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Benet

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The use of chemical potential to describe water transfer in complex media with strong solid-liquid bonding

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Abstract

We consider a complex medium composed of finely intertwined micro-skeletons and micro-compartments where water transfer can occur. In these media, at low moisture content, water pressure measurement is not longer possible. Mass transfer is then expressed in terms of chemical potential gradient. The assumption of local thermodynamic equilibrium, resulting in the uniformity of water chemical potential in all microstructures, is essential to define a sorption isotherm reflecting the relationship between water activity and average moisture content. In this case, it is also possible to describe water transfer by using the chemical potential gradient. Radial water transfer in wood is examined using a destructive method for calculating water flux and chemical potential gradient at the same position and at the same time. We deduce the variation of transport coefficient as a function of moisture content.

Keywords

Local thermodynamic equilibrium, transport coefficient, isotherm, wood, water flux, water diffusion.

1. Introduction

Biological tissue, gels, food products and soils are characterized by the juxtaposition of micro-skeletons (continuous solid or granular phases, network of polymers, membranes, cell walls), and micro-compartments (interstitial fluid, films, gas bubbles, micro cracks and intracellular phases). These micro-structures are of various shapes and sizes. Subsequently, the scale of these microstructures will be called α . For example, figure 1 shows the assembly of microstructures and micro-compartments in the case of two media: agar gel and coffee endosperm. For these products the scale α ranges from a micron to a few dozen microns. The macroscopic scale, noted β , corresponds to the assembly of a large number of N microstructures, such that any fluctuation around N does not change the properties measured at this scale. The existence of wide interfaces modifies the physical properties of certain constituents, in particular of water. This is due to the physical interactions between the constituents of liquid phase and solid phase. For a given porous media, the energy of interaction increases when the distance from the molecules of water to the surface decreases, and then when the water content decreases.

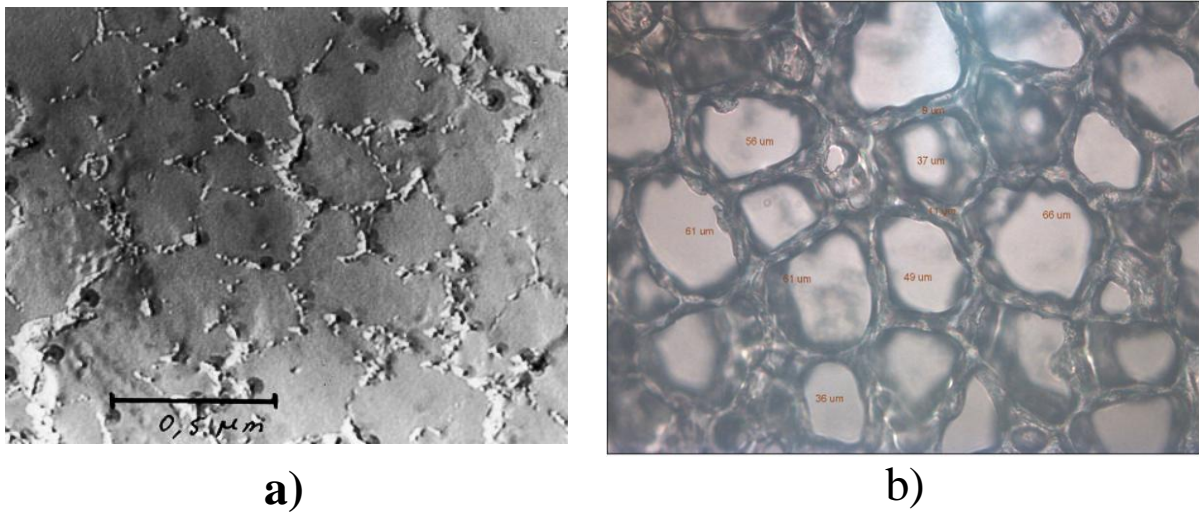
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Filtration of liquid water in porous media at β is generally described by Darcy's law. This law was initially introduced to describe the flow in saturated soils and then extended to other situations by introducing matrix, gravitational, and osmotic potentials [Corey & Klute, 1985; Niato & Bear, 1996]. Water flow is expressed in terms of the sum of these different potentials. The first potential comprises the action of the porous skeleton and the capillary effects. When the scale α is very small and the water is mostly contained in layers or intimately mixed with the micro-skeleton, pressure measurement becomes problematic or impossible [Baker & Frydman, 2009]. Therefore, in this case, variation of Darcy's coefficient in relation to moisture content cannot be analysed experimentally. For soils, one can try to extrapolate values of Darcy's coefficient from high moisture content values [Van Genuchten, 1980] to low moisture content values. However, simulations of very low moisture content profiles using this procedure are imprecise [Ouedraogo, 2008].

Studies on diverse natural media such as rubber [Auria et al 1990], agar gel [Mrani et al. 1995], pasta [Ponsart et al. 2003], and coffee [Ramirez-Martinez et al. 2013] show that a law similar to Fick's law correctly describes the global transfer of water at the β scale. The driving force used in these cases, was average moisture content. When moisture content is the only variable parameter, it is always possible, in a simulation, to write the flux of water in terms of moisture content gradient. In the case of Fick's law, an energetic variable such as pressure or chemical potential is replaced by a composition variable: water content. This is possible because of the relationship between energetic variables (pressure or chemical potential) and a composition variable (water content). This relationship is included in the mass transfer coefficient. In a case of composite material, water content is not a good parameter for the description of water transfer [Guillard V. et al. 2003]. A deeper discussion on this subject will be presented later in this article.

Considering that chemical potential is representative of the energetic bond between water and the rest of the media, its use as the driving force for mass transfer in porous media should be preferred [Job et al. 2006]. Moreover, it can replace pressure in situations where pressure measurements are no longer possible. It is also useful in situations where there is a mixture of different phases or electrolytes. At constant temperature, both at the α and β scale, the transfer of a chemical species takes place from regions where its chemical potential is higher toward regions where it is lower [Callen, 1985]. At equilibrium, the chemical potential value of a species is uniform throughout the medium at both scales. This equilibrium property allows the measurement of chemical potential for great variety of media (soils, gels, food products), at any moisture content value [Bénet et al., 2012]. Chemical potential measurement can be performed by well-known methods: the tensiometer for the lower absolute values, and the saturated saline solutions method for the higher absolute values. A mechanical method able to measure a wide range of chemical potential values has recently been developed [Ouoba et al., 2010].

The choice of chemical potential to describe mass transfer leads to adopting a thermodynamic approach. Therefore, the phenomenological relationship describing water transfer in structures at the α scale will be set using dissipation. At constant temperature, dissipation is defined as the product of the temperature by the entropy production per unit of volume and time. This relationship will then be extended to study complex media at the β scale, particularly, to interpret experimental water transfer results from wood (amaranth) in the radial direction of anisotropy.



99 Fig.1: Examples of microstructures of complex media. a) Agar gel b) Coffee bean endosperm.

100
101 **2. Thermodynamic equilibrium at α and β scales.**

102
103 **2.1 Chemical potential of water in complex media.**

104
105 The mass chemical potential is defined as the partial derivative of the internal energy (U) of
106 the whole media in relation to the mass of the considered species (m_i), where entropy (S),
107 volume (V) and the concentration of the other constituents (m_j) are kept constant
108 [Guggenheim, 1965]:
109

110

$$\mu_i = \left(\frac{\partial U}{\partial m_i} \right)_{V, S, m_j} ; j \neq i \quad (1)$$

111
112 This thermodynamics function presents the same level of generality as temperature and
113 pressure for pure phases [Job, 2006]. Therefore, chemical potential can also be interpreted
114 from a mechanical point of view in the case of complex media. According to definition (1),
115 the mass chemical potential of a chemical species i , for example water, corresponds to the
116 mechanical energy required for the extraction of a unit mass of i in a reversible, adiabatic,
117 constant volume transformation, the other species $j \neq i$ being kept in the media. The α
118 structures can be separated by physical membranes, superficial layers, or simply by free
119 surfaces, like for example, the surface between a liquid and a gas phase. The fundamental
120 property of the chemical potential stipulates that in a natural transformation at constant
121 temperature, a chemical species moves from the regions where its chemical potential is higher
122 toward the regions where it is lower. Movement can occur inside a phase or between phases.
123

124 At thermodynamic equilibrium, if a species i is present in several phases α and β , separated
125 by a permeable membrane only to constituent i , we have [Callen, 1985]:
126

127

$$(\mu_i)_{at\ phase\ \alpha} = (\mu_i)_{at\ phase\ \beta} \quad (2)$$

128
129 **2.2. Consequence of the assumption of a local thermodynamic equilibrium.**
130

131 We are interested in those media where the characteristic dimensions of structures at α are
 132 very small compared to the dimensions of the macroscopic objects (grain, cylinders or plates).
 133 We will consider these media at a uniform constant temperature. In coffee for example, the
 134 ratio between cell size and the grain is of the order of 10^{-3} . This ratio is of the order of 10^{-4} if
 135 compared to the cell wall. Considering the difference of ratio values, it is reasonable to
 136 suppose that the time to reach water chemical potential equilibrium between two structures at
 137 α , for example between the cell and the cell wall in the case of a coffee grain, is very fast
 138 compared to the characteristic time at which transfer occurs on a macroscopic scale. For
 139 example, at the macroscopic scale, the time it takes for water to transfer from the center to the
 140 surface of the coffee grain may be of the order of one day [Ramirez, 2011] in industrial
 141 drying.

142
 143 By adopting the hypothesis of local equilibrium, Equation (2) implies that the chemical
 144 potential of water (μ_w) is the same in all the structures contained in contained in a
 145 Representative Elementary Volume (REV) at all time. The moisture content of each structure
 146 (x_α) varies by mass transfer with the other structures in order to satisfy chemical potential
 147 equality. The chemical potential of water in each microstructure is characterized by a
 148 relationship between the water activity in the micro structure α and its moisture content x_α . By
 149 adopting free pure water as a reference at the same temperature, this relationship can be
 150 written as [Guggenheim, 1965]:

$$151 \mu_w = \frac{RT}{M_w} \ln(a_{w\alpha}(x_\alpha)), \forall \alpha \quad (3)$$

152
 153 $a_{w\alpha}(x_\alpha)$ represents the activity of water vapor in equilibrium with the water of the structure
 154 α . The relationship between $a_{w\alpha}$ and x_α is given by the desorption isotherm of the structure
 155 α if the determination of the latter is feasible. The average moisture content of the medium is
 156 defined by:
 157
 158

$$159 X = \frac{m_w}{m_s} = \frac{\rho_w}{\rho_s} = \sum_{\alpha} \frac{x_\alpha m_{s\alpha}}{m_s} \quad (4)$$

160
 161 Where m_w is the total mass of water in the REV, m_s is the total mass of solid in the REV and
 162 $m_{s\alpha}$ the mass of solid in the structure α of the REV with $m_s = \sum_{\alpha} m_{s\alpha} \cdot \rho_w$ and ρ_s are the
 163 apparent bulk densities of water and solid phase, respectively, at the β scale. In absence of
 164 dissolution or chemical reactions, the ratio $m_{s\alpha}/m_s$ remains constant, and knowing of the
 165 moisture content of the different structures at α (x_α), allows one to calculate the value of X
 166 by equation (4) and μ_w by equation (3). These relationships are monotonous, so there is a
 167 relationship between X and the water activity which is noted by $a_w(X)$:
 168

$$169 \mu_w = \frac{RT}{M_w} \ln(a_w(X)) \quad (5)$$

170

171 This relationship shows that regardless of the complexity of the structure, if local equilibrium
 172 is assumed, the chemical potential of water is a function of the average moisture content, the
 173 latter being accessible experimentally.

174

175 **2.3 Sorption isotherm**

176

177 It is therefore possible to characterize the thermodynamic state of the water at the β scale by
 178 a single isotherm, using the average moisture content (X). For example, the sorption isotherm
 179 for three media is given in Figure 2: wood [Anoua, 1986], agar gel [Mrani, 1995] and coffee
 180 [Ramirez-Martinez, 2011].

181

182 The GAB model (named after their three authors Guggenheim, Anderson, Boer) describes
 183 adsorption on a homogeneous surface, the adsorbed liquid being deposited in successive
 184 layers on the surface of the solid. It gives the relationship between the water content of the
 185 medium (X) and water activity (a_w) [E. Timmermann O. et al, 2001; Escalona et al, 2008].
 186

187

$$X = \frac{X_m C_g K_g}{(1 - K_g a_w)(1 + (C_g - 1)K_g a_w)} a_w \quad (6)$$

188

189 The model shows two constants: C_g associated with the adsorption energy of the first and
 190 second layers and K_g associated with the binding energies of the following layers. X_m is the
 191 water content corresponding to the first adsorbed layer.

192

193 Model parameters are calibrated to the experimental isotherms. The values of GAB
 194 parameters for wood, agar gel and coffee endosperm are Given in Table 1.

195

196 **Table 1: Parameters of the GAB model for the wood, agar gel and coffee endosperm.**

197

	X_m	C_g	K_g	$\partial X / \partial a_w (X = 0)$
Wood (amaranth)	0.0626	4.71	0.851	0.251
Agar gel	12.33	17.225	0.810	1.716
Coffee endosperm	0.0632	12.777	0.871	0.703

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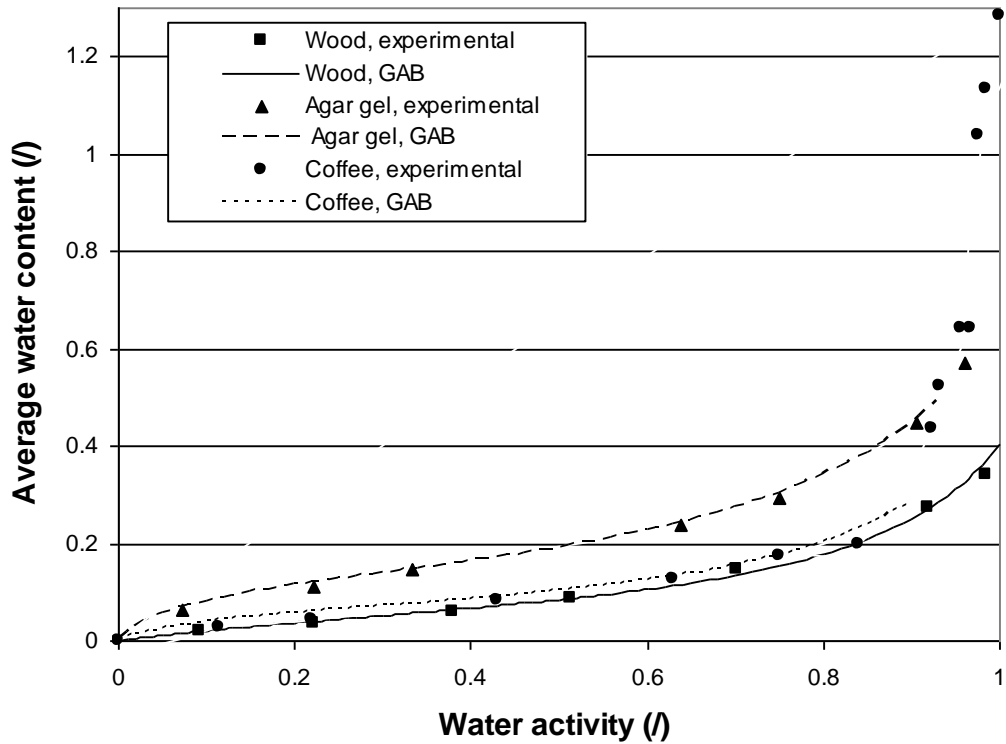
199 The GAB model gives a good fit for water activities less than 0.9. The final column of Table
 200 1 shows the derivative at the origin of X with respect to a_w , calculated from (6):
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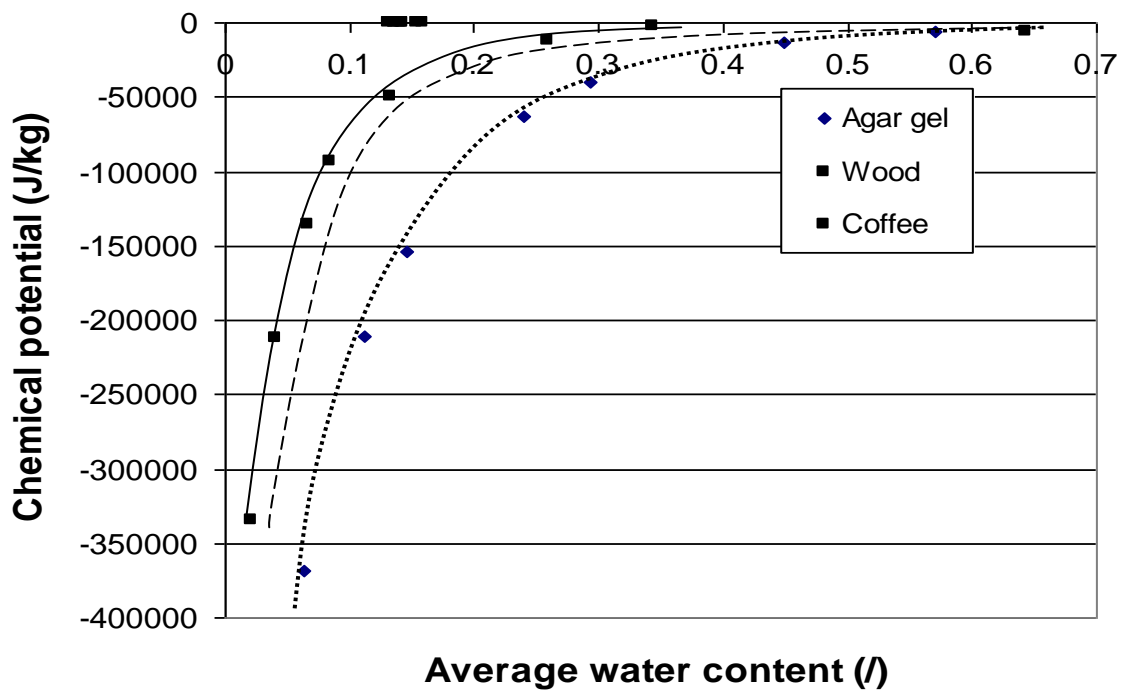
$$\left(\frac{\partial X}{\partial a_w} \right)_{a_w \rightarrow 0} = 1 / \left(\frac{\partial a_w}{\partial X} \right)_{X \rightarrow 0} = X_m C_g K_g \quad (7)$$

203

204 As the water activity of the saturated saline solutions employed are known [Norm NF X 15-
 205 119, 1999], it is possible to use equation (5) to establish the relationship between the chemical
 206 potential of the water in the medium and the moisture content at equilibrium (Fig 3).



207
 208 Figure 2. Isothermal desorption of three media: wood (solid squares), agar gel (solid triangles)
 209 and coffee (solid circles). The approximations obtained by the GAB model are also
 210 represented. For the agar gel, moisture content must be multiplied by 100.
 211



212
 213 Figure 3. Variation of chemical potential as a function of the average moisture content for
 214 wood, agar gel and coffee (reference state: free water at the same temperature as the medium).
 215 For the agar gel, moisture content must be multiplied by 100.
 216

217 According to the definition of chemical potential (1) the partial derivative of the internal
 218 energy must be evaluated at constant entropy. This is equivalent to a reversible adiabatic
 219 transformation. These conditions are approached during the establishment of an isotherm. The
 220 chemical potential can then be matched to the mechanical energy needed to extract the mass
 221 unit of the medium.

222
 223 Like any thermodynamic quantity, the chemical potential is defined using a reference state; in
 224 equation (5) it is free pure water at atmospheric pressure and room temperature, the activity is
 225 then set to 1. Under these conditions, according to (5), the chemical potential is negative and
 226 tends toward minus infinity when the water content tends to zero. Figure 3 shows that the
 227 energy required to extract the unit weight of water and bring it to the reference state increases
 228 as the water content decreases.

229
 230 For pure water which is assumed incompressible, when pressure measurement is possible,
 231 relative pressure is connected to chemical potential by: $p_w = \rho_w \mu_w$ [Guggenheim, 1965]. The
 232 pressure measurement is not possible in finely divided media like wood or coffee. For
 233 example, for a water content below 0.15, Figure 3 shows that the chemical potential is less
 234 than - 50 kJ / kg. The pressure calculated by the equation above is $500 \times 10^5 \text{ Pa}$. These values
 235 are far from the measurement capabilities of the pressure [Baker & Frydman, 2009]. This
 236 justifies the use of the chemical potential to describe water transfer, when water is strongly
 237 linked to the solid phase.

238 3. Mass transfer at scales α and β

239
 240
 241 In complex media, each structure at α scale is composed of components noted as α_i . It is
 242 assumed that the temperature is uniform and constant, there are no chemical reactions in the
 243 media and that the mechanical behavior of the medium is reversible (elastic). Neglecting
 244 gravity, dissipation D_{ir} (associated with transport phenomena in all structures), can be
 245 expressed as [Prigogine *et al.*, 1951; Bénét *et al.*, 1983; Müller, 2001]:

$$246 \quad D_{ir} = - \sum_{\alpha} \sum_i \rho_{\alpha i} v_{\alpha i}^k \mu_{\alpha i, k} \geq 0 \quad (8)$$

247
 248
 249 Where $\rho_{\alpha i}$ is the bulk density of the component α_i and $v_{\alpha i}^k$ is the velocity; $\rho_{\alpha i} v_{\alpha i}^k$ is the
 250 mass flux of the component α_i . It is assumed that water is the only moving component. The
 251 index w is reserved for the water component, therefore dissipation (equation 8) becomes:

$$252 \quad D_w = - \sum_{\alpha} \rho_{\alpha w} v_{\alpha w}^k \mu_{\alpha w, k} \geq 0 \quad (9)$$

253
 254
 255 According to the hypothesis of local equilibrium, the chemical potential gradient of water is
 256 the same for all structures. Dissipation (9) can be written:

$$257 \quad D_w = - \left(\sum_{\alpha} \rho_w v_w^k \right) \mu_{w, k} \geq 0 \quad (10)$$

258
 259
 260 Water movement occurs in structures occupying domains of different geometries. It can be
 261 assumed that the transport mechanisms in a structure at α scale are independent of
 262 phenomena that develop in other structures at α [Prigogine *et al.*, 1951; Bénét *et al.*; 1983].

263 In consequence, the dissipations $D_{w\alpha}$ due to the movement of water in the different structures
 264 α are separately positive:

$$265 \quad D_{w\alpha} = -\rho_{\alpha w} v_{\alpha w}^k \mu_{w,k} \geq 0 \quad (11)$$

267 The conditions imposed on this dissipation (positivity away from the equilibrium and
 268 equilibrium nullity), are achieved if the mass flux of water into the structure α satisfies the
 269 assumption of linearity in the vicinity of the equilibrium [De Groot et al., 1969; Kuiken,
 270 1994].

$$271 \quad \rho_{\alpha w} v_{\alpha w}^k = -K_{\alpha}(x_{\alpha}) \mu_{w,k} \quad (12)$$

272
 273 The quantity $K_{\alpha}(x_{\alpha})$ represents the coefficient of water transfer in the structure α . This
 274 quantity is positive and depends on the moisture content of the structure α . The question is
 275 whether we can express $K_{\alpha}(x_{\alpha})$ in terms of the average moisture content X . From equation
 276 (5), knowledge of X provides access to μ_w . This value introduced in (3) shows that the
 277 moisture content, x_{α} , is fixed in all structures α . X being fixed, x_{α} is also defined:

$$280 \quad x_{\alpha} = x_{\alpha}(X), \forall \alpha \quad (13)$$

281
 282 Equation (13) implies that all the coefficients $K_{\alpha}(x_{\alpha})$ of equation (12) can be expressed in
 283 terms of X . The overall flux of water is expressed by a relation of the form:

$$284 \quad \rho_w v_w^k = -\sum_{\alpha} \rho_{w\alpha} v_{w\alpha}^k = -K(X) \mu_{w,k} \quad (14)$$

285
 286
 287 With:

$$288 \quad K(X) = \sum_{\alpha} K_{\alpha}(x_{\alpha}(X)) \quad (15)$$

289
 290 Using (5), (14) can be written in terms of average water content gradient:

$$291 \quad \rho_w v_w^k = -\rho_s D(X) X_{,k} \quad (16)$$

292
 293 Setting:

$$294 \quad D(X) = K(X) \frac{RT}{\rho_s M_w a_w(X)} \frac{\partial a_w}{\partial X} \quad (17)$$

295
 296 The mass balance equation for water can be written as:

$$297 \quad \frac{\partial \rho_w}{\partial t} = \frac{\partial \rho_s X}{\partial t} = -div(\rho_w v_w^k) \quad (18)$$

300
 301
 302
 303

304 Using equation (16) and considering a uniform and constant bulk density of the solid phase
305 ρ_s , equation (18) takes the form of a diffusion equation:

306

$$307 \quad \frac{\partial X}{\partial t} = \text{div} (D (X) X_{,k}) \quad (19)$$

308

309 The coefficient $D (X)$ is expressed in m^2 / s . In the above equations, the energetic driving
310 force responsible for the transport (chemical potential gradient) is replaced by another, non
311 energetic driving force related to composition (moisture content gradient). Such substitution is
312 only possible if there is a local equilibrium traduced by a single isotherm linking the chemical
313 potential with the average moisture content as expressed in (5). Also, the bulk density of the
314 solid phase must be uniform and constant.

315

316 The variation of the function $\mu_w (X)$ is monotone (Fig.5), so an inverse function $X (\mu_w)$ can
317 be defined. Using (14), the mass balance equation (18) can be written as:

318

$$319 \quad \rho_s \frac{\partial X}{\partial \mu_w} \frac{\partial \mu_w}{\partial t} = \text{div} (K (X (\mu_w)) \mu_{w,k}) \quad (20)$$

320

321 Equation (20) is, in this form, analogous to the heat equation. It highlights the strong analogy
322 of the temperature T and chemical potential μ_w . This is due to the fact that temperature and
323 chemical potential are defined as the partial derivatives of a single thermodynamic potential,
324 here the internal energy (1). The term $\partial X / \partial \mu_w$ is similar to the specific heat and $K (X (\mu_w))$
325 to the thermal conductivity.

326

327 **4. Use of the chemical potential of water to describe water transfer in the radial** 328 **direction of wood on the β scale.**

329

330 We propose to validate relationship (14) in order to judge the validity of the two assumptions
331 on which it is based: the hypothesis of local equilibrium of all forms of water and the
332 assumption of linearity. Moreover, this study will establish the variation of the transport
333 coefficient K (X) as a function of the moisture content.

334

335 **4.1 Experimental study.**

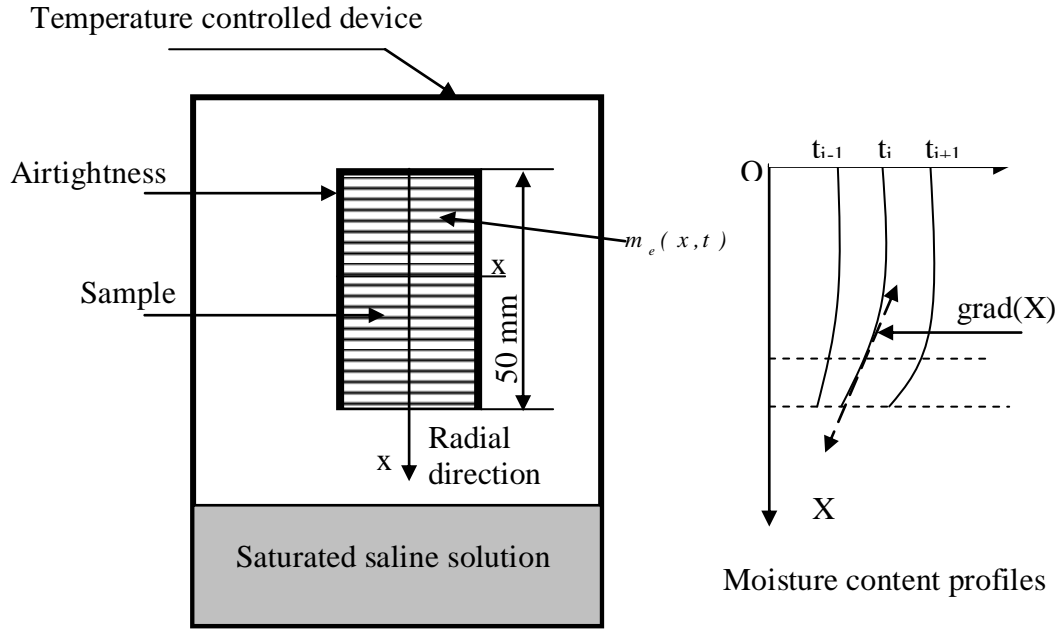
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337 As the solid skeleton of wood is anisotropic, we limit ourselves to the study of transfer in the
338 radial direction. The wood used in this study is amaranth whose desorption isotherm is shown
339 in Figure 2. The variation of the chemical potential of water as a function of moisture content
340 is given in Figure 3. As the contraction of wood (amaranth) is less than 4% and the range of
341 the studied moisture content values is less than 20%, the effect of contraction on water
342 transfer is neglected. The opposite is certainly not true.

343

344 The experimental setup is shown in Figure 4. Wood samples of 50x25x10 mm were cut from
345 a wood ridge. The dimension 50 corresponds to the radial direction, that of 25 to the
346 transverse direction and that of 10 to the longitudinal direction. Ten samples were placed in a
347 closed chamber in which the water activity was adjusted to 0.20 and the temperature to 60 °
348 C. Only the lower side of the samples was exposed. The other sides were sealed by an

349 aluminium film to assure the airtightness of the samples. To assure that water transfer was
 350 effectively occurring in the radial direction (Ox at Figure 4), a sample was suspended from a
 351 balance and its weight was measured continuously. To determine the profiles of moisture
 352 content at a given time (t_i), a sample was taken and cut into slices of 1 mm thickness
 353 perpendicularly to the radial direction. After measuring the moisture content of the slices, it
 354 was possible to trace the moisture content profiles at different times as shown schematically
 355 in Figure 4.



376 Figure 4. Schematic representation of the experimental device for measuring water flux and
 377 moisture content gradient.

378
 379 The radial flux, at the abscissa x , at time t is calculated by:

$$381 \quad \rho_w v_w(t, x) S_x = \frac{d}{dt} m_w(t, x) = \frac{d}{dt} \int_0^x X(t, \xi) \rho_s d\xi \quad (21)$$

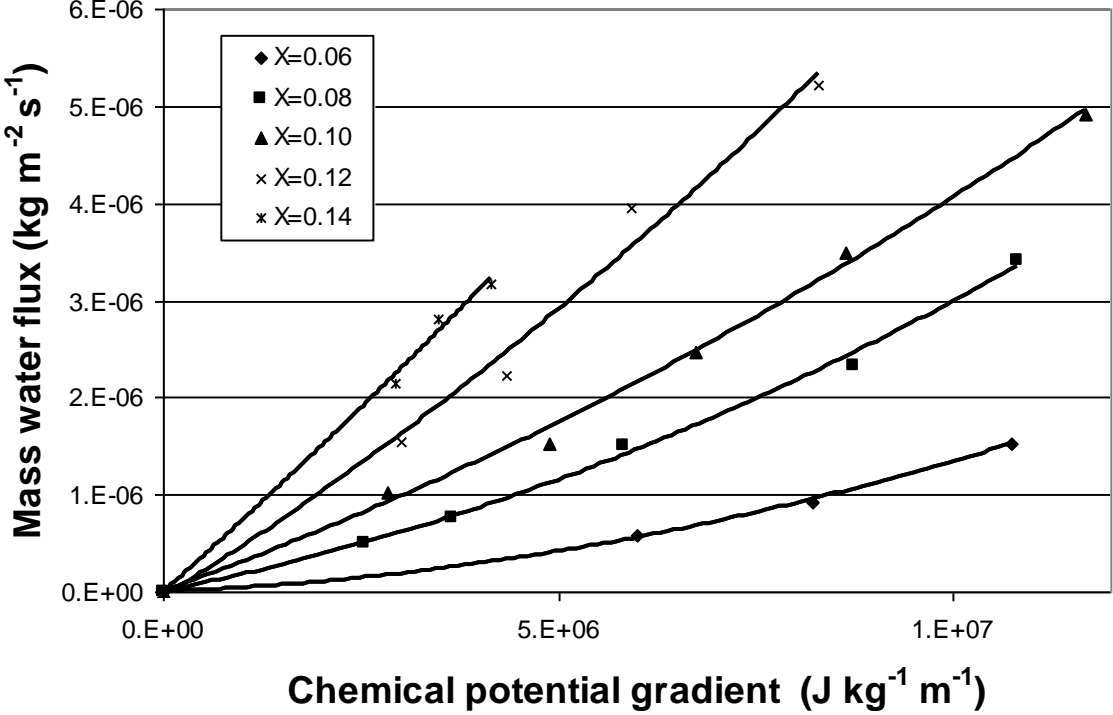
382
 383 Where S_x is the surface perpendicular to x axis, $m_w(t, x)$ is the mass of water contained in the
 384 sample between the upper surface ($x=0$) and the abscissa x at the instant t , ρ_s is the bulk
 385 density of the wood and ξ an abscissa between 0 and x . Relationship (21) gives, at different
 386 times, the flux $\rho_w v_w$ at x from experimental profiles of moisture content. The moisture
 387 content gradient is deduced directly from the tangent to the curve $X(t, x)$ (Figure 4). At any
 388 given time, the profile of X gives access to the chemical potential profile using the desorption
 389 isotherm equation (6) and the equation (5).

390
 391 For a given abscissa (values: $x = 4, 6, 10, 16, 20$ mm, are adopted) and a given time, water
 392 flux ($\rho_w v_w(t)$), the chemical potential gradient $\mu_{w,k}(t)$ and the moisture content $X(t)$ are
 393 known. The value of κ is calculated for a given moisture content X using (14). The open
 394 squares at Figure 6 are all the κ values determined for different abscissas and different times
 395 at 60°C .

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Fixing moisture content x_0 , the curve $x(t)$ allows to determine the instant when a moisture content is reached for a fixed abscissa x , also values from $\rho_w v_w(x_0)$ and $\mu_{w,k}(x_0)$ can be deduced. The relationship between water flux and the chemical potential gradient is shown in Figure 5 for $x_0 = 6\%$, 8% , 10% , 12% and 14% . This figure shows that the obtained relationships, parameterized by x_0 , do not satisfy the linearity assumption perfectly. However, its behaviour is not far from linearity, and is nearly attained in the vicinity of the origin. There is also better linearity at high moisture contents. The curves in Figure 5 are well approximated by quadratic functions. When the water content decreases (eg $X = 0.06$ in Figure 5) the binding energy increases; this hampers the movement of water and the value of K decreases.

When the chemical potential gradient approaches zero, values of $K(x_0, \mu_{w,k} \rightarrow 0)$ can be deduced from the slopes at the origin. These values at 60°C are shown in Figure 6 (solid squares). This figure also shows the values corresponding to the slopes of the curves in Figure 5 for a chemical potential gradient of 10^7 : $K(x_0, \mu_{w,k} = 10^7)$ (solid triangles).



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Figure 5. Variation of the water flux as a function of the chemical potential gradient at different moisture content values.

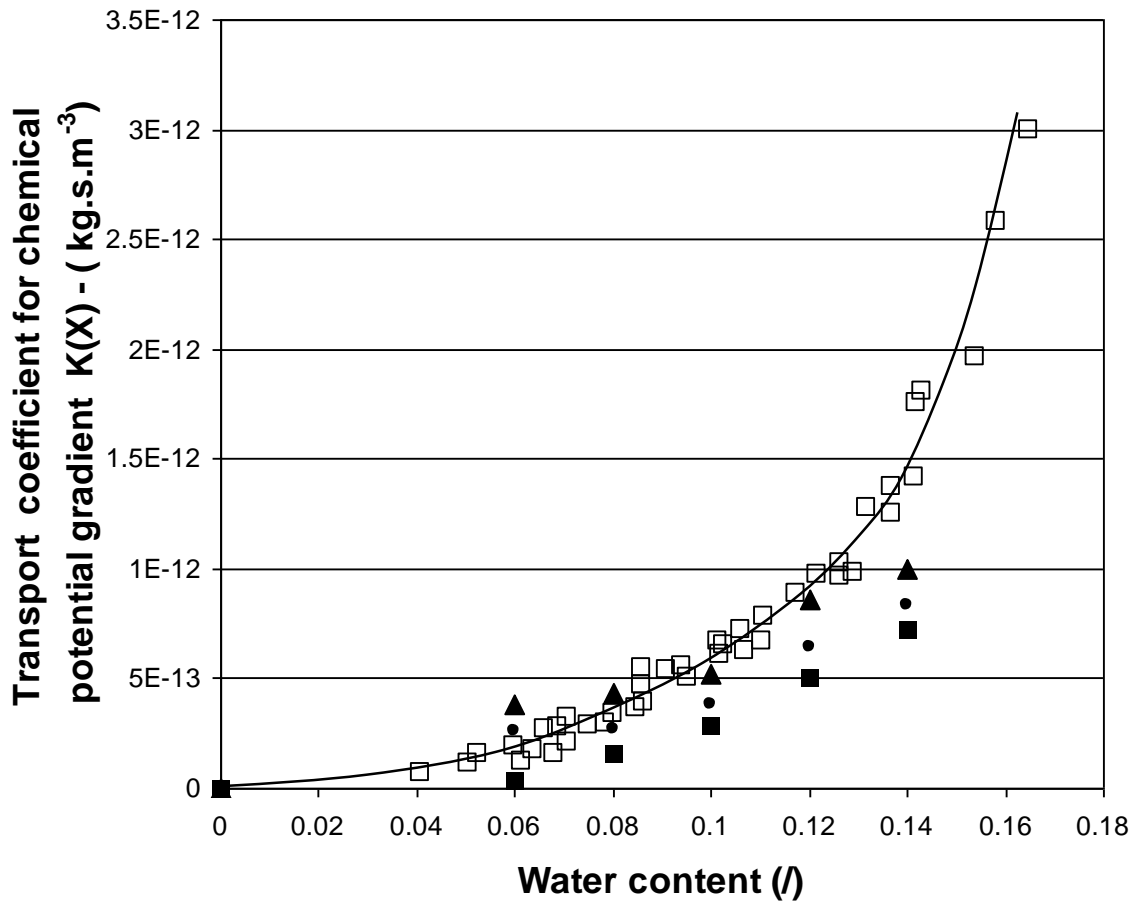


Figure 6. Variation of transport coefficient associated with the chemical potential gradient of water in the case of wood.

We can see that the points corresponding to the values of $K(X_0, \mu_{w,k} \rightarrow 0)$ (solid squares) are located below the points corresponding to measurements at different abscissas $K(X, 0 \leq \mu_{w,k} \leq 10^7)$ (open squares). Points corresponding to the values of $K(X_0, \mu_{w,k} = 10^7)$ (solid triangles) are similar to the latter. These observations confirm that the linearity assumption is not completely satisfied. However, the curves in Figure 6 are consistent, and related to the curves in Figure 5, they make it possible to model coefficient $K(X)$ in a wide region near the equilibrium. As expected, coefficient $K(X)$ tends to zero as moisture content value decreases. This can be explained by the increasing bonding of water in the wood quantified by an increase of the absolute value of the chemical potential as moisture content decreases.

5. Conclusion

When bonding between water and the other phases present in a medium is too strong and pressure measurement becomes impossible, chemical potential can be used to characterize the thermodynamic state of the water. Chemical potential can be measured by different methods even when its absolute value becomes very high.

440 The use of a single transport equation to describe water transfer in a complex medium, either
441 by the chemical potential or moisture content gradient, is subjected to the hypothesis of the
442 thermodynamic equilibrium of water in all its forms. In the case of experiments on wood, the
443 consistency of the results shows that the hypothesis of local equilibrium is consistent for the
444 experimental conditions used. The chemical potential can simply translate this assumption,
445 allowing water chemical potential to be defined at the macroscopic scale. Under this
446 condition, the equilibrium average moisture content can be used to define a single desorption
447 isotherm.

448

449 Another consequence of the assumption of local equilibrium is that dissipation can be
450 expressed as the product of the sum of the water flux by the gradient of a single chemical
451 potential. It is then possible to describe water transport in the vicinity of the equilibrium as a
452 linear relationship between water flux and the chemical potential gradient. In the case of
453 wood, experiments highlight a moderate nonlinearity. However, experiments were conducted
454 under drastic conditions ($T = 60^{\circ}\text{C}$ and $a_w = 0.2$) compared to normal conditions (natural
455 environment or drying process). Even under drastic conditions, there is a small deviation from
456 linearity behavior.

457

458 Transport coefficient is nil when the water content is zero. Under this condition, it is easy to
459 extrapolate the experimental results for moisture contents less than 0.04 (Figure 6). The
460 proposed method makes it possible to determine the transport coefficient associated with the
461 chemical potential gradient when liquid-solid interaction is strong. Developed for the case of
462 wood, the method can be extended to other media.

463

464 Use of the chemical potential gradient is limited by the two asymptotic behaviours shown in
465 Figure 3. At very low water content, a low water content gradient produces a high chemical
466 potential gradient. The coefficient K tends to zero and the relation (14) is presented as an
467 indeterminate form, which may introduce instabilities in the calculations. When the water
468 content tends toward saturation, water activity tends to 1 making determination of the
469 isotherm unclear. It is preferable, in this case, to measure the water pressure with a
470 tensiometer and use pressure gradient to describe the transfer of water. The combined use of
471 tensiometer and desorption isotherms allows the chemical potential and water content
472 relationship to be expressed in all the fields of water content (Bénet, JC, et al., 2009)

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