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Improvement in selectivity of oxygen bleaching

Submitted to

Indian Paper Manufacturers Association

by

AVANTHA

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Particulars of the Project

1.	Project No.	:	ACIRD/IPMA/0814-24/162
2.	Project Title	:	Improvement in selectivity of oxygen bleaching
3.	a. Project Team (ACIRD)	:	N. K. Bhardwaj (PI) Sandeep Tripathi (Co-PI) Nirmal Sharma (Co-PI) Ankush Gupta Amit Singhal Rahul Kumar O. P. Mishra R. Vardhan
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	c. Project Team (SPB)	:	P. Marimuthu (PI) D. Sundarakumar (Co-PI)
4.	Sponsoring Agency	:	Indian Paper Manufacturers Association
5.	Implementing Agency		Avantha Centre for Industrial Research and Development Central Pulp and Paper Research Institute
6.	Participating Agencies	:	Seshasayee Paper and Boards Limited Erode - 638 007, Tamil Nadu
7.	Date of Start	:	August 2014
8.	Duration of the Project	:	24 + 8 months

Contents

Nomenclature

AQ	:	Anthraquinone
CMC	:	Carboxymethyl cellulose
COD	:	Chemical oxygen demand
CPPRI	:	Central Pulp and Paper Research Institute
DTMPA	:	Diethylene triamine penta methylene phosphonic acid
DTPA	:	Diethylene triamine penta acetic acid
EDTA	:	Ethylene diamine tetra acetic acid
HEDP	:	Hydroxy ethylidene diphosphonic acid
IPMA	:	Indian Paper Manufacturers Association
NTA	:	Nitrilo triacetic acid
ODL	:	Oxygen delignification/ Oxygen bleaching
POM	:	Polyoxometalate
RAA	:	Residual active alkali
SPB	:	Seshasayee Paper and Boards Limited
°SR	:	Schopper Riegler

1. EXECUTIVE SUMMARY

Indian Paper Manufacturers Association (IPMA) sponsored this project to carryout research on improvement of selectivity during oxygen bleaching. Financial support for this project was granted by CESS Committee, Development Council for Pulp, Paper and Allied Industry, Department of Industrial Policy & Promotion, Ministry of Commerce & Industry, Govt. of India. Objectives of the project were:

- To find out most suitable conditions for ODL for different indigenous raw materials
- To study the effect of carbohydrate protectors to reduce cellulose degradation during ODL stage
- To reduce pulp shrinkage during ODL stage
- Plant scale trial using optimized conditions with identified additive

Under this project the lab scale studies were carried out at Avantha Centre for Industrial Research and Development (ACIRD), Yamuna Nagar. Results of the laboratory scale studies revealed that:

- Increase in alkali dose, temperature and oxygen pressure during oxygen bleaching improved the delignification but also increased the cellulose degradation.
- Magnesium hydroxide showed the considerable improvement in reduction of kappa number of pulp, brightness, viscosity and pulp yield when used during oxygen bleaching. With the use of magnesium hydroxide during oxygen bleaching stage brightness of pulp was improved by 7.0 points, reduction in kappa number improved by 5.2% and the viscosity of pulp improved by 1.0 point compared to control pulp. Use of magnesium hydroxide during oxygen bleaching stage also improved the final pulp brightness, whiteness, pulp yield and viscosity by 0.9, 1.1, 0.6 and 1.2 units, respectively.
- DTPA showed the highest efficiency in terms of brightness development and reduction in kappa number of pulp amongst the different chelating agents used during the study. EDTA was found the most effective in protecting cellulose degradation. Use of ETDA during oxygen bleaching improved pulp yield by 0.5%, viscosity of pulp by 0.8 units with reduced kappa number. Use

of ETDA also improved the final pulp brightness by 0.8 units, bleached pulp yield by 0.3% with comparable pulp viscosity.

- None of the polymeric additive improved the reduction of kappa number or brightness of pulp. Native starch and carboxymethyl cellulose (CMC) were found the most effective in protecting cellulose degradation amongst the different polymeric additives used during the study.

Plant scale study carried out with the addition of magnesium hydroxide in oxygen bleaching stage resulted in the following:

- With the addition of magnesium hydroxide in oxygen bleaching stage, kappa reduction was improved by 9-10%.
- During trial average final pulp brightness improved by about 0.6 points. Pulp brightness after oxygen bleaching stage and D_0 stage was improved by 2.1 and 3.5 units, respectively compared to control. Average final pulp whiteness was improvement by 2.4 units at $Mg(OH)_2$ dose level of 2.0 kg/TP.
- As expected viscosity of the pulp after oxygen bleaching stage was improved by 0.7 to 0.9 cP with the use of magnesium hydroxide. Cellulose and hemicelluloses content in the ODL and final bleached pulp were improved marginally with the use of magnesium hydroxide showing the improvement in selectivity during oxygen bleaching stage.
- Physical strength properties of the unrefined and refined oxygen bleaching stage and final bleached pulps were improved marginally with the use of magnesium hydroxide.
- With the addition of magnesium hydroxide in oxygen bleaching stage there was reduction in bleaching chemicals. A reduction of about 2.0 kg/TP in chlorine dioxide, 0.7 kg/TP in hydrogen peroxide and 1.8 kg/TP in caustic consumption was obtained during trial.

- With the use of magnesium hydroxide in oxygen bleaching stage, magnesium content in ODL stage pulp, bleached pulp was increased by 18-23%, whereas in weak black liquor (WBL) it was increased by 6% only showing that maximum portion of magnesium was retained along with the pulp. Magnesium content in the dregs was increased by 24% showing that most of the magnesium which came to the recovery cycle with the black liquor got removed along with the dregs.

2. INTRODUCTION

Oxygen is not very selective bleaching/ delignifying agent. Oxygen reacts simultaneously with lignin as well as carbohydrates. Selectivity of oxygen towards lignin depends on process variables and reaction stages. During oxygen bleaching stage if lignin reduction is in the range of 40-50%, yield loss due to carbohydrate dissolution is generally in the range of 2-3%. Metal ions present in unbleached pulp (Fe, Mn and Cu mainly) promote formation of hydroxyl radicals which attack/react with cellulose resulting in cleavage of cellulose chain, lower viscosity of pulp and higher shrinkage in pulp yield. Oxygen bleaching/ delignification is widely adopted across the world and in recent past few of the progressive Indian pulp and paper mills have also adopted this cleaner technology due to wide benefits.

Indian Paper Manufactures Association (IPMA) has sponsored this project jointly to Avantha Centre for Industrial Research & Development (ACIRD), Central Pulp and Paper Research Institute (CPPRI) and Seshasayee Paper and Boards Ltd. (SPB) to carryout research on improvement in selectivity of oxygen delignification. Financial support for this project was granted by CESS Committee, Development Council for Pulp, Paper and Allied Industry, Department of Industrial Policy & Promotion, Ministry of Commerce & Industry, Govt. of India.

Under this project the lab scale studies on hardwood pulp were carried out at Avantha Centre for industrial Research and Development (ACIRD), Yamuna Nagar on following areas:

- Effect of process conditions on oxygen bleaching
- Effect of different carbohydrate protectors (Chemical additives, chelating agents and polymeric additives) to improve selectivity

Validation studies on selected additives were carried out at Central Pulp & paper Research Institute (CPPRI), Saharanpur.

Pre-plant trial studies using mill pulp and the bleaching conditions were carried out at ACIRD.

Magnesium hydroxide and ethylene diamine tetra acetic acid (EDTA) were found most suitable among various chemicals studied to improve selectivity of oxygen bleaching in lab scale studies carried out at ACIRD. It was proposed to explore suitability of any one chemical on plant scale.

Plant scale trial using commercial magnesium hydroxide was carried out at Seshasayee Paper and Boards Ltd., Erode, Tamil Nadu with the objective to study the effect of carbohydrate protector (magnesium hydroxide) to reduce cellulose degradation during oxygen bleaching stage and to improve pulp quality.

3. LITERATURE REVIEW

Oxygen bleaching/ delignification is a green and clean technology and accepted worldwide very rapidly by paper industry. During oxygen bleaching/ delignification, the lignin is removed primarily from the interior of the fiber by breaking of bonds within the lignin structure. About 50% of the residual lignin left after pulping can be removed at this stage without severe damage to the cellulosic material. Beyond 50% delignification, degradation of pulp takes place due to severe cellulose depolymrization and consequently deterioration of pulp viscosity and strength of pulp. This is due to the lack of selectivity of oxygen delignification (Hsu and Hsieh, 1987).

The selectivity of reactive chemicals/ ions/ radicals formed during oxygen bleaching/ delignification towards lignin reactions compared to carbohydrates degrading reactions is mostly affected by the temperature and alkali charge. Selectivity worsens when extending the reaction time to achieve very low lignin contents. Selectivity is defined as oxygen reaction rate with lignin to the reaction rate with carbohydrate polymer present in pulp (Tao et al., 2011). High temperatures and increasing alkali charge have a negative impact on the selectivity, particularly towards the end of the delignification (Irabarne and Schroeder, 1997). At a fixed temperature high delignification is achieved with high dose of alkali and this is true for both high and low kappa pulp (Tao et al., 2011). Carbohydrate degradation reactions are described in terms of the decrease in viscosity of pulp. The reactions of the cellulose and hemicelluloses have been studied by many researchers. Usually, the reactions can be divided into two categories one is random chain cleavage and the other is carbohydrate peeling reactions. In the random chain cleavage, cleavage occurs at any glycosidic linkage along the carbohydrate chain, while peeling reactions occur on the sugar units at the reducing end of the chain, leading to successive removal of one sugar unit at a time. Both types of the reactions are responsible for viscosity drop. The degradation of the cellulose within the fibers is caused by oxygen radicals generated through lignin reactions and the reduction of oxygen species during the process. These radicals randomly oxidize the cellulose chain by forming carbonyl groups which, under alkaline conditions, undergo a β-elimination reaction resulting in cleavage of the cellulose chain. The net result is a decrease in pulp viscosity and ultimately in pulp strength. Degradation of the cellulose within the fibers is caused by hydroxyl radicals generated by the reduction of oxygen during ODL process (Sjostrom, 1981; McDonough, 1996; Guay et al., 1999).

Over the past many years several attempts were made to improve selectivity of oxygen delignification either with some process modification or using suitable cellulose protector during oxygen bleaching stage. $MgSO_4$ was widely reported to improve the selectivity of an oxygen bleaching stage. It is reported that $MgSO_4$ functions by precipitating as magnesium hydroxide, which adsorbs the metal ions, making them unavailable for catalysis of ions/ radicals or by forming complexes with them (Robert and Viallet, 1971; Gilbert and Pavlovova, 1973).

Several studies were carried out by different researchers to enhance the efficiency of oxygen bleaching/ delignification through optimization of process parameters, pretreatment of pulp and using different kinds of additives to protect carbohydrate portion of pulp (Gaspar et al., 2009; Suchy and Argyropoulos, 2002; Fu et al., 2005; Chen and Lucia 2002; Samuelson and Otjeg 1996)

Parthasarathy et al., 1990 reported that peroxide as additive in oxygen bleaching stage improved selectivity and delignification efficiency. It was also postulated that peroxide has to be added during the first stage of double stage oxygen bleaching to realize potential benefits from the second oxygen stage which may or may not be reinforced with hydrogen peroxide (Parthasarathy et al., 1990; Odermatt et al.,1994). Cao et al., 2007 studied on regulation of superoxide anion radical during oxygen delignification by using anthraquinone-2 sulphonic acid sodium salt. Use of hydrogen peroxide with different additives like magnesium sulphate and organophosphate during oxygen bleaching/ delignification improved lignin removal efficiency. Lignin removal up to 70% was reported with two stage oxygen bleaching using hydrogen peroxide (Sahu et al., 2008; Dan and Adrian, 2015). Vaino Sippola, 2006 studied the application of transition metal complexes as catalysts in softwood pulp and found that in the presence of Co-sulphosalen, oxygen is selectively transferred to the lignin model compounds and the carbohydrates are depolymerised solely by the generated hydrogen peroxide. Sodium borohydride treatment of fully bleached pulp prevents the carbohydrate degradation during oxygen bleaching. With borohydride treatment complexes are formed with metal ions and carbohydrate which inhibit the metal ions to damage cellulose (Barrau and Lachenal, 2001).

Using anthraquinone (AQ) during oxygen bleaching/ delignification was reported to improve selectivity and found effective for protection of cellulose (Ng et al., 2011; Liu et al., 2013). Use of Poly oxometalates (POM) as additive during oxygen bleaching/ delignification was studied. POM is a polyatomic ion consisting of three or more transition metal oxyanions linked together by shared oxygen atoms. POM is an environmentally friendly alternative to the chlorine based bleaching reagents. POMs are either used as re-generable stoichiometric oxidants or as catalysts. POMs with the Keggin-type structure have been generally considered for kraft pulp delignification (Evtuguin and Neto, 1997; Weinstock et al., 1997; Ira et al., 1998; Gaspar et al., 2007 & 2009). Potential of water soluble poly pyridine was explored as cellulose protector during oxygen bleaching stage (Perng et al., 1994). Suitability of magnesium hydroxide in refiner bleaching was studied in mill scale operation resulting in reduction in bleaching cost, reduced refiner specific energy, decreased BOD/COD, increased pulp yield and elimination of calcium oxalate scaling issue (Harrison et al., 2008). Presence of calcium is found to contribute negatively for the preservation of pulp viscosity during oxygen delignification. To limit the level of calcium present in brown stock pulp, its levels in the white liquor needs to be kept as low as possible. The dissolved solids concentration also plays an important role for limiting selectivity and loss of the strength (Tikka and Sundquist, 2001).

Several researchers have conducted the studies to reduce the degradation of cellulose during ODL stage. Van Tran, 2000 studied on different additives to enhance degree of delignification in oxygen bleaching stage like surfactants, chelating agents, TAED, AQ and urea. Violette and Heiningen, 2003 studied on a sugar based polymeric additive to improve selectivity during oxygen delignification; they found improvement in selectivity by 30%. Fu et al., 2005 studied the effect of hydroquinone compounds on oxygen delignification of softwood kraft pulp. Kontturi et al., 2008 studied on use of carboxymethyl cellulose during oxygen delignification of kraft pulp for improvement of strength properties. They found improvement in tensile strength by 25% and tear strength by 35%. Ni et al., 2001 studied on using sodium borohydried in significant quantity to increase the pulp brightness significantly. Pesman, et al. 2010 used it for reinforcement of oxygen delignification and they found that delignification was increased from 45 - 58% without selectivity loss. Solinas and Proust, 1997 studied the effect of using ethylene glycol during oxygen bleaching/ delignification and reported viscosity improvement of about 3 cP. Violette and Heiningen, 2003 reported the improvement in selectivity by 30% with the use of different additives like starch, carboxymethyl cellulose, galactomannan, xylan, and glucomannan.

4. OBJECTIVES

- To find out most suitable conditions for ODL for different indigenous raw materials
- To study the effect of carbohydrate protectors to reduce cellulose degradation during ODL stage
- To reduce pulp shrinkage during ODL stage
- Plant scale trial using optimized conditions with identified additive

5. MATERIALS AND METHODS

5.1. Experimental

Collection of raw material and pulp samples

During the study different hardwood chips were procured from wood based paper mills situated in northern and southern part of India. Different chemicals were procured from chemical suppliers.

Raw material preparation

Chips samples collected from mill were classified using standard chips classifier. Accept chips were collected and air dried to a moisture level of 15-20%, mixed thoroughly and kept in polythene bag to maintain uniform moisture. Moisture content was determined as per standard procedures prior to pulping experiments. Eucalyptus chips sample were analyzed for proximate analysis after grinding in Wiley mill and screening on 40 mesh sieve.

Pulping

Pulping experiments were performed in autoclave digester consisting six bombs of 2.5 l capacity, rotating in an electrically heated air/polyethylene glycol bath or in liquor re-circulatory stationary digester. The pulping conditions like time, temperature, and bath ratio were varied to get targeted kappa number pulp.

Bleaching

Oxygen delignification of pulp was carried out in oxygen bleaching reactor (electrically heated pressurized vessel having high shear mixing facility during the treatment) fabricated at ACIRD. Other bleaching experiments were performed simulating mill conditions to achieve desired brightness.

Effluent

Filtrate generated from each stage of bleaching was mixed in respective proportion and analysed for different properties.

Analytical techniques

Following standard test methods were followed to analyze different properties of pulp, black liquor and effluent generated during bleaching:

Test	Test method followed
Brightness	Tappi T 525
Cellulose	Updegroff (1969)
Chemical oxygen demand	IS: 3025 (Part 58)
CIE whiteness	Tappi T 560
Handsheet preparation	Tappi T 205
Hemicelluloses	Deschatelets (1986)
Kappa number	Tappi T 236
Klason lignin	Tappi T 222
Moisture	Tappi T 264
1% NaOH solubility	Tappi T 212
PFI Refining	Tappi T 248
pH	IS: 3025 (Part 11)
Physical testing of pulp handsheets	Tappi T 220
Silica	Tappi T 244
Solvent extractives	Tappi T 204
Viscosity	Tappi T 230

5.2. Facilities of ACIRD used

Pulping digesters

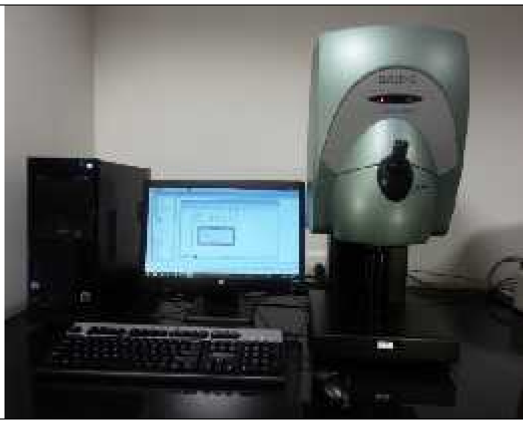
Oxygen bleaching reactor

Unbleached pulp analysis

Unbleached and bleached pulp testing lab

AOX analyzer

Image analyzer



Fiber Tester

Brightness Tester

Papermaking and paper testing lab

6. RESULTS AND DISCUSSIONS

Scope of the activities to be carried out was distributed as below:

ACIRD

- Detailed survey of literature on latest work on different carbohydrate protectors used in oxygen delignification of different raw materials.
- Fabrication of oxygen bleaching reactor for laboratory scale bleaching.
- Procurement of pulp from integrated pulp and paper mills.
- Proximate chemical analysis of raw material chips.
- Oxygen delignification of pulp from indigenous raw materials by varying process conditions like pH, temperature, time and initial kappa number in single as well as two stages.
- Procurement of different chemical additives and polymeric additives suitable to improve selectivity of oxygen bleaching.
- Oxygen delignification of pulp with different carbohydrate protectors and polymeric additives to improve pulp yield, viscosity and physical strength properties of the pulp.
- Screening of the most effective and suitable additive on the basis of results obtained in the project.
- Compilation of data and preparation of report.

CPPRI

- Validation of the results obtained with selected additive/chemical at ACIRD.
- Oxygen delignification to be carried out using quantum mixer.

SPB

- Plant scale study with selected additive and assessment of pulp properties

Based on the literature review following pathway was selected to increase selectivity of oxygen bleaching:

Fabrication of oxygen bleaching reactor

- Exploration of operating parameters like consistency, quantity of pulp, mixing speed and oxygen dosing etc.

Effect of process conditions during oxygen bleaching on pulp properties

- Alkali dose
- Initial kappa number
- Temperature
- Chemical oxygen demand (COD) carryover

Effect of carbohydrate protectors to improve selectivity

- Study on use of different chemical additives namely EDTA, $MgSO_4$, DTPA, H_2O_2, DTPA-H_2O_2, $Mg(OH)_2$, anthraquinone, $NaBH_4$, DTMPA, borax, thiourea, urea, sodium perborate, boric acid, sodium gluconate and ethylene glycol.
- Study on use of different polymeric additives namely cationic starch, native starch, CMC and guar gum.

Study on mill pulp with screened additives

Validation studies on selected process at CPPRI

Pre plant trial studies at ACIRD

Demonstration of results in the plant scale

Studies carried out and results obtained under each segment discussed above are described in detail in the forthcoming sections/chapters of the report.

Fabrication of oxygen bleaching reactor

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6.1. Fabrication of oxygen bleaching reactor

Laboratory scale oxygen bleaching reactor having capacity to bleach about 250 g oven dried equivalent pulp in pressurized mixing conditions was fabricated. The same is shown in Figure 6.1.1.

Figure 6.1.1: Oxygen bleaching reactor fabricated at ACIRD

Performance evaluation of oxygen bleaching reactor

To evaluate the performance of oxygen bleaching rector and further studies eucalyptus chips were collected from one integrated paper mill situated in northern part of India. Physical and chemical properties of eucalyptus chips were determined. Bulk density expresses the amount of wood that can be loaded to the digester. Bulk and basic density of collected chips were 265 kg/m^3 and 515 kg/m^3, respectively. Detailed results of physical properties of chips are given in Table 6.1.1.

Table 6.1.1: Physical properties of eucalyptus chips collected for study

Particulars	Value
Density of chips	
Bulk density of chips (kg/m^3)	265
Basic density of chips (kg/m^3)	515
Chips classification	
+45 mm hole (%)	5.8
-45 mm hole, +8 mm slot (%)	32.2
-8 mm slot, +7 mm hole (%)	55.8
-7 mm hole, +3 mm hole (%)	5.5
-3 mm hole (%)	0.7

Eucalyptus chips collected during the study had 3.3 % extractives, 0.64% ash content, 50.3% cellulose, 22.6% hemicelluloses and 26.3% lignin. Detailed proximate chemical analysis results of eucalyptus chips are given in Table 6.1.2.

Table 6.1.2: Chemical properties of eucalyptus chips collected for study

Particulars	Value (%)
Acetone extractives	1.2
Total extractives	3.3
DCM extractives	0.5
1% NaOH solubility	15.6
Cellulose	50.3
Hemicelluloses	22.6
Klason lignin	26.3
Holocellulose	74.6
Ash	0.64
Silica	0.06

Pulping optimization study was carried out in autoclave digester and unbleached pulp in bulk was produced in liquor re-circulatory digester for further study. Unbleached pulp having kappa number of 18.9 was produced using 16.0% active alkali, 162°C temperature for 90 minutes cooking time. Detailed results of pulping carried out in liquor re-circulatory digester are given in Table 6.1.3.

Table 6.1.3: Pulping results of eucalyptus chips

Particulars	Results
Pulping conditions	
Active alkali as Na_2O (%)	16.0
Sulphidity (%)	23.4
Cooking temperature (°C)	160
Cooking time (min)	90
Pulp properties	
Pulp yield (%)	47.9
Rejects (%)	0.20
Kappa no.	18.9
Brightness (% ISO)	30.0
Viscosity (cP)	14.1

Performance evaluation of oxygen bleaching reactor was carried out by varying amount of pulp, consistency and mixing speed. The reactor was found suitable for oxygen bleaching studies at consistency range of 8 to 12%, temperature range of ambient to 110 °C, oxygen pressure range of 0.5 to 5.5 kg/cm^2.

Effect of process conditions on oxygen bleaching

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6.2. Effect of process conditions on oxygen bleaching

As per the scope of the project effect of process conditions on oxygen delignification was studied in the initial stage of study. Effect of different process conditions like alkali dose, temperature, initial kappa number, COD carryover and single/ two stages oxygen delignification were studied on different pulp samples.

6.2.1. Effect of Sodium hydroxide dose on pulp properties

To evaluate the effect of alkali dose during oxygen bleaching on different pulp properties, sodium hydroxide dose was varied from 1.8 to 2.8% by keeping other conditions constant. Results showed that with increase of alkali dose kappa number and viscosity of pulp reduced and brightness of pulp improved. Effect of alkali dose on brightness and kappa no. of pulp is shown in Figure 6.2.1. Detailed results of effect of alkali dose on different properties of pulp are given in Table 6.2.1.

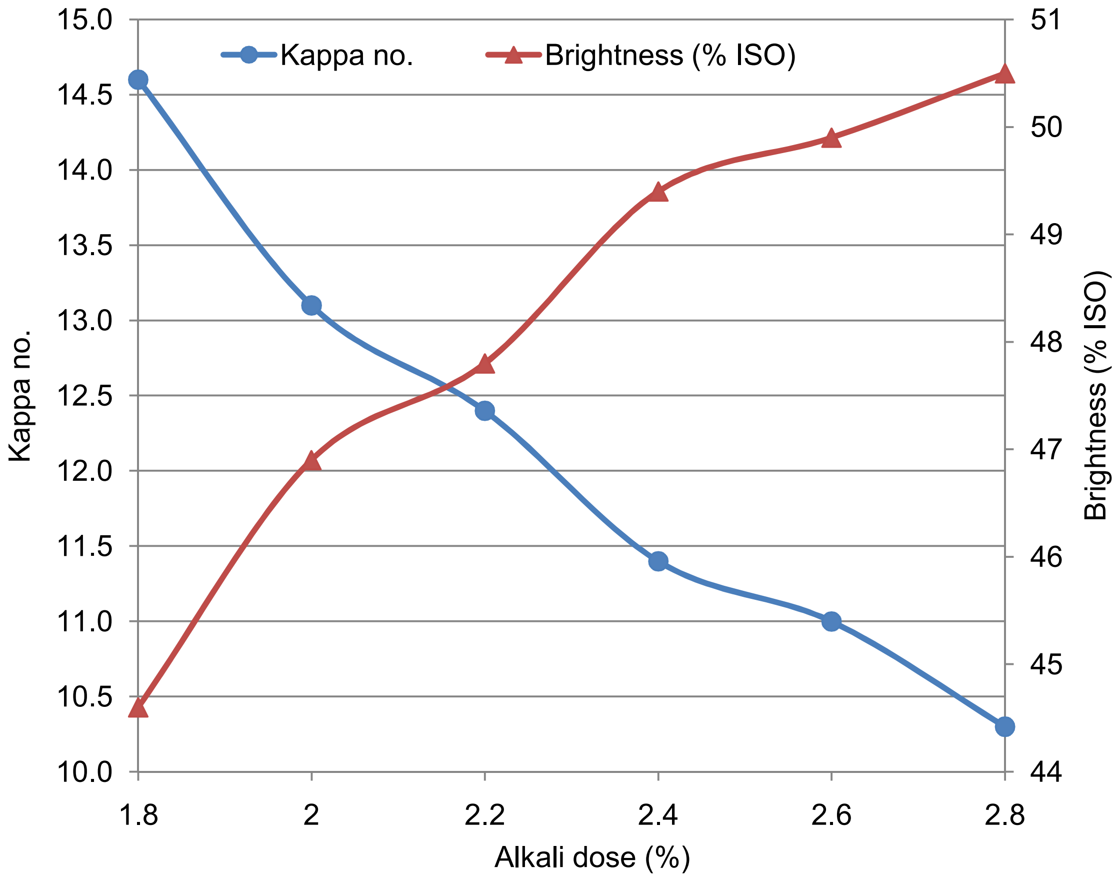

Figure 6.2.1: Effect of alkali dose on brightness and kappa no. of pulp

Table 6.2.1: Effect of sodium hydroxide dose on pulp properties

Particulars	Results					
Kappa no.	23.4					
Brightness (% ISO)	26.2					
Viscosity (cP)	11.6					
Oxygen delignification *(Consistency - 10%, Temperature - 80/100 °C, Time - 90 min, Oxygen - 1.8%)*						
NaOH (%)	1.8	2.13	2.2	2.4	2.6	2.8
pH	9.8	10.1	10.5	10.9	11.2	11.4
Kappa no.	14.6	13.1	12.4	11.4	11.0	10.3
Reduction (%)	37.6	44.0	47.0	51.3	53.0	56.0
Brightness (% ISO)	44.6	46.9	47.8	49.4	49.9	50.5
Improvement (Units)	18.4	20.7	21.6	23.2	23.7	24.3
Viscosity (cP)	9.4	9.1	8.9	8.6	8.5	8.4
Reduction (Units)	2.2	2.5	2.7	3.0	3.1	3.2

6.2.2. Effect of temperature on pulp properties

To evaluate the effect of temperature during oxygen bleaching on different pulp properties, treatment temperature was varied from 65 to 110°C by keeping other conditions constant. With the increase in temperature the kappa number of pulp was reduced and brightness of pulp improved. Detailed results of effect of temperature on different properties of pulp are given in Table 6.2.2.

Table 6.2.2: Effect of temperature on pulp properties

Particulars	Results		
Kappa no.	23.4		
Brightness (% ISO)	26.2		
Viscosity (cP)	11.6		
Oxygen delignification *(Consistency - 10%, Time - 90 min, NaOH - 2.3%, Oxygen - 1.8%)*			
Temperature (°C)	65/100	80/100	80/110
pH	11.1	10.6	10.3
Kappa no.	13.4	12.1	11.1
Reduction (%)	42.7	48.3	52.6
Brightness (% ISO)	46.8	49.1	53.5
Improvement (Units)	20.6	22.9	27.3
Viscosity (cP)	9.9	8.8	8
Reduction (Units)	1.7	2.8	3.6

6.2.3. Effect of initial kappa number

Three pulps of kappa no. 22.5, 18.6 and 15.3 were prepared to study the impact of kappa number on oxygen bleaching. All the pulps were subjected to oxygen bleaching using appropriate alkali doses and other conditions constant. Detailed results are given in Table 6.2.3. All the pulps were bleached with $DE_{OP}D$ sequence to know the bleaching response of different kappa number pulps. Detailed results of bleaching of pulps are given in Table 6.2.4. Bleached pulps were evaluated for physical strength properties and the results are given in Table 6.2.5.

Table 6.2.3: Effect of initial kappa number on pulp properties

Particulars	Results		
Kappa no.	23.4	18.6	15.3
Brightness (% ISO)	26.2	28.9	29.8
Oxygen delignification *(Consistency - 10%, Temperature - 80/100 °C, Time - 90 min, Oxygen - 1.8%)*			
NaOH (%)	2.3	1.9	1.6
pH	10.6	10.5	10.5
Kappa no.	12.1	10.0	8.4
Reduction (%)	48.3	46.2	45.1
Brightness (% ISO)	49.1	48.2	49
Improvement (Units)	22.9	19.3	19.2
Viscosity (cP)	8.8	8.6	8.4

Table 6.2.4: Bleaching response of different kappa number pulps

Particulars	Results		
Kappa no.	12.1	10.0	8.4
D_0 stage *(Consistency - 8%, Temperature - 55°C, Time - 30 min)*			
ClO_2 added (%)	1.11	0.91	0.77
E_{OP} stage *(Consistency - 10%, Temperature - 80 °C, Time - 120 min, H_2O_2 - 0.6%)*			
NaOH (%)	1.5	1.2	1.0
Final pH	10.5	10.6	10.6
CE kappa no.	1.9	1.5	1.4
Brightness (% ISO)	83.8	84.7	85.0
D stage *(Consistency - 10%, Temperature - 75 °C, Time - 180 min, ClO_2 - 1.0%)*			
Final pH	3.5	3.6	3.6
Brightness (% ISO)	88.0	88.4	88.9
CIE whiteness	73.8	74.0	74.4
ASTM yellowness	6.26	5.96	5.66

Table 6.2.5: Physical strength properties of bleached pulp

Particulars	Results		
Starting kappa no.	12.1	10.0	8.4
PFI revolutions (no.)	2500	2500	2500
°SR	29.0	30.5	31.0
Bulk (cc/g)	1.33	1.33	1.33
Tensile index (N.m/g)	58.4	54.7	52.4
Burst index (kN/g)	3.9	3.3	3.3
Tear index (mN.m^2/g)	8.6	8.5	8.2
Porosity (sec/100 ml)	30	33	35
Double fold (no.)	56	45	32
Smoothness (ml/min)	122	110	100

6.2.4. Effect of COD carryover

Proper washing of pulp is essential for better performance of oxygen bleaching stage as black liquor consumes oxygen and adversely affects selectivity (McDonogh 1996). To study the impact of washing on oxygen bleaching, unbleached pulps having different levels of COD carryover were subjected to oxygen bleaching. Results showed that with increase of COD carryover reduction in kappa number and viscosity of pulp was reduced. The effect was marginal till the COD carryover was up to 14.3 kg/TP after that delignification rate was affected significantly with loss of viscosity. Detailed results of oxygen bleaching of unbleached pulps having different COD carryover levels are given in Table 6.2.6.

Table 6.2.6: Effect of COD carryover on oxygen delignification

Parameters	Results					
Kappa no.	20.0					
Brightness (% ISO)	28.4					
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)						
COD carryover (kg/ TP)	12.3	12.8	14.3	15.9	17.4	18.4
Final pH	10.6	10.5	10.6	10.4	10.4	10.4
Kappa no.	10.9	11.2	11.3	11.6	11.9	12.6
Kappa reduction (%)	45.5	44.0	43.5	42.0	40.5	37.0
Brightness (% ISO)	46.5	45.0	44.4	44.1	41.7	39.0
Viscosity (cP)	11.0	11.0	10.7	10.7	10.5	10.8

To overcome/ reduce the effect of COD carryover alkali dose was increased. With the increase in alkali dose delignification rate was marginally improved but viscosity of the pulp got reduced further. Detailed results of oxygen bleaching of unbleached pulps having different COD carryover with increased dosage of alkali are given in Table 6.2.7.

Table 6.2.7: Effect of COD carryover on oxygen delignification (Increased dose of NaOH)

Parameters	Results				
Kappa no.	20.0				
Brightness (% ISO)	28.4				
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)					
COD carryover (Kg/ TP)	12.3	14.3	15.9	17.4	18.4
NaOH (%)	1.9	2.1	2.2	2.2	2.3
Final pH	10.6	10.7	10.7	10.6	10.6
Kappa no.	10.9	11.0	10.9	11.3	11.8
Kappa reduction (%)	45.5	45.0	45.5	43.5	41.0
Brightness (% ISO)	46.5	45.1	45.9	44.7	42.0
Viscosity (cP)	11.0	10.6	10.4	10.0	9.9

An additional study was carried out by increasing the alkali dose and addition of 0.2% EDTA to preserve the viscosity. Results showed that with the addition of EDTA and surplus alkali in oxygen bleaching stage the delignification improved and viscosity of pulp was protected for the pulps having higher COD carryover values. Detailed oxygen bleaching results of unbleached pulps having different COD carryover with surplus dose of alkali along with EDTA are given in Table 6.2.8.

Table 6.2.8: Effect of COD carryover on oxygen delignification (Increased dose of NaOH and use of EDTA)

Parameters	Results				
Kappa no.	20.0				
Brightness (% ISO)	28.4				
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)					
COD carryover (kg/ TP)	12.3	14.3	15.9	17.4	18.4
EDTA (%)	--	0.2			
NaOH (%)	1.9	2.1	2.2	2.2	2.3
Final pH	10.5	10.4	10.5	10.2	10.2
Kappa no.	10.9	10.5	10.8	11.0	11.5
Kappa reduction (%)	45.5	47.5	46.0	45.0	42.5
Brightness (% ISO)	46.5	47.1	46.7	46.3	46.7
Viscosity (cP)	11.0	11.9	11.5	10.9	10.7

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Effect of carbohydrate protectors to improve selectivity

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6.3. Effect of carbohydrate protectors to improve selectivity

Study was carried out using different chemical additives, chelating agents and polymeric additives as carbohydrate protectors in oxygen delignification stage base on literature review.

6.3.1. Effect of AQ on oxygen delignification

Anthraquinone (AQ) is generally used in alkaline pulping to accelerate delignification and protect cellulose by stopping peeling reaction. In present study different dosage of AQ (0.025-0.3%) were used along with alkali dose. Results showed an improvement of viscosity by 1.1 cP and pulp yield by 1.2% with marginal improvement in kappa reduction with the use of 0.2% AQ in oxygen delignification of pulp. Detailed results are given in Table 6.3.1.

Table 6.3.1: Effect of AQ during oxygen delignification

Particulars	Results					
Kappa no.	19.3					
Viscosity (cP)	11.3					
Brightness (% ISO)	29.7					
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)						
AQ (%)	--	0.025	0.075	0.1	0.2	0.3
Final pH	10.9	10.7	10.5	10.6	10.8	10.8
Kappa no.	10.8	10.6	10.5	10.5	10.3	10.3
Kappa reduction (%)	44.0	45.1	45.6	45.6	46.6	46.6
Brightness (% ISO)	44.0	44.0	45.2	45.1	45.9	46.4
Viscosity (cP)	9.0	9.3	9.7	9.7	10.1	10.4
Yield (%)	97.4	98.0	98.1	98.3	98.6	98.6

6.3.2. *Effect of H_2O_2 on oxygen delignification*

Effect of hydrogen peroxide in oxygen bleaching stage was studied in detail on mixed hardwood pulp. H_2O_2 dose applied on pulp was 0.5%, 1.0% and 1.5% keeping other conditions constant. Results showed that with the use of H_2O_2 during oxygen bleaching, kappa reduction and pulp brightness got improved significantly but viscosity of pulp reduced. Ng et al., 2011 also reported drop of viscosity with the use of hydrogen peroxide during oxygen delignification. Detailed results of oxygen bleaching using H_2O_2 are given in Table 6.3.2.

Table 6.3.2: Effect of using H_2O_2 during oxygen bleaching on pulp properties

Particulars	Results			
Kappa no.	19.3			
Viscosity (cP)	11.3			
Brightness (% ISO)	29.7			
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)				
H_2O_2 (%)	--	0.5	1.0	1.5
Final pH	10.7	10.6	10.2	10.0
Kappa no.	10.8	10.6	10.2	9.6
Kappa reduction (%)	44.0	45.1	47.2	50.3
Brightness (% ISO)	43.6	47.0	50.6	54.9
Viscosity (cP)	8.9	8.6	8.4	8.3
Yield (%)	97.0	97.0	96.8	96.4

6.3.3. Effect of H_2O_2 along with DTPA on oxygen delignification

Effect of using chelating agent diethylene triamine pentaacetic acid (DTPA) during hydrogen peroxide fortified oxygen bleaching stage was studied for improving efficacy of hydrogen peroxide and to preserve the pulp viscosity. Optical properties and viscosity of pulp were improved with the use of DTPA along with H_2O_2 compared to using H_2O_2 alone. Detailed results of using DTPA and H_2O_2 during oxygen bleaching stage are given in Table 6.3.3.

Table 6.3.3: Effect of DTPA-H_2O_2 during oxygen delignification

Particulars	Results				
Kappa no.	19.3				
Viscosity (cP)	11.3				
Brightness (% ISO)	29.7				
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)					
NaOH (%)	1.9	1.9	1.9	1.9	1.9
H_2O_2 (%)	--	--	0.5	1.0	1.5
Final pH	10.7	11.1	11.0	10.9	10.6
Kappa no.	10.8	10.4	9.7	9.4	8.7
Kappa reduction (%)	44.0	46.1	49.7	51.3	54.9
Brightness (% ISO)	45.0	48.9	51.8	55.1	58.5
Viscosity (cP)	9.0	9.3	8.9	8.7	8.4
Yield (%)	96.9	97.6	97.6	97.4	97.0

$DTPA-H_2O_2$ treated pulps were bleached using $D_0E_{OP}D$ sequence to observe its impact on final bleached pulp properties. With the use of $DTPA-H_2O_2$ final bleached pulp brightness was improved by 1.2 units, whiteness by 1.5 units and yellowness of the pulp reduced by 1.2 units compared to control. Detailed results of bleaching of $DTPA-H_2O_2$ treated pulps are given in Table 6.3.4.

Table 6.3.4: Bleaching results of $DTPA-H_2O_2$ treated pulps

Particulars	Control	DTPA	DTPA/ H_2O_2	DTPA/ H_2O_2	DTPA/ H_2O_2
Kappa no.	10.8	10.4	9.7	9.4	8.7
D_0 stage *(Consistency - 10%, Temperature - 55 °C, Time - 30 min)*					
ClO_2 added (%)	0.99	0.95	0.89	0.86	0.79
E_{OP} stage *(Consistency - 10%, Temperature - 80 °C, Time -120 min, H_2O_2 - 0.6%)*					
NaOH (%)	1.3	1.25	1.2	1.1	1.0
Brightness (% ISO)	82.5	83.9	84.2	84.9	85.2
D_1 stage (*Consistency - 10%, Temperature* - 75 °C, Time -180 min, ClO_2 - 1.%)					
Brightness (% ISO)	88.0	88.3	88.5	89.0	89.2
CIE whiteness	73.4	74.0	74.0	74.4	74.9
ASTM yellowness	6.8	6.38	5.94	5.68	5.63
L	95.0	95.2	95.32	95.68	95.73
a*	-0.34	-0.33	-0.33	-0.23	-0.23
b*	3.49	3.25	3.22	3.08	3.06

Bleached pulps were evaluated for physical strength properties. Detailed results of physical strength properties of bleached pulps are given in Table 6.3.5.

Table 6.3.5: Physical strength properties of pulps

Particulars	Control	DTPA	DTPA/ H_2O_2	DTPA/ H_2O_2	DTPA/ H_2O_2
PFI revolutions (no.)	2500	2500	2500	2500	2500
°SR	34.5	35.0	35.0	35.0	35.5
Bulk (cc/g)	1.27	1.22	1.24	1.23	1.24
Tensile index (N.m/g)	46.50	49.12	47.60	46.30	42.10
Burst index (kN/g)	2.95	3.20	3.20	2.82	2.92
Tear index ($mN.m^2/g$)	7.3	7.6	7.6	8.4	7.5
Porosity (sec/100 ml)	49.9	61.8	56.9	64.3	65.2
Double fold (no.)	45	64	45	46	61
Smoothness (ml/min)	214	239	205	199	182

6.3.4. Sodium borohydride

To assess the efficacy of sodium borohydride as cellulose protector, 0.05 - 0.1% dose of sodium borohydride were used during oxygen bleaching. Results showed that with the use of sodium borohydride in oxygen bleaching kappa reduction was improved by 5.2%, brightness by 6.8 units, viscosity by 1.0 unit compared to control. Detailed results are given in Table 6.3.6.

Table 6.3.6: Effect of Sodium borohydride during oxygen bleaching

Particulars	Results			
Kappa no.	19.3			
Viscosity (cP)	11.3			
Brightness (% ISO)	29.7			
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)				
Sodium borohydride (%)	--	0.05	0. 075	0.1
Final pH	10.8	10.8	10.8	10.9
Kappa no.	10.9	10.5	10.1	9.9
Kappa reduction (%)	43.5	45.6	47.7	48.7
Brightness (% ISO)	44.2	47.7	49.0	51.0
Viscosity (cP)	9.0	9.5	9.6	10.0
Yield (%)	97.0	97.5	97.7	98.0

6.3.5. Sodium perborate

Based on the literature 0.1-0.3% sodium perborate was used during oxygen bleaching to improve properties of pulp. With the used of sodium perborate during oxygen bleaching stage brightness of pulp was improved by 2.7 units, reduction in kappa number improved by 5.2% and viscosity of pulp improved by 0.7 units compared to control pulp. Detailed results of oxygen bleaching with different dosages of sodium perborate are given in Table 6.3.7.

Table 6.3.7: Effect of sodium perborate during oxygen bleaching

Particulars	Results			
Kappa no.	19.3			
Viscosity (cP)	11.3			
Brightness (% ISO)	29.7			
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)				
Sodium perborate (%)	--	0.1	0.2	0.3
Kappa no.	11.0	11.0	10.9	10.0
Kappa reduction (%)	43.0	43.0	43.5	48.2
Brightness (% ISO)	44.3	45.0	46.1	47.0
Viscosity (cP)	9.1	9.2	9.4	9.8
Yield (%)	97.0	98.0	98.3	98.4

6.3.6. Sodium gluconate

With the use of sodium gluconate during oxygen bleaching stage brightness of pulp was improved by 3.0 units, reduction in kappa number improved by 5.7% and viscosity of pulp improved by 0.5 units compared to control pulp. Detailed results of oxygen bleaching using different dosages of sodium gluconate are given in Table 6.3.8.

Table 6.3.8: Effect of sodium gluconate during oxygen bleaching

Particulars	Results		
Kappa no.	19.3		
Viscosity (cP)	11.3		
Brightness (% ISO)	29.7		
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)			
Sodium gluconate (%)	--	0.05	0.1
Kappa no.	11.0	10.2	9.9
Kappa reduction (%)	43.0	47.2	48.7
Brightness (% ISO)	42.0	44.3	45.0
Viscosity (cP)	9.0	9.2	9.5
Yield (%)	97.0	97.3	97.4

6.3.7. *Ethylene* glycol

With the use of ethylene glycol during oxygen bleaching stage brightness of pulp was improved by 4.9 units, reduction in kappa number improved by 4.2% but the viscosity of pulp marginally reduced compared to control pulp. Detailed results of oxygen bleaching using different dosages of ethylene glycol are given in Table 6.3.9.

Table 6.3.9: Effect of ethylene glycol during oxygen bleaching

Particulars	Results		
Kappa no.	19.3		
Viscosity (cP)	11.3		
Brightness (% ISO)	29.7		
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)			
Ethylene glycol (%)	--	0.05	0.1
Kappa no.	11.0	10.4	10.2
Kappa reduction (%)	43.0	46.1	47.2
Brightness (% ISO)	42.0	45.5	46.9
Viscosity (cP)	9.0	9.0	8.9
Yield (%)	97.0	97.0	96.8

6.3.8. Urea

With the use of urea during oxygen bleaching stage brightness of pulp was improved by 3.2 units, reduction in kappa number improved by 1.5% and the viscosity of pulp improved by 1.0 unit compared to control pulp. Detailed results of oxygen bleaching using different dosages of urea are given in Table 6.3.10.

Table 6.3.10: Effect of urea during oxygen bleaching

Particulars	Results			
Kappa no.	19.3			
Viscosity (cP)	11.3			
Brightness (% ISO)	29.7			
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)				
Urea (%)	--	0.5	0.75	1.0
Kappa no.	11.2	11.0	11.0	10.9
Kappa reduction (%)	42.0	43.0	43.0	43.5
Brightness (% ISO)	44.1	44.0	45.0	47.3
Viscosity (cP)	9.0	9.5	10.2	10.0
Yield (%)	96.9	97.0	97.6	98.0

6.3.9. *Thiourea*

With the use of thiourea during oxygen bleaching stage brightness of pulp was improved by 3.3 units, reduction in kappa number improved by 3.7% and the viscosity of pulp improved by 0.6 unit compared to control pulp. Detailed results of oxygen bleaching using different dosages of thiourea are given in Table 6.3.11.

Table 6.3.11: Effect of thiourea during oxygen bleaching

Particulars	Results			
Kappa no.	19.3			
Viscosity (cP)	11.3			
Brightness (% ISO)	29.7			
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)				
Urea (%)	--	0.5	0.75	1.0
Kappa no.	11.3	11.1	10.9	10.6
Kappa reduction (%)	41.5	42.5	43.5	45.1
Brightness (% ISO)	44.0	44.2	46.0	47.3
Viscosity (cP)	9.0	8.9	9.0	9.6
Yield (%)	97.0	97.0	97.3	97.7

6.3.10. Boric acid

With the use of boric acid during oxygen bleaching stage brightness of pulp was improved by 0.8 points, reduction in kappa number improved by 5.7% and the viscosity of pulp improved by 0.2 points compared to control pulp. Detailed results of oxygen bleaching using different dosages of boric acid are given in Table 6.3.12.

Table 6.3.12: Effect of boric acid during oxygen bleaching

Particulars	Results			
Kappa no.	19.3			
Viscosity (cP)	11.3			
Brightness (% ISO)	29.7			
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)				
Urea (%)	--	0.1	0.5	1.0
Kappa no.	11.1	10.3	9.9	10.0
Kappa reduction (%)	42.5	46.6	48.7	48.2
Brightness (% ISO)	44.0	45.2	45.5	44.8
Viscosity (cP)	9.1	9.0	9.3	9.2
Yield (%)	97.0	97.0	97.5	97.4

6.3.11. Effect of magnesium hydroxide

Efficacy of magnesium oxide, magnesium carbonate and magnesium hydroxide was studied to improve the selectivity of oxygen bleaching. Magnesium oxide and magnesium carbonate were not found effective in terms of improvement in selectivity or optical properties of pulp. Magnesium hydroxide showed the considerable improvement in reduction of kappa number of pulp, brightness, viscosity and pulp yield when used during oxygen bleaching. With the use of magnesium hydroxide during oxygen bleaching stage brightness of pulp was improved by 7.0 points, reduction in kappa number improved by 5.2% and the viscosity of pulp improved by 1.0 point compared to control pulp. Detailed results of oxygen bleaching using different dosages of magnesium hydroxide are given in Table 6.3.13.

Table 6.3.13: Effect of magnesium hydroxide during oxygen bleaching

Particulars	Results				
Kappa no.	19.3				
Viscosity (cP)	11.3				
Brightness (% ISO)	29.7				
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min,* *O_2 - 1.8%, NaOH - 1.9%*)					
$Mg(OH)_2$ (%)	--	0.05	0.1	0.2	0.3
Final pH	10.7	10.8	10.7	10.8	10.9
Kappa no.	10.8	10.0	10.2	10.1	9.8
Kappa reduction (%)	44.0	48.2	47.2	47.7	49.2
Viscosity (cP)	8.9	9.0	9.4	9.8	9.9
Brightness (% ISO)	44.0	49.2	50.1	50.5	51.0
Yield (%)	97.0	97.8	98.2	98.2	98.3

Oxygen bleached pulps with and without using magnesium hydroxide as cellulose protector were bleached by using $D_0E_{OP}D$ sequence. Detailed results of bleaching are given in Table 6.3.14.

Table 6.3.14: Bleaching results of pulps produced with and without using magnesium hydroxide during oxygen bleaching

Particulars	Control	0.05% $Mg(OH)_2$	0.1% $Mg(OH)_2$	0.2% $Mg(OH)_2$	0.3% $Mg(OH)_2$
Kappa no.	10.8	10.0	10.2	10.1	9.8
D_0 stage (Consistency - 10%, Temperature - 55 °C, Time - 30 min)					
ClO_2 added (%)	0.99	0.91	0.93	0.92	0.89
End pH	2.4	2.5	2.4	2.4	2.5
E_{OP} stage *(Temperature - 80 °C, Time - 120 min, H_2O_2 - 0.5%)*					
NaOH (%)	1.1	1.0	1.0	1.0	1.0
Brightness (% ISO)	81.9	82.0	82.3	82.3	82.4
Kappa no.	2.2	2.2	2.1	2.1	2.1
D stage (*Temperature* - 75 ℃, Time - 180 min, ClO_2 - 1.0%)					
Final pH	3.4	3.4	3.5	3.5	3.5
Brightness (% ISO)	88.0	88.0	88.0	88.1	88.0
CIE whiteness	75.9	75.9	75.8	75.9	75.9
ASTM yellowness	7.15	7.11	7.18	7.07	7.13
Yield (%)	95.7	95.8	95.9	96.0	96.0
Viscosity (cP)	8.5	8.6	8.9	9.2	9.3

Bleached pulps were evaluated for physical strength properties. Detailed results of physical strength properties of bleached pulps produced with and without using magnesium hydroxide during oxygen bleaching are given in Table 6.3.15.

Table 6.3.15: Physical strength properties of bleached pulps produced with and without using magnesium hydroxide during oxygen bleaching

Particulars	Control	0.05% $Mg(OH)_2$	0.1% $Mg(OH)_2$	0.2% $Mg(OH)_2$	0.3% $Mg(OH)_2$
PFI revolutions (no.)	2500	2500	2500	2500	2500
CSF (ml)	437	437	437	432	427
Bulk (cc/g)	1.318	1.326	1.322	1.313	1.310
Tensile index (N.m/g)	45.7	46.8	50.8	51.3	52.07
Burst index (kN/g)	2.88	2.93	3.00	3.26	3.37
Tear index ($mN.m^2/g$)	8.8	8.5	9.8	9.8	11.23
Porosity (sec/100 ml)	30.6	34.6	40.9	36.9	44.6
Double fold (no.)	41.0	44.0	46	51	61
Smoothness (ml/min)	192	153	130	140	118

6.3.12. Effect of chelating agents on oxygen delignification

Efficacy of different chelating agents namely hydroxy ethylidene diphosphonic acid (HEDP), nitrilotriacetic acid (NTA), ethylene diamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA) and diethylene triamine penta methylene phosphonic acid (DTMPA) were assessed during oxygen bleaching stage. DTPA showed the highest efficiency in terms of brightness development and reduction in kappa number of pulp amongst the different chelating agents used during the study. EDTA was found most effective in protecting cellulose degradation. Detailed results of oxygen bleaching using different chelating agents are given in Table 6.3.16.

Table 6.3.16: Oxygen bleaching of pulp using different chelating agents

Particulars	Control	HEDP	NTA	EDTA	DTPA	DTMPA
Kappa no.	19.3	19.3	19.3	19.3	19.3	19.3
Brightness (% ISO)	29.7	29.7	29.7	29.7	29.7	29.7
Viscosity (cP)	11.3	11.3	11.3	11.3	11.3	11.3
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)						
Additive dose (%)	--	1.0	0.5	0.2	0.07	0.07
Kappa no.	10.6	10.3	10.2	10.4	9.8	10.1
Reduction (%)	45.1	46.6	47.2	46.1	49.2	47.7
Brightness (% ISO)	46.9	47	48.1	44.4	49.3	47.8
Viscosity (cP)	9.3	9.5	9.9	10.8	9.6	9.3
Reduction (units)	2.0	1.8	1.4	0.5	1.7	2.0

6.3.13. Efficacy of polymeric additives

Efficacy of different polymeric additives namely cationic starch, native starch, carboxymethyl cellulose (CMC) and guar gum was assessed during oxygen bleaching stage. None of the polymeric additive improved the reduction of kappa number or brightness of pulp. Native starch and CMC were found most effective in protecting cellulose degradation amongst the different polymeric additives used during the study. Detailed results of oxygen bleaching using different polymeric additives are given in Table 6.3.17.

Table 6.3.17: Oxygen bleaching of pulp using different polymeric additives

Particulars	Results				
Kappa no.	19.7				
Brightness (% ISO)	30.0				
Oxygen bleaching (*Consistency - 10%, Temperature - 95 °C, Time - 60 min, O_2 - 1.8%, NaOH - 1.9%*)					
Additives	Control	Cationic starch	Native starch	CMC	Guar gum
Dose (%)	--	0.5	0.5	0.1	0.5
Kappa no.	11.0	11.6	11.9	11.4	13.0
Kappa reduction (%)	44.2	41.1	39.6	42.1	34.0
Brightness (% ISO)	45.8	44.4	43.3	44.5	43.0
Viscosity (cP)	9.0	9.6	9.9	9.8	9.4
Yield (%)	97.0	97.5	97.3	97.6	97.7

Bleached pulps were evaluated for physical strength properties. The highest tear index was obtained in the pulp treated with CMC in oxygen bleaching stage followed by native starch, cationic starch and guar gum. Detailed results of physical strength properties are given in Table 6.3.18.

Table 6.3.18: Physical strength properties of bleached pulp

Particulars	Control	Cationic starch	Native starch	CMC	Guar gum
PFI revolutions (no.)	2500	2500	2500	2500	2500
°SR	30	30.0	29.5	30.0	29.5
Bulk (cc/g)	1.38	1.40	1.40	1.40	1.42
Tensile index (N.m/g)	63.5	63.9	66.9	64.3	68.9
Burst index (kN/g)	4.06	4.40	4.21	4.50	4.80
Tear index (mN.m^2/g)	7.80	8.60	9.05	10.50	7.40
Porosity (sec/100 ml)	16.1	19.1	19.0	21.2	21.0
Double fold(no.)	65.8	139	91.5	145	89
Smoothness (ml/min)	132	120	116	105	100

Study on mill pulp with screened additives

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6.4. Study on mill pulp with screened additives

Efficacy of most effective additives was evaluated on mill pulps collected from paper mills situated in northern and southern part of India.

6.4.1. Efficacy of selected carbohydrate protectors on mill pulp (pulp collected from northern part of India)

Efficacy of EDTA, DTPA, magnesium hydroxide and hydrogen peroxide along with DTPA was assessed during oxygen bleaching stage on mill pulp collected from northern part of India. Detailed results of oxygen bleaching using different additives are given in Table 6.4.1.

Table 6.4.1: Oxygen bleaching of pulp using different additives

Parameters	Results				
Kappa no.	18.9				
Brightness (% ISO)	30				
Viscosity (cP)	14.1				
Oxygen bleaching (*Consistency - 10%, Temperature - 95/100 °C, Time - 30/90 min, O_2 - 5.0/4.5 kg/cm^2, NaOH - 2.0%*)					
Additive used	Control	EDTA	DTPA	$Mg(OH)_2$	DTPA-H_2O_2
Dose (%)	--	0.1	0.1	0.2	0.6 + 0.05
Kappa no.	10.7	10.4	10.7	9.8	9.7
Kappa reduction (%)	43.4	45.0	43.4	48.1	48.7
Brightness (% ISO)	47.7	48.1	47.6	49.4	53.3
Viscosity (cP)	9.2	10.0	9.9	10.3	9.6
Yield (%)	96.9	97.4	97.6	98.0	97.0

Effect of using different additives namely EDTA, DTPA, magnesium hydroxide and hydrogen peroxide along with DTPA during oxygen bleaching on black liquor properties was evaluated. Detailed results of using different selected additives in oxygen bleaching stage on black liquor properties are given in Table 6.4.2.

Table 6.4.2: Effect of using different selected additives in oxygen bleaching stage on black liquor properties

Particulars	Results				
	Control	EDTA	DTPA	$Mg(OH)_2$	DTPA-H_2O_2
SVR (ml/g)	35.6	39.4	35.8	41.3	36.8
Organic (%)	50.5	50.7	50.4	50.5	50.1
Inorganic (%)	49.5	49.3	49.6	49.5	49.9
GCV (kcal/kg)	3690	3620	3698	3601	3605

Pulps obtained after oxygen bleaching using different selected additives were bleached using $D_0E_{OP}D$ sequence. Final bleached pulp brightness was the highest 88.7% in the DTPA-H_2O_2 treated pulp followed by 88.6% in $Mg(OH)_2$, 88.5% in EDTA and 88.0% in DTPA treated pulps and 87.7% in control pulp. Viscosity of the final bleached pulp was highest 9.9 cP in the $Mg(OH)_2$ treated pulp followed by 9.0 cP in EDTA, 8.8 cP in DTPA-H_2O_2, 8.8 cP in DTPA treated pulps and 8.7 cP in control pulp. Detailed results on bleaching of pulps produced using different additives in oxygen bleaching stage are given in Table 6.4.3.

Table 6.4.3: Results on bleaching of pulps

Particulars	Control	EDTA	DTPA	$Mg(OH)_2$	DTPA-H_2O_2
Kappa no.	10.7	10.4	10.7	9.8	9.7
D_0 stage (*Temperature - 60 °C, Time - 45 min,* Kappa factor - 0.25)					
ClO_2 added (%)	1.02	0.99	1.02	0.93	0.92
E_{OP} stage *(Temperature - 80 °C, Time - 120 min, H_2O_2 - 0.6%)*					
NaOH (%)	1.3	1.34	1.2	1.2	1.3
Final pH	10.4	10.5	10.5	10.7	10.5
Kappa no.	2.0	1.9	1.9	1.8	1.6
Brightness (% ISO)	82.9	83.3	83.6	84.9	85.0
D stage *(Temperature - 75 °C, Time - 180 min,* ClO_2 - 1.0%*)*					
Final pH	3.5	3.5	3.6	3.5	3.6
Brightness (% ISO)	87.7	88.5	88.0	88.6	88.7
CIE whiteness	77.8	78.0	77.9	78.9	79.0
ASTM yellowness	6.13	5.79	5.83	5.72	5.60
Bleached yield (%)	43.4	43.7	43.7	44.0	43.5
Viscosity (cP)	8.7	9.0	8.8	9.9	8.8

Bleached pulps were evaluated for physical strength properties at two freeness levels. The highest tear index of 9.0 mN.m^2/g was obtained in the pulp using $Mg(OH)_2$ as additive in oxygen bleaching stage followed by 8.86 mN.m^2/g with DTPA, 8.6 mN.m^2/g with DTPA-H_2O_2, 8.4 mN.m^2/g with EDTA and 8.1 mN.m^2/g in control pulp. Detailed results of physical strength properties of bleached pulps obtained with and without using additives EDTA and DTPA in oxygen bleaching are given in Table 6.4.4. Detailed results of physical strength properties of bleached pulps obtained with and without using additives $Mg(OH)_2$ and DTPA-H_2O_2 in oxygen bleaching are given in Table 6.4.5.

Table 6.4.4: Physical strength properties of bleached pulps

Parameter	Control		EDTA		DTPA	
PFI revolutions (no.)	1800	2400	1800	2400	1800	2400
°SR	28.5	31	28	31.5	28.5	31.5
Bulk (cc/g)	1.44	1.38	1.43	1.37	1.43	1.38
Tensile index (N.m/g)	50.8	55.9	57.0	59.6	59.3	61.7
Burst index (kN/g)	3.4	3.8	3.4	3.9	4.2	4.6
Tear index (mN.m^2/g)	7.1	8.1	6.6	8.4	7.0	8.8
Porosity (sec/100 ml)	11.1	17.4	10.2	13.3	11.9	18.4
Double fold (no.)	30	44	47	56	36	60
Smoothness (ml/min)	120	101	131	115	104	81

Table 6.4.5: Physical strength properties of bleached pulps

Parameter	Control		$Mg(OH)_2$		DTPA - H_2O_2	
PFI revolutions (no.)	1800	2400	1800	2400	1800	2400
°SR	28.5	31	29	31.5	29	32
Bulk (cc/g)	1.44	1.38	1.42	1.38	1.41	1.36
Tensile index (N.m/g)	50.8	55.9	58.9	61.1	57.2	59.4
Burst index (kN/g)	3.4	3.8	4.3	4.5	3.4	4
Tear index ($mN.m^2/g$)	7.1	8.1	7.8	9.0	7.9	8.6
Porosity (sec/100 ml)	11.1	17.4	12.9	15.3	11.6	16.2
Double fold (no.)	30	44	54	72	41	54
Smoothness (ml/min)	120	101	129	103	117	93

Filtrate generated from different stages of bleaching was mixed in respective proportion and combined filtrate was analysed for different effluent properties. Detailed results on properties of effluent generated during bleaching are given in Table 6.4.6.

Table 6.4.6: Effect of using additives in oxygen bleaching stage on effluent generated during bleaching

Parameters	Control	EDTA	DTPA	$Mg(OH)_2$	DTPA - H_2O_2
COD (kg/t)	11.8	11.1	12.0	10.4	11.1
Colour (kg/t)	18.1	17.9	17.9	17.7	17.6
AOX (kg/t)	1.3	1.2	1.2	1.1	1.1
Total solids (%)	0.3	0.3	0.3	0.3	0.4

6.4.2. Efficacy of selected carbohydrate protectors on mill pulp (pulp collected from southern part of India)

Efficacy of most effective and economically viable additives suitable for use in mill scale operations namely $Mg(OH)_2$ and EDTA was evaluated on mill pulp collected from paper mill situated in southern part of India where plant trial was planned. Properties of the pulp collected from the mill are given in Table 6.4.7. Physical strength properties of unbleached and bleached mill pulp are given in Table 6.4.8.

Table 6.4.7: Properties of mill pulps

Particulars	Unbleached	ODL	Bleached
Kappa no.	21.9	14.9	--
Brightness (% ISO)	26.9	43.0	87.1
Viscosity (cP)	16.9	13.8	12.1

Table 6.4.8: Physical strength properties of mill pulps

Parameters	Unbleached	Bleached
PFI revolutions (no.)	3500	3100
°SR	35.5	36.0
Grammage (g/m^2)	60.9	61.2
Bulk (cc/g)	1.43	1.30
Tensile index (N.m/g)	56.8	53.5
Burst index (kN/g)	3.66	3.52
Tear index ($mN.m^2/g$)	8.56	7.81
Double fold (no.)	45	37

Oxygen bleaching of mill pulp was carried out with and without using $Mg(OH)_2$ and EDTA. Detailed results are given in Table 6.4.9.

Table 6.4.9: Oxygen bleaching of mill pulp with and without additives

Parameters	Control	$Mg(OH)_2$	EDTA
Kappa no.	21.9		
Brightness (% ISO)	26.9		
Viscosity (cP)	16.9		
Oxygen bleaching *(Consistency - 10%, Temperature - 85 °C, Time - 90 min)*			
Initial pH	12.5	12.5	12.4
Final pH	11.2	11.1	11.1
Kappa no.	13.6	13.0	13.4
Viscosity (cP)	12.9	13.8	13.4
Brightness (% ISO)	39.0	39.9	39.5
Kappa reduction (%)	37.9	40.6	38.8
Viscosity reduction (%)	23.7	18.3	20.7
Brightness improvement (units)	12.1	13.0	12.6
Pulp shrinkage in oxygen bleaching (%)	2.4	1.5	2.1

Pulps obtained after oxygen bleaching were further bleached using $D_0E_{OP}D$ sequence. With the use of $Mg(OH)_2$ in oxygen bleaching stage final pulp brightness was improved by 1.1 unit and viscosity by 0.9 units. Detailed results are given in Table 6.4.10.

Table 6.4.10: Bleaching results

Particulars	Control	$Mg(OH)_2$	EDTA
Kappa no.	13.6	13.0	13.4
D_0-Stage *(Temp. - 65°C, Time - 60 min, Cy - 10%)*			
ClO_2 added (%)	1.40	1.33	1.38
End pH	2.35	2.40	2.42
E_{OP}-Stage (Consistency - 10%, Temperature - 80 °C, Time - 90 min, H_2O_2 added - 0.6%, NaOH added - 2.0%)			
Final pH	11.2	11.2	11.3
Residual H_2O_2 (ppm)	13.6	10.2	6.8
H_2O_2 consumed (%)	0.58	0.59	0.59
Brightness (% ISO)	79.0	79.8	79.4
E_{OP} Kappa no.	1.7	1.5	1.6
D_1-Stage *(Consistency - 10%, Temperature - 65 °C, Time - 120 min, ClO_2 added - 0.6%)*			
Final pH	3.8	3.6	3.5
Residual ClO_2 (ppm)	81.0	108.0	91.8
ClO_2 consumed (ppm)	0.53	0.50	0.52
Brightness (% ISO)	86.8	87.9	87.2
CIE whiteness	74.2	75.5	74.5
ASTM yellowness	7.18	7.01	7.08
Viscosity (cP)	11.0	11.9	11.5

Handsheets of bleached pulps were prepared after refining the pulps to about 36 °SR level and evaluated for physical strength properties. With the use of selected additives in oxygen bleaching stage physical strength properties of final bleached pulp were improved marginally. Detailed results are given in Table 6.4.11.

Table 6.4.11: Physical strength properties lab bleached pulps

Parameters	Control	Additive-A	Additive-B
PFI revolutions (no.)	3100	3100	3100
°SR	35.5	36.0	36.0
Grammage (g/m^2)	61.3	60.7	61.1
Bulk (cc/g)	1.30	1.31	1.30
Tensile index (N.m/g)	58.8	59.5	59.3
Burst index (kN/g)	4.10	4.20	4.17
Tear index (mN.m^2/g)	8.55	8.63	8.63
Double fold (no.)	63	79	81

Validation studies on selected processes at CPPRI

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6.5. Validation studies on selected processes at CPPRI

The CESS project on Improvement in selectivity of oxygen bleaching was submitted by ACIRD/CPPRI with following objectives

OBJECTIVES

- To find out most suitable conditions for ODL for different indigenous raw materials
- To study the effect of carbohydrate protectors to reduce cellulose degradation during ODL stage
- To reduce pulp shrinkage during ODL stage
- Plant scale trial using optimized conditions with identified additive

QUANTIFIED DELIVERABLES

- Improvement in pulp yield
- Reduction in degradation of carbohydrates
- Improvement in pulp quality

The scope of activities was involved mainly application of various protectors and additives in order to preserve strength and yield during ODL treatment

Scope of CPPRI

- Validation of the results obtained with selected additive/chemical at ACIRD.
- Oxygen delignification will be carried out using quantum mixer.

In 1998, CPPRI had procured the quantum mixture to simulate the plant scale conditions and imparting the technical services in the areas of oxygen delignification in pre bleaching stage and extraction stage of pulp of various indigenous raw materials. Most of the large and medium scale pulp and paper mills which planned to introduce ODL in their fiber line have sponsored project to CPPRI to check its feasibility for their raw material.

This is why the scope of work under the project involved the cross verification of findings achieved by ACIRD by using quantum mixture at CPPRI before proceeding for plant trial.

EXPERIMENT AND RESULTS

After receiving the interim report from ACIRD, validation of the findings were carried out at CPPRI. The same are tabulated below compared with the results obtained at ACIRD.

Table 6.5.1: Pulping Results of Eucalyptus Chips

Parameters	**ACIRD**	**CPPRI**
Pulping conditions		
Active alkali as Na_2O (%)	16.0	16.0
Sulphidity (%)	23.4	23.4
Cooking temperature (°C)	160	160
Cooking time (min)	90	90
Pulp properties		
Pulp yield (%)	47.9	48.5
Rejects (%)	0.20	0.21
Kappa no.	18.9	19.2
Brightness (% ISO)	30.0	28.8
Viscosity (cP)	14.1	16.0

Table 6.5.2: Effect of selected additives on ODL stage pulp properties

Parameters	Control		EDTA (0.1%)		DTPA (0.1%)	
	ACIRD	CPPRI	ACIRD	CPPRI	ACIRD	CPPRI
Unbleached pulp properties						
Kappa no.	18.9	19.2	18.9	19.2	18.9	19.2
Brightness (% ISO)	30	28.8	30	28.8	30	28.8
Viscosity (cP)	14.1	16	14.1	16	14.1	16
Oxygen delignified pulp properties						
Kappa no.	10.7	11	10.4	10.8	10.7	10.7
Kappa reduction (%)	43.4	42.7	45.0	43.8	43.4	44.3
Brightness (% ISO)	47.7	48	48.1	49	47.6	49.5
Viscosity (cP)	9.2	10.2	10.0	11	9.9	11.5
Yield (%)	96.9	97	97.4	97.5	97.6	97.6

ODL stage conditions (Consistency - 10%, Temperature - 95/100 °C, Time - 30/90 min, O_2 - 5.0/4.5 kg/cm^2, NaOH - 2.0%)

Table 6.5.3: Effect of selected additives on ODL stage pulp properties

Parameters	Control		$Mg(OH)_2$ (0.2%)		H_2O_2+ DTPA (0.6+0.05%)	
	ACIRD	CPPRI	ACIRD	CPPRI	ACIRD	CPPRI
Unbleached pulp properties						
Kappa no.	18.9	19.2	18.9	19.2	18.9	19.2
Brightness (% ISO)	30	28.8	30	28.8	30	28.8
Viscosity (cP)	14.1	16	14.1	16	14.1	16
Oxygen delignified pulp properties						
Kappa no.	10.7	11	9.8	10	9.7	9.5
Kappa reduction (%)	43.4	42.7	48.1	47.9	48.7	50.5
Brightness (% ISO)	47.7	48	49.4	51	53.3	55
Viscosity (cP)	9.2	10.2	10.3	11.8	9.6	12.0
Yield (%)	96.9	97	98.0	98.0	97.0	98.0

ODL stage conditions (Consistency - 10%, Temperature - 95/100 °C, Time - 30/90 min, O_2 - 5.0/4.5 kg/cm^2, NaOH - 2.0%)

Observations:

The study on selectivity of oxygen bleaching carried out at ACIRD is repeated at CPPRI and data obtained are cited above.

It is observed that $Mg(OH)_2$ and combination of H_2O_2 and DTPA is more effective than EDTA and DTPA.

$DE_{OP}D$ Bleaching of ODL pulps

Table 6.5.4: Effect of using additive in ODL stage on pulp bleaching

Particulars	Control		EDTA (0.1%)		DTPA (0.1%)	
	ACIRD	CPPRI	ACIRD	CPPRI	ACIRD	CPPRI
Kappa no.	10.7	11	10.4	10.8	10.7	10.7
Brightness (% ISO)	47.7	48	48.1	49	47.6	49.5
Viscosity (cP)	9.2	10.2	10.0	11	9.9	11.5
Bleached yield (%)	43.4	42.0	43.7	41.0	43.7	44.0
Brightness (% ISO)	87.7	87.0	88.5	88.2	88.0	88.3
Viscosity (cP)	8.7	9.5	9.0	9.4	8.8	10.0

Table 6.5.5: Effect of using additive in ODL stage on pulp bleaching

Particulars	Control		$Mg(OH)_2$ (0.2%)		H_2O_2+ DTPA (0.6+0.05%)	
	ACIRD	CPPRI	ACIRD	CPPRI	ACIRD	CPPRI
Kappa no.	10.7	11	9.8	10	9.7	9.5
Brightness (% ISO)	47.7	48	49.4	51	53.3	55
Viscosity (cP)	9.2	10.2	10.3	11.8	9.6	12.0
Bleached yield (%)	43.4	42.0	44.0	43.8	43.5	44
Brightness (% ISO)	87.7	87.0	88.6	88.8	88.7	89.0
Viscosity (cP)	8.7	9.5	9.9	10.5	8.8	10.2

RECOMMENDATION

- The trial of ODL with additive $Mg(OH)_2$ and H_2O_2+DTPA have better performance as compared to control sample.
- Economically $Mg(OH)_2$ is a better option over H_2O_2+DTPA.

Pre plant trial studies at ACIRD

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6.6. Pre plant trial studies at ACIRD

A meeting was conducted on August 3, 2016 at Avantha Centre for Industrial Research & Development, Yamuna Nagar to discuss the outcome of the results obtained in lab scale study carried out at ACIRD and validation study conducted at CPPRI under the under the CESS sponsored project "Improvement in selectivity of oxygen bleaching". Following members were present in the meeting:

ACIRD	SPB	CPPRI
• Dr. N. K. Bhardwaj, Deputy Director • Mr. Sandeep Tripathi, Research Scientist cum Group Head	• Dr. P. Marimuthu, Deputy General Manager (R&D/ QC)	• Dr. Arvind Sharma, Senior Scientific Assistant

In the meeting it was decided to carry out lab study using commercial samples of magnesium hydroxide on mill pulp prior to conducting plant trial at SPB Ltd. One sample of commercial magnesium hydroxide was received on September 5, 2016 from SPB Ltd. Another sample of commercial magnesium hydroxide was procured by ACIRD.

Detailed results

Table 6.6.1: Properties of pulp samples received from the mill

Particulars	Unbleached	Oxygen delignified
Brightness (% ISO)	27.0	38.1
Kappa no.	19.1	12.5
Viscosity (cP)	14.1	11.4

Table 6.6.2: Effect of $Mg(OH)_2$ during oxygen bleaching of mill pulp

Parameter	Control	With $Mg(OH)_2$		
		Commercial grade (Received from SPB)	Commercial grade (Procured by ACIRD)	Lab grade
ODL stage *(Temperature - 85 °C, Time - 60 min, Consistency - 10%, O_2 - 1.8%, NaOH - 2.10%)*				
$Mg(OH)_2$ (%)	--	0.2		
Final pH	10.9	10.8	10.8	10.8
Kappa no.	11.2	10.8	10.7	10.7
Kappa reduction (%)	41.4	43.5	44.0	44.0
Brightness (% ISO)	40.0	41.1	41.3	41.2
Viscosity (cP)	10.4	11.3 (+0.9)	11.4 (+1.0)	11.3 (+0.9)
Yield (%)	97.5	98.4 (+0.9)	98.5 (+1.0)	98.5 (+1.0)

Table 6.6.3: Bleaching of oxygen bleached pulps

Particulars	Control		*$Mg(OH)_2$	
	Set 1	Set 2	Set 3	Set 4
Kappa no.	11.2		10.7	
D_0 stage *(Temperature - 65 °C, Time - 60 min, Consistency - 10%)*				
ClO_2 added (%)	1.23	1.23	1.18	1.18
Residual ClO_2 (ppm)	27.0	27.0	29.7	27.0
E_{OP} stage *(Consistency - 10%, Temperature - 80 °C, Time - 90 min, O_2 - 0.7%,* H_2O_2 - 0.6%, *NaOH - 1.7%)*				
Final pH	11.1	11.0	11.0	10.9
Residual H_2O_2 (ppm)	17.0	20.4	27.2	20.4
Kappa no.	2.2	2.2	2.1	2.1
Brightness (% ISO)	80.7	80.5	81.5	81.4
D stage *(Consistency - 10%, Temperature - 75 °C, Time - 180 min, ClO_2 - 0.9%)*				
Final pH	3.5	3.5	3.6	3.6
ClO_2 Residual (ppm)	5.4	8.1	12.1	13.5
Brightness (% ISO)	87.4	87.3	88.0	88.0
CIE whiteness	75.8	75.5	76.4	76.4
ASTM yellowness	6.74	6.78	6.65	6.62
Viscosity (cP)	9.6	9.6	10.7	10.6

*Received from SPB

Table 6.6.4: Physical strength properties of bleached pulps

Parameters	Control		*$Mg(OH)_2$	
PFI revolutions (no.)	0	2500	0	2500
°SR	20.0	29.5	20.5	29.0
Grammage (g/m^2)	59.3	59.2	59.6	59.0
Bulk (cc/g)	1.38	1.31	1.38	1.32
Tensile index (N.m/g)	21.0	54.4	23.7	56.6
Burst index (kN/g)	1.3	4.0	1.3	4.2
Tear index (mN.m2/g)	4.4	8.4	4.7	8.8
Double fold (no.)	2	52	2	66

*Received from SPB

Table 6.6.5: Magnesium content at different places of process

Particulars	Mg content (ppm)	
	Control	With $Mg(OH)_2$
ODL stage pulp	120	260
ODL stage filtrate	538	645
Dregs	15,815	17,986
Lime mud	4,005	4,778
White liquor	38.6	42.0

Salient findings

- Results obtained with the use of unbleached pulp collected from mill and using commercial magnesium hydroxide are similar to those obtained with lab produced pulp using lab grade magnesium hydroxide.
- Use of 0.2% $Mg(OH)_2$ during oxygen delignification improves the pulp yield by 1.0% and viscosity of pulp by 1.0 units with improved pulp brightness and reduced kappa number.
- Results showed that most of the magnesium remained with the pulp and maximum part of the remaining magnesium removed along with dregs. There is marginal increase in magnesium content in white liquor after using it in ODL stage.

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Demonstration of results in the plant scale

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6.7. Demonstration of results in the plant scale

Magnesium hydroxide and ethylene diamine tetra acetic acid (EDTA) were found most suitable among various chemical studied to improve selectivity of oxygen bleaching in lab scale studies carried out at Avantha Centre for Industrial Research & Development (ACIRD). It was proposed to explore suitability of any one chemical on plant scale trial at SPB, Erode (TN). Prior to carry out plant scale trial, suitability of both the chemicals was also validated at Central Pulp & Paper Research Institute (CPPRI).

Plant scale trial using commercial magnesium hydroxide was carried out at SPB with the objective to study the effect of carbohydrate protector (magnesium hydroxide) to reduce cellulose degradation during oxygen bleaching stage as well as improvement in pulp quality. The details on the trial are given below:

Trial date and time: November 30, 2016 to December 4, 2016

Chemical used: Commercial grade $Mg(OH)_2$ procured by the mill

Dosage used: 1.0 kg/TP (30.11.2016, 4:40 pm to 30.11.2016, 7:10 pm), 2.5 h

1.0 kg/TP (1.12.2016, 04:30 pm to 1.12.2016, 10:00 pm), 5.5 h

1.0 kg/TP (1.12.2016, 11:30 pm to 2.12.2016, 9:30 am), 10 h

2.0 kg/TP (2.12.2016, 1:30 am to 4.12.2016, 2:30 pm), 49 h

Place of addition: At BSW-3 repulper conveyer (oxygen bleaching stage inlet)

Dosing: Initially through reciprocating dosing pump (not succeeded due to depositions in valves). Finally slurry was added through centrifugal pump (successfully worked).

Quantity used: 2.0 tonne

Observations

- The trial run was smooth. There was no major interruption in plant running and desired parameters were maintained.
- Before conducting the trial average final pulp brightness, whiteness and ODL pulp kappa number were 84.7%, 71.7 and 11.8, respectively.
- With the addition of magnesium hydroxide in oxygen bleaching stage, kappa reduction during oxygen bleaching stage was significantly improved by 9-10%. (Please refer Figure 6.7.1 and Table 6.7.1).
- During trial average final pulp brightness obtained was 85.3% indicating the brightness improvement by about 0.6 points. During trial average ODL and D0 stage pulp brightness were improved by 2.1 and 3.5 units, respectively compared to control. (Please refer Figure 6.7.2 and Figure 6.7.3).
- During trial average final pulp whiteness obtained was 74.1 at a dose level of 2.0 kg/TP indicating the whiteness improvement by 2.4 units. (Please refer Figure 6.7.4).
- As expected viscosity of the pulp after oxygen bleaching stage were improved by 0.7 to 0.9 cP, showing the improvement in selectivity during oxygen bleaching stage (Please refer Figure 6.7.5).
- Cellulose and hemicelluloses content in the ODL and final bleached pulp was improved marginally with the use of magnesium hydroxide also showing the improvement in selectivity during oxygen bleaching stage (Please refer Table 6.7.4).
- Physical strength properties of the unrefined and refined ODL and final bleached pulp were improved marginally with the use of magnesium hydroxide (Please refer Table 6.7.5 and Table 6.7.6).
- With the addition of magnesium hydroxide in oxygen bleaching stage there was reduction in bleaching chemicals. A reduction of about 2.0 kg/TP in chlorine dioxide, 0.7 kg/TP in hydrogen peroxide and 1.8 kg/TP in caustic consumption was obtained during trial. (Please refer Table 6.7.1).
- No noticeable difference was observed in results of Bauer McNett classification of final bleached pulps (Please refer Table 6.7.3).

- There was marginal improvement in the morphological properties and other pulp properties with the use of magnesium hydroxide in oxygen bleaching stage. (Please refer Table 6.7.2 and Annexure 1).
- With the use of magnesium hydroxide in oxygen bleaching stage, magnesium content in oxygen bleaching stage pulp, bleached pulp was increased by 18-23%, whereas in WBL it was increased by 6% only showing that maximum portion of magnesium was retained along with the pulp. Magnesium content in the dregs was increased by 24% showing that most of the magnesium which came to the recovery cycle with the black liquor gets removed along with the dregs (Please refer Figure 6.7.6).
- No noticeable difference was observed in results of other metal ions in pulp and recovery cycle before and during the trial (Please refer Figure 6.7.7-9).

Tables and figures

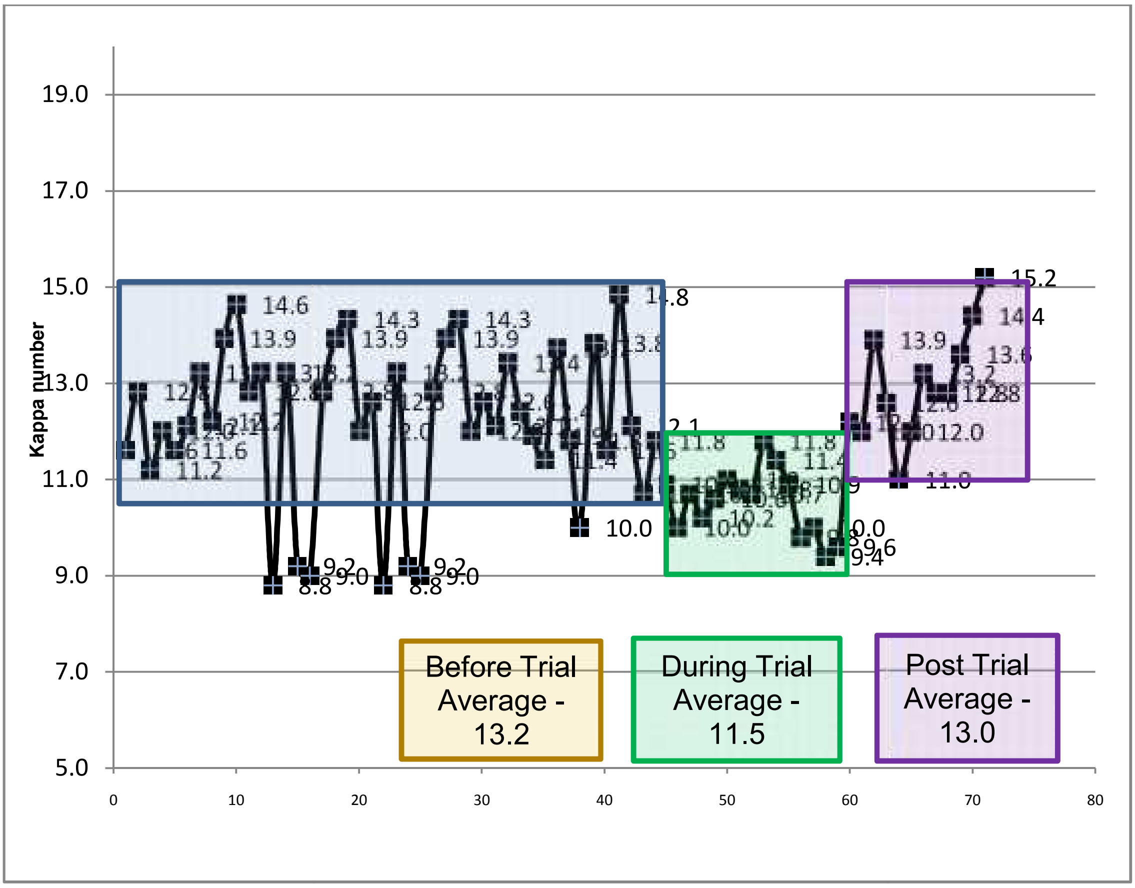


Figure 6.7.1: Effect of $Mg(OH)_2$ on ODL pulp kappa number

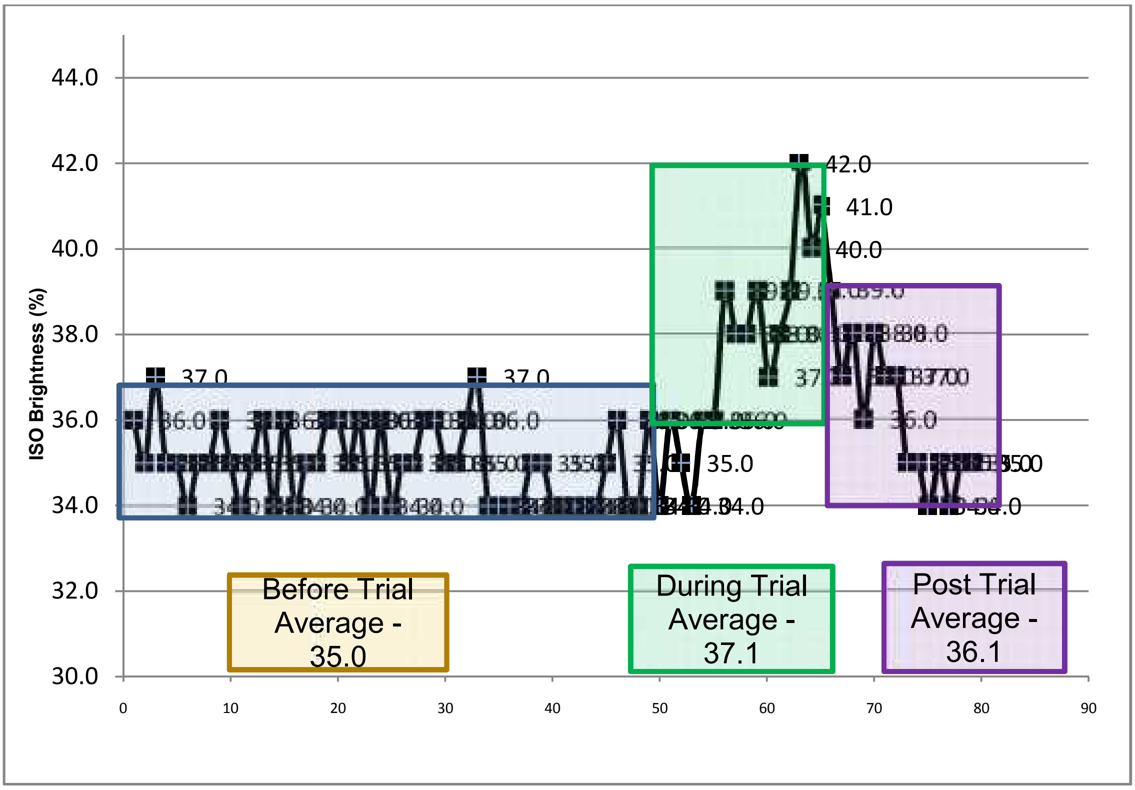


Figure 6.7.2: Effect of $Mg(OH)_2$ on ODL pulp brightness

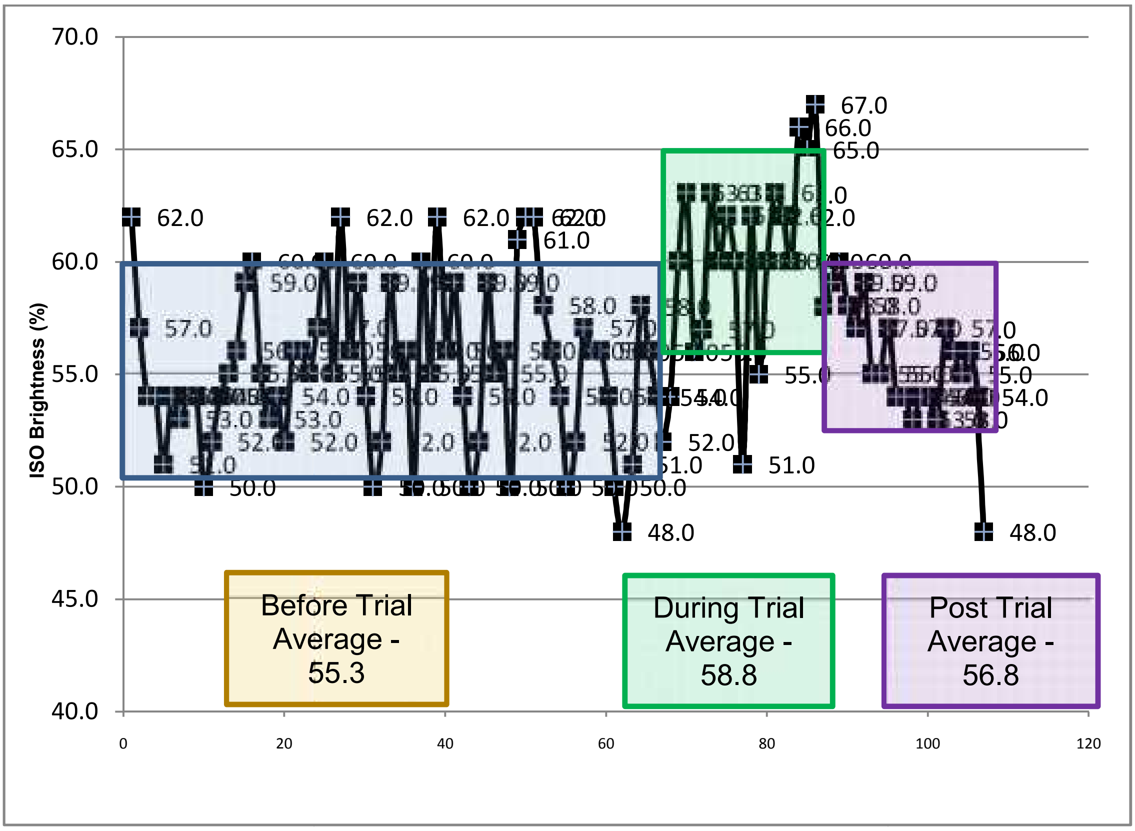


Figure 6.7.3: Effect of using $Mg(OH)_2$ in ODL stage on D_0 pulp brightness

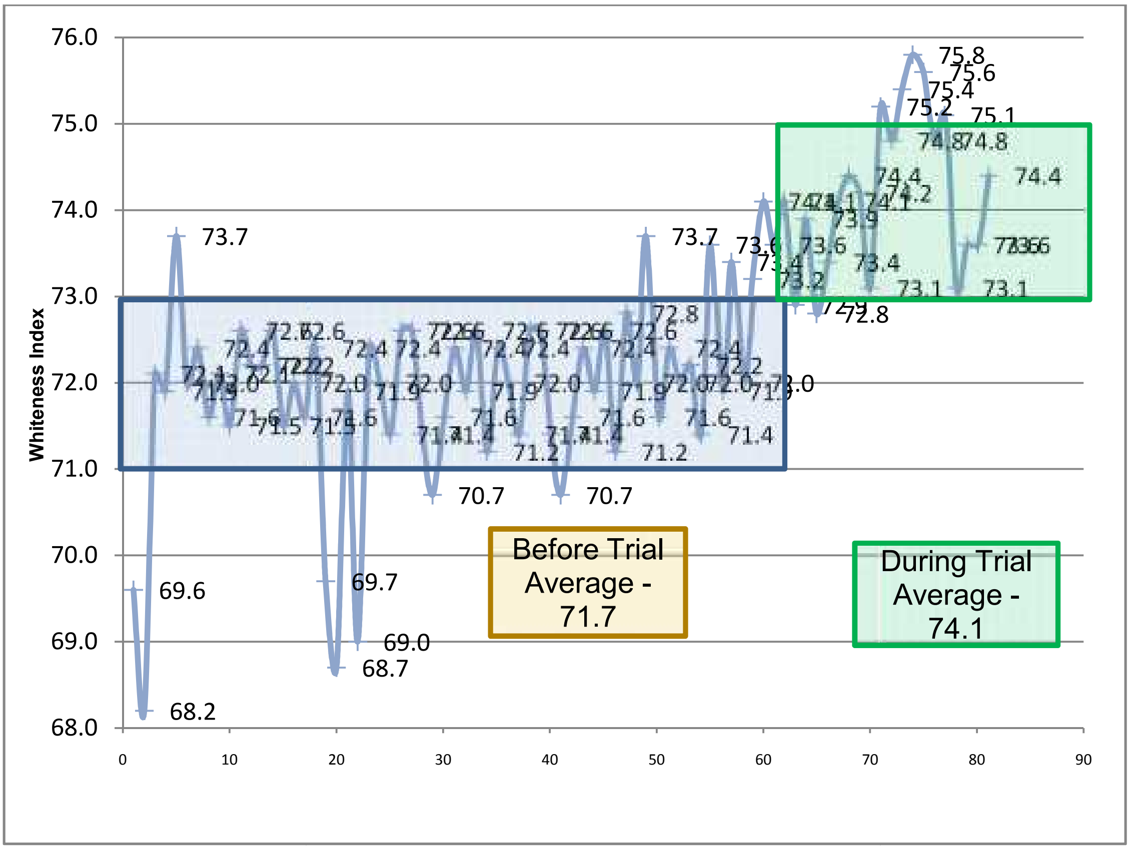


Figure 6.7.4: Effect of using $Mg(OH)_2$ in ODL stage on D_1 pulp whiteness

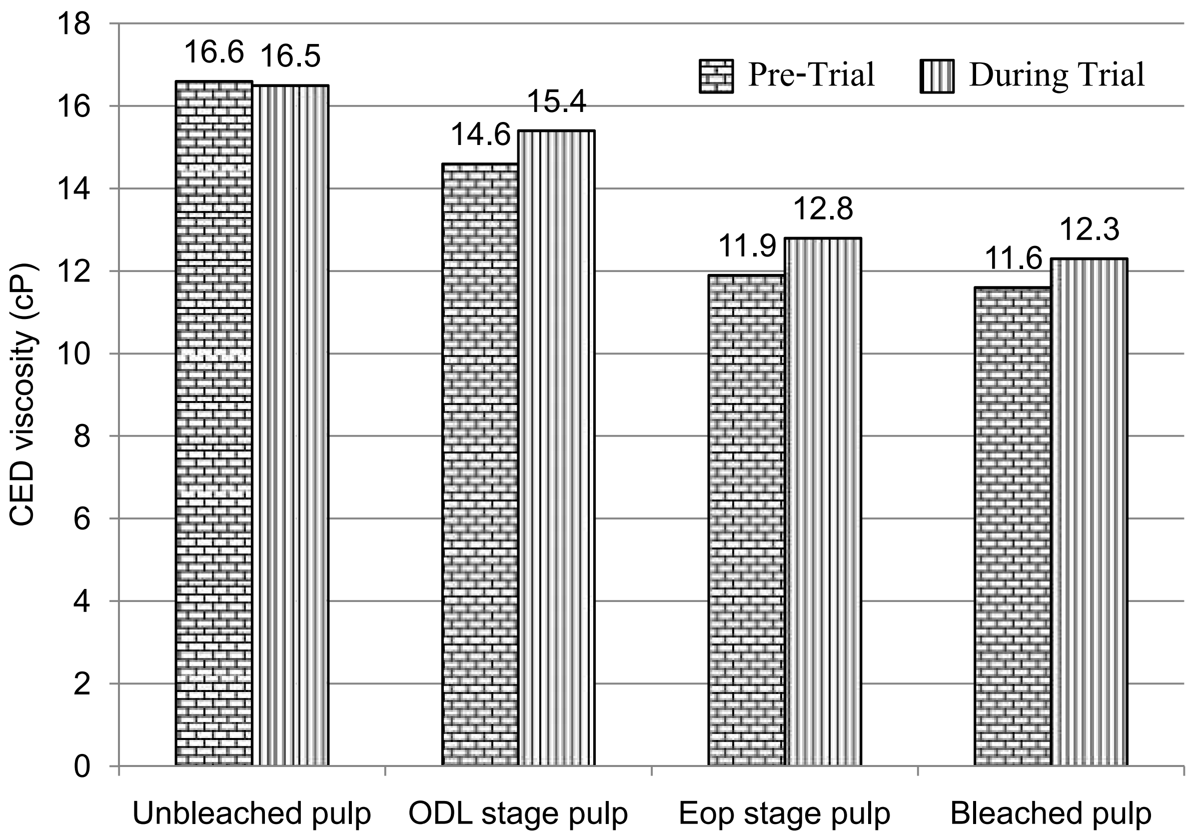


Figure 6.7.5: Effect of using $Mg(OH)_2$ in ODL stage on viscosity of pulps

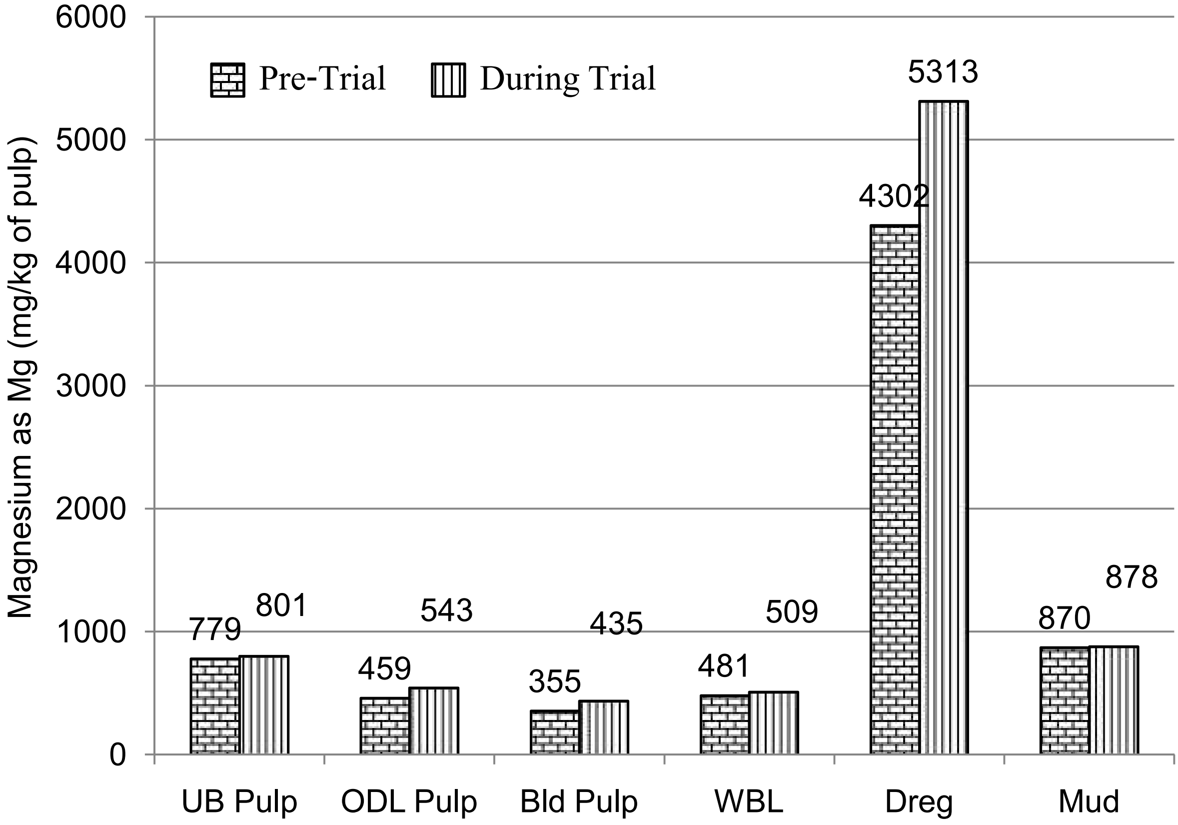


Figure 6.7.6: Magnesium content in pulp and recovery cycle before and during trial

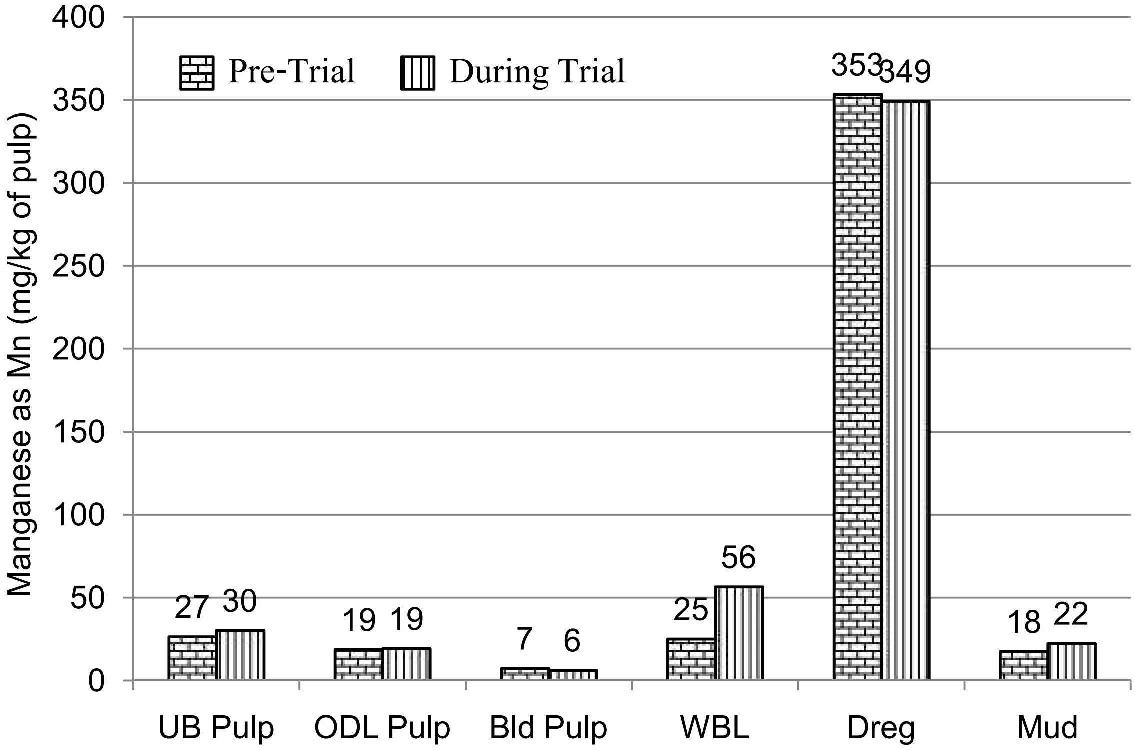


Figure 6.7.7: Manganese content in pulp and recovery cycle before and during trial

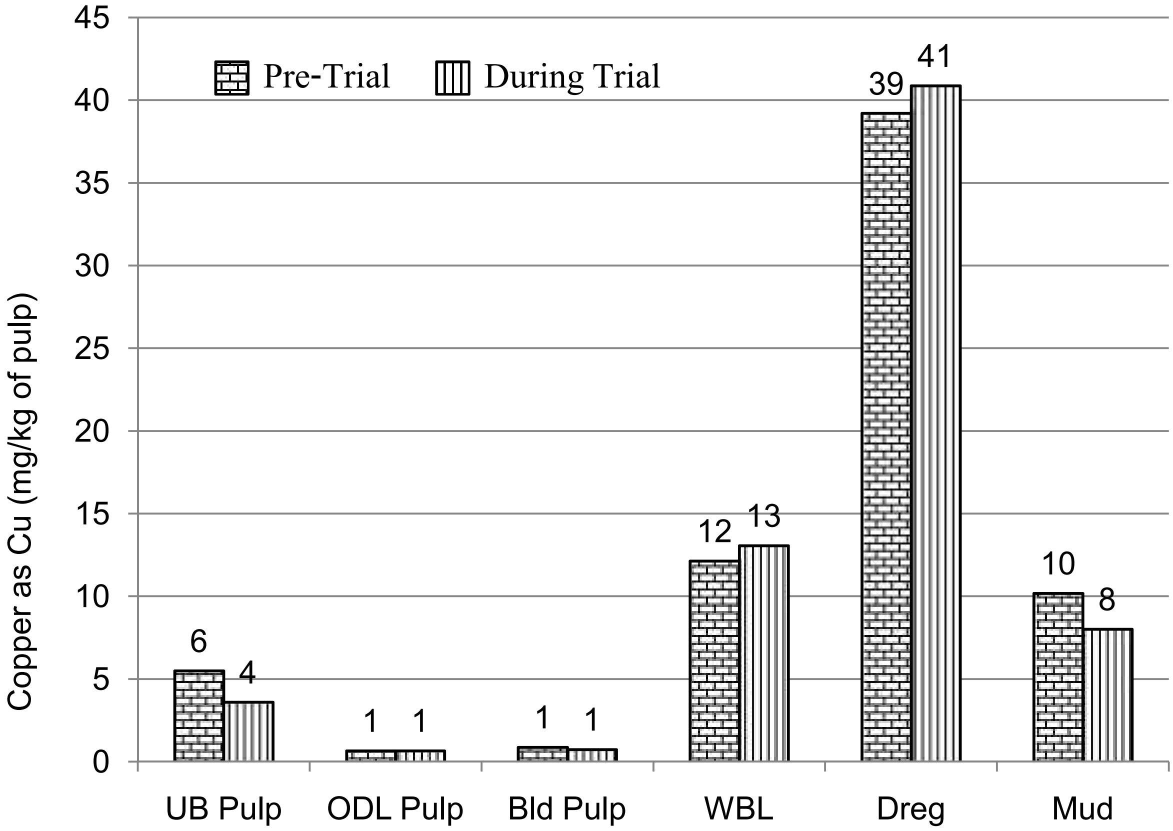


Figure 6.7.8: Copper content in pulp and recovery cycle before and during trial

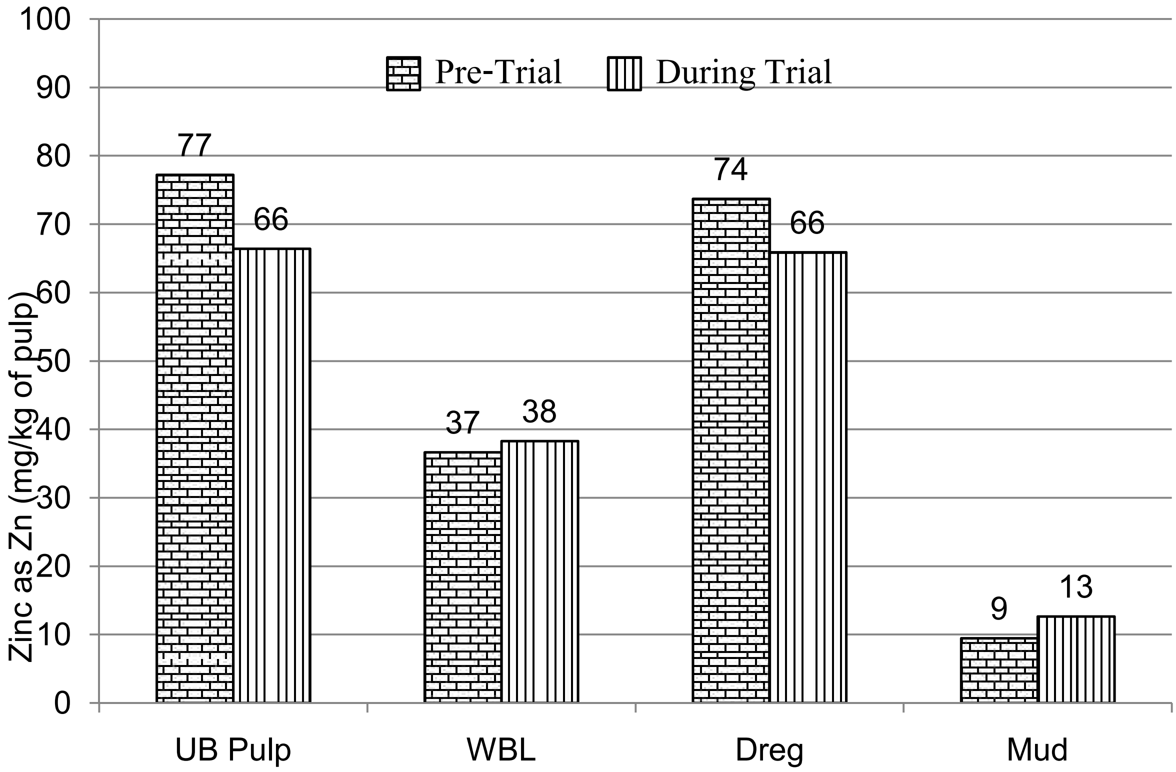


Figure 6.7.9: Zinc content in pulp and recovery cycle before and during trial

Table 6.7.1: Effect of using $Mg(OH)_2$ in ODL stage on bleaching chemical consumption

Particulars	Kappa reduction in ODL (%)	ClO_2 (kg/TP)	H_2O_2 (kg/TP)	NaOH (kg/TP)
Average (Pre Trial)	26.5	27.5	13.9	18.9
Average (During trial)	35.5	25.5	13.2	17.1
Difference (kg/TP)		2.0	0.7	1.8
Difference (%)	9.0	-7%	-5%	-10%

Table 6.7.2: Effect of using $Mg(OH)_2$ in ODL stage on properties of pulp at different stages

Particulars	Kappa Number			Brightness (% ISO)				Final Pulp	
	P. out	W-3	PO-2	W-3	PO-2	D0	E_{OP}	Brightness (% ISO)	Whiteness Index
Average (Pre Trial)	16.0	15.6	11.8	27.9	35.0	55.3	74.9	84.8	71.7
Average (During trial)	17.5	17.0	10.6	28.3	37.1	58.8	77.6	85.3	74.1
Difference(%)	9%	9%	-10%	1%	6%	6%	4%	1%	3%
Difference (Unit)	1.5	1.4	-1.2	0.4	2.1	3.5	2.7	0.4	2.3

Table 6.7.3: Bauer McNett classification of final bleached pulps

Particulars	Pre-Trial	During Trial
+28	9.7	9.8
+48	32.6	32.9
+100	22.4	22.3
+200	17.7	17.5
-200	17.6	17.5

Table 6.7.4: Effect of using $Mg(OH)_2$ in ODL stage on carbohydrate content in pulp

Particulars	Cellulose (%)		Hemicelluloses (%)	
	Pre-Trial	During Trial	Pre-Trial	During Trial
Unbleached pulp	70.4	71.3	19.7	19.5
ODL stage pulp	72.9	73.6	18.5	18.6
Bleached pulp	78.9	79.5	17.5	17.6

Table 6.7.5: Effect of using $Mg(OH)_2$ in ODL stage on physical strength properties of pulps (Unrefined)

Particulars	Unbleached		ODL		Bleached	
	Before trial	During trial	Before trial	During trial	Before trial	During trial
^{O}SR	16.5	17	15.5	15.5	15.5	15.5
Grammage (g/m^2)	61.49	62.3	61.57	61.03	62.63	61.1
Bulk (cc/g)	2.26	2.25	2.23	2.24	2.21	2.21
Tensile index (N.m/g)	23.0	25.0	14.1	14.3	10.3	10.7
Burst index (kN/g)	1.1	1.12	1.16	1.17	1.31	1.23
Tear index ($mN.m^2/g$)	3.7	4.0	2.2	2.3	1.79	1.91
Double fold (no.)	2	2	1	1	1	1

Table 6.7.6: Effect of using $Mg(OH)_2$ in ODL stage on physical strength properties of pulps (Refined)

Particulars	Unbleached		ODL		Bleached	
	Before trial	During trial	Before trial	During trial	Before trial	During trial
PFI revolutions (no.)	5000	5000	5700	5700	6000	6000
^{O}SR	34	34	35.5	35.5	35.5	35
Grammage (g/m^2)	59.61	58.7	62.5	61.76	63.37	62.95
Bulk (cc/g)	1.51	1.52	1.49	1.48	1.45	1.46
Tensile index (N.m/g)	50.9	52.5	46.9	48.1	44.7	45.7
Burst index (kN/g)	3.72	3.9	3.34	3.39	3.72	3.54
Tear index (mN m^2/g)	8.8	8.99	8.05	8.15	7.73	7.81
Double fold (no.)	28	32	24	26	23	25

Annexure 1

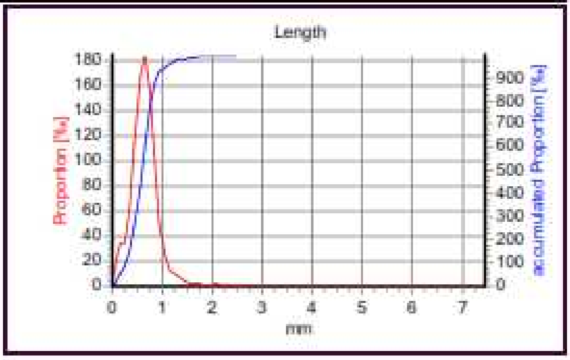
Lorentzen & Wettre

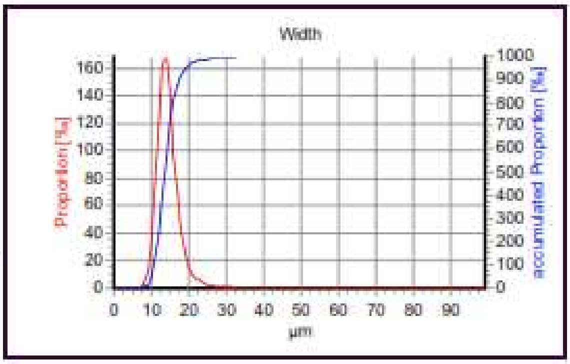
Sample name:	Before Trial	Number of fibers	15700 (20261)
Sample type:	Default	Number of images	1076
Time:	14-12-2016 16:28:26	Temperature	22.1 °C
Comment	Plant Trial in SPB		

Length weighted

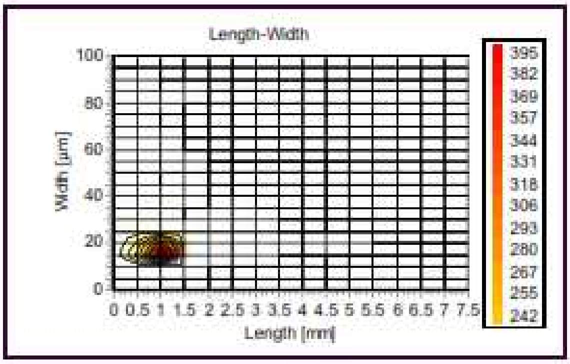
Variable	Value	Difference
Mean length	0.690 mm	0.009 mm
Mean width	15.0 µm	0.1 µm
Mean shape	90.1 %	-0.2 %

Length class	Proportion	Width	Shape
0.2-0.5 mm	0.219	15.3 µm	92.5 %
0.5-1.5 mm	0.762	14.9 µm	89.7 %
1.5-3 mm	0.017	17.7 µm	76.5 %
3-4.5 mm	0.001	17.2 µm	72.5 %
4.5-7.5 mm	0.000	16.5 µm	63.8 %





Variable	Weighting	Value
Length	Length	0.690 mm
Length	Volume	0.705 mm
Length	Arithmetic	0.595 mm
Length	Length-Length	0.831 mm
Width	Length	15.0 µm



Sample name:	Before Trial	Number of fibers	15700 (20261)
Sample type:	Default	Number of images	1076
Time:	14-12-2016 16:28:26	Temperature	22.1 °C
Comment	Plant Trial in SPB		

Variable	Value	Variable	Value
Number of objects measured	179	Number of objects in DB	179
Number of Objects in sample	6602	Number of object images	3732
Objects per 100000 fibers	269	Mean Object length	0.3242 mm
Object per gram	66020 g-1	Mean Object width	0.1506 mm
Object area/Fibre volume	0.943 mm-1		
Mean Object area	0.0493 mm2		

Proportion area weighted (%)

Width (µm) \ Length(mm)	0.10-0.20	0.20-0.30	0.30-1.00
100-120	1.2	4.8	5.2
120-150	1.6	9.3	19.7
150-1000	1.3	14.2	42.6

Number of Objects in sample

Width (µm) \ Length(mm)	0.10-0.20	0.20-0.30	0.30-1.00
100-120	184	553	369
120-150	221	885	1254
150-1000	148	996	1992

Sample name:	Before Trial			Number of fibers	15700 (20261)
Sample type:	Default			Number of images	1076
Time:	14-12-2016 16:28:26			Temperature	22.1 °C
Comment	Plant Trial in SPB				

Variable	Weighting	Value
Width	Width	16.0 µm
Width	Area	15.9 µm
Width	Volume	17.9 µm
Width	Arithmetic	15.0 µm
Width	Length-Length	15.2 µm
Shape	Length	90.1 %
Shape	Width	90.8 %
Shape	Area	89.8 %
Shape	Length-Length	88.6 %
Fines	Length	5.4 %
Fines	Width	29.8 %
Fines	Area	5.7 %
Fines	Arithmetic	29.1 %
Fines	Length-Length	1.0 %
Number of fibers		15700 (20261)
Number of images		1076

Variable	Weighting	Value
Temperature		22.1 °C
Sample weight		0.100 g
Coarseness adjust		1.000
Coarseness		54.7 µg/m
No. fibers in sample		2454659
Mean kink angle		44.4 °
Number of kinks per mm		0.710 mm-1
Number of large kinks per mm		0.143 mm-1
Number of kinks per fibre		0.453
Number of large kinks per fibre		0.091
Mean kink index		1.672
Mean segment length		0.529 mm
-	-	-
-	-	-
-	-	-
-	-	-

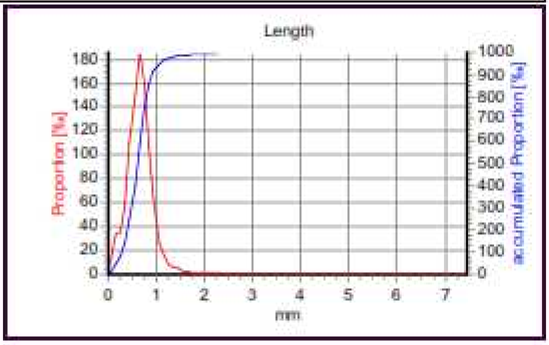
Lorentzen & Wettre

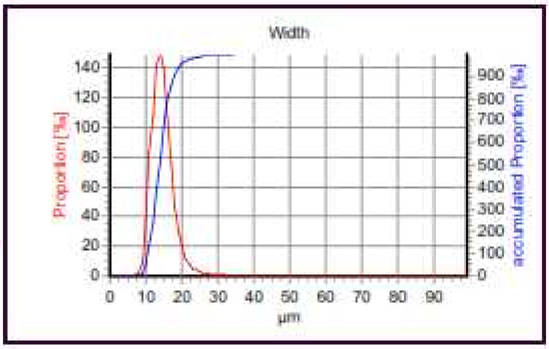
Sample name:	During trial	Number of fibers	15881 (20166)
Sample type:	Default	Number of images	1165
Time:	14-12-2016 14:45:39	Temperature	19.8 °C
Comment	Plant trial in SBP		

Length weighted

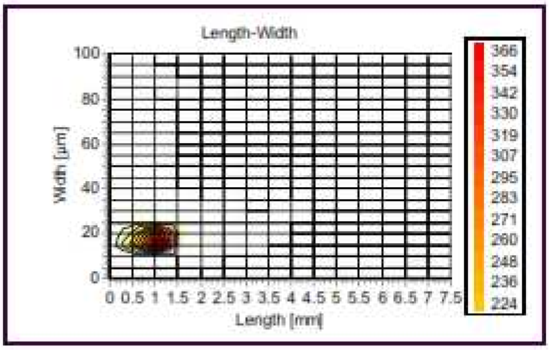
Variable	Value	Difference
Mean length	0.697 mm	0.001 mm
Mean width	15.2 µm	-0.1 µm
Mean shape	88.5 %	-0.2 %

Length class	Proportion	Width	Shape
0.2-0.5 mm	0.213	15.3 µm	90.8 %
0.5-1.5 mm	0.770	15.1 µm	88.3 %
1.5-3 mm	0.016	17.8 µm	71.5 %
3-4.5 mm	0.001	22.3 µm	67.0 %
4.5-7.5 mm	0.000	0.0 µm	0.0 %





Variable	Weighting	Value
Length	Length	0.697 mm
Length	Volume	0.711 mm
Length	Arithmetic	0.603 mm
Length	Length-Length	0.817 mm
Width	Length	15.2 µm



Sample name:	During trial	Number of fibers	15881 (20166)
Sample type:	Default	Number of images	1165
Time:	14-12-2016 14:45:39	Temperature	19.8 °C
Comment	Plant trial in SBP		

Variable	Weighting	Value
Width	Width	16.4 µm
Width	Area	16.2 µm
Width	Volume	18.8 µm
Width	Arithmetic	15.2 µm
Width	Length-Length	15.4 µm
Shape	Length	88.5 %
Shape	Width	89.3 %
Shape	Area	88.4 %
Shape	Length-Length	87.1 %
Fines	Length	5.1 %
Fines	Width	27.7 %
Fines	Area	5.3 %
Fines	Arithmetic	27.0 %
Fines	Length-Length	0.9 %
Number of fibers		15881 (20166)
Number of images		1165

Variable	Weighting	Value
Temperature		19.8 °C
Sample weight		0.100 g
Coarseness adjust		1.000
Coarseness		59.9 µg/m
No. fibers in sample		2239852
Mean kink angle		48.9 °
Number of kinks per mm		0.818 mm-1
Number of large kinks per mm		0.219 mm-1
Number of kinks per fibre		0.531
Number of large kinks per fibre		0.142
Mean kink index		2.013
Mean segment length		0.514 mm
-	-	-
-	-	-
-	-	-
-	-	-

Sample name:	During trial	Number of fibers	15881 (20166)
Sample type:	Default	Number of images	1165
Time:	14-12-2016 14:45:39	Temperature	19.8 °C
Comment	Plant trial in SBP		

Variable	Value	Variable	Value
Number of objects measured	155	Number of objects in DB	155
Number of Objects in sample	5883	Number of object images	3634
Objects per 100000 fibers	263	Mean Object length	0.3221 mm
Object per gram	58827 g-1	Mean Object width	0.1514 mm
Object area/Fibre volume	0.879 mm-1		
Mean Object area	0.0494 mm2		

Proportion area weighted (%)

Width (µm) \ Length(mm)	0.10-0.20	0.20-0.30	0.30-1.00
100-120	0.6	5.6	7.3
120-150	1.8	8.8	18.6
150-1000	1.3	13.5	42.7

Number of Objects in sample

Width (µm) \ Length(mm)	0.10-0.20	0.20-0.30	0.30-1.00
100-120	76	607	493
120-150	228	759	1025
150-1000	114	835	1746

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7. SALIENT FINDINGS

7.1. Findings of laboratory scale studies

Laboratory scale studies carried out using different additives in oxygen bleaching stage conclude the following:

- Increase in alkali dose, temperature and oxygen pressure during oxygen bleaching improved the delignification but also increased the cellulose degradation.
- Magnesium hydroxide when used during oxygen bleaching showed the considerable improvement in reduction of kappa number of pulp, brightness, viscosity and pulp yield.
- With the use of magnesium hydroxide during oxygen bleaching stage brightness of pulp was improved by 7.0 points, reduction in kappa number improved by 5.2% and viscosity of pulp improved by 1.0 point compared to control pulp.
- Use of magnesium hydroxide during oxygen bleaching stage also improved the final pulp brightness, whiteness, pulp yield and viscosity by 0.9, 1.1, 0.6 and 1.2 units, respectively.
- DTPA showed the highest efficiency in terms of brightness development and reduction in kappa number of pulp amongst the different chelating agents used during the study. EDTA was found most effective in protecting cellulose degradation.
- Use of ETDA during oxygen bleaching improved pulp yield by 0.5%, viscosity of pulp by 0.8 units with reduced kappa number. Use of ETDA also improved the final pulp brightness by 0.8 units, bleached pulp yield by 0.3% with comparable pulp viscosity.
- None of the polymeric additive improved the reduction of kappa number or brightness of pulp. Native starch and CMC were found most effective in protecting cellulose degradation amongst the different polymeric additives used during the study.

$Mg(OH)_2$ and EDTA were found most suitable among various chemicals studied to improve selectivity of oxygen bleaching in lab scale studies carried out at ACIRD. It was proposed to explore suitability of any one chemical on plant scale.

7.2. Findings of plant scale studies

Plant scale study carried out with the addition of magnesium hydroxide in oxygen bleaching stage resulted in the following:

- With the addition of magnesium hydroxide in oxygen bleaching stage, kappa number reduction was improved by 9-10%.
- During trial average final pulp brightness was improved by about 0.6 points. Pulp brightness after oxygen bleaching stage and D_0 stage was improved by 2.1 and 3.5 units, respectively compared to control. Average final pulp whiteness was improvement by 2.4 units at $Mg(OH)_2$ dose level of 2.0 kg/TP.
- As expected viscosity of the pulp after oxygen bleaching stage was improved by 0.7 to 0.9 cP with the use of magnesium hydroxide. Cellulose and hemicelluloses content in the ODL and final bleached pulp were improved marginally with the use of magnesium hydroxide showing the improvement in selectivity during oxygen bleaching stage.
- Physical strength properties of the unrefined and refined oxygen bleaching stage and final bleached pulps were improved marginally with the use of magnesium hydroxide.
- With the addition of magnesium hydroxide in oxygen bleaching stage there was reduction in bleaching chemicals. A reduction of about 2.0 kg/TP in chlorine dioxide, 0.7 kg/TP in hydrogen peroxide and 1.8 kg/TP in caustic consumption was obtained during trial.
- With the use of magnesium hydroxide in oxygen bleaching stage, magnesium content in ODL stage pulp, bleached pulp was increased by 18-23%, whereas in WBL it was increased by 6% only showing that maximum portion of magnesium was retained along with the pulp. Magnesium content in the dregs was increased by 24% showing that most of the magnesium which came to the recovery cycle with the black liquor got removed along with the dregs.

8. ACKNOWLEDGEMENT

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9. REFERENCES

- Barrau D.C. and Lachenal D., (2001) “Action of oxygen on the carbohydrates of a kraft pulp: The influence of a sodium borohydried pretreatment”. Journal of Wood Chemistry and Technology, 21(2): 169-179.
- Cao S., Zhan H., Fu S., Chen L., (2007) “Regulation of superoxide anion radical during the oxygen delignification process”. Chin. J. Chem. Eng., 15(1): 132-137.
- Chen S.L. and Lucia L.A., (2002) “Fundamental of insight into mechanism of oxygen delignification of kraft pulp: The influence of novel carbohydrate protective system”. Cellulose Chemistry and Technology, 36: 339-351.
- Dan G. and Adrian C.P., (2015) “Bleaching of softwood kraft pulp with oxygen and peroxide”. Cellulose Chemistry and Technology, 49(3-4): 341-346.
- Evtuguin D.V. and Neto C.P., (1997) “New polyoxometalate promoted method of oxygen delignification”. Holzforschung, 51: 338-342.
- Fu S.Y., Singh J.M., Wang S.F., Lucia L.A., (2005) “Investigation of chemistry of oxygen delignification of low kappa softwood kraft pulp using an organic inorganic chemical selectivity system”. Journal of Wood Chemistry and Technology, 25(3): 95-108.
- Gaspar A.R., Gamelas J.A.F., Evtuguin D.V., Neto C.P., (2007) “Alternatives for lignocellulosic pulp delignification using polyoxometalates and oxygen: a review”. Green Chem., 9: 717-730.
- Gaspar A.R., Gamelas J.A.F., Evtuguin D.V., Neto C.P., (2009) “Polyoxometalatecatalyzed oxygen delignification process: kinetic studies, delignification sequences and reuse of HPA-5-MnII aqueous solution”. Chem. Eng. Commun., 196: 801-811.
- Gilbert A. F., Pavlovova E., Rapson W.H., (1973). “Machanism of magnesium retardation of cellulose degradation during oxygen bleaching”. Tappi J. 56(6): 95-99.
- Guay D., Cole B.W., Fort Jr. R.C., Genco J.M., Hausman M.C., (1999) “Mechanisms of oxidative degradation of carbohydrates during oxygen

delignification". International symposium on wood and pulping chemistry (ISWPC), held at Yokohama.

- Harrison R., Parrish T., Gibson A., Knapp C., Wajer M., Johnson D., (2008) "Refiner bleaching with magnesium hydroxide and hydrogen peroxide". Tappi Journal, 7(9), 16-20.
- Hsu C.L., Hsieh J.S. (1987) "Oxygen bleaching kinetics at ultra-low consistencies". TAPPI Journal, 70(12): 107-112.
- Ira A.W., Kenneth E.H., Mark A.M., Lawrence L.L., Sally R., Cindy E.S. Richard S.R., (1998) "Selective transition-metal catalysis of oxygen delignification using water-soluble salts of polyoxometalate (POM) anions, Part II. Reactions of α-[SiVW11O40] 5-with Phenolic Lignin-Model Compounds" Holzforschung, 52(3): 311-318.
- Irabarne J. and Schroeder L., (1997) "High Pressure Delignification of Kraft Pulps: Kinetics". Tappi Journal, 80(10), 241-249.
- Kontturi E., Mitikka-Eklund M., Vuorinen T., (2008) "Strength enhancement of a fiber network by carboxymethyl cellulose during oxygen delignification of kraft pulp". Bioresources, 3(1), 34-45.
- Liu Z., Cao Y. and Wu S., (2013) "Oxygen delignification of wheat straw soda pulp with anthraquinone addition". Bioresources, 8(1): 1306-1319.
- McDonough T.J., (1996) "Oxygen delignification. In: Pulp Bleaching: Principles and Practice". Eds. Dence, C.W., Reeve, D.W. TAPPI Press, Atlanta. 213-239.
- NG S. H., Ghazali a. and LEH C.P. (2011) "Anthraquinone-aided hydrogen peroxide reinforced oxygen delignification of oil palm (Elaeis guineensis) EFB pulp: A two-level factorial design". Cellulose Chem. Technol., 45(1-2): 77-87.
- Odermatt J. R., Kordsachia P. O., and Troughton N., (1994) "TCF Bleaching of Conventional and EMCC® Softwood Kraft Pulp". Tappi Pulp Bleaching Conference Proceedings, 77-85.
- Parthasarathy V.R., R. Klein V.S.M. Sundaram H. Jammel and Gratzl J.S., (1990) "Hydrogen-Peroxide-Reinforced Oxygen Delignification of Southern

Pine Kraft Pulp and Short Sequence Bleaching”. Tappi Journal, 73(7): 177-185.

- Perng Y.S., Oloman C.W., Watson P.A. and James B.R. (1994) “Catalytic Oxygen Bleaching of Wood Pulp with Metal Porphyrin and Phthalocyanine Complexes”. Tappi Journal, 77(11): 119-125.
- Pesman E., Kalyancu E.E. and Kirci H., (2010) “Sodium perborate usage instead of hydrogen peroxide for reinforcement of oxygen delignification”. Fibers & Textiles in Eastern Europe, 18(83): 106-109.
- Robert A., Viallet A., (1971) “Degradation of polysaccharides by oxygen in the presence of alkali: protective action of magnesium salts and of silicates”. ATIP Rev. 25: 237-241.
- Sahu S.K., Pradhan S.K., Panigrahi J.C., and Dev U.K., (2008) “Additives for increased lignin removal efficiency in oxygen delignification”. IPPTA Journal, 20(2): 77-80.
- Samuelson O., and Otjeg U., (1996) “Oxygen bleaching of kraft pulps pretreated with nitrogen oxides”. Cellulose Chemistry and Technology, 30: 95-104.
- Sjostrom E., (1981) “Wood chemistry: Fundamental and applications”. Academic Press, Newyork Press, 169-189.
- Solinas M., Proust, A.M., (1997) “Oxygen bleaching process for cellulosic pulps with a polyhydric alcohol cellulose protector”. US Patent 5,609,723.
- Ni Y.H., Sommerville J., Heiningen, A. R. P. (2001). “Bleaching of recycled fibers by adding sodium borohydride to a peroxide reinforced oxygen stage”. TAPPI J., 84(6): 67.
- Suchy M. and Argyropoulos D.S., (2002) “Catalysis and activation of oxygen and peroxide delignification of chemical pulps: a review”. Tappi Journal 1(2): 1-18.
- Tao Li, Genco J.M., Cole B.J.W. and Fort R.C., J.R., (2011) “Selectivity of oxygen delignification for southern softwood kraft pulp with high lignin content”, Tappi Journal 10 (8): 29-38.

- Tikka P., Sundquist J. (2001). “Softwood fiber damage. Proceedings of 2001 pulping conference, Seattle, WA, USA, Session 12:10.
- Vaino Sippola (2006) “Transition metal-catalysed oxidation of lignin Model compounds for oxygen delignification of pulp”. Thesis, Industrial Chemistry Publication Series, Helsinki University of Technology.
- Van Tran A., (2000) “Utilization of additives in oxygen delignification of hardwood kraft pulp”. Appita Journal, 53(4): 300-304.
- Violette S and Heiningen A.V., (2003) “Oxygen delignification kinetics and selectivity improvement”. Ph. D. Thesis, University of Maine.
- Weinstock I.A., Atalla R.H., Reiner R.S., Moen M.A., Hammel K.E., Houtman C.J., Hill C.L., Harrup M.K., (1997) “A new environmentally benign technology for transforming wood pulp into paper. Engineering polyoxometalates as catalysts for multiple processes”. J. Mol. Catal. A Chem. 116: 59-84.