

# Drying of porous media: an introduction

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# Outlook

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# Porous materials

## The structure

A **porous medium**: any medium in which are present a **matrix** and a **void space**.

In a porous medium the water (or any other fluid) flows through a very complex network of **pores** and **capillaries**. The latter form the void space of the medium.

## The flow

The “boundaries” of this flow are the microscopic interfaces between solid and fluid(s).

⇒ the complete study of the hydrodynamics at the micro-scale is very involved!

# Continuum approach

To avoid such a difficulty, we may address the problem from a **macro-scale**.

At this scale the quantities involved in the problem can be measured.

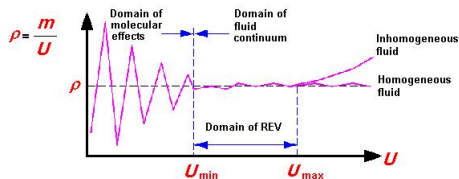
## Continuum approach:

the real medium it is substituted by an “artificial” model, in which any phase (liquid and air, for instance) is view as a continuum filling all the medium.

# Continuum approach: how can we define a quantity?

For instance: we want to know the density  $\rho$  of the medium in a point  $\mathbf{x}$ .

- ▶ Imagine to expand an ideal sphere (whose center is  $\mathbf{x}$ )
- ▶ At every step, measure the value of the density **averaged** on the sphere
- ▶ Increasing the radius: we get different values (random structure of the medium)



There is an interval of the sphere radius in which the value of  $\rho$  becomes stable!

# Continuum approach (ctd.)

We can fix a radius  $R$  belonging to this interval

We call **REV** (**R**epresentative **E**lement **V**olume) the sphere whose radius is  $R$ .

## Conclusion:

Any quantity defined at the macroscopic scale in a point  $\mathbf{x}$  has to be thought as a *quantity averaged on the REV centered in  $\mathbf{x}$* .

## Definitions:

- ▶ *Porosity*:  $\phi = \frac{\text{volume of the void space}}{\text{volume of the REV}}$
- ▶ *Saturation* (assume only one fluid flowing through the medium):

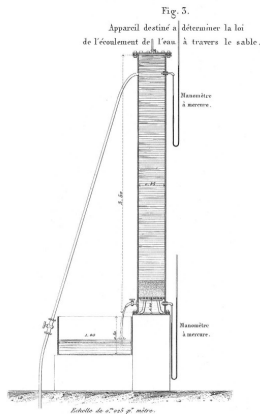
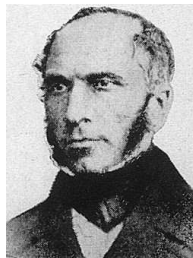
$$S = \frac{\text{volume of fluid}}{\text{volume of the void space}},$$

- ▶ The medium is *saturated* (namely all the void space is occupied by the fluid), if  $S = 1$ .
- ▶ *Specific discharge*,  $q$ : the **flux of fluid per unit area of the surface**, (dims.  $LT^{-1}$ ).

# Darcy's law (ctd.)

## Darcy's experiment

To determine the law linking  $q$  to the water pressure, the French engineer **Henry Darcy**, studying the system of water fountains of its city, Dijon, built up a particular experiment, reported in its famous book *Les Fontaines Publiques de la Ville de Dijon* (1856).



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# Darcy's law (ctd.)

Darcy measured the relationship between  $q$  and the *hydraulic head*  $h$ , defined as

$$h = z + p_w / \rho g,$$

where  $z$  is the quote at which the water is raised,  $p_w$  is the water pressure and  $g$  is the gravity acceleration.

He found a **proportionality relation** between **discharge**  $Q$  (volume of water per unit time) and increment of the hydraulic head with respect to the quote, i.e.

$$Q = K A \frac{h_1 - h_2}{L}$$

where  $A$  is the area of the column section and  $L$  its length. The coefficient  $K$  is called **hydraulic conductivity**.

# Generalization of Darcy's law

- ▶ In a differential form:

$$q = -K \frac{\partial h}{\partial z} = -K \frac{\partial}{\partial z} \left( \frac{p_w}{\rho g} + z \right)$$

- ▶ If density and/or the viscosity are not constant:

$$q = -\frac{k}{\mu} \frac{\partial}{\partial z} (p_w + \rho g z)$$

where  $k$  is the medium **permeability** and  $\mu$  is the fluid viscosity. We have:

$$K = k \frac{\rho}{\mu} g, [k] = L^2$$

$k$  : property of the medium;  $\rho, \mu$ : properties of the fluid

- ▶ Generalized form of Darcy's law:

$$\mathbf{q} = -\frac{k}{\mu} (\nabla p - \rho \mathbf{g}),$$

where  $p$  is the pressure and  $\mathbf{g}$  is the gravity vector.

# Heat and mass transfer in porous media

## Definitions and notation

### Three phases (unsaturated case):

- ▶  $a$  = air (inert gas)
- ▶  $v$  = vapour
- ▶  $w$  = water
- ▶  $\implies g = v + a$  = gas mixture = vapour + air
- ▶  $\phi$  porosity
- ▶  $S_\alpha$  = saturation of phase  $\alpha = w, g$
- ▶  $\rho_\alpha$  = density of phase  $\alpha = w, g$
- ▶  $\rho_i$  = density of species  $i$  (w.r.t. the gas volume),  $i = v, a$
- ▶  $\implies S_g = S_v + S_a$ ;  $S_w + S_g = 1$

# Definitions (ctd.)

- ▶  $p_w, p_v$  = water and vapour pressure
- ▶  $P$  = (total) gas pressure  $\Rightarrow (P - p_v)$  = air pressure
- ▶  $p_c = P - p_w$  = **capillary pressure** of the liquid phase (see later on)
- ▶  $\Rightarrow p_w = P - p_c$

$$\frac{\partial}{\partial t} (\rho_w \phi S_w) + \nabla \cdot \mathbf{J}_w = -\dot{\Gamma} \quad (1)$$

$$\frac{\partial}{\partial t} (\rho_v \phi S_g) + \nabla \cdot \mathbf{J}_v = +\dot{\Gamma} \quad (2)$$

$$\frac{\partial}{\partial t} (\rho_a \phi S_g) + \nabla \cdot \mathbf{J}_a = 0 \quad (3)$$

where  $\dot{\Gamma}$  is the **evaporation rate** and  $\mathbf{J}_\alpha$  is the total mass flux of phase  $\alpha$ .

# Expression of fluxes

## Vapour:

$$\mathbf{J}_v = \underbrace{\rho_v \mathbf{q}_v}_{\text{Darcy's flux due to pressure gradient}} + \underbrace{\mathbf{j}_v}_{\text{flux of (binary) diffusion}} \quad (4)$$

We have (gravity is neglected):

$$\mathbf{q}_v = -\frac{k_{sat} k_g}{\mu_g} \nabla P \quad (5)$$

$$\mathbf{j}_v = -\left( D \nabla \left( \frac{\rho_v}{P} \right) \right) \quad (6)$$

where

- ▶  $k_{sat}$ , saturated permeability
- ▶  $k_g = k_g(S_g)$ , relative permeability
- ▶  $\mu_g$ , viscosity

# Expression of fluxes (ctd.)

Similarly, for **air**:

$$\mathbf{J}_a = \underbrace{-\rho_a \frac{k_{sat} k_g}{\mu_g} \nabla P}_{\text{Flux due to pressure}} \quad \underbrace{- \left( D \nabla \left( \frac{P - p_v}{P} \right) \right)}_{\text{binary diffusion}} \quad (7)$$

# Expression of fluxes (ctd.)

**Water:**

$$\begin{aligned}\mathbf{J}_w &= \rho_w \mathbf{q}_w \\ &= -\rho_w \frac{k_{sat} k_w}{\mu_w} \nabla [(P - p_c) - \rho_w \mathbf{g}]\end{aligned}\quad (8)$$

Here the gravity may play a “significant” role, so that we include it in the Darcy’s flux.



# Constitutive eq.s

## Capillary pressure

$$p_c = p_c(S_w, T).$$

For instance, *Leverett' function*:

$$p_c(S_w, T) = \sqrt{\frac{\phi}{k_{sat}}} \sigma(T) f(S_w),$$

where:

$S_{w,r}$ , **irreducible water saturation**,

$T$ , temperature.

$\sigma(T) = \sigma_0 - \beta T$ , surface tension.

$$f(S_w) = 0.364 \left( 1 - e^{(-40(1-S_w))} \right) + 0.221(1 - S_w) + \frac{0.005}{S_w - S_{w,r}}.$$

...or many other forms (*vanGenuchten*, *Brooks & Corey*, etc.)

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# Constitutive eq.s (ctd.)

## Relative permeability:

$$k_w = k_w(S_w)$$

$$k_g = k_g(S_w).$$

Example (*Verma et al., 1985*):

$$k_w = (S_{eff})^3 = \left( \frac{S_w - S_{w,r}}{1 - S_{w,r}} \right)^3, \text{ for } S_w \geq S_{w,r}$$

$$k_g = a + bS_{eff} + cS_{eff}^2, \quad a, b, c = \text{const.}$$

or many other forms (e.g. *Mualem, Corey, Grant*).

**Liquid viscosity & density** (only in case of high temperature and/or pressure gradient):

$$\mu_w = \mu_w(T), \quad \rho_w = \rho_w(p_w, T).$$

# Constitutive eq.s (ctd.)

Moreover, the **perfect gas law** for vapour and air

$$\rho_v = p_v \frac{M_v}{RT} \quad (9)$$

$$\rho_a = (P - p_v) \frac{M_a}{RT} \quad (10)$$

with  $M_v$  and  $R$  constants.

## More on water flux...

In particular, exploiting the expression for the capillary pressure in the Darcian water flux  $\mathbf{q}_w$ , we have

$$\mathbf{J}_w = \underbrace{-\rho_w \frac{k_{sat} k_w}{\mu_w} \nabla (P - \rho_w \mathbf{g})}_{\text{Darcy's flux}} \underbrace{-D_s \nabla S_w - D_T \nabla T}_{\text{Capillary flux due to saturation \& temperature}}$$

$$\frac{\partial}{\partial t} \left( \rho_s(1 - \phi)h_s + \sum_{\alpha} \rho_{\alpha}\phi S_{\alpha} \right) + \sum_{\alpha} h_{\alpha}\mathbf{J}_{\alpha} = \nabla \cdot (\lambda_{mix}\nabla T) + (h_v - h_w)\dot{\Gamma}, \quad (11)$$

where:

- ▶ subscript  $( )_s$  refers to the solid matrix
- ▶  $h_{\alpha}$ , enthalpy of phase  $\alpha$
- ▶  $\lambda_{mix} = \lambda_s(1 - \phi) + \phi \sum_{\alpha} \lambda_{\alpha} S_{\alpha}$ , thermal conductivity of the mixture.

# Closure to the system

Exploiting the expression of fluxes and the constitutive laws in mass and energy balance, we have:

4	eq.s	(1), (2), (3), (11)
5	unknowns	$P, p_v, S_w, T, \dot{\Gamma}$
<b>-1</b>		

2 options for closure:

The description of evaporation can be based on either

1. *Equilibrium*
2. *Non-equilibrium*

condition

# Closure to the system (ctd.)

## Equilibrium:

we assume there is a water-vapour equilibrium relation:

$$p_v = \mathcal{F}(S_w, T) \quad (12)$$

and sum mass balance of water and vapour [(1) + (2)], so that  $\dot{\Gamma}$  disappears!

For instance, *Kelvin's equation*:

$$p_v = p_v^{sat}(T) \exp \left\{ \frac{-M_v p_c(S_w)}{\rho_w RT} \right\}, \quad (13)$$

which is derived from Clapeyron's eq., assuming a local thermodynamic equilibrium.

# Closure to the system (ctd.)

## Non-equilibrium:

we assume there is an equilibrium value for  $p_v$ ,

$$p_{v,eq} = \mathcal{F}(S_w, T) \quad (14)$$

and the evaporation rate is defined as

$$\dot{\Gamma} = \gamma(p_{v,eq} - p_v) \quad (15)$$

This approach has to be used **if** the time to reach the equilibrium is much longer than the time scale of the evaporation process (e.g. *fast drying process* in food industry).

In this case  $\dot{\Gamma}$  is a function of  $p_v$ , so that we have **4 eq.s** and **4 unknowns**.



# Boundary conditions on the external surface

In general, outside the domain, the following conditions are known:

- ▶ Air pressure
- ▶ Temperature
- ▶ **Relative humidity:**

$$H = \frac{p_v}{p_v^{sat}(T)}. \quad (16)$$

Assuming an equilibrium condition for the vapour pressure (Kelvin's eq.), (16) is related to  $S_w$ ,

$$H = \exp \left\{ \frac{-M_v p_c(S_w)}{\rho_w R T} \right\}$$

# Boundary conditions (ctd.)

Under these assumptions, the conditions on the boundary are:

1. Mass flux:  $\nabla H \cdot \mathbf{n} = \nu (H - H_{ext})$ .
2. Pressure:  $(P - p_v) = P_{ext}^{air}$
3. Temperature:  $T = T_{ext}$

*Remark:* in condition 1, the coefficient  $\nu$  represents the “interface effect” (**permeability of the boundary**).

As  $\nu \rightarrow \infty \Rightarrow$  high permeability: the effect vanishes and the condition is

$$H = H_{ext}$$

As  $\nu \rightarrow 0 \Rightarrow$  low permeability: **no flux condition**

# Possible simplifications

Analysing the physics of the process, one may assume:

1. Air (inert gas) is always at the same pressure.
  - ▶  $p_a = (P - p_v) = \text{const.}$
  - ▶ Only eq.s for water & vapour
2. Capillarity as primary mode,  $p_c \gg P$ 
  - ▶  $\nabla P \approx 0$
  - ▶ The process is driven by the capillary gradient  $\Rightarrow$  only equation for water.
3. Sharp interface
  - ▶ A sharp interface divides the *dry region* ( $S_w \equiv S_{w,r}$ ) to the *wet region*.
  - ▶ All the evaporation takes place at the interface
  - ▶ We obtain a *free boundary problem*
4. Isothermal condition, when  $T \approx \text{const.}$

# Generalization: *shrinkage*

If the initial porosity (= before the drying) is quite large, the loss of water may cause a significant stress within the structure of the medium.

Then, the **porosity  $\phi$  is no longer constant** and the problem becomes very involved!

**In particular:**

In the mass balance, among the fluxes, we have to include the one describing the movement of the matrix (since Darcy's law refers to flow relative to the skeleton!)

## Shrinkage (ctd.)

The simplest way to model this process is the definition of a constitutive law between porosity and water saturation,

$$\phi = \mathcal{F}(S_w) \quad (17)$$

For instance:

Linear:

$$\phi = \phi^{(0)} + c_1 \left( \frac{S_w^{(0)} - S_w}{S_w^{(0)}} \right).$$

Nonlinear (cubic):

$$\phi = \phi^{(0)} + c_2 \left( \frac{S_w^{(0)} - S_w}{S_w^{(0)}} \right)^3.$$

and many other forms (see Mayor, *J. Food Eng.*, 2004)

# The simpler problem in isothermal conditions ( $T = \text{const.}$ )

This approach can be applied whenever the drying takes place in a “natural” environment (=not forced drying).

## Assume also

- ▶ Constant air pressure,  $p_a = (P - p_v) = \text{const.}$   
Therefore: rescale  $p_a$  to 0, so that  $P = p_v$
- ▶ Equilibrium condition (Kelvin's equation):  $p_v = p_v(S_w)$ .

# The isothermal case (ctd.)

Under these conditions, the system simplifies to

$$\frac{\partial}{\partial t} [\rho_w \phi S_w + \rho_v \phi (1 - S_w)] = -\nabla \cdot \left\{ \left[ \rho_w \frac{k_{sat} k_w}{\mu_w} \left( \frac{dp_c}{dS_w} - \frac{dp_v}{dS_w} - \rho_w \mathbf{g} \right) + \rho_v \frac{k_{sat} k_g}{\mu_g} \frac{dp_v}{dS_w} \right] \nabla S_w \right\}$$

+ EOS:  $\rho_v = \rho_v(p_v)$ ;  $p_c = p_c(S_w)$ ;  $k_\alpha = k_\alpha(S_w)$

Only 1 equation (in  $S_w$ ), even if **strongly nonlinear!**

We assume a condition on the relative humidity. Since  $T = \text{const.}$ , saturated vapour pressure is a constant:  $p_V^{\text{sat}}$ . Therefore, the condition on the relative humidity becomes a condition on  $p_V$  (and in turn on  $S_w$ )!

Remember:

$$H = \frac{p_V}{p_V^{\text{sat}}} = \frac{1}{p_V^{\text{sat}}} p_V(S_w)$$

Thus, the B.C.  $\nabla H = \nu (H - H_{\text{ext}})$  reads as:

$$\nabla [p_V(S_w)] = \nu (p_V(S_w) - H_{\text{ext}} p_V^{\text{sat}})$$

which is a Robin's condition for  $S_w$ .

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## Some references

For a complete introduction on porous media:

- ▶ J. Bear, *Dynamics of fluids in porous media*, 1972 (or any other book by J. Bear).

For a rigorous derivation of the eq.s (from micro- to macro-scale):

- ▶ S. Whitaker, Simultaneous heat, mass and momentum transfer in porous media: a theory of drying, *Advances in Heat Transfer*, **13** (1972), 119–203.

A review on modelling the drying in food processes:

- ▶ A.K. Datta, Porous media approaches to studying simultaneous heat and mass transfer in food processes. I: Problem formulations, *Journal of Food Engineering*, **80**, Issue 1 (2007), 80–95.

A review on the shrinkage in food processes:

- ▶ L. Mayor and A. M. Sereno, Modelling shrinkage during convective drying of food materials: a review, *Journal of Food Engineering*, **61**, Issue 3 (2004), 373–386