

Kraft Pulp Bleaching with Hydrogen Peroxide and Peracetic Acid*

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Laboratory bleaching studies were carried out on kraft pulp to investigate the influence of two bleaching oxidizers and of operating variables, namely temperature and charge of oxidizers, on pulp properties. Totally chlorine-free bleaching sequences containing either hydrogen peroxide stage or peracetic acid stage were compared on the basis of the change in brightness and in zero-span breaking length measured for bleached pulp.

In recent years consumer demands have directed bleaching conditions to elemental chlorine-free (ECF) or totally chlorine-free (TCF) bleaching sequences. Hydrogen peroxide gains importance in chemical pulp bleaching [1–4]. Decomposition of hydrogen peroxide (H_2O_2) is necessary to delignify pulp, but the rate of decomposition into reactive intermediates must be controlled in order to achieve all the goals of peroxide bleaching. The bleached reaction species of alkaline hydrogen peroxide are the hydroperoxy anion HOO^- and its decomposition intermediates as hydroxyl HO^\bullet and superoxide anion $\text{O}_2^{\bullet-}$ radicals, which have generally undesirable influence in bleaching process and also attack the cellulose chains resulting in strength loss of the fibres. Some transition metal ions such as iron, manganese, and copper accelerate the catalytic decomposition of the active perhydroxyl ion. On the other hand, other ions (*e.g.* Mg^{2+} , Ca^{2+} , SiO_3^{2-}) inhibit this acceleration. Therefore, a chelation step influencing the pulp metal profile prior to bleaching is desirable. This step reduces the concentration of the transition metal within the pulp fibres, without removing the alkaline earth metals that stabilize peroxide. Of the hundred chelating agents known, diethylenetriamine pentaacetic acid (DTPA) with eight bonding sites, is a common chelant used in the pulp and paper industry due to its ability to chelate most metal ions in a 1 to 1 ratio [5].

Despite its remarkable bleaching potential, alkaline hydrogen peroxide alone does not affect the necessary delignification to achieve a sufficiently low kappa number before final bleaching. To improve bleaching effectiveness of existing equipments, a peracid stage can be usually located immediately after alkaline hydrogen peroxide [6, 7]. When used efficiently and selectively,

peracids eliminate the last traces of resistant lignin before final bleaching, hence considerably lifting the brightness ceiling.

In this paper, appropriate conditions suitable for TCF bleaching of kraft pulp the initial kappa number of which was less than 10 were tested. TCF bleaching sequences consisting of four or five stages included both treatment with chelating agent (Q) and several bleaching stages such as alkaline extraction stage with hydrogen peroxide addition (E_P), hydrogen peroxide stage without (P) and with oxygen (P_O), and peracetic acid stage (Paa).

EXPERIMENTAL

Oxygen-predelignified kraft pulp produced by AsisDomän Sepap (Štětí, Czech Republic) was subjected to three different bleaching sequences. In order to characterize the pulp fibres used in experiments, physical properties of kraft pulp were determined as well. The degree of delignification of pulp was expressed in terms of the kappa number the value of which was found to be 9.7. The Schopper—Riegler freeness value of unbleached pulp was 13 SR. Initial brightness of untreated kraft pulp was 41.4 % ISO. The pulp metal-ion content was measured with atomic absorption spectrophotometer AAS3 (Zeiss, Jena, Germany). The levels of metal ions in the untreated oven-dried pulp ($l(\text{Me}) = m(\text{Me})/m(\text{odp})$ were ($l(\text{Me})/(\text{mg kg}^{-1})$): 6.1 (Fe), 54.3 (Mn), and 326.1 (Mg).

The chelation (Q_1 , Q_2), alkaline extraction (E_P), hydrogen peroxide (P), and peracetic acid (Paa) stages were carried out in sealed polyethylene bags. The pulp samples were hand-kneaded for one minute and treated in a preheated water bath. Every tenth

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minute the pulp batch was hand-kneaded again for approximately ten seconds. The P_O stage at high temperature and pressure was carried out in stainless-steel autoclaves placed in a preheated oil bath. The consistency of pulp (*i.e.* mass fraction (*w*) of moisture-free fibres in suspension expressed in %) in each stage was maintained at a value of 10 %.

A chelation treatment with DTPA was always done before the extraction stage. The pulp was acidified to pH ranging from 4.5 to 5 with H₂SO₄ before adding the chelation aids. Hydrogen peroxide (*w* of 49.4 mass %) and/or peracetic acid (a 34 % solution equilibrium product of peracetic acid, hydrogen peroxide, acetic acid, and water) were used as bleaching chemicals. In order to reduce degradation of cellulose, the charge of 1 kg MgSO₄ per 1 tonne of oven-dried pulp was always added in each E_P and P_O stages. After each stage a washing at 4 % pulp consistency was performed with distilled water. The pulp was washed thoroughly and then pressed to 35 % consistency. To compare the effectiveness of bleaching sequences, distilled water was used to dilution/thickening washing for most experiments.

The first and second bleaching sequences designated Q₁ E_P Q₂ P_O and Q₁ Q₂ E_P P P_O, respectively, are illustrated schematically in Figs. 1 and 2. In these figures, one can find the charge of chelant or bleaching agents, retention time (*t*), pH value, and temperature (*θ*) which characterize operating conditions of each bleaching stage. The third Q₁ Q₂ E_P Paa P_O sequence comprises the Paa stage instead of P stage in comparison with the second bleaching sequence. The retention time in the Paa stage was equal to 4 h similarly as in P stage, but pH value was maintained only at 4.5. The charge of 5 or 10 kg of peracetic acid per tonne of oven-dried pulp was applied at either 70 °C or 80 °C.

Sample sheets were formed by means of a handsheet former. The handsheet amount varied from 75 to 85 g m⁻². Using Elrepho Zeiss Opton instrument, the brightness of kraft pulp was measured for twenty samples obtained in each bleaching sequence. Zero-span breaking length, under conditions when the length of a paper strip approaches zero and so the strength prop-

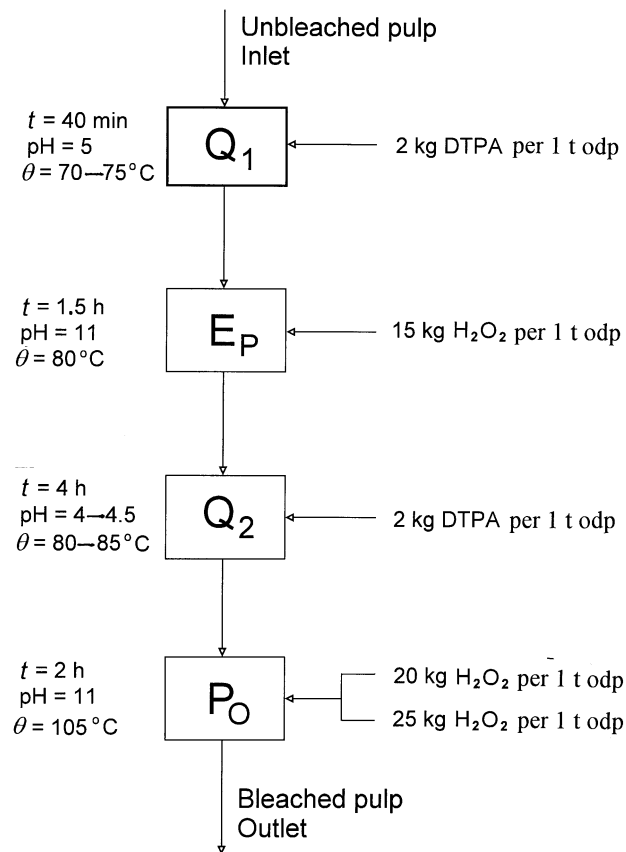


Fig. 1. Flowsheet of Q₁ E_P Q₂ P_O bleaching sequence.

erties of fibre bundles are determined, was measured for fifty samples of paper sheets by means of a breaking strength tester. Zero-span breaking length of unbleached pulp determined by this way had an average value of 3.915 km. Bleached pulp was also characterized by its intrinsic viscosity, $[\eta]$, which is a measure of its strength properties depending on molecular mass.

RESULTS AND DISCUSSION

A simple flowsheet of the first Q₁ E_P Q₂ P_O sequence is illustrated in Fig. 1. Cases examined are listed in Table 1. For unbleached kraft pulp having

Table 1. Bleaching Conditions and Content of Metal Ions for the First Q₁ E_P Q₂ P_O Sequence

Case	Wash liquid	Charge of H ₂ O ₂ in odp in P _O stage kg t ⁻¹	$[\eta]$ cm ³ g ⁻¹	<i>l</i> (Me) after Q ₂ stage		
				Fe	Mn	Mg
1A	Distilled water	20	540	10.1	0.2	62.9
1B	Distilled water	25	526	8.3	0.5	72.9
1C	Wash liquor	20	520	10.8	1.4	128.6
1D	Wash liquor	25	507	7.1	1.7	159.5

Table 2. Bleaching Conditions and Content of Metal Ions for the Second Q₁ Q₂ E_P P P_O Sequence

Case	Charge of H ₂ O ₂ in odp in P stage	Charge of H ₂ O ₂ in odp in P _O stage	Temperature in P _O stage	[η]	l(Me) after P stage		
	kg t ⁻¹	kg t ⁻¹	°C	cm ³ g ⁻¹	Fe	Mn	Mg
2A	15	20	90	475	9.8	0.6	289.9
2B	15	25	90	516	6.4	0.8	105.7
2C	10	20	90	495	8.0	0.8	262.6
2D	10	25	90	535	7.0	0.8	48.4
2E	15	20	105	481	8.6	1.4	295.6
2F	15	25	105	601	7.7	2.2	300.7
2G	10	20	105	462	9.4	2.8	287.9
2H	10	25	105	431	8.7	3.1	278.3

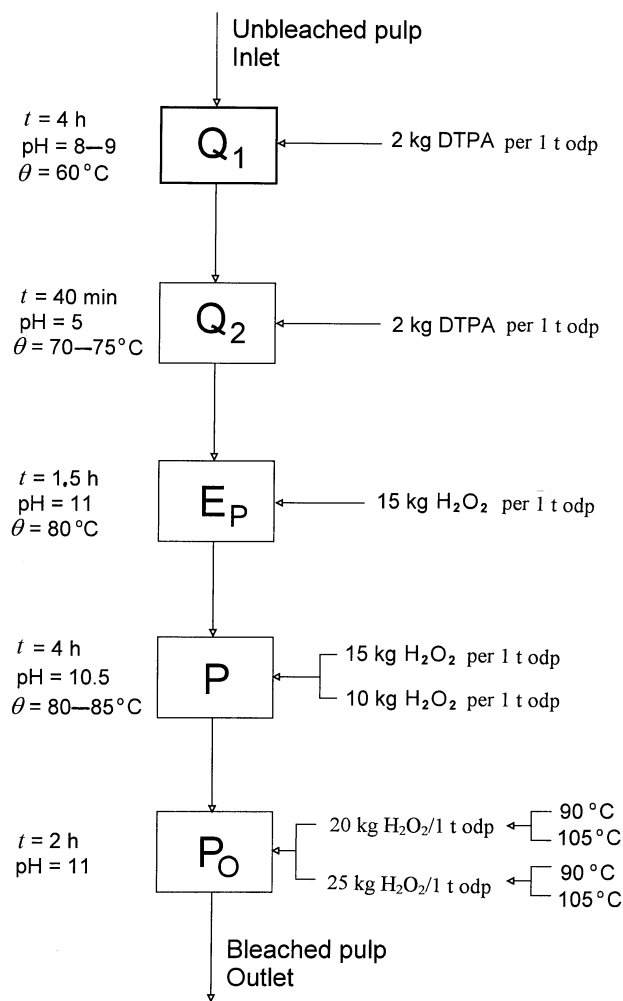
an initial brightness of 41.4 % ISO, bleaching in this sequence produces brightness increments of 14–15 points (see cases 1A and 1B in Fig. 3). Surprisingly, a higher charge of hydrogen peroxide (case 1B) did not improve the brightening capability of the P_O stage, although the zero-span breaking length had markedly lower value. It must be pointed out that DTPA addition brings down the concentration of Mn and Mg cations present in the pulp (Table 1), while the Fe level did not differ appreciably from the value for untreated pulp. Using the wash liquor to dilution/thickening washing, an increase in brightness by 3.8 (case 1C) and 9.2 points (case 1D) was attained in comparison with the cases 1A and 1B, respectively. The reason of this brightness increment can be quite simple. It can be supposed that in wash liquor residual hydrogen peroxide as well as metal cations were present.

In order to judge both properties of bleached pulp, *i.e.* brightness and zero-span breaking length, a selectivity factor can be employed. The selectivity factor, SF, was defined as

$$SF = \frac{PB_b - PB_{unb}}{ZSBL_{unb} - ZSBL_b} \quad (1)$$

It follows from Table 1 and Fig. 4 that the selectivity factor increases with increasing concentration of Mg and Mn cations as well as with decreasing intrinsic viscosity.

For the second sequence designated Q₁ Q₂ E_P P P_O (see Fig. 2 and Table 2), the results are grouped into two regions. The first region is a region of lower values of brightness (cases 2A–2D in Fig. 3), which represents the results obtained at the temperature of 90 °C in the P_O stage. The second region of higher values of brightness (cases 2E–2H) was obtained at the temperature of 105 °C in the P_O stage. The increase in pulp brightness by about 7 % ISO compared to the values at 90 °C is beneficial. For the higher temperature in the P_O stage, higher values of the selectivity factor as well as of zero-span breaking length were also measured (Figs. 3 and 4). This finding is in a good agreement with that reported by *Dence* and *Omori*

**Fig. 2.** Flowsheet of Q₁ Q₂ E_P P P_O bleaching sequence.

[1] who report that an increase in bleaching temperature not only enhances the rate of bleaching but also enhances peroxide decomposition. On the other hand, our results did not confirm the statement of these authors that an increase in peroxide charge results in an increase in brightness.

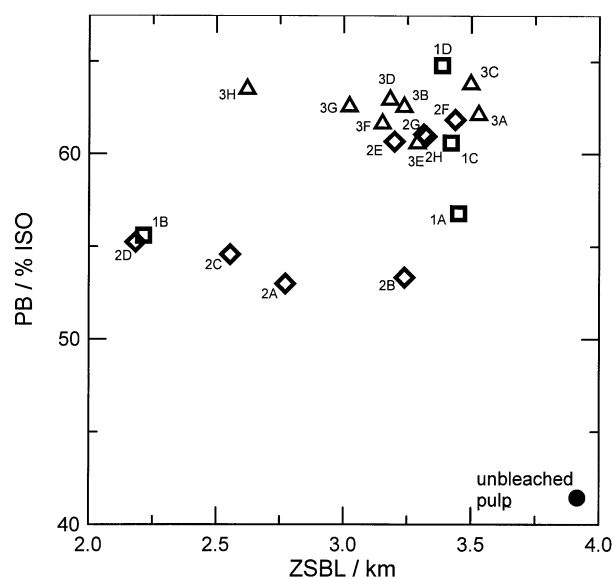


Fig. 3. Pulp brightness as a function of zero-span breaking length. Bleaching sequences are described in Tables 1–3.

The dependence of the selectivity factor on the concentration of Mn cations implies the following conclusion for the first and second sequences. With increasing content of Mn cations, the selectivity factor at

first increases rapidly, as follows from Fig. 5. After attaining a maximum of l in the region of approximately 2 mg kg^{-1} , the selectivity factor decreases. The low concentration of Mn cations is probably necessary to reach hydrogen peroxide decomposition at an optimum hydroperoxy anion concentration.

The third bleaching sequence denoted $Q_1 Q_2 E_P Paa P_O$ was similar to the second one except for the P stage which, in this case, was replaced by Paa stage. The effects of peracetic acid charge and a temperature in the Paa stage on pulp properties have been examined (Table 3). The unfavourable effect of higher temperature in the Paa stage, except for case 3H, on pulp brightness was observed (Fig. 3). For a temperature of 80°C , the zero-span breaking length decreased by about 10 %, although the concentration of Mg cations was higher in comparison with the cases 3A–3D where the temperature was 70°C . A decrease in the zero-span breaking length is in a good agreement with a decrease in the intrinsic viscosity in the case of a higher temperature in the Paa stage. A higher charge of peracetic acid improved the pulp brightness by about 1.5 % ISO, but the zero-span breaking length dropped by about 5 % in comparison with the Paa charge of 5 kg per tonne of oven-dried pulp.

Comparing this third $Q_1 Q_2 E_P Paa P_O$ sequence with the second $Q_1 Q_2 E_P P P_O$ sequence, it is evident that the presence of peracetic acid in the third

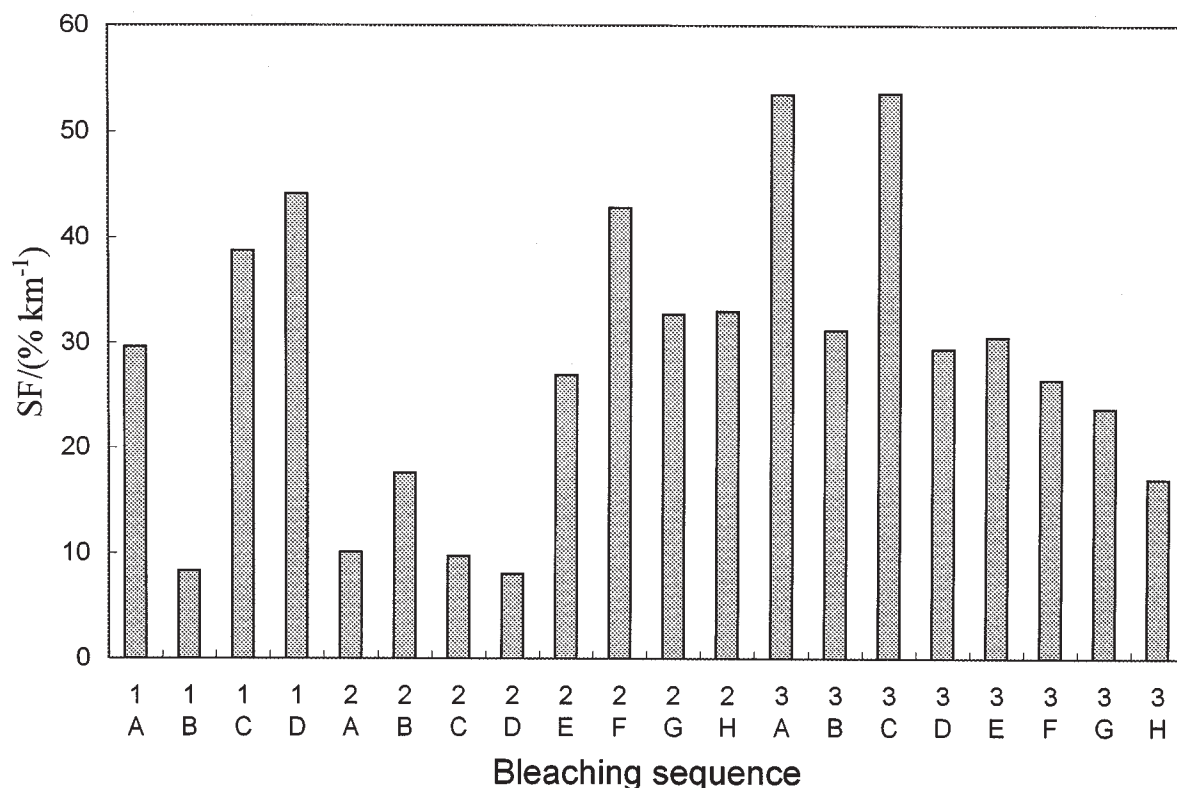
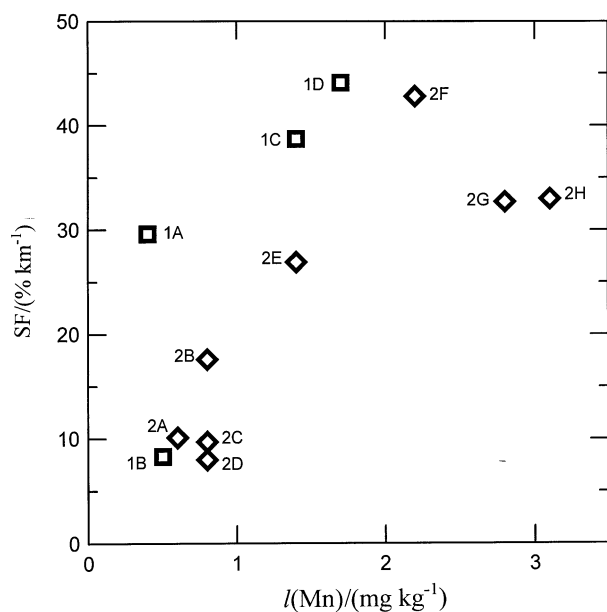


Fig. 4. The selectivity factor for bleaching alternatives measured (see Tables 1–3).

Table 3. Bleaching Conditions and Content of Metal Ions for the Third Q₁ Q₂ E_P Paa P_O Sequence

Case	Charge of Paa in odp in Paa stage kg t ⁻¹	Temperature in Paa stage °C	Temperature in P _O stage °C	$[\eta]$ cm ³ g ⁻¹	$l(\text{Me})$ after Paa stage mg kg ⁻¹		
					Fe	Mn	Mg
3A	5	70	90	542	5.9	0.6	50.5
3B	5	70	105	494	5.0	0.6	51.1
3C	10	70	90	555	9.4	0.8	58.4
3D	10	70	105	492	6.3	0.6	48.4
3E	5	80	90	509	6.5	1.0	99.2
3F	5	80	105	431	6.9	0.9	94.5
3G	10	80	90	535	6.5	1.0	87.2
3H	10	80	105	457	7.3	1.2	89.2

**Fig. 5.** The influence of the concentration of Mn cations on the selectivity factor for the first and second bleaching sequences (see Tables 1 and 2).

sequence led to an increase in brightness by approximately 6.5 % ISO. The third sequence gave the best results from the point of view of pulp brightness as well as of zero-span breaking length, especially in cases 3A and 3C. In comparison with untreated pulp, brightness increased by about 20 % ISO. It should be noted that one of possible reasons why poor final brightness was obtained in our laboratory experiments is that pulp washing was performed after each stage, except for cases 1C and 1D, using distilled water while, in bleaching plants, the wash liquor and pulp are flowing in opposite directions, *i.e.* as countercurrent flows. Also, the intensity of mixing of pulp suspension was less than that reached in industrial bleaching stages.

Our results showed that pulp properties, especially brightness, are influenced by a number of factors. That is why it is virtually very difficult to make generaliza-

tions about the relationships between the pulp brightness and operating variables. In spite of this fact, some conclusions valid within the framework of our study can be made. Firstly, when hydrogen peroxide is used as the only bleaching agent, the addition of a P_O stage at a temperature of 105 °C substantially improved the pulp brightness. It was furthermore found that the positive change in the pulp brightness as well as in the selectivity factor characterizing pulp properties was strongly dependent on an optimal concentration of metal cations, especially of Mg and Mn. Secondly, a sequence containing a peracetic acid bleaching stage appeared as the best alternative from those tested in our study. In this sequence, better results were obtained when a lower temperature of 70 °C was applied. When peracetic acid was applied in the bleaching sequence, no remarkable effect of cation concentration on the selectivity factor was observed.

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SYMBOLS

$l(\text{Me})$	level of Me ion in odp	mg kg ⁻¹
m	mass	kg, mg
PB	pulp brightness	% ISO
SF	selectivity factor	% km ⁻¹
t	time	h, min
ZSBL	zero-span breaking length	km
$[\eta]$	intrinsic viscosity	cm ³ g ⁻¹
θ	temperature	°C

Subscripts

b	referred to bleached pulp
unb	referred to unbleached pulp

Abbreviations

DTPA	diethylenetriamine pentaacetic acid
odp	oven-dried pulp
Paa	peracetic acid

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