Study of Penetration Kinetics of Sodium Hydroxide Aqueous Solution into Wood Samples

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The kinetics of unidirectional penetration of NaOH aqueous solution into rectangular samples of wood oriented parallel to a stern axis were studied. Scots pine (*Pinus sylvestris*), European larch (*Larix decidua*), blackthorn (*Prunus spinosa*), white willow (*Salix alba*), and horse-chestnut wood (*Aesculus hippocastanum*) were studied in this work. The time dependence of liquid incorporation was measured by the volumetric method as a change of total volume of coexisting liquid (NaOH/H_2O) phase. The total thickness of the swollen surface layer d and mean value of the apparent diffusion coefficient $\overline{D}_{app}$ of aqueous NaOH solution at 22 °C were determined.

Keywords: Incorporation; Diffusion; Liquid transport; Wood; Swelling; Alkali treatment

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INTRODUCTION

Cellulosic materials make up a very important group of raw materials used in many branches of industry, agriculture, and environmental technology. Because of their excellent properties, researchers are constantly searching for their novel, practical applications. Cellulosic research into the production of biofuels, phytomass and raw energy for chemistry and biotechnology, and cellulosic nanomaterial fabrication and application has received increased attention in the last ten years.

The utilization of lignocelluloses, as well as their structure and properties, have been expounded in numerous works (Ghose *et al.* 1972) in the past. The richest and most diversified phytomass material seems to be wood from trees, as a renewable product of photosynthesis (Blazek and Košík 1993). It has valuable aesthetic properties (texture, colour, touch feel, *etc.*), typically high strength and elasticity with respect to its specific mass, very low thermal expansion, good acoustic properties, appropriate resistance to corrosion with medium-concentrated acids, relatively good resistance to degradation, and good recyclability.

Wood is a material of plant origin characterized by a fibrous structure. Its high lignin content contributes to the unique rigidity of the structure and distinguishes wood from all the other plant materials. Its structural elements vary from a single fibre to aggregates of different sizes and geometries. It is a complex anisotropic material with an abundance of hydroxyl groups that have a high affinity to water molecules. The material can maintain equilibrium for a long time when exposed to external conditions. The moisture content has a profound influence on wood's properties, especially on the density and the other physical and chemical properties.

Wood is a natural heterogenic and colloidal system of many compounds that have very different chemical structures. General studies of the chemical structure of wood during the development of organic, colloidal, biochemical, and analytical chemistry methods have led to more detailed characterization of this material (Blazej and Kosik 1993). Cellulose, hemicellulose, and lignin are the main macromolecular components of wood. Their structural complexity is exemplified by the microfibrillar structure of cellulose in combination with branched rods of hemicelluloses chains in higher tertiary and quarternary ordered structures. Other main constituents comprise a wide diversity of low-molecular weight inorganic and organic substances, such as glucane, galactane, saccharidic acids, alkali chlorides and the other inorganic molecules. The overall picture of a wood cell wall at the supramolecular level is a crystalline, filamentous, solid phase material (the microfibril) composed almost exclusively of cellulose I crystal domains, which are impenetrable to water. There are also two interpenetrating solid phase systems, one composed of an extensively branched, three-dimensional, amorphous polymer (lignin), and the second composed of a complex of relatively linear polymers of a variety of molecular sizes and solubilities (hemicelluloses). Finally, the presence of water and air within the wood cell wall structure and the intermolecular free space should be considered as well (Mark 1981; Claesson and Engström 1977; Argyropoulos *et al.* 1995; Blazej and Kosik 1993 and many other authors) for the reason of hydrogen bond content lowering between carbohydrate chains during the swelling.

The world's supply of crude oil is running short, and the demand is likely to exceed the extraction capacity within the next few decades. Coal may last a few hundred years, but extensive mining and combustion will lead to serious environmental consequences. There is a shortage of fossil fuels (gas, liquid, and solid) as well as a deficit of fossil raw material resources. The current systems of production of organic compounds are based mostly on the conversion of fossil raw materials using a combination of chemical and biological methods in the last hundred years. Solutions to these energy shortage problems should be solved by:

- decrease the total energy consumption in all branches of human activity (industrial, commercial, cultural, and social),
- improve the knowledge of natural cycles of biomass production and realize the most intelligent methods for biotechnological processing,
- improve the effectiveness of solar energy conversion and storage, and
- increase the value of atmospheric carbon dioxide transformation into low molecular weight compounds and their utilization.

It has been estimated that 180 million tonnes of phytomass is produced on Earth annually (Blazej and Kosik 1993). Only a small part of this is used for industrial purposes such as the production of paper; various chemicals are used in synthetic fibre production, in the construction industry, and as an energy source; approximately 1% is used in the foodstuff industry (Hall 1978).

The following fundamental problems should be seen with respect to complex wood processing:

- regulation of the photosynthesis process, leading to a specific higher yield of directly utilizable products,
- economically improvement the process of plant body disintegration,

- complex utilization of all parts of trees and other components of plants (waste-free technology), and
- quantitative defibrilization in low-cost procedures

The thermal degradation of lignocellulosic materials has been studied very intensively (Shafizadeh *et al.* 1976). The main products of the combined biological, physical, and chemical degradation of wood are different types of coal, as well as humic and fulvic substances. The polysaccharidic part of wood is thermally more sensitive than the lignin component. The most characteristic feature of polysaccharides seems to be their cyclic arrangement and a variety of induction effects (Shafizadeh *et al.* 1976). These effects influence the properties of inter-glycosidic bonds as well as the bond strength between carbon atoms and they can be multiplied in the presence of acidic and alkaline compounds during the thermal destruction of wood. In such cases, polysaccharidic molecule transformation utilizes complicated isomerisation on a hemiacetal structure (Phillip et al. 1979; Horacek 2001; Bucko *et al.* 1988).

Theory

Diffusion treatments in which a high concentration of an electrolyte is applied to the outer surface of a wet wood specimen have been studied by many authors (Levy and Greaves 1978; Cussler 1984; Cranck and Park 1968; Smook 1989; Perre and Turner 2001). However, in spite of important developments and many fundamental studies in recent years (Tornqvist *et al.* 2001; Arevalo and Hernandez 2001; Schott 1992; Zmeskal *et al.* 1999), it seems that there are still some theoretical problems in the description of aqueous electrolyte solution diffusion in solid wood samples. The transport of external molecules in complex solid polymeric systems is generally governed by two simultaneous phenomena:

- diffusion, in which the mass flux is driven exclusively by a chemical potential gradient; and
- relaxation, where the major driving force is the distance of the system from the equilibrium state.

In the first period of mutual contact in the incorporation of aqueous NaOH solution into wood materials, there is strong swelling of the amorphous parts of cellulose aggregates, hemicelluloses, and lignin and the creation of a characteristic swollen surface layer (SSL) with a sharp interface boundary/solid sample complex. Many authors have found that during macromolecular compound swelling, dynamic overloading and a nonisotropic dissipation of stress tensors can be identified. In some cases, the overloading of internal polymeric chains results in free radical generation, characteristic of high reactivity to molecular oxygen. Many different peroxyradicals (ROO·) can be generated.

Diffusion of an aqueous electrolyte solution (1:1) may be regarded as an issue in which some of the components of a co-existing liquid system become immobilised when the incorporation of the liquid phase into the solid body proceeds. If the electrolyte molecules are immobilised by a first-order or pseudo-first-order reaction mechanism whose rate constant is *k*, the diffusion equation of these "active" species of the systems of one-dimensional semi-infinite media is given as (Eq. 1),

$$\frac{\partial c_i}{\partial t} = D_i \left(\frac{\partial^2 c_i}{\partial x^2} \right) - k_i \, c_i \tag{1}$$

where c_i is the i-th active species concentration (Me^{+n}, X^{-m}, H_2O), t is time, and x is distance, provided that the diffusion coefficient D_i is constant. In the diffusion formula for an infinite liquid body, the initial and boundary conditions are:

$$\begin{aligned} &c = 0, x = 0, t = 0 \\ &c = c_0, x = 0, t \rangle 0 \end{aligned} \tag{2}$$

According to Danckwerts (1970), the solution of Eq. (1) can be written in the form:

$$\frac{c_i}{c_i^0} = \frac{1}{2}\exp\left(-x\sqrt{\frac{k_i}{D_i}}\right) erfc\left\{\frac{x}{2\sqrt{D_i t}} - \sqrt{k_i t}\right\} + \frac{1}{2}\exp\left(x\sqrt{\frac{k_i}{D_i}}\right) erfc\left\{\frac{x}{2\sqrt{D_i t}} + \sqrt{k_i t}\right\} \tag{3}$$

The total amount of aqueous solution components incorporated into the solid body (G_t) during time t is given as follows:

$$G_t = \int_0^t -\sum_i D_i \left(\frac{\partial^2 c_i}{\partial^2 x}\right)_{x=0} dt = \sum_i c_i^0 \sqrt{\frac{D_i}{k_i}\left\{\left(k_i t + \frac{1}{2}\right) erfc\sqrt{k_i t} + \sqrt{\frac{k_i t}{\pi}} \exp\left(-k_i t\right)\right\}} \tag{4}$$

If the validity of an additive rule for all components in the solution is assumed, then G_t may be substituted by a volume of the incorporated liquid system and can be written (Schott 1992) as a ratio of the incorporated volume at infinite time (at equilibrium) $V_\infty^{(l)}$ to the time $V^{(l)}$, and under the supposition that $D_i = D_j = D_{k.....} = \overline{D}$, it can be written,

$$\frac{V_\infty^{(l)}}{V_\infty^{(l)} - V^{(l)}} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left\{\left[\frac{(2n+1)\pi}{d}\right]^2 \overline{D} t\right\} \tag{5}$$

and when

$$t \rangle\rangle 1; n \rangle\rangle 1; \ln\left(\frac{8}{\pi^2}\right) \approx 1 \tag{6}$$

then

$$\frac{V_\infty^{(l)}}{V_\infty^{(l)} - V^{(l)}} = \exp\left(\frac{\pi^2 \overline{D} t}{d^2}\right) = \exp(K t) \tag{7}$$

and finally

$$\ln \frac{V_{\infty}^{(l)}}{V_{\infty}^{(l)} - V^{(l)}} = \left(\frac{\pi^2 \, \overline{D}_{app} t}{d^2} \right) = K t \tag{8}$$

where $V_{\infty}^{(l)}$ is the total volume of aqueous solution incorporated into the solid specimen. d is the limiting value of the depth of penetration into the solid body, given as:

$$d = \frac{V_{\infty}^{(l)}}{\pi r^2} \tag{9}$$

$\overline{D}_{app}$ is an apparent integral value of the mutual diffusion coefficient, given as:

$$\overline{D}_{app} \approx \frac{d^2 K}{\pi^2} \tag{10}$$

EXPERIMENTAL

Materials

The studied wood samples were Scots pine (*Pinus sylvestris*) aged 67 years, European larch (*Larix decidua*) aged 20 years, blackthorn (*Prunus spinosa*) aged 21 years, white willow (*Salix alba*) aged 15 years, and horse-chestnut wood (*Aesculus hippocastanum*) aged 40 years, all taken from the same territory (Hranice na Morave, Czech Republic). Samples were selected from rectangular prismatic wooden boards with the same orientation shape and characteristic structural elements having dimensions of 2.5 cm x 4 cm x 0.5 cm. All samples were subjected to the same drying procedure, consisting of 18 h at 50 °C and atmospheric pressure, prior to measurement. Sodium hydroxide used in the study was purchased from Merci, Czech Republic. For preparation of all solutions, deionised distilled water (conductivity of 0.06 µS/cm) (Watek Demiwa 3ROS, Czech Republic) was used.

Methods

A schematic diagram of the experimental set-up used for the study of the kinetics of incorporation of aqueous solutions into the wood specimens is shown in Fig. 1.

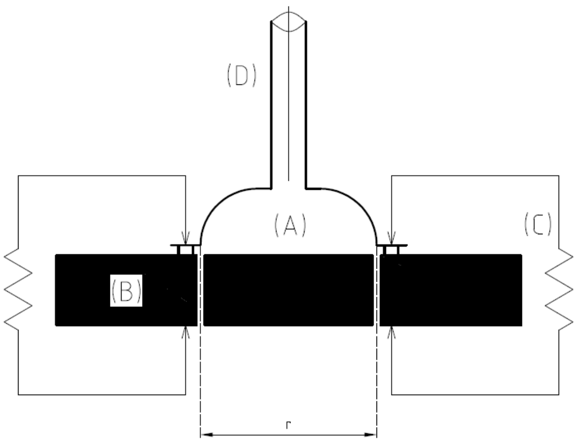


Fig. 1. Schematic representation of experimental set-up: A – aqueous solution of the electrolyte, B – rectangular solid wood sample, C – flexible tool holder, D – narrow capillary tubing

A simple experimental arrangement was realised using a glass reservoir (A) tightly connected to the surface of the studied wood sample by means of a mechanical holder (C). The reservoir (A) was capped by a Schelbach capillary with the volume reading ± (1×10^{-3}) cm^3. The volume of the liquid also can be read automatically, as described in a previous paper (Zmeskal *et al.* 1999). Penetration experiments were performed at the ambient temperature of 22 °C. The more detail information can be received in an older literature (Tomaschek 1938).

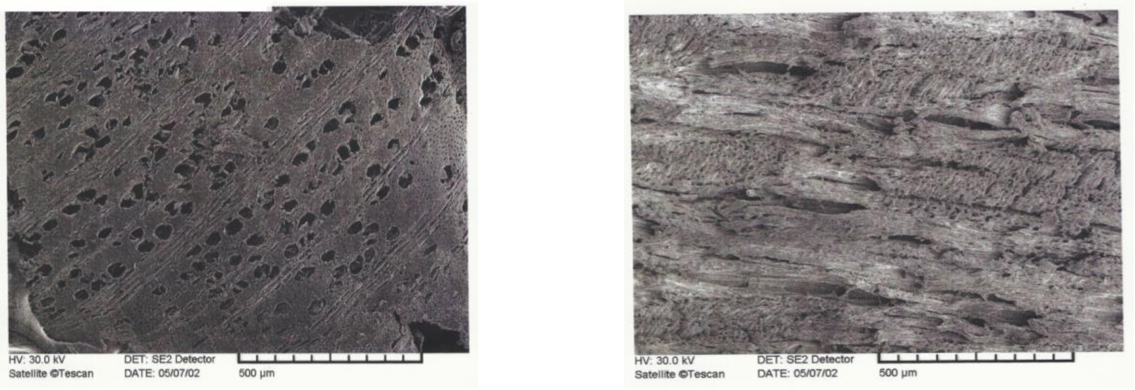
RESULTS AND DISCUSSION

Many factors influence the process of wood sample transformation and are reflected in the observed densities of wood solid matter. Photographic images of Scots pine (*Pinus sylvestris*) and European larch (*Larix decidua*) are shown in Figs. 2 and 3.

Fig. 2. Scots pine wood sample structure

Fig. 3. European larch wood sample structure

The physical and chemical properties of wood are determined by the chemical composition, the anatomy of the wood structure, previous wood sample history, properties of the ambient experimental atmosphere, and the applied testing methods. It is important to note that all of the aforementioned factors are reflected in the densities of wood samples. For the materials tested, the following densities were observed: Scots pine (*Pinus sylvestris*), 0.520 ± 0.005 g/cm^3 (see Fig. 2 for sample structure); European larch (*Larix decidua*), 0.592 ± 0.007 g/cm^3 (see Fig. 3 for sample structure); blackthorn (*Prunus spinosa*), 0.700 ± 0.005 g/cm^3 (see Fig. 4 for sample SEM structure); white willow (*Salix alba*), 0.450 ± 0.008 g/cm^3; and horse-chestnut (*Aesculus hippocastanum*), 0.440 ± 0.006 g/cm^3. The water content measured for all samples was 12 wt%.



(A) (B)

Fig. 4. SEM of the studied blackthorn wood sample: (A) – original, (B) – after sodium hydroxide treatment

The kinetics of the incorporation of an aqueous solution of NaOH in Scots pine wood is represented in Fig. 5.

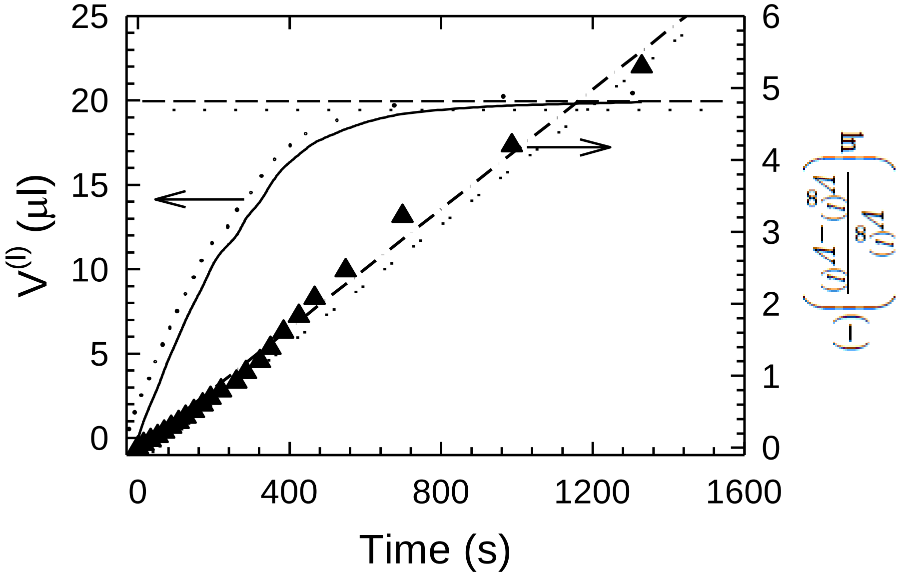


Fig. 5. Time dependence of the incorporated volume $V^{(l)}$ and of the linear dependence of $\ln\left(V_\infty^{(l)} / V_\infty^{(l)} - V^{(l)}\right)$ of 15 wt% aqueous NaOH solution in the Scots pine sample at 22 °C

This is characteristic of the linear increase of the time dependence of the quantity $V_\infty^{(l)}$ /[$V_\infty^{(l)}$ - $V^{(l)}$] for Scots pine wood. The rate of penetration of aqueous NaOH solutions in the wood samples was determined primarily by their apparent diffusion in the systems. The thickness *d* of the swollen surface layer (SSL) between the two phases in contact depended on temperature, time, and the thermal history of the complex polymer system. As an integral mechanism of the incorporation of water, it is similar to the process we described in previous papers (Lapcik *et al.* 1988; Valko and Lapcik 1967). The process of incorporation can be divided into two parts: the diffusion process of swelling and the proper process of diffusion of solvated molecules from the swelling surface layer into the co-existing surface solvent liquid layer. The complex process of the mutual transport is characterized with apparent diffusion coefficient $\overline{D}_{app}$, the internal pressure in SSL, the total thickness of the SSL, and the appropriate activation thermo-dynamic parameters of swelling and dissolution.

For the case of wood swelling in the aqueous NaOH solution, not only should the composition of the three principal polymers (cellulose, lignin, and hemicelluloses) be taken into account, but also some minor low-molecular weight organic and inorganic compounds. That is why the parameters of swelling and dissolution are denoted as apparent values. In Fig. 7, the concentration dependence of the apparent total thickness of the swollen surface layer (*d*) on NaOH concentration is shown. It is supposed that the governing process of NaOH solution incorporation is primarily diffusion in the cells wall. Calculated parameters obtained from the data for the model given in Eq. 8 for different concentrations of the aqueous sodium hydroxide solutions are summarized in Table 1.

Table 1. Kinetic Parameters of Sodium Hydroxide Aqueous Solution Penetration into Studied Wood Samples

c_{NaOH} [w. %]	$V_\infty^{(l)*}$ [mL]	K [s^{-1}]	d [cm]	$\overline{D}_{app}$ [$cm^2\ s^{-1}$]
Scots pine (*Pinus sylvestris*)				
0	20	0.67×10^{-2}	2.64×10^{-3}	0.47×10^{-8}
5	35	1.18×10^{-2}	4.61×10^{-3}	2.53×10^{-8}
10	30	0.62×10^{-2}	3.95×10^{-3}	0.98×10^{-8}
15	25	0.26×10^{-2}	3.30×10^{-3}	0.29×10^{-8}
20	34	0.59×10^{-2}	4.42×10^{-3}	1.17×10^{-8}
European larch (*Larix decidua*)				
0	33	1.51×10^{-2}	4.35×10^{-3}	2.89×10^{-8}
5	32	0.48×10^{-2}	4.22×10^{-3}	0.87×10^{-8}
10	29	0.33×10^{-2}	3.76×10^{-3}	0.47×10^{-8}
15	29	0.28×10^{-2}	3.82×10^{-3}	0.45×10^{-8}
20	35	0.53×10^{-2}	4.61×10^{-3}	1.14×10^{-8}
Blackthorn (*Prunus spinosa*)				
0	34	0.14×10^{-2}	4.48×10^{-3}	0.29×10^{-8}
5	25	0.19×10^{-2}	3.30×10^{-3}	0.21×10^{-8}
10	40	0.30×10^{-2}	5.27×10^{-3}	0.85×10^{-8}
15	40	0.76×10^{-2}	5.27×10^{-3}	2.14×10^{-8}
20	37	0.97×10^{-2}	4.88×10^{-3}	2.34×10^{-8}
White willow (*Salix alba*)				
0	36	0.35×10^{-2}	4.75×10^{-3}	0.80×10^{-8}
5	17	0.26×10^{-2}	2.24×10^{-3}	0.13×10^{-8}
10	40	0.96×10^{-2}	5.27×10^{-3}	2.70×10^{-8}
15	35	0.68×10^{-2}	4.61×10^{-3}	1.46×10^{-8}
20	33	0.40×10^{-2}	4.28×10^{-3}	0.74×10^{-8}
Horse-chestnut (*Aesculus hippocastanum*)				
0	35	1.40×10^{-2}	4.61×10^{-3}	3.02×10^{-8}
5	39	1.12×10^{-2}	5.14×10^{-3}	3.00×10^{-8}
10	38	1.03×10^{-2}	4.94×10^{-3}	2.61×10^{-8}
15	33	0.50×10^{-2}	4.35×10^{-3}	0.95×10^{-8}
20	20	0.79×10^{-2}	2.65×10^{-3}	0.56×10^{-8}

*Mean values from five measurements; Measurements done at 22 °C

It is evident from the experimental results that *d* values were dependent on NaOH concentrations and in some cases they increased, while in other cases they decreased, reflecting the broad variety of studied wood structures, their compositions, and internal free volume. The latter phenomenon can be explained by the swelling of cellulose and hemicelluloses in the surface layers of wood structural elements, leading to a reduction of the diameter of their open capillaries, thus decreasing the free volume part of the solid body. On the other hand, with increasing concentration of aqueous sodium hydroxide solutions, the viscosity and density also increased proportionally, thus affecting diffusion. The calculated kinetic parameters *d* and $\overline{D}_{app}$ changed with increasing sodium hydroxide concentration to a different extent. In the case of horse-chestnut wood, a spontaneous decrease of both determined quantities (*d* and $\overline{D}_{app}$) with increasing sodium hydroxide concentration was observed. As for the $\overline{D}_{app}$, a spontaneous decrease was also observed for European larch wood. The measured values of the kinetic parameters increased with increasing concentration of NaOH, reaction temperature, and reaction time. That is why the obtained results strongly reflected the heterogeneity of samples (see Fig. 4). These effects are reflected in the complicated patterns of the apparent diffusion coefficient dependencies, as shown in Fig. 6.

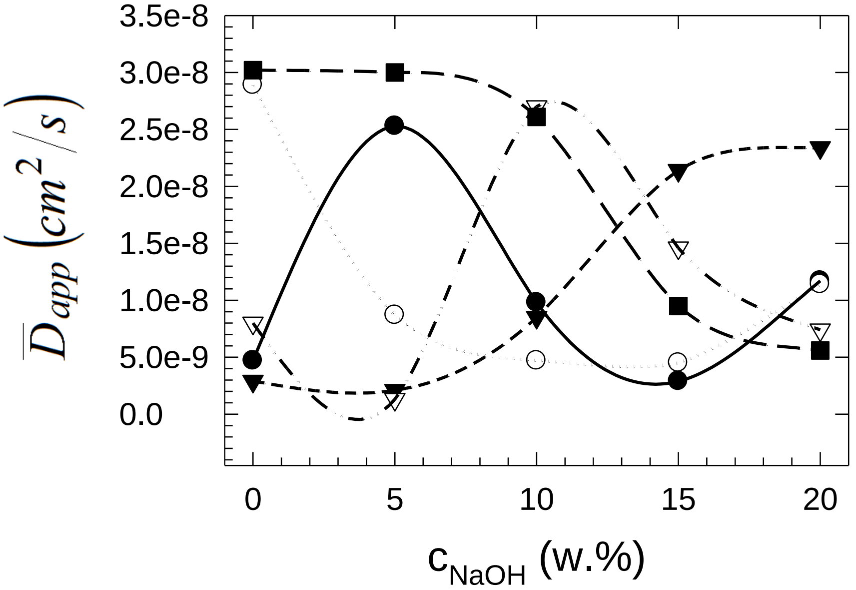


Fig. 6. The concentration dependency of the incorporated volume of NaOH water solution for the sample is reflected in the value of the mean apparent diffusion coefficient $\overline{D}_{app}$ (full circles – Scots pine, open circle – European larch, full triangle down – blackthorn, open triangle down – white willow, and full square – horse-chestnut).

The kinetic parameters *d* and $\overline{D}_{app}$ for NaOH in aqueous solution were changed with increasing sodium hydroxide concentration for different wood samples. In the case of horse-chestnut wood, there was an observable, spontaneous decrease in both parameters with increasing NaOH concentration. As for $\overline{D}_{app}$, the spontaneous decrease was also observed for European larch. In both samples, there were phenomena connected with the density of samples and probably with non-isotropic internal pressure distribution (Lapcik *et al.* 1988, 2010). This coefficient decreased with increasing sodium hydroxide concentration in the case of horse-chestnut wood and European larch wood. In the case of Scots pine and white willow, the mutual apparent diffusion coefficient was observed at low sodium hydroxide concentrations (5 wt% for Scots pine wood and 10 wt% for white willow wood) and increased, followed by a gradual decrease, as a result of the decreasing internal free volume.

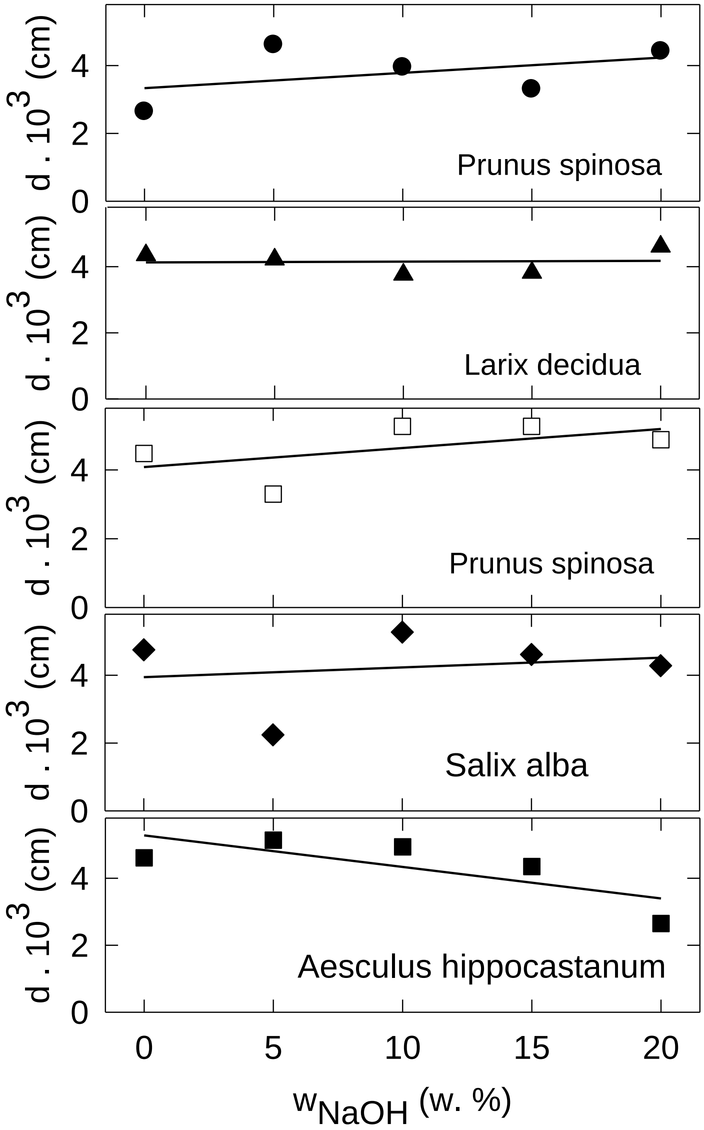


Fig. 7. Concentration dependence of total swollen surface layers thickness *d* on the concentration of aqueous solutions of NaOH in the studied wood samples.

However, a completely different pattern was found for blackthorn wood, where the apparent diffusion coefficient was not changed until 5 wt% sodium hydroxide concentration, followed by an asymptotic gradual increase reaching its maximum at 2.4 × 10^{-8} cm^2/s. Liberated water-soluble component spectroscopic analysis confirmed the uniform chemical composition of the studied woods, differing only in their mutual weight ratio. This fact was most visible from FTIR spectra, where the ratio of the absorbance of hydroxyl groups to that of aromatic ones (1.8) was identical for all studied samples. However, in the case of hydroxyl-to-carboxylic group ratio, relatively large differences were found, with values ranging from 5.8 for European larch wood to 2.6 for horse-chestnut wood.

Based on these facts, it can be concluded that the composition of the studied samples was based on the same type of basic building components, while their mutual mass ratio differs from case to case, depending on the individual supramolecular structure. With increasing sodium hydroxide concentration in aqueous solutions, the extent of chemical reactions increased as well. However, it was not confirmed that with increasing concentration of active components of the applied solutions, the transport rate of electrolytes into the wood mass increased. As shown in previous studies (Lapcik, Jr. *et al*. 2004), the tested wood samples can be used to manufacture fibrous and granular agglomerates filled with mineral fertilisers after alkali treatment, applicable as smart dosing systems suitable for direct nutrition into the plant root system. This might have positive effects on the economy and ecology of general agricultural production, especially when there is a deficit of organic carbon in the soil and the economic conditions of the country do not allow for increased synthetic fertiliser application.

CONCLUSIONS

1. The swelling activity of NaOH aqueous solutions strongly determines the kinetic parameters of the penetration process for all of the studied wood samples. The mechanism of the process is similar to that described for synthetic and natural polymers (Überreiter and Asmussen 1957; Valko and Lapcik 1967). The swelling of macromolecular components of wood (cellulose, hemicelluloses, and lignin) is also connected with the diffusion of low-molecular weight organic and inorganic compounds into a co-existing water solution phase. For these reasons, one can expect the intensification of microbial processes connected in topsoil creation and its reproduction in the cases of wood particular system as a part of carbon fertilizers.
2. The total thickness of the swollen surface layer situated in the boundary between the solid sample phase and the liquid NaOH aqueous solution is on the order of 10^{-3} cm. It is only dependent on alkali concentration in a small extent.
3. The mean apparent mutual diffusion coefficient of aqueous NaOH solution, water, and wood complexes are in the range of 10^{-8} cm^2/s and in the samples of horse-chestnut decreases with increasing NaOH concentration. This phenomenon may be caused by the higher concentration of hemicellulose, phenolic substances, and other low-molecular weight compounds.

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