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# Sodium Perborate Usage instead of Hydrogen Peroxide for the Reinforcement of Oxygen Delignification

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## Abstract

Oxygen has always been an attractive oxidant for the pulp and paper industry due to it being cheap and harmless for the environment. However, it has lower lignin-cellulose selectivity, therefore the degree of delignification achieved at the oxygen stage is ultimately limited by its industrial pulp strength – 45-50%. In this study, to enhance the degree of delignification, the addition of sodium perborate and hydrogen peroxide at the oxygen stage was examined. At the same active oxygen (approximately 0.5%) content, the degree of delignification increased from 45.56% to 49.42% using hydrogen peroxide and to 52.96% with sodium perborate. For the same selectivity parameter with control, the delignification degree can be increased to 57.59% with the addition of sodium perborate, which includes 1% active oxygen. Moreover, the costs of using sodium perborate and hydrogen peroxide were compared with respect to commercial employability. It was determined that the use of sodium perborate was more effective than that of hydrogen peroxide for delignification of the oxygen stage.

**Key words:** oxygen delignification, sodium perborate, selectivity, active oxygen, hydrogen peroxide.

## Introduction

During the kraft pulping process, extensive lignin fragmentation and degradation occurs, leading to the generation of new free phenolic hydroxyl groups. Under the alkaline conditions employed, these hydrophilic groups are ionised, resulting in approximately 90% of the lignin being dissolved in the cooking liquor [1]. By the end of the cooking, the majority of  $\beta$ -aryl ether structures have been cleaved, and consequently the ability to generate new phenolic sites decreases, making the residual lignin more resistant to dissolution. The remaining lignin is more resistant to hydrolytic degradation, requiring oxidative degradation over several stages to be removed [2]. Traditionally, chlorine and/or chlorine dioxide can be utilised, but environmental regulations are increasingly mandating the replacement of such chemicals. The major alternatives currently employed are oxygen-based chemicals such as molecular oxygen and hydrogen peroxide [2].

At present, oxygen delignification is widely used for lignin removal in pulping and bleaching. The chemical cost savings realised by displacing chlorine or chlorine dioxide with oxygen and caustic, as well as the ability to recycle the filtrate in the recovery furnace are the main advantages of oxygen delignification. However, the capital costs and lower lignin-cellulose selectivity compared to chlorine dioxide bleaching are handicaps of the oxygen delignification stages. The lower selectivity of oxygen delignifica-

tion leads to weaker pulp fibers and limits single stage delignification to ~50% [3]. Several researches, such as the pretreatment of pulp prior to oxygen delignification and the reinforcement of oxygen delignification with a reactant, have been undertaken to try and overcome this handicap. The first study about combining the effects of hydrogen peroxide and oxygen for the bleaching of chemical pulp was undertaken in 1980's, and a synergy was determined between oxygen and peroxide [4,5]. Parthasarathy and coworkers showed that peroxide with oxygen had additional effects on the delignification of pine kraft pulps, resulting in improved selectivity and delignification efficiency. The addition of 0.5% hydrogen peroxide at the oxygen delignification stage caused a 60% reduction in the kappa number as compared to a conventional oxygen delignification stage [6]. Parthasarathy and coworkers also examined the peroxide reinforcement of the double-stage oxygen delignification process. Using the (PO)(PO) process, the kraft pulps delignified showed a kappa number of about 73% of the original, as compared to 61% for the double oxygen stage with an addition of 0.5% hydrogen peroxide to the oxygen delignification media [6].

Besides hydrogen peroxide, similar oxidising agents such as sodium perborate can be utilised for the reinforcement of oxygen delignification. Sodium perborate monohydrate is used in the formulation of concentrated detergents as well as in certain medical, disinfectant, and cleaning preparations. Sodium

perborate monohydrate ( $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ ) contains 16% active oxygen, and it does not have a specific melting point. When heated, it decomposes by releasing oxygen and water. Sodium perborate monohydrate is preferred to tetrahydrate due to its higher oxygen content and faster dissolution rate. In addition, monohydrate is more stable than tetrahydrate in storage [7].

Meshcherova and coworkers conducted laboratory studies on the use of sodium and potassium perborates for bleaching softwood kraft pulps. They compared the physico-chemical and mechanical properties of the bleached pulps and concluded that it is more advantageous to bleach kraft pulp with potassium perborate than hydrogen peroxide [8]. Varennes and coworkers used sodium perborate tetrahydrate for bleaching thermomechanical pulp, reaching a brightness as high as 75% ISO with the addition of 6.5% sodium perborate tetrahydrate [9]. Moreover, by using sodium perborate monohydrate for the bleaching of SGW (Stone Ground Wood) pulp, the brightness of the pulp increased from 49.64% to 64.74% ISO with a 1% active oxygen dosage [10]. Based the information above, we used sodium perborate for the reinforcement of oxygen delignification.

In this study, the effects of sodium perborate monohydrate reinforcement on oxygen delignification was investigated as an alternative to hydrogen peroxide for enhancing the delignification capacity of the oxygen stage.

## Methodology

Eastern Spruce (*Picea orientalis* L.) kraft pulps were used for experiments, which had the following properties:

- Kappa Number – 33.2
- Pulp viscosity – 917 cm<sup>3</sup>/g
- Screened pulp yield – 47.2%

Oxygen delignification was carried out in a 15 L stainless steel reactor heated electrically, the temperature of which was controlled by an OMRON 55 CK digital process controller to within  $\pm 0.2^\circ\text{C}$ . Loading of the reactor was done manually, and 100 g o.d. of the spruce kraft pulp was used in each experiment. The pulp was diluted to a consistency of 12% with 0.2% MgSO<sub>4</sub> and 2% NaOH added to the pulp. For reinforcement of the oxygen delignification, peroxide and sodium perborate with a charge varying from 0.25% to 1.5% was used as active oxygen on oven dry pulp. The constant temperature was set at 90°C and the process time at 60 minutes. An oxygen pressure of 690 kPa was used in each experiment. For comparison, the charges of the reagents were selected according to the active oxygen content. The active oxygen content of peroxide and sodium perborate monohydrate is 47% and 15%, respectively.

Following oxygen delignification, the pulp was washed twice with distilled, deionised water at a consistency of 1% and then pressed to a high consistency (>25%) for yield determination.

The kappa numbers of the pulps were determined according to the TAPPI method T236. The viscosity of the pulps were determined according to the standard method SCAN cm 15:88. Correlation between the SCAN viscosity and DP was made using formula (1):

$$DP = (0.75 * [\eta_{\text{scan}}])^{1.105} \quad (1)$$

In order to expose the selectivity to oxygen delignification, selectivity parameter S, developed by Van Heinengen et al. was calculated as follows [3]:

$$S = \frac{\Delta K_c}{(1/DP_t - 1/DP_0)} \quad (2)$$

$\Delta K_c$  – Difference in Kappa number,  
 $DP_t$  – Polymerisation degree of Oxygen delignified pulp,  
 $DP_0$  – Polymerisation degree of the pulp

## Results and discussion

### Determination of the optimum alkaline charge for the oxygen delignification stage

Eastern Spruce (*Picea orientalis* L.) kraft pulp was exposed to oxygen delignification with a varying alkaline content, from 1% to 5%. Other process parameters were similar to those in conventional mill scale application (Pulp consistency – 12%, reaction temperature – 90°C, reaction time – 60 minutes, oxygen pressure – 690 kpa, MgSO<sub>4</sub> addition – 0.02%). Pulp properties subjected to oxygen delignification are shown in **Table 1**. At an alkaline charge of 2% and delignification degree of 45.6%, the minimum relative degradation of the pulp was determined. When other parameters were kept constant at a conventional mill-scale level, the optimal alkaline charge for oxygen delignification was selected as being 2%. (**Table 1**)

### Effects of peroxide and sodium perborate on delignification, viscosity and selectivity parameters

In optimum oxygen delignification conditions, a number of experiments were conducted with peroxide and sodium perborate added to the reaction media. **Table 2** gives the average of the dupli-

cate test result with peroxide and sodium perborate added. For comparison, the charges of the reagents were calculated as active oxygen on oven dry pulp.

However, both reagents increased the delignification, and sodium perborate caused significant delignification augmentation. With an addition of (as active oxygen to o.d. pulp) peroxide of 0.5%, the delignification degree rose from 45.56% to 49.41% in comparison with the control. Furthermore, with a sodium perborate addition of 0.5%, the delignification degree rose to 52.96% (**Figure 1** – see page 108).

Hydroperoxide anion (HOO<sup>-</sup>) is an active species and is responsible for the bleaching action of hydrogen peroxide under alkaline conditions. On the other hand, hydroperoxyl and hydroxyl radicals generated by the decomposition of hydrogen peroxide are responsible for delignification [6]. Hydroxyl radicals are capable of attacking practically all types of organic structures, including those containing hydroxyl and ether linkages [6]. Similar reactions occur with sodium perborate, but its alkalinity is higher than that of hydrogen peroxide; in this respect sodium perborate has significant effects on delignification at the same active oxygen charge. Parthasarathy and coworkers showed

**Table 1.** Properties of oxygen delignified eastern spruce kraft pulp.

Alkaline charge, %	Kappa Number	Scan viscosity, cm <sup>3</sup> /g	General yield, %	Process yield, %	Delignification degree, %	Relative degradation ( $\Delta\eta/\Delta k$ )
Pulp	33.3	917	47.2	–	–	–
1%	24.6	839	46.8	99.1	26.1	9.01
2%	18.1	793	46.4	98.4	45.6	8.20
3%	14.1	752	46.2	98.0	57.5	8.65
4%	13.1	713	45.5	96.4	60.7	10.1
5%	12.4	697	45.4	96.1	62.6	10.6

**Table 2.** Properties of the hydrogen peroxide and sodium perborate reinforced oxygen delignification stages.

Delignification	Charge of Reactives (active oxygen, %)	Pulp Viscosity, cm <sup>3</sup> /gr	Kappa Number	Brightness (ISO), %
Hydrogen peroxide reinforced oxygen delignification	0.00	793.00	18.10	37.10
	0.25	816.34	16.87	37.78
	0.50	814.40	16.82	39.83
	1.00	796.40	16.48	40.53
	1.50	790.00	15.74	41.96
Sodium perborate reinforced oxygen delignification	0.00	793.00	18.10	37.10
	0.25	790.35	16.67	39.41
	0.50	784.53	15.64	39.93
	1.00	766.61	14.10	42.55
	1.50	726.26	13.69	44.88

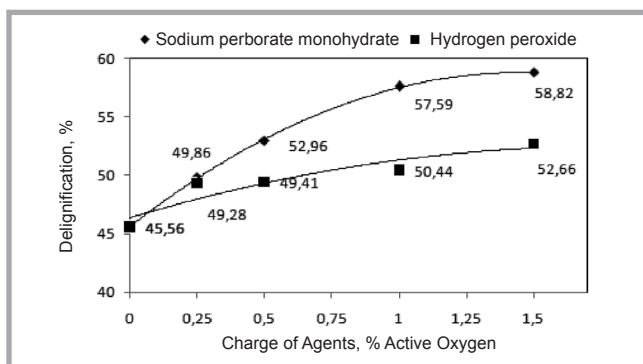


Figure 1. Effects of sodium perborate and hydrogen peroxide charges on the delignification degree of the oxygen stages.

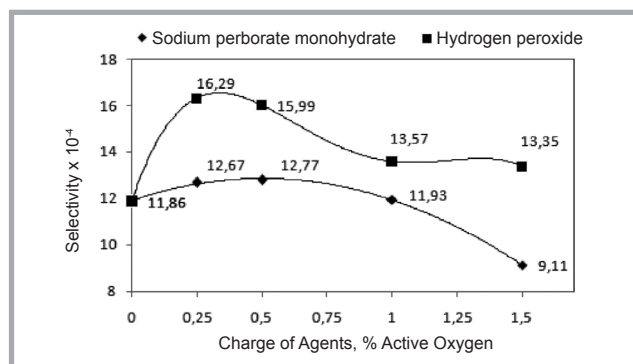


Figure 2. Effects of sodium perborate and hydrogen peroxide charges on the selectivity of the reaction during oxygen delignification.

that hydrogen peroxide with oxygen has an additional effect on the delignification of kraft pulps. Hydrogen peroxide charges of 0.2-0.5% applied at the oxygen stage resulted in pulps with a lower kappa number and higher viscosity [6]. In this study the viscosity of the pulp and the selectivity of the reaction increased with the addition of hydrogen peroxide. Nonetheless, with sodium perborate, the viscosity of the pulp decreased, whereas

Table 3. Cost of the chemical agents [9,11,12].

Chemical agent	Cost US\$/kg
Oxygen	0.0600
Magnesium sulfate	0.3527
Sodium hydroxide to 50%	0.3478
Hydrogen peroxide to 50%	0.3500
Sodium perborate tetrahydrate	0.4200
Sodium perborate monohydrate	0.7100

the selectivity of the reaction increased up to a 1% charge. This situation can be explained by detailed examination of the delignification and selectivity parameters all together. As can be seen in Figures 1 and 2, with an addition of peroxides of 0.5% (active oxygen), the selectivity increased from 11.86 to 15.99 and the delignification – from 45.56% to 49.41%. On the other hand, with a 0.5% addition of (active oxygen) sodium perborate, the selectivity increased to only 12.77, whereas the delignification increased to 52.99% (Figures 1 & 2).

In fact, with a 0.5% addition of sodium perborate, a delignification ratio of 7.43% was achieved without a loss of selectivity. For the same selectivity value with control (11.9), a 1% addition of sodium perborate increased the delignification degree from 45.56% to 57.59%. These results clearly indicate that, because of extra alkalinity, sodium perborate is more

effective than hydrogen peroxide for the reinforcement of oxygen delignification.

### Cost parameters of sodium perborate and hydrogen peroxide reinforced oxygen delignification

The costs of the chemical agents used in this work are summarised in Table 3 with respect to commercial employability. Sodium perborate is more expensive than hydrogen peroxide because of the use of peroxide during perborate production. On the other hand sodium perborate includes extra alkaline, and consequently it needs less alkaline charge than hydrogen peroxide for oxygen delignification.

For an active oxygen charge of 0.5%, 21.2 kg of hydrogen peroxide (50%) per ton of pulp, a 33.3 kg of sodium perborate monohydrate, and 49.02 kg of sodium perborate tetra hydrate per ton of pulp were needed.

As shown in Table 4, sodium perborate reinforced oxygen delignification is \$ 16.2 more expensive than hydrogen peroxide reinforced oxygen delignification for the same active oxygen charge; however, the delignification gained is 3.55%

Table 4. Cost of the reinforced oxygen delignification stages per ton of pulp.

Component	Charge, %		
	Hydrogen peroxide reinforced OD	Hydrogen peroxide reinforced OD	Sodium perborate monohydrate reinforced OD
Oxygen	2.49 (7 Bar)	2.49 (7 Bar)	2.49 (7 Bar)
Magnesium sulfate	0.05	0.05	0.05
Sodium hydroxide	2	2	2
Hydrogen peroxide	0.5 (activated oxygen)	1.5 (activated oxygen)	–
Sodium perborate	–	–	0.5 (activated oxygen)
Cost, US\$/ODMT	23.00	37.98	39.22
<b>According to the Control, Delignification and Selectivity Augmentation of Reinforced O.D.</b>			
Delignification, %	49.41	52.66	52.96
ΔDelignification, %	3.85	7.10	7.40
ΔSelectivity, Sx10 <sup>-4</sup>	4.13	1.49	0.91

higher than peroxide reinforced oxygen delignification without selectivity loss. In other words, to obtain a delignification ratio of 52.5%, a peroxide charge of 1.5% (as active oxygen to o.d. pulp) was needed, whereas with perborate monohydrate only an active oxygen charge of only 0.5% was enough. Consequently, peroxide reinforcement increased the oxygen delignification cost to \$ 37.983 (Table 4) for a higher delignification ratio (52.5%)

### Conclusions

The effects of sodium perborate and hydrogen peroxide reinforcement on the delignification ratio and selectivity of the oxygen stage have been demonstrated. Both reactants increased the degree of delignification without selectivity loss. Sodium perborate was more effective than hydrogen peroxide at a high delignification ratio, which is because of the increase in the alkalinity of the oxygen delignification media, as compared with hydrogen peroxide. Nevertheless sodium perborate is expensive because of the use of peroxide during perborate production

and the increase in the cost of oxygen stage. In addition to this, more residual lignin can be removed by sodium perborate instead of hydrogen peroxide. In this respect, the cost of the oxygen stage or the chemicals for following bleaching stage can be decreased by using sodium perborate. Moreover, it is a good alternative for peroxide because it is more stable and can be stored in a solid form.



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