Influence of ambient conditions on the process of clay-like body vacuum drying

G I Sukhinin, A V Fedoseev, V A Maltsev, I V Yarygin, V G Prikhodko and S A Novopashin

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

E-mail: Sukhinin@itp.nsc.ru

Abstract. The first experiments on the vacuum drying of spherical clay sample are presented and the theoretical model of the process is considered. The model is based on the solution of the heat and the moisture transfer equations with the effective thermal conductivity and water diffusion coefficients for wet porous clay-like medium. The time and radial dependence of the temperature and the moisture were calculated for different initial conditions. The results obtained for the time dependence of the moisture content are in good agreement with the experimental results obtained in the initial period, when all the moisture in the sample did not freeze to form an ice crust.

1. Introduction

Capillary-porous materials very often occur in nature and in industry. These are, for example, soil, clay and clay minerals, wood, fruits, vegetables and different food and technological products. A porous medium is a solid matrix with voids, or pores, which are continuously connected. These pores are usually filled with fluids or moisture, water vapor and air that can pass through the medium because the voids are interconnected. The void fraction in the solid matrix is referred to as the porosity, $\varepsilon$, and $(1 - \varepsilon)$ is volume fraction of the solid matrix. Porosity or void fraction is a measure of the void (i.e. "empty") spaces in a material, and is a fraction of the volume of voids over the total volume. The moisture content in porous media determines the properties of the porous body, its mechanical and thermo-physical properties, such as density, plasticity, viscoelasticity, swelling, cracking, and so on. Complex processes of heat and mass transfer occur in porous bodies when they are heated or cooled, during drying or freezing [1]. The course of these processes depends essentially on the physical-chemical composition of the solid matrix of the porous body, on its fractal dimension, porosity and morphology.

The clay and clay minerals are the most important porous materials in the history of the mankind [2]. Clay is a very fine grained, unconsolidated rock matter, which is plastic when wet, but becomes hard and stony when heated. It has its origin in natural processes, mostly complex weathering, transported and deposited by sedimentation within geological periods. Clay is composed of silica (SiO$_2$), Alumina (Al$_2$O$_3$) and water (H$_2$O) plus appreciable concentrations of oxides of iron, alkali and alkaline earth, and contains groups of crystalline substances such as quartz, feldspar, and mica. Building materials, bricks, and tiles, pottery, porcelain and faience are made from clay [2, 3]. Clay is used in the food and medical industry, and, not least, in the mining industry as a carrier containing...
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aluminum, silicon and other valuable elements, as well as metals (copper, gold) as constituents, contained in the pores in the form of micro- and nano-particles or grains.

The water content in the pores of clay determines such properties as plasticity, visco-elasticity, stickiness, which are important for the extraction of micro- and nano-particles of gold from clay rock. While particles with sizes larger than 35-50 μm are relatively easy washed out of clay rock, smaller particles are retained in clay minerals because of their plasticity and stickiness. To improve the gold extraction from the plastic and sticky gold-bearing clay pieces they should be disintegrated. It is well-known that in the drying process, the porous clay material undergoes significant mechanical stresses due to the non-uniform distribution of temperature and humidity inside it [4-10]. To enhance the effect of disintegration, we suggest the method of vacuum drying of clay matter. Spherical samples of clay expose a sharp pumping, which leads to their cooling and freezing of the moisture contained in them. As a result, significant stresses arise in clay samples, "breaking" or reorganizing a solid matrix consisting of clay mineral flakes and grains, changing the shape of the pores and facilitating the repeated extraction of micron-sized gold particles.

In the paper, the first experiments on vacuum drying of clay are given, and also the theoretical model of the process is considered.

2. Experiment

Experiments were carried out in the vacuum chamber presented in figure 1. The clay (kaolin) was carefully dried beforehand, and then impregnated with water to some moisture content $U_0$ (~ 0.15-0.30 kg/kg), at which the clay had plasticity. Then the spherical samples of clay were formed from this mix and placed in a small chamber with a volume of $V_0 = 22$ liters, pressure $p_0 = 1$ atm. Small chamber was connected with large vacuum chamber (receiver), $V = 5$ m$^3$, which was evacuated to a pressure of $p_f < 1$ Torr. The experimental setup is presented in figure 1.

First experiments were carried out with three clay spheres from kaolin: ($m_1 = 1.02$ kg, $R_1 = 5.0$ cm, $m_2 = 1.2$ kg, $R_2 = 5.25$ cm, $m_3 = 0.167$ kg, $R_3 = 2.7$ cm). The shutter suddenly opened, and the pressure in both chamber dropped to $p_T ~ 3$ Torr. Water from the clay began to evaporate rapidly. The initial stage of water expansion from the spherical clay samples with the formation of the cloud of frog around it can be seen in figure 2. Evaporated water carried away the energy associated with the latent heat of evaporation, which led to the cooling of the sample. After a while, the samples were significantly cooled, an ice crust appeared on the surface of the spherical samples. Since the specific volume of ice is larger than the specific volume of liquid water, the ice formation should lead to the occurrence of strong stresses in the near-surface layer of clay, to the cracking of sample surface, its deformation and shifts of clay mineral flakes or grains relative to each other.

![Figure 1. Vacuum drying setup.](image-url)
Measurements of the radius of the clay sample show that the radius increased by 1.5% after 5 minutes of evacuation, another 1% after 90 min, and 0.5% after 72 hours. This increase in radius can be explained by the action of the atmospheric gas pressure inside the sample, expanding it after sudden gas evacuation in the chamber. At longer times, when the pressure inside and outside the sample is already leveled, a further increase in radius may be due to freezing of water in the pores, since the specific volume of ice is greater than the specific volume of liquid water.

To measure the moisture content in the clay samples during vacuum evacuation they were weighed at some moments, and the results are shown in figure 3. It can be seen that the moisture content from the first minutes of evacuation (at positive sample temperatures) decreases logarithmically slowly. Apparently, this is due to a decrease in the effective diffusion coefficient of liquid water in the porous body with decreasing temperature. After the formation of the ice crust in the body, the moisture escape from the body is further slowed.

3. Model

The process of drying capillary-porous materials is extremely complicated, involves a variety of processes of heat and mass transfer [1]. Microscopic capillaries and pores can be filled with water in a bound, capillary or free (liquid) state. Nonstationary processes of heat and mass transfer in porous bodies can be accompanied by phase transitions to solid state (ice) or gaseous state (vapor) with the release or absorption of latent heat of the phase transition. The science of drying porous bodies and materials was laid by A.V. Lykov (or Luikov) [1] and the following half a century is actively developing in relation to soil, clay, wood, organic materials, etc. [4-10].

To describe the processes of heat and mass transfer inside a porous clay material placed in a

Figure 2. Two spherical clay samples in small vacuum chamber: in atmospheric pressure (left photo), and during evaporation (right photo). The cloud of fog can be seen around clay samples.

Figure 3. a): Moisture content time dependencies for sample with $R_1 = 5.0$ cm (circles), $R_2 = 5.25$ cm (triangles), and $R_3 = 2.7$ cm (squares). Initial moisture content was $U_0 = 0.1627$ kg / kg, $T_0 = 293$ K. Calculated moisture content dependence in the centre of large sample (solid line) and in small sample (dashed line). b): Calculated temperature time dependence in the centre of large sample (solid line) and small sample (dashed line).
vacuum chamber and subjected to a sudden pumping, the equations of thermo-conductivity and
diffusion of moisture are usually used:

\[
\rho C_{\text{eff}} \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \lambda_{\text{eff}} (U, T) \frac{\partial T}{\partial r} \right],
\]

(1)

\[
\frac{\partial U}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_{\text{eff}} (U, T) \frac{\partial T}{\partial r} \right],
\]

(2)
in which the density and heat capacity of wet clay, \( \rho(U, T) \), \( C_{\text{eff}}(U, T) \), the effective coefficients of
thermo-conductivity \( \lambda_{\text{eff}}(U, T) \) and diffusion of moisture \( D_{\text{eff}}(U, T) \) in porous bodies are the functions of
the local temperature \( T(r,t) \) and the moisture content \( U(r,t) \), \( r \) is the radial coordinate. The specific heat \( C_{\text{eff}} \)
of the wet porous material is expressed through the specific heat of the kaolin \( C_{p,s} = 1.1 \text{ kJ/kg/K} \) and of water \( C_{p,l} = 4.22 \text{ kJ/kg/K} \):

\[
C_{\text{eff}} = C_{p,s} + U C_{p,l} \frac{\rho_s}{1+U}.
\]

(3)
The sample density \( \rho \) is the function of the moisture content \( U \) and expressed through the mass of
solid dry sample \( m_0 \), its volume \( V \) and initial moisture content \( U_0 \):

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

(4)
The effective heat conduction coefficient \( \lambda_{\text{eff}} = (1-\varepsilon) \lambda_s + \varepsilon \lambda_l \) is the function of the porosity of
the sample \( \varepsilon \), where \( \varepsilon = U \rho_s / (\rho_l + U \rho_s) \), where \( \rho_s = 2600 \text{ kg/m}^3 \) is the solid phase density, and \( \rho_l = 1000 \text{ kg/m}^3 \) is the liquid phase density, \( \lambda_s = 1.18 \text{ W/m} \cdot \text{K} \) is the solid thermal conductivity, and \( \lambda_l = 0.6 \text{ W/m} \cdot \text{K} \) is the liquid thermal conductivity.

The effective diffusion coefficient \( D_{\text{eff}} \) (m²/s) is the function of temperature and moisture content,
and is taken in the form [5]:

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

(5)

At the initial time, the temperature \( T_0 \), and the moisture content \( U_0 \) were distributed uniformly over the
spherical porous body. As the boundary conditions, the Hertz-Knudsen-like conditions were used to transfer moisture and heat from the body to the vacuum chamber. The energy flux \( F_T \) from the spherical sample through its surface is due to evaporation of water from the sample surface to the vacuum chamber:

\[
F_T = -h_v F_U,
\]

(6)
where \( F_U \) is the rate of water evaporation at the surface, \( h_v \) is the latent heat of evaporation. The water
flux at the exchange surface is expressed as [5], without the term of water condensation from the vacuum chamber to the sample surface:

\[
F_U = \frac{k_v M_v \varphi_v P_{U, sat}(T_s)}{R_0 T_s},
\]

(7)
where \( k_v \) is the water vapor transfer coefficient, \( k_v = H_v / (\varphi_c) \), \( H_v = 40 \text{ W/m}^2/\text{K} \) is the convective heat
transfer coefficient, \( M_v \) is the water molecular weight, \( R_0 \) is the universal gas constant, \( \varphi_v \) is the relative
air humidity at the surface of the sample, \( P_{U, sat}(T_s) \) is the saturated vapor pressure temperature dependence [Buck’s formula]. For the air relative humidity at the sample surface, the expression from [5] was used:
\[
\varphi_s = \begin{cases} 
1, & \text{for } U \geq U_{cr} \\
1 - (1 - \varphi_a) \frac{U_{cr} - U}{U_{cr} - U_{eq}}, & \text{for } U_{cr} < U < U_{eq}, \\
0, & \text{for } U \leq U_{eq}, 
\end{cases}
\]

where \(U_{cr} = 0.135 \text{ kg/kg}\) and \(U_{eq} = 0.05 \text{ kg/kg}\) denote the critical and the final equilibrium moisture contents in dried sample were determined experimentally [5].

The model also takes into account the process of freezing water in the pores when the local temperature reaches \(T_f = 273.15 \text{ K}\) (is a variable parameter of the model). It is assumed that a phase transition of water into the solid state of (ice) takes place in the temperature interval from \(T_f\) to \(T_f - \Delta T_f\) with \(\Delta T_f \sim 1 \text{ K}\). This transition requires the latent heat \(h_f = 330 \text{ kJ/kg}\).

4. Results
The model was applied for the problem of vacuum drying of spherical kaolin samples with radii (\(R = 2.5, 5.0\) and \(10 \text{ cm}\)). In the paper, we considered for simplicity only the limiting case, when only the vapour flux from the sample was taken into account in expression (7), and the backflow from the ambient space to the sample was not taken into account. In figure 3, calculations of the time dependence of the moisture content and temperature for the vacuum pumping of spherical samples of kaolin used in the experiment are presented. It can be seen that at short times \((t < 10^4 \text{ sec})\), when the clay sample cooled, but the moisture did not have time to transfer into ice state, the moisture content in the calculation and experiment coincides with an accuracy of 5-10%. For large times, when an ice crust appears in the clay sample, the calculation apparently ceases to be adequate, since the sublimation of ice is taken into account, and the cessation of moisture diffusion through the crust is not

![Figure 4](image-url)

**Figure 4.** Time dependence of temperature (a) and moisture content (b) for clay samples with different radii. Averaged temperature (c) and moisture content (d) dependence on time normalized to the radius of sample \(R\).
Calculations of the radial temperature dependences \( T(r, t) \) and moisture content \( U(r, t) \) have been made for various initial and boundary conditions in a vacuum chamber, and for different radii \( R \) of clay samples. Figure 4 (a, b) shows the time dependences of the average temperature of the sample volume for spherical clay samples with radii \( R = 2.5, 5.0 \) and \( 10 \) cm. The initial temperature of the clay bodies is \( T_0 = 20^\circ \text{C} \), the initial moisture content is \( U_0 = 0.2 \text{ kg/kg} \). In figure 4(c, d), the time scales for samples with different radii are normalized to the corresponding radius \( R \). It can be seen that the dependences of the averaged over sample’s volume temperatures \( T(r, t) \) as well as the averaged moisture content \( U(r, t) \) in the modified coordinates practically coincide. This result has simple explanation: The initial energy reserve of a spherical sample is proportional to \( R^3 \), the energy loss during evaporation is proportional to \( R^2 \). This means that the characteristic cooling and freezing time of a sample is proportional to its radius \( R \).

5. Conclusions
First experiments and the model of vacuum drying of a kaolin spherical sample were presented. The model is based on the solution of the heat and the moisture transfer equations with the effective thermal conductivity and diffusion coefficients for wet porous clay-like medium. The results obtained for the time dependence of the moisture content are in good agreement with the experimental results obtained in the initial period, when all the moisture in the sample did not freeze to form an ice crust.

It is known that stresses induced in porous spherical clay samples are proportional to radial gradients of temperature and moisture content [10]. To obtain the formation of stresses the model should be modified to take into account the plasticity of clay sample and its expansion due to the influence of initial gas pressure in the sample and its disintegration due to water freezing.

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