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THE EFFECT OF PH OF HYDROGEN PEROXIDE SOLUTION ON KRAFT PINE PULP DELIGNIFICATION¹

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The investigated pulps are characterized by different reactivity to hydrogen peroxide both in acidic and alkaline conditions. Residual lignin of pulps with lower kappa number (30 and 16) was considerably degraded in acidic conditions. Acidified hydrogen peroxide solutions caused yet severe degradation of carbohydrates in all the studied pulps. Oxygen delignified pulp (kappa number 16) revealed the smallest differences in yield and selectivity of delignification in dependence of the reaction conditions (acidic/alkaline). The most efficient protection of Mg⁺² ions was found for the same pulp in alkaline conditions. Our results show that studies should be continued on the chemistry of hydrogen peroxide treatment of the kraft pulps before as well as after oxygen delignification.

Key words: kraft pine pulp, delignification, hydrogen peroxide

INTRODUCTION

The stringent ecological requirements of the last decade have forced the producers of wood pulp to use hydrogen peroxide, not only as the brightening reagent but also for delignification. Hydrogen peroxide together with other oxidizers (oxygen, ozone) can successfully reduce or totally eliminate the use of harmful chlorine and its compounds from pulp bleaching process (Rutkowski and Perlińska-Sipa 1991, Rutkowski 1994a, Rutkowski 1994b).

Hydrogen peroxide dissociates in an aqueous solution and forms perhydroxyl anion (O_2H^-) . However, efficient oxidation of lignin with O_2H^- requires the presence of carbonyl groups. Since the number of carbonyl groups in residual lignin of cellulose pulps is negligible, perhydroxyl ion can not be the important delignification factor (O_2H^-) ion itself can not oxidize the phenolic ring – Agnemo and Gellerstedt 1979). The most important factors in delignification process are the products of H_2O_2 decomposition: hydroxyl radical, superoxide anion radical and oxygen generated in free radicals

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reactions. Their strong delignificating activity is observed at high temperatures (min. 80°C) and high pH (approx.11). The negative aspect of such severe technological regime is the possibility of degradation of partially oxidized cellulose due to OH and O2 - free radicals (Chirat and Lachenal 1994). As an alternative to the treatment in alkaline conditions, H₂O₂ can be used in acidic conditions. Hydrogen peroxide was used together with acetic acid (Desprez et al. 1994, Glinski and Nicholls 1997, Jakubikova and Suty 1995, Liebergott 1996, Rutkowski 1994c) or with formic acid (Hortling et al. 1990). Delignification of cellulose pulps and wood with monopersulfurous acid produced by the addition of concentrated sulfuric acid to hydrogen peroxide solutions was also studied (Desperez et al. 1994, Liebergott 1996, Springer 1990). It was confirmed that hydrogen peroxide used in the two-stage treatment (in alkaline and acidic media) increases the efficiency of bleaching of the mechanical pulp (Hobbs and Abbot 1991, Kempf 1981, Lachenal 1986). Laser flash photolysis studies suggest that the efficiency of bleaching by hydrogen peroxide is mainly due to the elimination of α -carbonyl groups, irrespectively of the treatment conditions (Wójciak et al. 2002). It was also confirmed that acidified H2O2 solutions in combination with alkaline extraction could remove chromophoric groups from the cellulose pulp with the same efficiency as alkaline peroxide solutions (Wójciak et al. 2000). Although test results show the possibility of using H₂O₂ as the delignification and bleaching agent in acidic conditions, also for the so-called chemical paper-pulp, no sufficient literature is avilable on this subject (Fossum and Haggstrom 1980).

The aim of this work is the evaluation of chemical and technological factors of kraft pine pulp delignification by hydrogen peroxide in alkaline and acidic conditions.

MATERIALS AND TEST METHODS

Three types of kraft pine pulps were subject to the oxidation treatment:

- A: kraft pulp with kappa number 58, produced by the continuous cooking method at Frantschach S.A – pulp mill, Świecie.
- B: kraft pulp with kappa number 30, produced in the Institute of Chemical Wood Technology, Agricultural University of Poznań. Wood material in the form of air-dried industrial pine chips (*Pinus sylvestris* L.) was used. The chips cooks were carried out in stainless steel Hagglünd autoclaves heated in a glycerine bath. The conditions for the kraft cooks were as follows: total alkali 66.4 g/dm³, active alkali 58.4 g/dm³, liquor to wood ratio of 3.5:1, sulfidity 20.4% and heating-up time 90 min. The yield of pulp equalled to 47.9%.
- C: kraft pulp with kappa number 16 after oxygen delignification, produced in International Paper – pulp mill, Kwidzyń.

The material A was taken from the dewatering drum while material B was filtered off, manually disintegrated and then dried at room temperature. Material C was prepared in form of soft sheets (Modrzejewski et al. 1985).

In order to determine metals profile (before oxidation treatment), cellulose pulps were subjected to mineralization in microwave oven (Star 6 CEM) by nitric acid and hydrogen peroxide solution. Heavy metals (Pb, Cu, Mn, Fe) and Mg were determined by atomic absorbtion spectroscopy (AAS) using Perkin Elmer A Analyst 300. Limit of accuracy was less than or equal to 2 ppm for Pb, Cu, Mn and Fe and less than 5 ppm for Mg.

Decomposition of H_2O_2 depending on pH and metals profile in hydrogen peroxide solution (p.a.) was tested in zip-lock polyethylene bags at 80°C. The pH index of the reaction was controlled by the addition of NaOH (pH 11) or H_2SO_4 (pH 2.5). Measurements were also made at pH 5.3, which is the standard value of the commercial H_2O_2 solution. Metals were introduced with HNO3 solution (Pb, Cr, Mg, Fe, Cu, Mn – AAS standards) that adjusted hydrogen peroxide at pH 2 \pm 0.5. Concentration of metals in the solutions was equal to 0.12 μ g/cm³. Initial concentration of hydrogen peroxide was 0.13 M/dm3. The H_2O_2 consumption was determined by iodometric titration using saturated ammonium molybdate solution as a catalyst. Standard deviation of the results was less than or equal to \pm 0.34%.

Oxidation treatment of cellulose pulps was carried out with the use of $5\%~H_2O_2$ acqueous solution (p.a.). Prior to the addition of pulp, pH of hydrogen peroxide solution was adjusted: pH 2.5 by the addition of H_2SO_4 and pH 11 by NaOH. Hydrogen peroxide stabilizer $MgSO_4 \cdot 7H_2O$ (0.25% vs. o.d. pulp) was added to several pulps oxidized in alkaline conditions (Bouchard et al. 1995). The treatment was also conducted at pH 4.5. Pulps were oxidized in zip-lock polyethylene bags at 10% of pulp concentration. The bags were heated up in water bath (80°C). Reference samples (treated in the same conditions of pH, peroxide and pulp concentration as above) were kept at room temperature (22°C). Hydrogen peroxide consumption was determined by iodometric titration (see above). The treatment was continued for 3 hours. After completion of oxidation treatment, materials were washed in Büchner funnel to neutral reaction and then dried at room temperature. Some of the pulps after treatment in alkaline and acid conditions were subject to alkaline extraction with 2% acqueous NaOH solution with pulp concentration 10%, temperature 70° C, extraction time 1h (Allison et al. 1996). After extraction, pulps were washed to neutral reaction and dried as the other ones.

Moisture content, yield, kappa number (Modrzejewski et al. 1985) and viscosity according to TAPPI T 230 om – 89 were measured.

Delignification value was calculated as the decrease of the kappa number in relation to its initial value (Δ Kappa No / Δ Kappa No_{initial}) – (Rutkowski and Perlińska-Sipa 1998).

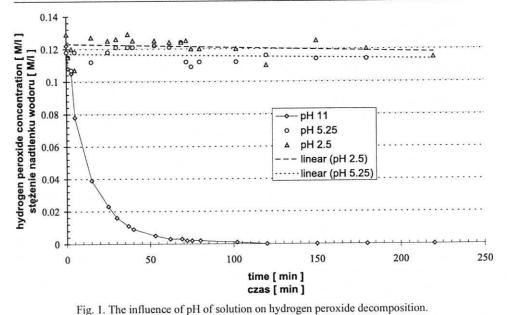
Selectivity of delignification was calculated by two methods:

- as the decrease of lignin content (conversion coefficient of the kappa number to lignin content 0.13) versus yield loss of pulps (ΔL/ΔΥ) (Rutkowski and Perlinska-Sipa 1998),
- as the quotient of percentage reduction of kappa number and viscosity (ΔKappa No / ΔViscosity) – (Brown and Dawe 1996).

ANALYSIS OF RESULTS

Catalytic decomposition of acidic hydrogen peroxide

As opposite to alkaline solutions, hydrogen peroxide in acid conditions shows stability in considerably wide range of pH 2.5 - 5.3 (Fig. 1). The influence of heavy



Trends are shown for pH 2.5 and 5.3

Rys. 1. Wpływ pH roztworu na rozkład nadtlenku wodoru. Zaznaczono linie trendu dla pH 2,5 i 5,3

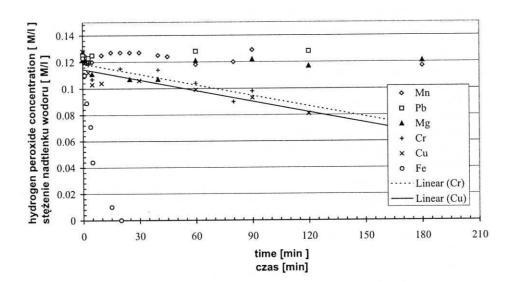


Fig. 2. The influence of heavy metal on hydrogen peroxide decomposition (pH 2 ± 0.5).

Trends are shown for Cr and Cu

Rys. 2. Wpływ metali ciężkich na rozkład nadtlenku wodoru (pH 2 ± 0,5).

Zaznaczono linie trendu dla Cr i Cu

Table 1

Tabela 1

Metals content in pulps

Zawartość metali w masach celulozowych

| Metals Metale | A | В | С | |
|------------------|-------|-----|-----|--|
| | [ppm] | | | |
| Mg | 149 | 750 | 228 | |
| Fe | 50 | 71 | 54 | |
| Mn | 107 | 214 | - | |
| Pb | 82 | 74 | 57 | |
| Cu | - | - | 1 % | |

Pulps codes in Table 2a

Oznaczenia literowe mas jak w tabeli 2a

Table 2a

Tabela 2a

Effects of pH of the H_2O_2 solution on chemical and technological indices of pulp treatment (treatment temperature 80°C)

Wpływ pH roztworu H₂O₂ na wskaźniki chemiczno-technologiczne obróbki mas celulozowych (temperatura obróbki 80°C)

| Pulp | рН | | | | | |
|-------------|--|------|------|---------------------------|--|--|
| Symbol masy | 2.5 | 4.5 | 11 | 11 Mg ⁺² added | | |
| | Yield [%] Wydajność [%] | | | | | |
| Α | 94.3 | 93.4 | 89.4 | 91.4 | | |
| В | 86.2 | 85.7 | 85.4 | 85.7 | | |
| С | 93.6 | 94 | 89.3 | 93.8 | | |
| | H ₂ O ₂ consumption [%] Zużycie H ₂ O ₂ [%] | | | | | |
| Α | 66.7 | 28.6 | 100 | 100 | | |
| В | 25 | 22 | 100 | 100 | | |
| С | 6.7 | 1 | 100 | 100 | | |
| | Kappa no Liczba kappa | | | | | |
| A | 45.0 | 44.1 | 24.8 | 27.9 | | |
| В | 9.6 | 15.8 | 8.1 | 9.8 | | |
| С | 9.8 | 11.1 | 5.2 | 5.7 | | |

A - pulp kappa number 58; B - pulp kappa number 30; C - pulp kappa number 16

A – masa celulozowa o liczbie kappa 58; B – masa celulozowa o liczbie kappa 30; C – masa celulozowa o liczbie kappa 16

Table 2b

Tabela 2b

Effects of pH of H_2O_2 solution on chemical and technological indices of pulp treatment(treatment temperature 80°C; pH code as in Table 2a)

Wpływ pH roztworu H₂O₂ na wskaźniki chemiczno-technologiczne obróbki mas celulozowych (temperatura obróbki 80°C; pH jak w Tabeli 2a)

| | * | $\Delta H_2O_2 / \Delta I$ | Kappa No | |
|---|------|----------------------------|--------------------------------|------|
| | | $\Delta H_2O_2 I$ | ∆L.kappa | |
| Α | 2.98 | 1.19 | 1.75 | 1.93 |
| В | 0.89 | 0.46 | 1.37 | 1.49 |
| С | 0.17 | 0.03 | 1.48 | 1.55 |
| | - t | ∆Kappa No / Ka | appa No _{initial} 100 | |
| | | ΔL.kappa / L.l | kappa _{pocz} .·100 | |
| Α | 22.4 | 24 | 57.2 | 51.9 |
| В | 68 | 47.3 | 73 | 67.3 |
| С | 38.8 | 30.6 | 67.5 | 64.4 |
| | | ΔL | <i>Ι</i> ΔΥ | |
| | | ΔL | / ΔW | |
| Α | 0.3 | 0.27 | 0.41 | 0.46 |
| В | 0.19 | 0.13 | 0.2 | 0.18 |
| С | 0.13 | 0.11 | 0.13 | 0.22 |

Pulp codes as in Table 2a Oznaczenia mas jak w Tabeli 2a

metals profile on hydrogen peroxide decomposition was diversified (Fig. 2). Iron ions due to their catalytic properties (Walling and Goosen 1973, Walling and El-Taliawi 1973) have caused fast decomposition of H₂O₂, while in the case of Cu and Cr ions, moderate catalytic effect was observed. Manganese, lead and magnesium (commonly used as H₂O₂ stabilizers) did not cause decomposition of hydrogen peroxide in acidic conditions. Investigations were carried out in the homogeneous system. Catalytic activity of metals to H₂O₂ may be changed if it is used in the heterogeneous system (Duke and Haas 1961), eg. as the components of cellulose pulp. Catalytic activity of metals is also influenced by pH as well as their oxidation level and concentration (Kitajama et al. 1978, Mooi and Selwood 1952). Decomposition kinetics of H₂O₂ in the heterogeneous system (with cellulose pulp) will be investigated separately. Quantities of iron and catalytically active lead in the heterogeneous system (Mooi and Selwood 1952), which were determined in cellulose pulps (Table 1) probably enabled the degradation of residual lignin by acidified H₂O₂ solution (Table 2 and 3).

Table 3

Tabela 3

Effects of the pH of H₂O₂ solution on chemical and technological indices of pulp treatment (pulps after alkaline extraction)

Wpływ pH roztworu H₂O₂ na wskaźniki chemiczno-technologiczne obróbki mas celulozowych (masy celulozowe po ekstrakcji alkalicznej)

| Pulp | pH | | | | | |
|-------------|---|-------|-------|---------------------------|--|--|
| Symbol masy | 2.5 | 4.5 | 11 | 11 Mg ⁺² added | | |
| | | Yield | 1 [%] | | | |
| | Wydajność [%] | | | | | |
| Α | 77.1 | 83.1 | 83.6 | 90.2 | | |
| В | 80.8 | 82.5 | 84.2 | 85.1 | | |
| С | 89.4 | 90.5 | 86.6 | 91.3 | | |
| | Kappa number | | | | | |
| | Liczba kappa | | | | | |
| Α | 25.7 | 30.9 | 22.5 | 25.8 | | |
| В | 5.3 | 5.4 | 6.4 | 8.1 | | |
| С | 5.6 | 3.9 | 4.5 | 5.1 | | |
| | ΔKappa No / Kappa No _{initial} 100 | | | | | |
| | ΔL. kappa / L. kappa _{pocz} .·100 | | | | | |
| A | 55.7 | 46.7 | 61.2 | 55.5 | | |
| В | 82.3 | 82 | 78.7 | 73 | | |
| С | 65 | 75.6 | 71.9 | 68.1 | | |
| | ΔL / ΔΥ | | | | | |
| | ΔL / ΔW | | | | | |
| A | 0.18 | 0.21 | 0.28 | 0.34 | | |
| В | 0.17 | 0.18 | 0.19 | 0.19 | | |
| С | 0.13 | 0.17 | 0.11 | 0.16 | | |

A - pulp kappa number - 58; B - pulp kappa number - 30; C - pulp kappa number - 16

Delignification with hydrogen peroxide solutions

Kraft pulps with different residual lignin content and production technology were used in the research. The differences in technologies have the influence on the content and quality of cellulose pulps. For example, residual lignin of pulp after oxygen delignification is different from the lignin contained in the standard kraft pulp with respect to the molecular weight and the lack of phenolic hydroxyl groups (Johansson and Ljunggren 1993). On the other hand, the so-called hard pulps (high kappa number) may contain certain quantities of hemicellulose. Since the delignification ability of hydrogen peroxide is relatively low (Rutkowski 1994b) and the range of kappa numbers

A – masa celulozowa o liczbie kappa 58; B – masa celulozowa o liczbie kappa 30; C – masa celulozowa o liczbie kappa 16

rather wide, 5% aqueous H_2O_2 solution was used in the studies. The use of such a high charge of peroxide (50%) in relation to dry cellulose pulp made the interpretation of results easier.

Differences in the degree of pulping and production technology were reflected in the reactivity of materials to hydrogen peroxide. This has been already observed during the analysis of reference tests at 22°C (not included in the paper). Pulp A (kappa number - 58), after treatment in alkaline conditions revealed the highest H2O2 consumption, the highest decrease of yield and kappa number in comparison to the other materials. Similar reduction of yield was noted for material A subject to high temperature treatment in alkaline conditions (80°C), (Table 2a). The other pulps (B and C) revealed less diversified effect of treatment conditions on yield, although the lowest value was also observed at pH 11 (no addition of H2O2 stabilizer). The total consumption of hydrogen peroxide in alkaline conditions occured at 80°C. In the acid medium the highest increase of H₂O₂ consumption was observed for the lowest pH (2.5) of treatment. In this medium also, the highest H2O2 consumption was noticed for the less delignified pulp (A). The relation of H₂O₂ consumption to the reduction of the kappa number ($\Delta H_2O_2/\Delta K$ appa No) in pulps with lower kappa numbers (B and C) was more advantageous in acidic than in alkaline conditions (Table 2b). This shows the possibility of using acidified hydrogen peroxide solutions, particularly in the initial stage of bleaching the pulps with lower kappa numbers. It should be pointed out that relatively low H2O2 consumption combined with high reduction of kappa number could be cost efficient, particularly if the remaining hydrogen peroxide is re-used in the productions. Experiments at 80°C have revealed considerable reduction of kappa number in all the studied pulps (Table 2a). A clear tendency of reducing differences between kappa numbers after treatment in acidic and alkaline conditions (particularly in the presence of Mg+2 ions) was observed in pulps with the lowest initial kappa numbers, especially in B. The most advantageous delignification value was obtained for material B in acidic conditions (pH 2.5), which was comparable to results obtained in alkaline conditions (Table 2 b).

However, it should be noticed that for pulp B it is not possible to balance out even approximately the values of yield and lignin removed during treatment (lignin was calculated as a difference of the kappa number before and after treatment, by multiplying the kappa number by 0.13). During the treatment process, considerable degradation of pulp carbohydrates system occurred. This is confirmed by the lowest viscosity values after acidic treatment for the three investigated materials (264.70 cm³/g), (Table 4). Reduction of the kappa number to 9.6 resulted in a simultaneous increase of selectivity of delignification (viscosimetric), which reached the highest value for pulp B (1.1), as compared to pulp A (0.8) and C (0.71), (Table 5).

Delignification value (hydrogen peroxide treatment at pH 2.5) of oxygen delignificated pulp is less adventageous than for pulp B, probably due to smaller number of reactive sites in the residual lignin (Table 2b). It should be pointed out that this pulp revealed distinct reduction of the kappa number already in slightly acidic conditions

Table 4

Tabela 4

The influence of pH of treatment on pulps viscosity

Wpływ pH obróbki na lepkość mas celulozowych

| рН | Viscosity [cm³/g] Lepkość [cm³/g] | | | | | | |
|------------------------------|--|----------------|--------|---|--------|--------|--|
| | Before alkaline extraction Przed ekstrakcją alkaliczną | | | After alkaline extraction Po ekstrakcji alkalicznej | | | |
| | Α | В | С | Α | В | С | |
| 2.5 | 547.33 | 264.70 | 378.84 | 197.03 | 242.96 | 245.86 | |
| 11 Mg ⁺² added | | 0 = | 514.13 | 579.45 | 534.49 | 411.96 | |

A – pulp viscosity 736.76 cm 3 /g; B – pulp viscosity 708.93 cm 3 /g; C – pulp viscosity 832.34 cm 3 /g A – masa o lepkości 736,76 cm 3 /g; B – masa o lepkości 708,93 cm 3 /g; C – masa o lepkości 832,34 cm 3 /g

Table 5

Tabela 5

The effect of pH of treatment on selectivity of delignification of pulps Wpływ pH obróbki na selektywność delignifikacji mas celulozowych

| pН | ΔKappa No / ΔViscosity ΔL.kappa / ΔLepkość | | | | | | |
|------------------------------|---|------|------|---|------|------|--|
| | No alkaline extraction Bez ekstrakcji alkalicznej | | | After alkaline extraction Po ekstrakcji alkalicznej | | | |
| | Α | В | С | Α | В | С | |
| 2.5 | 0.80 | 1.10 | 0.71 | 0.76 | 1.25 | 0.92 | |
| 11 Mg ⁺² added | : - | - | 1.74 | 2.60 | 2.97 | 1.35 | |

Pulps codes as in Table 2a Oznaczenia mas jak w Tabeli 2 a

(pH 4.5), in spite of minimum consumption of hydrogen peroxide (Table 2a). In this case, delignification can be related to the transfer of lignin macromolecule fragments into acidified solution rather than to H_2O_2 activity. Reduction of pH to 2.5 resulted in considerable decrease of the kappa number in pulps with the lowest initial kappa numbers (B and C), which is also related to increased H_2O_2 consumption. However, no influence of pH on delignification of pulp A has been found. Delignification of this material (with the highest lignin content) by acidified solutions was rather poor. At the same time, pulp A revealed the best selectivity of delignification among other materials treated with acidified H_2O_2 solutions (Table 2b). It should be explained by high lignin content, which creates protection against the degradation of carbohydrates. This is confirmed by viscosity results (Table 4), showing the lowest cellulose degradation

(among the studied pulps) in acidic conditions. Elimination of lignin during alkaline extraction has caused yet distinct decrease of pulp viscosity (Table 4). The comparison of selectivity of delignification (taking into account efficiency losses) for pulps processed in acidic and alkaline conditions revealed that the smallest differences in selectivity depending on reaction conditions are in pulps B and than for C and A, respectively (Table 2b).

It should be pointed out that acidic conditions (pH 2.5) have caused strong cellulose degradation as confirmed by viscosity measurements for pulp C (pH 2.5 - 378.84 cm³/g and pH 11 - 514.13 cm³/g), (Table 4). Degradation of cellulose in acidic conditions seriously decreased the selectivity of delignification in all studied pulps (Table 5). Since the decrease of viscosity and the kappa number was accompanied by slight consumption of hydrogen peroxide (approx. 7%) at the excess oxidizer, it would be useful to continue studies with the smaller doses of hydrogen peroxide.

Delignification with hydrogen peroxide solutions followed by alkaline extraction

Elimination by alkaline extraction step of the lignin fragments, which had been degraded during oxidation treatment, allowed for more comprehensive evaluation of H₂O₂ reactivity in relation to the treatment conditions (Table 3). Acidification has caused considerable yield loss in all pulps, however the highest value was obtained for material A and the lowest for C. Oxygen delignified kraft pulp revealed the smallest variations in yield depending on the treatment conditions (alkaline/acidic). Slight efficiency loss of this material was observed even during alkaline treatment without the addition of Mg⁺² ions (as compared to treatment in acidic or in alkaline medium with magnesium sulfate). Alkaline extraction stage had an influence on the kappa number as well. After treatment in acidic conditions, pulps B and C revealed relatively lower kappa numbers than in alkaline conditions. Comparable values of the kappa number for pulp A were determined at pH 2.5 and 11 (with MgSO₄). Delignification values for pulp B subjected to acid treatment were found to be higher than for treatment with alkaline H2O2 solution. Delignification value of pulp C was diversed respectively of the treatment conditions (acidic/alkaline), but not so much as it was in the case of pulp A. Reduction of pH from 4.5 to 2.5 had no effect on the delignification value of pulp B. In the case of oxygen delignified pulp (C), pH drop was accompanied by reduced delignification value and selectivity. In spite of comparable delignification values in alkaline and acidic conditions for material A with the highest lignin content, selectivity of delignification considerably decreased during treatment with acidified H₂O₂.

Viscosity measurements have confirmed degradation of cellulose pulps during treatment with acidified H₂O₂ followed by alkaline extraction (Table 4). The most significant decrease of viscosity was found for pulp A. Pulps B and C are characterized by similar resistance to degradation by hydrogen peroxide in acidic conditions. Delignification selectivity values confirm the influence of oxidizing treatment conditions on the main components of cellulose pulps: cellulose and residual lignin (Table 5). Treatment of pulps A and B in acidic conditions (with alkaline extraction) has resulted in double (B) and over triple (A) decrease of selectivity of delignification in comparison to alka-

line conditions. Pulp B had the highest selectivity of delignification (taking into consideration viscosity losses) both in alkaline and acidic conditions. It contains the highest amount of "native" magnesium (Table 1) which can perform protective function against carbohydrates both in alkaline and acidic conditions (Fossum and Haggstrom 1980). The lowest selectivity of delignification in acidic conditions was confirmed for pulp A and, slightly higher for C. These results are in correlation with magnesium profile in the pulps (Table 1). In the case of pulp C the essential thing are slight differences in selectivity of delignification irrespectively of the treatment conditions.

Results in Table 2 and 3 show that acidified H₂O₂ solutions, irrespectively of pH value, cause strong degradation of lignin, which can be quite easily removed by alkaline extraction. The most advantageous technological parameters were obtained for pulps with lower kappa numbers. Delignification values reflect reactivity of residual lignin of the studied pulps towards hydrogen peroxide. The results only to a certain extent can be explained using known mechanisms of reactions between hydrogen peroxide and lignin. Peroxide delignifie efficiently only the preliminary oxidized pulps, having enon and quinon groups (Agnemo and Gellerstedt 1979), and that is why less delignified pulp (A), as it would be expected, presented minor reactivity. Oxygen delignified pulp (C) should be more susceptible to delignification than other ones, but showed to be less reactive in comparison with kraft pulp not treated with oxygen (B). It was caused probably by lowered hydroxyl groups content and higher degree of condensation of the residual lignin.

Due to the potential degradation of cellulose, further research works should be focused on the use of slightly acidic solutions, shorter time of treatment or smaller peroxide charge as well as the use of H_2O_2 stabilizers, e.g. magnesium ions. Mg^{+2} ions prevent fast decomposition of H_2O_2 , which is catalyzed by metals contained in the pulps (Colodette et al. 1989). Slight protective effect of Mg^{+2} resulting in lower H_2O_2 consumption has been already found in reference tests (results not included).

The presence of Mg⁺² during treatment at 80°C increased the yield and kappa numbers of all the studied cellulose pulps in comparison with samples treated without magnesium sulfate addition (Table 3). The strongest effect of Mg⁺² was observed in pulp C (the highest increase of yield at the lowest increase of kappa number). In spite of very high initial charge of H₂O₂, this reagent was totally consumed during the reaction. Therefore, it seams that the mechanism of Mg⁺² activity is very complex and is not only limited to the precipitation or formation of complexes with metals which catalyse H₂O₂ decomposition (Jarrehult and Samuelson 1993, Linden and Ohman 1997). It is indirectly confirmed by the measurements of metals profile in the pulps (including "native" Mg⁺²). They show that in spite of different metal profiles, the efficiency of Mg⁺² added prior to the treatment has not decreased (Table 1). Apparent influence of Mg⁺² on the yield and the kappa number of kraft pulps seams to confirm the results of other studies showing possible interaction between magnesium ions and functional groups of lignin and cellulose (Abbot et al. 1992, Nunn and Van der Linde 1975).

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WPŁYW PH ROZTWORU NADTLENKU WODORU NA DELIGNIFIKACJĘ MAS CELULOZOWYCH SIARCZANOWYCH SOSNOWYCH

Streszczenie

Badano delignifikację mas celulozowych siarczanowych sosnowych różniących się stopniem roztworzenia i technologia produkcji, przy pomocy nadtlenku wodoru w środowisku kwaśnym i alkalicznym. Masy celulozowe po delignifikacji tlenowej, poddane obróbce nadtlenkiem wodoru, odznaczały się najmniejszym zróżnicowaniem wydajności i selektywności delignifikacji niezależnie od środowiska obróbki.

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