WOOD RESEARCH
55 (2): 2010
13-24

ALKALINE AND ALKALINE/OXIDATION PRE-TREATMENTS OF SPRUCE WOOD PART 2: PHYSICAL PROPERTIES OF THE PRE-TREATED WOOD AND THEIR INFLUENCE ON ITS DIGESTIBILITY UNDER CONDITIONS OF KRAFT COOK

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ABSTRACT

A series of comparable specimens of spruce wood were submitted to chemical pre-treatments. Chemical pre-treatments were carried out with diluted sodium hydroxide, or sodium hydroxide and then with diluted hydrogen peroxide, or per-acetic acid. All pre-treatments modified the physical properties of wood and caused its weight loss. The pre-treatments resulted in an increase in the facial swelling, coefficients of axial permeability and diffusion under stationary conditions of determination at ambient temperature. A deep, almost total deacetylation of spruce wood due to the pre-treatments influenced apparently the uptake of water by the pre-treated wood. All the mentioned alterations in physical properties of the pre-treated material are casually connected with its chemical changes and reflected improved digestibility of spruce wood under conditions of kraft cooks.

KEY WORDS: spruce, pre-treatments, mass loss, permeability, SEM, swelling, diffusion, uptake of water

INTRODUCTION

Alkaline pre-treatments are known to improve the digestibility of chips in the course of alkaline cooks. Their principle dwells in the preliminary deacetylation of wood, slight delignification and a partial dissolution of low molecular weight hemicelluloses in alkaline media. The above mentioned chemical alterations result in a moderate weight loss and increase in swelling of the pre-treated wood. The excessive swelling of the pre-treated wood is connected with the increased uptake of water by such a material which may influence positively the rate and completeness of its impregnation. The pre-treatments of chips based on the application of alkali or alkali followed by oxidation agents such as hydrogen-peroxide or per-acetic acid have also been tested (Solár et al. 2008 a, b and 2009 a, b). The combined pre-treatments improved the Kappa and brightness of the resulting kraft pulp noticeably, and in the case of hornbeam wood also higher mechanical strength was reported (Solár et al. 2009 a).

Treatment of hardwood and softwood chips with alkali (NaOH) and acidified peroximonosulphate connected with the subsequent alkaline extraction of lignin from the processed chips yielded pulp of high quality (Minor and Springer 1995).

This paper was focused on the presentation of data concerning alterations in physical properties of spruce wood pre-treated with alkaline and alkaline/oxidation media, especially those responsible for noticeably improved digestibility of chips under conditions of kraft pulping.

MATERIAL AND METHODS

Material

From a 75-year old spruce tree trunk the test specimens with dimensions of 2.5×2.5×1.0 cm were prepared. The longest dimensions were in radial and tangential directions. From the air-dry specimens a comparable series with proportional representation of mature and juvenile wood were selected (Solár et al. 2009 b).

Pre-treatments

A review of the applied sequences of pre-treatments is presented in Tab. 1, in which NaOH denotes solution in deionised water, P denotes hydrogen peroxide, PAA is per-acetic acid, and DCDA dicyandiamide (an activator) added to oxidation agent (P) in amount of 0.028g.g^{-1} of o. d. wood (approx. 10 % based on the lignin content). The wood to alkali (oxidation agent) solution ratio was 1:5 w/w. A more detailed description was given in Part 1 of the paper (Solár et al. 2009 b).

Tab. 1: The pre-treatment sequences of hornbeam and spruce wood specimens

Pre-treatment sequence	Agent/Time (h)/Temperature (°C)
1	2.5% NaOH/48/20
2	2.5% NaOH/48/20 + 7.5%P/72/20
3	2.5% NaOH/48/20 + 7.5% P/24/60 + DCDA
4	2.5% NaOH/48/20 + 8% PAA/72/20

Determination of physical properties

- Weight of both the sound and pre-treated series of the specimens in their oven dry state (drying in a desiccator over H_2SO_4 and then P_2O_5).
- Facial swelling of spruce wood specimens prior to pre-treatments was calculated from their dimensions in radial and tangential direction after 48 hours duration dipping in de-ionised water with the addition of Chelaton III (0.0155 mol.l^{-1}). The temperature

of the process was 20 ± 2°C. To remove the air from wood and promote its penetration, two 10-min vacuum treatments at 10 kPa were carried out at the beginning of soaking. Swelling of the pre-treated specimens was measured instantly after rinsing their surface with de-ionised water (determination was not performed according to the Standards with normalised moisture content of the specimens). For determination of facial swelling, the dimensions of sound wood with initial moisture content of 9.07 % were used as a reference.

- Coefficients of axial permeability of sound and pre-treated spruce wood were determined at a constant pressure gradient according to the method of Regináč et al. (1977). The method is based on the application of the Darcy law. The monitoring temperature was 20°C, and de-ionised water was used as a medium. The measurements were carried out on the specimens saturated with water after a 48-hour immersion in the de-ionised water.
- Diffusion coefficients of sound and pre-treated specimens of mature and juvenile spruce saturated with de-ionized water were determined under pseudo-stationary conditions from the conductivity of an electrolyte passing through them into the monitoring chamber. The method proposed by Reinprecht and Makovíny (1990) was used for the determinations. The conductivity in the chamber initially containing de-ionized water was measured within a 6-h period of the pseudo-stationary process. Sodium chloride was used as an electrolyte in order to avoid deacetylation and neutralization of acidic groups of sound wood with alkali solution when used. After these measurements, sodium chloride was removed from the specimens by continual washing in de-ionized water. The same specimens were immersed into 2.5 % NaOH at 20°C for 48 h, and their impregnation was promoted by a vacuum in the initial stage. The chemicals from the pre-treated specimens were removed prior to measurements by long-term continual washing with de-ionized water until the conductivity of de-ionized water and the extract from a 6-h cold water extraction (3 specimens/100 ml of water) almost equalled each other (0.029-0.031 μS for water, and 0.050-0.056 μS for the extracts).
- Uptake of water by sound and the pre-treated spruce wood specimens was determined from a difference between the weights of wet and oven dry specimens. In the case of the pre-treated specimens these were washed with de-ionised water almost to neutral pH of water extract.
- Scanning electron micrographs (SEM) of cut radial surfaces of sound and pre-treated spruce wood coated with Au were obtained using TESCAN Digital Electron Microscope VEGA TS 51-20.

RESULTS AND DISCUSSION

Tab. 2 represents the mass loss, facial swelling and coefficients of axial permeability of the pre-treated spruce wood and an increase in the uptake of water by spruce wood due to pre-treatments, as well.

Tab. 2: Mass loss (Δm), coefficient of axial permeability (K), facial swelling (F), and uptake of water (196 h of dipping) by sound and the pre-treated, washed specimens of a small series of spruce wood (n = 18, $w_{init.}$ = 9.07 %, $\rho_{w\ init.}$ = 0.4324 g.cm^{-3})

Pre-treatment	Δ m (%)	K (m^2)	F (%)	Increase in F (%)	Uptake of water in g/100 g o.d. wood	Increase in uptake of H_2O (%)
0	-	**2.21E-14 ***	**8.32**	-	**188.30**	-
v (%)		49,79	16.58		8,99	
1	**3.47**	**3.18E-13**	**10.57**	**27.04**	**217.81**	**15.67**
v (%)	24.04	120,10	16.56		4.23	
2	**3.94**	**3.53E-13**	**10.93**	**31.37**	**221.78**	**17.78**
v (%)	18.61	101.24	12.59		5.42	
3	**5.35**	**1.22E-13**	**11.12**	**33.65**	**228.74**	**21.48**
v (%)	20.21	95.23	13.88		7.83	
4	**10.02**	**9.80E-14**	**10,33**	**24.15**	**219.63**	**16.64**
v (%)	19.23	33.05	12.72		5.16	

*coefficient of permeability of cautiously dried mature wood dipped for 196 h in 0,0155 M solution of Chelaton III and in de-ionized water; dried juvenile wood soaked with water was impermeable, regardless whether it was sound or pre-treated

Note: Coefficient of permeability of fresh mature spruce wood was **6.45E^{-12}** (v = 22.12 %); in the case of mature wood pre-treated with 2.5 % NaOH the coefficient was was reduced to **3.12E^{-12}** (v = 47.31 %). A combined pre-treatment of fresh mature wood with NaOH/H_2O_2 equalled to **3.43E^{-12}** (v =42.15 %). Total number of specimens of mature wood in the sets before and after pre-treatments was 6.

As it follows from Tab. 2, the mass loss of spruce wood depended on the pre-treatment sequence applied. The deepest mass loss resulted from application of the pre-treatment sequence 4 (NaOH/per-acetic acid). The total deacetylation and partial delignification (Tab. 3) of wood, and to a lesser degree also a partial dissolution of hemicelluloses and alkali soluble extractives contributed mainly to this phenomenon. High delignification efficacy of the pre-treatment sequence No. 4 dwells in a progressive oxidation of lignin at low pH, including the decomposition of its aromatic nuclei (Chang and Allan 1971).

Tab. 3: Amount of acetyl groups and lignin removed from spruce wood due to the pre- treatments (%) (Solár et al. 2009 b)

Pre-treatment sequence	Removed acetyl groups (%)	Removed lignin (%)
Sound wood (**0**)	-	-
1	97.80	5.83
2	98,50	6.67
3	97.80	8.47
4	97.10	**39.65**

The chemical pre-treatments increased markedly the coefficients of axial permeability, however only in the case of wet mature wood (dried and soaked with water prior to pre-treatments) (Tab. 2). Chemical pre-treatments did not influence the permeability (w > FSP) of juvenile wood submitted to the same procedure. A difference between the axial permeability of mature and juvenile spruce wood may explain the following SEM images. From the space reasons only a few images of sound and the pre-treated juvenile and mature wood with sequences 2 and 4 are presented in Figs. 1 - 10.

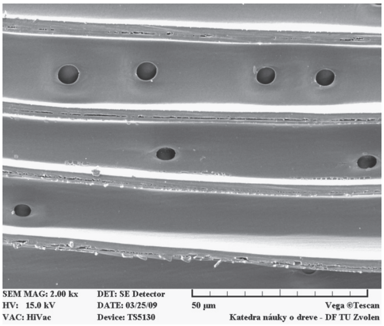

Fig. 1: Tracheids of sound early juvenile wood, untouched bordered pit between tracheids in closed position

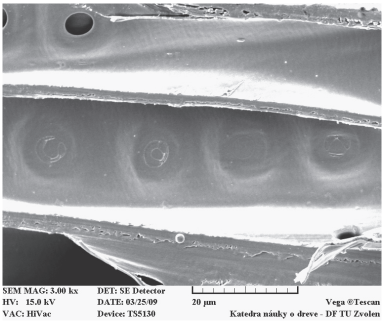

Fig. 2: Tracheids of sound early juvenile wood, bordered pits in closed state

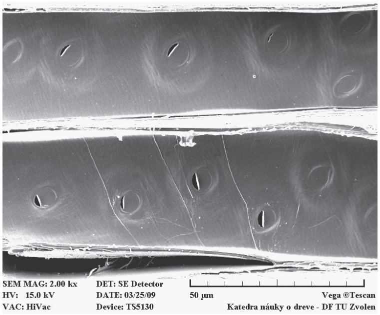

Fig. 3: Tracheids of sound early mature wood; slightly open bordered pits

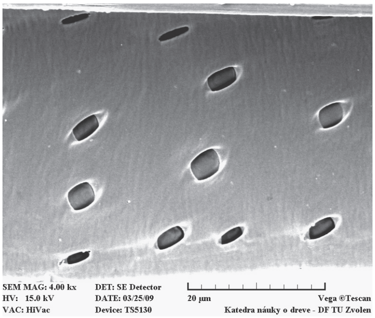

Fig. 4: Tracheid of sound early mature wood; partly open, rolled bordered pits (cross field)

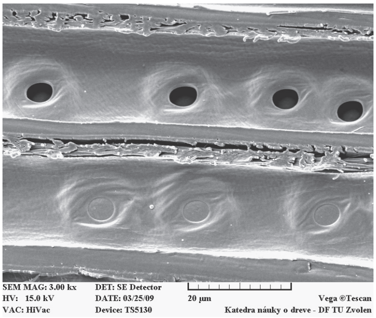

Fig. 5: Tracheids of early juvenile wood pre-treated with $NaOH/H_2O_2$ *(sequence 2); undamaged bordered pits, released middle lamellae*

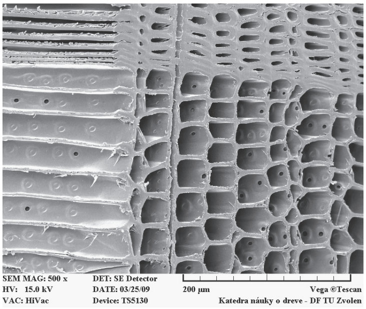

Fig. 6: Transverse and_radial plane of juvenile wood pre-treated with $NaOH/H_2O_2$ *(sequence 2); interface between late and early wood; closed untouched bordered pits between tracheids, ray of axial parenchyma*

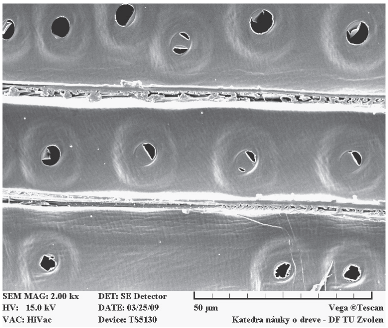

Fig. 7: Tracheids of early mature wood after pre-treatment with NaOH/H_2O_2 (seqence 2); defects in bordered pits, release in middle lamella

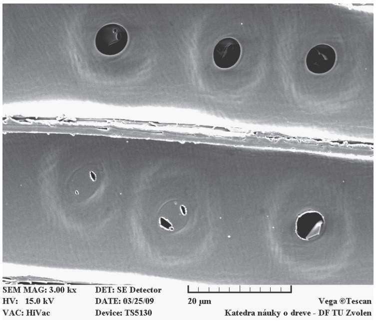

Fig. 8: Tracheids of early mature wood pre-treated with NaOH/H_2O_2 (sequence 2); corroded bordered pits

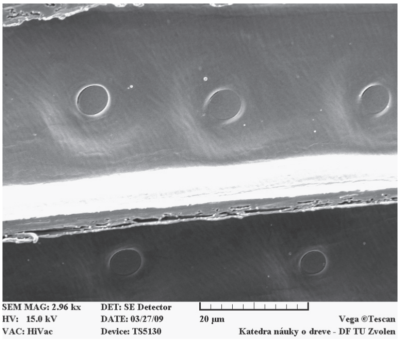

Fig.9: Juvenile wood pre-treated with NaOH/CH_3CO-OOH (sequence 4); uncorroded bordered pits

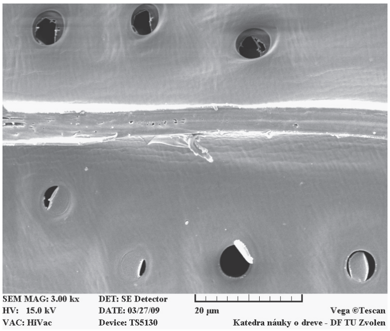

Fig. 10: Tracheids of mature wood pre-treated with a NaOH/CH_3CO-OOH sequence; partly corroded boarded pits

Despite an increased axial permeability of all samples of the pre-treated mature spruce wood, the contribution of this property to the course of impregnation (if considered separately form the other changes) might be negligible due to low value of the corresponding coefficients with an order of E-13 (m^2). When pulping chips representing a proportional mixture of the pre-treated mature and juvenile wood it is also necessary to consider the influence of impermeable portion of juvenile wood in the mixture. Extremely low permeability of once dried and then with water saturated juvenile spruce wood observed Lang et al. (2004).

Tab. 2 illustrates also an increase in the facial swelling of all series of the pre-treated spruce wood. This phenomenon results from improved accessibility of wood for water due to deacetylation (Sjöström and Haglund 1961, Sumi et al. 1964) and release in its micro- and sub-microstructure due to action of alkali. The apparently higher facial swelling and mass loss of the pre-treated wood give rise to an assumption of its deeply diminished "reduced density" ($\rho_{red.\ min.} = mo/V_{w\ max.}$) at a moisture content above FSP. These findings are in a good accordance with increased uptake of water by the pre-treated wood. The increase in the uptake of water may be a principal cause of improved digestibility of the pre-treated spruce wood due to a higher amount of pulping liquor delivered into the chips during the impregnation step of pulping.

The improved accessibility of the pre-treated wood for water contributes also to rate of diffusion because water is a medium for diffusion of water soluble compounds in the processed chips. In Tab. 4, the diffusion coefficients determined under "pseudo stationary" conditions in axial direction of the specimens from identical small sets of sound and afterward

As it follows from Tab. 4, the pre-treatment of selected specimens of spruce wood with alkali (NaOH) enhanced the rate of diffusion in their axial direction. It is surprising that the pre-treatment influenced more the diffusion through juvenile wood (five multiple increase in D), compared to mature wood where diffusion coefficient increased approximately two times. Despite such an apparent increase in the diffusion coefficients due to pre-treatment of spruce wood, its contribution to transport processes proceeding through such a material is manifold smaller, in comparison with those of hardwoods. As an example we present the values of diffusion coefficients determined for both sound and by alkali pre-treated hornbeam wood. These are two to three orders higher (D_{sound} = 0.81 E-7 and $D_{pre\text{-}treat.}$ = 1.55E-7) than those determined for spruce wood (Solár et al. 2008 a).

Tab. 4: Diffusion coefficients (D), surface swelling (F), mass loss (Δ m) and uptake of water (g H2O /g o. d. wood) by mature (n = 3) and juvenile (n = 3) spruce wood pre-treated 48 h with 2.5 % sodium hydroxide. Total time of immersion in sodium hydroxide and washing with deionised water was 240 h.

Mature wood						
Basic statistics	**g H_2O/g o. d. wood**	**Δ m (%)**	**F (%)**	**D ($m^2.s^{-1}$) sound wood**	**D ($m^2.s^{-1}$) pre-treated wood**	**Dp/Ds**
Avg.	**2.05**	**3.50**	**11.85**	**5.09 E-10**	**11.91 E-10**	**2.43**
Std.	0.064	0.375	1.58	2.50 E-10	4.86 E-10	0.28
v (%)	3.15	10.71	13.30	49.89	40.81	11.52
Juvenile wood						
Avg.	**2.14**	**5,59**	**9.98**	**1.14 E-10**	**5.23 E-10**	**4.87**
Std.	0.044	0.094	1.030	0,58	2.49	1.42
v (%)	2.07	14.30	10.31	50.94	47.78	29.15

For information, the properties (uptake of water, facial swelling and mass loss) of the selected comparable small series (n = 3) of mature and juvenile spruce wood resulting from a 240-h immersion in de-ionised water are presented in Tab. 5.

Tab. 5: Uptake of water (g H_2O /g of o. d. wood), mass loss (Δ m) and facial swelling (F) of sound mature (n = 3) and juvenile (n = 3) spruce wood immersed into de-ionizewater for 240 h

Mature wood			
Basic statistics	**g H_2O/g o.d. wood**	**Δ m (%)**	**F (%)**
Avg.	**1.74**	**0.54**	**8.82**
Std.	0.092	0.103	1.718
v (%)	5.30	19.07	19.48
Juvenile wood			
Avg.	**1.79**	**1.01**	**9.06**
Std.	0.025	0.203	0.489
v (%)	1.44	20.10	5.40

From the comparison of data concerning permeability, diffusion coefficients and "uptake" of water by the pre-treated spruce wood (Tab. 2, 3 and 4) it follows that the highest impact on its impregnation and digestibility represents more likely the increase in uptake of water or water solutions of pulping chemicals. This statement however, concerns especially the pulping of the air-dry pre-treated spruce chips. In the case of impregnation of the pre-treated wood saturated with water (w > FSP), the increased rate of diffusion may play more important part.

The contribution of better axial permeability of the pre-treated mature wood and of higher rate of diffusion through the pre-treated mature and juvenile wood (based on the data obtained at 20°C) to its digestibility seems to be less significant. Such a conclusion however, need not inevitably pay in the case of impregnation of chips at elevated temperatures of kraft cook (e.g., for pulping diagram: 2-h pre-heating from 80°C up to the pulping temperature of 170°C and a 2-h delignification at this temperature).

The influence of chemical alterations of the pre-treated spruce wood on its digestibility and quality of the resulting pulp has already been dealt with in Part 1 of this contribution.

CONCLUSIONS

Pre-treatment of spruce wood with diluted alkali, or alkali in combination with hydrogen peroxide or per-acetic acid, respectively, caused a number of alterations in its physical properties. Some of them may play an important part in semi-chemical and chemical processing of wood to pulps.

From the viewpoint of transport of pulping chemicals into chips of the pre-treated spruce wood an interesting finding is excessive swelling of wood resulting from a marked increase in the water uptake. This phenomenon may improve the digestibility of the pre-treated wood via more complete impregnation of chips with pulping media.

An excessive amount of water in the released and swollen ultra-structure of wood, together with its diminished "reduced density" also promote diffusion of chemicals through the cell walls and thus contribute to more complete impregnation and delignification of chips.

Formally, the least effect on the smooth impregnation of the pre-treated spruce chips might be attributed to increased axial permeability of the pre-treated mature wood. This statement is based on the generally low coefficients of axial permeability of conifers (regardless they were pre-treated, or not) and on the fact that the chips represent a mixture of mature and juvenile wood, the latter one remaining impermeable after the pre-treatments.

The real contribution of increased diffusion and permeability of the pre-treated spruce chips on the transport processes during kraft cooks is difficult to predict from the corresponding coefficients obtained at the ambient temperature. At the temperatures of impregnation and pulping the role of diffusion and permeability might be apparently higher due to reduced viscosity of pulping liquor, its surface tension and some other factors.

ACKNOWLEDGEMENT*S*

This research was supported by the Slovak Research and Development Agency under the contract No. APVV-0282-06.

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