Method of non-destructive control of the solvent diffusion coefficient in products made from anisotropic porous materials

V P Belyaev, S V Mishchenko and P S Belyaev

Technological Institute, Tambov State Technical University, 106 Sovetskaya St, Tambov, 392000, Russia

Abstract. The development of methods and means of non-destructive products testing in various industries is an actual task. The subject of this study is non-destructive testing of the solvents mass transfer processes in products made from anisotropic porous materials (PM) and the diffusion coefficient determination. The known methods for determining the diffusion coefficient in anisotropic porous media are developed for canonical forms. This leads to the necessity of destroying products for making experimental samples from them of a given configuration and size. The purpose of this study is to develop a dynamic method that allows us quickly determine the diffusion coefficient in products from anisotropic porous materials without destroying them. The method is designed to investigate the diffusion coefficient of solvents, for example, in reinforced building elements from materials having a porous structure. The task of constructing the method mathematical model is solved. The influence of the design and operating measuring device parameters on the accuracy of the determining diffusion coefficient is studied. A theoretical estimate of the error in the measurement result was made. The results of the method application are presented.

1. Introduction
At present, products in the form of blocks or panels made of fibrous composite materials are becoming increasingly widespread in the construction industry [1, 2]. They can have a significant properties anisotropy due to the orientation of the fibers during their production [1-4]. Measurement of the diffusion coefficient in building materials is associated with considerable time expenditure [5, 6]. To implement the known methods, it is often necessary to use expensive and cumbersome equipment that provides the measurement of spatial solvents distributions within the samples [7-9]. Most known methods use samples of special shapes and sizes [5-9]. This makes it difficult to control the diffusion coefficient in finished products from anisotropic porous materials [10]. The point pulse method of nondestructive testing presented by us in [11] is not suitable for the study of anisotropic materials. To calculate the technological processes for the production of anisotropic porous materials, data about the diffusion coefficients in the transverse direction to the fibers location are needed first of all, because diffusion in this direction is the limiting stage of the process [12, 13].

2. Formulation of the problem
The task was to develop a pulse method for measuring the diffusion coefficient of solvents distributed in the anisotropic porous materials (PM) solid phase. The method should provide an opportunity to
study products without destroying them and significantly reduce the time spent on monitoring. To achieve the goal it is necessary to solve the following tasks:

– to develop a physical and mathematical model of the method that ensures a fast flow mass transfer process in the controlled product and obtain the necessary measurement information for calculating the diffusion coefficient without destroying the product;

– to investigate the influence of measuring device design parameters and the regime variables of the measurement process on the accuracy and give recommendations about their rational values;

– to develop a mathematical model of measurement errors;

– to test experimentally the operability of the developed method on products from anisotropic porous materials.

3. Theory

The research results are based on the analytical theory of mass transfer, mathematical physics, mathematical modeling, the classical theory of metrology and mathematical statistics. The main idea of the developed method is to use a linear impulse action on anisotropic sample in the form of a solvent dose and to analyze the response in the solvent concentration change at a fixed distance from the source. When we use the proposed method, the conditions for diffusion of the solvent are specially created in the controlled samples, which from the point of the mathematical description view are analogous to the description of radial mass transfer in an unbounded medium when we apply a pulsed action from a linear source of mass. For this purpose, the samples must have a flat section of specified dimensions. This allows one-sided access to the product for placing the measuring device. In such case non-destructive control of the solvents diffusion coefficients is possible. At the beginning of the experiment, a solvent dose with power $W$ along a line of length $L$ and width $s$ is applied to the flat sample surface. After the impulse is applied, the flat product surface in the vicinity of the pulse line is waterproofed. With the help of the electrochemical converter electrodes [14], made in the form of rectilinear segments with length $l$, which located on both sides of the mass pulse application line at a distance $x_0$ from it, the change in the electromotive force $E(r,\tau)$ in time is measured.

The process of solvent distribution in an anisotropic product made of PM is described by the following equation for mass transfer boundary-value problem in an unbounded medium, when we apply a pulsed action from a linear source:

$$
\frac{\partial U(r,\tau)}{\partial \tau} = D \frac{1}{r} \frac{\partial}{\partial r} \left[ r \frac{\partial U(r,\tau)}{\partial r} \right] + \frac{W}{\rho_0} \delta(r,\tau),
$$

$$
\tau > 0, \ 0 \leq r < \infty, \ U(r,0) = U_0^0; \quad \frac{\partial U(0,\tau)}{\partial r} = 0; \quad U(\infty,\tau) = U_0^0,
$$

where $U(r,\tau)$ is the concentration of the solvent in the product at a distance $r$ from the linear source of the mass pulse at time $\tau$; $D$ – the diffusion coefficient; $\delta(r,\tau)$ – Dirac delta function; $\rho_0$ – the density of the absolutely dry material; $W$ – the power of the “instantaneous” solvent source acting at coordinate $r = 0$, calculated as the ratio of the solvent amount to the impulse line with length $L$ multiplied by the thickness $h$; $U_0$ – initial concentration of solvent in the material at the time $\tau = 0$.

The diffusion coefficient can be found from [15]:

$$
D = \frac{\rho_0^2}{4r_{\text{max}}}, \quad (1)
$$

where $r_{\text{max}}$ is the time corresponding to the maximum on the $U(r_0,\tau)$ curve of the concentration change at a distance $r_0$ from the source.

Due to the monotonicity of the electrochemical converter static characteristic [14], the moments of reaching the maximum values of the concentration $U(r_0,\tau)$ and the EMF of the converter $E(r_0,\tau)$ coincide. This makes it possible to implement the measurement method without preliminary calibration of the electrochemical converter (ECC). The experience [16, 17] shows that during the research it is expedient to use the range of the static characteristic near the value $0.5U_0$, characterized
by high sensitivity and stable signal. Here \( U_p \) - the concentration of the diffusing substance in the PM solid phase at equilibrium with saturated solvent vapors at a given temperature. Therefore, it is expedient to obtain the value of the maximum concentration \( U_{\text{max}} \) in the vicinity of the given value during the experiment:

\[
U_{\text{max}} \approx 0.5U_p
\]  

(2)

The values of the ECC location coordinate \( \tau_0 \) and the solvent dose \( W \), supplied at the beginning of the experiment active part exert a significant influence on the value \( U_{\text{max}} \). In this case, the change in the concentration of the solvent in the PM in the area of the source action is described by the function:

\[
U(r, \tau) - U_0 = W/(4\pi D\rho_0 \exp[r^2/4D\tau])
\]

(3)

From (3), taking (1) into account, assuming for simplicity \( U_0 = 0 \), it is possible to obtain the dependence of the attained maximum \( U_{\text{max}} \) at \( \tau = \tau_{\text{max}} \) from the solvent dose \( W \):

\[
U_{\text{max}}(r_0, \tau_{\text{max}}) = W/(4\pi D\rho_0 \tau_{\text{max}})
\]

(4)

Let us consider the influence of the measuring device design parameters and technological variables of the measurement process on the diffusion coefficient accuracy. The main design parameters for devices implementing the proposed method are: the minimum permissible dimensions of the flat area and the product thickness in the place of the linear pulse source; permissible dimensions of length \( L \) and width \( s \) of the substance dose line; coordinate \( r_0 \) of the ECC electrodes location relative to the location of the pulse line. The main technological variables are the parameters of the applied mass pulse: the duration \( t \) and the power \( W \). The basis for finding the design parameters of the device is the coordinate \( r_0 \) determination by measuring the EMF change after the application of the pulse.

The mathematical model of the root-mean-square estimate of the relative error \( \delta D \) in determining the sought diffusion coefficient from (1) has the form [16, 18]:

\[
\delta D = \sqrt{(4(\Delta r_0)^2 + (\Delta \tau_{\text{max}})^2 + (\delta r_m)^2)
\]

(5)

where \( \Delta r_0 = r_0 - r_0 \) and \( \Delta \tau_{\text{max}} = \tau_{\text{max}} - \tau_{\text{max}} \) are, respectively, the relative error in determining the coordinate of the calculated cross-section and the time to reach the maximum on the curve of the concentration change in the calculated section; \( \delta r_m \) is the total value of the methodical error due to the incomplete correspondence of the mathematical model used to real physical processes.

As an object of study, the cement-fiber board sample with a thickness of 50 mm and a density of 1320 kg / m\(^3\) in dry state with oriented cotton threads 0.4 mm in diameter is considered. The sample was prepared as follows. Cotton yarns were wound on a mandrel providing their orientation in a given direction, then the mandrel with the wound filaments was placed in a rectangular tray and filled with cement milk. After solidification, the process of setting the sample strength in an autoclave proceeded. Then the sample was dried to constant weight and the diffusion coefficient was investigated. It was shown in [14] that when ECC electrodes are placed on the equipotential product surfaces, value \( \pm a/r_0 \) can be used as an estimate of \( \delta_0 \), where \( a \) - the radius of the electrodes of the ECC. As for the value \( \delta \tau_{\text{max}} \) in (5), it essentially depends on the nature of the change in the concentration \( U(r_0, \tau) \) and the error of its determination [17]. Therefore, the choice of distance \( r_0 \) from (5), when \( \delta m - \text{const} \), is achieved by a compromise solution based on the error \( \delta r_0 \) and duration of the experiment. As a result of this analysis, it was decided to place the main electrodes of the electrochemical converter at a distance \( r_0 = 4 \) mm from the pulse-action line and additional electrodes at a distance of 3 and 5 mm. Removing the transducer from the source over a distance than 5 mm causes an increase in the experiment duration, in the dimensions of the flat products area and in the overall dimensions of the
measuring device with a slight increase in the accuracy. Using (4), and taking into account the calculated constants, it is possible to calculate in advance the required source power of the solvent dose \( W \) to ensure the maximum concentration in the calculated cross section \( r_0 \):

\[
W \approx 8.54 \rho_0 U_{\text{max}} r_0^2.
\]  

The remaining design parameters and regime variables of the diffusion coefficient measurement process was obtained by analyzing the methodical error \( \delta_m \). They were chosen from the condition of reaching negligibly small values \( \delta_m \) in comparison with the remaining components of the resulting error according to [17, 18]. The length \( L \) and width \( s \) of the impulse line, the dimensions of the measuring device and the minimum permissible dimensions of the product itself were chosen from the condition of ensuring mass transfer under linear impulse action in an unbounded medium [18]. The diffusion coefficient was measured by device pressed against a flat rectangular shape surface 100 × 120 mm. The measuring device had a rectilinear groove 90 mm long to accommodate a linear source of solvent mass. The product should have a flat surface area at least 120 × 120 mm. The permissible product thickness in the control zone is not less than 40 mm. The pulse durability \( t \) of the mass must not exceed \( 0.05 \times \tau_{\text{max}} \). This allowed us to take an upper bound estimate of 5% for the total methodical error \( \delta \) for distances up to a linear source 3, 4 and 5 mm, respectively, is 13; 12 and 12% when \( \delta E = 0.5 \% \) and doses for each \( r_0 \) optimally calculated by (6).

4. Experimental results

For carrying out experimental studies, we used the information-measuring system developed by the technology of "National Instruments" [19], with a modernized measuring device. Before carrying out the active experiment, we determined first the required pulse mass by formula (6). In Table 1, as an example, the ethanol diffusion coefficient in a cement-fiber board with a thickness of 50 mm and a density of 1320 kg/m³ in the dry state for a transverse direction to the reinforcing yarns is presented. The pulse application line of the solvent mass was oriented in the direction of the reinforcing filaments in the sample. The total number of studies for each PM-solvent system was at least 20 trials. The calculated value of the ethanol pulse for this example is \( 4.5 \times 10^{-4} \) kg, \( r_0=4 \) mm. Experimental studies have shown that the mathematical expectation of the ethanol diffusion coefficient in a cement-fiber board with a confidence probability \( \alpha = 0.95 \) is \( 2.9 \times 10^{-9} \text{ m}^2/\text{s} \). The random error of determining the diffusion coefficient is less than 8%. The duration of the experiment does not exceed 30 minutes.

| Parameter                  | Parameter Value for \( \tau_{\text{max}} \) (s) |
|----------------------------|-----------------------------------------------|
| \( D_t \cdot 10^9 \) (m²/s) | 1520.9 1716.7 1194.0 1133.1 1219.5            |
| \( \Delta D_t = (D_t - \overline{D}) \cdot 10^9 \) (m²/s) | -0.29 -0.59 0.43 0.61 0.36                     |
| \( \Delta D_t^2 \cdot 10^{18} \) (m⁴/s²)                  | 0.0841 0.3481 0.1849 0.3721 0.1296             |

| Expected value \( \overline{D} = 2.9 \cdot 10^{-9} \text{ (m}^2/\text{s}; \text{error} \ \delta D \approx 8 \% \). |

5. Discussion of the results
Presented method allows us to measure operatively the diffusion coefficient of the polar solvents in the products of anisotropic porous materials with a thickness more than 40 mm, having at least one flat surface with a size of 120 × 120 mm, without their damage. A significant increase in control performance ensured by:

– eliminating the need for preparing samples for study;
– using a more dynamic process of mass transfer under the pulsed action
– eliminating the need for preliminary calibration of applied electrochemical transducer for each new material and solvent.

The efficiency of this method was checked by comparison our results with the results of water and ethanol diffusion coefficients in samples of solid porous materials, by zonal [20] and adsorption [21] methods. The discrepancy in the numerical values of the desired coefficient does not exceed 10 ... 13 %, what can be considered a satisfactory result in the study of solvents diffusion in the PM.

6. Conclusion

The developed dynamic method allows significantly increase efficiency of the diffusion coefficient control for polar solvents in products made from anisotropic porous materials without their destruction. The method can be used in portable devices for operational diffusion coefficient control in the products. The result of these studies identified the minimum allowable dimensions of the flat surface of the product, on which we can place measuring device. We determined the rational value of the coordinate electrode arrangement for electrochemical transducer relative to the line of pulse impact application from the condition of achieving acceptable accuracy and duration for the measurement process. We also received the resulting equation for calculation the required power line solvent source for pulse exposure. Statistical processing of the obtained experimental data and their comparison with the results obtained from known methods demonstrate the efficiency of the proposed non-destructive testing method.

References

[1] Remond R and Almeida G 2011 Wood Mater. Sci. Eng. 1 23
[2] Nizovtsev M I, Stankus S V, Sterlyagov A N, Terekhov V I and Khairulin R A 2008 Int. J. Heat Mass Transf. 51 4161
[3] Roels S and Carmeliet J 2006 Int. J. Heat Mass Transf. 49 4762
[4] Koptyug I V and Sagdeev R Z 2002 Russian Chem. Rev. 71 789
[5] García-Gutiérrez M J L C, Cormenzana J L, Missana T, Mingarro M and Molinero J 2006 J. Iberian Geol. 32 37
[6] Mishchenko S V, Belyaev P S, Gladkikh V A, and Safonova E N 1999 Drying Technol. 17 2151
[7] Carslaw H S and Jaeger J C 1959 Conduction of Heat in Solids (Oxford: Clarendon Press) p 487
[8] Belyaev V P, Belyaev M P, Mishchenko S V and Belyaev P S 2014 Meas. Tech. 56 1190
[9] Belyaev V P, Mishchenko S V and Belyaev P S 2015 Meas. Tech. 58 574
[10] Gurov A V, Sosedov G A, Rodina A E and Ponomarev S V 2013 Meas. Tech. 55 1187
[11] Shashkov A G, Volokhov G M, Abramenko T N and Kozlov V P 1973 Methods to determine thermal conductivity and thermal diffusivity [in Russian] (Moscow: Énergiya) p 336
[12] Belyaev M P, Belyaev V P and Divin A G 2010 Vestn. Tambovsk. Gos. Tekh. Univ. 16 797
[13] Kartashov É M and Rudobashhta S P 2010 Diffusion in chemical-technology processes [in Russian] (Moscow: KolosS) p 478
[14] Scheffler G A and Plagge R 2011 Proc. 5th Int. Autoclaved Aerated Concrete Conf. September 2011, Bydgoszcz (Poland) 337