Mathematical Modeling of the Process of Humid Absorption in a Porous Medium on the Example of Moisture of Lime Composites

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Abstract. A mathematical description of the dependence of the equilibrium moisture content of the porous material of the lime composite on the relative humidity of the air - curves of moisture adsorption in the material under study is considered. Mathematical modeling of the moisture absorption process was performed on the basis of the representation of a certain elementary volume of a lime composite in the form of a volume-porous medium with averaged physicochemical parameters. Mathematical modeling is used for theoretical study of the laws of the process of wetting dry construction mixes. Comparison of calculated and experimental data is carried out, their good consistency is shown. The moistened material is a material with a developed surface throughout the volume and can be considered as a porous medium with effective characteristics distributed throughout the volume, such as porosity, thermal conductivity, mass diffusivity, adsorption characteristics, etc. In the process of moistening the material of the medium at each point of the porous space, an adsorption reaction occurs moisture, which has its macro and microkinetic patterns. Moist air is supplied to the internal, hard-to-reach areas of the porous material due to diffusion and air flow caused by various reasons. The speed of the microscopic reaction of wetting the surface of the composite granules should be taken into account in accordance with the theory of the dependence of the moisture content of the material on the relative humidity of the air. Analysis of the type of sorption curves makes it possible to notice that for a mathematical description of experimental dependence, it is advisable to distinguish two sections on each curve: a section with a bulge up and a segment with a bulge down. The basic equation of moisture transfer in a porous medium is a three-dimensional parabolic differential equation. Under certain conditions, the process of moistening a porous material has the same regularities on any straight line perpendicular to the air-medium interface, which makes it possible to reduce the equation to one-dimensional in spatial variables. The presented calculation results show that the value of the diffusion coefficient significantly affects the process of moistening a porous material and can be used as a measure of the possible moisture content of the composite.

1. Introduction
The problem of mathematical modelling allows us to study the properties of moisture distribution in the process of moistening of porous materials.

The moistened material is a material with a developed surface throughout the volume and can be considered as a porous medium with effective characteristics distributed throughout the volume, such
as porosity, thermal conductivity, mass diffusivity, adsorption characteristics, etc. In the process of moistening the material of the medium at each point of the porous space, an adsorption reaction occurs moisture, which has its macro and microkinetic patterns.

The most important driving forces for the penetration of moist air to the inner, hard-to-reach areas of the porous material are the diffusion mechanism and the air flow caused by natural or technological reasons. At the same time, the rate of the microscopic reaction of moistening the surface of the granules of the lime composite should be taken into account in accordance with the theory of the dependence of the moisture content of the material on the relative humidity of the air.

Description of the Macrokinetics of the porous system as a homogeneous medium under certain conditions of adsorption processes was proposed by Y. B. Zeldovich [1]. According to this theory, the moistened porous medium can be considered as homogeneous, at each point of which a kinetic moisture reaction takes place.

Naturally, all kinetic parameters, including the diffusion coefficient, have averaged values. These values may differ from the true values and are usually determined experimentally.

2. The mathematical description of the adsorption patterns of absorption
A characteristic form of the adsorption curve – the dependence of the equilibrium moisture content of the material \( W \) on the relative humidity \( \varphi \) is shown in figure 1.

\[ W(\varphi) \]

![Figure 1](image.png)

**Figure 1.** Type of dependence of equilibrium humidity of the material \( W(x) \) of relative humidity \( \varphi(x) \)

The existing descriptions of the dependence \( W = f(\varphi) \) (for example [2, 3, 4]) adequately describe the processes of moisture filling only within a sufficiently narrow range of changes in the relative humidity \( \varphi \).

Analysis of the type of sorption curves allows us to note that for the mathematical description of the experimental dependence it is advisable to allocate two sections on each curve: for \( 0 < \varphi(x) < \varphi_0 \) the area with the convexity up and for the \( \varphi_0 < \varphi(x) < 100\% \) area with the convexity down. Here \( \varphi_0 \) – some average parameter selectable, from the interval \( \varphi \approx 10\% – 60\% \), and having a certain value for each type of moist porous material.

On the basis of physical representations and logical reasoning, we deduce the analytical dependence of the equilibrium moisture content on the moisture content of the humidifying air \( W = f(\varphi) \). To do this, consider the rate of growth of moisture content from the current moisture content and relative humidity of the air flow \( \frac{dW}{d\varphi}(W, \varphi) \).
On the section of the adsorption curve “convexity down” it is logical to assume that the rate of growth of the adsorbed moisture volume is proportional, firstly, to its value at a given humidity $\phi$, since moisture molecules deposited on the material create additional adsorption centers, as well as differences $(W_M - W)$, where $W_M$ – the maximum possible moisture content of the material. These arguments lead to dependence:

$$ \frac{dW}{d\phi} = k \cdot W \cdot (W_M - W), $$

(1)

where $k$ is some constant of proportionality. To solve the equation (1), it is necessary to Supplement it with the initial value of the moisture content $W_N$ at a certain value $\phi = \phi_0$.

Equation (1) is a differential equation with separating variables and with a given initial condition - the Cauchy problem, which always has a unique solution. Divide the variables:

$$ \frac{dW}{k \cdot W \cdot (W_M - W)} = d\phi. $$

(2)

When calculating indefinite integrals from both parts of this equation, we use the method of indefinite coefficients to decompose the fraction:

$$ \int \frac{1}{W \cdot (W_M - W)} dW = \frac{1}{W} \cdot \frac{1}{W_M - W} + \frac{1}{W_M \cdot (W_M - W)}. $$

(3)

After such a representation of the right-hand side, equation (3) is easily integrated:

$$ \int \frac{1}{kW \cdot (W_M - W)} dW = \int \frac{1}{W \cdot W_M} dW + \int \frac{1}{W_M \cdot (W_M - W)} dW = \int d\phi + \text{const}; $$

$$ \frac{1}{kW_M} \ln W - \frac{1}{kW_M} \ln (W_M - W) = \phi + \text{const}; \quad \frac{1}{kW_M} \ln \frac{W}{W_M - W} = \phi + \text{const}. $$

The value of const is found from the substitution of initial conditions $W(\phi_0) = W_N$:

$$ \text{const} = \frac{1}{kW_M} \ln \frac{W_N}{W_M - W_N} - \phi_0. $$

Substitute the expression for const in the solution, we obtain:

$$ \frac{1}{kW_M} \ln \frac{W}{W_M - W} = \phi + \frac{1}{kW_M} \ln \frac{W_N}{W_M - W_N} - \phi_0; $$

$$ \ln \frac{W(W_M - W_N)}{W_N(W_M - W)} = kW_M (\phi - \phi_0); \quad \frac{W(W_M - W_N)}{W_N(W_M - W)} = \exp(kW_M (\phi - \phi_0)). $$

Solving the last equation with respect to the function $W$, we obtain finally:

$$ W = \frac{W_N}{\frac{W_N}{W_M} + \left(1 - \frac{W_N}{W_M}\right) \cdot \exp\left(- kW_M (\phi - \phi_0)\right)}. $$

(4)

Note that when $\phi = \phi_0$ from equation (4) is obtained $W = W_N$, and at a sufficiently large value $\phi$ can be taken $W \approx W_M$. 

3
In the second section, the “bulge up”, that is \( \phi \geq \phi_s \), when the mechanism of moisture filling of the capillary medium is activated, which has a monomolecular and, further, capillary character. In [5] suggested that the increase with the growth \( \phi \) must have exponential character. Following this assumption, we write:

\[
W = W_M \cdot \exp(k_1(\phi - \phi_s)),
\]

where \( k_1 \), and \( \phi_s \) – some regression constants, the value of which must be determined based on the curves obtained experimentally using methods of mathematical data processing, for example, the least squares method.

Thus, the expression \( W = f(\phi) \) can be written as:

\[
W = \begin{cases} 
\frac{W_N}{W_M} + \left( 1 - \frac{W_N}{W_M} \right) \cdot \exp(-kW_M(\phi - \phi_{0})) & \phi < \phi_s; \\
W_M \cdot \exp(k_1(\phi - \phi_s)) & \phi \geq \phi_s.
\end{cases}
\]

Let's perform a simple analysis of expression (6). Note that for small values \( \phi - \phi_0 \) (close to zero) both exponents are small numbers and \( W \approx W_N \) and the rate of growth of moisture content of the material is not high. Then there is an increase in speed \( \frac{dW}{d\phi} (W, \phi) \), and its maximum value it will reach when executed \( \frac{d^2W}{d\phi^2} = 0 \). Twice differentiating the right part of equation (6) and equating the obtained expression to zero, it is easy to obtain that the maximum increase in the rate of moisture filling is observed, at a value of \( \phi - \phi_0 = 1/W_Mk \cdot \ln(W_M/W_N - 1) \). The second term \( W_M \cdot \exp(k_1(\phi - \phi_s)) \) is decisive with further growth of the relative humidity \( \phi \) in expression (6).

Thus, for small values \( \phi \) for the mathematical description of moisture absorption by a porous material with a certain degree of accuracy, the expression (2) can be used, and for significant values of air humidity \( \phi \) expression (3).

### 3. Mathematical model of moisture absorption process

The basic equation of mass transfer of moisture in a porous medium can be written in the following General form [6]:

\[
\frac{\partial \phi}{\partial t} = -\vec{w} \cdot \frac{\partial \phi}{\partial x} + w_2 \frac{\partial \phi}{\partial y} w_3 \frac{\partial \phi}{\partial z} + D \left( \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} \right) - k \cdot S \cdot f(\phi).
\]

Here: \( \vec{w} = (w_1, w_2, w_3) \) – velocity vector of the conditioned air through a porous medium; \( D \) – effective diffusion coefficient; \( S \) – specific surface of the unit volume of the material, \( k \) – a constant.

We assume that the process of moistening the porous material has the same laws on any straight line perpendicular to the surface of the air – medium phase interface, which reduces the equation (7) to one-dimensional spatial variables:

\[
\frac{\partial \phi}{\partial t} = -\vec{w} \cdot \frac{\partial \phi}{\partial x} + D \frac{\partial^2 \phi}{\partial x^2} - k \cdot S \cdot f(\phi).
\]

Here \( 0 \leq x \leq L \), \( L \) is the thickness of the porous material. In addition, in the absence of forced convection in equation (8) there will be no first term in the right part:
\[
\frac{\partial \varphi}{\partial t} = D \frac{\partial^2 \varphi}{\partial x^2} - k \cdot S \cdot f(\varphi).
\]  

(9)

In the case where the humidification process is stationary, equation (9) is simplified to the form:

\[
D \frac{\partial^2 \varphi}{\partial x^2} - k \cdot S \cdot f(\varphi) = 0.
\]  

(10)

Using the results of the previous section, in particular equations (3), with significant initial values of air humidity can be taken \(k \cdot S \cdot f(\varphi) = W_M \cdot \exp(k_1(\varphi - \varphi_s))\) and write down the following equation to calculate the humidity of the porous medium:

\[
D \frac{d^2 \psi}{dx^2} - W_M \cdot \exp(k_1 \psi) = 0.
\]  

(11)

Here, for convenience of calculations, the designation \(\psi(x) = \varphi(x) - \varphi_s\) is introduced. We assume that the values of air humidity at the interfaces of air – porous material media: \(\varphi_0\) and \(\varphi_L\). The ordinary differential equation (11) is an equation with separating variables. Having previously designated \(W_D = W_M / D\), we perform the separation of variables: \(\exp(-k_1 \psi) \cdot d^2 \psi = W_D dx^2\).

We integrate both parts of the equation, respectively, by the variables \(\psi\) and \(x\),

\[
\int e^{-k_1 \psi} d^2 \psi = \int W_D dx^2,
\]

we will receive:

\[
\frac{1}{k_1} \cdot \exp(-k_1 \psi) d\psi + c_1 = W_D x dx.
\]

Integrating this equation for the same variables, we get the following expression:

\[
\frac{\exp(-k_1 \psi)}{k_1^2} + c_1 \cdot \psi + c_2 = x^2 \cdot \frac{W_D}{2}.
\]  

(12)

To determine the constants \(c_1\) and \(c_2\), we use the boundary conditions: \(\psi(0) = \varphi_0 - \varphi_s\) and \(\psi(L) = \varphi_L - \varphi_s\). Substituting in (12) first \(x = 0\), and then \(x = L\), we obtain the system of equations:

\[
\begin{cases}
\frac{\exp(-k_1 \psi(0))}{k_1^2} + c_1 \cdot \psi(0) + c_2 = 0 \cdot \frac{W_D}{2}; \\
\frac{\exp(-k_1 \psi(L))}{k_1^2} + c_1 \cdot \psi(L) + c_2 = L^2 \cdot \frac{W_D}{2}.
\end{cases}
\]

The solution of this system with respect to unknown \(c_1\) and \(c_2\) are the expressions:

\[
\begin{align*}
c_1 &= \frac{L^2 \cdot \frac{W_D}{2} - \frac{1}{k_1^2} (\exp(-k_1 \psi(L)) - \exp(-k_1 \psi(0)))}{\psi(L) - \psi(0)}; \\
c_2 &= \frac{-\exp(-k_1 \psi(L)) - \psi(0) \cdot \frac{L^2 \cdot \frac{W_D}{2} - \frac{1}{k_1^2} [\exp(-k_1 \psi(L)) - \exp(-k_1 \psi(0))]}{\psi(L) - \psi(0)}}{k_1^2}.
\end{align*}
\]

Turning to expressions \(W_D = W_M / D\), \(\psi(0) = \varphi_0 - \varphi_s\) and \(\psi(L) = \varphi_L - \varphi_s\), we get:
The calculated and experimental curves [7] presented in figure 2 show good agreement, and, consequently, the efficiency of the mathematical model.
Figure 2. The distribution of moisture content in the finishing coating, calculated: curve 1 – in the expanded vermiculite sand, curve 2 – in ash microspheres of aluminosilicate; experimental – points

4. Conclusions
Analyzing the results of calculations, we can conclude that, apparently, the value of the diffusion coefficient significantly affects the process of moistening the porous material and can be used as a measure of the possible moisture content of the composite.

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