

Oxygen Reinforced Peroxide Bleaching of Agricultural Residues

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INTRODUCTION

Environmental considerations and shifting market demand have generated interest in the production of high brightness pulp without use of chlorine compounds. Since all the chlorine based bleaching chemicals contribute to the production of absorbable organic halides (AOX), the trend in bleach plants have been to reduce the use of these chlorine chemicals. Commercial total chlorine free bleaching (TCF) apply oxygen, ozone and peroxide to produce market brightness pulp and require careful application to minimize pulp strength loss. There are many similarities among ozone, alkaline oxygen and hydrogen peroxide delignification; they have common reaction intermediate species and transients (1). For example, large quantities of H_2O_2 are produced during oxygen and ozone delignification (2). The goals when using these chemicals are to maximize delignification, brightness and selectivity towards lignin and minimize pulp strength loss.

The most significant development in peroxide bleaching technology is the advent of pressurized peroxide bleaching (PO), the rate of the bleaching reaction is significantly increased through increase in temperature upto $120^\circ C$. To carry out this, the peroxide stage must be run under to keep the bleach solution from boiling up and causing lack of bleaching agent mass transfer to the pulp (3). The higher temperature allows the peroxide stage to develop high brightness in relatively short (1-2 hr) reaction time. Pressurised peroxide bleaching also allows a higher brightness ceiling to be achieved (4). One recent development that utilizes the increased initial rate of reaction in peroxide bleaching is known as PHT process (5). In this process, the reaction is split into phases. One of the phase is carried out under temperature pressurised conditions in a short upflow reaction tube. The reaction time is reduced at high temperature, $110^\circ C$.

In all these peroxides, the hydrogen peroxide delignification and brightening reaction takes place in completion with decomposition reaction which can waste peroxide as well as degrade pulp strength.

The reacting species of the alkaline hydrogen peroxide are the hydroperoxy anion (HOO^-) and its decomposition intermediates, hydroxyl (OH^-) and superoxide anion (O^{2-}) radicals. Decomposition of H_2O_2 is necessary to delignify pulp (6), but the rate of peroxide decomposition into reactive intermediates must be controlled in order to achieve all the goals of peroxide bleaching. It is well known that transition metals such as manganese, iron and copper, which exist naturally in pulp catalyze the decomposition of peroxide too fast under alkaline conditions. Therefore the concentration of HOO^- and OH^- becomes too high, selectivity towards lignin is being lost and cellulose degradation as indicated by loss in CED viscosity is increased as well lignin degradation. Lignin degradation increases the hydrophilicity, which leads to pulp delignification, while cellulose degradation decreases the degree of polymerisation and eventually weaken the pulp. A slow hydrogen peroxide decomposition rate will also provide longer time of pulp exposure to HOO^- anions for better brightening. Therefore optimal peroxide bleaching requires the careful management of the profile of metal ions in pulps.

The object of this paper is to present a new process for oxygen peroxide bleaching using a chelant agent and thus EOP stage will have to be modified to run at higher temperature and time under pressure.

RESULTS AND DISCUSSION

Oxygen treatment

The significant reduction in pollution load through oxygen bleaching vis a vis conventional bleaching using chlorine can be clearly seen from the information available that reduction of 64% in colour and 65% in BOD can be achieved through oxygen bleaching. Partial replacement of chlorine with oxygen can significantly reduce the pollution load while

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Table-1

Effect of alkali on Kappa no. of wheat straw soda pulp

Experiment No.	Oxygen pressure psi	Reactor temperature °C	% Alkali charged as NaOH	Kappa No.	% Reduction Kappa no.	Brightness %
1	40	85	1.5	13.5	25.4	41.4
2	40	85	2.0	13.3	26.5	41.8
3	40	85	2.5	13.1	27.1	42.2
4	40	100	1.5	13.2	26.8	42.4
5	40	100	2.0	12.6	30.2	43.7
6	40	100	2.5	11.4	36.8	44.6
7	100	100	0.5	14.7	18.8	41.3
8	100	100	1.0	13.2	27.1	44.1
9	100	100	1.5	11.0	39.2	46.2
10	100	100	2.0	10.7	40.6	48.7

complete replacement can reduce the pollution by 75%. It has been proved that introduction of oxygen in a particular bleaching sequence produces pulp of the same quality and yield as obtained with conventional bleaching system with significant low pollution load. Additional advantage of oxygen bleaching is chemical saving. Oxygen bleaching can reduce operating costs while producing pulp of good quality.

The effect of alkali concentration at two oxygen pressure and two temperatures during treatment was studied. Table-1 indicates that at low oxygen pressure (40 psi) and low temperature (85 °C) at 2.0% alkali as NaOH, Kappa no. reduction was 26.5% and brightness gain was 41.8%. From Fig.1 it is observed that when temperature was increased to 100 °C there is about 10% more reduction in kappa number at 2.5% alkali. The brightness gain is only 3% more. At high temperature and pressure even at low alkali concentration (1.5%) significant reduction in kappa number (39.2%) and gain brightness (46.2%) was achieved.

Effect of Chelation (Q) on metal profile

It is well known that transition metals such as manganese, iron and copper catalyze the decomposition of hydrogen peroxide under alkaline conditions. Since these transition metals are insoluble under alkaline conditions as heterogenous surface-catalyzed reaction caused by colloidal transition metal oxides/hydroxides has been proposed to be the likely mechanism of this decomposition of peroxide under bleaching condition (7). In an attempt to create the optimal metal profile chelation was done using diethylene triamine pentaacetic acid (DTPA) at pH 4.5-5.5 for

30 minutes at 50 °C. The metal profile changes resulting before and after chelation is shown in Fig.2. The reduction in Fe^{+2} , Mn^{+2} and Cu^{+2} is observed after Q stage, whereas some ions i.e. Mg^{+2} and Ca^{+2} and SiO_3 are reported to have a stability effect on peroxide (8). Thus the chelation stage helps in removing metallic ions from the pulp during washing.

An attempt was also made to see the effect of pH on metallic ion removal from the pulp. It was found that chelation at pH less than 3 results in poorer bleaching; because of lower amount of Mg^{+2}

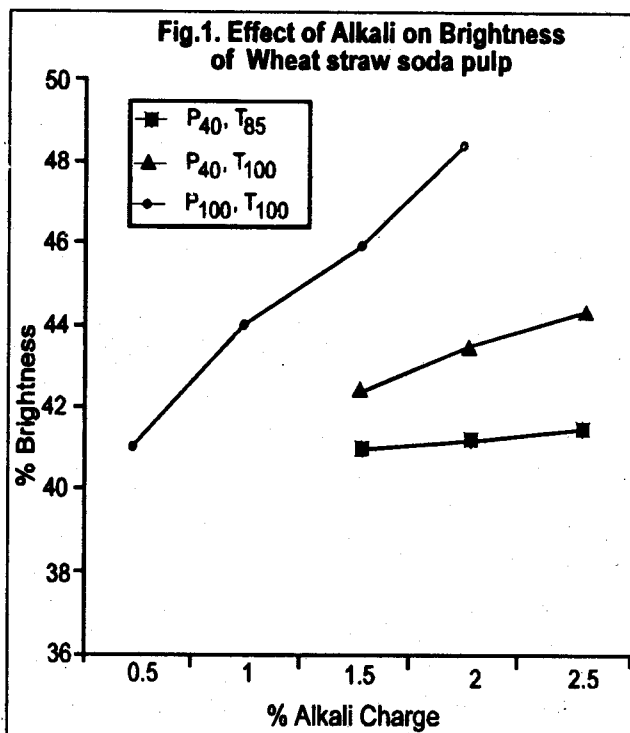


Table-2				
Chelating Pretreatment versus acid pretreatment				
Treatment	% Peroxide	Brightness	kappa No. reuction	Viscosity Cp
Q (P ₄₀ /T ₈₅)	1.2	49.3	30.7	19.2
Q (P ₄₀ /T ₁₁₀)	1.2	51.1	38.7	16.03
AQ (P ₄₀ /T ₈₅)	1.2	43.8	25.4	17.2
AQ (P ₄₀ /T ₁₁₀)	1.2	47.1	35.9	15.9
Q (P ₁₀₀ /T ₁₁₀)	1.2	56.0	49.2	15.1

in pulp, as addition of Mg⁺² to Peroxide improves peroxide bleaching and is believed to complex transition metal ions and thus lower their catalytic effect. Chelation treatment at pH above 8 also results in poor chelation because of large amount of Mn⁺² in pulp. For example at pH 10.8 the decreasing order of metal activity for peroxide decomposition is reported to be Mn⁺² >> Cu⁺² > Fe⁺² (9). The activity of chelant is a function of pH.

The performance of chelating agent was evaluated, first as a chelation stage followed by washing before peroxide bleaching and secondly in the peroxide bleaching stage. Using chelating agent in the peroxide stage directly, also gave the lower brightness than that of chelation stage followed by a wash before peroxide bleaching. Thus the washing step is critical and requires careful handling.

Effect of chelating agent on Oxygen-peroxide bleaching sequence

The following methods were adopted to control the effects of metals.

- i) Pretreatment with DTPA (Q)
- ii) Acid treatment (A) at pH ≈ 2 for 5 min. Followed by DTPA.

The impact of chelation stage alone (Q) and combining both acid treatment and chelation stage (AQ) were studied. From the results tabulated in Table-2, it is observed that Q stage followed by pulp washing results in higher brightness 51.1% ISO as compared 47.1% ISO for the combined stage with 1.2% peroxide charge based on the optimized conditions at same pressure and temperature (Pressure-40 psi and temperature 110 °C). The CED viscosity observed is also on higher side (16.03 cps) indicating that Q stage helps in removing metallic ions over AQ stage. The increase in temperature during reaction

also helps in achieving the higher brightness though CED viscosity is reduced. The alkali charged was 2.5% as NaOH based on results reported in Table-1. It was postulated that the acid stage could be used to desorb the metals from the pulp sites. Lower brightness and reduction in CED viscosity as observed during AQ from the Table-2 may be due to the fact that even though the metals have desorbed from the sites within the pulp, they may be difficult to remove completely in subsequent washing stage and catalytic activity of desorb the metals from the pulp sites within the pulp, they may be difficult to remove completely in subsequent washing stage and catalytic activity of desorb metallic ions is higher than the metal ions present. It is not possible to prepare a standard formula for a chelation stage applicable to all pulps, because the transition metals content change depending on the pulp origin and

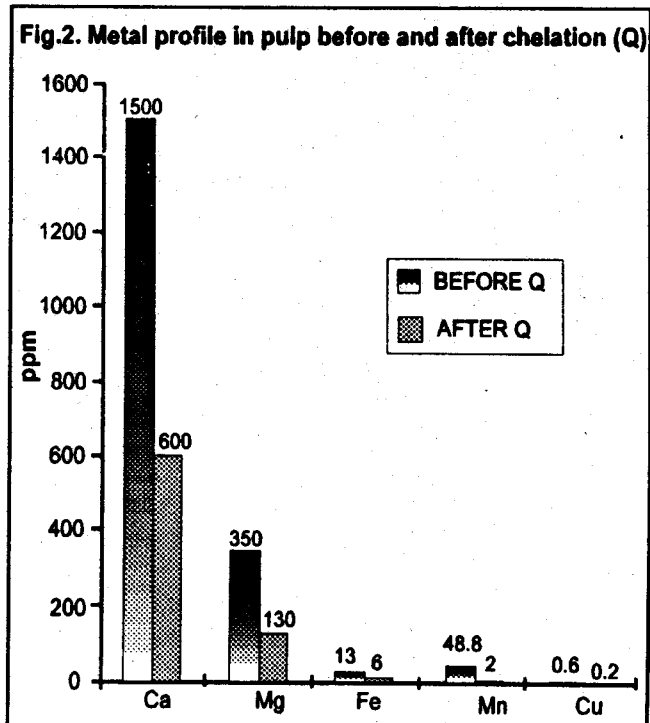


Table-3

Oxygen reinforced peroxide bleaching conditions of wheat straw soda pulp									
Experiment	First stage bleaching				Second stage bleaching				Brightness
	%Peroxide	Temp. °C	Residual peroxide g/l	pH	%Peroxide	Temp. °C	Residual peroxide g/l	pH	
1	1.2	85	0.68	10.8	1.2 (Pressurized)	110	0.12	10.4	68.2
2	1.2	85	0.68	10.8	1.2 (Atmospheric)	85	0.34	10.6	57.4

0.2% DTMPA, 2.5% NaOH, 1st stage oxygen at 40 psi

species. These differences can only be accounted for by difference in the strength of chemical binding of the metals to the pulp. The chelation stage therefore be optimised for each specific pulp.

Effect of Diethylene Triamine Pentamethylene Phosphoric Acid (DTMPA)

Phosphorous containing chelating agent has also been evaluated. DTMPA has been evaluated as a potential replacement for sodium silicate which can cause problems when mill close up its white water system (10). The experiment was carried out with use of MgSO₄, Na₂ SiO₃ and DTMPA. These were added directly in the washed chelated pulps during oxygen-peroxide bleaching keeping 2.5% alkali concentration. The best brightness was achieved with use of either MgSO₄ or DTMPA in the peroxide stage. Using DTMPA in peroxide stage gives higher viscosity pulp as compared to MgSO₄. Use of silicates in the peroxide stage results in lower brightness. The DTMPA dose was varied from 0.05% to 0.25% and effect was observed on brightness and viscosity. Optimum charge with respect to brightness and CED viscosity in the sequence is approximately 0.2% on pulp. High doses of DTMPA can result in lower brightness. Hence DTMPA can replace MgSO₄ and Na₂SiO₃ in peroxide bleaching.

Effect of temperature and pressure on Oxygen-peroxide bleaching sequence

Peroxide bleaching can be significantly enhanced by increasing the temperature and pressure of the reaction. All the experiments reported here have same initial starting pressure (40 psi) of oxygen for 20 min. and then vented to atmospheric pressure. Peroxide was added during initial oxygen treatment. The combined effect was observed. The oxygen pressure

was maintained during first stage of treatment. The effect of temperature was examined at 1.2% peroxide with 2.5% alkali as NaOH and 0.2% DTMPA in both the stages. Second stage of peroxide was performed under pressure and compared with atmospheric bleaching. The results in Table-3 indicate that at temperature 85 °C the residual peroxide is 0.68 g/l and pH of the effluent is 10.8. When second stage of bleaching was carried under pressure at high temperature there is 11% increase in brightness level as shown in Table-3 than the bleaching carried out under atmospheric condition at lower temperature. The results indicate that the pressure and temperature enhances the brightness level, but with 1.2% peroxide the targeted brightness could not be achieved. So it was decided to perform pressurized bleaching at higher peroxide doses.

Two stage peroxide pressurized bleaching

Pressurized peroxide stage was used as part of the bleaching sequence. The pressurized peroxide stage was run in a pressurized tumbling reactor. In first stage oxygen was used to pressurize the vessel. In this case the pulp tumbled through the oxygen atmospheric throughout the reaction resulting in good contact with oxygen. The system was pressurized with oxygen for 20 min. at 85 °C and 110 °C and vented to atmospheric pressure. This option is evaluated since it would be easier to modify EOP stage into pressurized Oxygen-peroxide stage. The results are shown in Table-4. The final brightness (72.2%) for the sequence containing temperature 85 °C in first stage and 110 °C in second stage is lower as compared to 78.36% for the sequence when both the stages were performed at 110 °C.

The residual peroxide is on lower side and pH of the effluent is around 10.4 during first stage of

Table-4									
Oxygen reinforced peroxide pressurised bleaching of wheat straw soda pulp									
Experiment	First stage bleaching				Second stage bleaching				Brightness %
	%Peroxide	Temp. °C	Residual peroxide g/l	pH	%Peroxide	Temp. °C	Residual peroxide g/l	pH	
1	2	85	0.83	10.42	2	110	0.34	9.83	72.2
2	2	110	0.23	10.37	2	110	0.23	9.8	78.36
0.2% DTMPA, 2.5 NaOH, 1st stage oxygen at 40 psi									

treatment in both the case but dropped less than 10 after second stage. CED viscosity is on lower side (11.2 cps) as compared 14.9 cps with lower temperature at first stage.

Both the pulps were beaten in PFI mill and evaluated for strength properties (Table-5). The breaking length and tear indices are on lower side in case of pulp bleached at 85/110 °C. The burst factor is on higher side. In all, the pulps obtained by both treatments possess, high strength properties.

When comparing with CEHH sequence, the increase in strength properties was observed by 13% in burst index, 3.8% in tensile index and 3% in tear index. The reduction in pollution load was 83% in BOD and 67% COD.

CONCLUSION

There are many similarities between oxygen and peroxide bleaching, they have common reaction intermediate species and transients. In the present paper, the oxygen and peroxide stages were combined. It was observed that high temperature and high pressure even at low alkali concentration (1.5%) significant reduction in Kappa number (39.2%) and gain in brightness (46.2%) was achieved. Hydrogen peroxide under alkaline conditions can both delignify and

brighten the pulp. The optimal metal profile is obtained by lowering as much as possible the concentration of transition metals that catalyse hydrogen peroxide decomposition. An attempt was also made to see the effect of removal of metallic ions from the before and during peroxide stage. Chelation with DTPA under appropriate conditions of pH, time and temperature was also studied with respect to gain in brightness. Oxygen followed by peroxide was carried out at two temperature levels. The results indicate that the pressure and temperature enhances the brightness. In other set of experiment both the stages were performed under pressure. It was observed that pressurised stage can be fully pressurised to obtain high level of brightness with high temperature and shortened retention time under pressure. The final brightness (72.2%) for the sequence at temperature 85 °C in oxygen reinforced stage and 110 °C in second peroxide stage under pressure is lower as compared to brightness of 78.36% for the sequence when both the stages were performed under pressure at 110 °C. Pulps obtained by both the treatment possessed high strength properties. Hydrogen peroxide can be produced at the mill site and minimal capital is required for implementation. The sequence chosen was OPP, since it can be retrofitted into existing bleach plant with slight modification.

Table-5					
Strength properties of wheat straw oxygen reinforced peroxide bleached pulp					
Pulp	CSF ml	Breaking length Km	Burst factor	Tear factor	CED viscosity Cps
I	370	6.08	27.5	11.3	14.9
	220	6.9	43.3	10.87	
	170	7.35	47.2	9.59	
II	360	6.2	30.0	11.78	11.2
	240	6.99	47.2	10.97	
	180	7.4	43.5	10.48	

EXPERIMENTAL

Wheat straw pulp was produced by cooking the raw material with 10% NaOH at 504 H factor. The pulp was washed and screened on flat vibrating screen.

Kappa number 18.1
 Brightness, ISO 37.3%
 CED viscosity 28.62 Cps

BLEACHING

Bleaching was carried out with pretreated chelated pulp. The chelation was performed at 5% consistency, pH 4.5-5.5, temperature 50 °C, for 30 min.. The chelation was done in the two following ways:

- i) Acid treatment (A) at pH \approx 2 for 5 min. followed by 0.2% DTPA (Q) with intermittent washing in between and after.
- ii) 0.2% DTPA (Q). followed by washing of pulp

Oxygen reinforcing peroxide treatment

The peroxide with oxygen was given at 40 and 100 psi with 2.5% alkali concentration 1.2% peroxide, temperature 85-100 °C and time at temperature 60 min (Pressure was released after 20 min. and reaction was continued).

DTMPA addition

DTMPA was varied. 05%, .1%, .15%, .2% and .25%.

REFERENCES

1. Johnson, A.P., Fitting together the ECF-TCF Jigsaco Appita, 47 (3): 243-251 (1994).

2. Francis, R.C. . Hydrogen peroxide delignification and brightness of chemical pulp bleaching, TAPPI Press, Anthology; 418-419 (1989).

3. Devenyns, J., Renders, A., Carlien, J. and Walsh, P. Proc. Pulping Conference: Chicago, p. 281 (1995).

4. Germgard, V.C., Norden, S. Proc. Int. Bleaching Cof., Vancouver, B.C., p.53 (1994).

5. Abot, J. JPPS, 17 (1): 10 (1991).

6. Backman, L. and Gellecstealt, G. Reactions of kraft pulp with alkaline hydrogen peroxide, 7th ISWPS Vol.1, Beizing, China, 223-229 (1993).

7. Desberg, F., Devenyns, N. and Troughten, P. One stage hydrogen peroxide full bleaching of previously delignified softwood kraft pulp. Application to TCF sequence, pulping Conference/443 (1993).

8. Bambrick, D.R. . The effect of DTPA on bleaching peroxide decomposition. TAPPI 68 (6) : 96-99 (1985).

9. Colodette, J.L., Rothenberg, S., & Dence, C.W. Factors affecting hydrogen peroxide stability in the brightening of mechanical and chemimechanical pulps. Part-II: Hydrogen Peroxide Stability in the presence of sodium silicate. J. Pulp and Paper Sci., 15 (1), J 10 (1989).

10. Dence, C.W. and Somori . Factors affecting hydrogen peroxide bleaching of mechanical and chemimechanical pulp. TAPPI, p. 120-123 (1986).