THE USE OF ACIDIFIED HYDROGEN PEROXIDE IN OXYGEN DELIGNIFIED KRAFT PINE PULP BLEACHING*

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SYNOPSIS. Bleaching of oxygen delignified kraft pine pulp with acidified hydrogen peroxide was investigated. The influence of pH of the bleaching solution, hydrogen peroxide charge, as well as the time and temperature of the treatment on chemical and technological indices of the process was evaluated. Hydrogen peroxide bleaching efficiency with the change of bleaching liquor reaction from acidic to alkaline was compared with reference to short-sequence OAP and OQP processes.

KEY WORDS: brightening, bleaching, oxygen delignified kraft pine pulp, hydrogen peroxide, acidic medium

INTRODUCTION

The users of bleached fibrous semi-finished products show interest in pulps which do not have to be necessarily characterized by high brightness and strength. These requirements were fulfilled traditionally by the kraft pulps bleached with chlorine or its compounds to the brightness of 60-70%. Due to stringent requirements of the environmental standards, today oxygen and hydrogen peroxide are used for the production of chemical pulps (RUTKOWSKI and PERLIŃSKA-SIPA 1991, 1998, RUTKOWSKI 1994 a, b). Peroxide, as both delignifying and bleaching agent, can be used for short-sequence bleaching of kraft pulps, e.g. acc. to OAP and OQP schemes (BOUCHARD et al. 1995, LAPIERRE et al. 1995, 2000). Taking into account lower quality of pulps obtained by this method, their production costs are, however, quite high. Factors which contribute to relatively high costs of bleaching

are the consumption of hydrogen peroxide and the requirement of pulp pretreatment (A or Q). Preliminary pulp acid treatment (A), as well as chelation (Q) create additional problems with the neutralization of effluent water.

Alternative solution allowing for costs reduction could be the use of peroxide reaction against lignin in acidic medium (FOSSUM and HAGGSTROM 1980, ECKERT 1982). As opposed to alkaline medium, acidified hydrogen peroxide remains relatively stable. However, at higher temperature, particularly in the presence of cations, e.g. Fe^{+2}, Cr^{+3} and Cu^{+2}, low pH of the solution does not prevent peroxide decomposition (WÓJCIAK 2002 a). The resulting products reveal degradation power against residual lignin which can be relatively easily removed by alkaline extraction (WÓJCIAK 2002 b). Two-stage treatment according to the schemes: hydrogen peroxide in acidic medium/alkaline extraction (P_{ac}/E) or again hydrogen peroxide but in alkaline medium (P_{ac}/P), can bring advantageous effects, particularly in case of highly delignified pulps.

The purpose of the present work is to define possible application of acidified hydrogen peroxide for bleaching of oxygen delignified kraft pine pulps, as well as comparison of efficiencies of the bleaching processes carried out according to schemes $OP_{ac}E$, OP_{ac}/P, as well as OAP and OQP.

MATERIALS AND TEST METHODS

Oxygen delignified kraft pine pulp (O) obtained from International Paper – Kwidzyn mill was used in the studies. Material parameters: kappa number 16.0, brightness 37.43% and viscosity 883 cm^3/g (conditions of oxygen delignification – pulp concentration 28%, oxygen pressure in high-pressure reactor 4-4.5 bars, stabiliser $MgSO_4 \cdot 7H_2O$ in quantity of 0.2% vs. o.d. pulp, NaOH 2% vs. o.d. pulp). The pulp was prepared in the form of soft sheets (MODRZEJEWSKI et al. 1985). All experiments on the pulp brightening were made in zip-lock PET bags placed in thermostatic water bath.

Hydrogen peroxide brightening in acidic medium (P_{ac}). The following initial parameters of hydrogen peroxide treatment in acidic medium were defined: treatment time – 1 h, temperature 70°C, H_2O_2 charge – 1% vs. o.d. pulp, pulp concentration – 10%. Pulp treatment was carried out in such conditions at variable pH parameters: 2.5, 3.0, 4.0, 5.2, as well as at pH 4.0 with variable time (30, 60 and 120 min.) and temperature (70, 80, 90°C) of the treatment.

The influence of peroxide charge on chemical and technological indices of the process was defined by charging 1, 2, 3, 4 and 5% of H_2O_2 vs. o.d. pulp, maintaining the above mentioned parameters of time (1 h) and pulp concentration (10%). Investigations were carried out at two different temperatures (70 and 80°C) and pH (2.5 and 4.0).

Pulp concentration of 10% was chosen for further investigations based on the analysis of brightening of thermo-mechanical pulps (TMP) with acidified peroxide – at lower concentrations, peroxide reaction was less efficient (WÓJCIAK 2002 b).

Alkaline extraction (E). 2% NaOH solution, time 1 h, temperature 70°C and pulp concentration 10% were used.

Acidified hydrogen peroxide brightening and alkaline extraction (OP$_{ac}$/E scheme). Oxygen delignified kraft pulp (O) brightening was carried out at pH 4.87 by charging 5% H$_2$O$_2$ vs. o.d. pulp during 1 h at temp. 80°C and pulp concentration 10%. The same parameters were applied for brightening in the presence of catalysts – Cr$_2$(SO$_4$)$_3$ and CuSO$_4$ added to hydrogen peroxide solution at 0.042 µg/cm^3 concentration. After termination of peroxide brightening, pulps were washed with distilled water and then subjected to alkaline extraction (as above). After alkaline extraction, pulps were washed with distilled water to neutral reaction and dried at room temperature.

Hydrogen peroxide bleaching in acidic and alkaline medium (OP$_{ac}$/P scheme). Oxygen delignified pulp (O) was bleached at pH 4.87 by charging 5% H$_2$O$_2$ vs. o.d pulp during 45 min. at 80°C and 10% pulp concentration. The same treatment parameters were used for bleaching in the presence of CuSO$_4$ catalyst added to hydrogen peroxide at 0.042 µg/cm^3 concentration. After termination of bleaching with acidic peroxide solution, reaction medium was alkalized without intermediate operations to pH 11 and bleached for 1 h. When bleaching was completed, pulps were washed with distilled water to neutral reaction and dried at room temperature.

Pulp bleaching according to OAP scheme. Oxygen delignified pulps (O) were subjected to acid pretreatment (A) during 1 h at 50°C, pH 2.5 and 8% pulp concentration. After washing with water up to neutral reaction, pulps were bleached by hydrogen peroxide (2% vs. o.d. pulp), adding 2% NaOH vs. o.d. pulp (bleaching solution pH 11) during 3 h at 90°C and using MgSO$_4$·7H$_2$O stabiliser – 0.1% vs. o.d. pulp and 10% pulp concentration. Magnesium charge was determined on the basis of earlier investigations (WÓJCIAK 2003).

Pulp bleaching according to OQP schemes. Oxygen delignified pulps (O) were chelated (Q) for 1 h at 60°C, using ethylenediaminetetraacetic acid (EDTA) in quantity of 5% vs. o.d. pulp (pH of suspension 4.33) and at 5% pulp concentration. After washing with water, pulps were subjected to hydrogen peroxide bleaching (2% H$_2$O$_2$ vs. o.d. pulp) with addition of 2% NaOH vs. o.d. pulp (bleaching solution pH 11), during 3 h at 90°C, using MgSO$_4$·7H$_2$O stabiliser in quantity of 0.1% vs. o.d. pulp and at 10% pulp concentration. Magnesium charge was determined from earlier investigations (WÓJCIAK 2003).

After completed bleaching, pulps were washed with distilled water to neutral reaction and dried at room temperature. All chemical charges used in this paper are expressed as percent on pulp, oven dry basis (o.d. pulp). Adjustment of pH was made by charging H$_2$SO$_4$ or NaOH to the bleaching solutions. Sequence of reagents addition: water, pH controller (H$_2$SO$_4$ or NaOH), stabiliser, hydrogen peroxide.

Since hydrogen peroxide treatment, alkaline extraction, acid treatment and chelation carried out in Institute of Chemical Wood Technology, The August Cieszkowski Agricultural University of Poznań are the elements of the technological cycle started with oxygen delignification operated in industrial conditions, this paper also uses symbol (O) to indicate integrity of the above mentioned stages of bleaching. Because of the bleaching effect of acidified peroxide solutions at limited delignification, in the discussion of test results of P$_{ac}$ and OP$_{ac}$E treatment we have used the term "brightening" to describe these processes. "Bleaching" was

used for the processes causing not only increased brightness but also pulp delignification (OP$_{ac}$/P, OAP, OQP).

Test methods. Reaction of hydrogen peroxide solutions (pH) was determined by pH meter CP-401 Elmetron with automatic temperature compensation at constant solution temperature 22°C and ±0.01 pH precision. Hydrogen peroxide consumption was determined with ±0.34% accuracy by iodometric titration using saturated ammonium molybdate as a catalyst. Brightness was determined by Zeiss leucometer (MODRZEJEWSKI ET AL. 1985). Brightness of the same paper sheets tested by L&W ELREPHO 2000 spectrophotometer following ISO 2470 standard (R457 with C-illuminant) was 2.15% higher than the results of the measurements with Zeiss apparatus reported in this paper*. Pulp yield was defined on the basis of humidity measurements by drying samples to constant weight (MODRZEJEWSKI ET AL. 1985). Degree of delignification (kappa number) was determined according to PN-70/P-50095 test method. Pulp viscosity was determined by viscosimetric method with Cuen solution (PN-92/P-50101/01). Metal ion concentration in the pulps after mineralization in CEM 2000 apparatus were determined as follows: Mn and Mg by AAS method (apparatus AAS N1 Zeiss Jena), and Cu, Pb, Fe by inversion voltammetry (ECO-TRIBO, PC-ETP apparatus produced by Institute of Physical Chemistry and Electrochemistry, Czech Academy of Sciences). Application of voltammetry allowed for the determination of metal content in quantities lower than 2 ppm. Analytically pure chemical reagents were used in the investigations.

Test results were evaluated by the following indices:

– delignification value, indicating decrease of kappa number vs. its initial value,

$$\Delta \text{ Kappa No/Kappa No}_{init},$$

– delignification selectivity, indicating decrease of lignin content (0.13 as the conversion coefficient of kappa number to lignin content in pulp was used) vs. yield loss of pulp,

$$\Delta L/\Delta Y,$$

and calculated as a quotient of percentage reduction of kappa number and viscosity,

$$\Delta \text{ Kappa No}/\Delta \text{ Viscosity},$$

– hydrogen peroxide consumption vs. kappa number decrease in percent

$$\Delta \text{ H}_2\text{O}_2/\Delta \text{ Kappa No},$$

ANALYSIS OF RESULTS

Optimisation of hydrogen peroxide brightening in acidic medium

The aim of the investigations was to define the influence of pH of hydrogen peroxide solution, peroxide charge, temperature and time of the pulp treatment on chemical and technological indices of the process.

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Investigation of the influence of pH of the reaction medium revealed that, although treatment with diluted acidified peroxide solutions had not caused significant delignification, it had apparently affected pulp chromophores (Table 1). Pulp brightness was increasing with pH increase, however, at peroxide solution pH 2.5 and 3.0, not only the lack of brightening effect but also slight reduction (vs. initial value) of pulp brightness were observed. Earlier studies (WÓJCIAK 1997, 1998, 2002 a, WÓJCIAK et al. 2002, KOPANIA and WANDELT 2003) had demonstrated delignification capacity of acidified peroxide solutions (also for pH 2.5), however, due to the use of smaller peroxide charges vs. o.d. pulp in the present work it was possible to determine optimum pH of the brightening solution. The highest brightness was obtained at pH 5.2 (Table 1). Difference in pulp brightness for pH 2.5 and 5.2 exceeded 10 units (already at pH 4.0 apparent increase of brightness to 44.89% was observed). Taking into account slight difference in pulp brightness at pH 4-5, this range should be considered as the optimum for hydrogen peroxide treatment in acidic medium. Correlation between initial pH value of the brightening solution and hydrogen peroxide consumption becomes noticeable – it increases with the increasing pH. Earlier literature (BOUCHARD et al. 1995, LAPIERRE et al. 2000) has reported dependence between H_2O_2 consumption and kappa number or brightness of peroxide bleached pulps. Therefore, by charging peroxide at definite pH, the effects of treatment could be anticipated.

Table 1. Effects of pH of the hydrogen peroxide solution on the chemical and technological indices of the oxygen delignified kraft pulp brightening treatment
Tabela 1. Wpływ pH roztworu nadtlenku wodoru na wskaźniki chemiczno-technologiczne obróbki rozjaśniającej mas siarczanowych po delignifikacji tlenowej

pH	Yield Wydajność [%]	H_2O_2 consumption Zużycie H_2O_2 [%]	ΔH_2O_2 $\dfrac{\dfrac{\Delta \text{Kappa No}}{\Delta H_2O_2}}{\Delta \text{L.kappa}}$	Kappa No Liczba kappa	Brightness Białość [%]	$\dfrac{\dfrac{\Delta \text{Kappa No}}{\Delta \text{Kappa No}_{init.}}}{\dfrac{\Delta \text{L.kappa}}{\Delta \text{L.Kappa}_{pocz.}}} \times 100$	$\dfrac{\Delta L}{\Delta Y}$ $\dfrac{\Delta L}{\Delta W}$
2.5	97.9	32.41	4.29	14.8	34.97	7.5	0.07
3.0	97.8	38.56	4.17	14.5	36.29	9.4	0.09
4.0	97.9	49.31	4.11	14.1	44.89	11.9	0.12
5.2	96.2	49.89	4.20	14.1	45.25	11.9	0.07

P_{ac} – treatment time 1 h, temperature 70°C, H_2O_2 charge 1% vs. o. d. pulp, pulp concentration – 10%).

P_{ac} – czas obróbki 1 h, temperatura 70°C, H_2O_2 – 1% w stosunku do b. s. masy, stężenie masy – 10%.

Investigation of the influence of hydrogen peroxide charge quantity on chemical and technological process indices were carried out in two variants, changing pH and temperature (variant I – pH 2.5, temperature 80°C and variant II – pH 4.0, temperature 70°C). Using the same peroxide charge in both variants (3% vs. o.d. pulp), better results (like delignification value and selectivity) were obtained for variant II (Table 2, Fig. 1). Also slightly higher pulp yields (by approx. 1%) were obtained in these conditions. The most advantageous level of brightness (48.85%), as well as delignification value and selectivity (13.1 and 0.07, respectively) were

Table 2. Effects of the hydrogen peroxide charges on the chemical and technological indices of oxygen delignified kraft pulp brightening treatment

Tabela 2. Wpływ ilości dozowanego nadtlenku wodoru na wskaźniki chemiczno-technologiczne obróbki rozjaśniającej mas siarczanowych po delignifikacji tlenowej

| H_2O_2 charge on o.d. pulp Ilość H_2O_2 w stos. do b. s. m. celulozy [%]	Yield Wydajność [%]	Kappa No Liczba kappa	Brightness Białość [%]	Viscosity Lepkość [cm³/g]	$\dfrac{\Delta \text{ Kappa No}}{\text{Kappa No}_{init.}}$ $\dfrac{\Delta \text{ L.kappa}}{\text{L.kappa}_{pocz.}}$	$\dfrac{\Delta L}{\Delta Y}$ $\dfrac{\Delta L}{\Delta W}$
1*	94.8	15.4	–	–	3.8	0.02
2*	94.8	14.6	–	–	8.8	0.04
3*	95.1	14.3	46.04	–	10.6	0.05
3**	96.3	14.2	46.79	–	11.3	0.06
4**	96.2	14.0	47.10	–	12.5	0.07
5**	96.1	13.9	48.85	634	13.1	0.07

*P_{ac} – pH 2.5 and temperature 80°C.
**P_{ac} – pH 4.0 and temperature 70°C, treatment time 1 h, pulp concentration – 10%.
*P_{ac} – pH 2,5 i temperatura 80°C.
**P_{ac} – pH 4,0 i temperatura 70°C, czas obróbki – 1 h, stężenie masy – 10%.
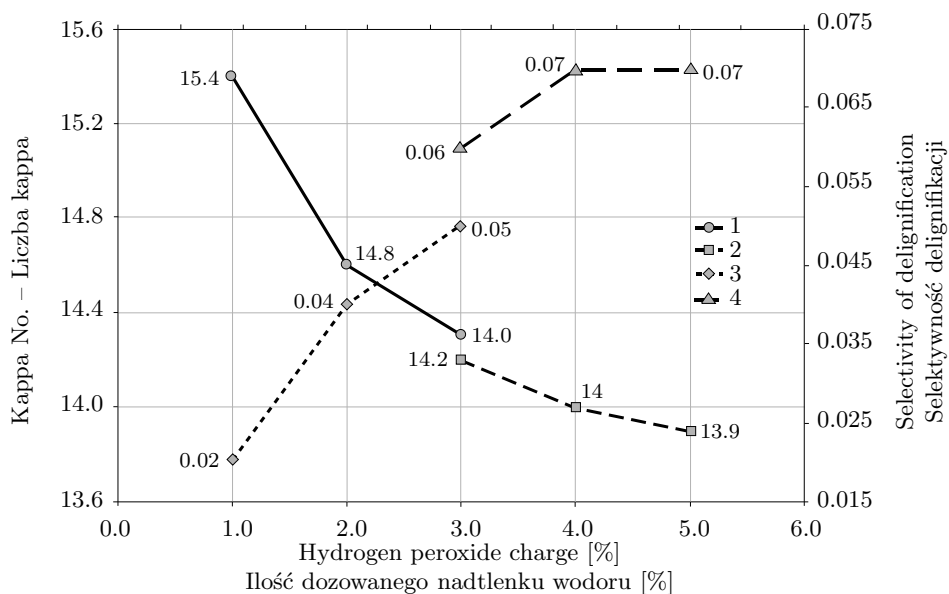
Fig. 1. The influence of hydrogen peroxide charge on kappa no and selectivity of delignification of oxygen delignified kraft pine pulp. Two variants of treatment: 1 and 3 – temperature 80°C, pH 2.5, 2 and 4 – temperature 70°C, pH 4.0

Rys. 1. Wpływ ilości dozowanego nadtlenku wodoru na stopień roztworzenia i selektywność delignifikacji masy celulozowej sosnowej po delignifikacji tlenowej. Dwa warianty obróbki: 1 i 3 – temperatura 80°C, pH 2,5, 2 i 4 – temperatura 70°C, pH 4,0

Table 3. Effects of temperature of the hydrogen peroxide solution on the chemical and technological indices of oxygen delignified kraft pulp brightening treatment

Tabela 3. Wpływ temperatury roztworu nadtlenku wodoru na wskaźniki chemiczno-technologiczne rozjaśniania mas siarczanowych po delignifikacji tlenowej

Temperature Temperatura obróbki [°C]	Yield Wydajność [%]	Kappa No Liczba kappa	Brightness Białość [%]	$\frac{\Delta\ \text{Kappa No}}{\text{Kappa No}_{init.}}$ $\frac{\Delta\ \text{L.kappa}}{\text{L.kappa}_{pocz.}}$ $\times\ 100$	$\frac{\Delta L}{\Delta Y}$ $\frac{\Delta L}{\Delta W}$
70	97.9	14.1	44.89	11.9	0.12
80	98.0	14.2	46.35	11.3	0.12
90	98.5	13.7	47.32	14.4	0.20

P_{ac} – treatment time 1 h, H_2O_2 charge 1% vs. o. d. pulp, pulp concentration – 10%.
P_{ac} – czas obróbki 1 h, H_2O_2 – 1% w stosunku do b. s. masy, stężenie masy – 10%.

Table 4. Effects of time of the hydrogen peroxide treatment on the chemical and technological indices of oxygen delignified kraft pulp brightening

Tabela 4. Wpływ czasu obróbki nadtlenkiem wodoru na wskaźniki chemiczno-technologiczne rozjaśniania mas siarczanowych po delignifikacji tlenowej

Time Czas [min.]	Yield Wydajność [%]	Kappa No Liczba kappa	Brightness Białość [%]	$\frac{\Delta\ \text{Kappa No}}{\text{Kappa No}_{init.}}$ $\frac{\Delta\ \text{L.kappa}}{\text{L.kappa}_{pocz.}}$ $\times\ 100$	$\frac{\Delta L}{\Delta Y}$ $\frac{\Delta L}{\Delta W}$
30	97.8	15.3	43.62	4.4	0.04
60	97.6	14.9	44.89	6.9	0.06
120	97.4	14.2	46.36	11.3	0.09

P_{ac} – temperature 70°C, H_2O_2 charge 1% vs. o. d. pulp, pulp concentration – 10%.
P_{ac} – temperatura 70°C, H_2O_2 - 1% w stosunku do b. s. masy, stężenie masy – 10%.

obtained with 5% H_2O_2 vs. o.d pulp. This charge was considered as the basis for further investigations on the two-stage treatment of kraft pulp with acidic and alkaline peroxide solutions. It should be emphasised that in variant II (lower temperature and higher pH of brightening solution) cellulose is less endangered by hydrolytic decomposition as compared to treatment in variant I. In spite of that, acidic kraft pulp treatment according to variant II resulted in cellulose degradation which was manifested by viscosity reduction from 883 cm^3/g to 634 cm^3/g after application of H_2O_2 (5% vs. o.d. pulp).

Investigations of the influence of temperature show (Table 3) that the highest delignification value and selectivity are obtained at 90°C. However, increase of these indices was not accompanied by comparable increase of pulp brightness which had been achieved with higher charge of H_2O_2 at lower temperature (5% vs. o.d. pulp; temperature 70°C – Table 2). Assuming possible intensification of cellulose degradation, it was decided to continue further studies at 80°C.

Investigations of the influence of treatment duration confirmed the growing tendency for delignification value and selectivity as the process proceeded in time

(Table 4). However, after 2 h, significant increase of pulp brightness was not observed. Due to a relatively high stability of hydrogen peroxide in acidic medium (as compared to alkaline), prolongation of treatment with acidified H_2O_2 solutions is not advisable since the final result of brightening depends on the peroxide charge used in the reaction. Assuming higher consumption of acidified peroxide in the presence of catalysts it was decided that the time of treatment in further investigations should not exceed 1 h.

It should be noticed that lower decomposition susceptibility of hydrogen peroxide in acidic than in alkaline medium justifies its use in the preliminary stages of bleaching process.

Continuation of experiments on pulp bleaching with acidic hydrogen peroxide is advisable in the following conditions: solution pH 4-5, H_2O_2 charge – 5% vs. o.d. pulp, temperature 80°C, treatment time not exceeding 1 h. Under these conditions, peroxide behaves, first of all, as a brightening reagent without causing considerable pulp delignification.

Two-stage hydrogen peroxide bleaching in acidic and alkaline medium

Investigations on the use of acidified hydrogen peroxide in the initial stage of bleaching were made in two variants:

1. Acidified hydrogen peroxide (with or without catalyst – chromium sulphate or copper sulphate)/alkaline extraction (pos. 1 and 2, Table 5).

2. Acidified hydrogen peroxide (with or without catalyst – copper sulphate)/hydrogen peroxide in alkaline medium (pos. 3 and 4, Table 5).

Results in Table 5 show that the use of alkaline extraction after hydrogen peroxide treatment is not advantageous. Although, certain reduction of kappa number was observed (down to 12.1 in case of hydrogen peroxide treatment without catalyst addition), yield decreased to 95% (pos. 1, Table 5). Alkaline extraction has also contributed to the reduction of pulp viscosity to 596 cm^3/g. The presence of catalyst (chromium sulphate), in spite of approximately 9% increase of peroxide consumption in acidic medium, had not significant effect on delignification value (similar results were obtained with copper sulphate catalyst). On the contrary, slightly higher kappa number (14.1) and yield (96.6%) were obtained as compared to hydrogen peroxide treatment without catalyst. On the basis of earlier investigations, Cr^{+3} and Cu^{+2} salts with moderate catalytic power were chosen for peroxide brightening in acidic medium (WÓJCIAK 2002 a). The lack of correlation between increase of peroxide consumption and delignifiction value could be, however, related to over-fast peroxide decomposition. It should be pointed out that similar results were obtained for acidified hydrogen peroxide brightening of TMP pulps in the presence of catalysts (WÓJCIAK 2002 b). Brightness numbers determined for both pulps (after acid peroxide treatment and alkaline extraction) were not significantly different from the results obtained for catalyst-free peroxide brightening (47.33% and 46.12% for treatment with and without catalyst, respectively). During alkaline extraction in the excess of sodium hydroxide, yellowing effect – as opposed to brightening, was observed. Results of earlier investigations (WÓJCIAK et AL. 2000 a, 2000 b, 2002) show that standard alkaline extraction efficiently re-

Table 5. Effects of the oxygen delignified kraft pulp treatment with hydrogen peroxide
Tabela 5. Efekty obróbki masy siarczanowej sosnowej po delignifikacji tlenowej (O) przy użyciu nadtlenku wodoru

No. L.p.	pH before treatment pH przed obróbką	H_2O_2 consumption Zużycie H_2O_2 [%]	Yield Wydajność [%]	Kappa No Liczba kappa	Viscosity Lepkość [cm³/g]	Brightness Białość [%]	$\dfrac{\Delta H_2O_2}{\Delta \text{Kappa No}}$ $\dfrac{\Delta H_2O_2}{\Delta \text{L.kappa}}$	$\dfrac{\Delta \text{Kappa No}}{\text{Kappa No}_{init.}} \times 100$ $\dfrac{\Delta \text{L.kappa}}{\text{L.kappa}_{pocz.}} \times 100$	$\dfrac{\Delta L}{\Delta Y}$ $\dfrac{\Delta L}{\Delta W}$	$\dfrac{\Delta \text{Kappa No}}{\Delta \text{Viscosity}}$ $\dfrac{\Delta \text{L.kappa}}{\Delta \text{Lepkość}}$
1	4.87	10.33**	95.0	12.1	596	47.33 ±0.16	0.42	24.4	0.10	0.75
2	4.97	19.83**	96.6	14.1	–	46.12 ±0.66	1.67	11.9	0.07	–
3	4.87 10.80*	94.49	97.8	9.7	678	58.44 ±0.27	2.40	39.4	0.37	1.70
4	4.87 10.80*	86.74	97.4	10.3	682	58.53 ±0.41	2.43	35.6	0.29	1.57
5	11.00	89.33	89.1	4.9	580	60.20 ±0.10	1.29	69.4	0.13	2.02
6	11.00	96.20	93.1	8.6	583	62.63 ±0.16	2.08	46.3	0.14	1.36

*pH of the brightening solution after alkalization.

**After P_{ac} stage.

1 – in acid medium and then alkaline extraction (P_{ac}/E), 2 – in acid medium with catalyst Cr^{+3} an then alkaline extraction, 3 – in acid and then in alkaline medium, 4 – in acid medium with catalyst Cu^{+2} and then in alkaline medium, 5 – with preliminary acid treatment (OAP), 6 – with chelation (OQP).

*pH roztworu rozjaśniającego po alkalizacji.

**Po stopniu P_{ac}.

1 – w środowisku kwaśnym wraz z ekstrakcją alkaliczną (P_{ac}/E), 2 – w środowisku kwaśnym w obecności katalizatora Cr^{+3}, wraz z ekstrakcją alkaliczną (P_{ac}/E), 3 – w środowisku kwaśnym, a następnie w środowisku alkalicznym (P_{ac}/P), 4 – w środowisku kwaśnym w obecności katalizatora Cu^{+3}, a następnie w środowisku alkalicznym (P_{ac}/P), 5 – z wstępną obróbką kwasową (OAP), 6 – z chelatacją (OQP).

moves residual lignin and reduces chromophores concentration but only if kraft pulps had been before then subject to long term action of peroxide excess in acidic medium (3 h). Such conditions, which are favourable for delignification, simultaneously cause strong cellulose degradation. In the present work, the time of acidic hydrogen peroxide brightening was reduced, taking into consideration necessary limitation of cellulose depolymerization. This, however, reduced lignin degradation and, in consequence, restricted its removal during alkaline extraction.

Better results were obtained for two-stage hydrogen peroxide treatment in acidic and, then, in alkaline medium (pos. 3 and 4, Table 5). Yield values exceeding 97% were obtained, no matter which variant of treatment had been used (with or without copper sulphate catalyst). Pulp brightness was also relatively high (taking into account the time and number of bleaching stages) and exceeded 58%. Viscosity results were improved in comparison to alkaline extraction. Pulp viscosity after acidic (no catalyst) and alkaline peroxide treatment was 678 cm^3/g and, in the presence of catalyst, 682 cm^3/g. The latter result should be related to lower H_2O_2 consumption. It should be also pointed out that the time of acidic treatment was reduced to 45 min. and the total time of bleaching (acidic and alkaline medium) was 1 h 45 min. For comparison: for oxygen delignified kraft pulp bleaching according to OAP scheme (total time of acid and peroxide treatment 4 h), the yield was 89.1% at peroxide consumption 89.33%. Delignification value apparently increased (69.4) but brightness was only slightly higher – 60.20% (pos. 5, Table 5). More advantageous results were obtained for bleaching according to OQP scheme (pos. 6, Table 5) – higher yield (93.1%) and brightness (62.63%). However, delignification value was lower than in OAP scheme and peroxide consumption ratio in relation to the change of pulping degree was also less advantageous (pos. 6, Table 5). Relatively long time of oxidation treatment in alkaline medium (P) has also reduced viscosity of pulps bleached in OAP and OQP schemes to 573 cm^3/g and 583 cm^3/g, respectively. This negative effect of reduced viscosity and, in consequence, lower pulp strength, is not compensated by the highest value of selectivity of delignification which reflects viscosity losses in relation to the change of kappa number (2.02) for pulps treated in OAP scheme (Table 5).

The results show that if semi-finished pulp products with lower brightness and strength (lower viscosity) are required, hydrogen peroxide treatment in acidic and then, alkaline medium could be an alternative solution (also from economical point of view) to short-sequence bleaching schemes, e.g. OAP (BOUCHARD et al. 1995). Taking into consideration possible application of efficient catalysts for hydrogen peroxide decomposition in acidic medium, as well as magnesium compounds as its stabilisers in alkaline medium, one could expect the improvement of pulp quality after acidic and alkaline peroxide bleaching. Bleaching can be carried out both in a single bleaching tower and in two-tower configuration with washing system between the reactors. The latter option, given in Figure 2, allows not only for good mixing of pulp and chemicals but also re-circulation of acidified peroxide solution. After completion of peroxide losses, this solution can be reused for brightening in acidic medium. Removal of acidic peroxide solution together with metal ions catalysing its decomposition at increased pH will also facilitate alkaline bleaching carried out in a separate tower. Pulp brightened with acidified hydrogen peroxide,
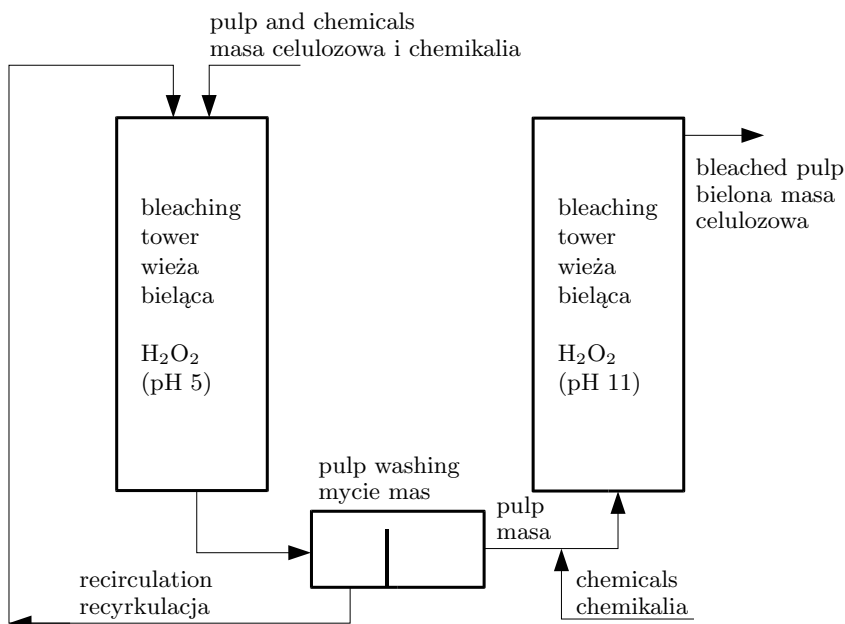
Fig. 2. A simplified schemat for the two-stage bleaching of oxygen delignified kraft pulp with acidic and alkaline hydrogen peroxide

Rys. 2. Uproszczony schemat dwustopniowego bielenia masy celulozowej siarczanowej po delignifikacji tlenowej nadtlenkiem wodoru w środowisku kwaśnym i alkalicznym

Table 6. Metal profile of oxygen delignified kraft pulp after acidic hydrogen peroxide treatment (P_{ac}), acid (A) and chelation step (Q)

Tabela 6. Zawartość metali w masie celulozowej siarczanowej po delignifikacji tlenowej poddanej obróbce zakwaszonym roztworem nadtlenku wodoru (P_{ac}), wstępnej obróbce kwasowej (A) i chelatacji (Q)

Metals Metale	Treatment* – Rodzaj obróbki*		
	P_{ac}	A	Q
	[ppm]		
Mn	< 0.05	< 0.05	< 0.05
Cu	0.85	0.60	1.80
Pb	2.42	1.96	0.12
Fe	31.89	10.08	42.53
Mg	130.76	105.00	122.89

*Treatment P_{ac}: pH 4.87, 5% H_2O_2 on o. d. pulp, temperature 80°C, pulp concentration 10%, time of treatment 1 h. Conditions for A and Q steps as in experimental parts (OAP, OQP schemes).

*Warunki obróbki P_{ac}: pH 4,87, 5% H_2O_2 w stosunku do b. s. masy celulozowej, temperatura 80°C, stężenie masy 10%, czas 1 h. Warunki obróbki A i Q – jak w schematach rozjaśniania OAP i OQP (część metodyczna pracy).

after washing with water revealed manganese, copper and lead concentrations comparable to acid treated (A) and chelated (Q) pulps (Table 6). Iron content was even lower than in chelated pulp, although acid treatment removed this metal most efficiently. Relatively high retention of magnesium (as compared to chelated and acid treated pulps), which can perform as a "native" peroxide stabiliser during alkaline bleaching, may be also advantageous. It is also important to notice that in spite of the increase of metals concentration in acidic solutions after re--circulation they are not built-up in cellulose (BOUCHARD et al. 1995). However, the increase of iron ions concentration could be a cycle limiting factor in peroxide solution re-circulation. Acidified hydrogen peroxide solutions reveal stability in the presence of metal ions that occur in pulps as for example Pb^{+2} and Mn^{+2}, while Cu^{+2} and Cr^{+3} ions contribute only to its moderate decomposition. Iron ions in these conditions are characterised by a very high catalytic activity (WÓJCIAK 2002 a). The risk of exceedingly fast peroxide decomposition due to the presence of iron is very likely to require limitation of the number of cycles and monitoring of metal content in the re-circulating solution.

CONCLUSIONS

1. Treatment of oxygen delignified kraft pine pulp with acidified hydrogen peroxide solution reduces chromophore concentration in the pulp and increases its brightness. Hydrogen peroxide brightening in acidic medium was not, however, as efficient as in alkaline medium. Considerable increase of brightness was obtained by two-stage pulp treatment when hydrogen peroxide in acidic and then in alkaline medium was used.

2. The following conditions are technologically justifiable for preliminary bleaching of oxygen delignified kraft pine pulp with acidified hydrogen peroxide: pulp concentration 10%, temperature not higher than 80°C, treatment time not exceeding 1 h, hydrogen peroxide charge not higher than 5% vs. o.d. pulp and solution pH not less than 4.0.

3. Two-stage treatment of oxygen delignified kraft pine pulp with hydrogen peroxide in acidic (with $CuSO_4$ catalyst) and alkaline medium allows to obtain semi--finished product with brightness 58.53%, viscosity 682 cm^3/g, yield 97.40% at hydrogen peroxide consumption 86.74%. Besides brightness which is 2% and 4% lower, the above mentioned indices are better than those obtained during bleaching of the same pulp according to OAP and OQP schemes, respectively.

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ZASTOSOWANIE NADTLENKU WODORU W ŚRODOWISKU KWAŚNYM W PROCESIE BIELENIA MAS CELULOZOWYCH SIARCZANOWYCH SOSNOWYCH PO DELIGNIFIKACJI TLENOWEJ

Streszczenie

Zbadano możliwość zastosowania nadtlenku wodoru w środowisku kwaśnym w procesie bielenia mas celulozowych siarczanowych sosnowych po delignifikacji tlenowej. Najkorzystniejsze rezultaty stwierdzono w przypadku dwustopniowej obróbki mas celulozowych nadtlenkiem wodoru, najpierw w środowisku kwaśnym, a następnie w alkalicznym. Dwustopniowe, krótkosekwencyjne bielenie nadtlenkiem (w środowisku kwaśnym z dodatkiem katalizatora $CuSO_4$) umożliwiło uzyskanie półproduktu o białości 58,53%, lepkości 682 cm^3/g, z wydajnością 97,4%, przy zużyciu nadtlenku wodoru – 86,74%.

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