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ANALYSIS OF THE CUP METHOD APPLICATION FOR DETERMINATION OF THE BOUND WATER DIFFUSION COEFFICIENT IN WOOD

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SYNOPSIS. The principles and basic assumptions of the cup method for the bound diffusion determination were discussed. A detailed analysis of the influence of the assumptions of surface bound water content, boundary condition of the first kind, the constant value of the diffusion coefficient and correction of relative humidity inside the cup was provided. A numerical example was presented to verify practical credibility of the discussed method.

KEY WORDS: bound water diffusion, transport properties, assumptions' credibility, prediction accuracy

INTRODUCTION

The accurate prediction of bound water transport in wood is of great importance not only for understanding timber drying under the fiber saturation point but also for the proper design and use of products, structures and building components made of already dried wood. Therefore, the credible data on wood properties responsible for bound water transport are especially important.

The bound water transport and the related wood properties have been studied extensively for the last century. It was early suggested that the transport is probably limited by the internal and the external resistance. The bound water migration in the solid (i.e. the transport related to the internal resistance) was traditionally called diffusion and described by Fick's laws in its original or modified form. The transfer in the interface between the ambient air and the surface of the solid was related to the so-called external resistance and determined by the appropriate boundary condition (Crank 1975). The two groups of methods for the transport properties determination were developed. The first one uses Fick's first law of diffusion with data from the steady-state experiments of bound water transfer and is traditionally called the cup method. The second group of methods is based on the unsteady-state experiments and Fick's second law of diffusion. The common name of this group is the sorption method. The distinct differences in the results of the determined properties for the both groups of the methods were reported by Söderström and Salin (1993), as well as by Wadsö (1993). The differences were related not only to the species variation but also to the applied method. Therefore, the basic question rose on the correctness of the assumptions applied during the development of these methods. Unfortunately, the most important references on the wood-water system (Siau 1984, 1995, Skaar 1988) and timber drying (Keey et al. 2000) report the principles of the methods for the determination of the wood transport properties but do not provide their critical review and do not refer to the possible causes of the differences in the obtained values.

The objective of this paper is to review the mathematical assumptions and the derivation procedures applied to develop the cup method for the diffusion coefficient determination. The analysis will be also completed by the practical application of the data obtained from the cup method. The results obtained from the modeling will be compared to the experimental data.

PRINCIPLES OF THE CUP METHOD

The detailed description of the cup method is given by Siau (1984, 1995). A diffusion cup is partially filled with a saturated salt solution or distilled water in order to obtain a specified relative humidity of moist air (RH_2) inside the cup (Fig. 1). The tested wood sample, which closes the cup from the top, has sealed edges in order to ensure the one-dimensional moisture transfer. The cup with the sample is placed on a balance inside the closed climate chamber with controlled relative humidity (RH_1) and controlled constant temperature (T). The mass of the cup with the tested sample is recorded in the constant time instants. The steady-state of the bound water transfer during the experiment is identified when a linear relationship between mass change and time is obtained. The flux of the bound water (J) through the sample is calculated as the ratio of the mass change (Δm) to the time interval ($\Delta\tau$) and the area of transfer (A):

$$J = \frac{\Delta m}{A \cdot \Delta\tau} \tag{1}$$

The bound water content based diffusion coefficient (D_M) is determined from the modified form of Fick's first law. The modification of the law is related to the replacement of the bound water concentration (c) defined as the ratio of water mass and wood volume, being the original driving force of diffusion, with the bound water content (M) defined as the ratio of water mass and mass of oven-dry wood. Skaar (1988) has shown that the selection of the driving force of diffusion does not influence the analysis of the process and the bound water transport coefficients

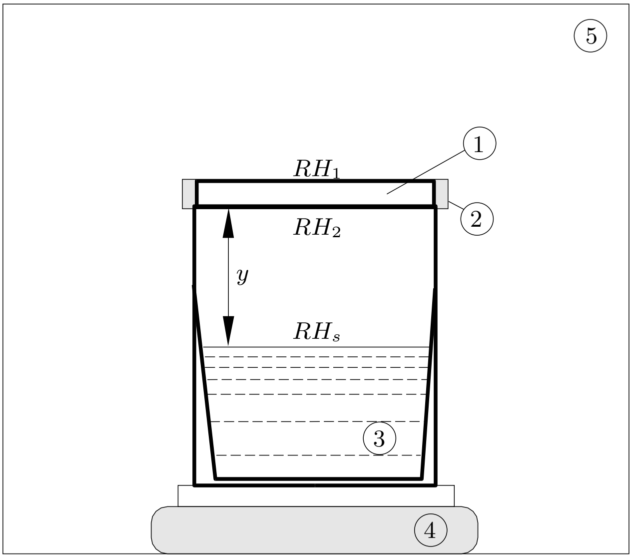

Fig. 1. Experimental set-up in the cup method for the diffusion coefficient determination: 1 – sample, 2 – sealing, 3 – salt solution, 4 – balance, 5 – climate chamber
Rys. 1. Układ pomiarowy do wyznaczania współczynnika dyfuzji metodą stanu ustalonego: 1 – próbka, 2 – powłoka uszczelniająca, 3 – roztwór soli, 4 – waga, 5 – komora klimatyczna

obtained for different potentials can be related to the original diffusion coefficient (D) calculated from the original form of Fick's first law in which the bound water concentration is assumed as the driving force of the process. The selection of the bound water content as the driving force has its important practical aspect because of much easier experimental determination of the property in comparison to the bound water concentration. The finite form of the modified Fick's first law is

$$J = D_M \frac{M_2 - M_1}{L} \tag{2}$$

where L is the sample thickness (i.e. bound water transport distance) and M_2, M_1 are the bound water contents on the surfaces of the tested sample. The diffusion coefficient is then calculated as:

$$D_M = \frac{J \cdot L}{M_2 - M_1} \tag{3}$$

If the bound water concentration is directly used in the calculations, e.g. COMSTOCK (1963), then the formula for the diffusion coefficient is written as:

$$D = \frac{J \cdot L}{c_2 - c_1} \tag{4}$$

The presented approach requires the assumption that the surfaces of the sample are immediately in equilibrium with the corresponding relative humidity values.

Therefore, the values of M_2 and M_1 have to be determined using the sorption isotherms data given in the form of graphs, tables or empirical models.

Siau (1984, 1995) suggests the correction of relative humidity value to be determined at the surface of the tested sample inside the cup (RH_2). The correction is due to the water vapor transfer between the salt solution surface and the sample surface. The difference of relative humidities (ΔRH) is defined as:

$$\Delta RH = RH_s - RH_2 \tag{5}$$

where RH_s is the relative humidity at the surface of the salt solution.

The correction procedure requires determination of the water vapor concentration gradient ($\Delta c/y$) given in the following form:

$$\frac{\Delta c}{y} = \frac{J}{D_a} \tag{6}$$

where Δc is the difference in water vapor concentrations, y is the distance between the surface of the tested sample and the surface of the salt solution, D_a is the diffusion coefficient of water vapor in air usually given by the empirical equation (Kneule 1970):

$$D_a = 23 \cdot 10^{-6} \frac{98100}{p} \left(\frac{T}{273.15} \right)^{1.75} \tag{7}$$

where p is air absolute pressure, T is absolute temperature. The difference of water vapor concentration is defined as follows:

$$\Delta c = \Delta \left(\frac{m_{\mathrm{H_2O}}}{V} \right) \tag{8}$$

where $m_{\mathrm{H_2O}}$ is mass of water vapor, V is volume. The difference can be calculated from the ideal gas law given as:

$$\Delta \left(\frac{m_{\mathrm{H_2O}}}{V} \right) = \frac{\Delta p}{R \cdot T} \tag{9}$$

where Δp is the difference of water vapor partial pressure at given temperature, R is the individual gas constant of water vapor $R = 462$ J/(kg·K).

Substituting equations (6) and (8) to (9) the difference of water vapor partial pressure is obtained as:

$$\Delta p = \frac{y \cdot J}{D_a} \cdot R \cdot T \tag{10}$$

From the definition of the relative humidity it results that

$$\Delta RH = \frac{\Delta p}{p_s} \tag{11}$$

where p_s is saturated water vapor pressure. Substituting (10) to (11) we get:

$$\Delta RH = \frac{y \cdot J}{p_s \cdot D_a} \cdot R \cdot T \tag{12}$$

CREDIBILITY OF THE CUP METHOD

The presented steady-state method for the diffusion coefficient determination required several assumptions in the mathematical derivation of Equation (3) from Fick's first law as well as in the experimental procedure. The most important assumptions will be listed and discussed below in order to present the consequences of their application with respect to the credibility of the method.

Surface bound water content

The application of the cup method is only possible when the assumption is made that both surfaces of the sample immediately obtain the equilibrium respectively with air inside the cup and inside the closed chamber. It has been already experimentally proved for the water transfer processes that the wood surface moisture content differs significantly from the equilibrium moisture content. Shmulsky et al. (2002) showed that the difference between the wood surface moisture content and the equilibrium moisture content increases with the air velocity decrease for the same values of the relative humidity and the air temperature. They reported that after 24 h of the 25 mm thick red oak drying at 43.3°C dry-bulb and 40.6°C wet-bulb temperatures the surface moisture contents were equal to ca. 21% and 18% for air velocities of 1 m/s and 3 m/s respectively. While the corresponding equilibrium moisture content obtained from the sorption data was 16.2% (Dry kiln... 1991). It has to be emphasized here that in moisture transfer experiments performed according to the cup method there is no air flow on either side of the tested sample and therefore high discrepancies between the surface and the equilibrium moisture contents should occur. Thus the resistance of moisture transfer in the interface between air and the wood surface cannot be neglected. It is in the opposition to the basic assumption allowing derivation of Equation (3) from Fick's first law.

The other problem related to establishing the surface moisture content from the sorption data is the wood species. The sorption data, which are available in the most common references on the wood-water system, were experimentally obtained for Sitka spruce. Skaar (1988) as well as Siau (1984, 1995) report the significant influence of wood species on the equilibrium moisture content for given air parameters. Therefore, it is suggested to use the sorption data for the analyzed species in order to determine the exact values of the equilibrium moisture content. The majority of studies, in which the cup method was applied, did not take into account the suggestion because of the lack of the sorption data for the investigated species.

Boundary condition of the first kind

The derivation of Equation (3) from Fick's first law is made with the assumption of the boundary condition of the first kind. This assumption is closely related to the moisture content determination of the wood surface. It is because of the physical interpretation of the boundary condition means that the moisture contents of wood surfaces have to be immediately equal to the equilibrium moisture contents. The consequence of this assumption is neglecting the so-called external resistance of the moisture transfer. In most cases, except the very thin wood samples, the assumption is not valid. It was already proved in different experiments and reported in the basic references on the wood-water system (Siau 1984, 1995, Skaar 1988).

The constant value of the diffusion coefficient

As it results from the mathematical derivation presented by Siau (1984, 1995) the very crucial assumption enabling the application of the cup method is the constant value of the diffusion coefficient. Choong (1965) made a series of experiments for western fir wood using the cup method with the constant air parameters inside the cup and with varying air parameters in the closed climate chamber. It enabled him to determine the diffusion coefficient values related to the variable differences of the surface moisture contents. He found that the values of the transverse diffusion coefficient were linearly increasing with the moisture content increase, while the opposite relationship for the longitudinal diffusion coefficient was found. The similar investigations were conducted by Comstock (1963) for yellow poplar wood. However, the exponential increase of the diffusion coefficient with increasing moisture content was found. The other investigations, e.g. Choong et al. (2001), also suggest the nonlinear relationship.

Another evidence of the diffusion coefficient dependency on moisture content was reported by Skaar (1954). He showed that the assumption of the constant value of the diffusion coefficient implies the linear distribution of the bound water content after obtaining the steady-state. He reported experiments in which the slicing technique was used to determine the distribution. The obtained results showed that the distribution was clearly non-linear and therefore the values of the diffusion coefficient depended on the driving force of the process. The same technique was used by Lee et al. (1991) after obtaining the steady-state in the cup experiments. Again nonlinear bound water content distributions were obtained.

The discussed results clearly show that the diffusion coefficient is not a constant. Therefore, it was suggested in some works that the values of the diffusion coefficient obtained in the cup method are not true. Skaar (1954) called the values as apparent or average.

Correction of relative humidity inside the cup

Although Siau (1984, 1995) suggested the need of the correction of relative humidity inside the cup, there were not found works applying the correction. Therefore, the question rises on the significance of the relative humidity difference. In order to estimate the difference (ΔRH) Equation (12) was used together with the following input data: temperature $T = 293.15$ K, the distance between the surface of the tested sample and the surface of the salt solution (y) varying from 1 to

5 cm. The typical values of the bound water flux (J) recorded during the cup experiments were taken from LEE et AL. (1991). The J values were varying from 1.5 to 10 g/(m^2·h). The obtained results of the estimation of ΔRH are presented in Figure 2. The minimum calculated value of the difference ΔRH was equal to 1%. However, it can be achieved only for very small values of the flux J and very small distances y. The majority of the calculated results were higher than 5%. In some cases the values as high as 30% may be obtained.

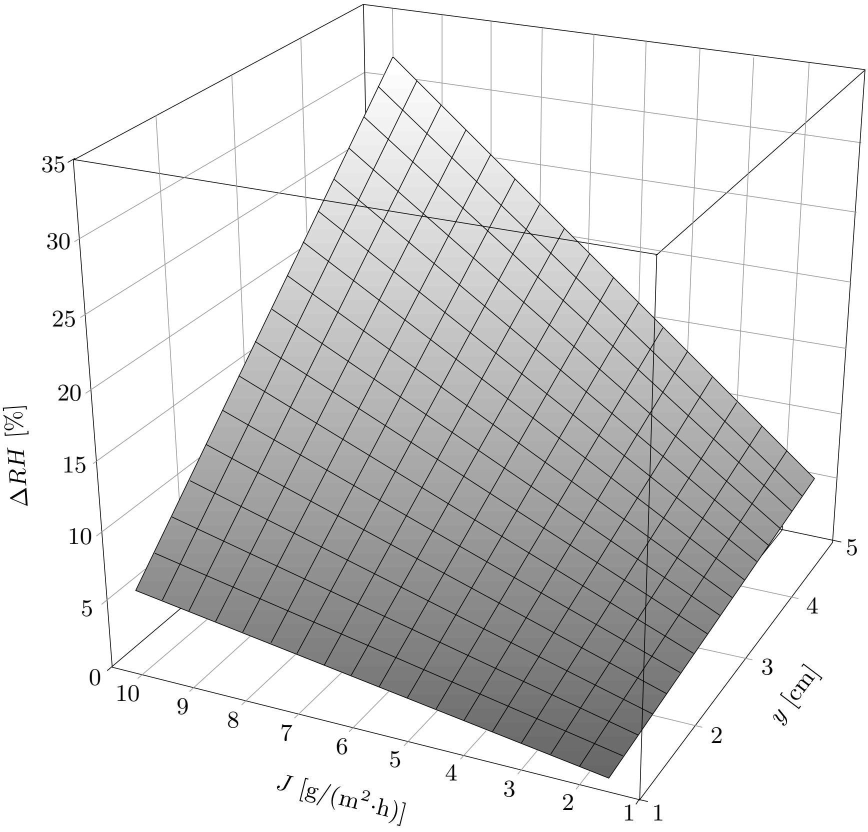

Fig. 2. Relative humidity difference inside the cup
Rys. 2. Różnica wilgotności względnej wewnątrz naczynia z roztworem soli

It is evident from the performed analysis that the conditions of the cup experiments may have significant influence on the difference in relative humidity values between the surface of the tested sample inside the cup and the salt solution surface. Therefore, neglecting the correction procedure proposed by SIAU (1984, 1995) may lead to additional errors in the cup procedure of the diffusion coefficient determination.

DIFFUSION PREDICTION – NUMERICAL EXAMPLE

The objective of the numerical example is to estimate the influence of the assumptions made during the cup method derivation on the results of the transient diffusion modeling. The analyzed problem of the transient diffusion is described by the differential form of the second Fick's law given by:

$$\frac{\partial M}{\partial \tau} = \frac{\partial}{\partial x}\left(D_M \frac{\partial M}{\partial x}\right) \tag{13}$$

where x is space dimension. Differential equation (13) is supplemented by the initial condition, here the constant value of the initial bound water content (M_0) in wood:

$$M(x,\ 0) = M_0, \qquad\qquad x \in \overline{\Omega} \tag{14}$$

where $\overline{\Omega}$ is geometric domain of the R^1 space with the boundary. The cup method implies the use of the boundary condition of the first kind also in the numerical example which is provided here. Therefore, the boundary condition is given as:

$$M(x,\ \tau) = EMC, \qquad (x,\ \tau) \in \Gamma \times [L/2,\ \tau_F] \tag{15}$$

$$M(x,\ \tau) = EMC, \qquad (x,\ \tau) \in \Gamma \times [-L/2,\ \tau_F] \tag{16}$$

where EMC is the equilibrium moisture content, Γ is the boundary, τ_F is time of the process investigation.

The assumption on the constant value of the diffusion coefficient lets to write differential equation (13) in the following form:

$$\frac{\partial M}{\partial \tau} = D_M \frac{\partial^2 M}{\partial x^2} \tag{17}$$

However, the boundary-value problem given by equations (14)-(17) has its analytical solution, a numerical method will be used here to solve the problem because of good accuracy of the method and the ease of its application. The numerical technique uses principles of the finite element method. The computer program was coded in Lahey Fortran 95 environment. The details on the applied numerical approach were described by Weres (1997).

The numerical solution was obtained for the following input data: $L = 0.008$ m, $M_0 = 0.08217$ kg/kg, $EMC = 0.1495$ kg/kg and the value of the diffusion coefficient D_M commonly considered as typical for Scots pine in the radial anatomical direction, i.e. $2 \cdot 10^{-10}$ kg/(m·s), as well as much lower than typical, i.e. 10^{-12} and 10^{-16} kg/(m·s). The empirical data presented earlier by Olek and Weres (2001) were used to validate the obtained values of the modeling. The numerically obtained bound water content changes in time as well as empirical data are presented in Figure 3. The bottom plot presents also values of the local relative error of prediction (e) calculated by the comparison of the bound water content values from experiments and computer simulations. The definition of the error is:

$$e(\tau_i) = 100\frac{|M_{\text{exp}}(\tau_i) - M(\tau_i)|}{M_{\text{exp}}(\tau_j)}, \qquad i = 1, \ldots, NT \tag{18}$$

where NT is number of time instants, subscript 'exp' denotes experimental values.

The results of transient diffusion modeling presented in Figure 3 were limited only to one performed case study, i.e. for $D_M = 2 \cdot 10^{-10}$ kg/(m·s) because of the insignificant influence of the lower values of the diffusion coefficient on the bound water content predictions. The calculated bound water contents obtained very early values equal to the equilibrium moisture content. It is clear from the results that the assumption of the boundary condition of first kind is the primary cause of the inadequate prediction of the process. The obtained high values of the relative error of predictions let to state that the analyzed model is not suitable for describing the process. Although, the better results of predictions for the steady-state can be expected, the numerical example of the transient diffusion was intentionally chosen here. It shows the scale of consequences of the full application of the assumptions used in the cup method.

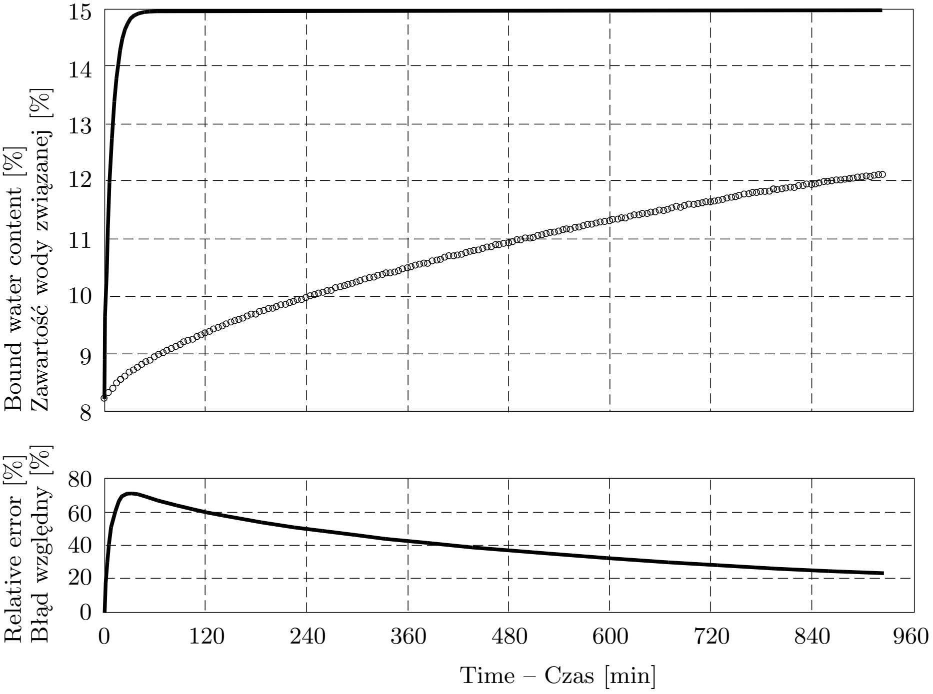

Fig. 3. Validation of the bound water content predictions by comparing with experimental data: ∘ – experimental data, —— – numerical modeling
Rys. 3. Ocena prognozowania zawartości wody związanej przez porównanie z danymi doświadczalnymi: ∘ – dane doświadczalne, —— – modelowanie numeryczne

CONCLUSIONS

1. The assumptions, which are required for the application of the cup method to determine the bound water diffusion coefficient, i.e. surface bound water content, boundary condition of the first kind and the constant value of the diffusion coefficient are not satisfied in the case of wood.
2. The cup method is unable to provide credible information on the transport resistance in the interface between air and wood surface.
3. The significant additional errors in the procedure of the diffusion coefficient determination may be produced by omitting the correction of air relative humidity inside a cup.
4. The cup method is not valid for the bound water diffusion coefficient determination in wood.

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ANALIZA ZASTOSOWANIA METODY STANU USTALONEGO DO WYZNACZANIA WSPÓŁCZYNNIKA DYFUZJI WODY ZWIĄZANEJ W DREWNIE

Streszczenie

Omówiono i uporządkowano metodykę wyznaczania współczynnika dyfuzji wody związanej w drewnie z zastosowaniem metody stanu ustalonego. Szczególną uwagę zwrócono na założenia metodyczne. Dokonano analizy wpływu założeń dotyczących zawartości wody związanej na powierzchni drewna w trakcie eksperymentów, wykorzystania warunku brzegowego pierwszego rodzaju, braku wpływu zawartości wody związanej na wartości współczynnika dyfuzji (tj. analizy stałej wartości współczynnika) oraz korekty wartości wilgotności względnej powietrza między powierzchnią drewna a powierzchnią nasyconego roztworu soli. Wykazano, że przyjęte najistotniejsze założenia teoretyczne są nieadekwatne do badanego systemu empirycznego. Tym samym nie można uznać omawianej metody za wiarygodną, a otrzymywane z jej zastosowaniem wartości współczynników dyfuzji wody związanej nie mogą stanowić wartościowych danych opisujących proces dyfuzji. Przedstawiono także przykład numeryczny wykazujący jednoznacznie, że zastosowanie omówionych w pracy założeń metodycznych do modelowania dyfuzji prowadzi do uzyskania wyników prognozowania procesu, które nie opisują prawidłowo przebiegu dyfuzji w układzie empirycznym.

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