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# CHARACTERISATION OF 2700-YEAR OLD WOOD FROM BISKUPIN

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## ABSTRACT

The article presents results of current investigations carried out on archaeological oak wood recovered during excavation works conducted in Biskupin in a Lusatian culture settlement from the $8^{th}$ century BC. The performed investigations comprised the determination of physical (maximum water content, conventional density and loss of wood mass) and chemical (percentage proportion of holocellulose, cellulose, lignin and ash as well as molecular weight, polydispersity and degree of polymerisation of cellulose) wood properties. In addition, microscopic observations of the cross section were carried out. In order to establish the deposition conditions of the examined wood on the site, pH changes, electrical conductivity, ground water level as well as changes in the redox potential (Eh) were measured.

KEY WORDS: chemical properties, physical properties, site characteristics

## INTRODUCTION

A defence settlement from the period of Lusatian culture situated in Biskupin which is dated back to the $8^{th}$ century BC remains the best known wet archaeological site in Poland. During excavation works which began at this site in 1934 on the area of (the peninsula of the Biskupin Lake), more than half of a 2 ha site was examined revealing remains of a wooden breakwater, rampart, gate, houses and streets excellently preserved in a layer of wet peat. The majority of recovered artefacts were made from oak wood. Archaeological excavations were terminated in 1974 and some parts of excavation works were either flooded or covered with earth or sand. As the excavation work was terminated, it was decided that the remaining archaeological material was to be preserved for future generations.

It is well known that archaeological wood which remains for many years in water or underground is exposed to the action of a wide rage of destructive factors (Björdal et al. 1999, Blanchette 2000) which result in characteristic physical, chemical and mechanical changes of the wood tissue. The rate of wood degradation depends on the deposition conditions of the artefacts. Even in near-anaerobic environments, a slow decomposition of the wood tissue by erosive bacteria cannot be ruled out (Björdal et al. 1999). It can be assumed that changes which have been observed to occur in Biskupin in recent years (including the lowering of the ground water table) can accelerate considerably the decomposition processes of the archaeological wood. With the aim to counteract the unfavourable phenomena, measures were undertaken in 1992 to increase the level of water in the Biskupin Lake which is adjacent to the archaeological site (Piotrowski and Zajączkowski 1993). This resulted in lifting the ground water level at the site leading to favourable changes in the conditions at which the remains of the settlement are deposited. In the year 2003, a research program was developed for the monitoring of some selected environmental deposition parameters of the Biskupin archaeological wood and the degree of its degradation was assessed (Babiński and Prądzyński 2004a, 2004b). The aim of this paper is to present the results of recent investigations carried out on the archaeological oak wood in Biskupin and to assess the conditions of its deposition on the site.

## MATERIAL AND METHODS

Experiments were carried out on specimens of oak wood (*Quercus* sp.) collected from a fragment of a pole about 70 cm long and 15 to 20 cm thick (Fig. 1.). The object was excavated from a pilot excavation dug in the western part of the site, at the place where a measuring station MS1 was established to monitor changes in physico-chemical properties of water and soil. The excavated fragment of a construction element was deposited horizontally in a layer of wet peat at a depth of about 100 cm. The degree of degradation of sapwood and heartwood of the examined oak wood was determined on the basis of selected wood physical properties, concentration of major chemical constituents and microscopic observations.


*Fig. 1: The fragment of oak pole from Biskupin*

The maximum water content of the archaeological wood ($U_{max}$) was determined on the basis of sample weight saturated many times with water at the pressure of 50 hPa and the weight of absolutely dry wood dried for 24 h at the temperature of 105 °C. Wood specific gravity was determined on the basis of correlations between the specific gravity and maximum water content as well as on the basis of the absolutely dry wood weight and the sample volume at the state of maximum saturation with water determined using the buoyancy method, in accordance with the formula given below:

$$d_{A-1} = \frac{100000}{U_{\max} + 66.7}, \tag{1}$$

$$d_{A-2} = \frac{m_0}{V_{\max}} \times 1000, \tag{2}$$

where:
$d_A$ – specific gravity of archaeological wood (kg·m$^{-3}$)
$U_{max}$– maximum water content (%)
$m_o$ – mass of absolutely dry wood (g)
$V_{max}$ – wood volume at the state of maximum saturation with water (cm$^3$)

The loss of wood substance (*LWS*) – expressed as the relative loss of specific gravity of archaeological wood – was calculated according to the formula given by Grattan and Mathias (1986):

$$LWS' = \frac{d_C - d_A}{d_C} \times 100, \tag{3}$$

where:
*LWS* – loss of wood substance (mass loss) (%),
$d_C$ – specific gravity of contemporary wood (kg·m$^{-3}$)
$d_A$ – specific gravity of archaeological wood (kg·m$^{-3}$)

Depending on the adapted wood specific gravity ($d_{A\text{-}1}$ or $d_{A\text{-}2}$), the loss of wood substance was presented either as $LWS_1$ or $LWS_2$. The specific gravity for sound, contemporary wood amounted to 577 kg·m$^{-3}$ (Dietz 1975). The chemical analyses (determination of the content of holocellulose, cellulose, lignin and ash) were carried out in compliance with the PN 92/P-50092 standard. The degree of cellulose polymerisation was assessed employing the method of gel chromatography using, for this purpose, a chromatographic system consisting of: Isocratic Pump HP 1050, Manual Injector (Model 7125-Rheodyne Inc.), Differential Refractometer Detector HP 1047A, Column Set: 3 × Plgel Mixed A, 20 µm + guard, PL Caliber GPC Software Ver. 5.1. The conditions of the chromatographic analysis were as follows: solvent DMAC/0.5 % LiCl, flow rate – 1 ml/min, concentration 0.05 %, injection volume 100 ml, temperature 80 °C.

Microscopic observations of the wood cross section were carried out on micro-samples measuring 6 × 6 × 2 mm (T × R × L). The wood samples were subjected to steaming at the temperature of 105 °C for 30 minutes. Following their drying, all micro-samples were covered in vacuum conditions with a layer of gold. The experimental material prepared in this way was placed in a scanning electron microscope Tesla TS5130 and subjected to observations.

The following measurements were performed in the place where the oak pole was excavated (measuring station *MS1*): *pH* changes, electrical conductivity, level of ground water as well as changes in the soil redox potential (*Eh*) at the depth of 100 cm below the ground level. Investigations were conducted during the period from September 2003 to August 2004.

## RESULTS

Tab. 1 presents the physical properties of the examined oak wood, whereas Tabs. 2 and 3 show its chemical composition and number and weight average values of the molecular weight (*Mn* and *Mw*), polydispersity (*Mw*/*Mn*) as well as the degree of polymerisation (*DP*) of cellulose isolated from this raw material. Figs. 2 and 3 present photos taken with the electron microscope, while Figs. 4–7 present changes in the level, reaction (*pH*) and electrical conductivity of ground waters as well as the redox potential of the soil.

*Tab. 1: Selected physical properties of investigated archaeological oak wood*

| Zone | Value | Maximum water content | Conventional density | | Loss of wood substance | |
|---|---|---|---|---|---|---|
| | | $U_{max}$ % | $d_{A\text{-}1}$ kg·m$^{-3}$ | $d_{A\text{-}2}$ kg·m$^{-3}$ | $LWS_1$ % | $LWS_2$ % |
| sapwood | min | 743 | 117 | 117 | 78.6 | 78.6 |
| | max | 785 | 123 | 124 | 79.7 | 79.7 |
| | mean | 757 | 121 | 121 | 79.0 | 79.0 |
| heartwood | min | 233 | 265 | 266 | 42.2 | 41.7 |
| | max | 311 | 333 | 337 | 54.1 | 53.9 |
| | mean | 263 | 307 | 309 | 46.8 | 46.5 |

*Tab. 2: Percentage content of chemical components in archaeological oak wood*

| Zone | Carbohydrate | | Lignin | H/L** | Ash |
|---|---|---|---|---|---|
| | Holocellulose | Cellulose | | | |
| sapwood | 26.54 (5.57)* | 16.78 (3.52)* | 71.28 (14.97)* | 0.37 | 6.72 (1.41)* |
| heartwood | 29.90 (15.94)* | 21.73 (11.58)* | 52.21 (27.83)* | 0.57 | 6.20 (3.30)* |

*Valve for non degraded wood – the original mass was calculating with taking into account appropriate losses of wood substance in the degraded wood, i.e. 79% for sapwood and 46,7% for heartwood
**H/L – relation of percentage content of holocellulose and lignin

*Tab. 3: Number-averaged molecular weight (Mn), weight-averaged molecular weight (Mw), polydispersity and degree of polymerisation (DP) of cellulose obtained from archaeological wood*

| Zone | *Mn* | *MW* | Polydispersity | *DP* |
|---|---|---|---|---|
| sapwood | 12988 | 61450 | 4.73 | 376.99 |
| heartwood | 18229 | 84372 | 4.56 | 517.62 |

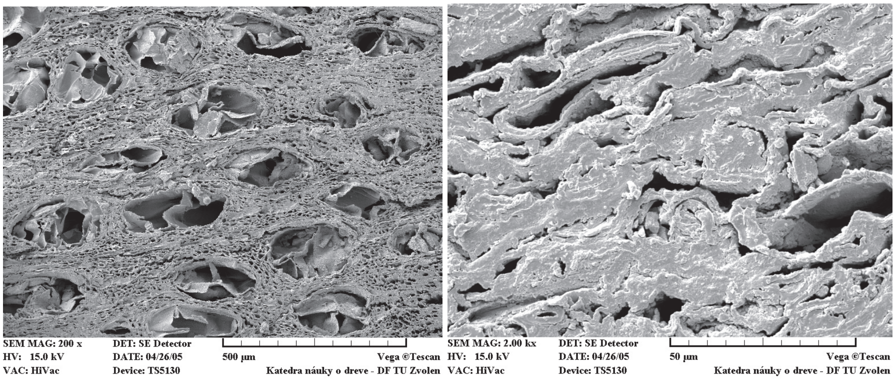


*Fig. 2: Collapsed wood cells at the periphery and the associated excessive shrinkage – cross section*

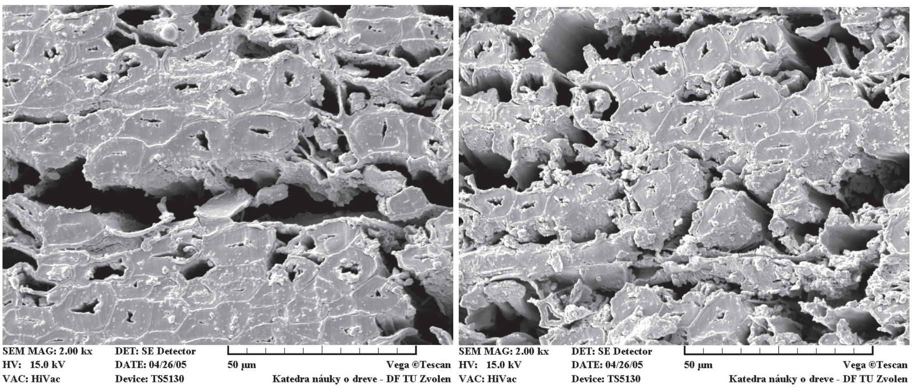


*Fig. 3: Degradation of cell walls of libriform fibres by biological agents – cross section*

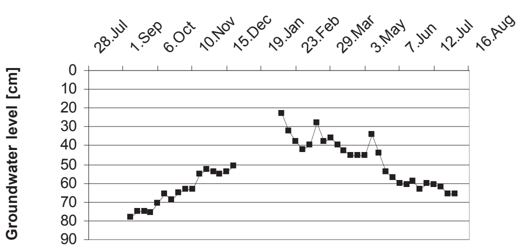


*Fig. 4: Changes in groundwater level (in cm below ground level) at the measuring station MS1*

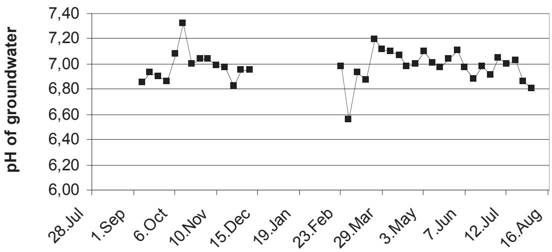


*Fig. 5: Changes in pH of groundwater at measuring station MS1*

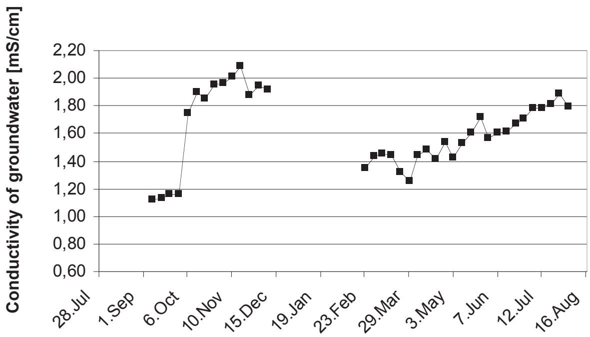


*Fig. 6: Changes in electrical conductivity of groundwater at measuring station MS1*

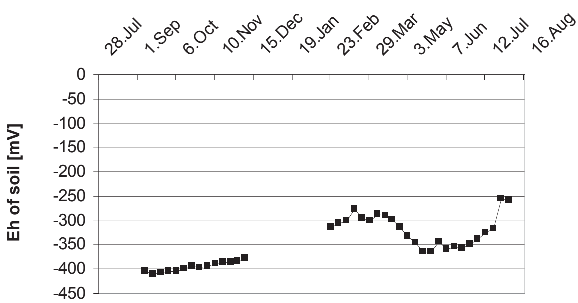


*Fig. 7: Changes in redox potential (Eh) of soil at measuring station MS1 at the depth of 100 cm*

On the basis of the determined physical properties a distinct difference was determined between the response of sapwood and heartwood of the examined oak wood. The sapwood part was degraded stronger. Its maximum water content – increasing with the progress of the wood tissue deterioration – ranged from 743 to 785 % (Tab. 1), whereas its specific gravity ranged in the interval from 117 to 124 kg·m$^{-3}$. The degradation of the examined zone was homogenous as confirmed by slight differences (about 3 %) between the mean, minimum and maximum values.

The loss of wood substance (mass loss) – on average amounting to 79 % – corroborates the very high extent of degradation of the examined wood zone. In comparison with the sapwood, the heartwood part was characterised by a distinctly lower extent of wood degradation. The maximum water content of heartwood ranged from 233 to 311 %, while its specific gravity was contained in the interval from 265 to 337 $kg{\cdot}m^{-3}$. Considerable variability was also determined in the case of the wood substance loss which – for the examined heartwood – ranged from 41.7 to 54.1 %. The wide range of the obtained results should be attributed to different degrees of degradation of individual heartwood layers. The layer adjacent to the sapwood zone underwent far stronger degradation (mass loss of about 54 %) than the internal (close to the pith) layers (mass loss of about 42 %). The mean loss of the wood substance for the entire heartwood zone of the examined pole – after taking into account the volume and the mass loss of two different heartwood layers – reached 46.7 %.

The performed chemical analysis of the softwood and heartwood of the examined raw material revealed changes in the proportion of chemical constituents making up the wood tissue (Tab. 2). The proportion of structural constituents (carbohydrate) decreased considerably. The content of holocellulose (after taking into account the mass loss) in the sapwood of the examined raw material amounted to 5.57 %, whereas in the heartwood – 15.94 %. Therefore, it can be said that the share of the analysed constituent in both zones was many times smaller than in the contemporary wood of the same species. In the case of sound, contemporary oak wood, cellulose makes up from 45 to 50 % of the wood tissue bulk, whereas in the analysed archaeological material the content of this constituent ranged from 3.52 % in the sapwood to 11.58 % – in the heartwood. This indicates significant degradation of this important structural constituent in both of the compared zones of the examined object. The comparison of the percentage proportion of the carbohydrate constituents in the sapwood and heartwood corroborated a clear difference in the behaviour of the examined material observed on the basis of investigations of physical properties. The degradation intensity of the next wood principal chemical constituent – lignin also turned out to differ in the compared zones. Whereas in the case of heartwood, the proportion of this most durable wood component amounted to 27.83 %, in other words, it did not deviate significantly from that of contemporary oak wood, in the case of sapwood, it made up only 14.97 % of wood tissue. This result is significantly lower than the mean proportions of lignin found in the sapwood of the contemporary wood raw material and confirms advanced degradation of the examined wood. The determination of the true lignin proportion in the analysed raw material was possible following the application of a conversion factor which took into account the bulk loss of wood tissue. The interpretation of the research results without the application of the above-mentioned conversion factor would refer to the so called apparent increase of lignin proportion frequently found in the literature dealing with archaeological wood (Obst et al. 1991, Iiyama et al. 1988, Blanchette et al. 1991). In addition, it would make it impossible to assess real quantitative changes that affected this constituent during the long period of wood deposition in the soil. The H/L coefficient (ratio of the percentage proportion of holocellulose to lignin) provides valuable and reliable information concerning the extent of degradation of archaeological wood (Babiński 2005); the lower its value, the more degraded is the raw material. This coefficient, in the contemporary oak wood, exceeds the value of 2, whereas in the heartwood of the examined samples, it amounted to 0.57 and in the sapwood – 0.37. Apart from the principal wood constituents, the content of minerals of the examined wood material was also analysed. Literature on the subject reports high content of minerals in archaeological wood (Hoffmann 1982, Grattan and Mathias 1986, Hedges 1990, Zborowska 2004). Also in our investigations, the proportion of this fraction reaching 6.72 % in the sapwood and 6.20 % in the heartwood exceeded many times values typical for contemporary wood.

In order to gain a better insight into the qualitative changes of cellulose in the examined raw material, its degree of polymerisation as well as polydispersity of this constituent were determined. The obtained results indicate well advanced depolymerisation of the cellulose component of the analysed wood tissue (Tab. 3). In the case of heartwood, the polymerisation degree (*DP*) of cellulose reached 518 and that of sapwood – 377. Bearing in mind that the *DP* of contemporary wood is about 1000, we can say that significant qualitative changes (degradation) occurred in this wood structural constituent and, consequently, in the entire analysed raw material.

The cross-section photos of the examined oak wood taken with the scanning microscope revealed changes in the wood anatomical structure. The microstructure of the analysed sapwood (Fig. 2) is deformed, cells collapsed and distorted, and the cell walls clearly thinner in comparison with the contemporary oak wood. Considerable destruction of cell elements was also observed in the heartwood (Fig. 3). The distribution of failures was irregular. The original state was altered either as a result of biological degradation by fungi and bacteria. It is not possible to specify unambiguously which of the two is the causal agent, the mycelium hyphae, however, present in the examined wood pointed to the first of them.

The ground water level measured at the MS1 station fluctuated from 78 to 23 cm below the ground surface (Fig. 4). The lowest ground water levels were recorded towards the end of summer (August/September). If, in the past, the ground water levels at the examined site decreased more than in the period 2003–2004, then the excavated element could have been exposed to the degradation not only by bacteria but also by fungi (Björdal and Nilsson 2002). On the other hand, the highest ground water levels were observed at the end of winter and beginning of spring – during the period of snow melting and heavy rainfalls. The water reaction (pH) varied during the entire measuring period from 6.56 to 7.32 (Fig. 5) and its electrical conductivity – from 1.12 to 2.09 $mS \cdot cm^{-1}$ (Fig. 6). It can be assumed that the observed slight salinity and near-natural ground water reaction did not have a significant influence on the preservation conditions of the wood deposited in Biskupin. Similar values were reported on numerous sites in Great Britain (Caple et al. 1997, Hogan et al. 2002).

The soil oxidative-reduction potential (*Eh*) - one of the principal indicators of the degree of its aeration (Bohn 1971) – ranged from –400 to –260 mV (Fig. 7). Similar values are characteristic for strongly reductive environments – close to anaerobic conditions. In the case of Flag Fen and Woodhall sites in Great Britain, where the deposited archaeological organic material was preserved best, the value of the redox potential ranged from –400 to –200 mV (Caple et al. 1997). The probable causes of increased Eh values at the MS1 measuring station in Biskupin are given by Babiński et al. (2004) who blame it on the possible contamination of the platinum electrodes by oxygen migration along the wire as well as the presence of oxidised forms (e.g. nitrates) in the ground water.

## CONCLUSIONS

The physical properties of the archaeological oak wood from Biskupin (maximum water content, specific gravity and mass loss) changed distinctly on the cross section of the excavated trunk going from the external sapwood through the heartwood part occurring close to the sapwood zone down to the near-pith heartwood. These changes illustrate a biological distribution classical for oak wood which is characterised by greater activity in the external zone of the object decreasing in the direction of the pith.

Significant changes in the content of chemical constituents were found in the analysed raw material. The observed very low proportion of carbohydrates – holocellulose and cellulose, poses a serious threat to the structural stability of the examined wood. The constituent which remained relatively well preserved until today is lignin which was degraded in 50 % in the sapwood but remained extremely well preserved in the heartwood. Distinct variations were also found in the degradation degree of the carbohydrate constituents of the compared wood zones. About three times less cellulose was determined in the sapwood in comparison with the heartwood. In addition, the cellulose quality was also found inferior as confirmed by low values of the molecular weight and polymerisation degree.

Advanced degradation processes characterised by considerable changes within carbohydrate components were also observed in the wood of black alder (*Alnus glutinosa* Geartn.) excavated from the same environment (Zborowska et al. 2005). The polymerisation degree of cellulose determined in this raw material was even lower and amounted to 175. The observed differences can probably be attributed to different resistance of the two compared materials to the degradation factors.

The results of monitoring of the deposited object (ground water level, its electrical conductivity, pH and soil redox potential) indicate that the wooden constructions deposited in the soil of the Biskupin site are significantly protected against degradation and the degradation processes are very slow.

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