

Project Details

Project Title	Improvement in selectivity of oxygen bleaching
Project Executed by	
Participating Agency	Seshasayee Paper and Boards Ltd., Erode, Tamilnadu Avantha Centre for Industrial R & D (ACIRD), Yamuna Nagar (Haryana) Central Pulp & Paper Research Institute (CPPRI), Saharanpur (UP)
Project Duration , Months	2 years
Date of Start	August, 2014
Date of Completion	March, 2017
Project Cost, Rs Lacs	62.36 (ACIRD - 27.0, CPPRI - 27.00, SPB – 8.36)
Funds Released	62.36
Balance Funds to be Released	Nil

Objectives

- To find out the 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

Work Progress (Summary)

Sl. No	Activities as per Work Plan	Status
1.	Literature survey	Completed
2.	Fabrication of oxygen bleaching reactor for laboratory scale bleaching	Completed
3.	Study on oxygen delignification of pulps by varying process conditions in single as well as two stages	Completed
4.	Oxygen delignification of pulp with different carbohydrate protectors to improve pulp yield, viscosity and physical strength properties	Completed
5.	Oxygen delignification of pulp with different polymeric additives to improve pulp yield, viscosity and physical strength properties	Completed
6.	Validation of the results obtained with selected additive/chemical	Completed
7.	Plant scale study with selected additive	Completed
8.	Preparation of report	Completed and submitted

Results

ODL reactor fabricated at ACIRD



Effect of process conditions on oxygen bleaching

Effect of sodium hydroxide dose

Particulars	Results					
Kappa no.	23.4					
Brightness (%)	26.2					
Viscosity (cP)	11.6					
Oxygen delignification (<i>Consistency - 10%, Temperature - 80/100 °C, Time - 90 min, Oxygen - 1.8%</i>)						
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 number	14.6	13.1	12.4	11.4	11.0	10.3
Brightness (%)	44.6	46.9	47.8	49.4	49.9	50.5
Viscosity (cP)	9.4	9.1	8.9	8.6	8.5	8.4

Effect of process conditions on oxygen bleaching

Effect of temperature

Particulars	Results		
Kappa no.	23.4		
Brightness (%)	26.2		
Viscosity (cP)	11.6		
Oxygen delignification (Consistency - 10%, NaOH - 2.3%, Time - 90 min, Oxygen - 1.8%)			
Temp. (°C)	65/100	80/100	80/110
pH	11.1	10.6	10.3
Kappa number	13.4	12.1	11.1
Brightness (%)	46.8	49.1	53.5
Viscosity (cP)	9.9	8.8	8.0

Effect of process conditions on oxygen bleaching

Effect of COD carryover

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
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

Effect of additives on ODL stage pulp properties

Following additives were studied in oxygen delignification stage as carbohydrate protectors :

Chemical additives:

- | | | |
|----------------------------|---------------------------------|-----------------------|
| (1) EDTA, | (2) MgSO_4 | (3) DTPA, |
| (4) H_2O_2 | (5) $\text{DTPA-H}_2\text{O}_2$ | (6) Mg(OH)_2 |
| (7) Anthraquinone, | (8) NaBH_4 , | (9) DTMPA |
| (10) Borax, | (11) Thiourea, | (12) Urea |
| (13) Sodium perborate | (14) Boric acid, | (15) Sodium gluconate |
| (16) Ethylene glycol | | |

Polymeric additives:

- | | | |
|---------------------|-------------------|---------|
| (1) Cationic starch | (2) native starch | (3) CMC |
| (4) Guar gum | | |

Effect of additives on ODL stage pulp properties

Parameter	Control	EDTA (0.1%)	DTPA (0.1%)	Mg(OH) ₂ (0.2%)	H ₂ O ₂ + DTPA (0.6+0.05%)
ODL stage <i>(Temp. - 95/100°C, Time - 30/90 min., O₂ pressure - 5.0/4.5 kg/cm², NaOH - 2.0% , Cy – 10%)</i>					
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

Initial brightness of pulp: 30% ISO, Kappa no.: 18.9, Viscosity: 14.1 cP

Effect of additives in ODL stage on BL properties

Parameter	Control	EDTA (0.1%)	DTPA (0.1%)	Mg(OH) ₂ (0.2%)	H ₂ O ₂ + DTPA (0.6+0.05%)
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

Effect of additives in ODL stage on bleaching

Particular	Control	EDTA (0.1%)	DTPA (0.1%)	Mg(OH) ₂ (0.2%)	H ₂ O ₂ + DTPA (0.6+0.05%)
Kappa No	10.7	10.4	10.7	9.8	9.7
D₀ stage (<i>Temp. - 60 °C, Time - 45 min, Kappa factor - 0.25</i>)					
ClO ₂ added (%)	1.02	0.99	1.02	0.93	0.92
Residual ClO ₂ (ppm)	60.7	64.4	60.7	118	134.8
E_{OP} stage (<i>Temp. – 80°C, Time – 120 min, H₂O₂ - 0.6%</i>)					
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

Effect of additives in ODL stage on bleaching

Particular	Control	EDTA (0.1%)	DTPA (0.1%)	Mg(OH) ₂ (0.2%)	H ₂ O ₂ + DTPA (0.6+0.05%)
D stage (<i>Temp. – 75 °C, time – 180 min, ClO₂ – 1.0%</i>)					
Final pH	3.5	3.5	3.6	3.5	3.6
Residual ClO ₂ (ppm)	26.9	30.4	26.9	33.8	35.4
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
Shrinkage (%)	4.7	4.6	4.6	4.5	4.6
Bleached yield (%)	43.4	43.7	43.7	44.0	43.5
Viscosity (cp)	8.7	9.0	8.8	9.9	8.8

Effect of additives in ODL stage on paper strength

Parameter	Control		EDTA (0.1%)		DTPA (0.1%)	
Revolutions	1800	2400	1800	2400	1800	2400
°SR	28.5	31	28	31.5	28.5	31.5
Grammage (g/m ²)	68.4	73.3	72.7	71.5	71.6	73.3
Bulk (cc/g)	1.44	1.38	1.43	1.37	1.43	1.38
Tensile index (Nm/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

Effect of additives in ODL stage on paper strength

Parameter	Control		Mg(OH) ₂ (0.2%)		H ₂ O ₂ + DTPA (0.6+0.05%)	
Revolutions	1800	2400	1800	2400	1800	2400
°SR	28.5	31	29	31.5	29	32
Grammage (g/m ²)	68.4	73.3	72.6	70.7	69.4	71.8
Bulk (cc/g)	1.44	1.38	1.42	1.38	1.41	1.36
Tensile index (Nm/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

Effect of additives in ODL stage on effluent

Parameter	Control	EDTA (0.1%)	DTPA (0.1%)	Mg(OH) ₂ (0.2%)	H ₂ O ₂ + DTPA (0.6+0.05%)
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

Oxygen delignification of mill pulp with and without additives

Parameters	Control	Mg(OH) ₂	EDTA
Initial kappa No.	21.9		
Brightness (%ISO)	26.9		
Viscosity (cP)	16.9		
ODL Stage (Temp. - 85°C, Time - 90 min., O ₂ pressure - 5.0 kg/cm ² , NaOH - 2.1% , Cy – 10%)			
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
Pulp shrinkage (%)	2.4	1.5	2.1

Effect of additives in ODL on bleaching of mill pulp

Particulars	Control	Mg(OH) ₂	EDTA
Kappa no.	13.6	13.0	13.4
D₀ Stage (<i>Temp. - 65°C, Time - 60 min., Cy - 10%</i>)			
ClO ₂ added (%)	1.40	1.33	1.38
End pH	2.35	2.40	2.42
E_{OP} Stage (<i>Temp. - 80°C, Time - 90 min., Cy - 10%, H₂O₂ – 0.6%, NaOH – 2.0%</i>)			
Final pH	11.2	11.2	11.3
Brightness (%ISO)	79.0	79.8	79.4
E _{OP} Kappa number	1.7	1.5	1.6
D Stage (<i>Temp. - 65°C, Time - 120 min., Cy - 10%, ClO₂ added - 0.6%</i>)			
Final pH	3.8	3.6	3.5
Residual ClO ₂ (ppm)	81.0	108.0	91.8
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

Physical strength properties of bleached pulps

Parameters	Control	Mg(OH) ₂	EDTA
PFI revolutions (nos.)	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 (Nm/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

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

Effect of selected additives in ODL stage

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

Effect of selected additives in ODL stage

Parameters	Control		Mg(OH) ₂ (0.2%)		H ₂ O 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

Effect of using additive on pulp bleaching

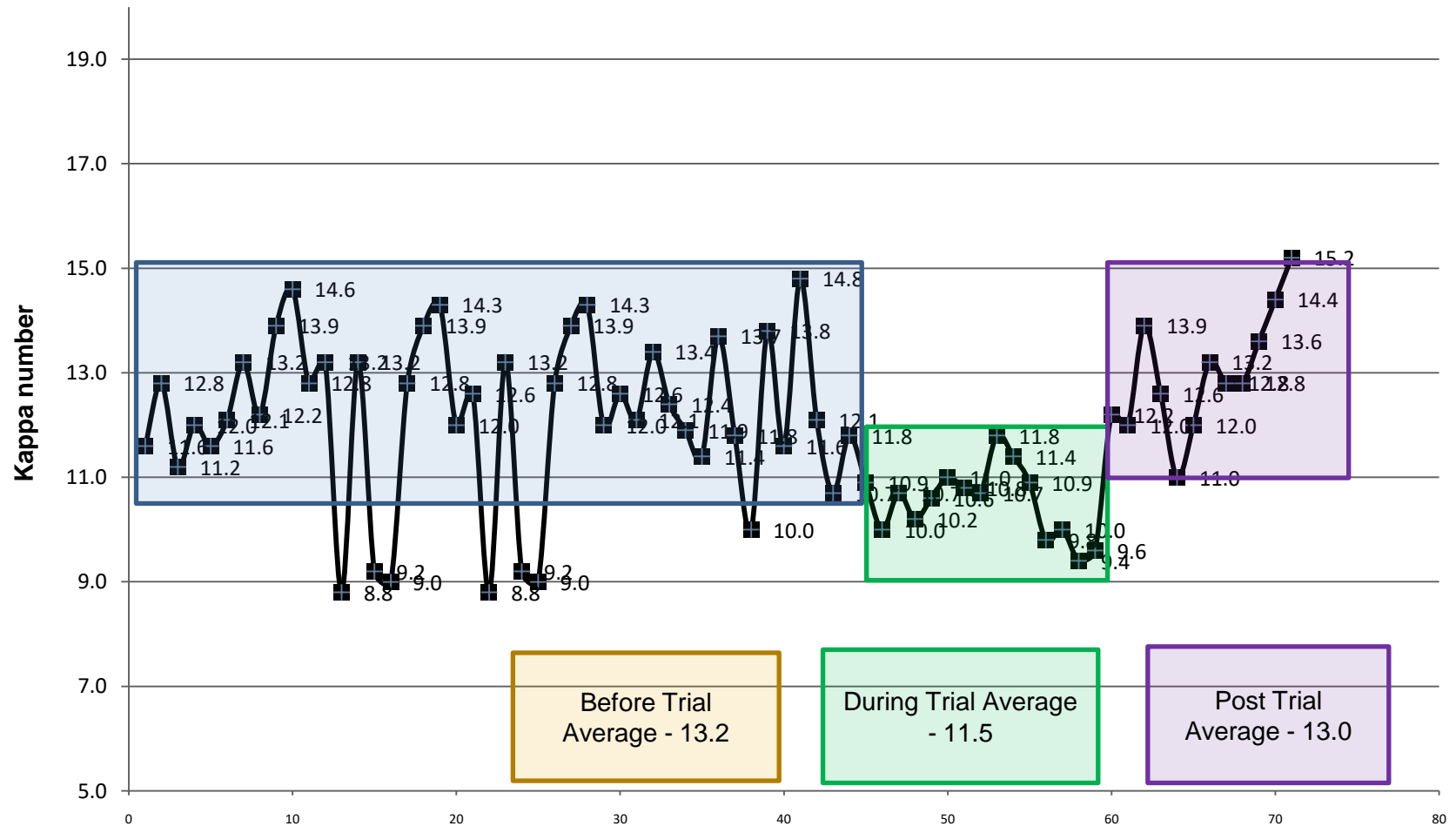
Particulars	Control		EDTA (0.1%)		DTPA (0.1%)	
	ACIRD	CPPRI	ACIRD	CPPRI	ACIRD	CPPRI
Kappa no.	10.7	11	10.4	10.8	10.7	10.7
Brightness (% ISO)	47.7	48	48.1	49	47.6	49.5
Viscosity (cP)	9.2	10.2	10.0	11	9.9	11.5
Bleached yield (%)	43.4	42.0	43.7	41.0	43.7	44.0
Brightness (% ISO)	87.7	87.0	88.5	88.2	88.0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

Effect of using additive on pulp bleaching

Particulars	Control		Mg(OH) ₂ (0.2%)		H ₂ O 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

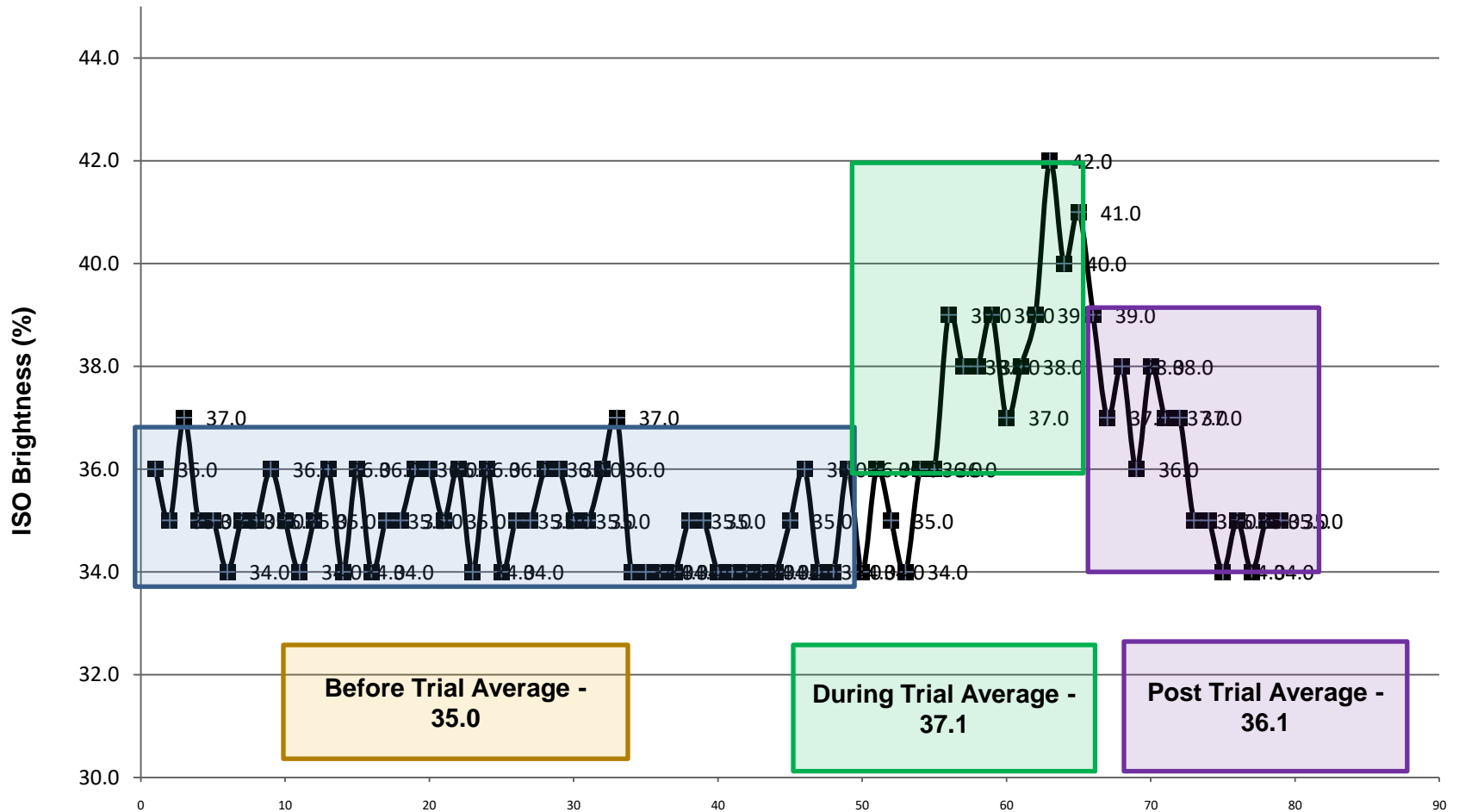
Plant scale trial results

Effect of $\text{Mg}(\text{OH})_2$ on ODL pulp kappa number



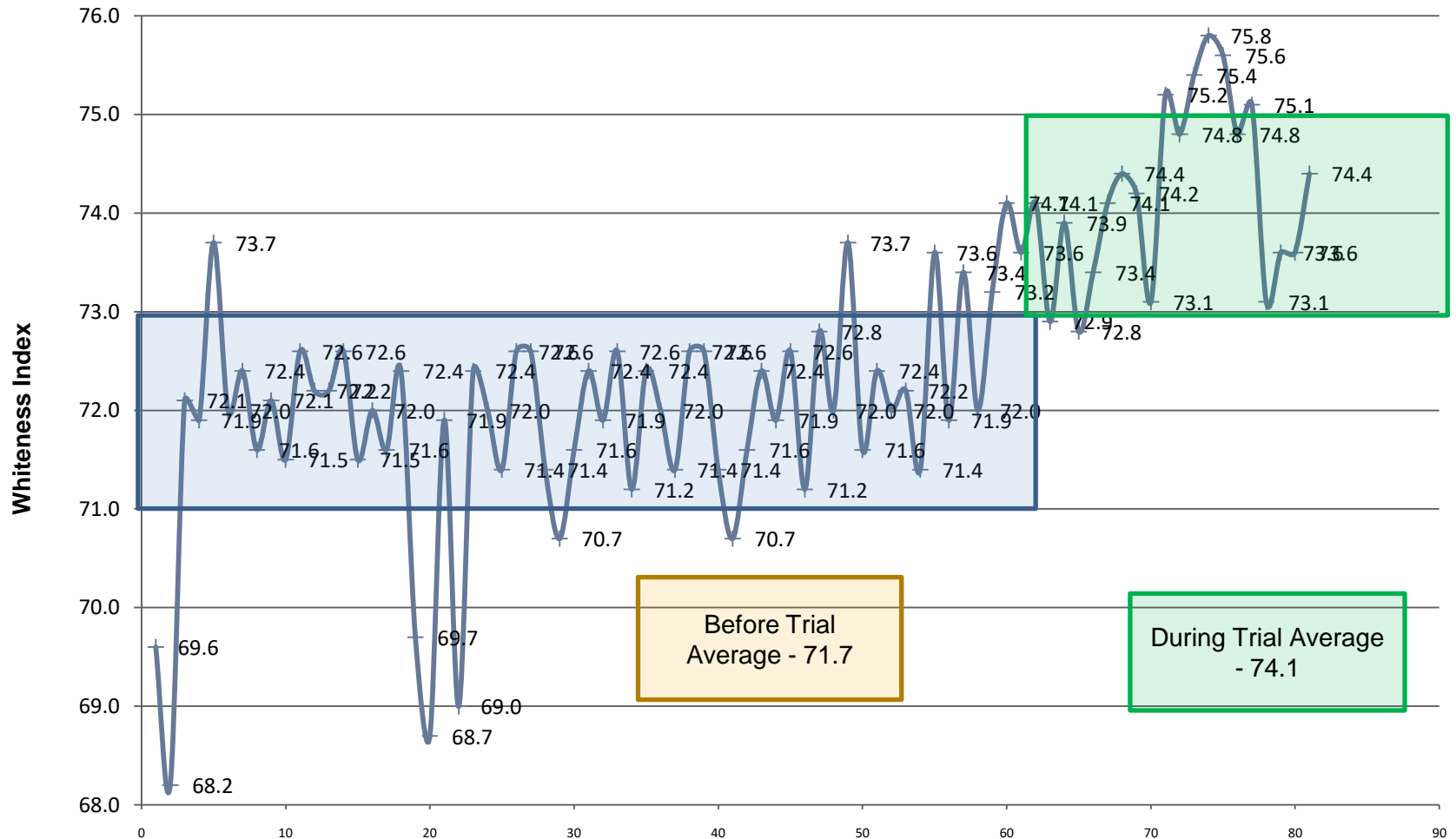
Plant scale trial results

Effect of $\text{Mg}(\text{OH})_2$ on ODL pulp brightness



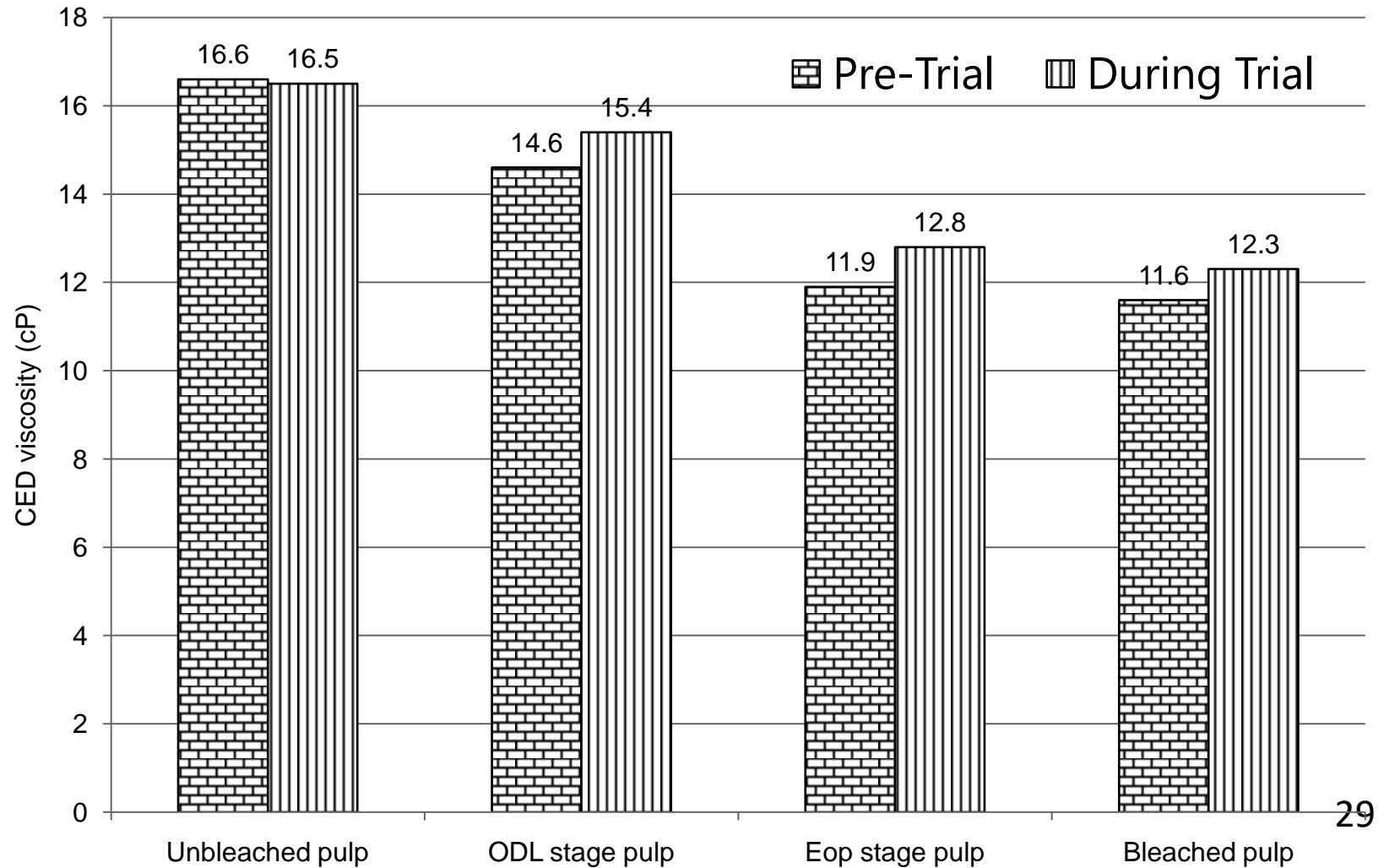
Plant scale trial results

Effect of $\text{Mg}(\text{OH})_2$ on final pulp whiteness



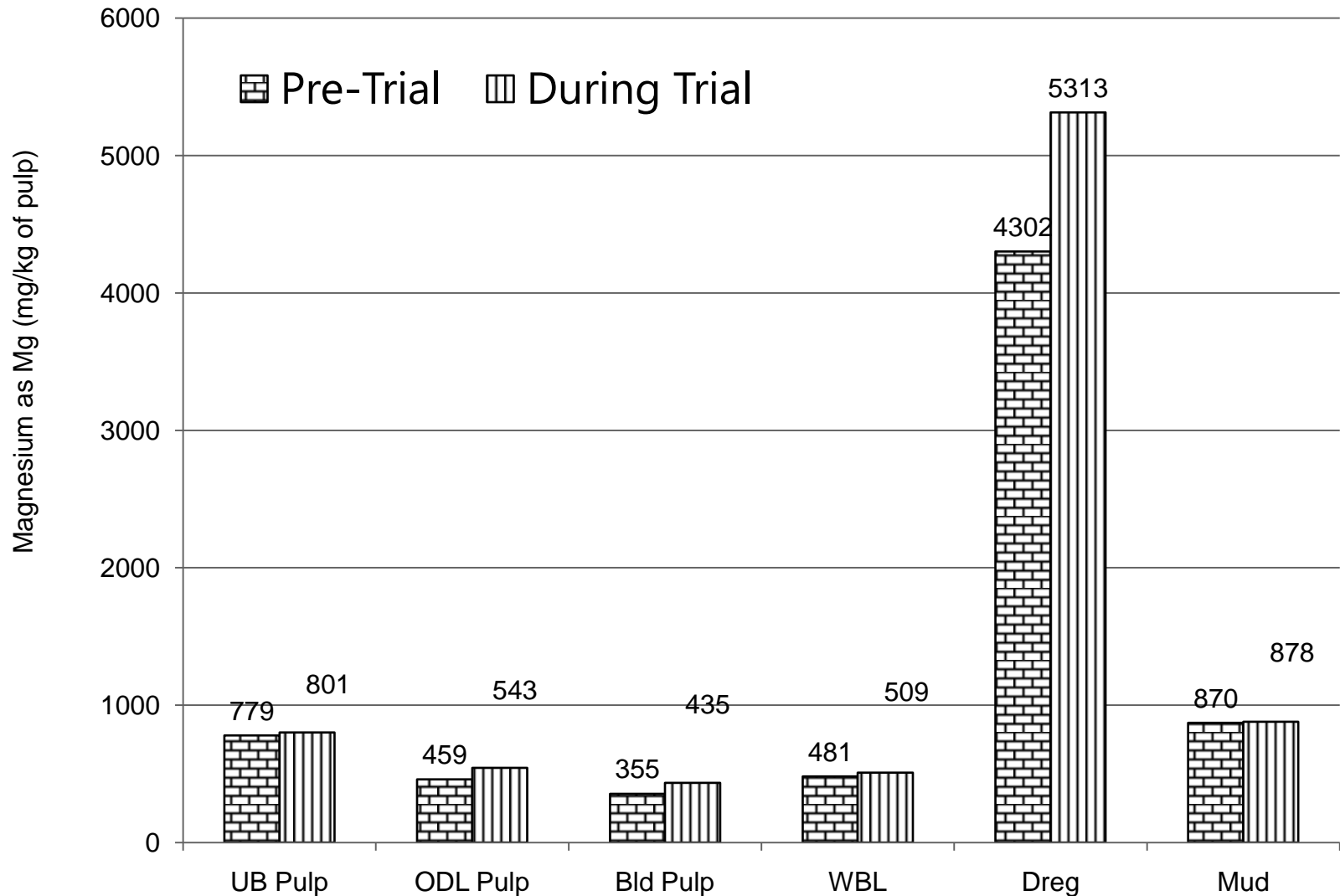
Plant scale trial results

Effect of $\text{Mg}(\text{OH})_2$ on ODL stage pulp viscosity



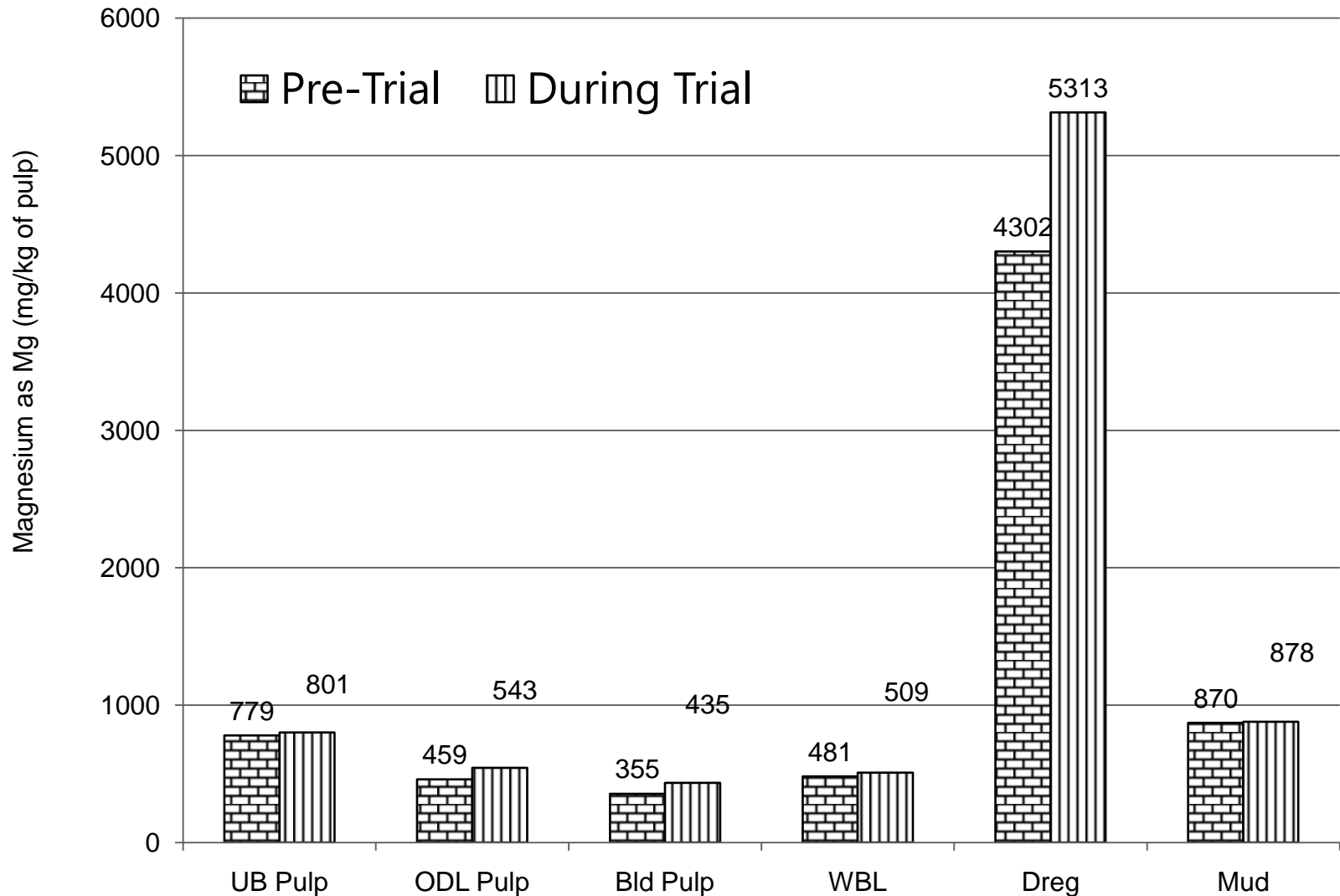
Plant scale trial results

Effect of $\text{Mg}(\text{OH})_2$ on Mg content in system



Plant scale trial results

Effect of $\text{Mg}(\text{OH})_2$ on ODL stage pulp viscosity



Plant scale trial results

Effect of using $\text{Mg}(\text{OH})_2$ 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%

Plant scale trial results

Effect of using $\text{Mg}(\text{OH})_2$ 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
°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

Major Achievements...

Laboratory scale studies...

- Following additives were studied in oxygen delignification stage as carbohydrate protectors :

Chemical additives:

- | | | |
|----------------------------|----------------------------------|------------------------------|
| (1) EDTA | (2) MgSO_4 | (3) DTPA, |
| (4) H_2O_2 | (5) DTPA- H_2O_2 | (6) $\text{Mg}(\text{OH})_2$ |
| (7) Anthraquinone | (8) NaBH_4 | (9) DTMPA |
| (10) Borax, | (11) Thiourea, | (12) Urea |
| (13) Sodium perborate | (14) Boric acid, | (15) Sodium gluconate |
| (16) Ethylene glycol | | |

Polymeric additives:

- | | | |
|---------------------|-------------------|---------|
| (1) Cationic starch | (2) native starch | (3) CMC |
| (4) Guar gum | | |

Major Achievements...

Laboratory scale studies

- Out of the different chemicals and polymeric additives used to improve selectivity of oxygen bleaching, EDTA and $\text{Mg}(\text{OH})_2$ were found the most suitable.
- Results along with salient findings in the form of interim report was shared with SPB, IPMA and CPPRI in April 2016.
- Validation studies of selected processes were carried out at CPPRI and validation report was shared with SPB, ACIRD and IPMA in July 2016 by CPPRI.
- It was decided to carry out pre-plant trial study using mill pulp prior to conducting plant trial at SPB Ltd., Erode (TN).

Major Achievements...

Plant scale studies...

- With the addition of $\text{Mg}(\text{OH})_2$ in ODL stage, kappa reduction was improved by 9-10%.
- Pulp brightness after oxygen bleaching stage and D0 stage was improved by 2.1 and 3.5 units, respectively compared to control. Average final pulp whiteness was improvement by 2.4 units. The viscosity of the pulp was improved by 0.7 to 0.9 cP.
- Cellulose and hemicelluloses content in the ODL and final bleached pulp were improved with the use of magnesium hydroxide showing the improvement in selectivity during oxygen bleaching stage.

Major Achievements

Plant scale studies

- 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.
- Mg content in 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.