Short ECF Sequences Involving Chlorine Di oxide to Bleach Bagasse Pulp to 90% ISO

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ABSTRACT

There has been a terrific increase in awareness for high quality products and at the same time the environmental issues are given primary importance. Currently, paper industry is being cornered by the quality awareness, cost reduction and environmental issues. Elimination of elemental chlorine is becoming an important thought in designing of bleaching sequence. This paper discusses short ECF sequences with chlorine di oxide to achieve 90% ISO brightness for bagasse kraft pulp.

INTRODUCTION

Quality consciousness has been increasing tremendously and there is excellent demand for the value added premium products as well as improved regular paper products. The demand is at competitive price. On the other hand, environment consciousness is also on an increase and there is an urgent need to minimise or eliminate pollutant generation. The two objectives, imporved quality and lower pollutants, warrants implementation of novel technologies in the pulp and paper industry. Quality improvement, in the paper products is primarily concerned with development of high bright varieties.

Bleaching to very high brightness, at the same meeting the pollution control board limits, does necessarily involves alternative bleaching technologies. The alternatives are required, not only to reach higher brightness targets, but also to preserve the cellulose from degradation. Most of the paper mills in India adopt the conventional CEH/CEHH bleaching sequence. But the mills will be forced to switch over to Elemental Chlorine Free sequences (ECF), involving chlorine dioxide, to reach high brightness targets.

Bagasse kraft pulp, with excellent bleaching response, lends itself more suitable to this change to ECF bleaching, helping us to reach 90% ISO, with short sequence at the same time generates lower pollutants not only in terms of chlorinated organics, but also in colour and COD, in comparison to the conventional CEH, where high brightness targets are not possible even at the expense of pulp properties.

EXPERIMENTAL

Unbleached kraft screened pulp of bagasse was collected from pulp mill. The characteristics of unbleached pulp is given in Table 1.

Table 1

Unbleached bagasse kraft pulp Characteristics		
Kappa No.	:	9.1
Brightness % ISO	:	46.9
Viscosity cPs	:	33.9

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BLEACHING EXPERIMENTS

Laboratory scale bleaching experiments were carried out in polythene bags, except chlorination which was performed in polythene bottles with air tight lid. Exploratory tests were carried out with 20 g (OD) pulp. The pulps, except chlorinated pulps, were brought down to 5% consistency, after the prescribed bleaching period and then dewatered with back water recirculation. The pulps were then washed with water equivalent to twenty times of the OD pulp taken. In case of chlorination, the pulp at 3% consistency was dewatered after bleaching period and then washed as mentioned above. The effluent generated from each stage was finally mixed and the combined pollution load from a specific sequence was determined. The condition maintained during bleaching at various stages are given in Table-2.

Table-2

Constant bleaching conditions

Parameter	C D/C	E	EOP EO	EP	H	DO	DI
Consistency %	8.0	8.0	12.0	8.0	8.0	11.0	11.0
Temperature °C	Amp.	60	90	60	40	65	70
Time mts	30	60	30	60	120	45	180
pH	2.0	>10.5	>10.5	>10.5	8.5-9.5	2.5-3.5	4-5
O_2 pressure kg/cm^2	--	--	2.0	--	--	--	--
Peroxide %	--	--	0.3	0.3	--	--	--

Oxidative extraction using oxygen was performed under specified conditions, in electrically programmable rotating digester.

ANALYSIS

Pulp Kappa number, brightness and pulp properties were determined according to ISO, SCAN standards. Effluent characterisation with respect to colour, COD were performed as per BIS. The optical properties were measured using Elrepho 2000 brightness tester.

RESULTS AND DISCUSSION

THE NEED FOR CHLORINE DIOXIDE

The conventional bleaching of chemical pulps involve chlorine and calcium hypo chlorite. These have no doubt proved to be the most versatile and most economic bleaching agents. But reaching high targets of brightness, merely by increasing the chemicals charge, does not serve the purpose and results only in extensive degradation of cellulose by hypochlorite.

Further more, chlorine is the main precursor for the formation of chlorinated organic matter in bleach plant effluent. Next to chlorine is calcium/Sodium hypochlorite. Whereas, Chlorine dioxide also contributes to AOX formation as well, but results only in 20% of AOX formation compared to same dosage of elemental chlorine. Also, reaching high brightness of 90% ISO is possible with chlorine dioxide brightening in the final stage.

Though chlorine dioxide bleaching is not a new aspect in bleaching, application of chlorine dioxide in bleaching of bagasse kraft pulp, and arriving at optimised sequences that are short, and capable to reaching 90% ISO was the aim of the study. The bleaching was compared with the existing conventional C-E-H with regards to brightness, pulp properties and

effluent quality. As an added advantage, bagasse pulp responds better than hardwood pulp to bleaching (2). Also achieving low kappa number, in case of bagasse is very easy and the unbleached kappa number of 9-11 facilitates easier bleaching to get high brightness.

In all the bleaching sequences, the total chlorine charge, as chlorine % was maintained constant.

C-E-H BLEACHING OF BAGASSE PULP

Conventional C-E-H bleaching of bagasse kraft pulp was carried out. Chlorine as Cl_2 in chlorination was 2.1% and Hypochlorite as Cl_2 in final stage was 1.5%. Extraction was performed with 1.5% alkali. The final brightness obtained was 86.8% ISO the C-E-H bleaching results are given in Table-3

Table 3

CEH bleaching of bagasse kraft pulp		
Chlorination C		
Chlorine as Cl_2%	Applied	2.1
	Consumed	1.9
pH	Final	2.0
Brightness % ISO		55.4
Extraction stage E		
Alkali as NaOH%	Applied	1.50
	Consumed	0.79
pH	Initial	12.0
	Final	11.7
Brightness % ISO		61.7
Kappa no.		1.8
Hyphochloride stage H		
Hypochloride as Cl_2%	Applied	1.50
	Consumed	0.97
pH	Initial	10.3
	Final	8.7
Brightness % ISO		86.8
Viscosity cPs		13.7
Yellowness %		6.7

The bleached pulp viscosity was 14.0 cPs.

The elemental chlorine and hypochlorite in the above sequence were replaced with chlorine-di-oxide, and total chlorine applied was maintained constant.

CHLORINE-DI-OXIDE BLEACHING

The C-E-H bleaching was replaced with D-E-D sequence. The first stage chlorine-di-oxide stage perfomed at 11% consistency for 45 minutes with same amount of ClO_2 as Cl_2, followed by extraction with 1.5% alkali resulted in E stage Kappa number of pulp entering the D stage should be less than 2.0 (3). Aiming at higher brightness of 90% ISO, the necessity of E stage Kappa number less than 2.0 was very much essential. With the above fact in view, to obtain desired E stage Kappa number, oxidative extraction involving peroxide, oxygen, both oxygen and peroxide was thought of.

OXIDATIVE EXTRACTION

oxidative extraction has been proved to be a very promising approach to achieve lower extracted pulp kappa number with lesser degradation and lower pollutants levels in terms of colour and COD. During alkaline extraction, in presence of peroxide, only unetherified phenolic neclei or monomer unit having side chains containing a carbonyl group appears to be susceptible to attack (4). Peroxide favours brightening of pulp than delignification (5), in the extraction stage. Likewise applications of oxygen during extraction stage has better delignification ability than regular extractions. Oxidative extraction involving both oxygen and peroxide has been very effective. Hence, the following sequences involving oxidation extractions were studied, which could result in 90% ISO brightness.

D-EOP-D

D-EP-D

D-EO-D

D-EOP-D bleaching results are given in Table 4. The final brightness was 89.6% ISO and pulp viscosity was high (29 cPs). The D 1.25 stage brightening was performed at 4-5 pH (6). The E stage Kappa number was 1.6. Instead of administering two oxidants, the influence of one oxidant was studied.

The D-EP-D bleaching sequence, with 0.3% peroxide in extraction stage, gave an ultimate

Table 4

D-E (OP)-D Bleaching of Bagasse kraft pulp		
D Stage		
ClO_2% as Cl_2%	Applied	2.30
	Consumed	2.22
pH	Initial	3.8
	Final	2.5
Extraction (EOP) stage		
Alkali as NaOH%	Applied	1.50
	Consumed	1.11
pH	Initial	12.1
	Final	11.1
Brightness % ISO		80.8
Kappa no.		1.6
D (1) stage		
ClO_2% as Cl_2%	Applied	1.25
	Consumed	1.08
pH	Initial	5.0
	Final	5.1
Brightness % ISO		89.6
Viscosity cPs		28.1
Yellowness %		4.5

Table 5

D-E (P)-D Bleaching of Bagasse kraft pulp		
D (O) Stage		
ClO_2% as Cl_2%	Applied	2.30
	Consumed	2.18
pH	Initial	3.5
	Final	3.6
Brightness % ISO		67.7
Extraction (EP) stage		
Alkali as NaOH%	Applied	1.50
	Consumed	1.11
pH	Initial	12.1
	Final	11.9
Brightness % ISO		80.0
Kappa no.		1.3
D (1) stage		
ClO_2% as Cl_2%	Applied	1.25
	Consumed	1.16
pH	Initial	4.8
	Final	4.2
Brightness % ISO		90.3
Viscosity cPs		27.2
Yellowness %		4.5

brightness of 90.3% ISO with preserved pulp viscosity of 27.0 cPs. The E stage Kappa number was only 1.2. Thus the necessity of oxygen along with peroxide was felt to be not necessary. As a comparison oxidative extraction using only oxygen in extraction was also perfomed.

The D-EO-D bleaching also reached 89.7 % ISO with E stage Kappa number of 1.6. All the oxidative extraction steps such as E (OP), E (P) and E (O) proved successful in reaching 90% ISO with same chlorine charge, in comparison to C-E-H.

It is but known fact that 50% replacement of chlorine, with chlorine di oxide is supposed to be the most effective, in terms of brightness achievement. In this regard, D/C-EOP-D bleaching with 50:50 ClO_2:Cl_2 was performed, though this cannot be termed under ECF.

As evident from table, brightness of 91% ISO with 24 cPs viscosity and extracted pulp Kappa number as low as 1.0 could be achieved.

PULP PROPERTIES

A comparison of pulp properties among various chlorine-di-oxide sequences and conventional CEH sequences is given in table 8.

Table 6

D-E (O)-D Bleaching of Bagasse kraft pulp		
D Stage		
ClO_2% as Cl_2%	Applied	2.30
	Consumed	2.16
pH	Initial	3.6
	Final	2.5
Brightness % ISO		66.8
Extraction (EO) stage		
Alkali as NaOH%	Applied	1.50
	Consumed	1.06
pH	Initial	12.7
	Final	11.0
Brightness % ISO		73.2
Kappa no.		1.6
D (1) stage		
ClO_2% as Cl_2%	Applied	1.25
	Consumed	1.06
pH	Initial	5.0
	Final	4.0
Brightness % ISO		99.7
Viscosity cPs		28.2
Yellowness %		4.1

Table 7

D/C - EOP-D Bleaching of Bagasse kraft pulp		
D/C Stage		
ClO_2% as Cl_2%	Applied	1.15
	Consumed	1.09
Chlorine as Cl_2%	Applied	1.15
	Consumed	1.10
pH	Final	2.2
Brightness % ISO		57.8
Extraction (EOP) stage		
Alkali as NaOH%	Applied	1.50
	Consumed	1.37
pH	Initial	12.1
	Final	10.7
Brightness % ISO		79.9
Kappa no.		1.2
D (1) stage		
ClO_2% as Cl_2%	Applied	1.25
	Consumed	1.03
pH	Initial	4.8
	Final	4.2
Brightness % ISO		91.0
Viscosity cPs		24.2
Yellowness %		3.7

The pulp strength properties at 300 ml CSF show better tear factor in case of chlorine-dioxide sequences, as expected.

POLLUTANTS

One of the major concerns with regard to bleach plant effluent being its pollution load, the colour and COD load as Kg/T of pulp was measured for C-E-H sequence and compared with the chlorine-di-oxide sequences.

No doubt, the oxidation extraction stage has provided an additional advantage of lowering the pollution load. It is interesting to note that, colour reduction is more in case of D-EP-D while COD reduction is maximum in D-EO-D, while D-EOP-D lies in between.

AOX

The absorbable organic halogens (AOX) generated from sequences involving chlorine and chlorine containing compounds are of great concern. Since literature survey shows (7) that ClO_2 accounts for only 20% of chlorinated organics in comparison

Table-8

Strength properties of bleached bagasse kraft pulp at 300 ml CSF

Sequence	Tensile Index Nm/g	Tear Index mN. m^2/g	Burst Index k. Pa. m^2/g
C-E-H	58.6	4.74	3.76
D-EOP-D	58.7	5.44	3.85
D-EP-D	57.9	5.57	4.12
D-EO-D	56.9	5.26	3.85
D/C-EOP-D	59.6	5.36	3.81

Table-9

Colour and COD generation from bagasse kraft pulp bleaching

Sequence	Colour kg/t	COD kg/t	Reduction % Colour	Reduction % COD
C-EH	19.3	38.4	--	--
D-EOP-D	8.7	34.4	54.9	10.4
D-EP-D	6.5	28.2	66.3	26.6
D-EO-D	11.4	24.0	40.9	37.5
D/C-EOP-D	8.7	32.6	54.9	15.1

to similar charge of chlorine, therefore, sequences suggested will straightaway have an AOX reduction of above 80%.

OBSERVATIONS AND CONCLUSIONS

Chlorine-di-oxide as expected helps in achieving high brightness 90% ISO targets, in case of bagasse kraft pulp also.

Introduction of oxidative extractions is a preferred necessary step, to achieve less than 2.0 extracted pulp kappa number.

ClO_2 substitution to level of 50% is most effective, though it cannot be termed under ECF sequence.

E (OP) extraction is not necessary for bagasse pulp as (E (P) or (E (O) serve the same purpose E (P) preferable owing to its simplicity in operation.

E (O) is most effective in COD reduction while E (P) in colour reduction. When compared to colour & COD of conventional sequence

The short three stage D-EP-D sequence is quite promising.

The strength properties, particularly tear factor

is improved, though brightness levels are higher.

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