Improved oxygen delignification for magnesium-based sulfite pulps

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ABSTRACT

Addition of a catalytic quantity of sodium borohydride to the magnesium-based oxygen delignification of sulfite pulps improves pulp yield, viscosity, and strength properties. A proposed mechanism to explain this behavior assumes that carbonyl groups on the cellulose molecules of sulfite pulps promote cellulose degradation during oxygen delignification. Treatment of pulp with sodium borohydride reduces the carbonyl groups to hydroxyl groups, thus stabilizing the cellulose against degradation during the oxygen delignification stage. It was found experimentally that sodium borohydride is reasonably stable under the conditions of a magnesium oxide-based oxygen delignification stage. Therefore, pulp reduction by sodium borohydride and oxygen delignification can be performed simultaneously in a single stage.

Application:

A very small amount of sodium borohydride can improve the performance of magnesium oxide-based oxygen delignification of sulfite pulps

EFFLUENT DISCHARGES MUST BE minimized to reduce the environmental impact of pulp and paper mills. Oxygen delignification is one of the available options for accomplishing this objective.

Conventional oxygen delignification uses sodium hydroxide as the alkali source, and its effluent can be incorporated into the chemical recovery system of the kraft process. On the other hand, the effluent from the sodium hydroxide-based oxygen delignification stage (referred to as an O_{NaOH} stage in the following text) cannot be sent to the recovery system of the magnesium-based sulfite process because the sodium salts are not compatible with the operation. Therefore, it was concluded *(1, 2)* that magnesium oxide-based oxygen delignification technology (referred to as an O_{MgO} stage in the following text) is preferred for the magnesium-based sulfite pulping process.

Because of the low alkalinity of MgO or $Mg(OH)_2$ relative to NaOH, the temperature of an O_{MgO} stage must be increased by about 30°C to achieve the same degree of delignification as an O_{NaOH} stage *(2)*. However, the O_{MgO} process can decrease the lignin-to-carbohydrate selectivity *(1)*, thus reducing pulp strength properties *(2)*. Since the strength properties of sulfite pulp are usually inferior to those of kraft pulp, a further decrease in strength properties of the sulfite pulps during the O_{MgO} process is not tolerated in most cases.

This paper reports on an improved O_{MgO} process for sulfite pulps. By adding a small quantity of sodium borohydride to the O_{MgO} stage, the lignin-to-carbohydrate selectivity, pulp yield, and pulp strength properties can be improved significantly.

EXPERIMENTAL

Pulp samples (kappa no. 25.2, viscosity 43.1 mPa·s) used in the experiments were received from a commercial mill (Fraser Paper, Edmundston, NB). The pulp was stored in a refrigerator at about 50–60% pulp consistency.

Borohydride reduction (R)

Sodium borohydride was first added to the pulp slurry in a plastic bag at 10% consistency. After kneading for a few minutes, the plastic bag was transferred to a temperature bath and maintained at a desired temperature. After 30 min, the pulp slurry was thoroughly washed with deionized water in preparation for the subsequent O_{MgO} treatment.

Oxygen delignification with MgO (O_{MgO})

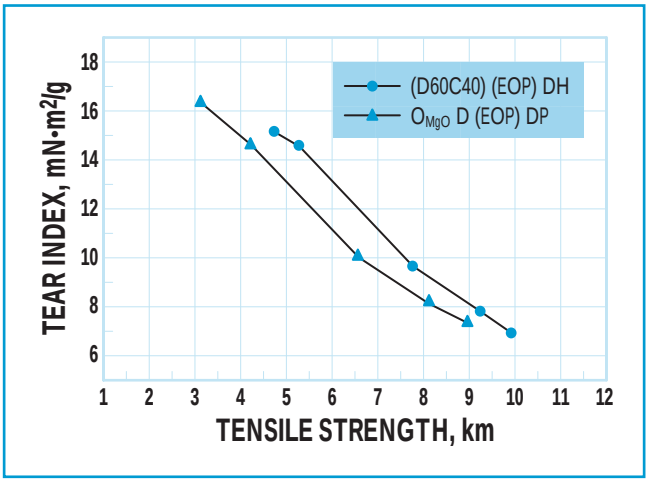
Magnesium oxide (equivalent to 2.0% on pulp) was added to the pulp suspension (10% consistency) in a plastic bag. Mixing was accomplished by kneading the bag. The pulp slurry was then transferred to a Parr reactor equipped with a mechanical stirrer and heated to 127°C under 100-psi pressure. After the specified reaction time, the pulp slurry was removed from the reactor and thoroughly washed with deionized water.

Sodium borohydride-assisted oxygen delignification (O_{MgO+R})

The required sodium borohydride was first added to the magnesium oxide slurry in a beaker. The mixture was then charged to the pulp suspension in a plastic bag, which was kneaded to ensure thorough mixing. After mixing, the contents of the plastic bag were transferred to the Parr reactor and subjected to oxygen delignification using the same conditions as the O_{MgO} process.

Other bleaching stages

Other bleaching stages were conducted following conventional procedures. Conditions for the various bleaching stages are given in **Table I**.



1. Strength properties of (D60C40)(EOP)DH- and O_{MgO}D(EOP)DP-bleached sulfite pulps

Measurement of pulp properties

Pulp viscosity, kappa number, copper number, and strength properties were measured in accordance with TAPPI test methods.

RESULTS AND DISCUSSION

Oxygen delignification and pulp strength

The Fraser Papers mill in Edmundston, NB, has a sulfite pulp production capacity of about 600 tons/day, with a typical kappa number of about 26. Its bleach plant is operated in a (D60C40)(EOP)DH sequence. A typical beating curve for the bleached sulfite pulp obtained following this bleaching sequence is shown in **Fig. 1**. For comparison, Fig. 1 also includes the strength properties of a bleached pulp by an ECF (elemental chlorine free) sequence including the O_{MgO} stage, namely O_{MgO}D(EOP)DP. Figure 1 shows that the O_{MgO}-based ECF bleaching process leads to the production of a fully bleached pulp with inferior strength properties than the conventional bleaching process. This is consistent with earlier reports that inclusion of the O_{MgO} process lowers the lignin-to-carbohydrate selectivity and thus reduces pulp strength *(2)*.

Presence of carbonyl groups

It has long been recognized that sulfite pulps can have more carbonyl groups on the cellulose molecules than kraft pulps *(3)*. A reduction treatment by sodium borohydride can increase the viscosity of sulfite pulps significantly *(3)*. However, the effect of sodium borohydride reduction on the strength properties of sulfite pulp has not been studied.

The presence of carbonyl groups on cellulose molecules of the sulfite pulps may have two negative consequences. First, carbonyl groups may reduce the hydrogen bonding capacity between cellulose molecules, thus resulting in poor strength properties. Second, the presence of carbonyl groups in the cellulose molecule may induce more carbohydrate degradation via the well-known β elimination mechanism under an alkaline condition, such as during oxygen delignification. This could be especially true during an O_{MgO} stage, since it is operated at a higher temperature to compensate for the lower alkalinity. In either case, it is desirable to eliminate the carbonyl groups in the sulfite pulps prior to an oxygen delignification stage.

$NaBH_4$ reduction and pulp viscosity

It is known that a post-treatment stage with sodium borohydride on an oxidized pulp, such as ozone-delignified pulp, leads to increased pulp viscosity. For example, it was reported that a reduction treatment stage with 0.1% sodium borohydride increased the viscosity of ozone-treated pulp—as measured by the degree of polymerization (DP)—from 710 to 920 *(4)*. The chemistry of sodium borohydride reduction is well understood. Carbonyl groups present in carbohydrates are reduced to alcohol functionalities *(5)*.

To study the effect of the reduction of sulfite pulp on the subsequent oxygen delignification, we treated the sulfite pulp with sodium borohydride under the conditions of 0.05% $NaBH_4$ charge, 50°C, pH 9.5, and 10% pulp consistency. After 30 min, the pulp slurry was thoroughly washed with deionized water. Pulp fibers were then collected for the subsequent O_{MgO} treatment under the typical conditions of 127°C, 100-psi pressure, 10% pulp consistency, 2% MgO, and 1 h. The resulting pulp had a kappa number of 13.8 and a viscosity of 39.5 mPa·s. Without the sodium borohydride pretreatment, the same sulfite pulp was subjected to an O_{MgO} stage under exactly the same conditions, yielding an oxygen-delignified pulp with a kappa number of 12.8 and a viscosity of 27.8 mPa·s. Therefore, it is evident that sodium borohydride reduction of the sulfite pulp significantly increases the viscosity of the oxygen-delignified pulp.

There could be two mechanisms to account for the increase in pulp viscosity, (a) greater dissolution of low-molecular-weight carbohydrates, such as hemicellulose and (b) less carbohydrate degradation. We believe that the second mechanism is dominant because the hemicellulose dissolution between the two cases is similar, while the reduction of sulfite pulp in a pretreatment stage stabilizes the carbohydrate, thus decreasing carbohydrate degradation during the oxygen delignification stage.

Combined $NaBH_4$ reduction and oxygen delignification stage

To enhance the practicality of the O_{MgO} process, coupled with borohydride reduction for sulfite pulps, we investigated the potential of combining the sodium borohydride reduction and O_{MgO} in a single stage. This consideration is reasonable because the pH requirement for borohydride reduction is similar to that provided

Process variables	O_{MgO}D(EOP)DP				(D60C40)(EOP)DH			
	D	EOP	D	P	D60C40	EOP	D	H
Consistency, %	3.5	10	11.5	10	3.2	10	11.5	3.5
Time, min	12	30	145	70	20	50	225	35
Temperature, °C	40	70	72	80	40	65	72	60
O_2 pressure, psi	…	40	…	…	…	35	…	…
Time at pressure, min	…	4	…	…	…	6	…	…
Chemical charge, % on pulp								
Cl_2	…	…	…	…	3.28	…	…	…
ClO_2	1.36	…	0.5	…	0.83	…	0.75	…
NaOH	…	1.8	…	1.0	…	3.0	…	…
H_2O_2	…	0.8	…	1.0	…	0.65	…	…
$MgSO_4$	…	…	…	0.05	…	…	…	…
NaOCl	…	…	…	…	…	…	…	0.14
pH	2.7	…	…	…	2.7	…	…	…
Final pH	…	11.8	3.9	10.5	…	12.1	3.8	10.8

I. Bleaching conditions for sulfite pulps

by the O_{MgO} process. However, a couple of questions needed to be addressed before continuing the project.

1. Can the reduction of sulfite pulp by sodium borohydride be completed in a reasonably short period of time?
2. What is the stability of sodium borohydride in the presence of oxygen and with magnesium oxide as the alkali source?

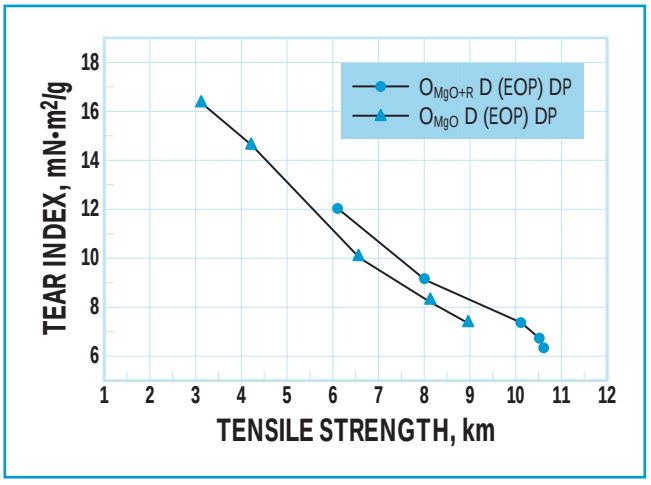
Speed of $NaBH_4$ reduction. Can the reduction of sulfite pulp by sodium borohydride be completed in a reasonably short period of time? We determined the residual sodium borohydride after being mixed with the pulp and magnesium slurry and found that the charged sodium borohydride is almost completely exhausted after a few minutes. Also, we found that varying borohydride reduction from a few minutes to a half hour followed by the O_{MgO} stage has a negligible effect on the viscosity of the resulting pulps, suggesting that the reduction time does not affect the response of the subsequent oxygen delignification. Therefore, we conclude that the reduction of carbonyl groups on the cellulose molecule is a fast reaction. The implication is that it may not be necessary to perform sodium borohydride reduction of sulfite pulp as a separate stage to ensure completion of the reaction.

	OXYGEN DELIGNIFICATION STAGE			
	O_{MgO}	O_{MgO+R}	O_{NaOH}	O_{NaOH+R}
Conditions				
Base chemical	MgO	MgO	NaOH	NaOH
Base charge, % on pulp	2	2	2	2
$NaBH_4$ charge, % on pulp	…	0.1	…	0.1
Temperature, °C	127	127	90	90
Time, min	60	60	60	60
Pressure, psi	100	100	100	100
Final pH	9.0	9.0	10.8	10.8
Pulp properties				
Pulp viscosity, mPa·s	24.4	43.0	25.6	40.4
Kappa number	12.8	12.4	13.7	13.8
Pulp yield, %	96.0	98.5	94.2	95.9

II. Conditions of oxygen delignification during O_{MgO}, O_{MgO+R}, O_{NaOH}, and O_{NaOH+R} stages and sulfite pulp properties

Stability of $NaBH_4$ under reaction conditions. What is the stability of sodium borohydride in the presence of oxygen and with magnesium oxide as the alkali source? A sodium borohydride solution at around pH 9 (in 2% MgO slurry) was bubbled with an oxygen stream in a gas wash bottle that was submerged in a temperature bath of 70°C. The residual sodium borohydride was titrated at various reaction times. We found that the sodium borohydride concentration is practically unchanged after 45 min. We also studied the stability of sodium borohydride (7.2 g/L $NaBH_4$ solution) at pH 9.5 (adjusted with the addition of magnesium oxide slurry), 70°C, and 100-psi oxygen pressure. The titration results showed that after 30 min, about 92% of sodium borohydride initially present still remains. Therefore, we conclude that sodium borohydride is reasonably stable under the conditions of a magnesium oxide-based oxygen delignification stage.

Pulp yield. Based on these results, we propose that the sodium borohydride reduction and the oxygen delignification can be combined in a single stage. This is done by mixing the pulp slurry, magnesium oxide, and sodium borohydride first



2. Tear–tensile relationship of the O_{MgO}D(EOP)DP- and O_{MgO+R}D(EOP)DP-bleached sulfite pulps

and then transferring this mixture to a preheated Parr reactor and feeding oxygen until reaching the desired pressure. We call this process the sodium borohydride-assisted oxygen process and denote it as O_{MgO+R}.

Table II shows the comparison of pulp properties obtained from the O_{MgO}, O_{NaOH}, O_{MgO+R}, and O_{NaOH+R} processes. In order to reach a similar delignification, the MgO-based oxygen delignification stages (O_{MgO} and O_{MgO+R}) were operated at 127°C as opposed to 90°C for the NaOH-based stages (O_{NaOH} and O_{NaOH+R}). Evidently, all the processes under the present conditions lead to well-delignified pulps with similar residual kappa numbers. On the other hand, the pulp yield after the oxygen stage is lowest for O_{NaOH} and O_{NaOH+R} and highest for O_{MgO} and O_{MgO+R}. The greater yield loss of the O_{NaOH} process than the O_{MgO} process was also observed by Luo and Christensen *(2)*, who operated both processes at the same temperature of 95°C.

The greater yield loss for O_{NaOH}-treated pulps is explained by the fact that sulfite pulps usually contain large amounts of hemicellulose and that the higher alkalinity of the O_{NaOH} over the O_{MgO} process dissolves more hemicellulose. It is interesting to note that the pulp yield of the O_{MgO+R} process is even higher than that of the O_{MgO} process. When the yield loss due to delignification is considered (where percent lignin = 0.147 × kappa number), we can conclude that the pulp yield loss caused by carbohydrate dissolution is minimal during an O_{MgO+R} stage. Also, the viscosity of the O_{MgO+R}-delignified pulp is 43.0 mPa·s, similar to that of the unbleached pulp (43.1 mPa·s), supporting the supposition that the addition of sodium borohydride essentially eliminates carbohydrate degradation during the MgO-based oxygen delignification of sulfite pulp.

Using the same sulfite pulp, we also studied the addition of sodium borohydride to the O_{NaOH} process. The same sulfite pulp was mixed with 2% NaOH, 0.1% $NaBH_4$, and 0.2% $MgSO_4$ and subsequently transferred to the preheated Parr reactor. The properties of the resulting pulp are included in Table II. Based on these results, we conclude that the addition of sodium borohydride to a sodium hydroxide-based oxygen delignification of sulfite pulps is equally effective in minimizing carbohydrate degradation and yield loss.

Pulp strength. So far we have shown that addition of sodium borohydride during oxygen delignification of sulfite pulp significantly increases both viscosity and yield, most likely because the $NaBH_4$ minimizes carbohydrate degradation during the oxygen stage. This leads to the question of whether the strength properties of the O_{MgO+R}-treated pulp are also higher than those of the O_{MgO}-treated pulp.

We performed the O_{MgO+R} process under the conditions of 0.05% sodium borohydride, 10% pulp consistency, 2% MgO, 0.2% $MgSO_4$, 127°C, and 1 h. The resulting pulp with a kappa number of 13.9 and pulp viscosity of 41.9 mPa·s was then bleached to a full brightness (90% ISO) using the D(EOP)DP sequence described previously. The tear–tensile beating curve of the O_{MgO+R}D(EOP)DP-bleached pulp is compared with that of the O_{MgO}D(EOP)DP-bleached pulp in **Fig. 2**. It is evident that the strength of the O_{MgO+R}D(EOP)DP-bleached pulp is superior to that of the O_{MgO}D(EOP)DP-bleached pulp, indicating that the addition of a small amount of sodium borohydride improves the strength properties of sulfite pulp.

We therefore propose that the reduction of carbonyl groups to hydroxyl groups enhances the hydrogen bonding ability of cellulose molecules of the fibers. Furthermore, elimination of the carbonyl groups on the cellulose stabilizes it against degradation during the oxygen delignification stage.

Effect of $NaBH_4$ charge. We further studied the effect of sodium borohydride charge on the performance of the O_{MgO+R} process. A sulfite pulp with a kappa number of 25.2 and viscosity of 43.1 mPa·s was used. The sodium borohydride charge varied from zero to 0.02%, 0.035%, 0.05%, 0.1%, and 0.2%. The kappa number, viscosity, and pulp yield of the O_{MgO+R}-delignified pulps at various $NaBH_4$ charges are given in **Table III**. These results clearly show that the pulp viscosity is significantly improved when sodium borohydride is present during the oxygen stage. In addition, it shows that a sodium borohydride charge as low as 0.035% is sufficient to achieve the desired beneficial effects.

It has been hypothesized that the improved performance of the $NaBH_4$-

$NaBH_4$ charge, % on pulp	Kappa number	Pulp viscosity, mPa·s	Brightness, % ISO
0	12.8	27.8	57.7
0.02	15.3	29.4	56.6
0.035	15.5	38.8	56.6
0.05	13.9	41.9	59.6
0.1	12.4	43.0	62.5
0.2	14.6	43.0	60.9

III. Effect of $NaBH_4$ charge on oxygen delignification of sulfite pulp

Samples	Copper number
Unbleached pulp	2.16
O_{MgO}-delignified pulp	1.60
O_{MgO+R}-delignified pulp*	1.35

*0.1% $NaBH_4$

IV. Comparison of copper numbers

O_2 delignification process	Kappa number	Pulp viscosity, mPa·s	Brightness, % ISO
O_{MgO}	12.8	27.8	57.7
O_{MgO+R}*	12.4	43.0	62.5
RO_{MgO}*	13.8	39.5	59.9
$O_{MgO}R$*	12.0	32.9	63.3

*0.1% $NaBH_4$

V. Effect of sequence of $NaBH_4$ addition on oxygen delignification of sulfite pulp

assisted oxygen delignification can be ascribed to the effective reduction of carbonyl groups on the cellulose molecules. We estimated the carbonyl content of the sulfite pulps in accordance with the copper number test *(6)*. The results are shown in **Table IV**. It is evident that the copper number of the O_{MgO+R}-treated pulp is lower than that of the O_{MgO}-delignified pulp, which confirms the hypothesis that carbonyl groups are reduced with the addition of sodium borohydride.

Sequence of $NaBH_4$ addition. We also studied the effect of different sequences of $NaBH_4$ addition on oxygen delignification:

1. Reduction with $NaBH_4$ during the oxygen stage, O_{MgO+R}
2. Reduction with $NaBH_4$ first, followed by an oxygen stage, RO_{MgO}
3. An oxygen stage first, followed by reduction with $NaBH_4$, $O_{MgO}R$.

The results are summarized in **Table V**. One can observe that the RO_{MgO} and the O_{MgO+R} processes can deliver well-delignified pulps with similar viscosity, higher than that of the O_{MgO}-delignified pulp. On the other hand, the $O_{MgO}R$ sequence leads to a delignified pulp with significantly lower viscosity compared with the RO_{MgO} and the O_{MgO+R} process, although moderately higher than the O_{MgO} process alone. These results clearly show the superior performance of the RO_{MgO} and O_{MgO+R} processes and support the hypothesis that removal of the carbonyl groups on the cellulose molecules of sulfite pulps suppresses carbohydrate degradation during the subsequent oxygen delignification stage.

CONCLUSIONS

The presence of carbonyl groups on the cellulose molecules of sulfite pulps increases carbohydrate degradation during oxygen delignification. Sodium borohydride can efficiently reduce the carbonyl groups, thus improving the lignin-to-carbohydrate selectivity and pulp yield without affecting delignification during the oxygen stage.

The strength properties of fully bleached sulfite pulp using a sodium borohydride-assisted oxygen delignification stage were superior to those of a bleached pulp produced by the same bleaching sequence without sodium borohydride. The higher pulp strength was achieved because the sodium borohydride removed the carbonyl groups, which improved the bonding capability of cellulose fibers and minimized carbohydrate degradation during the bleaching stages.

It was found that sodium borohydride reduction is very fast, so that practically no retention time is needed. The reaction conditions for sodium borohydride reduction are also compatible with those of oxygen delignification. Furthermore, sodium borohydride is reasonably stable under the conditions of oxygen delignification. Therefore, it should be possible to combine oxygen delignification and sodium borohydride reduction within a single process, thus eliminating the need for a separate reduction stage.

Sodium borohydride-assisted oxygen delignification can be performed by mixing the pulp slurry with magnesium oxide and sodium borohydride first, followed by the desirable retention time in the pressurized reactor. This improved oxygen delignification process for sulfite pulps may be economically feasible because the sodium borohydride charge required to achieve the expected results is rather low, typically in the range of 0.02–0.05%. TJ

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LITERATURE CITED

1. Bokstrom, M. and Tigerstrom, A., *Pulp Paper Can.* 92(11): 38(1992).
2. Luo, J. and Christensen, P. K., *Tappi J.* 75(6): 183(1992).
3. Hartler, N., *Svensk Papperstid.* 65(14): 535(1962).
4. Chirat, C. and Lachenal, D., *Holzforschung* 48(Suppl): 133(1994).
5. Browning, B. L., *Methods of Wood Chemistry*, Vol. 2, Interscience, New York, 1967, p. 165.
6. Browning, B. L., *Methods of Wood Chemistry*, Vol. 2, Interscience, New York, 1967, p. 430.