

# Application of peroxymonosulfuric acid as a modification of the totally chlorine-free bleaching of acacia wood prehydrolysis-kraft pulp

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**Abstract** The totally chlorine-free (TCF) bleaching process avoids the generation of organochlorine substances. In this study, the application of peroxymonosulfuric acid ( $\text{H}_2\text{SO}_5$ ;  $\text{P}_{\text{sa}}$ ) to TCF bleaching was proposed as a modification of the bleaching process of hardwood prehydrolysis-kraft pulp. *Acacia mearnsii* pulps were treated by oxygen bleaching, followed by  $\text{P}_{\text{sa}}$  treatment, ozone bleaching, alkali extraction, and finally, hydrogen peroxide bleaching. The  $\text{P}_{\text{sa}}$  treatment was conducted with 10 % pulp consistency at pH 3 and 70 °C. The use of  $\text{P}_{\text{sa}}$  increased the removal of hexenuronic acid from the pulp and improved pulp brightness. After the final hydrogen peroxide bleaching, pulp brightness increased to 86.0 % ISO with a 0.6 %  $\text{P}_{\text{sa}}$  dosage. The  $\text{P}_{\text{sa}}$  treatment showed better selectivity, i.e., kappa number decrement per unit of viscosity, compared with ozone bleaching. A dosage of 0.2 %  $\text{P}_{\text{sa}}$  afforded a 3.4 kappa number decrement with a 10.9 cP viscosity loss, while ozone treatment with a dosage of 0.5 % resulted in a 2.6 kappa number decrement with a 12.5 cP viscosity loss.

The results showed that the  $\text{P}_{\text{sa}}$  treatment can enhance pulp quality in terms of brightness and reduce ozone consumption, which improves the TCF bleaching process.

**Keywords** Peroxymonosulfuric acid · Prehydrolysis-kraft pulp · Totally chlorine-free bleaching · Hexenuronic acid · Hardwood pulp

## Introduction

Indonesia is the ninth largest pulp producer and is the sixth in production of paper and paper board in the world, with the largest volumes generated by two pulp and paper mill groups, Asia Pulp and Paper and Asia Pacific Resources International Limited [1]. The pulp production capacity in Indonesia was 8.8 million tons in 2013, and should increase to 10 million tons by 2017. During production, almost all the Indonesian pulp bleaching mills use chlorine dioxide in elemental chlorine-free (ECF) bleaching.

The switch from chlorine bleaching to ECF bleaching has significantly lowered the quantity of organochlorine substances released in effluent streams and, accordingly, has reduced environmental toxicity. In Japan, the 2007 emissions of adsorbable organic halogen (AOX) or organochlorine substances were reduced to one-fifth of 1997 levels by the switch to ECF bleaching [2, 3]. However, ECF bleaching still discharges organochlorine compounds in the form of chloroform from the bleaching and wastewater treatment processes [2, 4]. In addition, organochlorine species are still present in the effluent and accumulate in the activated sludge during wastewater treatment.

In contrast, totally chlorine-free (TCF) bleaching is a process that eliminates the possibility of AOX formation. The interchange of ECF with TCF bleaching will further

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diminish AOX emissions as well as the amounts of organochlorine substances found in effluents, activated sludge, and the air. However, we must also note that TCF bleaching can produce harmful non-chlorinated environmental pollutants [5]. Furthermore, based on investigations [6], the TCF bleaching process also has the potential to produce halogenated compounds. Even in low concentrations, chloride ions can be incorporated into halogenated byproducts. In a practical sense, to diminish AOX formation in the system, all processes should be totally free from supplemental chloride ions, including the closed water system.

Hexenuronic acid (HexA) is considered to cause the brightness reversion (yellowing) of pulp and increases the consumption of bleaching reagents [7–9]. HexA is an unsaturated molecule that contributes to the consumption of permanganate during the determination of the kappa number, which is proportional to the lignin content, and results in higher values during lignin determinations. It has been reported that the removal of HexA from TCF pulp affects the pulp properties [10].

Peroxymonosulfuric acid ( $\text{H}_2\text{SO}_5$ ;  $\text{P}_{\text{sa}}$ ) has been identified as a promising alternative reagent for the delignification of wood and the bleaching of chemical [11–13]. During oxygen delignification, the treatment of a chelated pulp with  $\text{P}_{\text{sa}}$  was shown to afford kappa number reduction [14].  $\text{P}_{\text{sa}}$  can improve the brightening of chemical pulp from the perspective of ECF bleaching [15], as well as solubilize lignin [16] and decompose HexA [17, 18]. Recently, it was found that highly stable  $\text{P}_{\text{sa}}$ , as Caro's acid (a mixture of concentrated sulfuric acid and hydrogen peroxide) could be produced on industrial scale [19], and was successfully incorporated in the bleaching process in Japanese paper mills as a substitute for the acid washing stage during hardwood ECF bleaching [20].

In this study, to determine a new sequence for TCF bleaching, the application of  $\text{P}_{\text{sa}}$  as a modification of the TCF bleaching process was investigated on hardwood prehydrolysis-kraft (Ph-kraft) pulp.

## Experimental

### Materials

Acacia (*Acacia mearnsii*) wood chips were obtained from South Africa.  $\text{P}_{\text{sa}}$  was synthesized by dropping 95 % sulfuric acid (Wako Pure Chemical Industries, Ltd.) into 45 % hydrogen peroxide aqueous solution (Mitsubishi Gas Chemical Company, Inc.) at 70 °C. The molar ratio of  $\text{H}_2\text{SO}_4$  to  $\text{H}_2\text{O}_2$  was 3.0. After mixing, the solution was immediately diluted with chilled water. The  $\text{P}_{\text{sa}}$  concentration was determined by subtracting the amount of redox titration with cerium (IV) sulfate, which can oxidize

residual  $\text{H}_2\text{O}_2$ , from the total amount of peroxide determined by iodometric titration using  $\text{Na}_2\text{S}_2\text{O}_3$ . Oxygen-bleached hardwood kraft pulp (LOKP) was prepared from eucalyptus–acacia mixed hardwoods as a non-prehydrolysis-kraft pulp, and was provided by the Niigata Mill, Hokuetsu Kishu Paper Co., Ltd., Japan.

### Prehydrolysis and kraft cooking

Acacia wood chips were prehydrolyzed at 147 °C for 90 min, and kraft-cooked with 18 % active alkali and 30 % sulfidity at 150 °C for 1–3 h (H-factor: 165–496). The liquor-to-wood ratio was 4 mL/g.

### $\text{P}_{\text{sa}}$ treatment

Laboratory-prepared pulps and the Niigata mill LOKP were treated with  $\text{P}_{\text{sa}}$  for 70 min at 70 °C at a pulp consistency (PC) of 10 %. A target amount of  $\text{P}_{\text{sa}}$  solution and aqueous sodium hydroxide to adjust the acidity to pH 3 was added to the pulp suspension.

To determine the required dosage of  $\text{P}_{\text{sa}}$  to the pulp, it was considered that the required molar ratio of  $\text{P}_{\text{sa}}$  to a HexA model compound (hexenuronosyl-xylotriose:  $\Delta\text{-X3}$ ) for degradation was about 3.4 [21]. When the  $\text{P}_{\text{sa}}$  dosage is 1.0 % of the pulp weight, it is estimated that 87.7 mmol  $\text{P}_{\text{sa}}$  is added to 1 kg pulp. It is expected that approximately 26 mmol HexA can be removed from 1 kg pulp.

### TCF bleaching

Pulps were treated under the following conditions:

#### 1. Oxygen bleaching (O)

PC: 30 % (high consistency); oxygen pressure: 0.5 MPa; NaOH dosage: 1 %; reaction temperature and time: 115 °C for 60 min.

#### 2. $\text{P}_{\text{sa}}$ treatment ( $\text{P}_{\text{sa}}$ )

Conditions are as described above.

#### 3. Ozone bleaching (Z)

PC: 30 % (high consistency); pH 3; ozone dosage: 0.5 %; reaction temperature and time: 28 °C for 15 min.

#### 4. Alkali extraction (E) and hydrogen peroxide bleaching (P)

E: PC:10 %; NaOH dosage: 1 %; reaction temperature and time: 60 °C for 60 min.

P: PC:10 %;  $\text{H}_2\text{O}_2$  dosage: 1.4 %; NaOH dosage: 1 %; reaction temperature and time: 70 °C for 60 min.

## Pulp testing

Kappa number, viscosity and brightness were determined according to TAPPI Test Methods: T236 om-13, T254 cm-10 and T452 om-08, respectively [22]. The brightness (ISO) was measured using a Tokyo-Denshoku Digital Color Meter Model TC-1500 SX. HexA content was determined from 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid after formic acid hydrolysis at pH 2.5 and 120 °C for 3 h, using high-performance liquid chromatography with 4:1 acetonitrile–water (pH 2.5) solution as eluent and a detection wavelength of 265 nm [23]. A Zorbax ODS column ( $\Phi$  4.6  $\times$  250 mm) was used. Acid-insoluble lignin was measured using the Klason lignin method (TAPPI Test Method T222 om-11 [22]), and acid-soluble lignin was determined by UV–Vis spectrophotometry [24]. The carbohydrate composition of the pulp and the monosaccharide and oligosaccharide contents of the hydrolyzate were determined using a Dionex ICS 3000 ion chromatograph after 4 % sulfuric acid hydrolysis at 121 °C for 1 h [25].

## Calculations of selectivity and effectiveness

Selectivity was calculated as the kappa number decrease per unit of decreased viscosity ( $\Delta$ kappa number/ $\Delta$ viscosity), while effectiveness was calculated as the kappa number decrement per unit chemical dosage ( $\Delta$ kappa number/unit chemical dosage).

## Results and discussion

### Characterization of raw materials

The prehydrolysis process is an important step for producing dissolving pulp with kraft cooking, which consists of removing part of the hemicelluloses [26]. As shown in Table 1, xylan was a major component removed during the prehydrolysis process. The prehydrolysis also removed a very small part of the lignin.

Table 2 shows that the kappa number of the Ph-kraft pulp was lower than that of the non-Ph-kraft pulp,

indicating a lower lignin content. It was reported that holes that are created in the cell walls of the material after the dissolution of amorphous hemicellulose would allow the favorable penetration of chemicals in the subsequent cooking [27]. In addition, the final conditions of the prehydrolysis treatment are acidic (pH 4.5), which may cause the cleavage of lignin–carbohydrate complex bonds, and thus improve the subsequent alkaline delignification.

### Effects of $P_{sa}$ treatment on kappa number and HexA content

Kuwabara et al. [8] reported on the relationship between  $P_{sa}$  dosage and the decomposition of HexA in pulp. A higher dosage of  $P_{sa}$  contributes to increased HexA decomposition. The reaction displays a linear correlation in the range of 0.5–1.5 %  $P_{sa}$  dosage for LOKP. This implies that a 1.0 %  $P_{sa}$  loading contributes to the decomposition of 13–15 mmol/kg HexA. If HexA in the pulp could react with  $P_{sa}$  with an efficiency similar to that of the HexA model compound  $\Delta$ -X3, a 1.0 %  $P_{sa}$  dosage to the pulp would contribute to the decomposition of 26 mmol/kg HexA [21]. In fact, the efficiency of HexA removal from the pulp was almost half that of the model  $\Delta$ -X3, because the pulp contained other components such as residual lignin which can react with  $P_{sa}$ , in addition to the reactions limited to the solid phase of the pulp.

Ph-kraft pulps with various kappa numbers were treated with  $P_{sa}$  before oxygen bleaching. The results showed that the kappa number and HexA content decreased while brightness increased. Niigata LOKP was also treated with several  $P_{sa}$  dosages, resulting in decrements of kappa number and HexA, while the brightness was increased (Table 3). The experimental data indicated that  $P_{sa}$  treatment effectively lowered the kappa number, which is an indicator of lignin removal. Furthermore, the effects were dose related: a higher dosage of  $P_{sa}$  contributed to a larger decrement in the kappa number. Thus, the  $P_{sa}$  treatment was able to reduce a part of the residual lignin in the pulp.

Comparing the Ph-kraft pulp and LOKP, the HexA decrement at a 1.0 %  $P_{sa}$  dosage for the former was in the range 9.0–12.0 mmol/kg, whereas that for LOKP was in the range 19.3–21.5 mmol/kg. It was found that HexA in

**Table 1** Chemical composition of *Acacia mearnsii* wood, hydrolyzate, and Ph-kraft pulp

Samples	Yield (%) <sup>a</sup>	Acid-insoluble lignin (%) <sup>a</sup>	Acid-soluble lignin (%) <sup>a</sup>	Glucan (%) <sup>a</sup>	Xylan (%) <sup>a</sup>	Other sugars (%) <sup>a</sup>	Ash (%) <sup>a</sup>	Unknown (%) <sup>a</sup>
Wood		20.3	2.9	41.5	17.1	2.1	0.5	15.4
Hydrolyzate	2.6	0.2	0.1	0.1	1.1	0.4	0.1	0.6
Ph-kraft pulp	45.2	0.7	0.4	39.2	4.3	0.8	0.1	0.03

<sup>a</sup> % based on wood

the pulp was degraded more easily by  $P_{sa}$  treatment when the content was higher.

These experiments showed that the  $P_{sa}$  treatment decreased both the kappa number and HexA content, while increasing the brightness. The application of  $P_{sa}$  in TCF bleaching, using the sequence O- $P_{sa}$ -Z-E-P, was next investigated.

Effects of  $P_{sa}$  treatment on kappa number determined using vanillyl alcohol

Figure 1a (symbol filled diamond) shows the relationship between the HexA content and  $P_{sa}$  dosage applied to oxygen-bleached Ph-kraft pulp. Application of  $P_{sa}$  to the oxygen-bleached Ph-kraft pulp caused the removal of HexA. The 0.5 %  $H_2SO_5$  dosage means that 44 mmol  $H_2SO_5$  is added to the 1 kg of pulp during the treatment, and the HexA decrement was 7 mmol/kg at this dosage. Meanwhile, the kappa number decrement as shown in Fig. 1b (symbol filled diamond) was 3.5. A previous study has shown 1 mmol/kg of the HexA decrement corresponds to approximately 0.086 of the kappa number decrement [28]. The 7 mmol/kg of the decrement indicated 0.6 of the kappa number decrement in this study, and then the difference in 3.5 of the observed decrement and 0.6, which was equal to 2.9, should be caused by the oxidation of residual lignin. To confirm this phenomenon, the kappa number decrement using vanillyl alcohol as a free-phenolic

lignin model compound was estimated after the  $P_{sa}$  treatment.

First, 0.244 mmol (37.5 mg) or 0.061 mmol (9.3 mg) of vanillyl alcohol as a lignin model was mixed with 1 ml (789 mg) of ethanol as a carbohydrate model. Then, 9 ml of water containing 0.044–0.132 mmol (0 as control) of  $H_2SO_5$  was added to the mixture. After the  $P_{sa}$  treatment for 70 min at 70 °C, 400 ml of water, 50 ml of 20 %  $H_2SO_4$  and 50 ml of 0.1 N  $KMnO_4$  were poured into a total mixture, and then the consumed  $KMnO_4$  was determined according to TAPPI Test Method T236 om-13. Figure 2 shows that 0.044 mmol of  $H_2SO_5$  addition contributed to the 1.6–3.1 of the kappa number decrement. It was confirmed that a part of the kappa number decrement observed in the  $P_{sa}$  treatment was caused by the lignin oxidation.

Application of  $P_{sa}$  to TCF bleaching

*Effects of  $P_{sa}$  on HexA removal from oxygen-bleached Ph-kraft pulp*

Figure 1a agreed with previous results for LOKP [8, 21] in which  $P_{sa}$  was an effective reagent for reducing HexA. Next, the HexA contents of oxygen-bleached Ph-kraft pulps treated with  $P_{sa}$  after ozone bleaching were examined. After ozone bleaching, the HexA content of the  $P_{sa}$ -treated pulp was further reduced (Fig. 1a, symbol filled triangle). HexA increases the consumption of bleaching reagents [7, 8]. Therefore, the reduction of HexA content would imply that  $P_{sa}$  treatment has the potential to reduce ozone consumption in the next stage.

Figure 1b shows that after treatment with  $P_{sa}$  at a dosage 0.1 %, ozone treatment did have an effect on kappa number decrement. Notably, ozone treatment showed no significant kappa number decrement after the 0.2–0.6 %  $P_{sa}$  treatment. This was an unexpected result, because the acidic oxidation treatment could lead to modification of the molecular structure of lignin [29].

**Table 2** Effect of Prehydrolysis on yield, kappa number, and HexA content of pulp

	Yield (%)	Kappa number	HexA (mmol/kg)
Non-Ph-kraft pulp	53.5	24.5	55.0
Ph-kraft pulp	45.2	13.2	18.0
Oxygen-bleached Ph-kraft pulp	–	5.3	19.1

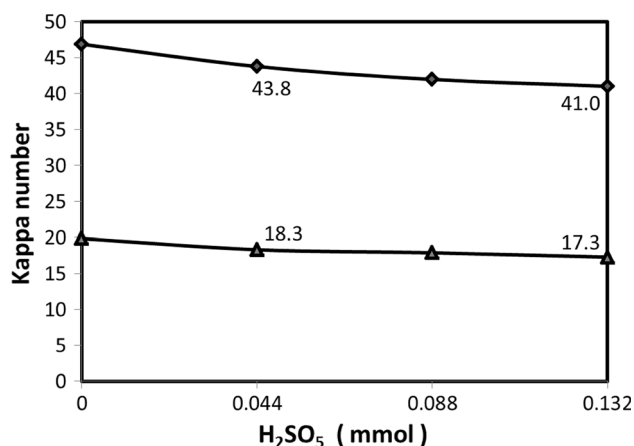
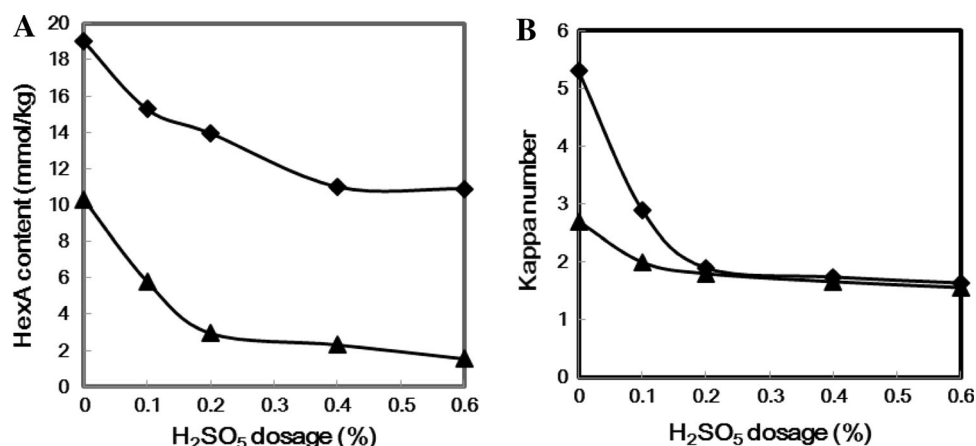
**Table 3** Effect of  $P_{sa}$  dosage on kappa number, HexA content, brightness, and viscosity of pulp

	$P_{sa}$ dosage (%)	Kappa number		HexA (mmol/kg pulp)		Brightness (% ISO)		Viscosity (cP)	
		Before	After	Before	After	Before	After	Before	After
Ph-kraft pulp <sup>a</sup>	0.20	21.5	20.7	12.6	10.8	41.4	45.9	85.3	39.3
	0.25	15.7	14.3	15.0	12.3	41.7	46.3	49.0	29.7
	0.30	13.2	11.0	18.0	14.4	41.9	47.9	46.1	27.0
LOKP <sup>b</sup>	0.20	9.1	8.4	60.4	56.1	62.3	66.1	18.2	17.3
	0.40	9.1	7.6	60.4	52.7	62.3	67.0	18.2	15.3
	0.60	9.1	7.1	60.4	47.5	62.3	69.0	18.2	11.7

<sup>a</sup> *Acacia mearnsii* pulp by kraft cooking for 1–3 h

<sup>b</sup> Eucalyptus–acacia mixed hardwood oxygen-bleached (non-prehydrolyzed) kraft pulp

**Fig. 1** HexA content and kappa number of the pulp after  $P_{sa}$  treatment of oxygen-bleached Ph-kraft pulp, with and without 0.5 % ozone application. Filled diamond  $P_{sa}$  treated; filled triangle  $P_{sa}$ -Z bleached



**Fig. 2**  $P_{sa}$  treatment of vanillyl alcohol. Filled diamond 0.244 mmol; filled triangle 0.061 mmol

#### Effects of $P_{sa}$ on brightness and viscosity

The relationship between the  $P_{sa}$  dosage and brightness showed that a higher dosage of  $P_{sa}$  increased pulp brightness. Figure 3a shows that a brightness above 85 % ISO was achieved with a  $P_{sa}$  dosage above 0.2 %. It was found that a  $P_{sa}$  dosage of 0.1 % could increase the final brightness by 1.0 unit % ISO, while at a 0.6 % dosage, brightness was increased by 2.2 unit % ISO.

However,  $P_{sa}$  applications from 0.1 to 0.6 % decreased pulp viscosity by 6.7–15.1 cP (Fig. 3b), which indicates that cellulose is partly degraded. The treatment may have low selectivity due to residual  $H_2O_2$  in the solution. For example, the loss of viscosity during ozone treatment is reportedly due to the reaction between carbohydrates and hydroxyl and perhydroxyl radicals generated as by-products [29]. It is presumed that the viscosity loss during  $P_{sa}$  treatment would be caused by hydroxyl radicals formed from the residual  $H_2O_2$ . This residual oxidant remains from the synthesis of peroxymonosulfuric acid in which 55 %

hydrogen peroxide reacts with sulfuric acid at equilibrium. The viscosity loss, as similarly observed during alkaline hydrogen peroxide treatment to improve TCF performance, might be mitigated by the addition of a chelation (Q) stage, but the effects would not be totally identical.

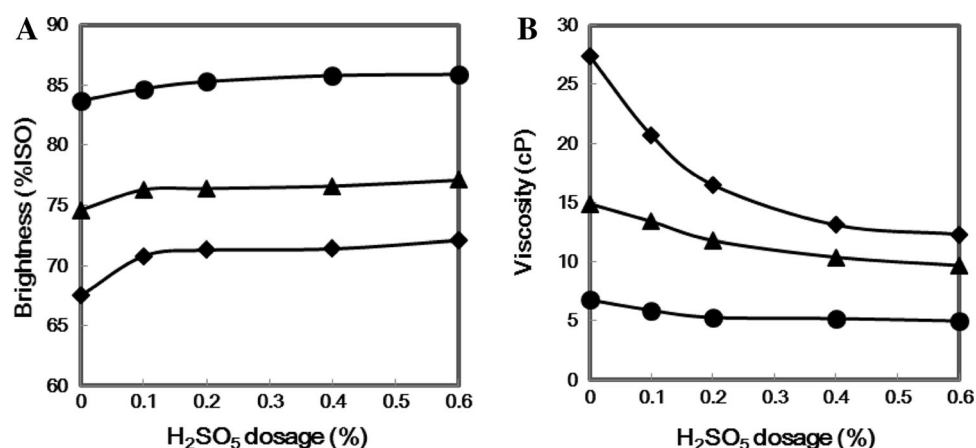
The decreasing pulp viscosity is an indicator of carbohydrate degradation in the pulp. According to Brasileiro et al. [16], peracids could be applied in the bleaching process without harming pulp strength properties, and could therefore be used in TCF bleaching without reducing pulp quality. As a result, further research is required to investigate pulp strength properties and viscosities after the application of  $P_{sa}$  in TCF bleaching. Next, the selectivity of the  $P_{sa}$  and ozone treatments is compared based on kappa number and viscosity.

#### Selectivity and effectiveness of $P_{sa}$ based on kappa number decrement

Figures 1b and 3b show plots of changes in the kappa number and viscosity vs  $P_{sa}$  dosage, respectively. A dosage of 0.2 %  $P_{sa}$  resulted in a kappa number decrease of 3.4 and a 10.9 cP viscosity loss, whereas ozone treatment at a dosage of 0.5 % gave a lower decrement of kappa number (2.6) but a higher loss of viscosity (12.5 cP). The selectivity was calculated from the kappa number and viscosity data in Figs. 1b and 3b. Table 4 reveals that ozone treatment had a selectivity of 0.21 at a dosage of 0.5 %, whereas  $P_{sa}$  application exhibited selectivity in the range 0.36–0.25 with 0.1–0.6 % dosages. Thus,  $P_{sa}$  demonstrates better selectivity than ozone treatment. The effectiveness as determined from the kappa number decrement, and the chemical dosage of  $P_{sa}$  or ozone was calculated on the basis of the data in Fig. 1b. The  $P_{sa}$  treatment has a higher effectiveness than ozone: ozone treatment with a 0.5 % dosage had an effectiveness of 5.2, whereas  $P_{sa}$  treatment had an effectiveness range of 24.0–6.2 for  $P_{sa}$  dosages of 0.1–0.6 %.



**Fig. 3** Brightness and viscosity of pulp produced by modified TCF bleaching with  $P_{sa}$  application to oxygen-bleached Ph-kraft pulp. Filled diamond  $P_{sa}$  treated, filled triangle  $P_{sa}$ -Z bleached, filled circle  $P_{sa}$ -Z-E-P bleached



**Table 4** Selectivity and effectiveness of  $P_{sa}$  and ozone treatment

$P_{sa}$ dosage (%)	Selectivity ( $\Delta$ kappa number/ $\Delta$ viscosity)		Effectiveness ( $\Delta$ kappa number/1.0 % chemical used)	
	$P_{sa}$ treated	$P_{sa}$ -Z <sup>a</sup> bleached	$P_{sa}$ treated	$P_{sa}$ -Z <sup>a</sup> bleached
0.0	–	0.21	–	5.2
0.1	0.36	0.12	24.0	1.8
0.2	0.31	0.03	17.0	0.2
0.4	0.25	0.00	9.0	0.0
0.6	0.25	0.00	6.2	0.0

<sup>a</sup> Ozone dosage 0.5 %

These results suggest a potential benefit the decreased consumption of oxidant in the Z stage. The selectivities calculated for the Z and  $P_{sa}$  stages indicate that we may theoretically decrease ozone consumption by increasing the peroxymonosulfuric acid dosage.

Bleaching was conducted using the sequence O- $P_{sa}$ -E-P, with a  $P_{sa}$  dosage of 0.2 %. The final pulp brightness achieved was 82.2 % ISO, implying that  $P_{sa}$  is a promising alternative reagent for pulp bleaching. However, the application of  $P_{sa}$  as a main bleaching agent without ozone treatment is still under further investigation.

## Conclusions

1. The application of  $P_{sa}$  to the TCF bleaching of *Acacia mearnsii* Ph-kraft pulp using the sequence O- $P_{sa}$ -Z-E-P indicated the potential for obtaining high brightness. The experiments resulted in a lower HexA content and a lower kappa number. When the  $P_{sa}$  dosage was in the range 0.2–0.6 %, the brightness reached 85–86 %ISO.
2. Although the application of  $P_{sa}$  in bleaching effectively removed HexA, cellulose was partially depolymerized during the treatment, resulting in a loss of pulp viscosity. The viscosity loss was presumed to result

from attack by hydroxyl radicals, which must originate from residual hydrogen peroxide.

3.  $P_{sa}$  application also strongly suggested the possibility of decreased ozone consumption. Compared with 0.5 % ozone treatment, the application of  $P_{sa}$  demonstrated higher selectivity and effectiveness, based on kappa number and viscosity decrements. The preliminary results suggest that  $P_{sa}$  can be applied as an alternative to ozone.

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