	30	90	1	9.6	21.1	69.7	88.3
		158	120	30	90	0	5.6	27.3	60.8	91.2
		159	120	30	90	0	7.4	24.2	65.3	90.0
		160	120	30	90	0	9.2	21.4	69.3	88.3
		161	110	45	90	1	6.8	29.0	58.4	91.3
		162	110	45	90	1	8.2	27.0	61.3	90.6
		163	110	45	90	1	10.0	21.8	68.7	88.6
		164	110	45	90	0	6.0	29.3	58.0	91.0
		165	110	45	90	0	7.8	25.6	63.3	90.1
		166	110	45	90	0	9.4	22.8	67.3	89.0
O	29.0	167	110	30	90	0	1.0	23.5	19.0	98.4
		168	110	30	90	0	1.5	20.6	29.0	97.1
		169	110	30	90	0	2.0	18.3	36.9	97.5
		170	110	30	90	0	2.5	16.5	43.1	96.7
		171	110	30	90	0	3.0	15.0	48.3	96.9

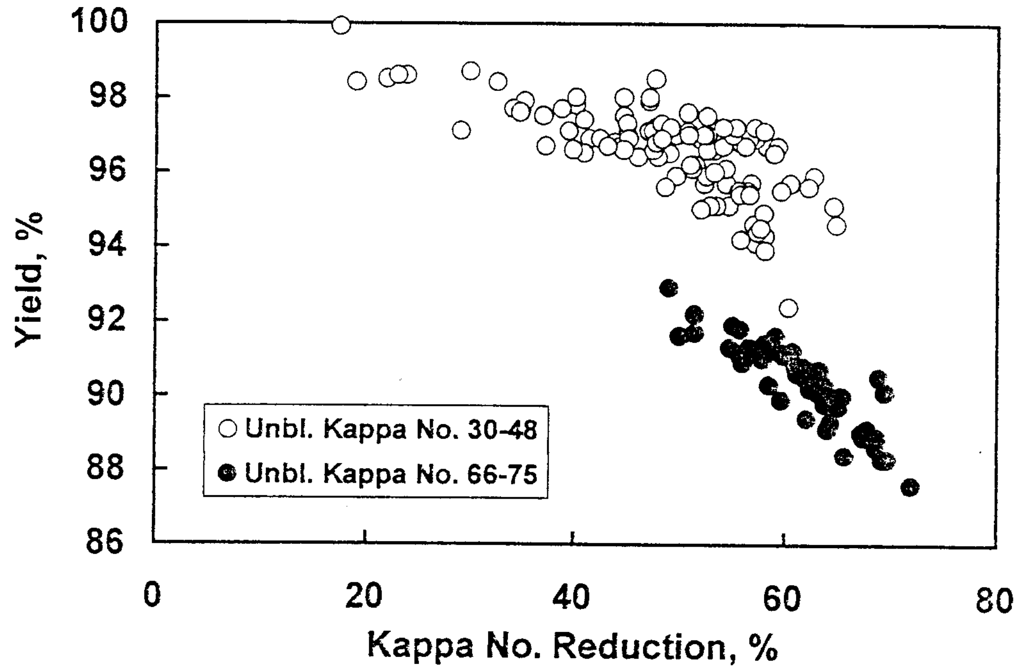

Figure 1. Yield for all pulps vs. degree of delignification

Much of the remaining variation is due to differences in temperature and time, but a significant component was attributable to an unknown characteristic of two of the pulp samples, A and E. These two behaved the same as one another, but differently from all the rest. The other thirteen pulps were also indistinguishable from one another with respect to yield retention and its dependence on the process variables studied. The difference between the two groups was that that the former (pulps A and E) gave a yield that was higher than all the rest by an average of 0.8%, regardless of conditions. This was due either to a systematic laboratory error or to some unknown property of these two pulps. In either case, the model described below appears quite general, inasmuch as it accurately predicts the yield of 13 of the 15 pulps studied, and it accurately describes the dependence of yield on process variables for all 15 pulps. The anomalous behavior of pulps A and E was accommodated in the regression model by including an additional constant term in the equation for these two pulps.

To facilitate the regression analysis, the original variables were nondimensionalized and scaled ("coded"). The defining relationships for the coded variables are given in Table III.

The final regression model is as follows:

$$\text{Yield, \%} = 95.77 + 0.76XA - 0.42XTMP - 0.23\ XTM - 1.18XKA - 1.20XKR - 0.27XTMP^2 - 0.38XKA^2$$
$$- 0.07XKR^2 + 0.19XTM\cdot XKR - 0.54XKA\cdot XKR$$

The R^2 value is 0.980 and the root mean square error is 0.46. The 95% confidence for the mean yield at a given set of values of the independent variables depends on what those values are, but is typically ±0.25%. Figure 2 shows good agreement between observed and predicted values. Figure 3 shows the agreement between observed and predicted yields for three sample cases. For yield prediction, the equation may be used with XA set equal to zero, since the yields of 13 of the 15 pulps were accurately predicted with XA set to zero.

Table III. Defining relationships for the coded variables

Original Variable	Coded Variable	Coding Relationship	Sample Values
Pulp characteristic	XA	1 for pulps A and E; 0 otherwise	
Temp., °C	XTMP	XTMP = (Temp. - 120)/10	-1 when Temp. = 110; +1 when Temp. =130
Time, min	XTM	XTM = (Time - 20)/10	-1 when Time = 10; +1 when Time = 30
Unbl. Kappa no.	XKA	XKA = (Kappa - 45)/15	-1 when Kappa = 30; +1 when Kappa = 60
Kappa reduction (KR),%	XKR	XKR = (KR - 50)/10	-1 when KR = 40%; +1 when KR = 60%

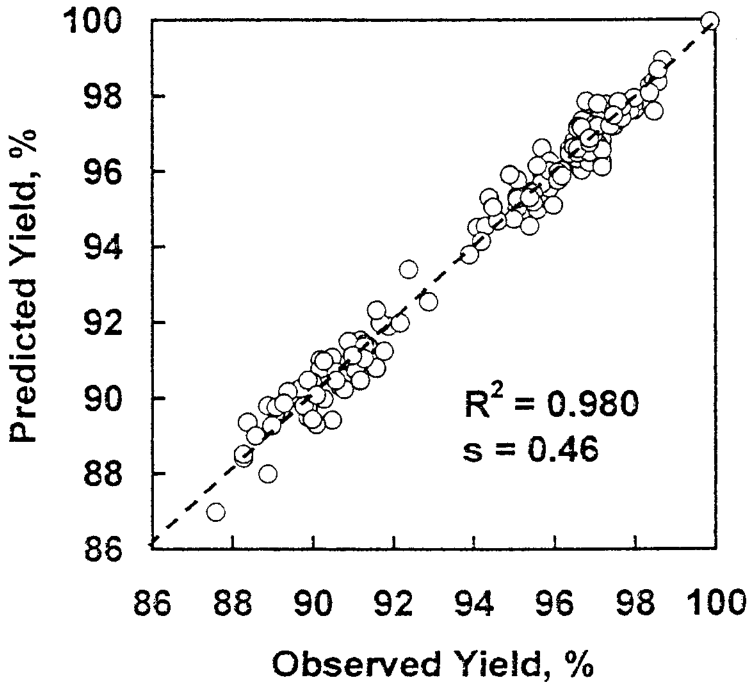

Figure 2. Yield predicted by the model vs. observed yields.

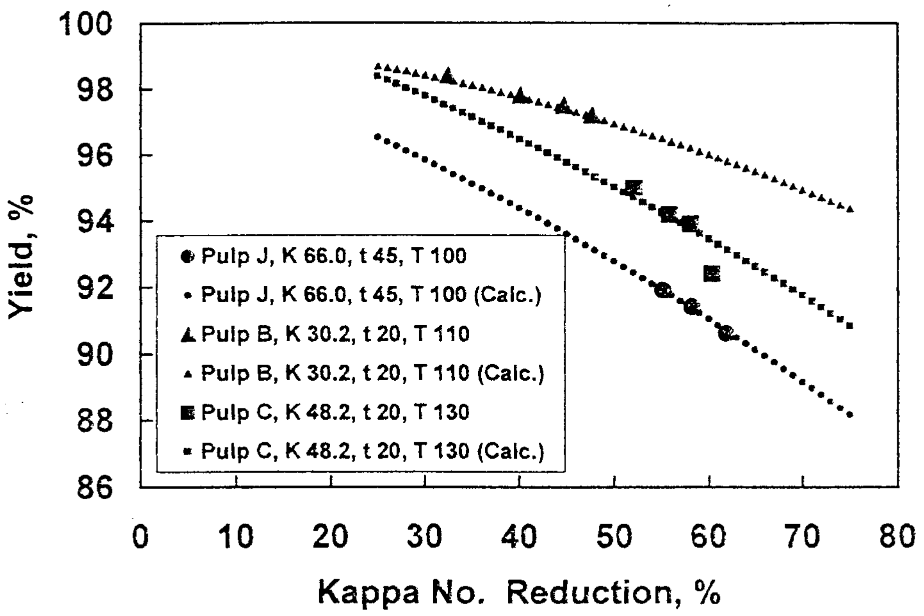

Figure 3. Examples of the agreement between observed and predicted yields.

Examination of values predicted by the model reveals interesting features of the behavior of the system. Figure 4 shows the predicted yield of a Kappa 30 pulp as a function of degree of delignification at different temperatures. It is apparent that increasing the temperature decreases the yield at temperatures above 120°C, while there is little effect below 120°C. This is consistent with the assumption that there are two opposing effects of raising the temperature at a given degree of delignification. One is to decrease the alkali charge needed, which is beneficial for yield preservation, while the other is to increase the rate of carbohydrate degradation relative to that of lignin degradation. The temperature dependence of the latter effect is greater, with the result that yield suffers at very high temperatures.

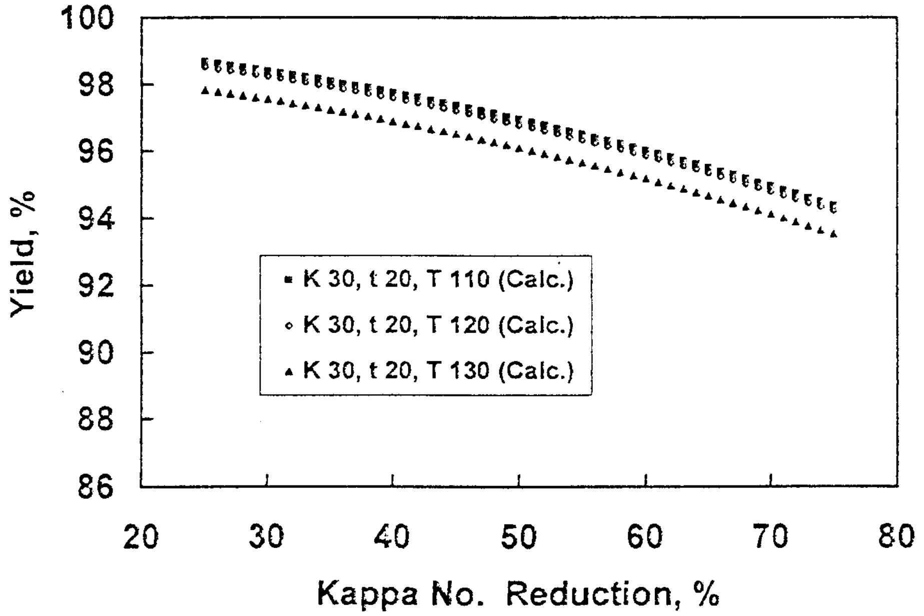

Figure 4. Effect of temperature on predicted yield.

Figure 5 shows the effect of increasing time, which is negligible at high degrees of delignification, but negative at low degrees of delignification. This effect also could be interpreted in terms of two opposing effects. One is the decrease in alkali charge allowed by increasing time when the necessary alkali charge is high, leading to less alkali-induced carbohydrate degradation. The detrimental effect of increasing time when the alkali charge is low suggests the existence of carbohydrate degrading reactions that become important as the pH falls below 10.

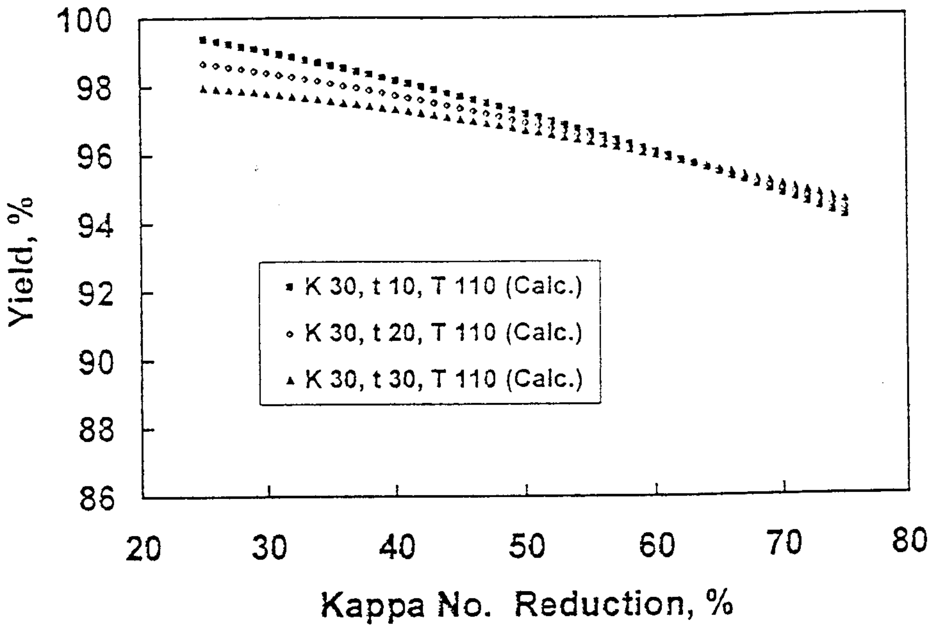

Figure 5. Effect of time on predicted yield.

Figure 6 compares the predicted behavior of pulps at three different unbleached kappa number levels. High kappa pulps, not surprisingly, lose more yield. What is more surprising is that at lower degrees of delignification, the effect of unbleached kappa number is not greater, especially in the kappa no. range from 30 to 45. This is even more apparent when the predicted yield is plotted against unbleached kappa number, as in Figure 7. When the kappa number reduction is maintained constant at 40%, very little yield loss is predicted when the unbleached kappa number is increased from 30 to 50. This implies a smaller carbohydrate loss at the higher kappa number level, since more lignin is lost. It suggests that the lignin in high kappa number pulps is much more reactive towards oxygen and alkali than that present at lower unbleached kappa number. A similar observation has been made by Magnotta *et al.* [1].

Despite their robustness at low degrees of delignification, the high kappa pulps become increasingly vulnerable as the extent of delignification is increased. This is shown by the greater separation of the curves in Figure 6 at high degrees of delignification and the increase in the negative slope of the curves in Figure 7 as the degree of delignification is increased. Table IV illustrates this effect in terms of specific shrinkage (shrinkage per unit of kappa number decrease). At low degrees of delignification, specific shrinkage is sharply lower for high kappa pulps, but this advantage disappears as the extent of delignification is increased. Conversely, increasing the degree of delignification has little effect on the already high specific shrinkage of low kappa number pulps, but when the initial kappa number of the pulp is high, increasing the degree of delignification sharply increases specific shrinkage. In terms of specific shrinkage, combinations of high unbleached kappa number and moderate degrees of delignification are far superior to any other combination of unbleached kappa number and delignification degree.

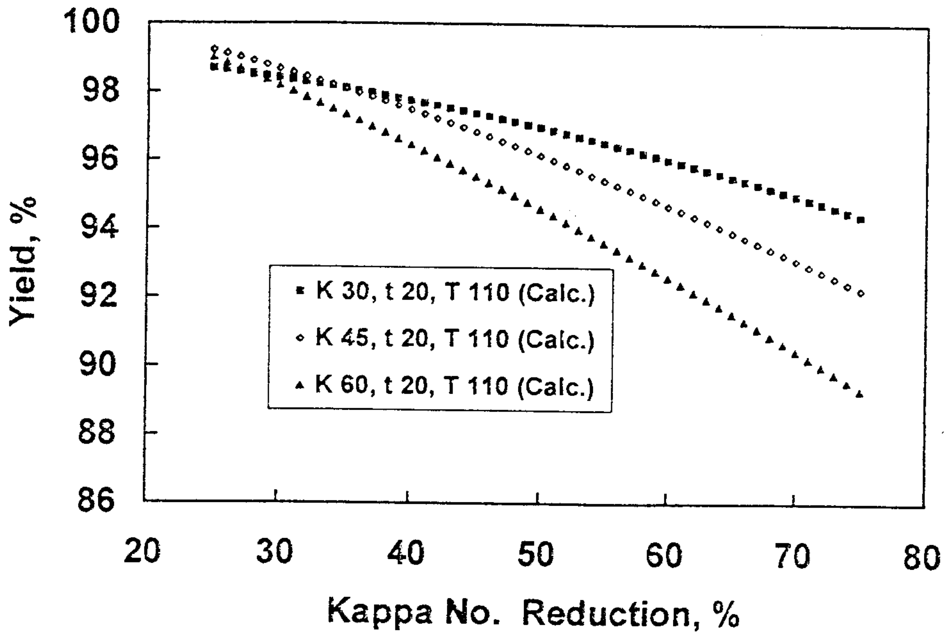

Figure 6. Effect of unbleached kappa number on predicted yield.

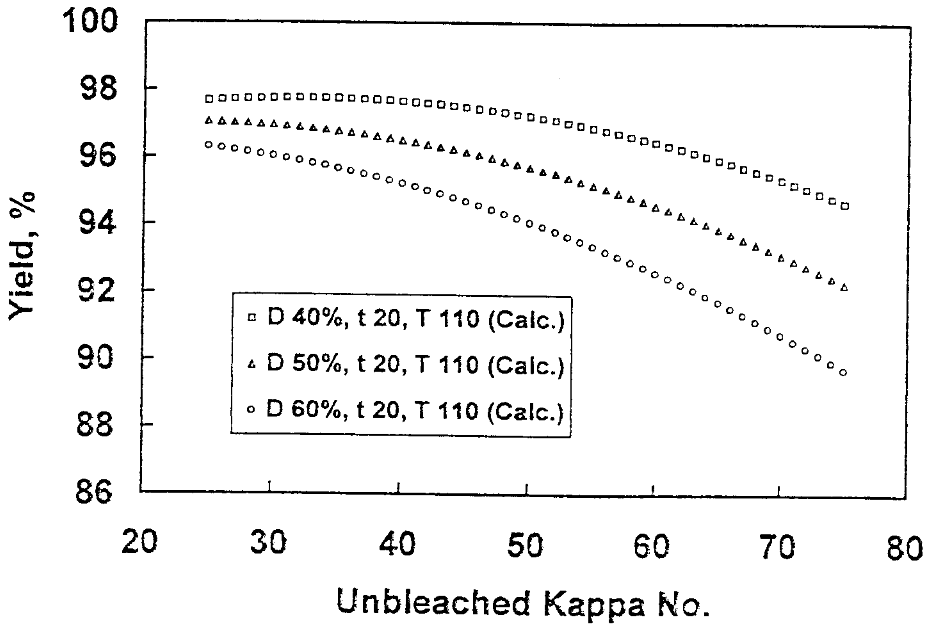

Figure 7. Yield vs. unbleached kappa number at different degrees of delignification.

Table IV. Shrinkage (%/ kappa unit) for different degrees of delignification and unbleached kappa number.

Kappa No. Reduction, %	Unbleached Kappa No. 30	Unbleached Kappa No. 40	Unbleached Kappa No. 50	Unbleached Kappa No. 60
30	0.26	0.18	0.15	0.14
40	0.24	0.18	0.17	0.17
50	0.23	0.19	0.19	0.19
60	0.23	0.21	0.20	0.21
70	0.24	0.22	0.22	0.23

Magnotta *et al.* [1], after approximately 60% delignification, observed specific shrinkages of 0.21 for a 59 kappa pulp, 0.17 for a 50 kappa pulp, and 0.19 for kappa 29 and 38 pulps. These values are in reasonably good agreement with the above data, even though they were obtained in a medium consistency system. This suggests that the model derived here may also be applicable to medium consistency oxygen delignification.

A final observation with respect to the regression model is that it has no terms related to oxygen pressure or type of alkali used (oxidized white liquor or caustic). It may be concluded that these variables do not significantly affect yield.

SUMMARY AND CONCLUSIONS

1. A predictive model has been obtained for yield in the high consistency oxygen delignification of softwood kraft pulps. The model is based on a large number of experimental data and is generally applicable to southern and western North American softwood pulps. This is shown by its ability to predict effects of time, temperature, degree of delignification and unbleached kappa number for the entire set of 15 diverse softwood kraft pulps evaluated. It was also shown to accurately predict the absolute yield level for 13 of the 15 pulps.
2. The model predicts that increasing the temperature will decrease yield, but only at temperatures above 120°C. This suggests that there are two opposing effects of raising the temperature at a given degree of delignification. One is to decrease the alkali charge needed, which is beneficial for yield preservation, while the other is to increase the rate of carbohydrate degradation relative to that of lignin degradation. The temperature dependence of the latter effect is greater, with the result that yield suffers at very high temperatures.
3. Another prediction of the model is that increasing time will have no effect at high degrees of delignification, but will decrease yield at low degrees of delignification. This effect also could be interpreted in terms of two opposing effects. One is the decrease in alkali charge allowed by increasing time when the necessary alkali charge is high, leading to less alkali-induced carbohydrate degradation. The detrimental effect of increasing time when the alkali charge is low suggests the existence of carbohydrate degrading reactions that become important as the pH falls below 10.
4. When kappa number reduction is maintained constant at 40%, very little additional yield loss is predicted when the unbleached kappa number is increased from 30 to 50. This implies a smaller carbohydrate loss at the higher kappa number level, since more lignin is lost. It suggests that the lignin in high kappa number pulps is much more reactive towards oxygen and alkali than that present at lower unbleached kappa number.

5. High kappa pulps become increasingly vulnerable as the extent of delignification is increased. At low degrees of delignification, specific shrinkage is sharply lower for high kappa pulps, but this advantage disappears as the extent of delignification is increased. When the initial kappa number of the pulp is high, increasing the degree of delignification sharply increases specific shrinkage.

6. Neither oxygen pressure nor type of alkali used (oxidized white liquor or caustic) significantly affect yield.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the guidance of Dr. Douglas H. Andrews. We also thank Kvaerner Chemetics, Inc. for supporting this research.

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Effect of Kappa Number on the Bleaching Response of Soda and Kraft Pulps from Bagasse

Subrahmanyam, S.V., Sharma, A.K., Godiyal, R.D., Janbade, V.T. and Gupta, H.K.

ABSTRACT

Bagasse is used by small, medium and big paper mills in India. The fiber line operations are different depending on the capacities of the mills. Hence, it is imperative to standardise the pulping and bleaching operations, keeping the merits of the processes and economic considerations and the requirement of mills of different capacities of the mills in view. The present study on bagasse pulping and bleaching of the pulp produced evaluates the merits and deficiencies of Kraft and soda pulps with special reference to bleach plant effluent in addition to strength and optical properties of the pulps. The studies indicated that it is advisable to produce pulps with a kappa number around 15 for bleach grades. Kappa numbers below 15 have not shown any significant benefit in terms of bleaching requirement, pulp strength and bleach effluent quality.

INTRODUCTION:

The paper mills in India are broadly catgorised in to three groups ie. Big (>100 TPD); Medium (30-100 TPD); and Small (<30 TPD) and total number being ≃ 500. Paper industry is considered to be one of the major contributors to gaseous and liquid pollution. The environmental norms are becoming more stringent due to public awareness. The major toxic liquid pollutants are the chloro-organics in bleach streams, since the chlorine in various forms is used in the bleaching process. Shortage in wood supply and the forest regulations and prohibitive cost of pulpwood made the technocrats to opt for agro residues as a major furnish in the papermaking. The bagasse is the prime raw material in the non-wood based fiber, which is available for the Indian paper industry. Due to its sustained availability all over the country makes the raw material a choice fiber to the paper industry. A good number of Indian mills of different capacities are using bagasse to produce bleached varieties. The fiberline operations vary from Soda pulping, Alkaline sulphite pulping and Kraft pulping. In general, the pulps produced are bleached by following CEH/ CEHH bleaching sequences. Oxygen delignification is one of best choice to significantly improve the pulp as well as effluent quality (Rajesh, K.S. et al, 2000). But it may not be practically feasible for the entire Indian paper industry to implement ECF and TCF processes by using chlorine free chemicals like Oxygen and Hydrogen peroxide. Hence, it is imperative to judiciously use existing bleaching processes to make the mills more productive without sacrificing the product quality. Keeping these limitations in view, the present work was carried out on bagasse Kraft and Soda pulps of different kappa number and CEH bleaching sequence in order to find out the optimum process conditions like kappa number of the unbleached pulp, impact on pulp quality, environmental and cost considerations. Similar studies were already conducted on other raw materials like rice straw (Gupta et al., 1988) and wheat straw (Gupta et al, 1992) and optimum kappa number for the bleachable grade pulp have been established for the better quality of the pulp and economical consideration.

Pulp Morphology:

Pulp from sugar cane (*Sachharum officinarum*) residue, commonly known as bagasse contains diverse cell types. The fibers are up to 4000 μ in length with an average of about 1750 μ. The fiber width ranges from 10 to 60 μ with an average of 23 μ. They are thick to thin walled, usually with straight, pointed ends with relatively more numerous

Central Pulp & Paper Res. Inst.,
PO Box 174,
Saharanpur - 247 001(UP) INDIA

slit-like or lenticular pits.

The wider fibers are usually shorter, frequently with blunt, oblique or forked ends. Parenchyma cells are very abundant, usually appreciably larger. They are up to 900 μ in length with an average of 375 μ and up to 180 μ in width with an average of 100 μ, and serve to easily identify bagasse. Vessels have length ranging from 180 to 1600 μ (average 600 μ) and 30 to 220 μ (mean 100 μ) in width. Epidermal cells are narrow and rectangular with undulating. Stomata may also be rarely present.

EXPERIMENTAL METHODS:

The bagasse raw material was collected from Sarsawa Sugar Mill near Saharanpur. The whole bagasse dry depithed in the laboratory. The pith content of whole bagasse was 21.4%. The bagasse used in the present experiments is assessed for its chemical composition to verify the quality of bagasse.

Pulping:

Soda and Kraft pulps were prepared in the laboratory using depithed bagasse. Kraft liquor with 19% sulphidity was used for pulping. Different chemical dosages were applied to obtain pulps in the Kappa number range of 10 to 35.

Pulping conditions:

Ambient to 100°C	30 min
100°C to 168°C	90 min.
At 168°C	90 min
Bagasse (each bomb)	200g OD
Bath ratio	1 : 5

Bleaching:

Bagasse pulp was bleached using CEH bleaching sequence to ≃ 85% ISO brightness using the following conditions:

__CEH bleaching sequence:__

Cl_2 Stage Consistency : 3%
Retention time : 30 min
Temperature : Ambient
pH : < 3

Alkali extraction consistency : 8%
Retention time : 60 min
Temperature : 65°C
pH : ≃ 10

Hypo stage Consistency : 8%
Retention time : 120 min
Temperature : 40 °C
Final pH : ≃ 9

Standards followed for testing:

Kappa number	T-236-OS-76
Bauer & McNett fiber classification	T-233-OS-75
Pentosan	CPPRI method
Viscosity	Scan C15:62
Brightness	ISO:2470

RESULTS AND DISCUSSION:

The whole bagasse was collected from a sugar mill in baled form. The whole bagasse was depithed in the laboratory and chemical proximate analysis was conducted on whole bagasse, depithed bagasse and the pith. The depithed bagasse has 71.3% holo-cellulose content (Table 1). The acid insoluble lignin in depithed bagasse is slightly on the higher side as compared with the samples collected analysed in different location (Mishra et.al. 1994). The variations in the chemical composition in bagasse are possibly due to variety of bagasse and location influence.

Table 1. Chemical Proximate analysis of Bagasse

Sl.No.	Property	Unit	Bagasse	Depithed	Pith
1	Moisture	%	26.8	26.2	24.5
2	Ash	%	1.8	1.7	2.2
3	Cold water solubility	%	1.4	1.3	8.1
4	Hot water solubility	%	3.1	2.8	9.7
5	1%NaoH solubility	%	28.9	25.8	39.9
6	Holo-cellulose	%	70.2	71.3	64.3
7	Pentosans	%	26.4	25.5	16.2
8	Acid insoluble Lignin	%	25.2	24.9	23.2

Table 2. CEH Bleaching of Kraft and soda pulps from bagasse

Dosage as NaOH	Unbleached Pulp					CEH Bleaching										
	Yield.	Screen rejects	Kappa no	Pentosan	viscosity (unbld.) pulp	Cl_2 dosage	Res. Cl_2	Alkali Extr,	Hypo as Cl_2	Res. Cl_2	Bld Yield	Pentosans	Viscosity (Bld)	Brightness	P.C.	Viscosity drop
%	%	%		%	cm^3/g	%	ppm	%	%	ppm	%	%	cm^3/gm	%	No.	%
Soda Pulp																
12	48.2	0.5	34.8	22.1	907	6.95	2900	3.0	3.0	240	43.5	19.5	430	85.4	1.55	52.6
14	45.9	0.4	28.4	22.0	886	5.67	2840	2.5	2.5	160	41.9	18.1	426	85.1	1.45	51.9
16	43.2	0.3	19.3	20.7	863	3.85	2560	2.0	2.0	140	39.8	20.3	430	87.7	1.37	50.2
18	42.1	0.2	15.5	19.4	857	3.10	2500	1.5	1.5	80	39.5	18.8	453	84.9	1.34	47.1
20	41.7	-	13.7	18.1	849	2.74	900	1.5	1.5	-	39.3	15.3	488	85.0	1.37	42.5
22	40.4	-	12.4	17.6	795	2.47	640	1.5	1.5	-	38.2	16.6	392	84.1	1.56	50.7
Kraft Pulp																
8	54.3	0.6	49.1	24.5	1073	9.82	380	3.5	3.5	40	48.5	18.7	591	86.5	0.85	44.9
9	52.4	0.4	33.4	22.3	1023	6.68	360	3.0	3.0	30	47.7	17.6	576	87.4	0.92	43.7
10	49.9	0.2	25.1	21.5	945	5.02	300	2.5	2.5	40	45.9	17.4	556	87.2	0.65	41.2
12	48.0	0.1	15.0	21.3	890	3.00	85	1.5	1.5	30	45.1	17.4	551	87.3	0.67	38.1
14	44.0	0.0	11.0	21.1	756	2.20	90	1.5	1.5	20	41.5	18.7	504	86.0	1.56	33.3
16	40.6	0.0	10.3	19.8	741	2.07	50	1.5	1.5	10	38.5	17.8	481	85.4	1.17	35.1

The depithed bagasse was cooked in laboratory digester using different chemical doses so as to obtain soda and Kraft pulps having kappa numbers in the range of 10 to 35 (Table 2). The yield levels reduced with reduction in kappa number in general. The yield levels of Kraft pulps are comparatively on the higher side to the yield from the soda cooking at any given kappa number. The pentosan content in the pulps is better preserved in Kraft pulping compared to soda pulping (Table 2). The cellulose degradation is also low in Kraft pulping as compared to soda pulping as indicated by the intrinsic viscosity of the pulps.

Table 3. Pulp yield and raw material requirement to produce one Bone dry Ton Bleached pulp.

Sl. No.	Chemical dose	Screen Yield	Kappa No.	Chlorine dose		Shrinkage	Bleached yield	Raw material/ BD Ton Pulp
	%	%		Ele. Cl_2	Hypo (Cl)	%	%	Ton
Soda as NaOH								
1	12	48.2	34.8	6.95	3.0	9.8	43.5	2.30
2	14	45.9	28.4	5.67	2.5	8.7	41.9	2.39
3	16	43.2	19.3	3.85	2.0	7.9	39.8	2.51
4	18	42.1	15.5	3.10	1.5	6.2	39.5	2.53
5	20	41.7	13.7	2.74	1.5	5.7	39.3	2.54
6	22	40.4	12.4	2.74	1.5	5.5	38.2	2.62
Kraft as Na_2O								
7	8	54.3	49.1	9.82	3.5	10.6	48.5	2.06
8	9	52.4	33.4	6.68	3.0	8.9	47.7	2.10
9	10	49.9	25.1	5.02	2.5	8.1	45.9	2.18
10	12	48.0	15.0	3.0	1.5	6.0	45.1	2.22
11	14	44.0	11.0	2.2	1.5	5.6	41.5	2.41
12	16	40.6	10.3	2.07	1.5	5.1	38.5	2.50

Kraft and soda pulps with different kappa number were bleached using CEH sequence in such a way that pulps would attain a brightness level ~85% ISO. The total chlorine requirement for Kraft and soda pulps varied from a minimum of 4% to a maximum of 10% depending up on the kappa number of the pulp (Table 2). It was observed that the residual chlorine level in the bleach effluents from soda pulps in elemental chlorine stage to be extremely high. The Kraft pulps on the other hand generated bleach effluent with considerably lower chlorine level. Similar trends were observed in residual chlorine levels in hypo stage bleach effluents. These observations indicate that the Kraft pulps respond more efficiently to CEH bleaching.

Cost analysis:

The bleached yields of the soda pulps are in the range of 43.5% to 38.2% (Table3). The requirement of fibrous raw material to produce one ton of bone dry bleached pulp from bagasse using soda process varies from 2.3 tons to 2.62 tons (Table 3). The cost analysis of bleach pulp production from soda pulping indicates continuous increase in cost as the kappa number of the pulps reduces. Since the environmental regulations are becoming more stringent on AOX discharge levels (Gupta et al, 1998), the Indian pulp and paper industry is left with no options other than reducing the chlorine consumption. Reducing the kappa number of the pulp, as it has empirical relation with AOX formation, can only control AOX formation. Hence, the desired kappa number in this case is below 15. The soda requirement is about 18% to produce a pulp with 15 kappa. The bleached pulp produced using 15 kappa pulp has good intrinsic viscosity and lowest brightness reversion (Table4). The bleached yield of the Kraft pulps fall in the range of 48.5% to 38.5% in the present study. The fiber requirement for producing one ton of bone dry bleached bagasse pulp using Kraft process varies from 2.06 tons to 2.50 tons (Table 3). The cost analysis of bleach pulp production from Kraft process was carried out assuming 80% chemical recovery of pulping chemical. As evident from table 4, the cost of bleached pulp gradually reduced with reduction in kappa number up to 15. Lowering of pulp kappa below 15 has negative impact on the production cost. The quality of bleached pulp from 15 kappa Kraft pulp is superior (Table 4). The strength of 15 kappa pulp is good as indicated by the intrinsic viscosity of the pulp. The brightness reversion is also lowest for this pulp (Table 4).

Table 4. Cost of raw material, pulping and bleaching chemicals per ton of bleached pulp

Sl. No.	Raw material		Pulping chemical		Bleach chemicals Chlorine						Total cost	AOX generation	Visco sity	P.C. No.
Un it	Ton	Cost (Rs.)	Kg	Cost (Rs.)	Caustic (Kg)	Cost (Rs.)	Cl_2 gas (Kg)	Cost (Rs.)	Hypo as Cl_2 (Kg)	Cost (Rs.)	Rs.	Kg/Ton	Cm^3/g	
Soda Pulping														
1	2.30	4,600	276.0	3864	33.27	466	77.07	771	33.27	50	9,611	6.96	430	1.55
2	2.39	4,780	334.6	4684	27.43	384	62.20	622	27.42	41	10,511	5.68	426	1.45
3	2.51	5,020	401.6	5622	21.68	304	41.73	417	21.68	33	11,396	3.86	430	1.37
4	2.53	5,060	455.4	6376	15.98	224	33.01	330	16.00	24	12,014	3.10	453	1.34
5	2.54	5,080	508.0	7112	15.90	223	29.04	290	15.90	24	12,729	2.74	488	1.37
6	2.62	5,240	576.4	8070	15.87	222	28.99	290	15.87	24	13,846	2.48	392	1.56
Kraft Pulping														
7	2.06	4,120	164.8	328	39.17	548	109.89	1,099	39.17	59	6,154	9.82	591	0.85
8	2.10	4,200	189.0	378	33.00	462	73.48	735	33.00	50	5,825	6.68	576	0.92
9	2.18	4,360	218.0	436	27.23	381	54.67	547	27.23	41	5,765	5.02	556	0.65
10	2.22	4,440	266.4	533	15.99	224	31.98	320	15.99	24	5,541	3.00	551	0.67
11	2.41	4,820	337.4	675	15.90	223	23.32	233	15.90	24	5,975	2.20	504	1.56
12	2.50	5,000	375.0	750	15.23	213	21.01	210	15.23	23	6196	2.06	481	1.17

Cost (in Rs.) of raw materials considered are – Bagasse @ 2,000/ton; NaOH @ 14/kg; Chlorine gas @ 10/kg; Hypo @ 15/kg; Salt cake @ 10/kg

The above observations indicate that in the light of stringent environmental regulations on the quality of liquid effluent discharges, the Indian pulp and paper industry is left with no choice other than producing low kappa pulps. The chloro-organics in effluents can only be reduced by lowering the chlorine usage (Kumar, S. et al. 1999) or by splitting the chlorine doses. Production of low kappa pulps from conventional soda process is not feasible with the existing know-how, due to the extent of chemical losses. So, the Kraft process with chemical recovery is the only viable alternative today keeping in view the cost of pulp production, quality of product and environmental considerations.

CONCLUSIONS:

1. Kraft pulps respond with better brightness and low reversion level compared to soda pulps at any given kappa number and chlorine consumption.
2. Loss in viscosity of Kraft pulps during bleaching is low compared to those of soda pulps.
3. Residual chlorine levels of Kraft pulp bleaching is significantly lower compared those of soda pulps.
4. Kappa number has significant effect on AOX production levels due to lower chlorine requirement.
5. Pulps with a kappa number around 15 are ideal for CEH bleaching to meet the product quality requirement and environmental regulations.

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Application of post-treatments to the ozone bleaching of eucalypt kraft pulp to increase the selectivity. Part A

M. BLANCA RONCERO*, JOSÉ F. COLOM† AND TERESA VIDAL†

SUMMARY

The effect of different Z stage post-treatments on the selectivity of bleaching processes using ozone has been studied. There are some contradictions in the literature as to the ideal post-treatment to increase the selectivity of ozone bleaching. The agents used as post-treatments in this study were formamidine sulfinic acid, sodium borohydride, sodium hydrosulfite and sodium hydroxide applied as an alkaline wash. Properties of the treated pulps (Kappa number, viscosity and brightness) were measured and compared to those of pulps bleached without post-treatment. Post-treatment with the agents tested gave an improvement in selectivity, which showed a remarkable difference depending on the agent applied with sodium borohydride being the most efficient. The behaviour of this agent was also analysed through the study of the chain scission number (CS) of the cellulose chain.

Keywords
Eucalypt, bleaching, TCF, ozone, post-treatments, selectivity, chain scission number, formamidine sulfinic acid, sodium borohydride, sodium hydrosulfite

Bleaching sequences including an ozonation stage usually lead to a phenomenon that negatively influences the selectivity of the process. It is well known that treatment with strong oxidants, such as ozone (Z), leaves pulps more sensitive to degradation in a subsequent alkaline treatment. During the Z stage, large quantities of carbonyl groups are formed all along the cellulose chains. These carbonyl groups cause a rapid degradation of the cellulose in an alkaline medium, which reduces viscosity and therefore lowers the selectivity (*1-3*). Since an alkaline stage generally follows ozonation, the study of post-treatment to the Z stage is of great interest to avoid this strong degradation of the carbohydrates in the next stage.

In the literature, there are some contradictions as to what is the more suitable treatment to be performed after ozonation. The post-treatment can influence the efficiency and selectivity of the process since a significant part of the lignin oxidised during the ozone treatment is not eliminated. Several researchers (*4-8*) proposed an alkaline extraction (E) after ozonation since the Z stage increases the formation of hydrophilic groups in lignin (*9*), thus facilitating its solubilisation in an alkaline medium, which improves the bleaching process by saving bleach chemical and in-creasing the pulp brightness. Some authors (*5,7*) also carried out studies to increase the elimination of lignin during the E stage through the addition of oxidants compatible with alkali such as oxygen and hydrogen peroxide. Colodette et al. (*5*) considered that alkaline extraction seemed to be more effective when the pulp was not washed after the Z stage, as long as a sufficient alkaline charge was applied. Lindholm (*10*) suggested neutralisation followed by washing with hot water as an alternative to the E stage.

Nevertheless, other researchers (*11,12*) consider that it is not advisable to perform the alkaline extraction after ozonation since it gives rise to a loss of viscosity and a decrease of the physical-mechanical properties of the pulp could take place. Chirat et al. (*13*) considered that the negative effect of the E stage on viscosity and physical properties of the pulp could be decreased with reducing agents.

The standard sequence in this work was of the XOZP type, in which a hydrogen peroxide stage in alkaline medium was carried out after the ozone stage. Therefore, significant degradation of the carbohydrates was very possible if a suitable treatment between the two stages (Z and P) was not included.

This work studied the application of different post-treatments to the Z stage. Several reducing agents were used, such as formamidine sulfinic acid, sodium hydrosulfite and sodium borohydride. An alkaline post-treatment consisting of an alkaline washing was also performed, since some authors recommend this treatment after the Z stage.

MATERIALS AND METHODS

The unbleached pulp used in this study was *Eucalyptus globulus* kraft pulp from an industrial source, with 13.6 Kappa number, 31.7% ISO brightness and 1090 mL/g viscosity.

Table 1
Conditions for the different bleaching stages (X, O, Z and P).

Condition	X	O	Z	P
Stock Conc.,%	10	10	40	10
Temperature,°C	45	110	Amb	70
Reaction time, min	180	60	-	120
Initial pH	6.5-8	-	-	10.5
Xylanase doses, EXU/kg on o.d. pulp	550	-	-	-
Pressure O_2, MPa	-	0.6	-	-
O_3 consumed, % on o.d pulp	-	-	0.8	-
H_2O_2 charge, % on o.d. pulp	-	-	-	2
NaOH charge, % on o.d. pulp	-	1.5	-	-
$MgSO_4 \cdot 7H_2O$ charge, % on o.d. pulp	-	0.5	-	0.2
O_3 inlet concentration, mg/L	-	-	30-40	-
Flow O_3/O_2, LN/h	-	-	150-200	-

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* Researcher, PhD,
† Professor, Department of Textile and Paper Engineering, E.T.S.E.I. Terrassa, Polytechnical University of Catalonia.
Colon 11, 08222 Terrassa. Spain.

Table 2

Agents used as post-treatments and conditions applied.

	FAS	Sodium borohydride		Sodium hydrosulfite	Alkaline washing
Post-treatment	**F**	**B_1**	**B_2**	**Y**	**W_E**
Initial washing temp,°C	50	-	-	-	-
Stock Conc.,%	10	10	10	4	2
Reaction time, min	90	60	60	60	10
Temperature,°C	70	Amb	Amb	70	Amb
NaOH charge, % on o.d. pulp	0.4	-	-	-	-
$CH_4N_2O_2S$ charge, % on o.d. pulp	1	-	-	-	-
$NaBH_4$ charge, % on o.d. pulp	-	0.5	0.1	-	-
Na_2CO_3 charge, % on o.d. pulp	-	1	1	-	-
$Na_2S_2O_4$ charge, % on o.d. pulp	-	-	-	1.2	-
DTPA charge, % on o.d. pulp	-	-	-	0.3	-
pH	-	-	-	-	11-12

The standard TCF bleaching sequence studied was XOZP where X is an enzymatic pre-treatment with xylanases, O an oxygen delignification, Z an ozone bleaching and P a hydrogen peroxide bleaching. The conditions of the different bleaching stages are shown in Table 1. The equipment and methods used for the different bleaching stages were published earlier (*14,15*).

The post-treatment (Post) consisted of performing a medium consistency treatment after the ozone bleaching stage using a given agent. After the post-treatment, the pulp was thoroughly washed before the following P stage.

The agents applied as post-treatments were: formamidine sulfinic acid, F, ($CH_4N_2O_2S$); sodium borohydride, B, ($NaBH_4$); sodium hydrosulfite, Y, ($Na_2S_2O_4$) and alkaline washing with soda, W_E, (NaOH). Table 2 shows the post-treatment conditions. In the case of sodium borohydride, two post-treatments with different doses were performed.

Characterisation of the pulps (Kappa number, brightness and viscosity) was done according to ISO standards 302, 3688 and 5351/1 respectively. These properties were measured after each bleaching stage to analyse the outcome of the process and to understand the effect of each post-treatment applied.

RESULTS AND DISCUSSION

The initial pulp was bleached with enzymatic, oxygen delignification and ozone bleaching treatments consecutively, which yielded XOZ pulp with 75.7% ISO brightness, 1.75 Kappa number and 456 mL/g viscosity.

Samples of this XOZ pulp were treated with the several post-treatments and then with hydrogen peroxide. Simultaneously a control bleaching sequence (XOZP) was performed without post-treatment. This allowed evaluation of the effect on pulp properties of each post-treatment applied after the Z stage.

Comparison of the different post-treatments applied

Comparison of the results of the control bleaching sequence XOZP with those of sequences with a post-treatment (XOZPostP), shows an improvement of the pulp properties when post-treatment was applied. The improvement extent varies with the post-treatment applied.

Figure 1 shows the selectivity of the process, being more effective when high viscosities and low Kappa numbers are obtained, since the bleaching aims to remove the maximum quantity of lignin while maintaining a high viscosity. Kappa number values obtained are very similar for all pulps. Viscosities following treatments with sodium hydrosulfite (Y) and formamidine sulfinic acid (F) are slightly higher than for the control pulp, whereas significantly greater viscosities were found for pulps post-treated with sodium borohydride (B_1 and B_2).

The alkaline washing (W_E) does not show a significant difference compared to the control pulp. These results are inconsistent with those reported by other authors (*4-8*) indicating that an alkaline extraction or a neutralisation increases the delignification and brightness while preserving the viscosity. Nevertheless, Kordsachia et al. (*12*) found that alkaline extraction after ozone bleaching did not increase brightness. As shown in Figure 2,

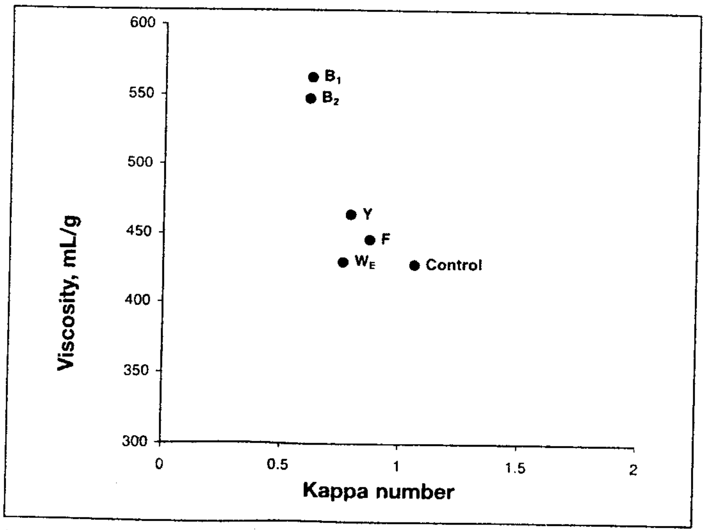

Fig. 1 Viscosity vs. Kappa number of the post-treatments studied and the control, measured after the P stage.

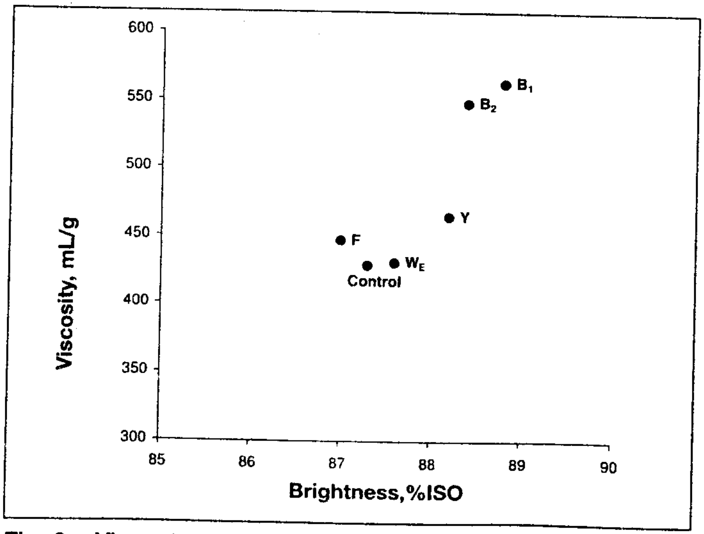

Fig. 2 Viscosity vs. brightness of the post-treatments studied and the control, measured after the P stage.

brightness and viscosity values for the alkaline washing (W_E) post-treated pulps are similar to that for the control bleaching. Although this post-treatment is not harmful, since it does not impair the pulp properties, it might dissolve more carbohydrates due to alkali-labile degradation (*3,16*). Therefore, the W_E treatment can be considered ineffective.

Figure 2 also illustrates that the highest brightness and viscosities are achieved with sodium borohydride. Post-treatment with formamidine sulfinic acid gives similar results to the control pulp, which is not in agreement with the results obtained by Colodette et al. (*5*), who found a decrease in Kappa number and an increase in brightness and viscosity using this reagent. Sodium hydrosulfite increases brightness only half a point without significantly affecting the pulp viscosity, in agreement with results obtained by Colodette et al. (*5*). However, results reported by Chirat et al. (*13*) showed an increase in brightness, but at the expense of a decrease in viscosity.

Figure 3 shows viscosity versus residual peroxide in the P stage for the different post-treatments. The greater the residual peroxide, the less peroxide has reacted with the pulp, and this gives an idea of the charge necessary for this stage. Very high residual values can allow a reduction of the initial charge of hydrogen peroxide or even of ozone, and therefore, a saving in chemicals. Again, the post-treatments with sodium borohydride are the most effective, since they show the greatest viscosities and highest residual peroxide values, with only 30% of the H_2O_2 added in the P stage being consumed. This suggests that the same brightness, viscosity and Kappa number could be obtained with a smaller charge of hydrogen peroxide. Therefore, the post-treatments with sodium borohydride not only provide greater brightness and viscosities, but also allow savings of hydrogen peroxide in the P stage.

It can be concluded that the best post-treatment among those evaluated is sodium borohydride, since it increases brightness by ~1.5 units while using a lower dose of hydrogen peroxide in the P-Stage. Moreover, the viscosity loss was reduced by 18% during the bleaching sequence. This agrees with the results obtained by Chirat et al. (*13*), who also tested different reducing post-treatments and concluded that the most efficient was sodium borohydride.

Lindholm (*7*) also applied sodium borohydride as an additive in alkaline extraction and this increased delignification and reduced the viscosity loss but without completely preventing it. This could be due to the high alkalinity used in the alkaline extraction. A high alkaline pH increases stability of the $NaBH_4$ but reduces its reactivity. Therefore, the pH of this stage must be kept between 9 and 10 in order to prevent hydrolysis of $NaBH_4$ and to maintain maximum reactivity towards the carbonyl groups present in the cellulose chains. If large doses of NaOH are used, this pH range can be exceeded giving rise to the β-elimination reaction of cellulose, which takes place under strongly alkaline conditions. In this study sodium carbonate (Na_2CO_3) was used to achieve the appropriate pH since it is a good agent for keeping pH between 9 and 10, which is high enough for the sodium borohydride to work efficiently and low enough to avoid cellulose depolymerisation (*17*).

Table 3
Cellulose chain scission number (CS) for the bleached samples and results from equation 5.

	CS	$CS_{C=O}-CS_{NoRedC=O}$
XOZP	1.91	0
XOZFP	1.79	0.13
$XOZB_1P$	1.16	0.76
$XOZB_2P$	1.22	0.69
XOZYP	1.67	0.25
$XOZW_EP$	1.90	0.01

The disadvantage of sodium borohydride as a post-treatment lies in its high price and the need for high doses (*18*). However, the present study reveals that the two post-treatments with sodium borohydride (B_1 and B_2) give rise to very similar results with the difference that the $NaBH_4$ charge in the B_1 treatment was 0.5% on o.d. pulp whereas in the B_2 treatment it was only 0.1%. Therefore, an improvement in pulp properties can be achieved with the application of a small dose of sodium borohydride as a post-treatment to ozone bleaching, which corroborates the results recently presented by Odermatt et al. (*16*).

Why is sodium borohydride so effective?

As mentioned previously, during ozone bleaching many carbonyl groups are formed, which makes the cellulose more susceptible, in an alkaline medium, to rapid degradation

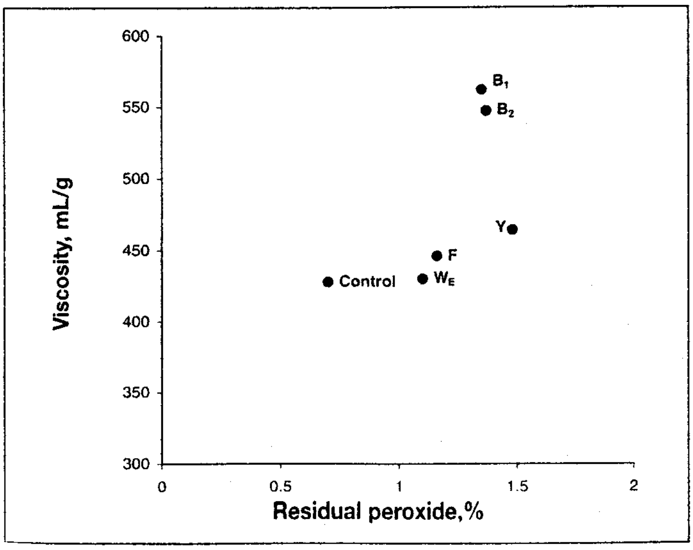

Fig. 3 **Viscosity vs. residual of the different post-treatments and the control.**

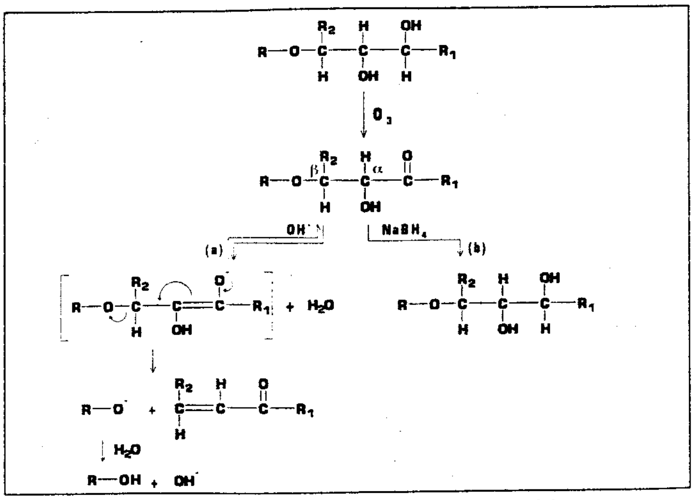

Fig. 4 **Example of a carbonyl group formed by ozone oxidation of cellulose. (a) Alkaline hydrolysis mechanism. (b) Reduction of the carbonyl group through the action of sodium borohydride.**

and therefore a decrease in viscosity. This reduction in viscosity can cause a decrease in the physical-mechanical paper properties. Fuhrmann et al. (*19*) reported that tear index could be increased by TCF bleaching using a sequence containing a Z stage if the content of carbonyl groups was reduced before proceeding to the following alkaline stage of bleaching.

An example of the oxidised cellulose degradation produced in an alkaline medium is shown in Figure 4 (a). The carbonyl group formed in the oxidative stage promotes the breaking of the cellulose chain in an alkaline medium, giving rise to the β-elimination reaction. A possible solution to this drawback is to inactivate the carbonyl groups by reducing them to alcohol, which will prevent excessive cellulose degradation in the alkaline stage. This effect can be attributed to the sodium borohydride, due to the reaction mechanism shown in Figure 4 (b).

Another way to assess the degradation of pulp during ozonation is by calculating the cellulose chain scission number (CS) in the cellulose from the DP values using the following equation (20,21):

$$CS = \frac{DP_O - DP}{DP} \qquad [1]$$

where DP_O is the degree of depolymerisation of samples after oxygen delignification (XO pulp) and DP is the degree of depolymerisation after the hydrogen peroxide stage (XOZP or XOZPostP pulps). This degree of depolymerisation is calculated from viscosity values (Vis) using the following expression (SCAN C-15: 62):

$$DP^{0.905} = 0.75 \cdot Vis \qquad [2]$$

The CS value of the bleaching sequence without post-treatment (Table 3) expresses the sum of the chain scission number produced by the direct attack of ozone and the radicals generated during the Z and P stages (CS_G) plus the chain scission number produced by the β-elimination reaction when the carbonyl groups are present ($CS_{C=O}$):

$$CS_{XOZP} = CS_G + CS_{C=O} \qquad [3]$$

On the other hand, CS values from post-treated samples (Table 3) express the sum of CS_G plus the chain scission number produced by the β-elimination reaction promoted by carbonyl groups that have not been reduced by the post-treatment used ($CS_{NotRedC=O}$):

$$CS_{XOZPostP} = CS_G + CS_{NoRedC=O} \qquad [4]$$

The difference between equations 3 and 4 is the degradation that would be avoided when the post-treatment is applied (or the degradation that would be produced by the carbonyl groups that have been reduced with the post-treatment applied):

$$CS_{C=O} - CS_{NoRedC=O} = CS_{XOZP} - CS_{XOZPostP} \qquad [5]$$

The results from equation 5 are also shown in Table 3. High values for this difference mean that more carbonyl groups were reduced by the post-treatment, and in consequence less cellulose degradation will be produced during the P stage. Therefore, the more efficient the post-treatment the greater this difference is.

As shown in Figure 5, alkaline washing produces no difference in pulp properties with respect to the control pulp, and thus does not produce a significant reduction in the carbonyl groups either.

Alternatively, the other post-treatments reduce some of the carbonyl groups. These treatments can be classified by their reducing power in the following order: $F < Y < B_2 < B_1$, with sodium borohydride reducing more of the carbonyl groups. Moreover, these results confirm that the reduction of the carbonyl groups formed during the Z stage can eliminate part of the cellulose degradation that takes place during the P stage due to the carbonyl groups, thereby increasing the selectivity of the bleaching process. Overall, sodium borohydride is the most effective reducing agent of carbonyl groups.

The viscosity values after each stage of the control bleaching sequence (XOZP), and of the bleaching sequence with sodium borohydride as post-treatment ($XOZB_1P$), are shown in Figure 6. It is seen that for the sequence XOZP, the greatest degradation of cellulose (viscosity loss) takes place during ozone bleaching, with the decrease in viscosity ongoing in the P stage. In the sequence with post-treatment, there is also an important loss of viscosity during the Z stage, but viscosity increases during the B_1 stage, which is inconsistent since this would mean that cellulose chains are rebonding during this B_1 stage, which cannot really occur.

In fact, the viscosity measured after the Z stage is not a 'real' viscosity. The highly alkaline conditions that are used in determining standard viscosity (measurement performed in alkaline medium with

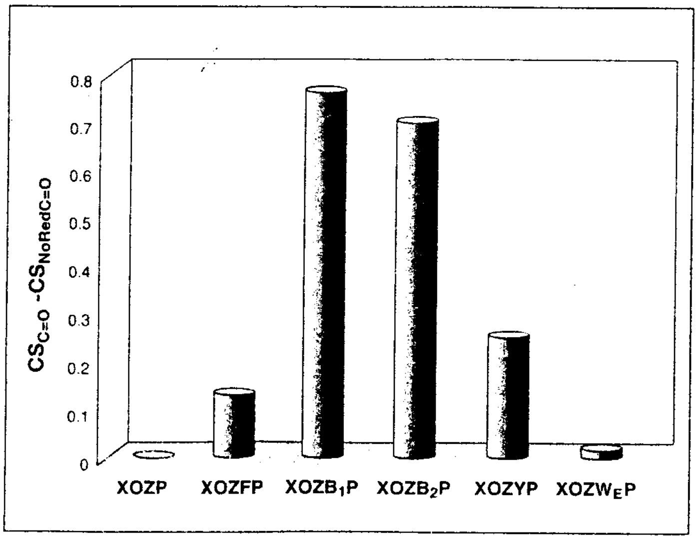

Fig. 5 Cellulose chain scission number which is avoided when a post-treatment is applied.

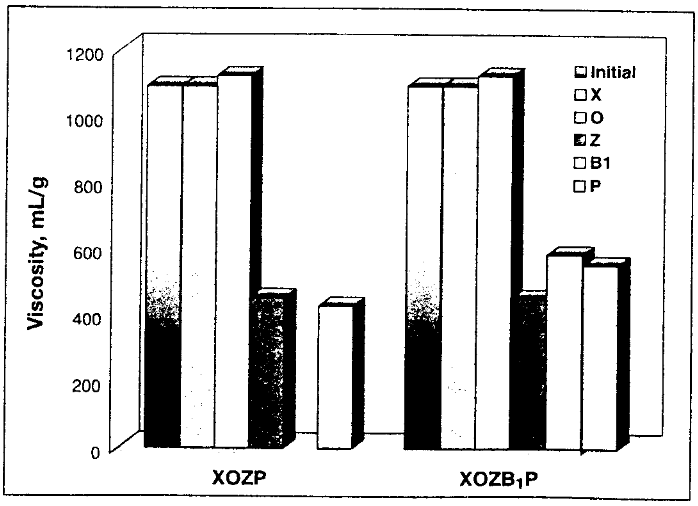

Fig. 6 Viscosity values after each bleaching stage of the XOZP control sequence and of the sequence with borohydride as post-treatment ($XOZB_1P$)

cupriethylene-diamine) can produce breakages in the cellulose chains due to the presence of the carbonyl groups formed during the Z stage, giving rise to viscosity values that are lower than the 'real' ones. Actually, some authors make reference to 'apparent' viscosity of the Z stage when measured using this standard method, and a new concept is introduced, 'borohydride viscosity', which is the viscosity measured by the same standard procedure but after performing a treatment with sodium borohydride to decrease the alkali labile effect of the cellulose (*1,2,3,6,11,19*).

These carbonyl groups that affect the determination of viscosity are responsible for the pulp degradation in the P bleaching stage, as is shown by the values obtained after the peroxide bleaching in both sequences (Fig. 6). Therefore, the post-treatment with sodium borohydride allows a more selective final process, due to its high reducing power.

It is worth highlighting that this reducing treatment would not be necessary if a chlorine dioxide bleaching (acid stage) were performed (*5*) instead of using a subsequent alkaline bleaching with hydrogen peroxide. However, our work is based on applying a TCF (Totally Chlorine-Free) sequence.

CONCLUSIONS

Different post-treatments were applied after an ozone bleaching stage and before the hydrogen peroxide stage in order to increase the selectivity of the process.

Contrary to what has been reported by several authors, alkaline washing does not increase delignification or pulp brightness and, therefore, does not improve the selectivity.

Post-treatments with formamidine sulfinic acid and with sodium hydrosulfite produce pulps with properties similar to or slightly higher than those of the control pulp. Therefore, their effect can be considered negligible regarding pulp properties, and does not justify application in the process from an economic point of view.

The best results were obtained with sodium borohydride. This agent produced an increase in brightness (1.5 points) and, especially, a higher viscosity of up to almost 150 units. This improved selectivity is attributed to reduction of the carbonyl groups formed during ozone bleaching since they promote cellulose degradation during an alkaline stage such as when using hydrogen peroxide. The effective reducing power of the sodium borohydride is confirmed by calculating the cellulose chain scissions number (CS). Hence, $NaBH_4$ reduces the sensitivity of the cellulose to alkaline attack.

The disadvantage of the application of this agent is its high price. Nevertheless, the results obtained show that only a small dose of 0.1% on o.d. pulp is needed to obtain the beneficial effect.

Achieving the appropriate activity of sodium borohydride requires an alkaline pH between 9 and 10. This pH should be produced using sodium carbonate instead of sodium hydroxide, since the latter could give rise to the β-elimination reaction of cellulose.

ACKNOWLEDGEMENTS

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Increasing the selectivity of ozone bleaching of eucalypt kraft pulp. Part B

M. BLANCA RONCERO*, JOSÉ F. COLOM†, AND TERESA VIDAL‡

SUMMARY

Ozone appears to be an effective bleaching agent for the TCF process. However, bleaching sequences involving a Z stage require optimisation to overcome low selectivity. In this work, various reagents were used in treatments preceding the ozone bleaching stage in order to increase its selectivity. Eight reagents were used under different conditions to test 26 different pretreatments. Two additional treatments consisting of a combination of a pretreatment and an additive (Pret+Addit) were also studied. Overall, the pretreatments had favourable effects (particularly those involving chelating agents or acids). Pret+Addit treatments were found to be even more efficient, probably due to the additive effect in the Z stage.

Keywords
Eucalypt, bleaching, TCF, ozone, pretreatments, additives, selectivity

The introduction of totally chlorine free (TCF) sequences has faced scientists with new problems, which has prompted the need to study and optimise the resulting new bleaching sequences. Avoiding the use of chlorine and its derivatives in order to obtain TCF pulp entails using alternative bleaching agents such as oxygen or hydrogen peroxide. However, a combination of these two agents has proved inadequate to match the efficiency of chlorination. Incorporation of an ozone stage (Z) appears to be a good choice for circumventing this shortcoming, as ozone possesses a high oxidation potential.

Unlike oxygen and hydrogen peroxide, ozone reacts with most chemical groups present in residual lignin. However, it also reacts with carbohydrates reducing considerably pulp viscosity and hence the selectivity of the process (*1-4*).

The selectivity problem associated with ozone bleaching hinders its use in TCF bleaching processes as the resulting pulp is of substandard quality. It is therefore essential to raise the selectivity of the process (i.e. increase the ratio of the Kappa number decrease or the brightness increase to the fall in viscosity during the Z stage) by using ozone efficiently during TCF bleaching in order to ensure adequate pulp brightness.

Some investigations into ozone bleaching have focused on developing an effective pulp treatment to prevent ozone reacting with carbohydrates (*5-9*). Such studies have provided various approaches to increasing the selectivity of the Z stage. One involves restricting the availability of ozone to cellulose by controlling the nature of the medium (*10,11*). Another avoids the formation, or inhibits the activity, of reactive secondary species such as hydroxyl radicals, which are believed to cause cellulose degradation (*12-14*). Additional treatments seemingly improving the selectivity of the bleaching process involve removing metal ions prior to ozone bleaching (*15,16*) and increasing the stability of ozone and/or its solubility in organic solvents and acids (*10,17,18*). There is an extensive literature on the topic, however no consensus exists with regard to the best treatment for improving selectivity in the ozone bleaching stage.

In this paper, an attempt was made to raise the selectivity of the TCF sequence by using various reagents in a stage preceding ozone bleaching. Such a preliminary stage, designated 'Pretreatment' (Pret), involved the use of medium consistency, an appropriate reagent and a final wash prior to the Z stage. Two additional treatments consisting of the combination of a pretreatment and an additive (Pret+Addit) were also studied. The aim was to maximise delignification while preserving the carbohydrates, i.e. improving the selectivity of ozone towards cellulose.

MATERIALS AND METHODS

The unbleached pulp used in this study was *Eucalyptus globulus* kraft pulp from an industrial source, with 13.6 Kappa number, 31.7% ISO brightness and 1090 mL/g viscosity.

The standard TCF bleaching sequence studied was XOZRP, where X is an enzymatic pretreatment with xylanases, O an oxygen delignification stage, Z an ozone bleaching stage, R a reductive treatment with sodium borohydride and P a hydrogen peroxide bleaching stage.

The conditions for the different bleaching stages are shown in Table 1. The equipment and methods used for the different bleaching stages were published earlier (*19,20*). The post-treatment R after the Z stage, described in a previous study

Table 1
Bleaching stage (X, O, Z, R and P) conditions.

Condition	X	O	Z	R	P
Stock conc., %	10	10	40	10	10
Temperature, °C	45	110	Amb	Amb	70
Reaction time, min	180	60	–	60	120
Initial pH	6.5-8	–	–	–	10.5
Xylanase dose, EXU/kg	550	–	–	–	–
Pressure O_2, MPa	–	0.6	–	–	–
O_3 consumed, % on o.d. pulp	–	–	0.7	–	–
$NaBH_4$, charge, % on o.d. pulp	–	–	–	0.5	–
H_2O_2 charge, % on o.d. pulp	–	–	–	–	2
NaOH charge, % on o.d. pulp	–	1.5	–	–	–
$MgSO_4{\cdot}7H_2O$ charge, % on o.d. pulp	–	0.5	–	–	0.2
O_3 inlet concentration, mg/L	–	–	30-40	–	–
Flow O_3/O_2, LN/h	–	–	150-200	–	–
Na_2CO_3 charge, % on o.d. pulp	–	–	–	1	–

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* Researcher, PhD,
† Professor,
‡ Professor,
Department of Textile and Paper Engineering, E.T.S.E.I. Terrassa, Polytechnical University of Catalonia, Colon 11, 08222 Terrassa, Spain.

(*21*) has been included in the standard sequence.

The pretreatment (Pret) was a treatment at medium or low stock concentration involving the use of a suitable reagent and a washing of the pulp prior to the Z stage. The resultant final sequence was XOPretZRP. The reagents used included various organic and inorganic chemicals, which were applied in various proportions under conditions derived from the literature (*5, 8*). The agents used were:

Organic: Acetic acid, DTPA and EDTA.
Inorganic: Sulfuric acid, hydrogen peroxide, sodium borohydride, sodium sulfite and sodium thiosulfate.

Overall, 24 different pretreatments were performed. Moreover, two combinations of a pretreatment and an additive (PAA1 and PEA16) were studied. Treatment PAA1 involved a pretreatment with 10% acetic acid at 12% stock concentration (s.c.) and 60°C for 60 min. The pulp was thoroughly washed and then treated with 2.6% acetic acid as the additive (which provided a pH of 3.2) at 12% s.c. and 60°C for 70 min. When the reaction was finished, the pulp was thickened to 40% s.c. for ozone bleaching, whereby 0.53% of additive (acetic acid) was retained and carried over to the Z stage. Treatment PEA16 also involved a pretreatment with 1% EDTA, at 10% stock concentration, room temperature and pH 3 for 10 min. Then, the pulp was thoroughly washed, followed by the addition of sulfuric acid at 2% s.c., pH 2.5 and room temperature for 30 min. Finally, the pulp was thickened to 40% s.c. for subsequent ozone bleaching, with 0.05% sulfuric acid present during the Z stage.

Table 2 shows the different reagents and conditions used in the treatments studied.

Characterisation of the pulps (Kappa number, brightness and viscosity) was achieved, according to ISO standards 302, 3688 and 5351/1 respectively. These properties were measured after each bleaching stage to study the outcome of the process and to understand the effect of each pretreatment applied.

The content of iron (Fe), copper (Cu) and manganese (Mn) metal ions was determined by atomic absorption spectroscopy after a dry digestion of the sample, according to TAPPI T 266 om-94.

Table 2
Application conditions for agents used as pretreatments.

Agent	Ref	Dose (% on o.d. pulp)	Stock conc. (%)	Temp. (°C)	Time (min)	pH
Acetic acid	PA1	10	12	70	60	–
	PA2	0.5	10	70	30	6
	PA3	1.5	3.5	70	30	2
	PA4	0.5	10	70	30	–
DTPA	PD1	0.5	3.5	70	30	6
	PD2	0.5	3.5	70	30	2
	PD3	0.5	3.5	70	60	6
	PD4	0.5	8.5	70	30	6
EDTA	PE1	1.0	10	Amb.	60	–
	PE2	1.0	10	90	40	–
Sulfuric acid	PS1	1.5	12	70	60	–
	PS2	3.0	3.5	70	60	–
Hydrogen peroxide*	PP1	0.2	12	60	60	–
	PP2	0.2	12	60	60	–
	PP3	1.6	12	60	60	–
	PP4	1.6	12	60	60	–
	PP5	0.2	12	90	60	–
	PP6	0.8	12	90	60	–
	PP7	1.5	3.5	70	30	2
	PP8	0.5	10	70	30	11
Sodium borohydride	PB1	1.5	3.5	70	30	–
Sodium sulfite	PY1	1.0	10	40	10	–
	PY2	10	10	80	180	–
Sodium thiosulfate	PT1	1.5	3.5	70	30	–

*Addition of H_2SO_4 and DTPA (in %), respectively: 0 and 0.2 for PP1; 2 and 0.2 for PP2; 0 and 0.2 for PP3; 2 and 0.2 for PP4; 1 and 0.2 for PP5 and PP6; no addition in PP7 and PP8.

RESULTS AND DISCUSSION

The pulp was initially treated with enzyme (X) and then delignified with oxygen (O) to obtain an XO pulp with a Kappa number of 7.5, 51.6% ISO brightness and a viscosity of 1127 mg/L.

The XO pulp was treated with the different pretreatments (Table 2) and then washed and bleached with ozone (Z), completing the XOPretZ sequence. A control sequence (XOZ) was also performed. The pulp properties were determined (Table 3) and pretreatments preliminarily screened in terms of efficiency. Subsequently, R and P stages were carried out and pulp properties determined (Table 4). Figure 1 depicts the operational sequence used.

Preliminary screening

A comparison of the results (Table 3) provided by the control sequence (XOZ) and those including pretreatment (XOPretZ) reveals that the latter increased brightness while slightly decreasing the Kappa number of the pulp. Viscosity was similar for both sequences, or slightly lower with XOPretZ.

In order to discard inefficient reagents used in the pretreatments, those conditions leading to the best results, and those with similar efficiency and involving the lowest reagent doses, shortest reaction times or highest compatibility with the bleaching process, were preliminarily adopted.

With acetic acid (pretreatments PA1-PA4), pulp properties exhibited no clear-cut dependence on the operating conditions. Thus, a high acetic acid dose and a long reaction time (PA1) did not give significantly better results; rather, this pretreatment produced the lowest pulp brightness. The most suitable conditions were those of PA4, followed by those of PA3; both pretreatments used less reagent and shorter reaction times, and provided pulps with higher brightness, than did PA1.

With DTPA (pretreatments PD1 – PD4), the pH seemingly had some influence, since pulp brightness was maximal at pH near six, consistent with results reported by Colodette et al. (*8*). However, Süss et al. (*9*) found that an acid pH was required for maximum efficiency. An extended reaction time (PD3) evidently

Table 3
Pulp properties after the Z stage of sequences with pretreatments (XOZPretZ), combined treatments (XO(Pret+Adit)Z) and control (XOZ).

		PH	Kappa number	Brightness (% ISO)	Viscosity (mL/g)
Control (XOZ)		–	1.9	73.1	527
Pretreatment					
Acetic acid	PA1	3.3	1.7	75.6	496
	PA2	6.1	1.7	76.2	500
	PA3	1.9	1.6	76.9	485
	PA4	4.7	1.5	78.9	473
DTPA	PD1	6.3	1.6	78.1	438
	PD2	1.8	1.5	76.9	479
	PD3	6.1	1.5	77.1	487
	PD4	6.3	1.5	77.5	476
EDTA	PE1	5.2	1.4	78.4	455
	PE2	5.5	1.6	77.6	466
Sulfuric acid	PS1	2.0	1.4	76.4	491
	PS2	2.0	1.4	77.4	469
Hydrogen peroxide	PP1	8.3	1.7	75.8	480
	PP2	1.8	2	75.7	500
	PP3	8.2	1.8	77.4	486
	PP4	1.9	1.8	77.5	481
	PP5	2.3	1.7	77.3	482
	PP6	2.3	1.7	77.4	504
	PP7	2.1	1.8	77.3	501
	PP8	11.3	1.7	75.6	496
Sodium borohydride	PB1	10.1	1.3	78.3	472
Sodium sulfite	PY1	8.6	1.5	74.9	501
	PY2	8.5	1.6	76.8	490
Sodium thiosulfate	PT1	6.4	1.8	75.5	517
Pret+Addit					
	PAA1	3.2	2.5	81.4	573
	PEA16	3.5	2.7	82	606

helped to preserve pulp viscosity.

With EDTA, pretreatment PE1 was more efficient than PE2. Raising the temperature did not improve pulp quality, which contradicts results given by Chirat et al. (*7*) who reported greater delignification when temperature was increased.

The two pretreatments involving sulfuric acid (PS1 and PS2) were carried out at the same pH, reaction time and temperature, but using different amounts of acid and stock concentration. The extent of delignification was similar in both cases. The lower quantity of acid and a medium s.c. (PS1) ensured higher viscosity, less cellulose degradation and lower brightness, than the PS2 treatment (with a higher quantity of acid and a low stock concentration). Therefore, pretreatment PS1 was adopted, as it was more compatible with the bleach sequence.

With hydrogen peroxide (pretreatments PP1-PP8), increasing the amount of reagent increased pulp brightness while preserving viscosity. No other variable had a significant effect; however, alkaline media (pH 8 to 11) were found to boost delignification, whereas in acid media (pH 2) there was a bleaching effect. Viscosity was very similar in all cases. Taking into account the brightness values, these treatments can be distributed into two groups: 1) PP1, PP2 and PP8, with values of ~76% ISO, and 2) PP3, PP4, PP5, PP6 and PP7, with values around 77.5% ISO. Thus, the latter group was selected, but PP4 was discarded as it was applied using the same conditions as PP3 except that it involved the addition of sulfuric acid to obtain the appropriate pH.

Finally, both sodium sulfite pretreatments (PY1 and PY2) resulted in very similar viscosities. However, brightness was two units higher with PY2. Even so, PY1 was adopted as PY2 used 10 times more reagent, a higher temperature and a longer reaction time.

Therefore, the pulp samples selected to carry out the final bleaching stage were PA3, PA4, PD3, PE1, PS1, PP3, PP5, PP6, PP7, PB1, PY1 and PT1.

The combined treatments (Pret+Addit) had a more favourable effect than the pretreatments alone; in fact, they provided higher brightness and viscosity, nevertheless a slightly higher Kappa number was obtained. PEA16 (the treatment involving EDTA and the use of sulfuric acid as additive) was the more efficient.

Final bleaching

The previously selected samples were bleached using a reductive treatment (R) and a hydrogen peroxide (P) stage. The results obtained after the P stage are shown in Table 4. Kappa number values are not provided, as they were less than unity in all instances. Instead, the P stage hydrogen peroxide residuals are given.

With sample PP5, brightness and viscosity after the P stage could not be measured; in any case, the results obtained after the R stage were similar to those from the other hydrogen peroxide-based pretreatments.

Figure 2 shows viscosity vs. brightness values for the selected pretreatments (XOPretZ), the two Pret+Addit treatments (XO(Pret+Addit)ZRP) and the control treatment (XOZRP). Most of the pretreatments resulted in a slightly decreased viscosity and a markedly increased brightness. The pretreatment with EDTA (PE1) provided the highest brightness (4 units above the control level). Treatments PY1 and PT1, based on sodium sulfite and sodium thiosulfate, respectively, stood out from the rest; these two reducing agents increased pulp brightness only slightly as the likely result of chromophores in the pulp being bleached, which is consistent with results reported by Colodette et al. (*8*).

The most interesting effects were those of the two combined treatments (Pret+Addit), which markedly increased brightness while preserving viscosity. The essential difference with the pretreatments was the use of an additive during ozone bleaching. Consequently, the improvement can be unequivocally ascribed to the presence of the additive.

Another factor to be considered was the amount of residual hydrogen peroxide (Fig. 3), based on which the treatments can be split into two groups:

1. Those with proportions above 1% (PA3, PD3, PE1, PS1, PAA1 and PEA16), where less than 50% of the hydrogen peroxide was consumed in the P stage.
2. Those with proportions below 0.8% (PP3, PP6, PP7, PB1, PY1 and PT1), where more than 60% of the initial amount of hydrogen peroxide was consumed.

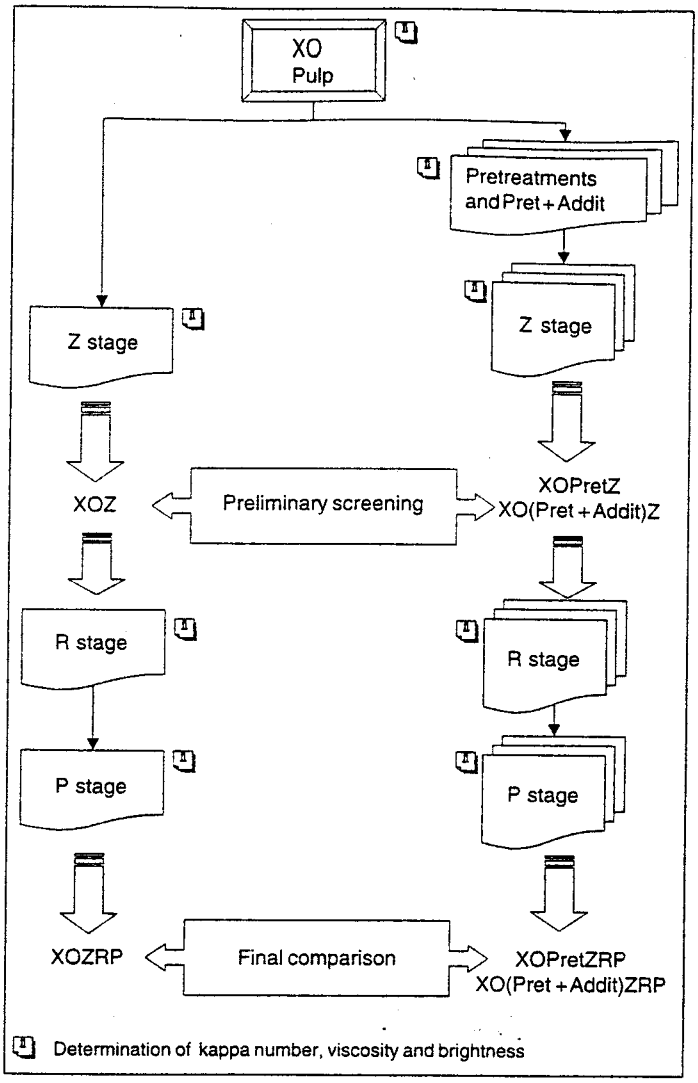

Fig. 1 **Work outline in the study of pretreatments and Pret+Addit applied to an XOZRP sequence.**

Hydrogen peroxide consumption below 50% suggests that a lower proportion of peroxide could be used in the P stage, which would save reagent without modifying the properties of the final pulp. Alternatively, using a smaller amount of ozone in the bleaching sequence would have the same effect.

All the pretreatments tested improved pulp properties. The highest brightness was obtained with EDTA, sodium borohydride, hydrogen peroxide, acetic acid, sulfuric acid and DTPA. Sodium borohydride treatment resulted in little residual hydrogen peroxide, so it would not allow the amount of hydrogen peroxide used in the P stage to be reduced. This would also be the case with hydrogen peroxide used for pretreatment; which in addition would need additional reagents (sulfuric acid and DTPA). Acetic acid, sulfuric acid and DTPA, in addition to EDTA, the reagent providing the highest brightness, were suitable choices. Acids and chelating agents thus yielded the best results.

Overall, the most efficient treatments were those involving the use of an additive during the Z stage (PAA1 and PEA16); they provided increased brightness and viscosity relative to the control treatment, and hydrogen peroxide residuals exceeding those of the other pretreatments.

Metal ions

The fact that acids and chelating agents were more efficient than the other reagents used in pretreatments may be related to their ability to remove metal ions. Pulp usually contains metal ions such as Fe(II), Mn(II), Cu(II), Co(II), Na(I), Ca(II) and Mg(II) with Fe, Cu and Mn being the most harmful (*8, 22-25*).

The metal ions quantified in the present study were Fe, Cu and Mn in the unbleached X, O and XO pulps. The pulp sample was digested (dry digestion) to eliminate the organic material and then the ash dissolved with hydrochloric acid. The metal ion content was then calculated using a calibration line obtained from standard solutions. Results are shown in Table 5.

The Mn content was about 37 μg/g in the unbleached pulp, 15 μg/g in the X pulp, 9 μg/g in the O pulp and 6.5 μg/g in the XO pulp. Therefore, the content of Mn ion was reduced by enzymatic treatment and oxygen delignification.

Table 4
Pulp properties after the P stages of sequences with pretreatments (XOPretZRP), combined treatments (XO(Pret+Adit)ZRP) and control (XOZRP).

		Residual peroxide (% on o.d. pulp)	Brightness (% ISO)	Viscosity (mL/g)
Control (XOZRP)		**1.2**	**84.7**	**618**
Pretreatment				
Acetic acid	PA3	1.27	87.9	564
	PA4	–	87.7	558
DTPA	PD3	1.41	87.8	577
EDTA	PE1	1.18	88.5	558
Sulfuric acid	PS1	1.16	87.6	562
Hydrogen peroxide	PP3	0.79	88.0	537
	PP5	0.64	–	–
	PP6	0.71	88.2	557
	PP7	0.67	87.7	554
Sodium borohydride	PB1	0.39	88.3	546
Sodium sulfite	PY1	0.08	86.0	601
Sodium thiosulfate	PT1	0.47	86.5	624
Pret+Addit				
PAA1		1.55	89.2	680
PEA16		1.43	90.7	732

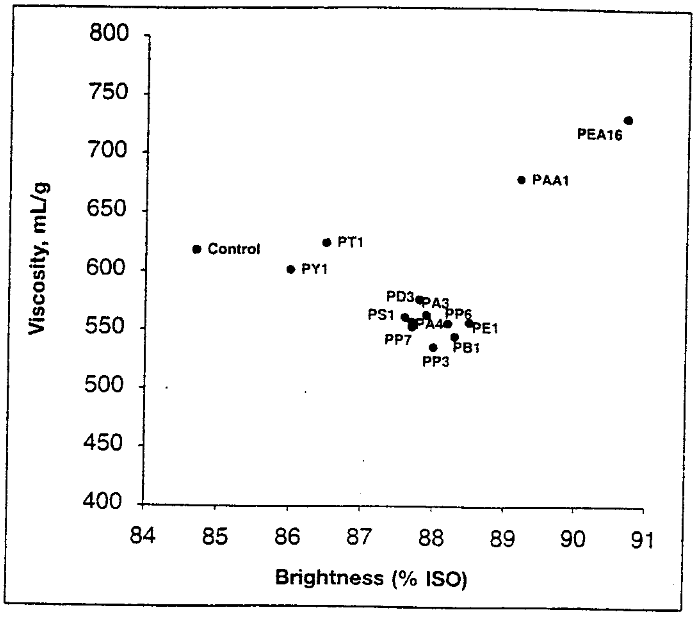

Fig. 2 **Viscosity vs. brightness for pretreatments (XOPretZRP), combined treatments (XO(Pret+Adit)ZRP) and the control (XOZRP), measured after the P stage.**

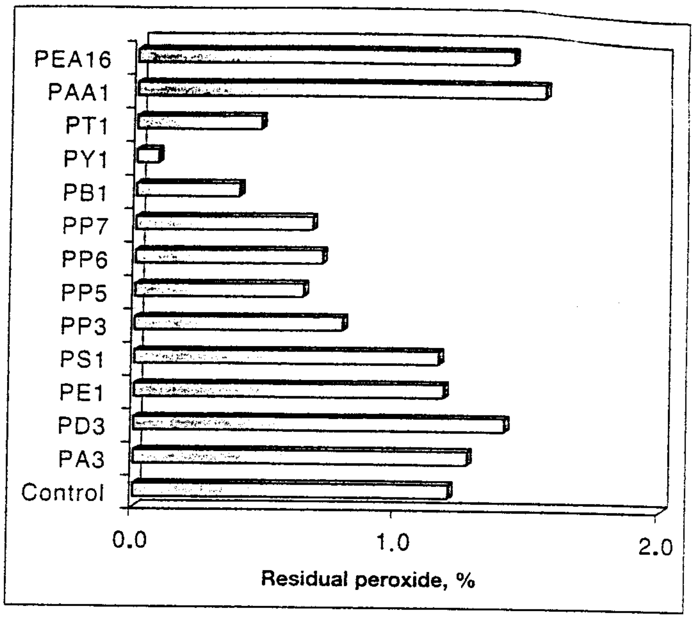

Fig. 3 **Residual hydrogen peroxide for pretreatments (XOPretZRP), combined treatments (XO(Pret+Adit)ZRP) and the control (XOZRP).**

This reduction is more evident when two stages (X and O) were carried out. The Cu ions were also partially eliminated (final value of 11 µg/g in XO pulp) during these treatments. Thus, an elimination of metal ions takes place during the X and O stages, but a certain quantity of these ions remains in the XO pulp entering the Z stage. These metal ions can have a detrimental effect on the subsequent bleaching stages.

Regarding the Fe content, it was not possible to obtain a clear conclusion, since an increase in Fe was obtained after oxygen delignification. This effect could be due to contamination of the sample by the reactor used for the oxygen delignification stages (O and XO).

The effects of metal ions on the Z stage have been studied by several authors (*7,26,27*). Metal ions in pulp catalyse the decomposition of ozone, thereby boosting the formation of hydroxyl radicals (°OH) (*4,14,16*). Hydroxyl radicals are strong oxidants, which react readily with organic substrates and exhibit a selectivity 10^5 to 10^6 times lower than that of molecular ozone (*12,13,28*). Therefore, hydroxyl radicals are considered the principal cause of cellulose degradation in the Z stage.

Both treatment with an acid and a chelating agent remove or inactivate metal ions, thereby increasing selectivity in the Z stage. In fact, the pretreatments using an acid (sulfuric or acetic) or a chelating agent (EDTA or DTPA) were those yielding the best results, particularly the latter. This may be because chelating agents more readily capture metal ions that interfere strongly with the bleaching process. Colodette et al. (*8*) refer to 'good' metal ions (Ca^{2+}, Na^+ and Mg^{2+}) and 'bad' ones (Fe^{2+}, Cu^{2+} and Mn^{2+}). Heijnesson et al. (*29*) classify the metal ions into two groups: those that have a catalytic effect (causing cellulose degradation and destruction of the bleaching agents) and those that have a stabilising effect (a protective effect against cellulose degradation). There are various theories on this topic, most of which, however, agree that Fe^{2+} is one of the most detrimental metal ions in bleaching systems. According to Süss et al. (*9*), ferrous ions require highly acidic conditions for their removal from fibres: however, the process can be expedited by adding a chelating agent to the medium. Thus, Chirat et al. (*7*) found that EDTA removed about 50 to 60% of Fe^{2+} and Cu^{2+}, and 90% of Mn^{2+}, whereas sulfuric acid eliminates only 20% of Fe^{2+}, 30% of Cu^{2+} and 85% of Mn^{2+}.

Abubakr et al. (*30*) indicate that metal ions are retained in the pulp by two mechanisms: by ionic exchange with acidic functional groups and by formation of complexes. Removal of the latter needs strong acidic conditions since these complexes are more firmly attached to the fibres. Adjustment of the pH is effective in eliminating metal ions that are attached by ionic exchange. However, a different chemical mechanism is necessary to eliminate metal ions that form complexes.

Soteland (*22*) also noted detrimental effects, particularly on brightness, from iron, copper and manganese. He found the most suitable pretreatment depended markedly on the particular type of pulp (i.e. on the specific metals it contained).

According to Zhang et al. (*14*), cobalt ions form complexes with hydroxyl radicals in the substrate, so they have no effect on ozone decomposition.

One other possible cause of the decreased pulp viscosity selectivity of acids relative to chelating agents is the extended carbohydrate hydrolysis during the acid treatment, which does not happen with chelating agents.

Treatments PAA1 and PEA16 were found to increase the process efficiency. They increased brightness (by 2 units in the more effective treatment) while preserving viscosity (about 150 units above the control value). These enhanced effects can be ascribed to the use of an additive in both treatments. The difference between these combined treatments and the other pretreatments is that the additive is present during the ozone stage.

Table 5
Metal ions in X, O and XO pulps.

Pulp	Mn (µg/g)	Cu (µg/g)	Fe (µg/g)
Initial	37	16	32
X	15	14	38
O	9	11	74
XO	6.5	11	79

Thus, the effect of acid (acetic acid in PAA1 and sulfuric acid in PEA16) is more beneficial since the acid can inhibit the action of metal ions during the reactions taking place in the Z stage and can increase ozone stability (*10, 17, 18*). The results are similar to those obtained by Lachenal and Bokström (*26*), who found the additive exerted an additional effect, less marked than that observed in this work, which they ascribed to the removal of metal ions. Pretreatments thus have favourable effects on ozone bleaching; however, the results provided by the two treatments including an additive suggest that simply using an additive during the Z stage may be enough. A study of additive application in the Z stage is in progress.

CONCLUSIONS

Pretreating pulp prior to ozone bleaching provides some advantages such as preserving viscosity while increasing brightness (by up to four units).

Pretreatments using an acid or a chelating agent yield the best results, which confirms that metal ions present during ozone bleaching of pulp can catalyse the decomposition of ozone, thereby favouring the formation of hydroxyl radicals and hence increasing cellulose degradation.

A metal ions study showed that a certain quantity of metal ions (Fe, Cu and Mn) remains in the pulp before the Z stage. Chelating agents are more efficient than acids in protecting against the effects of these metal ions, possibly because of their easier access to some metals and their greater ability to remove the more strongly interfering metals. Acids may result in more extensive cellulose hydrolysis and hence decrease polymerisation.

The EDTA-based pretreatment, particularly, produced the highest pulp brightness and a high proportion of residual peroxide, which could lead to hydrogen peroxide savings during the P stage or to ozone savings in the Z stage, while preserving viscosity.

The two treatments including an additive are the most efficient; in fact, they provide higher brightness and viscosity than the other pretreatments studied. These additional effects can be ascribed to the use of the additive during the ozone bleaching stage, since the acid reagent present during the ozone reactions inhibits the metal ion action and decreases ozone decomposition.

ACKNOWLEDGEMENTS

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The effects of alkaline leaching on pulp bleachability and physical properties

Jian Li and J. Martin MacLeod

ABSTRACT: The effects of alkaline leaching on pulp bleachability and physical properties were studied. Pulps with kappa numbers in the range of 16 to 48 were leached for 15 min at 100° C with 0.9 M NaOH. Delignification in alkaline leaching was between 17 and 30%. Successive delignification of unbleached kraft softwood pulp by alkaline leaching and oxygen delignification resulted in 25% more lignin removal than O_2 delignification alone. Relative to normally washed pulp, leached pulp could be C_DE-bleached to a lower kappa number with the same bleaching chemical charge; AOX production was proportional to the kappa number of either type of pulp. Leached pulp was slightly harder to beat, and had slightly higher tear and lower breaking length. Alkaline leaching can produce pulp with a lower kappa number for a given overall physical strength.

KEYWORDS: Alkaline pulping, bleachability, delignification, kraft pulps, leaching, oxygen, physical properties.

Because of the public concerns about chlorinated organic compounds in pulp bleaching effluents, researchers have been seeking better chemical pulping processes or process conditions for maximum lignin removal prior to bleaching. One such direction is research on better pulping processes for extended delignification (e.g., MCC®, RDH®, and Super-Batch®) *(1-3)*.

A different approach is to find suitable process conditions to ensure a more efficient removal of degraded, soluble lignin still in the unbleached pulp after normal washing. Recently, we found that significant amounts of lignin could be removed from washed, unbleached kraft pulp by alkaline leaching *(4)*. The amount of lignin removal increased with caustic concentration. Compared with pulp soaked in fresh tap water overnight at 1% consistency, the leaching of bleachable-grade kraft pulp in strong caustic solutions (pH 13-14) for relatively short times (15–30 min) at 100°C removed about 30% more residual lignin. Cellulose was not affected as long as alkaline leaching was performed under oxygen-free conditions at temperatures up to 100°C, but the extraction of hemicelluloses in 1 M NaOH was four to five times higher than that in 0.1 M NaOH.

A reduction of kappa number will obviously result in a reduction in bleaching chemical consumption and AOX production, but would alkaline leaching change the bleachability of the pulp? How might hemicellulose extraction affect pulp properties? Answers to such questions will help assess the potential for mill applications of the alkaline leaching concept.

In this report, results from oxygen delignification and C_DE bleaching of leached pulps are presented, and differences in the physical properties of normally washed and alkaline leached pulps are evaluated.

Experimental procedures

The pulp samples used in the leaching experiments were obtained by cooking 2- to 6-mm-thick black spruce chips to a given kappa number in a 20-L digester with forced liquor circulation. The pulping conditions were: 18% active alkali (as Na_2O, on oven-dry wood), 30% sulfidity, 90 min to 170°C, liquor-to-wood ratio of 4 L/kg, and H-factors appropriate to reach the target kappa numbers. Half of the cooked chips were disintegrated in and rinsed by tap water until the filtrate was clear. Then the pulp stood in cold water overnight at 1% consistency, was screened on a vibrating flat screen with 0.25-mm slots, and was thickened to 35% consistency for storage at 4°C. The other half of each batch of cooked chips was

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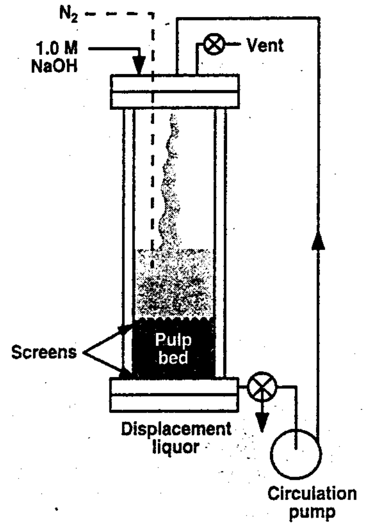
Li is an associate scientist and MacLeod is a senior scientist at Paprican, 570 St. John's Blvd., Pointe Claire, PQ H9R3J9, Canada.

1. Experimental setup used to leach kraft pulps in 0.9 M NaOH at 100°C



I. Kappa numbers and viscosities of the reference and leached pulps

Pulp no.	Pulp type	Kappa no.	Delignification, %	Viscosity, mPa·s	Viscosity loss, %
1-R	Reference	16.0		16.6	
1-L	Leached	11.4	28	16.0	4
2-R	Reference	28.9		28.0	
2-L	Leached	20.0	31	28.0	0
3-R	Reference	37.0		35.1	
3-L	Leached	27.6	25	34.0	3
4-R	Reference	47.8		42.1	
4-L	Leached	39.9	17	38.4	9

processed in the same way, but with deionized water. The pulp washed with tap water was used as the reference sample, and the pulp washed with deionized water was used as the starting sample in alkaline leaching experiments.

Figure 1 is a schematic of the leaching setup, a 20-L digester with flow circulation capability. A 200-mesh screen was placed at the bottom of the digester. The pulp [400 g oven-dry (o.d.) weight] was disintegrated and diluted with deionized water to 0.5% consistency. The dilute pulp suspension was added to the digester, and water was drained from the bottom. After pressing out the excess water, the pulp bed formed for leaching was about 39 cm high, 16 cm in diameter, and had 5% consistency. Another screen plate was placed on top of the bed to protect it. After the top cover of the digester was closed, the void space above the pulp bed was flushed with 20 equivalent volumes of nitrogen to eliminate oxygen in the gas phase.

The leaching liquor, one molar NaOH, was preheated to 100°C in a separate liquor accumulator. A leaching experiment was started by displacing the water in the pulp bed with NaOH solution. A 50 kPa nitrogen pressure was maintained above the bed to provide the force for liquor displacement, which started after about 4 L of NaOH solution had been added to the digester; NaOH solution was continuously added during the displacement. The displacement volume was about two times the water volume in the pulp bed, and displacement lasted for about 10 min. The total liquor volume in the digester before heating was about 19 L. After the pressure was released to the atmosphere, the leaching liquor was circulated at about 3 L/min, and the temperature was raised to 100°C in less than 2 min. Leaching was conducted at 100°C with liquor circulation for 15 min.

At the end of leaching, the liquor was forced out by nitrogen pressure, and the pulp bed was quickly dropped into 40 L of deionized water in a tank at room temperature to cool the pulp. The disintegrated pulp was washed with deionized water for about half an hour. Then the pulp stood in the water overnight at 1% consistency and was concentrated to 35% consistency for storage at 4°C.

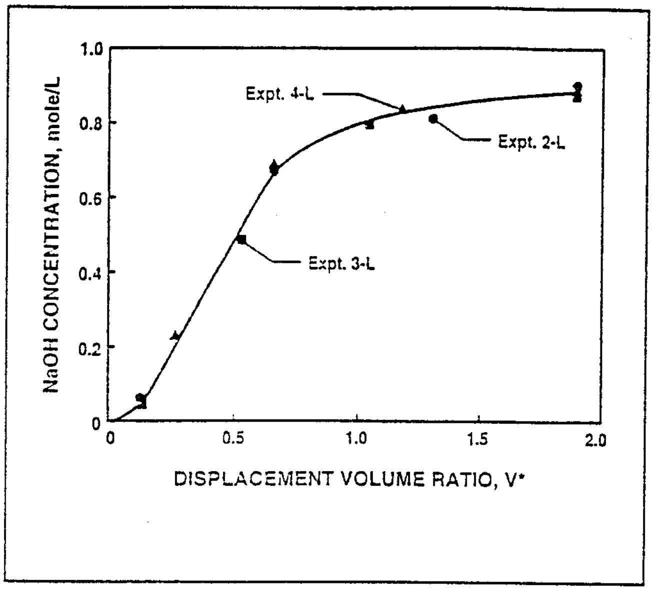
Oxygen delignification was performed with 20 g of each reference pulp and each leached pulp in a laboratory apparatus *(5)*. The experiments were conducted at 25% consistency, 100°C, and 400 kPa oxygen pressure for 45 min; NaOH and $MgSO_4$ charges were 1.5% and 0.025%, respectively, on o.d. pulp.

The reference and alkaline leached pulps were also tested in a conventional C_DE bleaching sequence. Chlorination was performed with a mixture of 90% Cl_2 plus 10% ClO_2, using an active chlorine multiple of 0.22 (i.e., the charge was 0.22 x kappa number). Treatment conditions were 30 min at 30°C and a consistency of 3.5%. Chemical consumption was 98–99% of the charge. Caustic extraction was done with an NaOH charge of 0.55 x C_D charge at 70°C for 90 min.

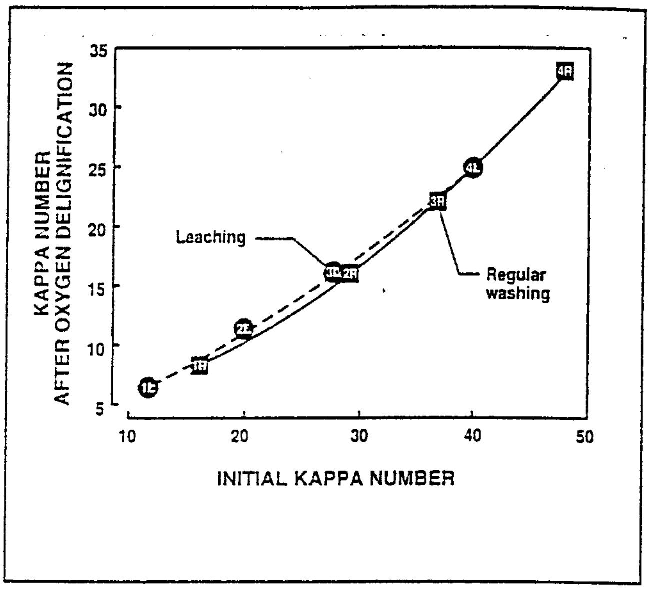
The kappa numbers and viscosities of the pulps after each treatment were determined. The α-, ß-, and γ-cellulose contents of the reference and leached pulps were measured according to CPPA Standard Test Method G.29P.

To assess physical properties, the reference and leached pulps were beaten in a PFI mill, made into 60 g/m^2 handsheets, and tested according to CPPA standard test methods.

2. Sodium hydroxide concentration reached a relatively constant level after two volumes of displacement.



3. Overall, the leached pulps reached lower kappa numbers after oxygen delignification.



Results and discussion

Alkaline leaching

The displacement stage in the 20-L digester was designed to replace all the water in the pulp bed by NaOH solution. Figure 2 shows the NaOH concentration measured in the outgoing liquor plotted as a function of the displacement volume ratio, V^*. This is the liquor volume displaced, V, divided by the initial water volume, V_0.

The breakthrough curve had very long tailing, perhaps due to low displacement efficiency and/or adsorption of sodium by the fibers. The concentration of NaOH began to rise at a very low displacement volume ratio, indicating that penetration of NaOH into the bed was quite high. In turn, this would result in dilution of the NaOH concentration above the pulp bed. This was confirmed by the measurement of NaOH concentration during the leaching period. The NaOH concentration was quite constant during the entire leaching time; in all four leaching experiments, the value was 0.90 ± 0.02 mole/L. Despite the low displacement efficiency and the dilution of NaOH, the reproducibility of the effect ensured that all the leaching experiments were performed at a reasonably constant NaOH concentration.

Table I lists the kappa numbers and viscosities of the four pairs of reference and leached pulps. The kappa number range of the reference pulps was reasonably wide, more than covering the bleachable range. The kappa number reductions by alkaline leaching were 4.6, 8.9, 9.4, and 7.9 units for the four pulps. With Pulps 1, 2, and 3, kappa number reduction increased with initial kappa number, and the amount of lignin removed was 25–31%. The lower leaching efficiency with Pulp 4-R may have been due to less uniform flow of the leaching liquor through the pulp bed. The small decreases in pulp viscosity indicated that leaching had little effect on cellulose.

One advantage of alkaline leaching can be illustrated by comparing Pulps 2-R and 3-L. The kappa numbers of these two pulps were close, but the viscosity of the leached pulp was significantly higher.

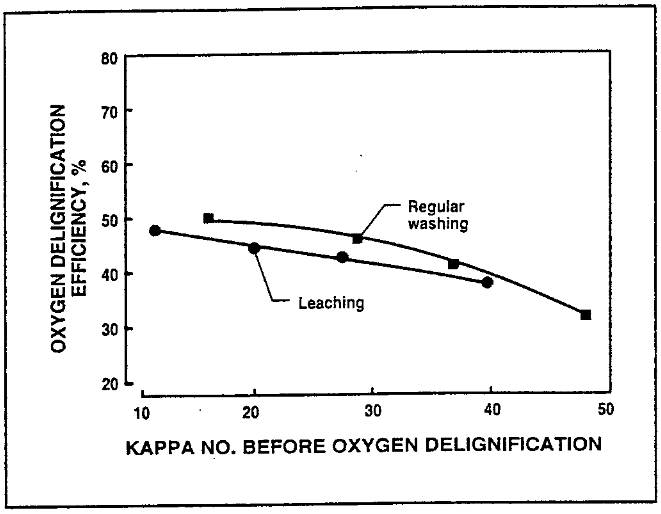
Oxygen delignification

Figure 3 illustrates kappa number after oxygen delignification as a function of initial kappa number. Comparing the post-O_2 kappa numbers of each pair of pulps (washed vs. leached), the alkaline leached pulps had lower kappa numbers after oxygen delignification (e.g., 15.9 for 3-L against 21.9 for 3-R), indicating that the effects of alkaline leaching and O_2 delignification were additive. The advantage of extra lignin removal via alkaline leaching before an O_2 stage is well demonstrated by this result.

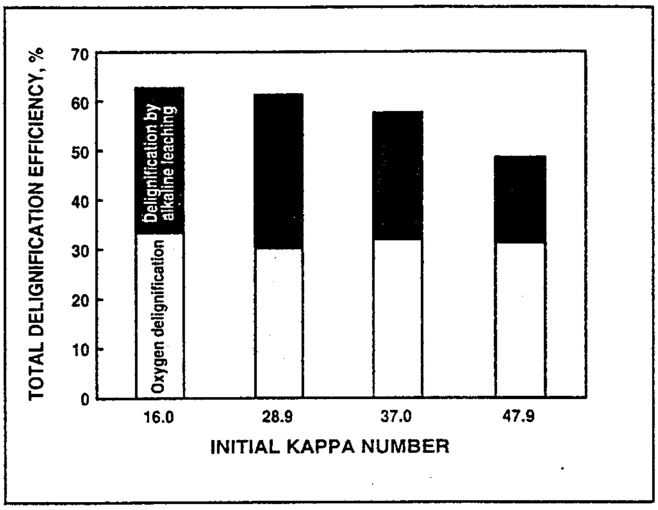
The two delignification effects were not 100% additive, however, because the line for the leached pulps was above the line for the normally washed pulps. This is more effectively demonstrated in Fig. 4. The two solid lines give the delignification efficiency of the oxygen stage; it was slightly lower for the leached pulps than for the normally washed pulps.

The nature of this lower efficiency can be explained by postulating that water-washed pulps contain a significant amount of alkali-soluble lignin, which could be removed without extensive degradation. This kind of lignin, however, is probably what has been removed during alkaline leaching. Oxygen delignification has two phases, and the first phase is very fast *(6, 7)*. In fact, this fast first stage may be mainly a leaching effect.

4. Oxygen delignification efficiency was slightly lower with leached pulps than with normally washed pulps when the comparison was made at the same kappa number before oxygen delignification.



5. Total delignification efficiency after leaching and oxygen delignification ranged from 48% to 63%.



The total delignification efficiency of alkaline leaching plus O_2 delignification is shown in **Fig. 5**. Despite the slightly lower O_2 delignification efficiency with the leached pulps, the total delignification efficiency was between 48% and 63%.

A further advantage of alkaline leaching can be seen from the pulp viscosities after O_2 delignification (**Table II**). The final viscosities of each pair of pulps were similar. Thus, the alkaline leached pulps have higher viscosities than the normally washed pulps when compared at common kappa numbers. For example, Pulps 2-R and 3-L had similar kappa numbers after O_2 delignification (15.7 and 15.9, respectively), but the leached pulp had a much higher viscosity.

II. Viscosities of the reference and leached pulps after oxygen delignification

Pulp no.	*Pulp type*	*Viscosity, mPa·s*	*Viscosity loss, %*
1-R	Reference	13.0	22
1-L	Leached	13.7	14
2-R	Reference	17.7	37
2-L	Leached	20.5	27
3-R	Reference	25.8	27
3-L	Leached	24.9	27
4-R	Reference	32.0	24
4-L	Leached	30.2	21

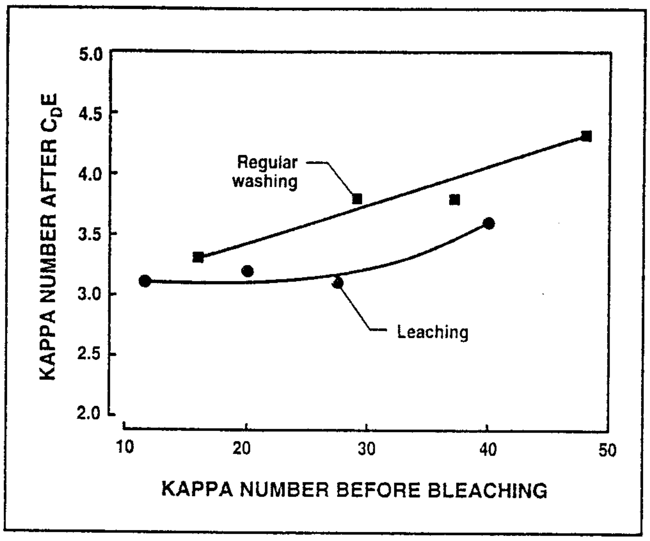
C_DE Bleaching

C_DE bleaching was performed with the four pairs of pulp samples listed in Table I. **Figure 6** shows the kappa numbers of the C_DE bleached pulps as a function of the kappa numbers before bleaching. Using C_D and E charges proportional to the ingoing kappa numbers, it was expected that the C_DE kappa numbers would decrease with initial kappa number *(8)*. Because the leached pulps had lower initial kappa numbers, the final C_DE kappa numbers of these pulps were naturally lower than those of their reference pulps. The unusual result in Fig. 6 is that the line for the leached pulps is lower than that for the reference pulps. More specifically, at a given initial kappa number, C_DE bleaching was more effective with alkaline leached pulps.

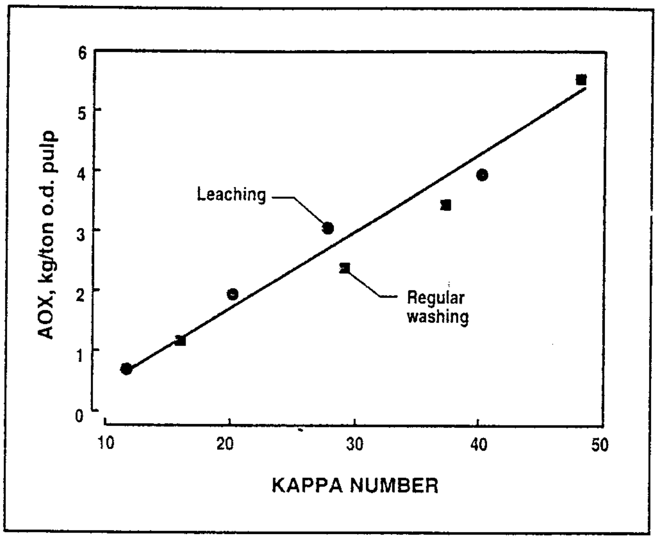
There is information indicating that soluble material in organic carryover is easily chlorinated to form highly chlorinated compounds, and that lignin in black liquor consumes more bleaching chemicals than residual lignin still in the pulp *(9)*. The net effect is that less chemicals would be available for degradation of the insoluble residual lignin. However, the nature or mechanism of enhanced delignification efficiency via leaching is not fully understood from the limited amount of information currently available.

The viscosities of the pulps after C_DE bleaching are listed in **Table III**. For each pair of pulps, the viscosities are about same, indicating that the effects of the bleaching chemical on cellulose are about the same whether or not the pulps were leached. The viscosity loss in C_DE bleaching, 8–17%, was comparable to literature values *(10)*.

6. Overall, the leached pulps had lower C_DE kappa numbers; this was also true at any initial kappa number.



7. AOX production in C_DE bleaching was linearly proportional to kappa number.



III. Viscosities of the reference and leached pulps after C_DE bleaching

Pulp no.	*Pulp type*	*Viscosity, mPa.s*	*Viscosity loss, %*
1-R	Reference	15.0	10
1-L	Leached	14.7	8
2-R	Reference	25.7	8
2-L	Leached	23.5	16
3-R	Reference	29.4	16
3-L	Leached	29.5	13
4-R	Reference	34.9	17
4-L	Leached	32.6	15

Figure 7 shows the AOX production from the combined C_D- and E-stage effluents as a function of kappa number before C_DE bleaching. AOX production decreased linearly with kappa number, which agrees well with results obtained by others *(11, 12)*.

A straight-line extrapolation in Fig. 7 does not go through the origin, and has an x axis intercept of kappa number 5. This agrees well with results reported by Liebergott *et al. (11)*. The reason for the nonzero intercept may be that AOX production is directly proportional to kappa number reduction instead of initial kappa number. The absolute values of these results are about 20% lower than literature data *(4, 11, 12)*. This may be due to effects during sample storage *(13)* or systematic error in the AOX analysis. If these effects on AOX value are proportional to the original value (20% in this case), the two conclusions drawn from Fig. 7 (i.e., a linear relationship and a nonzero intercept) would still stand.

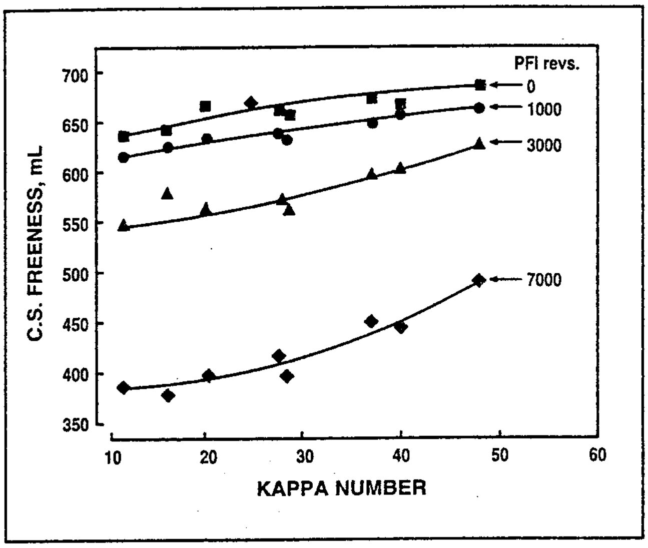
Physical properties

The comparison of pulp beatability should not be made with pulps in the same pair (i.e., a parent pulp and its leached version) because of the difference in lignin content. It is known that beatability becomes more difficult with increasing lignin concentration *(14)*. This was confirmed by the results shown in **Fig.** 8. At any fixed number of PFI revolutions, the freeness of both the leached and normally washed pulps increased with kappa number. Therefore, beatability is more fairly judged by comparing pulps of similar kappa numbers. Such a comparison of Pulps 2-R and 3-L (**Fig.** 9) indicates that the leached pulp was slightly harder to beat than the normally washed pulp.

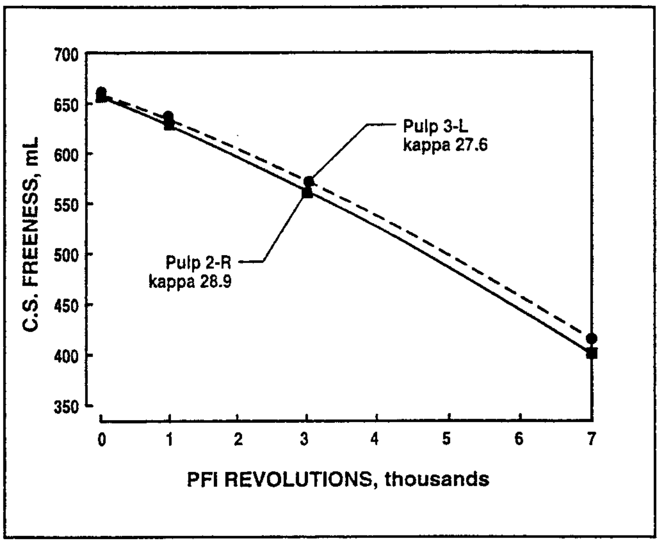
Tear-tensile performance is compared in **Fig. 10**, which contains results from the four pairs of pulps. The data representing each type of pulp have been enclosed in a bounded area. The large overlap of the two areas in the breaking length range of 9–13 km suggests that the overall physical strength of leached pulp is similar to that of normally washed pulp. The only distinct difference between the two sets of data is that the values for leached pulp are shifted to higher tear index and lower breaking length.

Although the results shown in Fig. 10 indicate that there is no physical strength loss as a consequence of alkaline leaching, the way in which tear-tensile strength changes as a function of lignin content cannot be deduced from this figure. To do so, the tear index of each pulp, interpolated at a

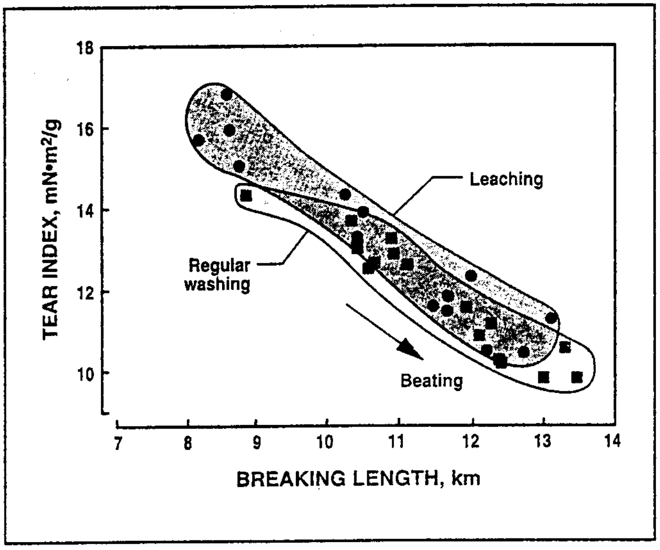
8. Canadian Standard Freeness decreased with kappa number at any value of PFI revolutions.



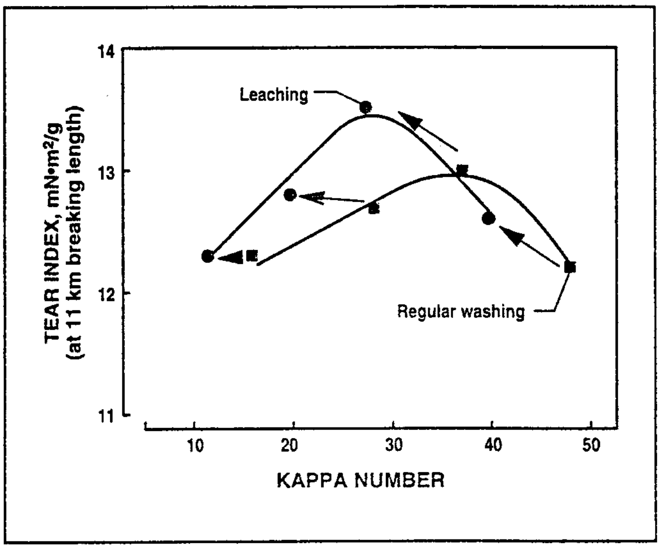
9. For a given kappa number, alkaline leached pulp was slightly harder to beat.



10. Leached pulps had higher tear indexes and lower breaking lengths.



11. Alkaline leaching did not change the overall physical strength of the pulp.

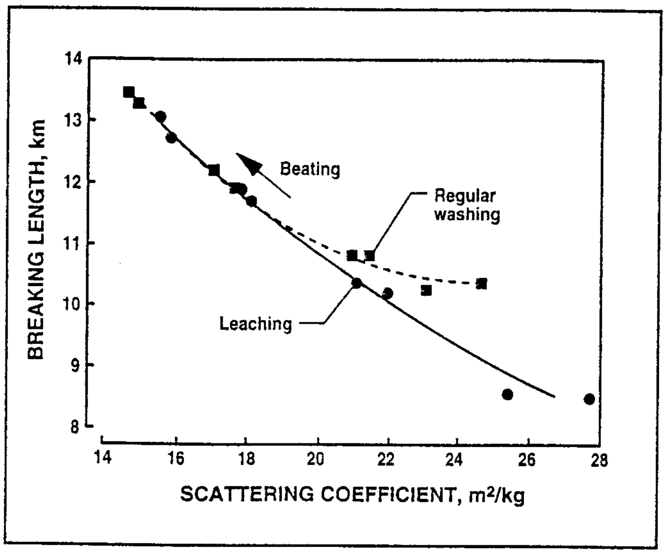


constant breaking length of 11 km, was plotted against its kappa number (Fig. 11); the arrows connect the pairs of pulps. The significant feature of Fig. 11 is that the arrows are either horizontal or slope upward. More specifically, the tear index at 11-km breaking length remains constant (1-L, 2-L) or increases slightly (3-L, 4-L). This means that alkaline leaching can produce a pulp with a lower kappa number while retaining a given strength level.

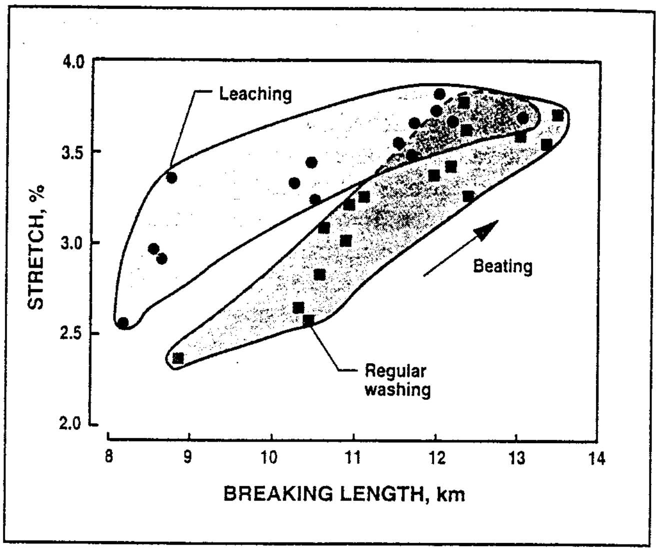
The fact that the leached pulps are shifted to higher tear index and lower breaking length (Fig. 10) cannot be explained by their relatively lower lignin contents, because lower lignin content should improve inter-fiber bonding and result in lower tear and higher tensile strengths. Are other factors at work here? It is well known that hemicelluloses can significantly influence fiber bonding *(15)*. We previously reported *(4)* that when the NaOH concentration in leaching was increased from 0.1 M to 1.0 M, significant amounts of hemicelluloses were extracted, while lignin removal was moderate.

In this work, we measured the α-cellulose content of the holocellulose of each pulp. The remaining portion of the holocellulose is ß- and γ-cellulose, representing the degraded cellulose and hemicellulose. The results are listed in **Table IV**. All the leached pulps have higher α-cellulose contents and lower hemicellulose contents. Higher

12. Alkaline leached pulps had higher scattering coefficients and slightly lower bonded areas and tensile strengths.



13. The higher stretch values of the leached pulps were probably due to extra pulp processing steps needed to perform the alkaline leaching.



IV. α-cellulose content of chlorite-delignified pulps

Pulp no.	*Pulp type*	*α-cellulose, %*	*Difference*
1-R	Reference	87.3	
1-L	Leached	89.3	+2.0
2-R	Reference	87.0	
2-L	Leached	89.3	+2.3
3-R	Reference	87.6	
3-L	Leached	88.9	+1.3
4-R	Reference	85.3	
4-L	Leached	87.9	+2.6

α-content would, in general, result in fibers that are somewhat stiffer and harder to beat; this may be the reason for the higher tear indexes of the leached pulps. Hemicellulose contributes to fiber–fiber bonding in two ways: increasing the plasticity of fiber walls so their surfaces are more conformable, and acting as a binder via hydrogen bonding of their hydroxyl groups *(15)*. This would explain the higher tensile strengths of the normally washed pulps.

The higher inter-fiber bonding of the normally washed pulps was confirmed by plotting the scattering coefficients against breaking lengths (**Fig.** 12). To minimize the effect that residual lignin might have on scattering coefficient values, only two pairs of pulps are compared: 2-R vs. 2-L and 3-R vs. 3-L. The entire scattering coefficient range of the normally washed pulps was shifted to lower values. The PFI mill beating revolutions were the same (0, 1000, 3000, and 7000) with both types of pulps; thus, a lower scattering coefficient was obtained for the normally washed pulps at any given beating value. We conclude that the small difference in tear-tensile performance was due to removal of some of the hemicellulose during alkaline leaching.

The data in Table IV can also be used to estimate the carbohydrate loss in alkaline leaching, and hence the pulp yield. Assuming that α-cellulose is stable under alkaline leaching conditions and that no carbohydrate material is lost during holocellulose preparation, the loss of hemicellulose during leaching can be calculated as:

$$\mathrm{Loss}_H(\%) = \left(1 - \frac{\alpha_R}{\alpha_L}\right)\left[100 - (kappa_R \times 0.147)\right] \quad (1)$$

where α_R and α_L are the percentages of α-cellulose in the reference and leached pulps, respectively, based on holocellulose, and $kappa_R$ is the kappa number of the reference pulp. The calculated losses of hemicellulose using the data in Tables I and IV are 2.2%, 2.5%, 1.4%, and 2.8%, respectively, based on the four reference pulps. Taking 50% as the approximate yield of unbleached pulp, we calculate that the yield loss (based on wood) is less than 1.5%.

Figure 13 shows that there is a significant difference in stretch between the reference and the leached pulps, at least initially. The higher stretch values of the leached pulps are probably the result of the extra pulp processing steps needed to perform the leaching operation. It was shown by MacLeod *(16)* that stretch increases along a brownstock fiber line as the pulp is subjected to more processing steps such as screening and pumping.

Conclusions

Successive delignification of unbleached kraft softwood pulp by alkaline leaching and oxygen delignification resulted in 25% more lignin removal than O_2 delignification alone. Relative to normally washed pulp, leached pulp could be C_DE-bleached to a lower kappa number with the same bleaching chemical charge; AOX production was proportional to the kappa number of either type of pulp. Leached pulp was slightly harder to beat and had slightly higher tear and lower breaking length. Alkaline leaching can produce pulp with a lower kappa number for a given overall physical strength. The difference in the tear-tensile performance of the reference and the leached pulps is probably due to the small amount of hemicellulose extracted during alkaline leaching with 0.9 M NaOH.

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Appita

Options for bleaching mechanical pulp with a lower effluent COD load

This paper, by H U. SUESS, M DEL GROSSO†, K SCHMIDT‡ AND B. HOPF§ is based on a presentation at the 55th Appita Annual Conference in Hobart, April 2001*

Peroxide bleaching of mechanical pulp requires alkaline conditions, which cause a solubilisation of wood substances, detectable as an increase of the effluent COD. Sodium carbonate could be applied as an alternative to sodium hydroxide as the alkali source; however, it is only capable of replacing sodium hydroxide by mass in equivalent amounts within a narrow range. The instability of in situ formed percarbonate is responsible for this limitation. The buffering action of sodium carbonate results in a lower COD and also in a lower consumption of H_2O_2.

Magnesium oxide, or hydroxide, is another alternative but this is limited by poor solubility. This necessitates very effective mixing to guarantee an even distribution. $Mg(OH)_2$ not only replaces NaOH but also most of the sodium silicate, which can be very attractive in terms of cost. COD is between 30% and 40% lower, but for very high brightness, a higher than normal peroxide charge is required.

Mechanical pulp is bleached industrially in a well-established process using hydrogen peroxide, caustic soda (NaOH) and sodium silicate. High brightness levels are achieved without difficulty if the stock concentration (s.c.) is high and retention time and temperature are within 'reasonable' ranges. The alkaline conditions of the process are responsible for hydrolysis of the acetyl groups bound to the hemicellulose. In addition hemicellulose and low molecular mass lignin compounds become water-soluble.

It is generally accepted that the perhydroxyl anion, generated from H_2O_2 and OH- (equation 1) is responsible for the bleaching effect. There is a competing decomposition reaction of the peranion at higher pH (equation 2) with additional H_2O_2, which generates oxygen.

$$H_2O_2 + OH^- \rightarrow HOO^- + H_2O \quad [1]$$

(bleaching reaction)

$$HOO^- + H_2O_2 \rightarrow O_2 + OH^- + H_2O \quad [2]$$

(decomposition reaction)

Thus alkaline conditions are required for bleaching, but conditions too alkaline are detrimental. Figure 1 describes the effect of bleaching with four different H_2O_2 amounts and different charges of caustic soda.

For every given amount of H_2O_2 a 'best' amount of caustic soda exists. Under the conditions of the conventional process the pH decreases continuously during bleaching. Quinones and conjugated double bonds are destroyed by oxidation generating carboxylic acids, which neutralise the solution. A rapid, initial phase of brightness increase is followed by a much slower phase of brightness growth and peroxide consumption. When the amount of caustic soda is too small a high residual of H_2O_2 remains; when it is too high, peroxide is consumed totally. In both cases the brightness increase is inferior (Fig. 1).

Because more caustic soda is required with increasing peroxide input and target brightness, bleaching with high H_2O_2 charges generates a higher COD load. The linearity of this increase becomes apparent from Figure 2. There is obviously a small potential to decrease the COD, namely to select the lowest possible charge of alkali for the activation. Staying on the lower part of the curves of Figure 2 allows generation of about 10% less COD without using significantly more bleaching chemical. The dissolved organic material not only requires effluent treatment; there is in addition a direct correlation between COD and pulp yield. The question is whether more buffered conditions could yield similar brightness and simultaneously give a lower COD load.

EXPERIMENTAL

All laboratory trials were run in plastic bags in a water bath. The pulp was preheated to temperature. The standard procedure was premixing of caustic soda, sodium silicate and chelant in a small amount of water; kneading of the chemicals into the pulp and adjusting the stock concentration with diluted peroxide and the exact amount of water. At the end of the test the pulp was repulped at 2% s.c. and samples for COD and residual were separated. Handsheets were prepared for brightness testing. The procedure was modified for the pulp pretreatment with DTPA and to mix $Mg(OH)_2$ effectively with the pulp: Pulp was stirred at 2% s.c. with the chelant using mill water, $Mg(OH)_2$ was added after 30 min., stirred for 3min. and dewatered to a concentration of above 30%. The bleaching chemicals (H_2O_2, Na silicate) were added after preheating the pulp. Brightness was analysed according to ISO 2470 using handsheets formed in a Büchner funnel on filter paper. Residual peroxide was decomposed with catalase before COD was determined.

RESULTS AND DISCUSSION

Bleaching with strong buffering

The use of soda ash (Na_2CO_3) as an alternative to NaOH was described earlier (*1*). This replacement is possible, however, with economical amounts only within a rather narrow H_2O_2 range. Figure 3 shows the required amounts of alkali as NaOH or Na_2CO_3 for different peroxide levels. Only at about 2% H_2O_2 were the amounts of NaOH or Na_2CO_3 nearly identical. For a lower input of H_2O_2 more soda ash is required. This could be expected on the basis of a stoichiometric calculation. On the other hand with high peroxide addition even a higher charge of Na_2CO_3 does not generate the brightness achieved with NaOH. This sets a limit to the applicability.

All bleaches with soda ash had a higher peroxide residual. Only a very high soda ash input decreases the residual, but this does not increase the brightness. On the positive side, there is a significant effect of buffering on the COD level;

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* Director Applied Technology, Degussa, Hanau, Germany.

† Business Director, Degussa (SEA) Pty. Ltd., Singapore.

‡ Applied Technology Manager, Degussa, Hanau, Germany.

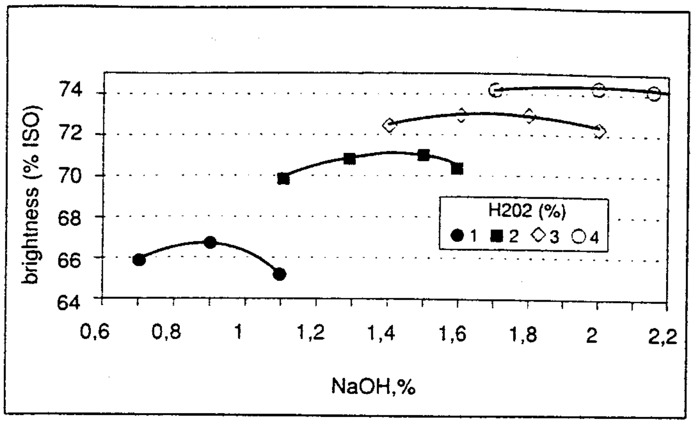

Fig. 1 **Effect of optimised charges of NaOH and different peroxide amounts on brightness. Bleaching at 65°C, 3h, 20% s.c. and with 2% Na silicate addition.**

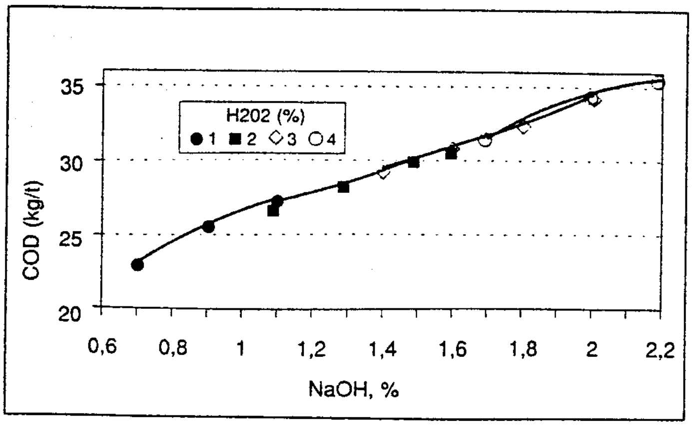

Fig. 2 **COD load increase with increasing caustic soda addition.**

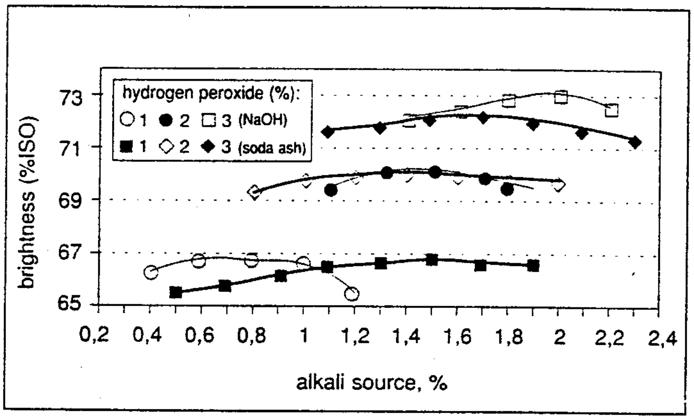

Fig. 3 **Bleaching of TMP with activation by caustic soda or soda ash – development of brightness after 3h at 70°C.**

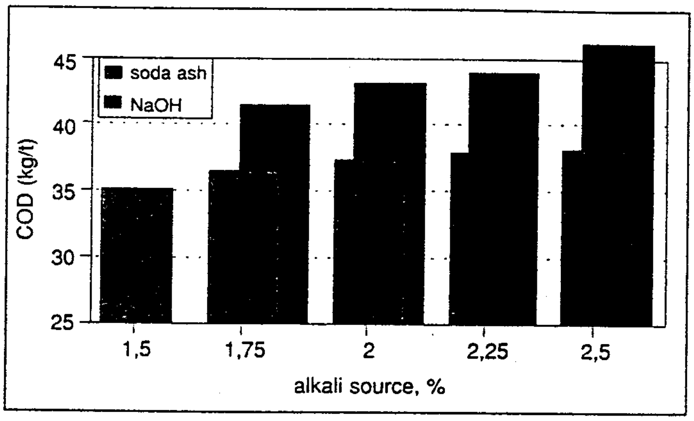

Fig. 4 **Comparison of the COD load with NaOH or Na_2CO_3 application in bleaching of a softwood TMP with 4% H_2O_2.**

the amount of dissolved organic material decreases (Fig. 4).

The buffering effect is even higher with sodium bicarbonate. This compound was also described as an alternative to caustic soda (*2*). If applied under conventional conditions, i.e. at about 70°C and 3 h retention time it produces similar effects: a limited consumption of peroxide and an inferior brightness gain. Brightness remains one to two brightness points lower if $NaHCO_3$ is used to replace NaOH.

The most obvious options to achieve a better consumption of H_2O_2 are an increase of the amount of bicarbonate, a longer retention time or a higher temperature. Surprisingly neither of these measures yields a better result. Despite the buffering, which should suppress the decomposition reaction (*2*), peroxide was consumed without any brightness improvement. There are obviously unknown side reactions. A comparison of the stability of diluted H_2O_2 at 70°C in the presence of 0.5 mol/L of different buffering compounds gave a surprising result. In contrast to the statement about a poorer stability at high pH, the drop in H_2O_2 concentration was most pronounced in the presence of the well buffering carbonates (Fig. 5). The concentration of peroxide decreased rapidly in the presence of carbonate ions. Therefore the pH cannot be the only reason for the loss of peroxide – there has to be some other reason.

Thus in addition the temperature dependence was measured for the H_2O_2 decomposition in a bicarbonate solution (Fig. 6). The data show a significant acceleration of the decomposition above about 50°C. This explains why a temperature increase will not improve the bleaching result. At higher temperature only the decomposition reaction will be accelerated. This acceleration takes place in the presence of carbonate or bicarbonate; therefore a decomposition of intermediately formed percompounds is very likely.

Peroxide is not decomposed in the presence of CO_2 under weak acidic and neutral conditions. Therefore it is very likely that the bicarbonate peranion has a limited thermal stability. Reaction 3 describes this potential decomposition path:

$$HOCOO^- + H_2O_2 \rightarrow HOOCOO^- + H_2O$$

$$HOOCOO^- + H_2O_2 \rightarrow HOCOO^- + O_2 + H_2O \qquad [3]$$

In kraft pulp bleaching the substitution of NaOH with Na_2CO_3 in the E stage was reported to give a poor response to H_2O_2 addition (*3*). The authors did not offer an explanation; however, the results presented in Figure 6 indicate the reason for the poor performance. Styrene derivatives are epoxidised at room temperature with bicarbonate-buffered peroxide solutions (*4*). Thus the percarbonate anion is readily formed; however, it decomposes rapidly at elevated temperature. As a consequence it is only possible to apply carbonates in the very narrow window described above or under rather impractical conditions of low temperature with an extreme retention time. Therefore carbonates are not the

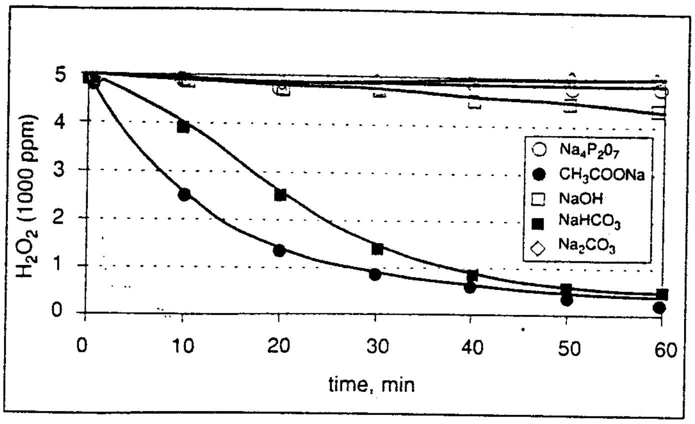

Fig. 5 **Stability of alkaline peroxide solutions in the presence of different buffers at 70°C, 5000ppm H_2O_2, 0.5mol/L buffer and distilled water. Initial pH values: NaOH, 13; Na_2CO_3, 11.1; $Na_4P_2O_7$, 9.8; $NaHCO_3$, 9.2; CH_3COONa, 8.2.**

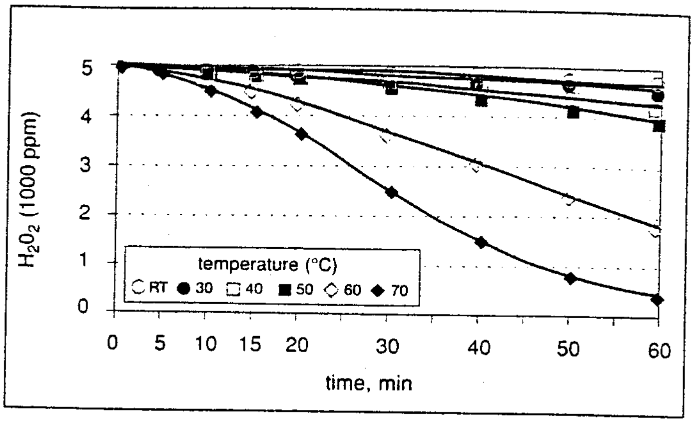

Fig. 6 **Stability of bicarbonate buffered peroxide solutions in distilled water at different temperatures with a constant charge of 20 g/L $NaHCO_3$.**

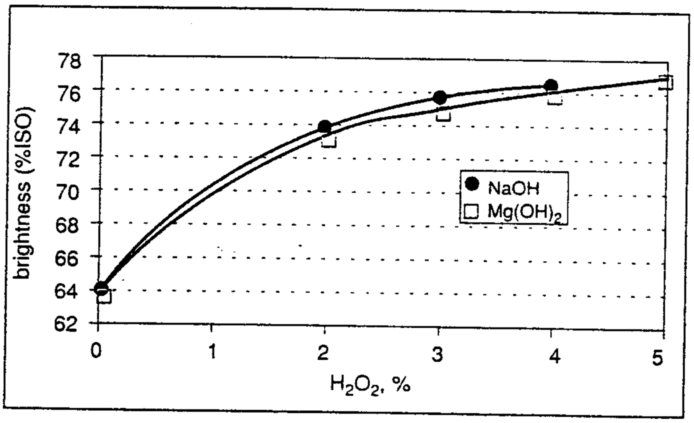

Fig. 7 **Bleaching of PGW pulp with H_2O_2 using NaOH or $Mg(OH)_2$ as the alkali source. Optimised charges of NaOH were used; $Mg(OH)_2$ input was 0.75% at 2% H_2O_2 and 1% for all other bleaches; constant charge of 2% Na silicate; 70°C, 3 h and 20% s.c.**

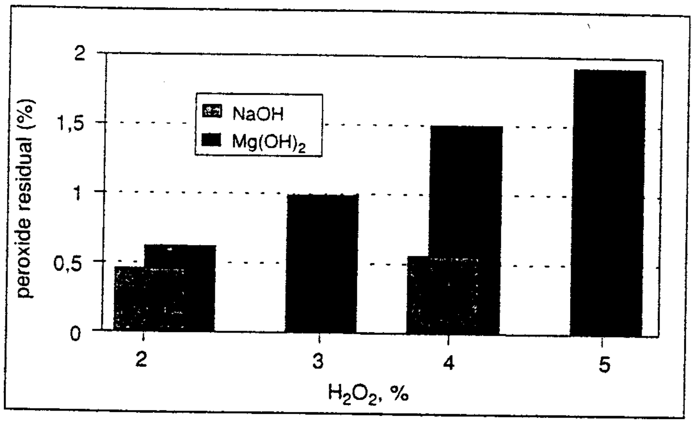

Fig. 8 **Peroxide residual in peroxide bleaching using NaOH or $Mg(OH)_2$ as the alkali source. (Conditions as for Fig. 7).**

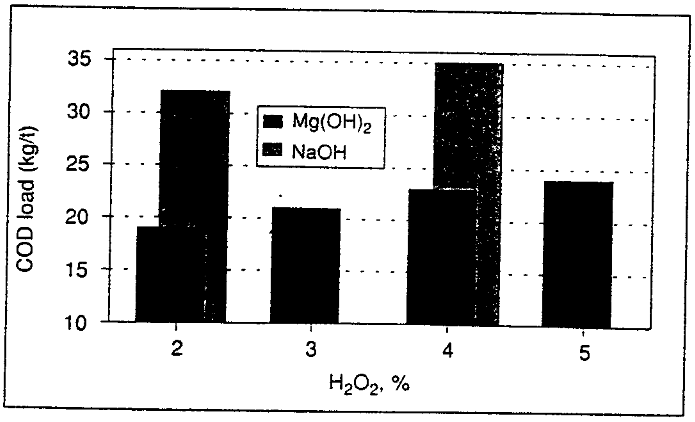

Fig. 9 **COD load in peroxide bleaching using NaOH or $Mg(OH)_2$ as the alkali source. (Conditions as for Fig. 7).**

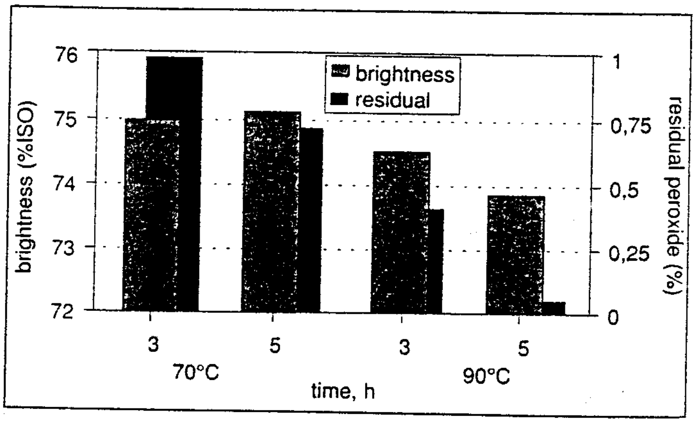

Fig. 10 **Bleaching with $Mg(OH)_2$ for prolonged time and higher temperature. Bleaching at 20% s.c., with 3% H_2O_2, 1% $Mg(OH)_2$ and 2% Na silicate.**

chemicals of choice for buffering.

On the other hand, the results indicate the potential of bleaching at a lower pH. As an alternative, the poorly soluble magnesium compounds, either magnesium oxide (MgO) or magnesium hydroxide ($Mg(OH)_2$), could become the chemical of choice as it will not produce a high pH.

Bleaching with magnesium hydroxide

The application of magnesium oxide in mechanical pulp bleaching has been described earlier in several papers; the papers cited here is an incomplete list (*5-9*). Despite this frequent description, no widespread industrial application resulted, an indication of severe difficulties to establish a reliable process configuration. The question is: Can

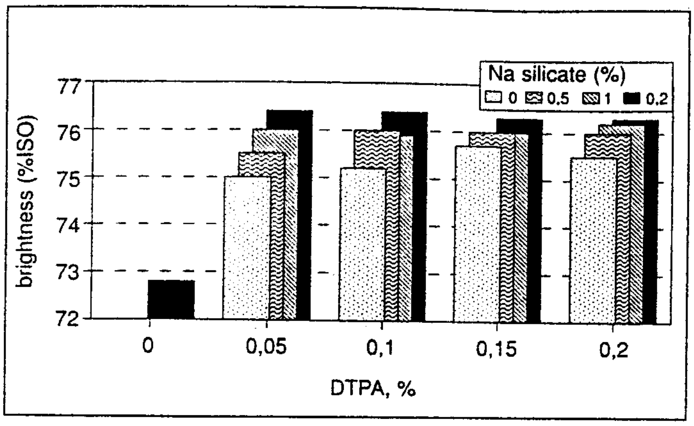

Fig. 11 **Effect of DTPA, sodium silicate and peroxide charge on brightness. DTPA pretreatment at 2% s.c. for 30 min. Bleaching with 3% H_2O_2, 1% $Mg(OH)_2$, at 70°C and 20% s.c.**

obvious existing problems with the application be solved?

There is one very important property of magnesium oxide: it is nearly insoluble in water. This is an attractive feature;
it would slowly dissolve with the generation of acidic groups during the bleaching process. Thus the pH would be rather constant. On the other hand the insolubility of the MgO has a negative side effect. It cannot be expected that MgO or $Mg(OH)_2$ particles would be capable of diffusing within the pulp mixture, especially not at high stock - concentration. Therefore it is extremely important to use fine particles and to distribute them as evenly as possible in the pulp.

The first laboratory tests with MgO showed poorly reproducibility. The MgO powder formed aggregates, which were as large as 1 mm in diameter. An even distribution was difficult to achieve. It was therefore decided to run the laboratory tests with technical grade magnesium hydroxide slurry, precipitated from seawater and never dried.
The $Mg(OH)_2$ particle size was between 2 μm and 5 μm. It was added to the pulp at 2% s.c. with stirring and the pulp was dewatered to high stock concentration. Because of the very low solubility of the magnesium salt it was retained completely in the pulp.

The bleaching tests were run under normal conditions of 70°C, with 3 hours retention time, at 20% s.c. and with 2% sodium silicate addition. Figure 7 compares the brightness response of a pressurised groundwood pulp using either caustic soda or magnesium hydroxide for activation. The graph shows a very similar brightness development. Only at very high charges of H_2O_2 did the brightness gain with magnesium hydroxide activation become inferior requiring a higher input of peroxide to achieve the same target brightness.

Variation of the amount of $Mg(OH)_2$ had very little effect due to its limited solubility. Table 1 shows the impact of higher or lower $Mg(OH)_2$ charges. While 0.5% is obviously too low a charge, there is no significant difference between the addition of 0.75% or 1%. Obviously the $Mg(OH)_2$ charge must be high enough to guarantee an end pH above 7. If this is not the case the brightening reaction stops and the H_2O_2 residual stays high. The amount of acidic groups generated during bleaching decides the demand for $Mg(OH)_2$ to maintain a final pH above 7. Consequently there is potential for cost savings as the demand for caustic soda is higher than that for $Mg(OH)_2$ on a mass basis. For example an input of 4% H_2O_2 requires about 2.4% NaOH for the activation; with $Mg(OH)_2$ an addition of 1% is sufficient. Bleaching with only 2% H_2O_2 requires only about half the alkali; 0.75% $Mg(OH)_2$ or 1.4% NaOH. This correlates with the molecular mass of the compounds and the stoichiometry.

The H_2O_2 residual measured after bleaching with $Mg(OH)_2$ is shown in Figure 8. The H_2O_2 residual is much higher compared with the caustic soda reference. It becomes clear from Figure 6 that a higher input of peroxide is required to achieve a high brightness. Therefore the increasing residual indicates less side reactions compared with the reference. The lower pH generates much less COD: the decrease is higher than 30% (Fig. 9).

Table 1

Effect of the addition of different amounts of Mg(OH)2 in groundwood bleaching with constant 2% H_2O_2. (Conditions as for Fig. 6).

Mg(OH)2 (%)	Final pH H_2O_2	Residual (%)	Brightness (% ISO)
0.5	6.8	0.91	72.9
0.75	7.2	0.62	73.4
1	7.4	0.5	73.5

These results raise additional questions: Is it necessary to operate with such a high excess of peroxide? Could there be a better use of the excess with other bleaching conditions?

Figure 7 gives a clear answer to the first question: higher end brightness results only if more peroxide is applied. Thus under the given conditions the high residual appears to be inevitable. A higher temperature or prolonged reaction time appears to be the only options to push the peroxide consumption and achieve an even better brightness. However Figure 10 shows only a moderate increase in brightness with longer retention time. It also shows the poor response to higher temperature: this increases peroxide consumption but does not lift the brightness.

The $Mg(OH)_2$ used in the tests had a low level of impurities; the iron content was less than 100 ppm Fe_2O_3. In peroxide bleaching, chelating agents are normally applied to suppress the decomposition caused by transition metals. However, chelates are formed not only with transition metals but also with alkaline earth metals like magnesium. In the presence of a high amount of magnesium a competition between metals might cause problems with peroxide stabilisation.
It was therefore important to learn about the demand for chelants. The pulp used in these experiments was analysed for its content of iron and manganese. The iron content was found to be 410 ppm and the manganese level 76 ppm. This translates into a total amount of 410 g Fe/t (7.34 mol) and 76 g Mn/t (1.38 mol). Thus the demand for a chelation agent should be as high as 8.7 moles.

However, Figure 11 demonstrates a much lower demand for chelant DTPA. The use of only very small amounts of DTPA improved the bleaching result significantly and an input of about 0.15% DTPA was sufficient to give a high brightness. The theoretically required 8.7 moles of chelant for iron

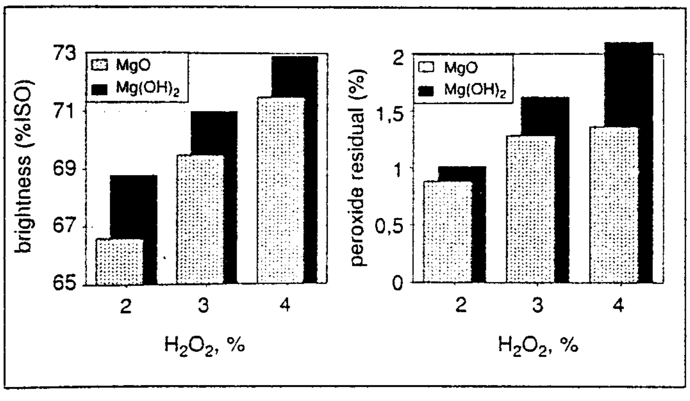

Fig. 12 **Effect of bleaching with MgO containing high iron and maganese levels on brightness and peroxide residual.**

and manganese would translate into a demand of 1.1% DTPA. This is without considering interference by magnesium. In reality the addition of 0.15% DTPA (1.2 mol) gives enough stabilisation (Fig. 11). Obviously the availability and the diffusion ability of the transition metals are much lower.

The positive effect of the silicate addition is clearly seen from Figure 11. Precipitation of transition metals by silicate appears likely. The amount of silicate can be much smaller compared with the conventional process; an amount around 0.5% on pulp appears to be sufficient.

The potential to apply low quality magnesium oxide containing a higher level of impurities was tested in additional experiments. This MgO, a mined product, was heavily contaminated with iron and maganese; the impurity level was 3000 ppm Fe and 330 ppm Mn. The bleaching results are given in Figure 12. Despite the high level of metals contamination a peroxide residual was measured in all experiments. This residual was significantly lower compared with the use of the 'pure' magnesium compound and the brightness was about two to three points lower with the poorer quality MgO. These experiments demonstrate the flexibility of Mg-activated bleaching in dealing with high contamination levels.

Table 2

Chemicals demand in bleaching with $Mg(OH)_2$ and NaOH. (H_2O_2, NaOH and $Mg(OH)_2$ as 100%, silicate and chelant as supplied. Conventional process: bleaching with 4% H_2O_2 to 76.5 % ISO).

Chemical (%)	Conventional process	$Mg(OH)_2$ process
H_2O_2	4	4.0 to 4.2
NaOH	2.4 to 2.6	—
$Mg(OH)_2$	—	~1.0
Na silicate	2 to 3	~0.5

Table 2 shows the demand for chemicals for conventional bleaching and the magnesium activated alternative. The lower demand for activation alkali, the decrease in sodium silicate demand and the higher pulp yield would more than offset the higher price per kg for a top quality magnesium hydroxide compared with caustic soda.

CONCLUSIONS

In mechanical pulp bleaching buffering of the bleaching process decreases the amount of dissolved organic compounds; it lowers the effluent COD load.

Buffering with carbonate-containing compounds results in either incomplete brightening or peroxide losses due to the decomposition of intermediately formed percarbonate.

The application of magnesium hydroxide as the alkali source has been shown to be a cost effective alternative to NaOH with the following characteristics:

- Conventional bleaching conditions are suitable.)
- The effluent COD decreases by about 30% to 40%.
- The demand for $Mg(OH)_2$.is about half that for NaOH.
- The demand for sodium silicate can be lowered to around 0.5%.

It is of extreme importance to adjust the water circuits and to apply the best technology in mixing for the addition of magnesium hydroxide to achieve these benefits.

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Control of AOX Discharges in Pulp & Paper Industry- The Role of New Fibreline

S. Panwar, R.M. Mathur, A.G. Kulkarni

Central Pulp and Paper Research Institute, P.O. Box No. 174, Saharanpur-247001 (U.P.)

ABSTRACT

The increased environmental awareness, cost competitiveness and quality consciousness particularly about high brightness chlorine free paper have forced the pulp and paper industries switch over to new fibre line with cleaner production options like ECF & TCF bleaching process to control the discharge of AOX below the toxicity level. However, the Indian pulp and paper industry is still persisting with the use of conventional pulping and high dosage of chlorine to produce high brightness product due to technological and economic constraints. With the emergence of regulation of discharge of AOX as an environmental issue in recent times, Indian pulp & paper industry is at cross road as it is faced with the challenge of becoming both cost competitive as well as environment friendly to survive in the international market. The present paper highlights the status of AOX level, level of technology, integrated approach and constraints to adopt the new fibre line to reduce the discharge of AOX to make Indian pulp & paper Industry more eco-friendly and internationally competitive.

INTRODUCTION

The bleaching of pulp with chlorine based chemicals produces toxic chlorinated phenolic compounds some of which are bioaccumlable and persist in environment for a long time. The increased environmental awareness, customer preferences for ecofriendly (chlorine free) products and imposition of stringent discharge norms have forced the pulp mills to adopt cleaner production options to reduce the kappa number of unbleached pulp so as to minimize /eliminate the use of chlorine based bleaching chemicals. The development process to reduce the kappa number of unbleached pulp is depicted in Fig. 1. With the development of technologies like extended delignification, oxygen delignification, improved pulp washing, chlorine dioxide bleaching etc., most of the pulp mills in developed countries have introduced new fiber line to produce paper products of high brightness ranging from 85-90% with AOX generation below toxicity level. The advantages of consistent supply of uniform wood based fibrous raw materials and high scale of operation have facilitated the switchover in these mills. Indian pulp and paper industry is still employing conventional pulping and bleaching process and have limitations to adopt the new modified fibre line to produce quality paper of international standards primarily because of low scale of operation and use of mixed fibrous raw materials. However inspite of all these limitations the Indian paper mills are managing to produce paper of brightness above 80% ISO which obviously is at the cost of increased chlorine consumption resulting in high level of AOX generation.

Technological status of Indian pulp & Paper Mills

The pulp and paper industries in India are scattered, old and vary in terms of size, use of fibrous raw material, process employed, machinery used and end products. These mills use a wide range of fibrous raw materials to produce variety of paper. In view of AOX discharge the paper mills are categorised broadly into :

Large Scale Mills (with chemical recovery process)

Small Scale Mills (without chemical recovery process)

The technological status of these mills is discussed below:

Scale of Operation

The scale of operation in large scale pulp and paper mills ranges from 100- 275 tonnes of pulp per day which in small mills is in range from 20-70 tonnes pulp per day. The low scale of operation of Indian paper mills is primarily due to scarcity of wood and inconsistent supply of other forest based raw materials. Further, the resource constraint is another reason for low scale of operation. Almost all the small scale mills are operating without chemical recovery system because of size constraint and are discharging their black liquor along with other streams.

Level of Technology

Pulping process

The kappa number of the unbleached pulp produced varies between 18-26. The reason for maintaining high kappa are the mixed raw material pulping and capacity limitation of chemical recovery boiler . By the same process the integrated agro residue based mills are producing pulp of kappa number between 14-16. J.K. Paper Mills, Orissa is the only mill employing modified RDH pulping process and oxygen delignification process i.e. advanced pulping technologies to produce pulp of better quality and low kappa number between 12-14 by using bamboo and eucalyptus.

Almost all the small scale agro based mills are employing soda pulping for producing pulp of high kappa number i.e 30-32 due to economic reasons as conventional chemical recovery system is not practiced and major part of lignin is removed in subsequent conventional bleaching process using elemental chlorine and hypochlorite .

Pulp washing system

The large integrated mills normally use conventional brown stock washers (BSW) with counter current washing for extraction of black liquor and washing of pulp. The efficiency of BSW's is defined in terms of soda losses and carry over of organic matter along with pulp entering the bleaching section. Due to inherent quality of fibers in the pulp from these raw materials and washing technology employed, the carryover of the organic matter, in terms of COD is generally on higher side. The washing efficiency of existing BSW's operating in small mills are even more lower as 50-70% higher carry over of COD alongwith pulp compared to large wood based mills has been observed which results in increase of demand of bleaching chemicals.

Bleaching process

Most of the large integrated mills are using conventional CEHH sequence for bleaching of pulps to a brightness level of 80-85% ISO, primarily to produce quality products of international standards. Some mills have started the use of chlorine dioxide alongwith elemental chlorine during chlorination and in final stages of bleaching only to get higher and stable brightness of pulp. The consumption of total chlorine in these mills varies from 60-100 kg/ tpulp . Most of these pulp mills are now using oxidative alkali extraction bleaching to increase pulp brightness and improve the quality of pulp and bleach plant effluent. The small scale mills based on agro residues also use conventional CEHH/ HH sequence to bleach the pulp to a brightness level of 75-80%. The consumption of chlorine in these mills is comparatively high and vary around 140-160 kg/t pulp primarily because of high kappa number of unbleached pulp and also high carry over COD along with pulp .

The pulp mills in developed countries have incorporated various measures to changeover to new fibre line in pulp mills which includes extended delignification, improved pulp washing, oxygen delignification , chlorine dioxide bleaching etc. However , the application of these technological development is mostly limited to developed countries primarily due to advantages of consistent supply of wood based fibrous raw materials and high capacity of pulp mills. The use of mixed fibrous raw materials, low scale of operation , high capital investment are the major constraints which restrict Indian pulp and paper mills to switch over to new cleaner production fibre line. The techno-economics of the modern pulping and bleaching technologies in Indian perspective is indicated in Table-1.

Status of AOX level in Pulp and Paper Mills Indian perspective

In the last decade, extensive R&D studies were conducted by CPPRI related to formation of AOX during bleaching of pulp produced from various fibrous raw materials commonly used by Indian pulp and paper mills . assessment of status of technology and level of AOX in both large and small scale mills producing bleached variety of paper and also the measures to control the discharge of AOX.

Table 1 Techno-economics of New Pulping & Bleaching Process in Indian Perspective

Technologies	Minimum Investment Rs. Crore	Level of Operation t/d	Limitations
Extended Delignification raw materials	55-60	>350	Low level of operation Use of mixed fibrous
Oxygen Delignification	20-25	>300	High capital investment
Chlorine dioxide bleaching (2.0-2.5 t/d)	32-35	~ 300	Age of mills Require new infrastructure

Source : Information available in literature and from association of mills

Table 2 Status of AOX in Indian Pulp and Paper Mills

Type of product	Kappa No.	COD Carry over during washing kg COD/T pulp	Consumption of Chlorine kg/t pulp	AOX level kg/t Paper	
				Gen.	Final Discharge
Rayon grade Pulp	12 - 16	Kappa No. Differ 1.5 units	25 - 28	0.7-1.0	<0.50
Newsprint chemical pulp	20 - 22	—	20 - 25	0.50-0.60	<0.50
Writing & Printing Paper:					
Large Mills	15 - 26	20 - 25	35 - 110	2.0-4.50	1.0-2.50
Small Mills (Agro-based)	30-32	30 - 40	140 - 160	6.0-10.0	4.0-6.50

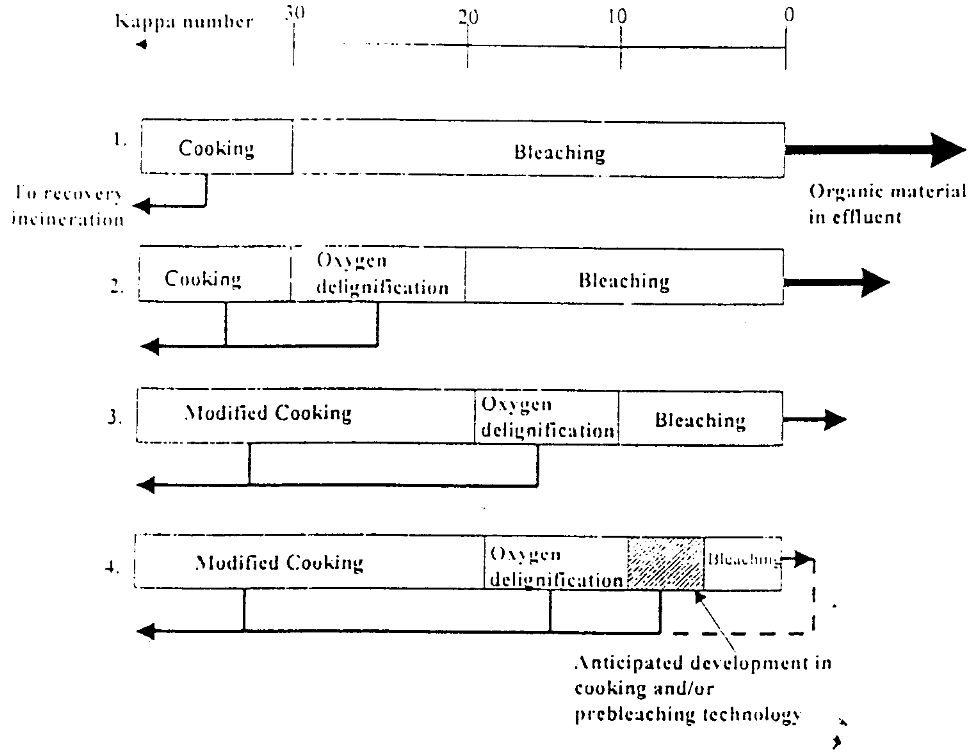


Fig. 1 Development of alternate pulping process

The level of AOX in large scale integrated mills varies between 2.0 -4.5 kg/t paper . Low level of AOX was observed in the mills using RDH , oxygen delignification and chlorine dioxide bleaching as compared to mills using conventional CEHH bleaching process. In small scale mills the scenario of AOX discharge is more alarming as these mills are using high dosage of chlorine to bleach pulp of high kappa number due to economical reasons . The generation of AOX in these mills varies from 6-10 kg /t paper . The high level of AOX is primarily due to following reasons :

- High kappa number of pulp due to absence of chemical recovery.
- High carryover of black liquor alongwith pulp going to bleaching plant.
- Use of high dosage of elemental chlorine.
- Obsolescence in technology & equipments.

The level of AOX generated and finally discharged in Indian pulp and paper mills is given in Table 2.

Integrated approach to reduce AOX level

In view of increased global competitiveness, preference for eco-friendly paper products, imposition of stringent environmental regulations, Indian pulp and paper mills particularly large mills are required to adopt energy efficient and environmentally friendly new fibre line to efficient and environmentally friendly new fibre line to become at par with the international status. This appear to be a difficult task primarily due to low scale of operation and use of mixed fibrous raw materials. However the level of AOX and other pollutants may be reduced to maximum extent in Indian paper mills by adoption of integrated approach involving better house keeping . process optimisation and other measures. These measures as given below. may be implemented with minor process modification and some capital investment to reduce the level of AOX :

Controlled Pulp Mill Operation

The large integrated as well as small scale mills are producing unbleached pulp of high kappa number with a fear of drop in pulp strength if kappa number reduces below 20. Laboratory studies conducted at CPPRI reveals that kappa number can be reduced to around 18 without any degradation in pulp properties. However to obtain pulp around kappa number 18, the mills will be required to operate the pulp mills under controlled and uniform cooking conditions to avoid any degradation in pulp properties.Small mills are also required to produce bleachable grade pulp below kappa number 25.

Imporved Pulp Washing

Usually the soda loss and carry over of organic matter along with pulp during washing observed was comparatively higher in Indian mills.The high carry over of organic matter along with pulp increases the bleaching chemical demand and ultimately contributes significant quantity of AOX in bleached plant effluents. It is desirable that the pulp mills should minimise the carryover of black liquor along with pulp i.e. below 15 kg COD/t pulp through modified pulp washing system to reduce the bleach chemical demand .

Substitution of Elemental Chlorine with Chlorine dioxdide

Most of the pulp mills in developed countries have eliminated the use of elemental chlorine as it is the major contributor of AOX . However the chlorine dioxide generation system is little bit expensive and use of chlorine dioxide requires new anti corrosive infrastructure in bleach plants including washing sysytem. However mills particularly large mills should use the chlorine dioxide to the maximum possible extent along with elemental chlorine as its use minimize the AOX formation substantially as well as improves the quality and pulp brightness.

Oxidative Alkali Extraction Bleaching

The studies conducted at CPPRI indicates 12-15% AOX can be reduced by using oxygen or peroxide in alkali extraction bleaching stage. The pulp and paper mills producing bleached variety of paper must use oxygen or hydrogen peroxide in oxidative alkali extraction stage of bleaching since the process can be used without any major changes in existing bleaching system.

Improved Chemical mixing in the bleach plant

Improved mixing of chemicals in bleach plant is an important step. If the bleaching chemicals are not rapidly & uniformly distributed through the pulp. there is chance of a portion of pulp being over bleached.

Increased Use of Recycled Fibre

The utilization of waste paper (recycled fiber) for paper production has now been on high priority all over the globe as an approach towards resource conservation and becoming environmentally compatible. The paper mills particularly the small scale agro based mills . where achieving kappa number of unbleached pulp below 20 is not economically viable in absence of chemical recovery system should restrict their bleachable grade pulp production and supplement the rest fibre furnish by blending with secondary fiber or purchased pulp. Similarly large paper mills should also explore the possibility of using maximum proportion of recycled fiber to supplement the fiber furnish for production of bleached variety of paper grades. Such supplementary recycled fibre must be bleached with hydrogen peroxide to reduce the overall level of AOX in the effluents.

Post Digester leaching of pulp

The conventional pulping process has limitations to avoid degradation of cellulose during cooking of fibrous raw material to produce the unbleached pulp of kappa number below 20. In order to preserve the strength properties of pulp . CPPRI developed a process known as alkali leaching or post digester leaching primarily for leaching out the lignin and its degraded products adsorbed onto the fiber surface of pulp produced from agro residues . The process has been found effective to reduce the kappa number of pulp having kappa number more than 25. The process coupled with efficient pulp washing system can be used in agro based mills producing the pulp of high kappa number in absence of chemical recovery and also in large mills which are forced to produce pulp of high kappa number due to capacity limitations of chemical recovery boiler.

Enzymatic prebleaching

An extensive R& D studies were conducted by CPPRI on potential and application of enzymatic biobleaching to reduce the consumption of chlorine in order to reduce the formation of AOX in bleach plant effluent. The results achieved in laboratory and mill scale trials reveal that the enzymatic treatment of unbleached pulp reduces the total chlorine requirement by about 10-15% and about 2-3 units gain in brightness level depending on the pulp quality and enzyme used. Some of the large mills have started the use enzymatic pre bleaching to achieve high brightness of pulp.

Elimination of Chlorination Stage Filtrate Recycle.

Recycling of chlorination filtrate (without treatment) for wet dilution is usually practiced in mlls which results in build up of AOX level. Hence it is desired that in absence of any suitable treatment system like ultrafiltration, reverse osmosis, chemical treatment etc. the chlorination stage filtrate recycling should be avoided.

Biological Treatment process

Biological methods i.e. activated sludge process, aerated lagoon etc have been found effective in removal of organo chlorine compounds. Biological effluent treatment plants can remove of COD,BOD & AOX to the tune of 70-80%,90-95% & 45-70 % respectively. The reduction in AOX level in different categories of mill by conventional biological effluent treatment plants is indicated in Figure-4. Anaerobic treatment can efficiently destroy chlorophenolics compounds, mutagenicity & acute toxicity. Anaerobic reactors have been reported to reduce the AOX by 40-45 %. However the anaerobic microbes are very sensitive and many chlorinated phenolics including H_2O_2 have been reported to cause severe inhibition & toxic effect to anaerobic microbes when exceed beyond tolerance limit. Thus regular & proper monitoring of ETP is necessary to avoid overloading so as to achieve desired removal efficiency of pollution loads.

CONCLUSION

In the changed scenario, the need to switch over to new fiber line involving the technologies such as extended delignification, oxygen delignification, chlorine dioxide bleaching has become a necessity of pulp and paper industry to address the environmental issues particularly control of discharge of AOX related compounds below toxicity level. Most of the pulp mills indeveloped countries have switched over to new fiber line with cleaner production techniques because of consistent supply of wood based fibrous raw materials and high capacity of pulp mills. The low scale of operation, use of mixed fibrous raw materials and high capital investment are the major bottlenecks which restrict the Indian pulp and paper mills to adopt these new technological developments by. As such these mils continue to rely on conventional pulping and bleaching technologies to produce high brightness paper of international standard. However inspite of these constraints, the mills will have to adopt the appropriate measures / strategies to address the above environmental issues for its survival. Thus an integrated approach involving better house keeping, optimisation of process variables ,restricting the chemical pulp production, increasing the recycled fiber proportion in the fiber furnish, operation of effluent treatment plants under optimum conditions etc. is required to be adopted by the Indian pulp and paper industry to become internationally competitive and environmentally compatible.

Environmental Prospects and status of Adsorbable Organic Halogens (AOX) Released in Pulp & Paper Industry.

S. Panwar*, M.K. Gupta*, S. Mishra*, R. M .Mathur* & A.G.Kulkarni**

ABSTRACT:

The release of chlorinated phenolic compounds formed during bleaching of pulp with chlorine-based chemicals has been reported to cause acute and chronic toxicity to the aquatic life. Some of the chlorinated phenolic compounds released are mutagenic and carcinogenic in nature and have tendency to accumulate & persist in environment for long time. The increased environmental awareness, stringent discharge norms, customer preference for ecofriendly paper products have resulted the pulp and paper industry to adopt the cleaner production techniques to control the discharge of toxic AOX, Dioxins and Furans. As a result, most of the pulp mills in developed countries have adopted modified pulping and bleaching processes to reduce the discharge of AOX below toxicity level. However, Indian mills are still using conventional pulping process and use high dosages of elemental chlorine and hypochlorite to attain the desired brightness target. Consequently, the level of AOX released in Indian pulp and paper mills are normally high compared to mills operating in developed countries. The present paper highlights the formation of AOX in raw materials commonly used by Indian mills, methodology for quantification of AOX, level of AOX in Indian mills and its environmental impacts.

*** Scientists, CPPRI, Saharanpur**

**** Director, CPPRI, Saharanpur**

INTRODUCTION

The bleaching of chemical pulp with chlorine & chlorine based chemicals became an issue in early 1970's when toxic chlorinated phenolic and dioxins compounds were detected in paper products, mill effluents and ETP sludges. The hazardous effect of bleach effluent was considered related to use of elemental chlorine for bleaching of pulp. In early 70's, the major portion of lignin was usually removed in subsequent bleaching stage of pulp produced with high kappa number (35 to 40) as the conventional pulping process was having limitations to produce pulp of kappa number below 20 and secondly, because environmental issues were not given priority due to non availability of analytical method for testing of effluent for the organo chlorine compounds. The consequences of toxic chloro compounds discharged in mill effluents were recognized by developed countries when high concentration of organo chlorine compounds were detected in fish fat stocks receiving bleach plant effluent. The elemental chlorine widely used for bleaching of pulp was found major contributor of organo chlorine compounds and more toxic dioxins, which has tendency for bioaccumulation, & persist in the environment. The amount of chlorinated organic compounds produced during pulp bleaching varies with raw materials, kappa number of the pulp, bleaching sequences & conditions employed.

The detection of toxic chlorinated phenolics, increased public awareness, imposition of stringent norms have necessitated the pulp and paper industry around the world to identified areas and development of technologies to minimize the requirement of bleaching chemicals to reduce the discharge of chlorinated phenolics. Some of these developments implemented are listed below:

- Extended & oxygen delignification process to reduce kappa number of pulp.
- Improved pulp washing techniques to minimize the carry over of organic matter alongwith unbleached pulp.
- Elimination of use of oil based defoamers in pulp washing.
- Substitution of elemental chlorine with chlorine dioxide .
- Use of oxidative alkali extraction bleaching.
- Elimination of hypochlorite bleaching.

Figure – 1 indicates the process development to reduce the kappa number of unbleached pulp & now most of the pulp mills in developed countries have adopted the modified pulping and bleaching process to reduce the kappa number of pulp around 10. The efforts are still continued to achieve the kappa number of unbleached pulp below 10.

BLEACHING PRACTICES:

The elemental chlorine, hypochlorite, chlorine dioxide, peroxide are used to bleach the pulp. However, elemental chlorine and hypochlorite are the dominating chemicals used for bleaching of pulp. The pulp mills in developed countries have almost adopted elemental chlorine free (ECF) bleaching technologies and some of the pulp mills particularly in Scandinavian countries have adopted total chlorine free bleaching techniques to produce the ecofriendly paper products.

Indian mills are still using elemental chlorine and hypochlorite in conventional CEHH bleaching sequences. Some of the wood based large mills have started the use of chlorine dioxide alongwith elemental chlorine in chlorination stage and in subsequent bleaching stages (C/DE$_P$H, C/DE$_P$HD) to minimize the formation of AOX related compounds in their mill effluents. Small mills use normally conventional CEH, CEHH & HH bleaching sequences. The chlorine consumption in large mills varies normally from 60-110 kg/t of pulp, while in small mills it varies from 140 – 160 kg/t of pulp.

The typical chlorine requirement for different raw materials used commonly by the pulp mills are given below:

Chlorine Requirements

Raw Material	Kappa No.	Cl_2 in C-Stage, %	Total available Chlorine required, %
Wood (Eucalyptus)	25	Kappa x 0.18 = 4.5	6-8
Bamboo	25	Kappa x 0.25 = 6.3	8-10
Bagasse	25	Kappa x 0.22 = 5.5	8-10

LEGISLATION TO CONTROL AOX DISCHARGE:

In the 1960's,when environmental consciousness was made related to the discharge of pollutants in mill effluents, the biological treatment plants were introduced in many of pulp & paper industry to reduce the pollution loads especially from bleach plant effluents which is the major source of pollution in large integrated pulp and paper mills.

The main emphasis was given for characterization & identification of hazardous chloro-organics present in bleach effluents when analytical methods & instruments were available. The new analytical methods and studies conducted created a basis for development of legislation for regulation of the level of chlorophenolics in discharge of pulp mills.

In the convention held in Paris ,for the prevention of pollution from land based sources & rivers. The AOX limit in general was set at 1.0 kg/t effective from1995 to all types of bleached chemical pulp mills and the proposed AOX limit in general has been accepted by Belgium, Denmark, France, Germany, Ireland, Luxemburg, The Netherlands, Norway, Portugal, Spain, Sweden and U.K.

Government agencies around the world have reacted by imposing standard for emissions of TOCl, AOX or dioxins in mill effluents and in some cases, limiting the levels of these compounds found in paper products. Most countries have specified the maximum discharge limit for AOX or TOCl in mill effluent. A typical example is the Swedish TOCl standard of 0.10 kg/t by the year 2010.

The U.S. Environmental Protection Agency (EPA) on the other hand has issued a guideline to regulate the discharge of AOX & chlorinated compounds under so called **cluster rules** for several categories of pulp mills **(Table-2)** .

Based on studies conducted by CPPRI on Assessment of AOX level in Indian Pulp and Paper Industry, Central Pollution Control Board (CPCB) has finalised to impose the limit for discharge of AOX in mill effluents. The regulation for discharge of AOX in various countries are given in **Table 1**.

FORMATION OF CHLOROPHENOLIC COMPOUNDS:

The nature & extent of formation of chlorophenolic compounds are determined primarily by the residual lignin content in the pulp and type of bleaching chemicals employed. The formation of chlorinated phenolic compounds during bleaching of pulp with chlorine based chemicals are given in **Table 3 & Fig. 2** which include chlorinated resin acids, fatty acids , chlorinated phenolics, dioxins & furans.

Fig-3 illustrates that about 80% of chlorine is bound with high molecular weight lignin material (MW>1000D) commonly referred as chlorolignin. These chlorinated compounds was thought to contribute little to acute toxicity due to their inability to penetrate the bacterial cell membranes. Studies conducted revealed that these high molecular weight chlorinated phenolics are slowly decomposed in recipient water, sediments into more active biologically chlorinated catechols and guaiacols. About 20% of low molecular weight chlorinated organic material(MW<1000D) is of main environmental concern. In recent years a considerable research efforts have been made in characterizing with respect to its individual chlorinated compounds particularly this fraction is considered to contain compounds which are toxic due to their ability to penetrate the bacterial cell membranes and has tendency to bioaccumulate in the fats of higher organism.

Carcinogenic & Mutagenic Compounds:

Bleach plant effluents contain chloroform and carbon tetra chloride which have been classified as carcinogens. The hypochlorite bleaching is the major contributor of chloroform & is reported as high as 0.30 kg/t of pulp. The various chlorinated benzenes, phenols, epoxystearic acid and dichloromethane present in bleach effluent have also been classified as suspected carcinogens. Some of the chlorinated compounds formed in chlorination stage have been identified as strong mutagens. However a very limited information regarding tendency of mutagens to bioaccumulation is available.

Polychlorinated Dioxins And Furans:

Among the chlorinated phenolics, the dioxins and dibenzofurnas are a group of chlorophenolics which have been found to have toxic effects. The prominent among the dioxins are 2.3.7.8 tetra chloro dibenzodioxin (TCDD) and 2,3,7,8 tetra chloro dibenzofuran (TCDF) **(Fig-4.)**

It is clear that out of 100% AOX **(fig.-3)** the percentage of dioxins is less than 0.1% which is supposed to be highly lypophyllic and bioaccumulable compunds. Such compounds are formed when unchlorinated dibenzodioxin (DBD) and dibenzofuran (DBF) present in unbleached pulp are chlorinated in chlorination stage. The oil based pulp mill additives particularly brown stock defoamer have been identified as potential sources of such compounds. Laboratory studies indicate a sharp increase in quantity of PCDD & PCDF when elemental chlorine consumption increased beyond 10-15 kg /t pulp.

The major source of chlorinated dioxins was found to be the C-Stage and the formation of dioxins is mainly dependent upon :

- Brown stock kappa number
- Active chlorine multiple
- Mixing conditions during chlorination
- Carryover of COD and
- Wash water quality

ENVIRONEMENTAL IMPACT OF CHLORINATED ORGANIC COMPOUNDS:

The chlorinated organics compounds formed during bleaching of pulp with chlorine and chlorine based chemicals are partly responsible for contributing effluent colour, acute, chronic toxicity, mutagenicity and carcinogenicity.

The toxicity of chlorinated compounds increase with an increase in the number of chlorine atoms in an organic compounds. The chlorinated organic compounds present in alkali extraction stage (E) bleach effluent are found more toxic and contributes more than 90% of acute toxicity. The major species of the chlorocompounds like trichlorophenol, tri & tetra chloroguaiacols have tendency to accumulate in fish & are responsible for acute toxicity. The formation of these compounds are directly proportional to the consumption of chlorine. **Fig-5** indicate that there is a sharp increase in the formation of tri & tetra chloroguaiacols when active chlorine multiple increased from 0.15 to 0.20. Chloroform and carbon tetra chloride produced during bleaching of pulp have also been classified as carcinogenic. Some of the chlorinated phenolics compounds like chloro catechols formed in C- stage have been identified as strong mutagens.

Fish exposed to chlorinated phenolics discharge by bleached pulp mill demonstrated impaired function of liver, enzyme system, metabolic cycle as well as increase in the incidence of spinal deformities and reduced gonad development in both laboratories and field studies. Some of the biological affects observed in laboratories and field studies are summarized below:

Effects on fish:

- **Acute toxicity:**
    - Egg mortality
    - Percentage of fertilised egg.
    - Acute toxicity to newly hatched fry.
- **Late effects: Survival and stress tolerance of fry from exposed parents.**
- **Effects on behavior: Response to rotory flow**
- **Physiological and Histological sublethal effect:**
    - Growth rate
    - Histological changes in lever.
    - Occurrence of parasitic in gills of flounder
- **Bioaccumulation:**

- Effect on primary production in natural mixed phytoplankton populations.

- **Genotoxic effects:**
  - Mutagenic effects
  - Carcinogenic effects.

Dioxin have received extensive media attention and it is reported that 2,3,7,8 Tetra chlorodibenzo dioxins is extremely toxic and bioaccumulative. Studies conducted in US focused mainly on effect of dioxins on humans and preliminary results obtained indicated no adverse effect on humans. However Greenpeace claims that there is no safe level of dioxin.

The extensive studies conducted on toxicity of dioxins on humus yielded contradictory findings. However, recently it was accepted that dioxins even in trace amounts may cause a wide range of other adverse effects on human health condition including :

- Disruption of regulatory hormones.
- Reproductive and immune system disorders and
- Abnormal fetal development.

The toxic effect and toxic levels of dioxins fixed by different countries and agencies are given below:

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

* - Picograms of 2,3,7,8 TCDD.kg of body weight/day

** - The studies have not established the safety levels.

Chlorate is still another pollutant which has recently aroused environmental concerns. The formation of chlorate is largely dependent on the amount of ClO_2 used during bleaching.

It is a well known herbicide and biocide used especially for plyso-physeae or brown algae. Conventional bleaching sequence produces about 3-6 kg of chlorate per ton of bleached pulp depending on ClO_2 substitution.

Adding ClO_2 & Cl_2 sequentially instead of simultaneously can decrease the chlorate concentration. The chlorate production can be reduced by:

- Increasing the end pH of chlorination
- Improving washing efficiency between stages, which reduces ClO_2 consumption only
- Avoiding conditions that lead to over ClO_2 consumption

METHODOLOGY FOR ANALYSIS OF CHLORINATED PHENOLICS:

The identification and quantification of individual chlorinated organic compounds are exceedingly complex & time consuming. However the identification & quantification of these chlorinated compounds can be done by gas chromatograph on high resolution. Therefore, the generic terms were developed for collective measurement of organically bound chlorine, some of them are given below.

TOCl : Total Organic Chlorine
TOX : Total Organic Halogens
AOX : Adsorbable Organic Halogens.
EOX : Extractable Organic Halogens
POX : Purgeable Organic Halogens

The basic principle of all methods is same, which involves the combustion of chlorinated organic compounds followed by microcoulometric measurement of chlorine content present in test sample.

TOCl & AOX are the terms which are used as a regulatory parameter for discharge of organochlorine in mill effluents. The brief of both TOCl & AOX methods is given below:

TOCl measures the quantity of chlorine associated with organic compounds. The method involves the determination of total chlorine and inorganic chlorine followed by organic chlorine by difference. The method has limitations for recovery of highly volatile chloro organics as most of these are evaporated during drying stage of sample. TOCl is a lengthy , complex and manual method.

a) Determination of Total Chlorine (TCl)

Effluent sample absorb on filter paper

↓

Drying at 105 °C for 15 mins.

↓

Ignition in combustion flask containing electrolyte (H_2O) in O_2 atmosphere :

$$(R\text{-}X + H_2O \xrightarrow{O_2} H\text{-}X + CO_2 + H_2O)$$

↓

Argentometric titration

$$(H - X + Ag \longrightarrow AgX)$$

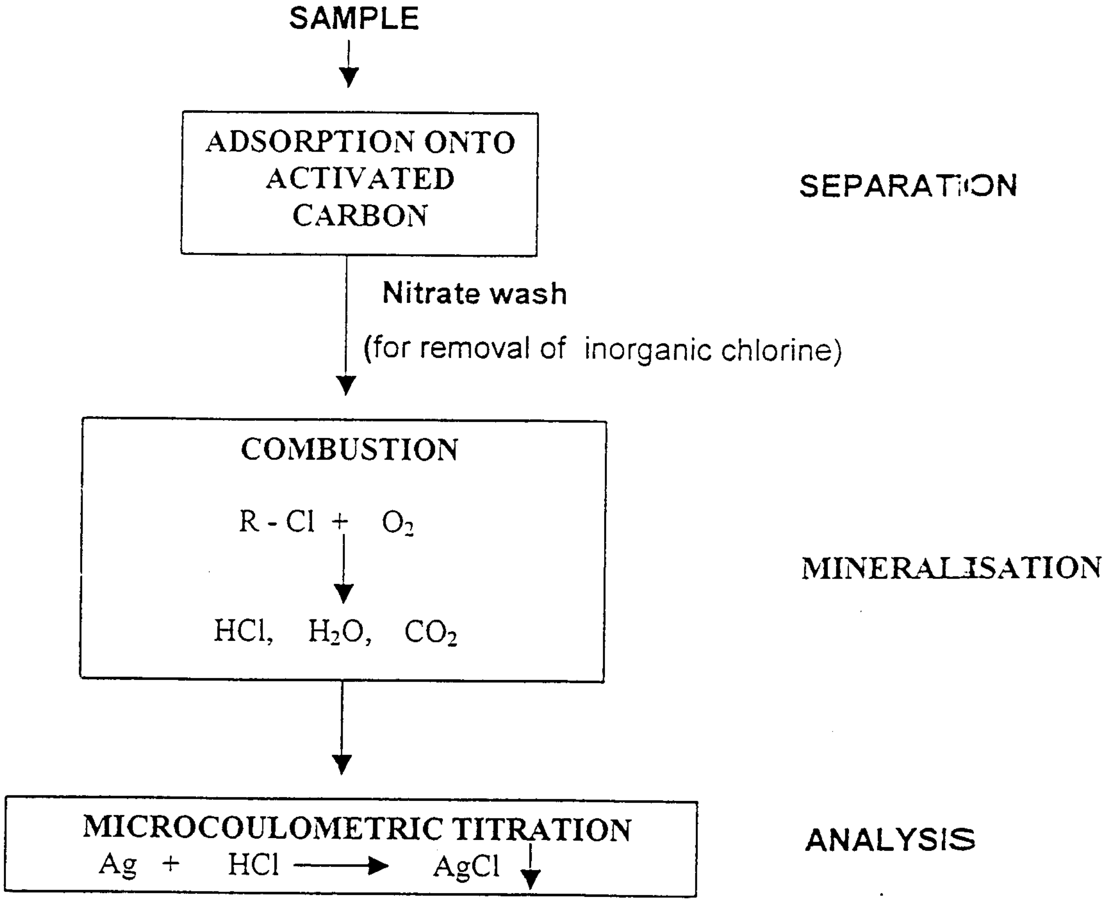
b) Determination of Inorganic Chlorine (ICl).

Analyse the effluent sample for Cl_2, ClO_2, Cl, ClO_2, ClO_3

c) Determination of Organic Chlorine(TOCl)

TOCl = TCl - ICl

AOX measures the amount of chlorine associated with the organic compounds, which is adsorbable on to the activated carbon. Method is accepted worldwide and is used for analysis of pulp mill effluents. The determination involves the following steps:



AOX method has following advantages over TOCl method:

- Better reproducibility
- Lower detection limit
- Higher percentage recovery of volatile chloro organics.

EOX measures the amount of chlorine associated with organic compounds present in sludge, paper & soils which is extractable with organic solvent.

POX measures the amount of organo chlorine which is highly volatile like chloroform etc.

STATUS OF AOX RELEASED IN PULP & PAPER INDUSTRY:

An extensive R & D studies were carried out at CPPRI related to the characterisation o bleached effluents generated in laboratory, generation of AOX in different raw materials using modified bleaching sequences. The result of AOX measured is given in **Table 4 & 5.** The chlorine consumption depends primarily on initial kappa number & bleaching response of pulp produced from different fibrous raw materials. **Table - 4** indicates that the requirement of total chlorine is higher for pulp produced from bamboo & eucalyptus. The level of AOX measured for pulp produced from bamboo, eucalyptus & bagasse was 4.60, 4.20 & 3.0 kg/t pulp respectively.

The chlorine requirement was reduced drastically from 50-65%, when the unbleached pulp produced from same raw materials were subjected to oxygen delignification followed by conventional CEH bleaching sequences. As a result the level of AOX was also reduced from 60-70%.

The modified bleaching sequences like OC/DEOD, ODEOD were also used to bleach the pulp in order to evaluate the level of AOX. **Table- 5** clearly indicates that with the use of modified bleaching process the level of AOX can be reduced below 1.0 kg, to the level of AOX generated in pulp mills operating in developed countries.

The effect of kappa number & active chlorine multiple on the formation of AOX were also studied and it was observed that the generation of AOX can be reduced effectively by lowering kappa number of pulp and use of low active chlorine multiple below 0.20.
The split addition of elemental chlorine in C-stage also reduced the generation of AOX by 8-10% compared to AOX generated in one time charge of elemental chlorine.
The use of oxidative alkali extraction reduces AOX by 12-15%.

MILL STUDIES:

CPPRI has conducted a exhaustive studies on assessment of status of technology & level of AOX in Indian mill producing writing and printing paper, newsprint, rayon grade pulp. The result of AOX are given in **Table -6**.

The level of AOX in mill producing writing and printing paper varies from 2.0 -4.5 kg/t paper. The low level of AOX i.e. 2.0 kg/t paper was measured in mill employing RDH, oxygen delignification & ClO_2 bleaching, while in small agro based paper mills, the situation is more alarming and level of AOX varies from 6.0-10.0 kg/t paper.

The reasons for high level of AOX in these categories of mills are:

- Use of mixed fibrous raw materials.
- High kappa number of unbleached pulp.
- High carry over of black liquor alongwith pulp entering to bleach section.
- Use of high dosages of elemental chlorine.
- Requirement of high brightness.
- Obsolescence in technologies and equipments.

CONCLUSIONS:

Today the environmental issues particularly control of AOX are the major challenges before the pulp and paper industry when discharge norms are becoming more and more stringent. Due to increased environmental awareness, imposition of stringent discharge norms, change in customer preferences for ecofriendly paper products, the pulp and paper industry in most of developed countries have already adopted the new modified pulping and bleaching processes in order to reduce the environmental impact of chlorinated phenolics & dioxins discharged in pulp and paper industry.

Indian pulp and paper industries are still continuing with conventional pulping and bleaching processes and use high dosages of chlorine for bleaching of pulp to achieve the high brightness level.

The pulp and paper mills particularly the mills producing writing and printing paper are facing severe problem due to its high level of AOX. The situation of AOX is even more alarming with small agro based mills. The adoption of new technologies are capital intensive. The use of mixed fibrous raw materials and also the low scale of operation restrict the Indian mills to adopt these new technologies to reduce the level of AOX below toxicity level. The Indian mills are at cross road as these are facing challenges of cost competitiveness, quality improvement and environmental friendly to survive in changed global scenario.

There is need of time before arising any alarming situation, industries must come forward with short term & long term strategies to develop and adopt new technologies in order to make pulp and paper industry more cost competitive and environmentally compatible.

TABLE – 1

REGULATIONS FOR DISCHARGE OF AOX (KG/T)

Country	**1994**	**1995-2000**	**2000-2005**
Australia	1.0	-	-
Austria	0.76- 1.5	0.5-1.0	-
Canada	1.5	-	1.0
Germany	1.0	-	-
India	2.0	2.0	1.0*
Japan	1.5	-	-
Norway	1.0-2.0	-	-
Sweden	1.2 – 1.5	0.3 – 1.0	0.3- 0.50
USA	-	0.62	-

- Proposed limit

TABLE – 2

POLYCHLORINATED PHENOLIC COMPOUNDS PROPOSED FOR REGULATION BY THE U.S.E.P.A.

Polychlorinated phenols	**Minimum level, ppb (µg/L)***
Pentachlorophenol	5.0
2,3,4,6 - Tetrachlorophenol	2.5
2,4,5 - Trichlorophenol	2.5
2,4,6 - Trichlorophenol	2.5
3,4,5 - Trichloroguaiacol	2.5
3,4,6 - Trichloroguaiacol	2.5
4,5,6 - Trichloroguaiacol	2.5
3,4,5 - Trichlosyringal	2.5
3,4,5,6 - Tetrachlorocatechol	5.0
3,4,6 - Trichlorocatechol	5.0
3,4,5 - Tetrachlorocatechol	5.0
3,4,5, 6 - Tetrachloroguaiacol	5.0

- The minimum level is defined as the concentration at which the analytical system gives recognizable mass spectra (corrected for background) and acceptable calibration points, using EPA method 1653

TABLE-3

CHLORINATED PHENOLIC COMPOUNDS GENERATED DURING BLEACHING OF PULP WITH CHLORINE BASED CHEMICALS

Type	No. of Species,	Amounts
Chlorinated acids	40	Upto 500g/t pulp
Chlorinated phenolics	40	Upto 100g/t pulp
Chlorinated aldehydes, Ketone and lactones	45	----
Chlorinated hydrocarbons	45	----
Chlorinated others	20	----
High molecular weight Materials	--	Upto 4kg.Cl/t pulp

TABLE 4

LEVEL OF AOX IN DIFFERENT PULPS BLEACHED IN LABORATORY

Raw Material	Kappa No.	CEH Bleaching			OCEH Bleaching		
		Cl_2 Demand kg/t pulp	AOX kg/t pulp	AOX After Sec.treat Kg/t	Cl_2 demand kg/t pulp	AOX kg/t pulp	AOX after sec.treat. kg/t
Eucalyptus	19	60.0	4.18	2.10	30.0	1.27	0.72
Bamboo	18	80.0	4.63	2.54	30.0	1.32	0.84
Bagasse	15	45.0	2 93	1.84	17.0	0.86	0.50

TABLE-5

LEVEL OF AOX IN DIFFERENT PULPS BLEACHED IN LABORATORY.

Raw Material	**Kappa No.**	AOX kg/t pulp			
		CEH	OCEH	OC/DE$_O$D	ODE$_O$D
Eucalyptus	19	4.18(2.1)	1.27(0.72)	0.83(0.46)	0.40(0.23)
Bamboo	18	4.63(2.54)	1.32(0.84)	0.90(0.63)	0.4[illegible](0.26)
Bagasse	15	2.93(1.85)	0.86(0.5)	0.6(0.30)	0.31(0.10)

TABLE-6

STATUS OF AOX IN INDIAN PULP AND PAPER MILLS

Type of product	Kappa No.	COD Carry over during washing Kg.COD/t. pulp	Consumption of Cl_2 Kg./t. pulp	AOX Level Kg./t. Paper	
				GEN-	FINAL Discharge
Rayon grade Pulp	12 - 16	--	25 - 28	0.7-1.0	< 0.50
News print chemical pulp	20 - 22	--	20 - 25	0.50-0.60	<0.50
Writing & Printing Paper:					
Large Mills	15 - 26	20 – 25	35 - 110	2.0 – 4.5	1.0 - 2.5
Small Mills (Agro-based)	30 - 32	30 – 40	140 - 160	6.0-10.0	4.0 - 6.5

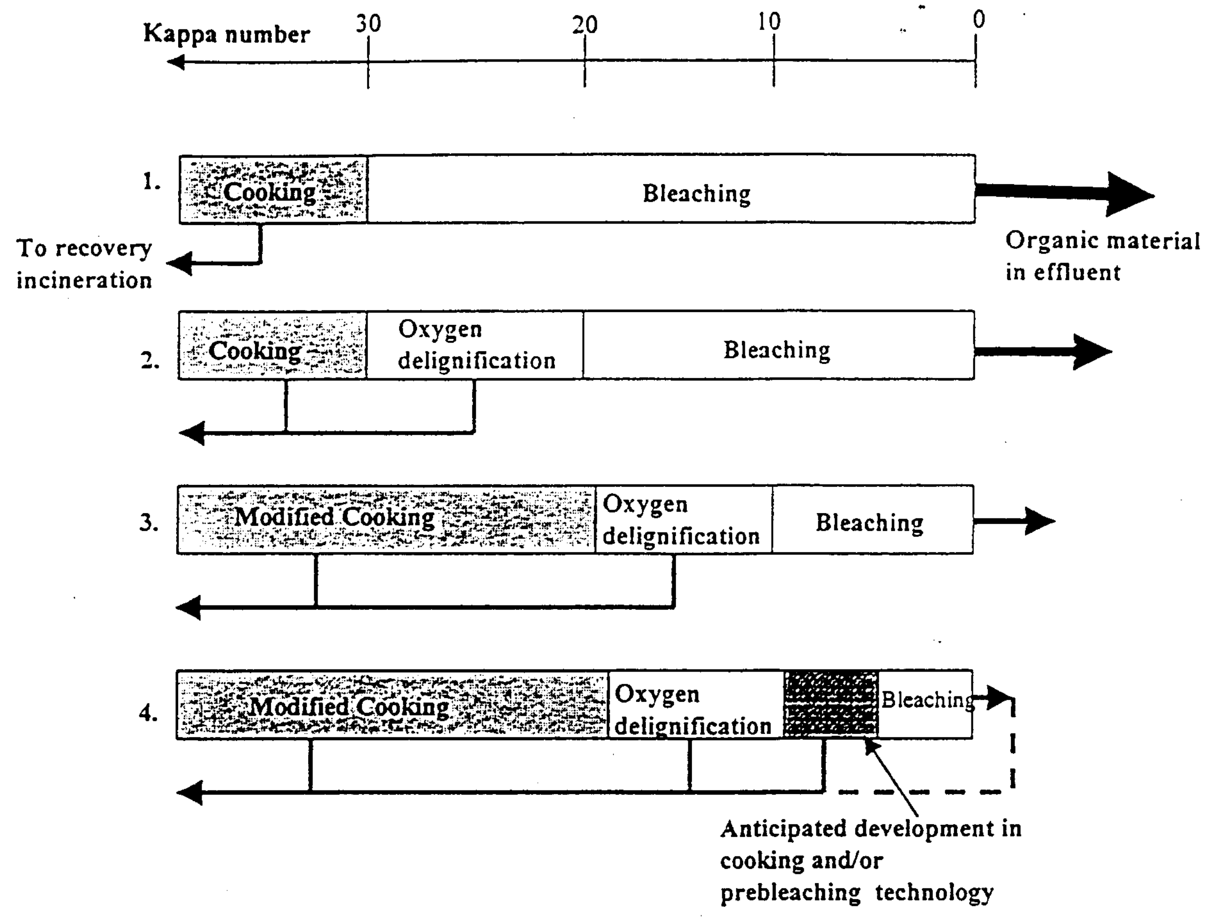


Fig-1. DEVELOPMENT OF ALTERNATE PULPING PROCESS

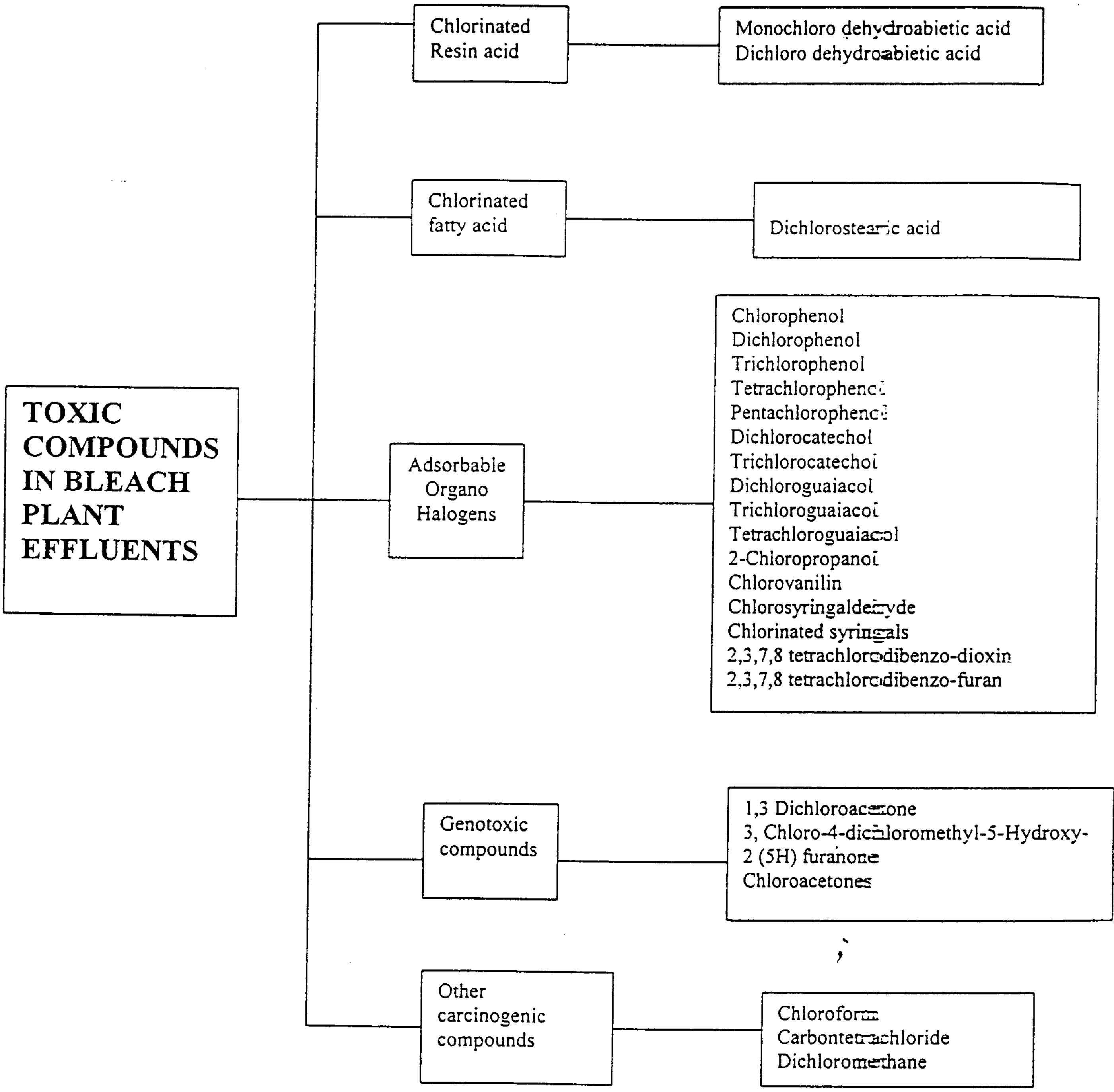
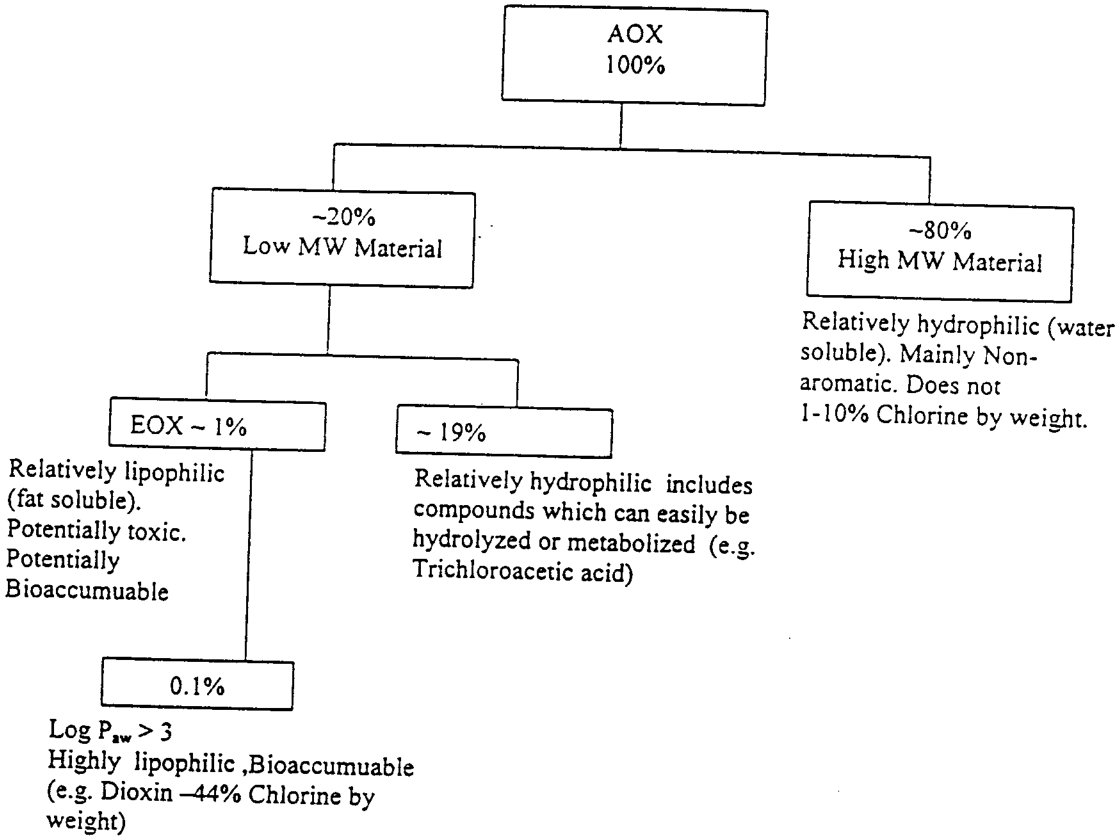


FIG.- 2 TOXIC COMPOUNDS IN BLEACH PLANT EFFLUENTS



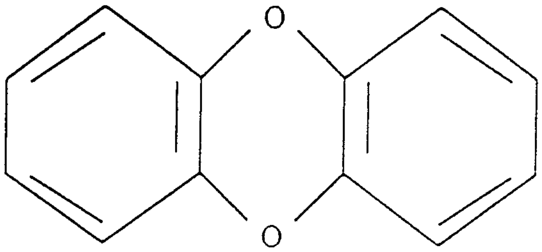
Relatively hydrophilic (water soluble). Mainly Non-aromatic. Does not 1-10% Chlorine by weight.

Relatively lipophilic (fat soluble). Potentially toxic. Potentially Bioaccumuable

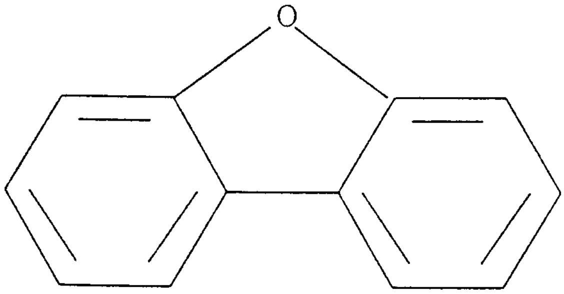
Relatively hydrophilic includes compounds which can easily be hydrolyzed or metabolized (e.g. Trichloroacetic acid)

Log $P_{aw} > 3$
Highly lipophilic ,Bioaccumuable (e.g. Dioxin ~44% Chlorine by weight)

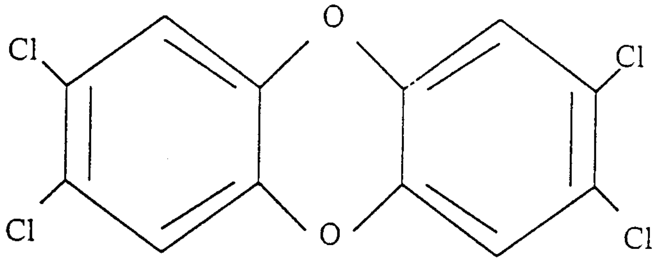
FIG-3: DISTRIBUTION OF CHLORO PHENOLIC COMPOUNDS



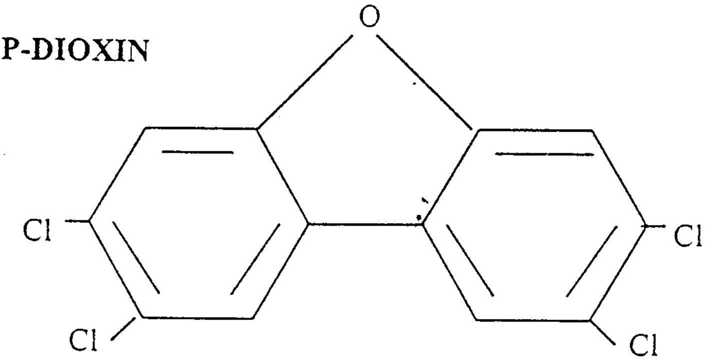
DIBENZO-P-DIOXIN(DPD)



DIBENZOFURAN(DPF)



2,3,7,8-TETRACHLORO-DIBENZO-P-DIOXIN
(2,3,7,8-TCDD)



2,3,7,8-TETRACHLORO-DIBENZOFURAN
(2,3,7,8-TCDF)

FIG.-4 STRUCTURES OF CHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS

Effects of kappa number variability on pulp properties

SHERRY L. THOMSON AND RICHARD R. GUSTAFSON

ABSTRACT

Documented pulp uniformity issues are available for the pulp and paper industry, but no clear understanding exists for the effect of nonuniformity on pulp properties. The project examines effects of nonuniformity by comparing pulp with variable kappa number distributions for bleachability and mechanical properties. Two mixtures with different kappa number distributions were compared with a uniform control pulp with the same average kappa number with analysis for brownstock strength and fiber morphology. The pulps were also bleached using ECF and TCF bleaching sequences. The pulps in this study did not show significant differences in strength or bleachability compared with the control pulp. Some limited differences existed in brownstock strength. The laboratory pulping and bleaching conditions were too mild to produce the negative effects that traditionally affect fiber strength. The pulps in this study therefore showed limited differences compared with the control pulp. Intrinsic fiber strength was maintained. Even with kappa number variability, all the pulps behaved similarly.

Application:

No differences in brownstock strength or bleachability for the mixtures tested occurred when mechanical factors in a pulp are minimized. Lignin content alone does not have a negative impact on fiber performance.

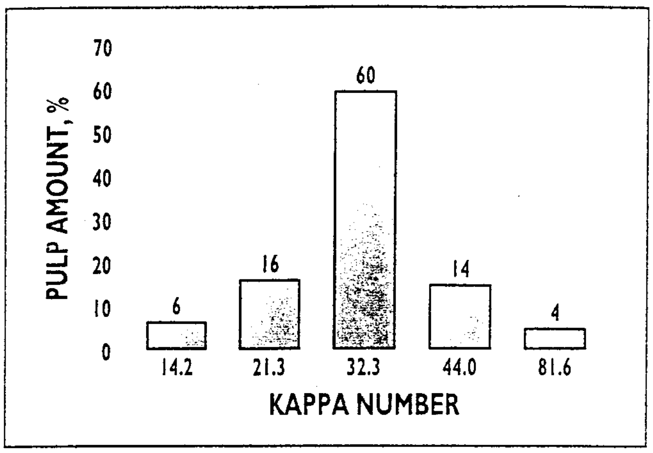
ACHIEVING PERFECTLY UNIFORM pulp in a mill is difficult. Every batch of pulp comes from a different source and may contain various amounts of knots and debris. Besides the effects of the raw material, the digesters themselves can have performance deficiencies including uneven or inadequate liquor distribution, inefficient pre-steaming, and poor chip impregnation *(1)*.

With all these possible conditions creating nonuniform pulp, many documented cases of nonuniformity exist. A density gradient column may be used to determine the kappa number for each fiber and establish a kappa number distribution for a pulp mixture. Mill pulps show a larger standard deviation in lignin content than more uniform laboratory pulps *(2)*. In recent years, MacLeod and others have used hanging baskets to measure the variability of kappa number in different areas within a digester *(3)*. With these baskets, pulp uniformity correlated with damage resistance during a digester blow. More uniform pulp is more likely to resist damage from a blow. MacLeod also showed that pulp strength loss resulted from a digester blow by comparing samples from points within the digester *(3)*.

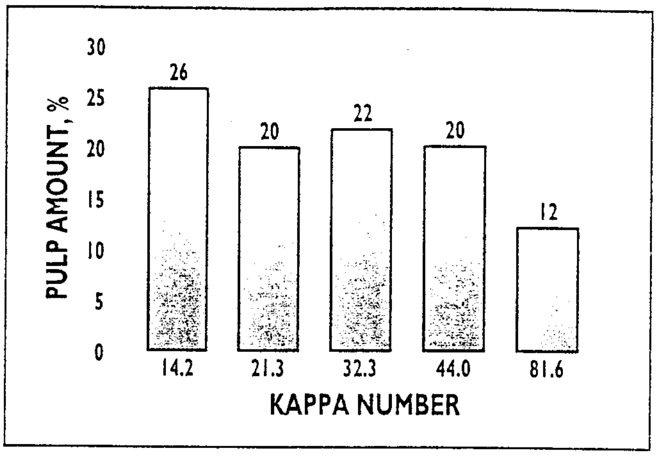
Since pulp uniformity is a concern in mills, companies have developed new pulping processes to produce uniform pulp. Kamyr extended modified continuous cooking (EMCC) is a pulping process that gives lower target kappa numbers but maintains brownstock pulp strength. If a mill could produce a lower kappa pulp by reducing the higher lignin fraction, the pulp would be easier to bleach and would therefore save money for the mill. New pulping technologies use the idea of pulp uniformity.

What effect does uniformity have on pulp properties and bleachability? Previous work has shown that nonuniform pulp is weaker and harder to bleach *(4, 5)*. Tichy and Procter compared pulp with different standard deviations of lignin content. The nonuniform pulp required more chlorine to reach the same permanganate number up to the CE stage using a CEHDED bleaching sequence. Comparing non-Gaussian distribution pulps showed that a nonuniform mixture had a decrease in bleach and brownstock strength and a higher chlorine demand. Hunt and Hatton measured the bleaching rates of pulps with varying lignin concentrations using a CED bleaching sequence *(5)*. A higher lignin pulp was harder to bleach than a lower lignin pulp. Kappa number variation should consequently be minimum. Higher lignin pulp required more chemical to achieve the same brightness endpoint.

An inadequate understanding still exists for what kappa variability does to pulp quality. Although a digester blow inflicts more damage on nonuniform pulp than uniform pulp, is uniform pulp intrinsically stronger than nonuniform pulp even without exposure to the damage of a digester blow? Past work showed that bleached nonuniform pulp was weaker and required more bleaching chemical. That work did not investigate why the nonuniform pulp was weaker. The research primarily used chlorine as the main bleaching chemical. Such chlorine use is no longer feasible. With most mills today switching their bleach plants to elemental chlorine free (ECF) and



1. Kappa number distribution of moderately uniform pulp



2. Kappa number distribution of poorly uniform pulp

totally chlorine free (TCF) bleaching sequences, the question is whether this kappa variability problem is worse without chlorine use.

OBJECTIVE AND APPROACH

This work investigated the effect of kappa number variability on pulp performance. A question that arose concerned the effect of kappa number variability on pulp properties and bleachability when the processing does not damage the fibers. In this study, the wood was carefully pulped to avoid detrimental effects to the fiber while still targeting different final kappa numbers. The raw material underwent scrupulous screening to obtain the optimum chip size of 4-6 mm. Specific pulping conditions used prevented depletion of cooking chemicals, lignin condensation, and overcooking. The ultimate goal was to remove the lignin selectively without affecting the integrity of the fibers.

Using the uniform pulping conditions, five kappa numbers of 10-80 were targeted. The kappa no. 30 pulp was used as the most uniform or control pulp. Two mixtures were created with the same average kappa number but with different distributions of the five pulps. The pulps underwent testing for strength and fiber morphology characteristics. The control pulp and the two mixtures were bleached under constant bleaching conditions using ECF and TCF bleaching sequences. The bleached pulps were also tested for strength and fiber morphology characteristics.

Pulp	Kappa no.	*H-factor*
1	14.2	1853
2	21.3	1250
3	32.3	800
4	44.0	625
5	81.6	360

I. Kappa numbers and H-factors of pulps before blending

MATERIALS AND METHODS

Five uniform pulps varying from kappa no. 14 to kappa no. 82 were produced. Douglas-fir chips were screened with a 6-mm thickness screen and accepted on a 7-mm round screen to remove any excessively thick chips, pins, and fines. Hand sorting removed compression wood and bark. Except the time of the cook, pulping conditions were constant *(6)*: 6/1 L/kg liquor/wood ratio (L/W), 24.8% effective alkali (as Na_2O), and a 40% sulfidity based on active alkali (AA). The chips were pre-steamed for 5 min at atmospheric pressure before the cooking liquor addition. The digester was ramped for 90 min to obtain the final cooking temperature of 160°C. Five different kappa values were targeted for the project. **Table I** contains the H-factors and measured kappa numbers. Kappa number measurement used TAPPI T235 cm-85.

Using these five uniform pulps, two mixtures were created that varied in their kappa number distribution. The two mixtures had the same average kappa no. 32, but they varied in their distributions of the starting pulps as **Figs. 1 and 2** show.

Stages	**D_0**	**E_0**	**D_1**
Charge	2.95% ClO_2	0.4% NaOH	0.60% ClO_2
Time, min	60	60	180
Temperature, °C	50	85	70
Consistency, %	10	5.5	10

II. ECF bleaching conditions

Stages	**O_2**	**Q**	**Z**	**P**
Charge	1.5% NaOH	0.5% DTPA	1.1% O_3	3% H_2O_2
Time	1 h	10 min	80 s	150 min
Temperature, °C	105	55	25	90
Consistency, %	5.5	5	10	12
NaOH, %	-	-	-	2.5
$MgSO_4$, %	0.5	-	-	0.5
DTPA, %	-	-	-	0.5

III. TCF bleaching conditions

Target kappa no.	Kappa value	Yield, %	Rejects, %	Time at 160°C, min	H-factor
10	14.2	44.0	0.05	275	1853
20	21.3	46.7	0.04	176	1250
30	32.4	49.6	0.07	112	800
40	44.0	49.6	0.12	85	625
80	81.6	54.4	0.47	46	360

IV. Results of kraft cooks at various target kappa numbers

Pulp	Weight mean curl	WAFL, mm	Kink index	Kink angle	Coarseness, mg/100m
Kappa no. 14	0.067	3.04	0.62	23.5	24.2
Kappa no. 82	0.059	3.22	0.52	19.7	32.1
Uniform	0.067	3.07	0.58	22.8	26.6
Moderate	0.066	3.09	0.57	20.9	27.0
Poor	0.068	3.07	0.58	22.2	25.7

V. Brownstock mixture and starting pulp fiber morphology data

The moderately uniform mixture mimicked typical pulp. The poorly uniform mixture was more extreme. The two mixtures were compared with a uniform original pulp having the same kappa no. 32. The kappa no. 32 pulp was the most uniform pulp or the control pulp. As MacLeod showed, a pulp with a kappa value from the low 20s to the middle 30s is the strongest softwood kraft pulp when compared with other pulps with a smaller or larger value of lignin *(7)*.

The two brownstock mixtures and the control pulp were analyzed for fiber morphology and physical strengths. The pulps were analyzed for PFI refining at 0, 500, 1500, 3000, and 8000 revolutions. CSF was determined using TAPPI method T 205. The brownstock pulp was tested for wet zero-span tensile index strength on the unrefined pulp. The tear strength and bulk properties were tested at all the refining levels. The pulps' tear and tensile strengths were measured using TAPPI T 414 and T 494, respectively. Fiber morphology data was measured with a Fiber Quality Analyzer (FQA) and the Kajaani FS100 (TAPPI T 271).

The pulps were bleached using a DEOD bleaching sequence. A duplicate bleach tested reproducibility. A target brightness of 85 was chosen to avoid the region of the brightness scale where the addition of more chemical produces little change in brightness. **Table II** shows the conditions used for the ECF bleaching sequence.

The chlorine dioxide bleaching used bag cooks in a hot-water bath. The pulps were washed and screened after each stage. The alkaline extraction stage used a commercially available digester at 35 psi. The second chlorine dioxide stage also used bag cooks in a hot-water bath.

The brightness value was determined with the GE brightness scale (TAPPI T218 om-83). The kappa numbers and viscosity were tested after the alkaline stage and after the last chlorine dioxide stage using TAPPI 246 and T 230, respectively.

The TCF bleaching sequence in this study was an OQZP. **Table III** shows the bleaching conditions.

The oxygen bleaching used a commercially available digester at 100 psi. The pulp was chelated before ozonation to remove any metals. The pulp was chelated with diaminetrietylenepentaacetic acid (DTPA) at pH 4–5. The ozone bleaching used 10% consistency in a commercially available high intensity mixer and reactor. A commercially available generator produced the ozone. Two-hundred grams of pulp were used with a total mixing time of 80 s. The peroxide bleaching used bag cooks in a hot-water bath.

RESULTS

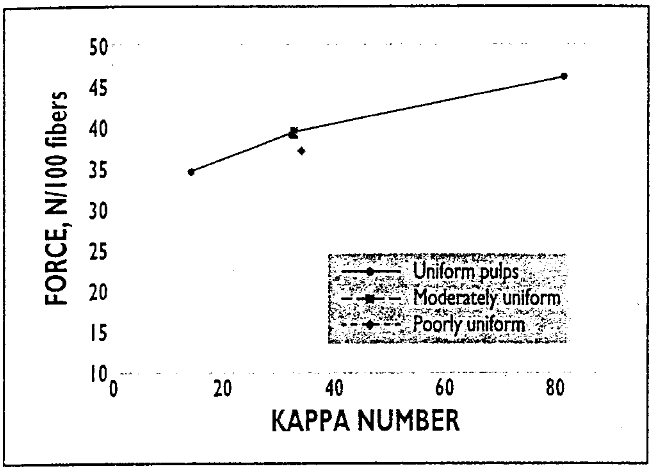
Table IV shows the kraft pulping data. The rejects were all very low due to the effective chip screening and mild pulping conditions. Even the kappa no. 82 pulp had low rejects. The pulp necessary to create the two mixtures was weighed and combined. The linear rule of mixtures provided a calculation of the weight percentage of each pulp necessary to achieve kappa no. 32 for the mixture. The calculated average kappa number value for the moderately uniform mixture was 33.1 but the actual value was 33.5. The calculated average kappa number for the poorly uniform pulp was 33.7, and the actual value was 33.5. Consequently, the pulp kappa numbers for these mixtures follow the linear rule of mixtures.

Pulp	Capillary viscosity, mPa·s
Uniform	63.2
Moderately uniform	51.2
Poor uniform	40.3

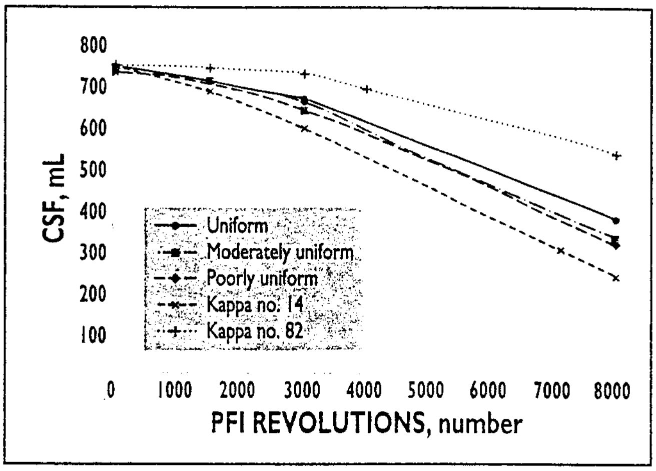
VI. Pulp viscosity results

Table V shows the fiber morphology data. The kappa no. 82 fibers are longer, straighter, and coarser than the kappa no. 14 fibers. No fiber morphology differences exist between the uniform pulp and the two mixtures. Pulp viscosity measurement on the uniform, moderately uniform, and poorly uniform mixtures used TAPPI T230. **Table VI** shows the results. The control pulp had 36% higher viscosity than the poorly uniform mixture and 19% higher viscosity than the moderately uniform mixture.

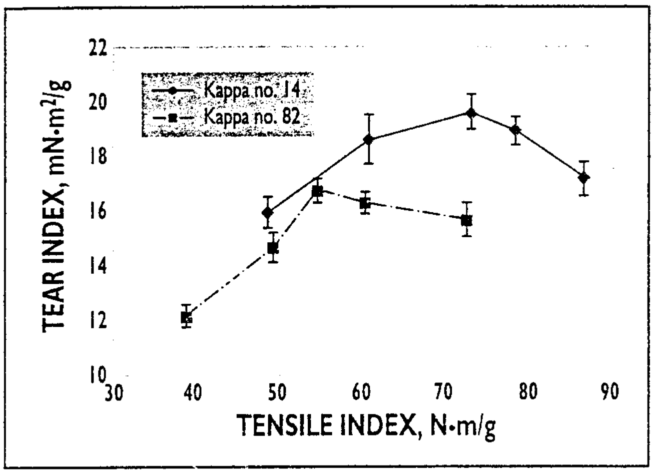
Table VII shows the wet zero-span tensile index data. The data represent the wet zero-span tensile index of the brownstock mixtures and the kappa nos. 14, 22, 44, and 82 unblended pulps. The error in the table is the 95% least significant difference.



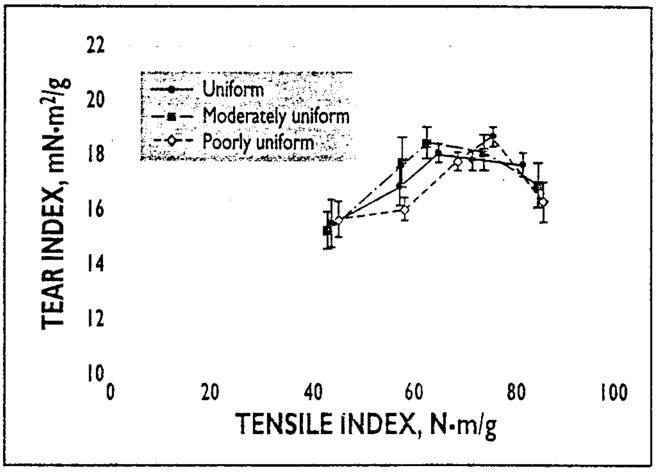
3. Comparison of wet zero-span tensile indices normalized using coarseness values



4. Refining response of mixtures and pulps with extreme kappa numbers



5. Tear vs. tensile index for kappa nos. 14 and 82 pulps



6. Tear vs. tensile index for the pulp mixtures

Sample	Wet Z-span tensile index, N·m/g	LSD
Control, kappa no. 32	148.90	3.86
Moderate mixture	145.68	5.86
Poor mixture	144.56	7.79
Kappa no. 14	143.73	5.21
Kappa no. 22	148.91	3.72
Kappa no. 44	150.16	4.41
Kappa no. 82	143.70	8.30

VII. Wet zero-span tensile index data for brownstock

The wet zero-span tensile data shows lower pulp strength for the kappa no. 14 and kappa no. 82 pulps, but the data are not statistically significant. A trend exists in the mixtures. When a pulp mixture contains a larger amount of higher and lower lignin content fibers, the brownstock strength is lower but not statistically significant. In addition, the reproducibility of the mechanical properties becomes poorer with increased kappa number variability. The kappa no. 82 and poorly uniform mixture have poorer reproducibility represented by the higher LSD.

The wet zero-span tensile index data does not show differences for the control pulp and the two mixtures. Apparently, an insufficient amount of low and high kappa pulp was present to affect the mixture. Even with viscosity differences, little strength difference existed for the moderately uniform, poorly uniform, and the control pulps.

Figure 3 shows the wet zero-span tensile data corrected for differences in coarseness by normalizing the strength. The differences in the normalized strength data of the mixtures compared with the control are insignificant. Consequently, the total intrinsic fiber strengths are similar. Even at a kappa no. 14, the fibers are not markedly degraded.

Figure 4 shows the freeness vs. number of revolutions for the mixtures and the control. The kappa no. 14 and kappa no. 82 pulps showed significant differences in their refining potential, but the control pulp vs. the mix-

Pulp	Final brightness
Control	85.3
Moderately uniform mixture	85.6
Poorly uniform mixture	85.9

VIII. Final brightness values for pulp mixtures after ECF bleaching

Pulp	Weight mean curl	WAFL, mm	Kink index	Kink angle	Coarseness, mg/100m
Uniform	0.096	1.02	1.02	39.5	25.9
Moderate	0.096	0.92	0.92	35.0	26.0
Poor	0.089	0.95	0.95	36.1	26.0

IX. ECF bleached misture and starting pulp fiber morphology data

tures did not show any differences in their refining responses.

Tear and tensile index were measured on a PFI refining curve. **Figure** 5 shows the tear vs. tensile index for the kappa no. 14 pulp compared with the kappa no. 82 pulp. The error is the 95% LSD.

The kappa no. 82 pulp is weaker even with a longer fiber length (WAFL) because the high amount of lignin remaining in the fiber decreases the fiber bonding. Fibers from the kappa no. 82 pulp were also not as compressible as shown earlier by the high coarseness values of Table IV.

Figure 6 shows the tear vs. tensile relationship for the control pulp compared with the two mixtures. The error is the 95% LSD.

Correlating with the wet zero-span data, there is no statistical difference between the two mixtures and the control pulp. As mentioned earlier, all the pulps were inherently strong and remained undamaged in the mild pulping process. The poorly uniform pulp does develop strength more slowly. The peak in the tear vs. tensile curve develops later than the uniform and moderately uniform mixtures. As noted above, the poorly uniform pulp contained more kappa no. 82 pulp that had more lignin. The three mixtures did not have any significant differences in coarseness or fiber length.

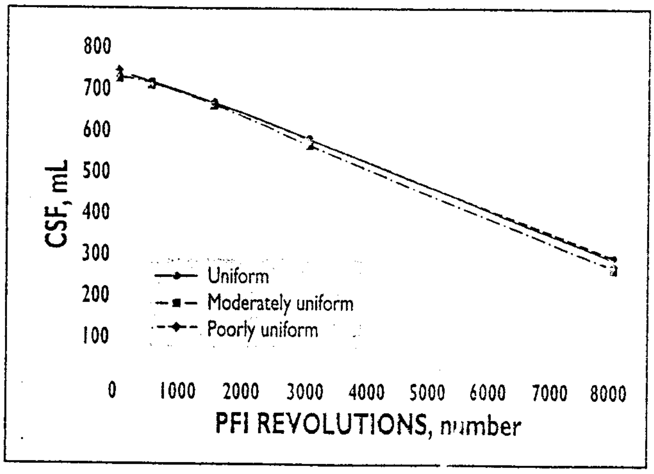
After ECF bleaching, only small differences existed between the pulps of different kappa number uniformity. **Table VIII** shows no differences in final brightness values. **Table IX** shows the fiber morphology values measured on the bleached pulps. No significant differences exist in fiber morphology for the bleached pulps. **Table** X shows the ECF wet zero-span tensile data. The error calculated is the 95% LSD. As expected from the previous brownstock wet zero-span tensile data, no statistical differences existed in zero-span tensile indices for the ECF bleached pulps.

Sample	Wet Z-span tensile index, N·m/g	LSD
Control	136.98	2.75
Moderately uniform	138.96	3.09
Poorly uniform	135.64	2.75

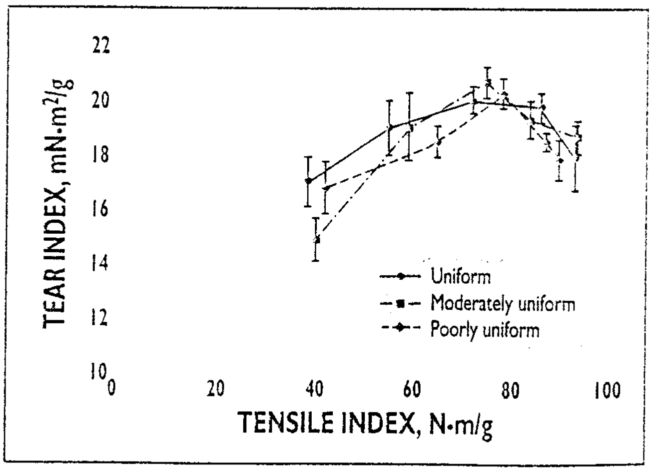
X. Wet zero-span tensile indices of ECF bleached pulps

Figure 7 shows no differences in refinability. The bleached stock refining response is not surprising since no refinability differences occurred in the brownstock results between the mixtures and the control pulp. **Figure** 8 shows no strength differences between the mixtures and the control as shown by the tear vs. tensile index curves. The error is the 95% LSD. Even after bleaching with an ECF sequence, the fibers maintained the same strength properties shown by the brownstock results. The pulp strength was independent of uniformity.

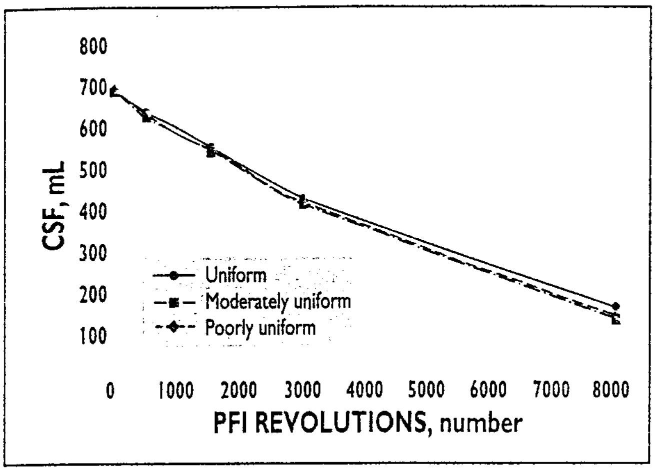
Table XI contains the final brightness values for the pulps after the TCF bleaching sequence. The moderately uniform mixture has higher brightness than the control and poorly uniform mixture. After application of the TCF bleaching sequence, the pulps did show some strength differences as **Table XII** indicates. The error is the 95% LSD.



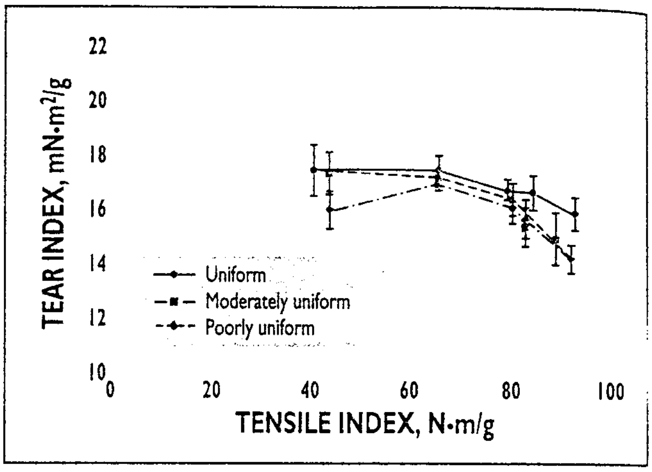
7. Refining response for ECF bleached pulp mixtures



8. Tear vs. tensile indices for ECF pulp mixtures



9. Refining response for TCF bleached pulp mixtures



10. TCF tear vs. tensile index PFI refining curves

Pulp	Final brightness
Control	81.6
Moderately uniform mixture	83.8
Poorly uniform mixture	80.6

XI. Final brightness values for pulp mixtures after TCF bleaching

Sample	Wet Z-span tensile index, N·m/g	LSD
Control	120.1	3.45
Moderately uniform	113.4	4.99
Poorly uniform	119.7	3.04

XII. Wet zero-span tensile indices of TCF bleached pulp

The moderately uniform pulp has a lower tensile index than the uniform pulp, but the result is not statistically significant. The poorly uniform and control pulps were similar. The moderately uniform mixture may have received a higher dose of ozone especially since the moderately uniform pulp had the highest brightness and the lowest zero-span tensile. Applying consistent ozone doses is more difficult because ozone is applied as a gas mixture.

Figure 9 shows that the refining potential for the pulps after TCF bleaching was similar to the ECF results. No refining potential difference existed between the pulps. **Figure 10** shows the tear vs. tensile index relationship for the TCF pulp. The error is the 95% LSD.

The control pulp was 8.4% stronger than the poorly uniform mixture at 40 tensile index and was 10.6% stronger at 90 tensile index. Figure 10 shows that the poorly uniform mixture has a lower tear and tensile index for the entire refining curve. At an 80 tensile index, the moderately and poorly uniform pulp strengths decline more rapidly than the control pulp. More work is necessary to confirm the response to the TCF bleaching.

CONCLUSIONS

This study compared two mixtures with varying kappa number distributions with a uniform control pulp having the same average kappa number. Bleachability and strength were measured. Previous workers did similar experiments, but the pulping conditions in this experiment created pulp with varying kappa numbers while minimizing fiber damage. Consequently, the chemical effect of lignin resulting from pulping to varying kappa numbers on pulp strength was measured. The results indicate that the kappa uniformity did not affect strength. This implies that lignin content alone may not reduce strength and decrease bleachability in nonuniform pulps. Under normal conditions, lignin content links strongly to other factors such as mechanical effects that weaken the fibers. Temperature, chemical concentration, blow temperature, washing, and many other factors within the pulp mill and bleach plants can contribute to damaging fibers. Curl, kink, twists, and dislocations can be due to the loss in pulp strengths *(8)*.

Even after bleaching, the pulps did not show any differences. This lack of strength loss is not surprising since previous work showed that laboratory pulps show little bleach strength loss. In a mill, pulp typically loses strength in the bleach plant and may have a strength delivery of only 75% of the original brownstock strength *(9)*.

The results of this study show no differences in brownstock strength or bleachability for the mixtures tested if the mechanical factors in a pulp are minimum. The lignin content alone does not have a negative impact on fiber performance over this range of kappa variability. Pulp uniformity is still an issue because the factors minimized in this work still exist in a mill to influence pulp quality. **TJ**

Thomson is scientist at Weyerhaeuser Co., WTC2B22, P. O. Box 2999, Tacoma, WA 98477, and Gustafson is professor at University of Washington, Anderson Hall, Box 352100, Seattle, WA 98195.

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