The investigation of drying and freezing of spherical samples of porous materials with second order nonlinear differential equations

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Abstract. The purpose of the current investigation is to present the results of the model, which allows obtaining the temperature distribution in a spherical sample of porous clay for the processes of rapid drying (heating) and freezing (cooling). Solutions are one-dimensional nonlinear temperature distributions for each point in time. The temperature of the external surface of the sample was set equal to the ambient temperature.

1. Introduction
Among the porous materials, the clay is strikingly different in that in some cases it can contain particles of gold. Such a clay is called gold-bearing. The clay is plastic and sticky, which makes it difficult to wash out small fractions of the precious metal. To date, after industrial processing, gold particles with an effective radius of $R_0 < 40 \, \mu m$ are not extracted. This means that half of the gold contained in the clay is discarded. To discover the best way to extract precious metal from a piece of clay, it is necessary to thoroughly examine clay itself.

Porous materials, such as clay, the voids are partially filled with moisture. The moisture content determines the properties of the sample, both mechanical and thermophysical, for example, density, viscoelasticity, and ductility. The course of the processes occurring in it, such as heating or cooling, will strongly depend on the properties of the clay [1, 2, 3]. The evolution of drying or freezing processes is strongly influenced by the porosity and humidity of the body, the amount of moisture in its pores and the state of water contained in pores [4, 5].

In industrial processes it happens that the clay is subjected to non-stationary heat treatment, in order to permanently change its properties. In such cases, changes in the moisture content of the sample significantly lag behind the temperature changes. This occurs because the diffusion coefficient of moisture content is small compared with the similar coefficient associated with the heat transfer (referred to as the thermal diffusivity). Thus, in the case of a fast non-stationary heating or cooling of a porous body in the numerical model describing the process the change in the moisture content can be neglected [6, 7].

In this paper a numerical model is presented which calculates a one-dimensional nonlinear temperature distribution over a spherical clay sample for the processes of drying and freezing under various initial and boundary conditions.
2. Model

The model presented below was first used in work [8], where it is considered in the most detailed way, and therefore, in this article, the focus will be placed only on its main details.

As mentioned in the introduction, in non-stationary thermal processes, where heat is exchanged between the environment and the material, the change in the moisture content of the sample is delayed, lagging behind the change in the temperature distribution inside the sample. This allows omitting the mass-exchange and makes it possible to study the changes in temperature distribution as a result of the heat-exchange process, where heat is transferred only through heat conduction. In this consideration, the distribution of heat over the body can be described by the equation of heat conduction:

\[ c_{\text{eff}} \rho \frac{\partial T}{\partial t} = -\text{div}(\lambda \text{grad} T) \pm q, \]  

where \( c, \rho \) and \( \lambda \) depend on \( T \) and \( u \), i.e. \( c = c(T,u), \rho = \rho(T,u) \) and \( \lambda = \lambda(T,u) \), where \( u \) – moisture content. The moisture contained in the pores can be both liquid and could turn into ice. The heat capacity of liquid water at 0°C is 4237 J·kg\(^{-1}\)·K\(^{-1}\), and ice is 2261 J·kg\(^{-1}\)·K\(^{-1}\), i.e. two times less.

The effective heat capacity \( c_{\text{eff}} \) is described by the following equation:

\[ c_{\text{eff}} = c + c_{bw} + c_{fw}, \]  

where \( c \) is the porous body heat capacity, \( c_{bw} \) is the heat capacity of bound water, \( c_{fw} \) is the heat capacity of free water. In the absence of an external heat source \( (q = 0) \) and for the case of an isotropic spherical body, equation (1) can be represented in spherical form:

\[ c_e \rho \frac{\partial T}{\partial t} = \frac{\lambda}{r^2} \left( \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) \right) + \frac{\partial \lambda}{\partial T} \left( \frac{\partial T}{\partial r} \right)^2. \]  

In this model, the temperature conductivity is assumed to be linear:

\[ \lambda = \lambda_0 \gamma (1 + \beta(T - 273.5)). \]  

where \( \lambda_0, \gamma \) and \( \beta \) are functions of temperature and moisture content, discussed in more detail in [8].

It was experimentally confirmed that for \( u > u_{sp} \) and for temperature values close to -2°C the dependence of temperature on time experiences a jump. Here, \( u_{sp} \) is the critical moisture content. It is the value after which the body can no longer absorb moisture:

\[ u_{sp} = u_{sp}^{20} - 0.001 (T - 293.15), \]  

where \( u_{sp}^{20} \) is the critical moisture content at 20°C. Also in the model \( u_{nfw} \) is used. It is the part of moisture that is not frozen.

\[ u_{nfw} = 0.12 + (u_{fw} - 0.12) \exp[0.0567 (T - 293.15)]. \]  

Heat capacity (3) is determined by the following set of equations:
1) For \( T > 271.15 \) or \( T \leq 271.15 \), while \( u < u_{nfw} \)

\[
c = \frac{2097 u + 826}{1 + u} + \frac{9.92 u + 2.55}{1 + u} T + \frac{0.0002}{1 + u} T^2, \quad u < u_{sp}
\]

or

\[
c = \frac{2862 u + 555}{1 + u} + \frac{5.49 u + 2.95}{1 + u} T + \frac{0.0036}{1 + u} T^2, \quad u \geq u_{sp}
\]

2) For \( T \leq 271.15 \), while \( u \geq u_{nfw} \)

\[
c = \left(1.06 + 0.04 u + \frac{0.00075 (T - 271.15)}{u_{nfw}}\right) \left(526 + 2.95T + 0.0022 T^2 + 2261 u + 1976 u_{nfw}\right) \frac{1}{1 + u}.
\]

\[
c_{fw} = 3.34 \cdot 10^4 \frac{u - u_{sp}}{1 + u}, \quad 271.15 < T \leq 272.15 \text{ & } u > u_{sp}
\]

\[
c_{bw} = 1.8938 \cdot 10^4 \left(u_{sp} - 0.12\right) \frac{\exp\left[0.0576 (T - 271.15)\right]}{1 + u}, \quad u > u_{nfw}
\]

The density of the material itself is determined by the following empirical formula:

\[
\rho = \rho_b \frac{1 + u}{1 - 9.3 \cdot 10^{-4} \rho_b (u_{sp} - u)}, \quad u \leq u_{sp}
\]

\[
\rho = \rho_b (1 + u), \quad u > u_{sp}
\]

where \( \rho_b \) is the density of an absolutely dry porous body.

The model presented above was used to calculate the temperature distributions of an absolutely isotropic perfectly spherical sample of porous clay, where changes in moisture content were assumed to be insignificant, and the moisture content itself was taken as a parameter.

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**Figure 1.** Temperature distribution over a spherical clay sample at various points in time \((r_0 = 5\text{cm}, T_0 = -20^\circ C, T_m = 20^\circ C)\).

**Figure 2.** The dependence of temperature on time in a clay sample, at various points in the sample \((r_0 = 5\text{cm}, T_0 = -20^\circ C, T_m = 20^\circ C)\).
3. Results

In this work, an isotropic spherically clay sample is considered, the density of which in an absolutely dry state is given by a constant equal to $\rho_b = 1800 \text{ kg/m}^3$. All experiments were set in such a way that the clay of the initial temperature $T_0$ is placed in an environment with a temperature $T_m$, and then the evolution of the temperature distribution over the entire sample, or at its various points, is considered.

First of all, the heating of a clay ball is considered in detail. The results of the experiment are presented in figures 1 and 2. The initial temperature of the sample is taken equal to $T_0 = -20^\circ\text{C}$, while the ambient temperature (drying apparatus) is set to $T_m = 20^\circ\text{C}$.

The first graph shows the temperature distribution across the clay ball at different points in time. From the evolution of the distribution, it can be seen that, as the temperature curve approaches the value $T_0 = -2^\circ\text{C}$, the region of constant values appears, which are equal to $-2^\circ\text{C}$. This is explained by the fact that the ice contained in the sample pores, when heated, turns into water not instantly, but gradually heats up and gradually melts. The deeper into the sample, the longer it takes to heat the solid phase of the liquid, and therefore the area of constant values, closer to the center of the sphere, is getting wider.

Figure 2 shows the dependence of the temperature distribution on time at different points in the sample, at which a region of constant values can be considered in more detail. The curves in this graph support the previous assumption that the zone of constant temperatures remains longer in the center of the sample due to the lower heating rate. It is clearly seen that, when approaching the center, the time it takes to transform ice into water increases.

Figure 3 shows the results of a series of experiments on sample heating with a drying machine, where the temperature of the latter was set in the range from $T_m = -2^\circ\text{C}$ to $T_m = 40^\circ\text{C}$. The temperature, the dependence of which is shown in figure 3, was measured at the very center of the sample, where the heating occurred most slowly. It is obvious from the graph that the region of constant values is broadened with the decrease of the $T_m$, and when the $T_m = -0^\circ\text{C}$, the temperature of the sample center remains equal to the -2$^\circ\text{C}$ until the end of the measurements. An additional, more thorough measurement showed that in this experiment the temperature of clay ball center reached -0$^\circ\text{C}$ only eight hours later, lagging behind all other curves by 5-6 hours.

Figure 4 shows the reverse graph - the results of the experiment, where a frozen clay ball with different initial temperature ranged from $T_0 = -40^\circ\text{C}$ to $T_0 = 0^\circ\text{C}$ is placed in a drying chamber, the temperature of which is equal to $T_m = 20^\circ\text{C}$. From these dependences it can be seen that the
“temperature front” reaches the center of the spherical sample approximately six to ten minutes after the start of heating, however, in the case of an initial temperature equal to $T_0 = -2^\circ C$, the center of the ball does not change its temperature so that it remains in the zone of constant temperatures and subsequently merging with the other dependencies. Later on, these dependencies, with a small time lag, depart from the areas of constant values and almost simultaneously, including the dependence, which started with $T_0 = 0^\circ C$, reach the value of $T_m$. From these two graphs it can be concluded that it does not matter what sample initial temperature is chosen - only the temperature of the drying apparatus influences the heating time.

Next, an experiment was conducted on the cyclic heating and cooling of a spherical sample of porous clay. This experiment simulates the process when a frozen ball of a porous soil is first placed in a drying apparatus heated to $T_{m,1} = 20^\circ C$, and then, when it is fully warmed up, the sample is taken out and placed in the refrigerator $T_{m,2} = -20^\circ C$, for the same time. The series of experiments was carried out with clay spheres of radii $r_0 = 5$, 10 and 20 mm. Figure 5 shows the evolutionary temperature curves measured at the centers of these three samples. The data of the time abscissa were divided into the square of the radii ratios of these samples, in other words, the time was normalized.

It can be seen from the figure that, despite the fact that the temperatures ultimately come to the same boundary values, the way that dependencies change is different for heating and cooling processes, which creates a figure on the graph similar to hysteresis. In addition, despite the different sizes of the samples, normalization of the data to the ratio of the squares of the radii gives absolute coincidence of the data. This result seems to be only partially correct - with further increase in the size of the ball, the heating time will be large enough to take into account the change in moisture content, and therefore this normalization will most likely no longer be valid.

4. Conclusions
The evolution of temperature distributions within an isotropic clay ball is investigated in this article. A thorough study of heating has been carried out. The dependency of temperature on time at different points in the sphere and temperature distribution in the clay sample for individual moments of time are considered. A number of measurements have been carried out for different initial and boundary conditions of the clay sample. An experiment was conducted to cyclically change the temperature of samples of different radii.

Almost all the presented data demonstrate the appearance of a region of constant values in temperature dependences, which is associated with non-instantaneous melting of frozen water in clay pores. The closer to the center of the sample, the longer this area remains.
According to the data obtained, it is established that heating to zero degrees Celsius occurs very slowly, which may be due to the fact that the ice in the pores does not melt and, until the very end of heating, participates in heat transfer. It was determined that the initial temperature of the sample does not affect the heating time—all evolutionary curves reach the boundary values almost at the same moment.

From the results of the experiments on cyclic temperature changes, it can be concluded that the object subjected to cyclic temperature change experiences irreversible changes in its internal structure. In addition, for sufficiently small clay samples, such cyclic changes will take place uniformly, and the distribution curves will coincide when normalizing the time abscissa by the square of the radii of the clay spheres.

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