Vacuum freezing of clay porous material

A V Fedoseev*, M V Salnikov, N A Demin, G I Sukhinin, I V Yarygin, V G Prikhodko and S A Novopashin

Institute of Thermophysics SB RAS, Lavrentyev Ave. 1, Novosibirsk 630090, Russia

*E-mail: fedoseev@itp.nsc.ru

Abstract. The results of experimental measurements of a temperature distribution in a clay layer of finite thickness for a vacuum drying process are demonstrated. The results of the experiment were compared with the results of the numerical model. An incomplete correspondence between two approaches was obtained. The effect of width of the clay layer on the course of the vacuum drying process is shown.

1. Introduction

Clay is one of the most important materials in the history of mankind, and it is impossible to overestimate its significance [1]. This fine-grained rock, in addition to being used in the food and medical industry, sometimes contains particles of precious metals. Clay is a porous material, which is, microvolumes usually filled with air, liquid or liquid vapors occur in solid rock. It is these pores that sometimes contain particles of foreign materials, such as gold. To date, gold from these pores is extracted in the mining industry only by half - grains smaller than 40 μm are dumped.

The ratio of the aggregate microvolume of pores to the volume of the continuous medium in the rock is called porosity. The moisture contained in the pores and the state of this moisture determine the course of thermal processes that the rock is exposed to [2, 3], such processes as, for example, cooling or drying [4]. In addition, the moisture content of the clay determines: density, plasticity, viscoelasticity, swelling, cracking, and other physicochemical parameters of the sample. [5].

Drying is a process of simultaneous heat and mass transfer. Drying in the industry is an incredibly widespread material processing mechanism [6]. If the power of the dryer is too large for the clay in the working volume, then the clay sample is deformed [7–10] due to the uneven distribution of temperature and humidity inside [11]. In order to achieve more efficient extraction of gold from gold-bearing clay, in previous works, the authors of this paper proposed a method of vacuum drying [12]. The method is to expose the clay sample to low pressure, whereby the moisture in its pores crystallizes. Because of this, stresses appear in the porous material, and the clay sample is significantly deformed.

This article explains the experimental setup and the numerical model, which determine the one-dimensional non-linear temperature distribution over a clay layer of a certain thickness for the vacuum drying process. The aim of the work is to compare the results obtained using a numerical model with an experiment on vacuum drying of clay.

2. Experimental setup

The clay layer was placed in a small chamber of volume $V_0 = 22$ liters, the pressure in which at the initial moment of time was $p_0 = 1$ atm. The small chamber was connected with a large vacuum
chamber, the volume of which was equal to \( V = 5 \text{ m}^3 \). An analog-digital converter, two pressure sensors, a display, a control unit for pneumatic valves, a computer, and a vacuum pump were connected to the experimental setup. A digital camera was used to visualize the processes. The experimental setup diagram is shown in Figure 1.

![Experimental setup of vacuum drying](image)

**Figure 1.** Experimental setup of vacuum drying. 1 – receiver, 2 – pressure gauge (MKS Baratron 722), 3 – ADC, 4 – computer, 5 – control unit, 6 – camera, 7 – weight sensor in a small chamber, 8 – atmospheric valve, 9 – pumping valve, 10 – vacuum pump, 500 l/s.

The experiment algorithm was as follows. Clay kaolin was placed in a small chamber. Then the vacuum pump 10 pumped out the air in the small chamber to a pressure of \( \sim 15 \text{ Pa} \). Low pressure in the chamber was maintained for almost an hour, and then the first valve 9 was closed to disconnect the receiver, and the second valve 8 was opened to connect the working chamber with the atmosphere.

The experiments were carried out with three clay layers of kaolin of thickness: \( L_1 = 11.0 \text{ mm} \), \( L_2 = 22.0 \text{ mm} \), \( L_3 = 35.0 \text{ mm} \). The end result of vacuum drying can be seen in Figure 2. As a result of the evaporation of water, the energy associated with the latent heat of evaporation was carried away and this led to icing of the surface of the layer. Since the specific volume of liquid water is less than the specific volume of ice, such freezing led to the occurrence of strong stresses, which led to the destruction of the surface of the layer that was even at the initial stage.

![A layer of porous clay 11 mm wide deformed as a result of vacuum pumping](image)

**Figure 2.** A layer of porous clay 11 mm wide deformed as a result of vacuum pumping.
3. Model

In numerical model, an isotropic layer of finite thickness acts as a sample of clay. The liquid evaporates only from the surface of this layer. When the sample is cooled, only processes that are associated with the liquid and solid phases are considered; the phases in the model have the same temperature and are incompressible. The sample was placed in such a way that its largest faces lay in the XY plane. The evolution of the temperature and moisture distributions in this model is considered only depending on the depth, that is, along the Z axis.

The distribution of temperature \( T \) and moisture \( U \) in a layer of isotropic clay of finite thickness is described by the equations:

\[
\rho c \frac{\partial T}{\partial t} = \lambda_{\text{eff}} \frac{\partial^2 T}{\partial z^2} + \frac{\partial \lambda_{\text{eff}}}{\partial z} \frac{\partial T}{\partial z}, \tag{1}
\]

\[
\frac{\partial U}{\partial t} = D_{\text{eff}} \left( \frac{\partial^2 U}{\partial z^2} + \frac{\partial D_{\text{eff}}}{\partial z} \frac{\partial U}{\partial z} \right), \tag{2}
\]

\( c \) and \( \rho \) are the specific heat capacity of the material and density, respectively, \( D_{\text{eff}} \) and \( \lambda_{\text{eff}} \) are the effective coefficients for water diffusion and thermal conductivity. All coefficients in equations (1) and (2) are the functions of local temperature \( T \) and moisture content \( U \): \( \rho = \rho(U,T) \), \( c = c(U,T) \), \( \lambda_{\text{eff}} = \lambda_{\text{eff}}(U,T) \), \( D_{\text{eff}} = D_{\text{eff}}(U,T) \).

Specific heat is given by the expression:

\[
c = \frac{C_{p,s} + UC_{p,l}}{1+U}.\]

where \( C_{p,l} = 4.22 \text{ kJ/kg/K} \), \( C_{p,s} = 1.1 \text{ kJ/kg/K} \), are the heat capacity of the liquid water and the heat capacity of the crystallized water, respectively.

The density of the sample \( \rho \) determines the initial moisture content \( U_0 \), the volume of the sample \( V \) and its sample mass \( m_0 \):

\[
\rho = \frac{m_0 (1+U)}{V(1+U_0)}.\]

The coefficient of thermal conductivity is determined through the formula [9]:

\[
\lambda_{\text{eff}}(U,T) = (1 - \phi) \lambda_s + \phi \lambda_l, \tag{3}
\]

where \( \rho_l = 1000 \text{ kg/m}^3 \) is the density of the liquid phase, \( \rho_s = 2600 \text{ kg/m}^3 \) is the density of the solid phase, \( \phi = U \rho_s / (\rho_l + U \rho_s) \) is the porosity of the clay layer, \( \lambda_s = 1.178 \text{ W/m/K} \) is the thermal conductivity of crystallized water and \( \lambda_l = 0.597 \text{ W/m/K} \) thermal conductivity of liquid water. It should be noted that formula (3) is a limit case of well-known inequality of Wiener \( \left( \sum \phi_i \lambda_{i,j} \right)^{-1} \leq \lambda_{eff} \leq \sum \phi_i \lambda_{i,j} \). A detailed discussion about electrical and heat conductivity of the mixtures see in [13].

The diffusion coefficient \( D_{\text{eff}}(\text{m}^2/\text{s}) \) is defined as [10,13]:

\[
D_{\text{eff}}(U,T) = 5.61 \cdot 10^{-10} \left( 7.5 + \exp \left( \frac{44U}{1.6+U} \right) \exp \left( -\frac{510}{T} \right) \right).\]

The density of the moisture \( q_U \) and thermal \( q_T \) flows are given as:

\[
q_T = -\lambda_{\text{eff}} \frac{\partial T}{\partial z},
\]

\[
q_U = -D_{\text{eff}} \frac{\partial U}{\partial z}.
\]

The heat flux onto the surface of a clay layer of finite thickness is determined by the sum of the heat \( q_{\text{heat}} \) and the convective \( q_{\text{conv}} \) terms, as well as the term associated with the evaporation of water from the surface of the layer:
\[ q_T = h_c(T_s - T_m) + h_\nu q_U, \]
where \( h_c = 40 \text{ W/m}^2\text{K} \) is the coefficient of convective heat transfer, \( h_\nu = 2500 \text{ kJ/kg} \) is the latent heat of evaporation of water, \( T_m \) is the temperature of the drying apparatus, \( T_s \) is the temperature of the sample surface.

The flow of vapor from the layer surface:
\[ q_U = \frac{k_\nu M_\nu}{R_0} \left( \frac{\varphi_m P_{\nu,\text{sat}}(T_s)}{T_s} - \frac{\varphi_s P_{\nu,\text{sat}}(T_m)}{T_m} \right), \]
where \( M_\nu \) is the molecular weight of water, \( k_\nu \) is the water vapor transfer coefficient \( (k_\nu = h_c/\rho/c) \), \( R_0 \) is the universal gas constant, \( \varphi_m \) and \( \varphi_s \) are the relative humidity of the drying apparatus and the clay surface, \( P_{\nu,\text{sat}}(T) \) is the pressure of saturated vapors. In this paper \( \varphi_s \) is determined by the formula [10]:
\[ \varphi_s = \begin{cases} 1, & \text{for } U \geq U_{cr} \\ 1 - (1 - \varphi_m) \frac{U - U_{cr}}{U_{cr} - U_{eq}}, & \text{for } U_{cr} \geq U \geq U_{eq} \end{cases} \]
where \( U_{eq} = 0.05 \text{ kg/kg} \), \( U_{cr} = 0.135 \text{ kg/kg} \), are the critical and final equilibrium moisture content in the dried layer [10].

4. Results
In the calculations and experiments in this paper a layer of clay of finite thickness was used. In the numerical model, the initial humidity and temperature were set constant throughout the volume \( T(r,t_0) = T_0, U(r,t_0) = U_0 \). The numerical calculations were organized according to the experiments performed - the clay of the initial humidity \( U_0 \) and temperature \( T_0 \) was placed in an airless environment, and then the evolution of the temperature and moisture distributions throughout the entire layer was calculated.

As a result of the experiment, the time dependences of the one-dimensional temperature distributions \( T(t) \) were obtained for different depths into which the temperature sensor was placed. Temperature measurements were carried out for three different depths: one sensor was placed on the surface of the clay layer, the second sensor was put in the center of the layer, and the third sensor was at the deepest point of the layer. Experiments were carried out for layers with a depth of 11, 22, and 33 mm. The results of experimental measurements are shown in Figure 3. The left side of this figure shows the temperature as a function of time, as measured by a sensor located on the surface of the clay layer. The right side shows the temporal temperature dependence obtained from the sensor placed at the maximum depth of the layer.

First of all, it is worth noting the emergence of a small region of constant temperature values, which appears after a slight bias as the temperature approaches 2 °C. As it has been repeatedly noted in [14,15], the appearance of such a region is directly related to the non-instantaneous freezing of water and the formation of ice in the pores of the clay — some time elapses before full crystallization. From the right side of Figure 3 it can be seen that this area grows with increasing width of the clay sample layer. This, in turn, is due to the fact that heat transfer in a thick layer takes more time. The lifetime of this area grows in a quadratic way. If for a sample 35 mm wide, the life span of the constant temperature region is about 15 seconds, for a layer of 11 mm depth this time becomes equal to approximately 3 seconds.

Dependences also show that the temperature to which samples are cooled increases with increase of the clay layer width. This suggests that the evaporation of a liquid into a vacuum through an external surface decreases with increase of width. This is probably due to the fact that in a more massive volume, the liquid has time to crystallize inside the material as a result of heat transfer.
Figure 3 Evolutionary temperature curve on the surface (left) and in the maximum depth (right) of a finite clay layer for three different layer thicknesses.

Figure 4 shows the temperature evolution curve measured on the surface of a clay layer of finite thickness. This graph shows a comparison of the experimental data obtained for a 35 mm thick clay layer with the results obtained using the one-dimensional numerical model described above. From this graph, it can be concluded that the numerical model does not fully satisfy the experimental data in a qualitative manner, if only because the numerical model does not form on the layer surface a region of constant values that is present in the experiment. This is due to the specificity of the boundary conditions, as a result of which the temperature and moisture content instantly react to the influence of the external environment (vacuum), whereas in the experiment the process of atmosphere evacuation is not instantaneous and there is an active heat exchange of the atmosphere with the external surface of the clay.

Nevertheless, although the calculated curve does not repeat the experimental curve with a good accuracy, it describes well the general tendency, i.e. the temperatures to which the clay cools in the experiment and the calculation coincide.

Figure 4 The temperature evolutionary curve measured on the surface of a clay layer. Comparison of experimental data (solid line) obtained for a 35 mm thick clay layer on the sample surface with results obtained using a numerical model (dashed line) for initial moisture content $U_0 = 0.2$ and initial temperature $T_0 = 17.5^\circ C$. 
Conclusions
In this article, one-dimensional distributions of moisture content and temperature inside a layer of clay of finite thickness, which is subjected to a vacuum drying process, are investigated.

An experiment was carried out on the vacuum pumping of clay layers for various thicknesses. It is shown that the sample is rapidly cooled to temperatures below -20 °C. The appearance of a region of constant values was observed when the layer temperature reaches -2 °C, which is associated with non-instantaneous crystallization of water in the pores of the material.

A one-dimensional numerical model that allows us to determine non-linear one-dimensional evolutionary curves of moisture content and temperature has been developed. The curves obtained for the temperature change do not fully coincide with the experimental curves, but they describe well the overall quantitative characteristics — the cooling time and the final temperature of the material.

Acknowledgement.
This research was funded by the Russian Ministry of Education and Science. Project Identifier: RFMEFI60417X0193.

References
[1] Mukherjee S 2013 The Science of Clays. Applications in Industry, Engineering and Environment (Germany: Springer-Heidelberg)
[2] Twardowski K, Rychinski S, Traple J 2006 Faculty of Drilling, Oil and Gas (AGHUST, Krakow) 208–12
[3] Luikov A V 1997 Mass and Momentum Transfer in Porous Media: A Theory of Drying. Advances in Heat Transfer 13 119–20
[4] Zhang Z, Yang S, Liu D 1999 Heat Transfer – Asian Research 28 (5) 337–51
[5] Luikov A V 1966 Heat and Mass Transfer in Capillary Porous Bodies (Pergamon Press)
[6] Miujumdar A 2014 Handbook of Industrial Drying (Fourth Edition. Boca Raton: CRC Press)
[7] Chua K J, Miujumdar A S, Hawlader M N A, Chou S K, Ho J C 2001 Drying Technology 19 (8) 1949–60
[8] Heydari M, Khalili K, Ahmadi Y 2017 Journal of Computational Applied Mechanics 48 (2) 171–84
[9] Hammouda I, Mihoubi D 2014 Mechanics of Time-Dependent Materials 18 97–111
[10] Kowalski S J, Pawlowski A 2010 Drying Technology 28 (8) 1023–31
[11] Kowalski S J, Mustielak G, Rybicki A, and Sliwa T 2012 Drying Technology 30 1176–89
[12] Sukhinin G I, Fedoseev A V, Maltshev V A, Yarygin I V, Prikhodko V G and Novopashin S A 2018 Journal of Physics: Conference Series 1105 (1) 012049
[13] Edvabnik V G 2015 Scientific Journal Modern Problems of Science and Education 1 2
[14] Salnikov M V, Fedoseev A V, Sukhinin G I 2018 Journal of Physics: Conference Series 1105 (1) 012063
[15] Fedoseev A V, Demin N A, Salnikov M V 2018 Journal of Physics: Conference Series 1105 (1) 012048