Oxygen Bleaching of a Mixture of Bamboo and Mixed Hardwood Unbleached Pulps

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SUMMARY

The literature on oxygen bleaching has been reviewed. Oxygen bleaching is mainly helpful in pollution abatement as the material dissolved during the oxygen-alkali stage of oxygen bleaching process can be recycled through the recovery system. Insoluble magnesium compounds especially the complexes are helpful in avoiding the attack of oxygen on cellulose fibres. 0.04% $MgCo_3$ as Mg^{++} on pulp is found to be a good inhibitor for protecting the cellulose fibres on the oxygen-alkali stage. Usually sodium hydroxide is used as an alkali during the oxygen-alkali stage. But sodium carbonate as well can be used in its place, the quantity required being the same. During the oxygen-alkali treatment stage, the Kappa Number of the unbleached pulp is to be reduced by nearly 50%. The subsequent bleaching stages to be adopted depends upon the quality of the final pulp required. Introduction of a C/D stage after the oxygen stage is helpful in getting better brightness and viscosity. But from the point of operational and economic consideration it may not be feasible. However, using a chlorination stage after the oxygen-alkali stage, a pulp having brightness, viscosity and strength properties, the same as that of the conventionally (CEHH) bleached pulp can be obtained. The experimental work carried out in the Research Centre show that oxygen bleaching helps in achieving 75% reduction in total volume of effluent discharged, 70–75% reduction in COD and BOD of effluents and 90% colour reduction of the effluents, compared to the conventional CEHH bleaching.

INTRODUCTION

In 1915 a U.S. patent was issued to Muller of Germany for oxygen bleaching(1). But until 1960, not much work was published regarding oxygen bleaching. Around 1960, American, Russian, Japanese, and French investigators reported encouraging results on oxygen bleaching of wood pulps. The discovery that Magnesium carbonate addition, decreases the degradation of cellulose was one of the important findings.

The oxygen bleaching has assumed very much importance due to its considerable reduction of pollution load, simplicity of the process and economic advantages over the conventional bleaching sequence. Already number of commercial oxygen bleaching plants are working in Europe and U.S.A.(2).

Dr. Liebergott said, "Oxygen bleaching has established itself as a principal bleaching stage in today's commercial processes. The use of oxygen in the first stage of bleaching has definitely shown that bleaching chemical costs can be reduced. Also, it eliminates the bulk of pollution usually associated with the first two stages of bleaching by recycling, through the recovery system, the material dissolved out in this stage ....." (1).

WHAT IS OXYGEN BLEACHING ?

Oxygen bleaching is a process, where the unbleached pulp is treated with oxygen in the presence of an alkali under given conditions of temperature, pressure and time.

Many workers like I. Croon, et al, tried to establish the chemistry of oxygen bleaching(2). The work carried out by these research workers indicate close similarities between the degradation of lignin during peroxide bleaching and oxygen bleaching. A substantial part of the degradation of lignin may thus proceed via oxidation of phenolic units followed by degradation to aliphatic acids, as has been demonstrated for the degradation of lignin by hydrogen peroxide. Oxydative cleavage of the C–3 side chain of lignin monomers seems to constitute another important part of lignin degradation. An anology may be drawn with the oxidation of lignosulphonate to vanillin.

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Degradation of cellulose and other wood polysaccharides may be reflected in decreased yield and viscosity. Peeling reactions are generally the most important source of yield loss in alkaline process. During oxygen bleaching of hydrocellulose, however, it was found that peeling reactions were of little sginificance. A higher yield was obtained compared with alkaline treatment in the absence of oxygen under otherwise identical conditions. Reactions leading to decreased viscosity may sometimes be considerable during oxygen bleaching. Similar reactions occur during ageing of alkali cellulose and have also close similarities with degradative reactions which occur under various bleaching conditions.

Undesirable degradation of polysaccharides during oxygen bleaching is diminished by the presence of magnesium carbonate. Despite considerable investigation, the mechanism of this effect has not been fully elucidated. The use of other magnesium salts in this connection has disadvantages. When a water soluble salt, e.g. magnesium sulphate is added to the pulp, alkali mixture, magnesium precipitates as virtually inactive magnestium hydroxide, with a resultant decrease in alkali concentration. If magnesium carbonate is used, a relatively high concentration is required to provide sufficient protection. However, if suitable magnesium complexes are added to the pulp alkali mixture, they will not precipitate during the operation. Thus recirculation of the waste liquor allows recovery of the most of the active constituents. Furthermore, the high efficiency of the magnesium complexes permits the use of very low additions, say, 0.03 to 0.05% as magnesium ions based on pulp. The cost is less then 20 cents per tonne of pulp.

PROCESS VARIABLES OF THE OXYGEN STAGE

Despite incomplete knowledge of the chemistry of oxygen bleaching, technical control of the process has been amply demonstrated. Optimum conditions for oxygen stage depend on process variables in that stage, Kappa Number of the unbleached pulp, conditions of any preceding bleaching stage, the type of subsequent bleaching stages and desired properties of the final pulp. The conditions for the oxygen stage and the most suitable sequence are predetermined, by pulp requirements and mill operation. This does not mean that oxygen bleaching is a complicated method but rather demonstrates its flexibility.

The range of conditions applicable when oxygen is used for kraft pulp is –

Pulp consistency	..	25–30%
Pressure (oxygen)	..	2–8 kg/cm^2
Temperature	..	90–120°C.
Time	..	Less than one hour
Alkali	..	2–5%
Mg	..	<0.05% (as Mg^{++})

To obtain a specific degree of delignification and bleaching, a certain alkali concentration is required. Thus, as pulp consistency is increased, decreasing amounts of alkali are required to obtain a selected Kappa Number. Excessive concentration causes a lowering of pulp viscosity. High pulp consistency contributes to more efficient contact between oxygen and pulp, eliminates the need for mechanical agitation and lowers steam consumption. A high oxygen pressure increases the rate of delignification and pulp yield. If oxygen bleaching is to be used, pulping to higher Kappa Number than is normally practiced may be advantageous.

Oxygen bleaching in combination with chlorine and chlorine dioxide mixtures promotes effective removal of shives. A general misconception is that oxygen bleaching will invariably produce a pulp of poor quality. But results of work carried out by many, and our present work show that it is not so. Both the plant and laboratory experiments indicate savings to the extent of $3 – $4 per tonne of bleached pulp.

POLLUTION ABATEMENT

Using countercurrent washing and an appropriate combination of the brown stock washing system, the screening operation and the oxygen stage, it is possible to burn the oxygen effluent. Water pollution due to bleach plant would thereby be reduced considerably. In addition, recovery of caustic could be achieved. BOD reduction is around 40–50% and COD reduction is about 40%. Colour of the effluent is reduced by approximately 60%.

Oxygen-alkali delignification, when correctly used, provides advantages in bleaching economics and pulp quality together with favourable prospects for pollution control.

RECOVERY ASPECTS

Oxygen bleaching alone does not decrease pollution to any considerable extent unless the dissolved solids from the oxygen stage are recovered in some way or the other. This fact leads to the concept of a truly countercurrent recovery system where the recovery liquor from the oxygen stage is used for washing on the last brown stock washer. By putting into use an appropriate method, it is possible to recover 80–90% of the dissolved solids from the oxygen stage without any additional dilution of the black liquor to the evaporators as compared with the practice of today in most brown stock washing systems. This means a reduction in COD and BOD values, and recovery of sodium hydroxide equivalent to 85–95% of salt cake per tonne of pulp.

EXPERIMENTAL

Unbleached pulps of bamboo and eucalyptus in 90:10 ratio with a Kappa Number of 30 and 43.2, prepared in the Research digester in Research Centre, and unbleached pulps of a mixture of bamboo, eucalyptus and mixed hardwood of Kappa Number 23,

collected from pulp mill, were used for the oxygen bleaching experiments.

For preliminary investigation, to establish optimum dosage of alkali, oxygen and inhibitors, bomb digesters of 2 litres capacity, heated in a glycol bath were used. After the establishment of optimum conditions, rotary digester of 16 litres capacity, electrically heated with 2 rpm was used.

In all the experiments the following method and conditions were used for oxygen-alkali treatment.

The required quantity of unbleached pulp was taken in the rotary digester and the alkali with the inhibitors were added to the pulp, mixed thoroughly and the consistency was adjusted to 10%. After securing the lid tightly, the whole mass was heated to 80°C and then the required quantity of oxygen was injected and 7 Kg/cm² total pressure was maintained. Then again the heating was started upto 120–125°C. At this temperature it was held for 30 to 40 minutes, and then the pressure was released. The oxygen-alkali treated pulp was washed in a hydroextractor thoroughly and then was bleached further using various sequences, as mentioned in the tables furnished in this paper.

TESTING

The following tests were carried out :

(1) Kappa Number and brightness of alkali-oxygen treated pulps, brightness, viscosity and the strength properties of the final bleached pulps.

(2) Analysis of the effluents of oxygen bleached pulps and conventionally bleached pulps. In this paper, the following points were studied :

(1) Effect of varying amounts of alkali and magnesium carbonate on the quality of the final bleached pulps (Table—I).

(2) Effect of various subsequent bleaching sequences on the pulp quality, after oxygen-alkali treatment (Table—II).

(3) Comparative effect of sodium hydroxide and sodium carbonate on the pulp quality of the final bleached pulps (Table—III).

(4) Analysis of effluents from oxygen and conventionally bleached pulps to ascertain the pollution rate (Table—IV).

(5) Costing of oxygen bleached pulps compared to conventionally bleached pulps (Table-V).

DISCUSSION

(1) In experiment 1 to 4 the quantity of sodium hydroxide used was varied between 2.5 to 4.0%. The final results show that 2.5% sodium hydroxide is sufficient in oxygen-alkali treatment to attain the brightness, viscosity and strength properties nearer to that of conventionally bleached pulp. In Experiment No. 1–4 after oxygen-alkali treatment H_1 H_2 sequence was used for further bleaching. However, while studying the effect of various amounts of inhibitors, CEH sequence was used as proved good in some other experiment. 0.04% $MgCO_3$ as Mg ions is sufficient to protect the cellulose from more severe attack of alkali.

(2) To ascertain the best subsequent bleaching sequence after alkali-oxygen treatment, number of different sequences were tried. They were O.H.E.H.; O.H.E.D.; O.C.E.H.; O.C./D.E.H. in comparison with conventional C.E.H.H. In all the cases, oxygen-alkali treated pulp of 15.7 Kappa Number was used. The conditions of bleaching of different sequences are recorded in Table—II. The results show that O.C.E.H. is more suitable than other sequences. However, O.C./D.E.H. gave highest brightness and viscosity than other sequences. But due to operational and economic consideration O.C.E.H. appears more feasible. Strength properties of O.C.E.H. bleached pulps were better than other sequences and almost same as that of conventional bleached pulps.

(3) Earlier experiments showed that sodium hydroxide during oxygen-alkali treatment degrades pulp more. Hence few experiments were carried out using different amounts of sodium carbonate instead of sodium hydroxide. The results are tabulated in Table—III. The results clearly indicate that sodium carbonate is better than sodium hydroxide with respect to brightness, viscosity and the strength properties of the bleached pulps. 2.5% sodium carbonate with 2.5% oxygen gives better results than 2.5% sodium hydroxide and 2.5% oxygen.

(4) **POLLUTION ABATEMENT**—Having established the conditions for oxygen bleaching to get satisfactory brightness and strength properties, few experiments were planned to minimise the pollution load. It is known that chloride ions, whether from elemental chlorine or chlorine dioxide do exist in the pulp mill effluent, which is a major contributor for pollution. One way of eliminating the presence of chloride ions to a large extent, is to have the Kappa Number of the oxygen treated pulps of 10 minus. As recorded in Table—IV, by using 4.0% NaOH and 3.0% oxygen it is possible to obtain a pulp of 8.4 Kappa Number. This Pulp was further bleached using only H_1H_2 sequence. Earlier experiments showed that it was not possible to obtain final brightness more than 78%. Hence the pH of H_1 stage was reduced by using hydrochloric acid. This has helped in getting brightness

TABLE—I

EFFECT OF VARYING AMOUNTS OF ALKALI AND MAGNESIUM CARBONATE ON PULP QUALITY AND STRENGTH PROPERTIES IN OXYGEN BLEACHING

Particulars	Experiment No. 1	2	3	4	5	6	7	8	9
Sodium hydroxide (on pulp), %	2.5	3.0	3.5	4.0	2.6	2.6	2.6	2.6	..
Magnesium carbonate (on pulp), %	0.06	0.06	0.06	0.06	0.04	0.06	0.08	0.10	..
Oxygen (on pulp), %	2.0	2.5	2.0	2.5	2.5	2.5	2.5	2.5	..
Brightness of O_2 treated pulp (Elrepho), %	30.1	31.4	32.0	32.9	31.8	31.4	30.9	28.6	..
Kappa Number of O_2 treated pulp	18.7	17.7	16.8	15.7	16.7	17.4	16.9	20.5	..
Bleaching sequence after O_2-alkali treatment	H.H.	H.H.	H.H.	H.H.	C.E.H.	C.E.H.	C.E.H.	C.E.H.	C.E.H.H.
Total chlorine added (on pulp), %	6.90	6.50	6.00	5.60	5.95	6.25	6.05	7.35	10.00
Total chlorine consumed (on pulp), %	6.28	5.68	5.25	4.85	5.34	5.73	5.31	6.85	8.85
Bleached pulp yield, (on raw material) %	47.4	46.3	47.5	47.0	45.8	45.9	46.5	46.4	47.6
Brightness (Elrepho), %	77.6	77.6	78.0	77.9	80.9	80.4	81.5	77.2	80.4
Viscosity, (CED) cps.	13.5	14.2	13.5	13.7	15.7	15.5	15.7	18.2	16.9
Strength properties									
Lampen ball mill, revolutions	8000	8000	8000	8000	8000	8000	8000	8000	8000
Slowness, °SR	42.0	41.5	40.0	40.0	44.0	41.0	41.0	40.0	41.0
Breaking length, kms.	5.71	5.81	5.48	5.60	5.14	5.48	5.31	5.39	6.23
Strength index	1810	1780	1760	1640	1910	1870	1810	1940	1960

Note : Unbleached pulp of bamboo and eucalyptus with Kappa Number 30 was used.

TABLE—II

EFFECT OF VARIOUS SUBSEQUENT BLEACHING SEQUENCES ON THE PULP QUALITY AND STRENGTH PROPERTIES OF OXYGEN-ALKALI TREATED PULP

Particulars	Experiment No. 10	11	12	13	14
Sodium hydroxide (on pulp), %			3.0		
Magnesium carbonate (on pulp), %			0.04		
Oxygen (on pulp), %			2.5		
Brightness of O_2-treated pulp (Elrepho), %			32.8		
Kappa Number of O_2-treated pulp			15.7		
Bleaching sequence after O_2-alkali treatment	H.E.H.	H.E.D.	C.E.H.	C/D.E.H.	C.E.H.H.
Total chlorine added (on pulp), %	5.6	5.6	5.6	5.6	10.00
Total chlorine consumed (on pulp), %	4.8	5.1	4.9	5.2	8.85
Bleached pulp yield (on raw material), %	46.8	47.0	46.4	47.4	47.6
Brightness (Elrepho), %	80.1	82.6	82.5	84.0	80.4
Viscosity, (CED) cps.	13.9	16.3	15.2	20.4	16.9
Strength properties					
Lampen ball mill, revolutions	8000	8200	8200	8200	8400
Slowness, °SR	40.0	42.5	40.0	38.0	41.0
Breaking length, kms.	5.06	5.17	5.34	5.20	6.20
Strength index	1810	1860	1900	1890	1960

Note : Unbleached pulp of bamboo and eucalyptus of 30 Kappa Number was used.

TABLE—III

COMPARATIVE EFFECT OF SODIUM HYDROXIDE AND SODIUM CARBONATE IN OXYGEN BLEACHING

Particulars	Experiment No. 15	16	17	18	19	20
Sodium hydroxide (on pulp), %	2.5	..	..	..	..	..
Sodium carbonate (on pulp), %	..	2.5	2.5	3.0	4.0	..
Magnesium carbonate as Mg^{++} (on pulp), %	0.04	0.04	0.04	0.04	0.04	..
Brightness of O_2-alkali treated pulp, %	35.5	32.3	26.5	34.1	34.0	..
Kappa Number of O_2-alkali treated pulp	17.8	21.1	22.7	17.2	16.5	..
Bleaching sequence after O_2-alkali treatment	C.E.H.	C.E.H.	C.E.H.	C.E.H.	C.E.H.	C.E.H.H.
Total chlorine (on pulp), %	6.45	6.20	9.00	5.25	6.14	14.30
Total chlorine consumed, %	4.61	5.68	8.18	4.08	4.96	12.79
Bleached yield (on raw material), %	43.1	44.0	43.7	42.4	41.7	43.6
Brightness of bleached pulp, %	82.0	82.0	79.0	80.3	80.6	81.2
Viscosity (CED), cps.	8.0	14.7	17.0	19.4	11.1	15.1
Strength properties						
Slowness, °SR	40	40	40	40	40	40
Breaking length, kms.	7.20	7.85	8.04	6.74	7.45	7.90
Strength index	2060	2410	2530	2440	2180	2510

Note : Unbleached pulp of bamboo and eucalyptus of 43.2 Kappa Number was used.
In Expt. No. 17, O_2, = 1.7%
In rest Expt., O_2 = 2.5%.

TABLE—IV

OXYGEN BLEACHING OF MILL UNBLEACHED PULP AND EFFLUENT ANALYSIS OF H.H. AND C.E.H.H. SEQUENCE

Particulars	Experiment No. 21	22	Reduction %	ISI Std. No. IS:2490–1963	Notes
Subsequent bleaching sequence after O_2-alkali treatment	H.H.	C.E.H.H. Blank			Unbleached pulp from plant with 23 Kappa Number was used for alkali-O_2 treatment under the following conditions: NaOH=4.0%; O_2=3.0% Brightness of Oxygen–Alkali treated pulp, % =41.3 Kappa No.=8.4.
Total chlorine added, %	3.50	9.85			
Total chlorine consumed, %	3.16	8.23			
Bleached pulp yield (on pulp),%	95.0	93.5			
Brightness (Elrepho), %	84.0	81.6			
Viscosity (CED), cps.	7.0	8.1			
Strength Properties					
Slowness, °SR	40.0	40.0			In bleaching in Expt. 21 acedic pH was maintained in H_1 stage by using hydrochloric acid.
Breaking length, kms.	6.60	6.60			
Strength index	1890	1950			
Analysis of Effluent					
Total effluent discharged per tonne of unbleached pulp, m^3	51.7	116.74	55.8	..	
C.O.D., ppm	216	380	..	250 Max.	
C.O.D. load in Kgs per tonne of unbleached pulp	11.1	44.3	75.0	..	
B.O.D., ppm	48	71.5	..	30 Max.	
B.O.D. load in Kgs per tonne of unbleached pulp	2.47	8.35	70.5	..	
Colour, Pt. Co. Units	90	465	..	..	
Colour load in Kgs per tonne of unbleached pulp	4.63	54.6	91.5	..	
Suspended solids, ppm	139	33	..	100	

TABLE—V

COST OF CHEMICALS FOR THE CONVENTIONAL AND OXYGEN BLEACHING OF ONE TONNE OF UNBLEACHED PULP BASED ON EXPT : 21 AND ITS BLANK (22)

Chemicals	Rate of chemicals	C.E.H.H. sequence		O.H.H. sequence	
	Rs. / Kg	Quantity Kgs	Total amount Rs	Quantity Kgs	Total amount Rs
Chlorine	0.95	60.0	57.00	..	..
Sodium hydroxide	2.40	15.0	36.00	40.0	96.00
Oxygen	2.50	..	..	30.0	75.00
Magnesium carbonate	2.60	..	..	1.40	3.64
Calcium hypochlorite	1.32	39.0	51.60	35.0	47.20
Hydrochloric acid	0.15	..	..	20.0	3.00
Total amount	..	..	144.50	..	224.84
Recovery of NaOH	..	..	..	36.0	86.40
Net cost, Rs/Tonne	..	..	144.50	..	138.44

Note : 90% of sodium hydroxide can be recovered.

of 84% and strength properties equivalent to that of conventional bleached pulp (Table —IV). The combined effluent of C.E.H.H. and O.H.H. were analysed separately for colour, C.O.D. and B.O.D. values. The results are tabulated in Table—V. The results clearly show that there is an overall reduction in the effluent discharge by 55.8% and reduction in COD and BOD to the extent of 70–75%. The colour reduction was more than 90%.

(5) **COSTING.**—Cost of both the conventional and oxygen bleaching were calculated. This is based on the assumption that 90% of the sodium hydroxide used can be recovered. The calculations show saving of Rs. 6 per tonne of bleached pulp (Table—V).

CONCLUSIONS

(1) About 50% reduction in Kappa Number of the unbleached pulp should be achieved in the oxygen alkali stage.
(2) For an unbleached pulp of Kappa Number 30, 2.5% NaOH and 2.5% oxygen is required for reducing the Kappa Number by 50% in oxygen alkali stage.
(3) A temperature of 120°C is found to be optimum for the oxygen alkali stage.
(4) 0.04% $MgCO_3$ as Mg^{++} on pulp is found to be a good inhibitor for protecting the cellulose fibre in the oxygen alkali stage.
(5) A subsequent C.E.H. stage of bleaching is suitable in the oxygen bleaching.
(6) Sodium carbonate is more advantageous than sodium hydroxide in the oxygen-alkali stage, the dosage being the same in both the cases.
(7) An overall reduction of 55.8% in the volume effluents discharged is achieved in the oxygen bleaching, compared to the conventional C.E.H.H. sequence. Also 70–75% reduction in C.O.D. and B.O.D. is achieved. The colour of the effluents is reduced by 90%.

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