Drying comparison of nonhygroscopic and hygroscopic materials

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Abstract. This paper investigates and presents the simulation of drying for hygroscopic and nonhygroscopic materials. This present work used a coupled mathematical model of mass, heat and gas transfer that implemented to finite element method in two dimensional and numerically compute using Skyline solver to capture highly nonlinear transient process. Bound water contribution was taken into account in the drying of hygroscopic materials by incorporating constitutive equation of bound water. The results showed drying process can be divided into three periods named constant rate period (CRP), first falling rate period (FRP1) and second falling rate period (FRP2). Capillary action is dominated during CRP before vapour diffusion takes place in FRP1. Bound water movement is generated by vapour pressure gradient exists that represent hygroscopic material.

Introduction

In reality of porous material consists of three types of water that indentified as free, capillary and bound water. Free water is able to flow under an applied pressure gradient, capillary water is immobile water held by capillary forces in regions of microporosity, i.e. dead-end pores. Meanwhile, bound water includes both the water strongly held to negatively charged particles surfaces and the water of hydration associated with the mineral charge-balancing unit. The difference level of these types of water will exhibit different properties of porous material that generally known as hygroscopic and nonhygroscopic materials. Drying of nonhygroscopic materials only involve free and capillary water that easily experimentally can be determined and measured with specific equipment. In contrast to that, drying of hygroscopic materials not only involves free and capillarity water but also a tightly bound water that strongly attach to the solid matrix up to hydration temperature [1]. Previous studies on drying of hygroscopic and nonhygroscopic have present different equations and formulations as well as the concept that had been derived [1, 2, 3, 4, 5]. Bound water movement is expressed in terms of the diffusion of sorbed water driven by a gradient in the chemical potential of the sorbed water molecules [2]. This similar approach had been used by Kolhapure and Venkatesh[1] during studies of an unsaturated flow of low moisture for porous hygroscopic media. During low moisture contents, pores mainly consist of bound water and vapour. Stanish et al[3] in their development had derived a uniquely explicit expression for bound-water flux in terms of temperature and vapor pressure gradients. Meanwhile, Zhang et al[4] and Haghi[5] revealed that the bound water transport mechanism only effective when saturation irreducible is reached. The movement of bound water in hygroscopic materials is also known as liquid moisture transfer near dryness or sorption diffusion with driving force of vapor transport and without liquid transport [6]. Although substantial efforts have been made in the studies of hygroscopic materials, there are limited references available on modeling drying of hygroscopic ceramic.

In this proposed model which is an extended work from previous study [7] that implemented coupled mass, heat and gas transfer in two dimensional for nonhygroscopic porous materials will be used. The transport mechanism of liquid by capillary action, vapor by diffusion and gas by vapor diffusion and bulk air flow in convective drying phenomena were taken into consideration in this model. In this present work, an improved model to accommodate hygroscopic material, which
emphasized on bound water on later period (FRP2) of drying, was developed by referring previous related work [4, 5].

**Theoretical Formulation**

Drying is represented by capillarity action, diffusion by vapor and air, gas transport, heat transport and bound water at hygroscopic zone. Three measured primary variables; water pressure, \(P_h\), temperature, \(T\) and gas pressure, \(P_g\) will be used.

\[
\frac{\partial (\phi_p S_l)}{\partial t} + \frac{\partial (\phi_v S_g)}{\partial t} = -\nabla (\rho_v V) - \nabla (\rho_p V) - \nabla (\rho_v V_g) - \nabla (\rho_p V_b)
\]

For water velocity, \(V_l\) and gas velocity, \(V_g\) can be easily derived from Darcy’s law [5, 7]. Meanwhile vapor velocity by diffusion is defined as;

\[
V_v = -\frac{D_{vm} \rho \alpha \theta_a}{\rho_v} \nabla \rho_v
\]

Rearranging the above equation according to the measured variables gives;

\[
V_v = -\frac{D_{vm} \rho \alpha \theta_a}{\rho_v} \left\{ \frac{\partial h}{\partial P_i} \nabla P_i + (\rho_v + \rho_o) \frac{\partial h}{\partial T} \nabla T + \rho_o \frac{\partial h}{\partial P_g} \nabla P_g \right\}
\]

When water content reached the maximum irreducible water content, the bound water flux is taken into account into equation. The bound water velocity was derived from Zhang[4] and Haghi[5] as;

\[
V_b = -D_h \nabla \theta_b
\]

Rearranging the above equation according to the measured variables gives;

\[
V_b = -D_h \phi_p \left( \frac{\partial S_l}{\partial P_i} \nabla P_i + \frac{\partial S_l}{\partial T} \nabla T + \frac{\partial S_l}{\partial P_g} \nabla P_g \right)
\]

By applying a mass balance to the flow of dry air within the pores of the material body dictates that the time derivative of the dry air content is equal to the spatial derivative of the dry air flux.

\[
\frac{\partial (\phi_p S_p)}{\partial t} = -\nabla (\rho_v V - \rho_p V_b)
\]

The effect of conduction, latent heat and convection are considered in the energy equation as given as below;

\[
\frac{\partial ((1-\phi) c_p \rho_s + \sum_{i=1}^{n} \phi_i c_{pi})}{\partial t} = \nabla (\lambda \nabla T) - \nabla (\rho_v V + \rho_p V_b) L - \nabla (\sum_{i=1}^{n} \rho_i c_{pi} V_i)
\]

**Thermodynamic Relationship**

The existence of a local equilibrium at any point within the porous is assumed. Kelvin’s law is applied to the equation below.

\[
h = \exp \left( \frac{P_w - P_g}{\rho_i R_v T} \right)
\]

The vapour partial pressure can be defined as a function of local temperature and relative humidity where the saturation vapour pressure, \(\rho_o\) is estimated using equation in [8] with saturated vapour density as a function of temperature. The degree of saturation, \(S\) is an experimentally determined function of capillary pressure and temperature.

\[
S_l = S_l (p, T)
\]

Saturation if expressed as combination of temperature effect [9] as in equation below.

\[
S_l = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \left( \frac{1}{1 + \alpha \phi(T)^{n}} \right)
\]
where the parameters $\alpha$, $n$ and $m$ are dependent of porous material properties and influence the shape of the water retention curve. The permeability of water and gas are based on Muelem’s model [10].

Material Data
Material properties of the two dimensional porous slab exposed to convective drying is listed in Table 1. Porous slab ($0.0003 \times 0.01$ m) which had 30 elements and 117 nodes are assumed to be a porous medium that is homogeneous, isotropic and composed of solid phase, water and vapor phase, gas phase and dry air phase. The boundary condition of convective drying is applied to node 1 until 7. Nodes 1 to 7 are also assumed to remain under atmospheric condition, while the rest of the wall surfaces are assumed to be insulated and impermeable. The temperature is set for slow convective drying with temperature at 25 °C and heat and mass coefficient are $2 \, \text{W/m}^2\text{K}$ and $0.009 \, \text{ms}^{-1}$. The simulation is conducted onto 2 different set for the material, nonhygroscopic material and hygroscopic material.

<table>
<thead>
<tr>
<th>$\rho_s$ (kg/m$^3$)</th>
<th>$\phi$</th>
<th>$K$ (m$^2$)</th>
<th>$C_p$</th>
<th>$\lambda$</th>
<th>$S_{irr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>0.2</td>
<td>$1 \times 10^{-17}$</td>
<td>920</td>
<td>1.8</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Boundary Condition
The general boundary condition is applied for convective mass and heat transfer.

$$J_m = h_m (P_w^* - P_g^*)$$

$$J_m = h_{tf} (T_f - T_w)$$  \hspace{1cm} (11)

$$J_m = h_{tg} (T_g - T_w)$$  \hspace{1cm} (12)

Solution of Governing Equations and Numerical Method
The coupled heat and mass transfer equations described above, in 2-dimensions can be written into a matrix form as follows;

$$[C(\Phi)] \frac{d}{dt} \{\Phi\} = \nabla [(K_{cx} (\nabla \Phi)]_{i_x} + [K_{cy} (\nabla \Phi)]_{i_y}] \{\Phi\} + R(\nabla Z)$$  \hspace{1cm} (13)

where $\{\Phi\} = \{P_w, T, P_g\}$ is the column of unknowns; $[C]$, $[K_{cx}]$ and $[K_{cy}]$ are 3x3 matrices. Each element of the matrix is a coefficient for the unknown $\{\Phi\}$; $i_x$ and $i_y$ are the unit direction vectors. In order to discretize this simplified second order non-linear coupled partial differential equation, finite element method is used. Afterwards, Galerkin method is used to minimize the residual error before the application of Greens theorem, to the dispersive term involving second order derivatives; this simplified combined equation set can be expressed in the following form.

$$K(\Phi)\Phi + C(\Phi)\Phi + J(\Phi) = \{0\}$$  \hspace{1cm} (14)

The transient matrix and nonlinear second order differential equations above are then solved by using a fully implicit backward time stepping scheme along with a Picard iterative method which is taken into account for non-linearity.

Results and Discussion
Fig. 1 shows the variation of average saturation generated by proposed model and Przesmycki and Sturmillo[11] are in close agreement. Presemycki and Sturmillo[11] studied the drying of brick that refer to hygroscopic materials. In their works, the brick slab had an area of 20 cm$^2$ and was 5 cm thick. From the simulated plot it obviously shows that the curve consists of three periods. These drying stage were elaborated in detail with the plot of pore water pressure curve, temperature and gas variables that represent the coupled model of this drying process.
The first period is a straight line from point A to B in Fig. 1 called constant rate period (CRP). In CRP stage, free water will evaporate steadily and continuously. This is obviously shown by both plot of hygroscopic and nonhygroscopic materials from 0-3 hours that show an unchanges of pore water pressure (refer Fig. 2). The CRP lasted as long as the surface is supplied with liquid and depended strongly on the drying conditions and medium properties [5, 12]. The temperature profiles along the thickness of the samples increased slowly (refer Fig. 3). At the beginning of CRP, gas pressure is constant or only show a slightly increased in value(refer Fig.4).

Eventually, when CRP is finished the water saturation reaches its critical free water value, which is 0.3 for most material [4, 7, 13]. This stage of drying is known as first falling rate period (FRP1) that shown by point B to C in Fig. 1. This mechanism is demonstrated by temperature, pore water pressure and gas pressure evolutions that show significant changes especially at the top exposed surface area. Pore water pressure increases drastically as material drying front starts to move inside the porous network as capillary action slowly diminished, as water is strongly bonded to the wall of porous material (refer Fig. 2). At this time, vapor mechanism starts to take place as liquid been replaced by gas. Concurrently, temperature and pressure gas increased simultaneously (refer Fig. 3 and Fig. 4). Thereby, gas pressure inside the solid is at its maximum value whereas outside is maintained at atmosphere level. As further drying proceed where there would be no more free water on the surface, water saturation decays slowly or nearly remain constant. Subsequent water content exceeds 0.09 shows irreducible water value for most non-hygroscopic material [4, 13]. This indicates the second falling period (FRP2) as shown in fig. 1 from point C to D. Drying process in this stage for nonhygroscopic is accomplished as pore water pressure, gas pressure and temperature started to decay towards the ambient condition. Conversely, for hygroscopic materials, this is particularly important stage of the drying process where bound water will continue to be drawn from very fine and dried and brittle capillaries inside porous structures. The bound water
exist in this stage is strongly attached to solid matrix [1] that shown by increasing of pore pressure water (refer Fig. 2). Driving force being the gas phase or vapour pressure gradient [4, 5] mean higher gas pressure as shown in Fig 3.

Conclusion
The computed critical variables during the drying process of nonhygroscopic and hygroscopic materials were investigated. Both nonhygroscopic and hygroscopic show similar distributions of drying in CRP and FRP1. Results clearly demonstrated that the capillary action is dominant force in CRP before the vapour diffusion starts to take place in FRP1. When in FRP2 moisture content exceeded to irreducible value, the mechanism of bound water mechanism will start to take place that indicates hygoscopic material. The bound water mechanism will take place within high capillary bound water that strongly attached to solid matrix with driving force is in gas phase or vapour pressure gradient. Thus, consequences of this, determination of drying characteristics for hygroscopic materials is vitally important for optimizing the drying stage.

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References: