Hydrogen Peroxide Bleaching of Chemical Pulps - A Case Study

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Use of elementary chlorine and chlorine based chemicals during bleaching generates Organo - Chloro compounds which cause toxicity in the effluent. In the charter for Corporate Responsibility For Environment Protection (CREP), stipulations are made to reduce the AOX levels to 1.0 kg/tonne and below within five years. Besides, Proposal to levy an ECO - Tax on pulp and paper industry as disincentive on consumption of Elementary Chlorine and removal of 16 % rebate under VAT for chlorine are being fiercely persued. The option for the industry lies in substitution of Chlorine by gradual phasing out with Dioxide or Hydrogen Peroxide. Hydrogen Peroxide offers an excellent method to bleach pulp to requisite brightness level without generation of toxic chemicals during the bleaching process. Century Pulp And Paper has successfully introduced Peroxide bleaching in all three fibre lines it operates with significant reduction in Chlorine / Hypo Chlorite and subsequent AOX levels. Successful trials towards ECF pulp for Bagasse have been completed. The paper outlines the gains of peroxide bleaching in terms of reduced degradation of pulp and brightness achieved in different furnishes. Details on the usage of "Stabilizers" towards optimum utilization of Hydrogen peroxide and gains there of are also discussed.

INTRODUCTION

During the last couple of years, attention on pollutants has shifted from conventional pollutants such as Biological Oxygen Demand (BOD) ,Chemical Oxygen Demand (COD) and suspended solids (SS) to Adsorbable Organo Chloride (AOX) and to Dioxins and Furaus because of their apparent toxicity. The AOX level in the bleach plant using Chrorine / Hypochlorite etc. is of the order of 4 - 6 kg/tonne of pulp.In the modern mills with Oxygen delignification ,Dioxide and Hydrogen peroxide Bleaching, the AOX level can be as low as 0.2 kg/tonne. High capital investment on infrastructure in oxygen Delignification is the limiting factor .Hydrogen -per - oxide is an excellent chemical that can be put to good use by the paper mills irrespective of size, to attain pulp brightness without causing damage to the fibre as well as to the environment, with negligible investment on infrastructure.

Besides successfully adopting Enzyme prebleaching for all its fibre lines, which is a pioneer work in the field, the company has introduced Hydrogen peroxide in the bleaching sequence to derive significant benefits in the terms of preserving the fibre strength at requisite brightness levels of pulp,besides reducing the Hypochlorite dosage to appreciable extent and resultant AOX in effluents.

EXPERIMENTAL

Hydrogen Peroxide decomposes in water and Oxygen ,OH (Hydroxyl) and OH H^- (perhydroxyl) Ion are being intermediate and the concentration of these ions is pH dependent. Perhydroxyl ions react with lignin based Chromophoric group through nucleophillic reaction. Higher temperature 70 - 90 °C improves the performance of Hydrogen Peroxide significantly.Thus alkali extraction stage in CEHD sequences fulfills all requirement of H_2O_2 Bleaching ,therefore no additional investment is required in the H_2O_2 Bleaching sequence.

Unbleached pulps were collected from plant. AOX quantity was calculated using Germgard Equation;

AOX as CI Kg/t = 0.1 (C+0.526 D)

Where C = Chlorine as Cl_2 Kg/t and D = Dioxide as ClO_2 Kg/t

RESULTS AND DISCUSSION

Elimination Of Hypo stage in Wood based paper

Details and processing condition and results are given in Table -1. It is evident from the results that substituting Hypo stage with one additional H_2O_2 stage @ 1.0 % improve brightness by 0.6 points with improved viscosity and about 43 % reduction in AOX . If capacity allows introduction of one Dioxide Stage between two peroxide stage improves Brightness and viscosity further.

Elimination Of Hypo In Dissolving Grade Pulp

Results and processing conditions are enclosed in table II. In the first step the Hypo is eliminated and ClO_2 dose

Table -I

	Kappa No. : 17.46					
	Unbleached Brightness : 23.40					
Bleaching Experiment:	Set No.1		Set No. II		Set No.III	Set No.IV
Enzyme Treatment						
Enzyme Dosage %:	0.03		0.03		0.03	0.03
Retention mint :	60		60		60	60
Temperature °C :	50 – 55		50-55		50 - 55	50-55
pH :	8.5		8.5		8.5	8.5
Chlorination Stage (C/D)						
Cl_2 % :	3.0		3.0		3.0	3.0
ClO_2 % :	0.15		0.15		0.15	0.15
Extraction Stage (E / p_1)						
NaOH % :	2.0		2.0		2.0	2.0
H_2O_2 % :	0.5		0.5		0.5	0.5
Dioxide Stage (D_1)						
ClO_2 % :	X		X		X	0.2
Hypo Stage						
Hypo % :	2.5		X		X	X
Extraction Stage (E / p_2)						
NaOH % :	X		0.5		0.5	0.5
H_2O_2 % :	X		0.75		1.0	0.5
Dioxide Stage (D_2)						
ClO_2 % :	0.4		0.4		0.4	0.4
AOX KgCl/T(Calculated)	5.78		3.28		3.28	3.39
Properties:						
	Set No.I		Set No.II		Set No.III	Set No.IV
Brightness % :	87.8		87.5		88.4	88.6
Yellowness % :	8.18		8.01		7.19	6.55
Viscosity cps :	5.1		5.9		5.7	5.9
Bleaching Conditions:						
	C/D	E/p_1	D_1	Hypo	E/ P_2	D_2
Consistency % :	3	10	10	10	10	10
Retention mint :	45	90.	90	90	90	150
Temperature °C :	Ambient	60 – 65	75 – 80	50-55	60-65	75 – 80
pH	20 - 2.1	11.8/10.7	5.6 / 5.8	9.1/8.7	10.8/10.7	5.4/5.7

was increased by 0.1 % , Marginal improvement in brightness but significant improvement in viscosity observed. Considering the capacity limitation of ClO_2 generation ,addition of H_2O_2 increased keeping ClO_2 constant @ 0.5 %. Significant improvement in brightness by 2.9 points, 83.7 % increase in viscosity was observed at H_2O_2 addition level of 1.25 %. Yellowness also reduced significantly by 2.20 points.

ECF Bleaching of Bagasse pulp

Kappa No of unbleached bagasse pulp at thickener remains in the range of 10 - 12 and the brightness at present sequence of Ez ,Cd,EO,D achieved in the range of 87 - 88 % Study was conducted to bleach the bagasse pulp in ECF sequence (Ez D,Ep,D) with comparable brightness using Hydrogen per oxide at extraction stage.Cl_2 is completely eliminated and ClO_2 increased to 0.5 % to 0.7 % in both stages .With 1.25 % addition level of H_2O_2 Brightness comparable to normal sequence was achieved. 77 % reduction in AOX level was observed.

The elimination of Hypo stage in the Bleaching of wood based paper and Rayon Grade sequence and elimination of Elemental Chlorine for ECF (Bagasse) has brought down the Chlorine consumption

Table - II

		P. No.	: 12.60			
Bleaching Experiment:		Set No.1	Set No.II	Set No.III	Set No.IV	Set No.V
Enzyme Treatment						
Enzyme Dosage %:		0.03	0.03	0.03	0.03	0.03
Chlorination Stage (C/D)						
Cl_2	%:	4.0	4.0	4.0	4.0	4.0
ClO_2	%:	0.2	0.2	0.2	0.2	0.2
Extraction Stage (E / p_1)						
NaOH	%;	2.5	2.5	2.5	2.5	2.5
H_2O_2	%:	0.5	0.50	0.75	1.00	1.25
Hypo Stage (Sodium)						
Hypo	%:	1.0	X	X	X	X
Dioxide Stage (D_1)						
ClO_2	%:	0.5	0.6	0.5	0.5	0.5
Sulpher Dioxide Stage						
SO_2	%:	0.4	0.4	0.4	0.4	0.4
AOX Cl Kg/t (Calculated)		5.37	4.42	4.36	4.36	4.36
Properties						
		Set No.I	Set No.II	Set No.III	Set No.IV	Set No.V
Brightness (PV) % :		87.0	87.2	88.3	88.7	89.6
Yellowness %:		8.26	7.26	6.75	6.32	6.06
Viscosity cp :		16.0	28.3	29.3	29.4	29.4
(1% Cupra Ammonium)						

Bleaching Conditions:

	Enz.	C/D	E/p_1	D_1	Hypo	E/ P_2	O_2	SO_2
Consistency % :-	8 – 9	3	10	10	10	10	10	10
Retention mint:	60	45	90	90	90	90	150	30
Temperature °C :	50-55	Ambient	60–65	75 - 80	50–55	60-65	75–80	Ambient
pH	8.8 – 9.2	2.0 - 2.1	11.8/10.7	5.6/5.8	9.1/8.7	10.8/10.7	5.4/5.7	4.9/5.3

significantly as shown in Fig.1.

Optimization Of H_2O_2 By Using Stabilizer

Presence of metal ion like Fe ,Mn & Cu etc promotes the decomposition of H_2O_2,which is highly exothermic reaction.Peroxide stabilizers check the decomposition of H_2O_2 thus making the H_2O_2 available for bleaching of pulp. A study was conducted to see the effect of Stabilizers on H_2O_2 consumption. Details are given in Table: IV .0.8 % stabilizer on H_2O_2 (100 %) was added and brightness improved by 1.2 points. Alternatively H_2O_2 dose reduction @ 20 & 30 % resulted in comparable brightness with 20 % less H_2O_2.The savings anticipated are as shown in Table V.

CONCLUSION

Hypo stage can be substituted by Peroxide stage with better brightness, viscosity and reduction in yellowness. Significant reduction in AOX level can be achieved which is order of the day.The company has already achieved the AOX level well below 1 kg/t of product During ECF bleaching also peroxide can play a major role. With arrival of new generation of H_2O_2 stabilizers it is possible to reduce H_2O_2 consumption by 20 to 30 % thereby saving of Approx Rs. 11 Lacs per annum on

Table: III

Unbleach pulp Kappa No. : 10.20	(Normal) Set No. I	ECF Set No. II	Set No. III	Set No. IV
Enzyme				
Dosage %:	0.03	0.03	0.03	0.03
Chlorination Stage				
Cl_2 %:	3.0	X	X	X
ClO_2 %:	0.2	0.5	0.5	0.7
H_2SO_4	X	added for adjusting the Initial pH		
Extraction Stage				
NaOH %:	2.0	2.0	2.0	2.0
H_2O_2 % :	0.5	0.5	1.0	1.25
Dioxide Stage				
ClO_2 % :	0.4	0.5	0.7	0.7
AOX KgCl/T(Calculated)	3..31	0.526	0.63	0.736
Properties				
	Set No.I	Set No.II	Set No.III	Set No.IV
Brightness % :	87.64	86.64	87.26	87.86
Yellowness %:	5.97	6.31	5.86	5.46
Bleaching Conditions:				
	Enz.	C/D	E/P_1	D_1
Consistency % :	8 – 9	3.0	10	10
Retention mint :	60	45	90	90
Temperature °C :	50 – 55	Ambient	60-65	75 - 80
pH :	8.8 - 9.2	2.0 . 2.2	11.8/10.7	5.6/5.8

Table-IV

	Kappa No. : 17.46			
	Unbleached Brightness: 23.40			
Bleaching Experiment:	Set No.I	Set No.II	Set No.III	Set No.IV
Enzyme Treatment				
Enzyme Dosage %:	0.03	0.03	0.03	0.03
Retention mint;	60	60	60	60
Temperature °C :	50 – 55	50–55	50– 55	50 – 55
pH	8.5	8.5	8.5	8.5
Chlorination Stage (C/D)				
Cl_2 % :	3.0	3.0	3.0	3.0
ClO_2 % :	0.15	0.15	0.15	0.15
Extraction Stage (E/p_1)				
NaOH % :	2.0	2.0	2.0	2.0
H_2O_2 % :	0.5	0.5	0.4	0.35
H_2O_2 Stabilizer % :		0.004	0.0032	0.0028
Hypo Stage				
Hypo % :	2.0	2.0	2.0	2.0
Dioxide Stage (D_1)				
ClO_2 % :	0.4	0.4	0.4	0.4
Properties				
	Set No.I	Set No.II	Set No.III	Set No.IV
Brightness % :	87.2	88.4	87.5	86.9
Yellowness % :	7.68	7.43	7.59	7.72
Viscosity cps :	6.2	6.1	6.0	6.1
Bleaching Conditions:				
	C/D	E/p_1	Hypo	D_2
Consistency % :	3.0	10	10	10
Retention mint:	45	90	90	150
Temperature °C :	Ambient	60 – 65	50 – 55	75 – 80
pH	20 - 2.1	11.8/10.7	9.1 / 8.7	5.4/5.7

Table V Saving after using H_2O_2 Stabilizer with H_2O_2.
(Based on R&D Experiment with reducing 20 % H_2O_2)

Without Stabilizer :		
Dosing rate of H_2O_2	:	590 ml / minute
	:	35.4 ltr / hrs
	:	42.126 kg/ hrs.
Per hour Production @ 100 TPD	:	4.2 tonne / hrs.
Dosing Quantity of H_2O_2	:	10.03 kg/tonne of pulp
Cost of H_2O_2 @ Rs. 25/kg	:	Rs. 250.75 / tonne of pulp.
With Stabilizer :		
Dosing rate of H_2O_2	:	472ml /minute
	:	28.32 ltr. / hrs
		33.70 kg/ hrs.
Per hour Production @ 100 TPD	:	4.2 tonne / hrs.
Dosing Quantity of H_2O_2	:	8.02 kg/tonne of pulp
Cost of H_2O_2 @ Rs. 25/kg	:	Rs. 200.6 / tonne of pulp.
Cost of H_2O_2 Stabilizer	:	0.4 % of H_2O_2 Dosing Rate * 550
	:	0.032 * 550
(Assumed rate of Stabilizer Rs. 80.0 /kg)	:	Rs.17.60 / tonne of pulp.
Saving per tonne of pulp	:	Rs.(250.75- 200.6) - 17.60
	:	Rs.32.55 / tonne of pulp
Saving per Day	:	Rs. 3255/day (Based on 100 tonne production)
Saving per year	:	Rs.11.88 lac / year.

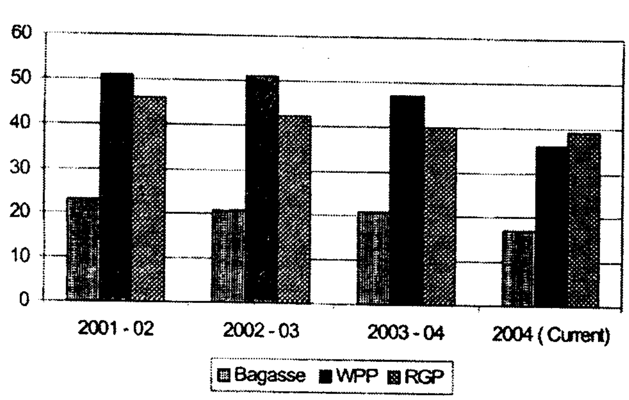

Fig. 1 . Trend of Chlorine Consumption (kg/tonne)

account of H_2O_2 consumption.

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REFERENCES

- Gupta R. K, IPPTA J. 11, (4), p. 9, 1999
- Sarma G.S.R.P., Satyanarayanarao P.V.V., Vidya Sagar, Ch. V, Annamraju P.V., Murthy N.V.S.R. & Satyanarayana U.V., IPPTA J. 12, (4) p.13, 2000
- Tendulkar S.R. IPPTA J. 13, p. 51, 2001