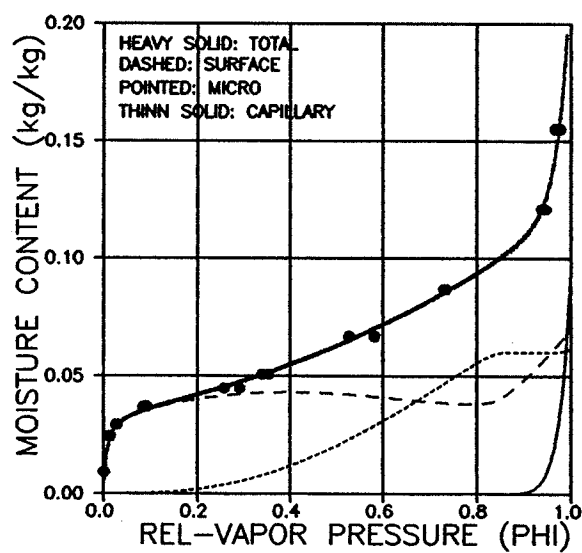


A research note on

***SORPTION, PORE SIZE DISTRIBUTION, AND SHRINKAGE  
OF POROUS MATERIALS***

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# SORPTION, PORE SIZE DISTRIBUTION, AND SHRINKAGE OF POROUS MATERIALS

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**Abstract:** Moisture is attracted by the pore system in porous materials. Attraction is associated with internal forces on the solid structure which responds by deformation according to its stiffness and geometrical complexity. The present paper deals with this phenomenon such that shrinkage/swelling of porous materials can be predicted from a relatively few number of sorption (moisture uptake) experiments. Two auxiliary "tools" have been developed to obtain this result: A very efficient sorption fit method is presented by which the basic thermodynamical pore parameters (BET-parameters) can easily be deduced from experimental data. A consistent pore size analysis is presented which simultaneously considers both pore volume and pore surface. Examples are given on cellular concrete and hardened cement paste in damp atmosphere. A computer program developed to consider any aspect of the analysis presented is described in a special report.

## I. INTRODUCTION

Moisture is attracted by the pore system in porous materials. Attraction is associated with internal forces on the solid structure which responds by deformation according to its stiffness and geometrical complexity. The present paper deals with this phenomenon in the following three steps procedure by which moisture induced shrinkage/swelling of porous materials can be predicted from experimentally obtained information on the moisture uptake potential of the material considered:

- A method is presented by which total sorption graphs can be predicted from relatively few experimentally obtained data. (Sorption graphs consider the ability of a porous material to impregnate itself by liquefying an ambient gas atmosphere. The results of sorption tests are frequently presented in a sorption graph where weight at equilibrium of condensed gas is plotted against relative vapour pressure).
- A method is developed where sorption graphs are used to predict simultaneously the internal geometrical complexity and stress states of porous materials. Consistent pore size distributions are deduced which at the same time consider both surface and volume.
- Finally, a method is developed where shrinkage (or swelling) of porous materials is predicted as a result of internal stress and geometrical complexity.

A number of symbols are used in the analysis. They are summarized and briefly explained in the following list. The terms "radius" and "vapour

pressure" are used in the meaning "hydraulic radius" and "relative vapour pressure" respectively unless otherwise indicated.

### 1.1 List of notations

R gas constant (8.314 J/(Mol\*K<sup>0</sup>))

#### Liquid (water in parenthesis)

M molecule weight (0.01802 kg/Mol)

Γ surface energy (0.0728 N/m, T = 293 K<sup>0</sup>)

d<sub>L</sub> density (1000 kg/m<sup>3</sup>, T = 293 K<sup>0</sup>)

D molecule diameter (0.30\*10<sup>-9</sup> m, T = 293 K<sup>0</sup>, average of D in free and adsorbed state)

#### Solid and porous material

c porosity

d<sub>S</sub> density of solid (kg/m<sup>3</sup>)

$d^* = (1 - c)d_S$  density of porous material (kg/m<sup>3</sup>)

$V_{TOT} = c/d$  pore volume (m<sup>3</sup>/kg solid)

$V_{SOL} = (1 - c)V_{TOT}/c$  solid phase volume (m<sup>3</sup>/kg solid)

K<sub>S</sub> solid phase bulk modulus

K<sub>o</sub> porous materials bulk modulus

$k_o^* = K_o^*/K_S$  relative bulk modulus of porous material

E<sub>S</sub> solid phase Young's modulus

ν<sub>S</sub> solid phase Poisson's ratio

E<sub>o</sub> porous materials Young's modulus

μ<sub>o</sub> shape factor of pore system

σ<sub>P VOL</sub> external volumetric stress

ε<sub>P VOL</sub> volumetric pore strain

σ<sub>P VOL</sub> volumetric pore pressure

$\sigma_P = \sigma_{P VOL}/3$  pore pressure

ε<sub>VOL</sub> volumetric external strain

$\epsilon_{LIN}^* = \epsilon_{VOL}^*/3$  linear external strain

#### Pore system

r (hydraulic) pore radius (see subsequent list on sorption)

r<sub>MAX</sub> max (hydraulic) pore radius

θ = r/D normalized radius (with respect to molecule diameter)

θ<sub>MAX</sub> normalized max pore radius

S<sub>TOT</sub> total pore surface (see subsequent list on sorption)

S = S(θ) Surface of pores with radii ≤ θ

V = V(θ) Volume of pores with radii ≤ θ

G = G(θ) = S/S<sub>TOT</sub> accumulated pore surface distribution

H = H(θ) = V/V<sub>TOT</sub> accumulated pore volume distribution

g = g(θ) = dG/dθ density function of pore surface distribution

h = h(θ) = dH/dθ density function of pore volume distribution

#### Sorption

Φ relative vapour pressure

Φ<sub>FOG</sub> relative vapour pressure at Φ = 1<sup>-</sup>

α contact angle between pore wall and capillary meniscus

α<sub>∞</sub> contact angle in large pores

u moisture content in porous material (kg/kg solid)

$Q, P, M, Q_{AD}, P_{AD}, M_{AD}$	fit parameters for sorption descriptions
$C$	heat property factor – so-called BET-parameter
$u_{UNI}$	weight of uni-molecular layer on solid surface (kg/kg solid) – so-called BET-parameter
$u_{AD}$	weight adsorbed on solid surface (kg/kg solid)
$N = u_{AD}/u_{UNI}$	number of molecule layers adsorbed on solid surface as a function of relative vapour pressure
$u_{TOT} = V_{TOT} \cdot d_L$	total moisture content (kg/kg solid)
$u_{AD}$	adsorbed moisture (kg/kg solid)
$u_{FOG}$	max. moisture content held by adsorption and capillary forces at $\Phi = 1^-$ (fog) (kg/kg solid)
$u_{FILL} = u_{TOT} - u_{FOG}$	"fill up" moisture at $\Phi = 1$ (kg/kg solid).
$u_M$	moisture in pores (micro pores) completely filled with adsorbed moisture (kg/kg solid)
$u_S$	moisture adsorbed on pore surface not associated with micro pores (kg/kg solid)
$u_C$	moisture in pores bound by capillary forces (kg/kg solid)
$U_I = u_I/u_{UNI}$	normalized moisture content of porous material (I is type of moisture content previously defined)
$S_{TOT} \approx u_{UNI}/(D \cdot d_L)$	Total surface of pores ( $m^2/kg$ solid)
$r_C$	(hydraulic) capillary pore radius (m)
$\theta_C = r_C/D$	normalized capillary radius
$r = N \cdot D + r_C$	pore radius (definition) (m)
$\theta = N + \theta_C$	normalized pore radius
$r_o = V_{TOT}/S_{TOT}$	Mean pore radius (m)
$\theta_o = r_o/D = u_{TOT}/u_{UNI}$	normalized mean pore radius
$\Phi_{CR}$	( $\approx 0.995$ ) critical vapour pressure beyond which no further capillary moisture is added (gravity forces dominate)
$\gamma$	film pressure in adsorbed moisture (N/m)
$\sigma_M$	hydraulic pressure in micro pore moisture
$\sigma_v$	normal pressure on total solid phase surface caused by adsorption
$\sigma_C$	hydraulic tension in capillary moisture

## II. SORPTION

Two mechanisms are responsible for sorption in porous materials: The adsorption mechanism where gas molecules liquefy on a solid surface as a result of surface force attraction – and the mechanism of capillary condensation where liquefaction is made possible by surface tension in curved vapour-liquid interfaces.

### 2.1 Adsorption

#### 2.1.1 Moisture content

The phenomenon of adsorption has been studied by Brunauer, Emmett and Teller (1) who developed an expression – the so-called BET-equation – which relates amount of adsorbed liquid to vapour pressure. The BET-equation

shown in Equation 1 is generally accepted to apply very well at relative vapour pressures less than 40 %. It is developed considering a plane surface, ignoring forces of gravity and assuming that heat of condensation does not vary from the second to higher molecule layers of adsorbed moisture.

#### **BET-RELATION**

$$u_{AD} = \frac{C \cdot u_{UNI} \Phi}{(1 - \Phi)[1 + (C - 1)\Phi]} \quad \text{adsorbed moisture} \quad (1)$$

$$N = \frac{u_{AD}}{u_{UNI}} = \frac{C \Phi}{(1 - \Phi)[1 + (C - 1)\Phi]} \quad \text{number of molecule layers}$$

#### **MODIFIED BET-RELATION FOR POROUS MATERIALS**

$$N = \frac{u_{AD}}{u_{UNI}} = \frac{C \Phi h_{AD}}{1 + (C - 1)\Phi} \quad ; \quad N(1) = Q_{AD} + M_{AD} \quad (2)$$

$$h_{AD} = h[Q_{AD}, M_{AD}, P_{AD}] \quad \text{from Equation 3 with}$$

$$(Q_{AD}, P_{AD}) = (Q, 1) \text{ and } M_{AD} \text{ from pore analysis}$$

#### **POROUS MATERIALS - NORMALIZED MOISTURE CONTENT**

$$U = \frac{u}{u_{UNI}} = \frac{C \Phi h}{1 + (C - 1)\Phi} \quad ; \quad U(1) = Q + M$$

#### **h-FUNCTION** (3)

$$h = h[Q, M, P] = h(\Phi) = \frac{1 - \Phi^Q}{1 - \Phi} + \Phi^{PQ} \frac{1 - \Phi^{PM}}{1 - \Phi^P} \quad ; \quad h(1) = Q + M$$

$$(Q, M, P) \geq (1, 1, 1) \quad (\text{deduced from sorp-data, see Appendix A})$$

Thus, some limits apply to the BET-equation when used in practice to describe moisture content of porous materials. However, as indicated before many years of experience show that fine results are obtained at relative vapour pressures,  $\Phi < 0.4$  (also in porous bodies). The results, however, become increasingly bad at higher vapour pressures, and quite impossible as  $\Phi \rightarrow 1$  (fog) where  $N \rightarrow \infty$  is predicted. The present analysis is therefore based on the modified BET-equation shown in Equation 2 developed by the present author in (2) to describe sorption in the whole range of vapour pressures. This expression includes the original BET-relation at  $\Phi \rightarrow 0$ , and "predicts" a finite number of  $N(1)$  adsorbed molecule layers at  $\Phi \rightarrow 1$ .  $N(1)$  is considered by the present author to be a pore specific thermodynamical property which can only be determined from sorption tests on porous

materials. The plane surface quantities  $N(1) \approx 5 - 7$  generally accepted in adsorption theory are used as first estimates in the pore size analysis subsequently presented where a pore specific, modified BET-relation is one of the principal results obtained by iteration. An effective absolute maximum of  $N(1) \approx 10$  is a cautious estimate based on the authors experience from running the computer algorithm developed in Section 3.2 on a number of porous materials.

### 2.1.2 Adsorption stresses

A number of authors have studied the stress state of adsorbed moisture. The "film pressure" and "micro pore pressure" results presented in this section are based on well-known principles in the field of surface chemistry (summarized in (3) for example).

**Film pressure:** An effective film pressure  $\Gamma$  (N/m) is developed in moisture being adsorbed on a free surface. Its magnitude is given by the so-called "Gibbs-equation" developed in (4) and presented in Equation 4 as the former expression.

**Micro pore pressure:** Micro pores are defined in this paper as pores which are not wide enough to contain the number of molecule layers predicted by Equation 2. Micro pores are filled with adsorbed moisture the (hydrostatic) pressure of which is determined by the so-called "disjoining pressure equation" developed in (5,6) and presented by the second expression in Equation 4. Micro pore pressure reduces the film pressure (in micro pores) such that film pressure in general  $\gamma$  should be expressed as given by the latter expression in Equation 4 (developed by the author).

#### ADSORPTION EFFECTS

*Film pressure in adsorbed moisture outside micro pores:*

$$\Gamma = \Gamma(\Phi) = \frac{RTDd_L}{M} \int_0^{\Phi} \frac{N}{\Phi} d\Phi$$

*Pressure in pore of radius  $\theta = N(\Phi_N)$  (micro pore)*

$$\sigma_M = \sigma_M(\Phi, \Phi_N) = \begin{cases} \frac{RTd_L}{M} \ln \left( \frac{\Phi}{\Phi_N} \right) & \text{when } N(\Phi) \geq 1 \text{ and } \Phi \geq \Phi_N \\ 0 & \text{otherwise} \end{cases} \quad (4)$$

*Film pressure in mic-pores (and general  $\because \sigma_M \equiv 0$  outs. mic-por.):*

$$\gamma = \gamma(\Phi, \Phi_N) = \Gamma(\Phi) - \sigma_M(\Phi, \Phi_N)[N(\Phi) - N(\Phi_N)]D$$

*( $\Phi_N$  is rel vapor pressure when micro pore is filled)*

## 2.2 Capillary condensation

The well-known Kelvin and Laplace relations (e.g. 7) describe meniscus radius of, and moisture stress in capillary condensed moisture. For the present purpose where pore systems are considered in general (cylindrical pores as well as slit shaped pores, a.o.) the Kelvin-Laplace relations can be written as shown in Equation 5 where  $\theta_c$  and  $\Phi$  denote hydraulic radius of pore (cross-sectional area divided by respective circumference) and ambient relative vapour pressure respectively. Notice that  $\theta_c$  is hydraulic radius normalized with respect to molecule diameter.

A constant contact angle ( $\alpha$ ) between pore wall and meniscus is normally assumed. This choice is reasonably well justified when materials are considered with relatively simple pore systems with large mean pore radii ( $\theta_o > \approx 100$ ). It is, however, hard to believe that a constant  $\alpha$  can be maintained in complicated pore systems with many pores of very small radii. The authors suggestion is that a mean contact angle  $\alpha$  is related to mean pore radius as shown in Equation 5 where  $\alpha_o$  is contact angle in large pores. ( $\alpha_o = 0$  is subsequently assumed when materials are considered with no hydrophobic extracts). The factor  $K_a$  introduced in the  $\alpha$ -expression in Equation 5 is suggested to increase with amount of pores with small radii.

Obviously capillary tension cannot exceed the moistures tensile strength which can be estimated from Equation 5 with a meniscus radius of  $\theta_c \approx 2$  (below which no real meniscus can be defined).

**Comment:** The  $\alpha$ -variation suggested in Equation 5 summarizes the authors experience from a limited number of pore size analysis on pore systems with many coarse pores (higher  $\theta_o$ ) and pore systems with few coarse pores (lower  $\theta_o$ ) respectively. This means that the  $\alpha$  estimate in Equation 5 is subject to modification if abnormalities show up in the pore size analysis presented in a subsequent section.

### CAPILLARY EFFECTS

$$\begin{aligned} \theta_c &= - \frac{M \Gamma}{RTDd_L} \frac{\cos \alpha}{\ln \Phi} && \text{capillary pore radius} \\ \sigma_c &= - \frac{RTd_L}{M} \ln \Phi ; \left( = \frac{\Gamma \cos \alpha}{D \theta_c} \right) && \text{capillary pore tension} \\ \alpha &\approx \alpha_o + (90^\circ - \alpha_o) * \text{MIN} \left[ 1, \exp \left( \frac{2 - \theta_o}{K_a} \right) \right] && \text{contact angle} \end{aligned} \quad (5)$$

**NOTE:**  $\theta_c$  and  $\sigma_c$  are non-existing (zero) when above predicted  $\theta_c < 2$ .  $K_a$  is high (50-100) in systems with many narrow pores

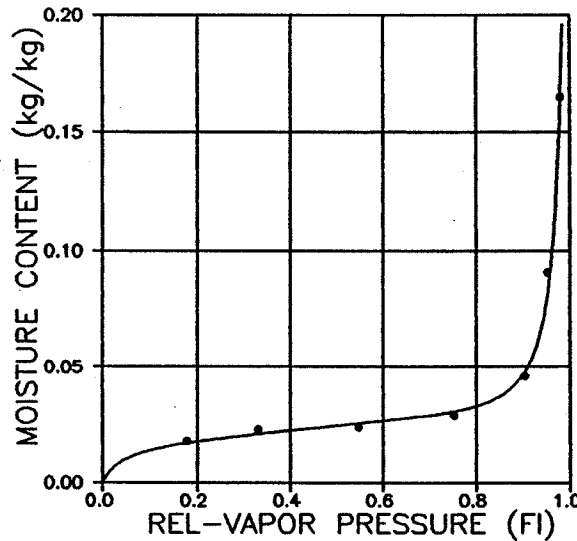
## 2.3 Sorption description

The modified BET-relation previously referred to is a special version of the fit method developed by the author in (2) and presented in Equation 3 to describe total sorption in porous materials. The present analysis is based on this description which offers a number of useful features in moisture research on porous materials: ■ The original BET-relation is included at  $\Phi \rightarrow 0$ . ■ A high quality fit of experimental sorption data in general is produced – also at higher vapour pressures where sorption is increasingly influenced by capillary condensation. The "fit" parameters (Q,P,M) and the BET-parameters (C,  $u_{UNI}$ ) are easily determined from experimental data by the regression method suggested in Appendix A at the end of the paper.

The rate of sorption is of interest in the pore size analysis subsequently considered. Information on this point is also given in Appendix A.

An example on sorption data fit is shown in Figure 1 where water sorption in cellular concrete is considered with experimental data as compiled in (8). General trends of the method are: Higher Q's and M's increase described moisture contents at lower vapour pressures and at higher vapour pressures respectively. Higher P's "flatten" moisture description at medium vapour pressures.

Useful information on sorption data for a variety of porous materials are given in (8,9,10,11,12).



*Figure 1. Adsorption data for cellular concrete ( $d^* = 500 \text{ kg/m}^3$ ). Fitted by Eq. 3 with  $(Q, M, P) = (2, 25, 5)$  producing  $C = 26.4$  and  $u_{UNI} = 0.01705 \text{ kg/kg solid}$ .*

## III. PORE SIZE AND MOISTURE DISTRIBUTION ANALYSIS

### 3.1 Basics

The subsequent pore size analysis is based on the following concepts:

- A) Moisture in a porous materials is adsorbed moisture and capillary condensed moisture. Adsorbed moisture is subdivided in pore filling moisture (micro pore moisture) and surface moisture on pore surface not associated



with micro pores. Adsorbed moisture is added first and is not influenced by capillary moisture. A similar concept is well-known from the literature on pore size analysis (e.g.13,14)

■ B) Capillary condensed moisture is not added at relative vapour pressures greater than a critical vapour pressure  $\Phi_{CR}$  where gravity forces dominate and capillary tension predicted by Equation 5 is less than approximately 2/3 MPa. ( $\Phi_{CR} = 0.995$  when water is considered at 20 °C). The critical vapour pressure is introduced to explain the large amount of moisture which can still be added (in this paper defined as "fill up" moisture) to the pore system at  $\Phi = 1$  – and which is usually not considered by traditional sorption graphs.

■ C) Pore radius is defined as thickness of adsorbed moisture plus hydraulic radius of capillary condensed moisture. Normalized with respect to liquid molecule diameter this means,  $\theta = N(\Phi) + \theta_c(\Phi)$  at  $\Phi < \Phi_{CR}$  and  $\theta = N(\Phi) + \theta_c(\Phi_{CR})$  at  $\Phi \geq \Phi_{CR}$ .

The definition of real pore radius as the sum of thickness of adsorbed moisture and capillary radius is quite common in pore size analysis where cylindrical pores and slit shaped pores are considered in separate pore size analysis. The present definition based on hydraulic pore radius has the advantage that more general pore shapes are considered in one approach.

■ D) Increase of pore volume at a certain radius (as just defined) is pore radius multiplied by increase in pore surface.

<i>PORE SIZE DISTRIBUTION</i>	
$G(\theta) = \frac{S}{S_{TOT}} = \int_0^\theta g(x) dx$	; accumulated pore surface distribution
$H(\theta) = \frac{V}{V_{TOT}} = \int_0^\theta h(x) dx$	; accumulated pore volume distribution
$\left. \begin{aligned} g(\theta) &= \frac{dG}{d\theta} \\ h(\theta) &= \frac{dH}{d\theta} \end{aligned} \right\}$	respective density functions
$\left. \begin{aligned} \frac{h(\theta)}{g(\theta)} &= \frac{dH}{dG} = \frac{\theta}{\theta_o} \rightarrow \\ \theta_o H(\theta) &= \theta G(\theta) - \int_0^\theta G(x) dx \end{aligned} \right\}$	pore systems presently considered

The former four relations presented in Equation 6 (G, H, g, h) are general mathematical distribution formulations. The correlations of density functions (latter two expressions in Equation 6) specify distributions to meet concept D stated above – and ensure consistency with respect to surface and volume distributions. Note that g and h are always positive which means that G and H are monotonically increasing with pore radius.

### 3.2 Pore size distributions

At any (relative) vapour pressure ( $\Phi$ ) moisture content is considered as the sum of moisture (adsorbed and capillary) in filled pores and adsorbed moisture (thickness  $N$ ) on pore surfaces not associated with filled pores. This statement is expressed mathematically by the first expression in Equation 7 from which pore surface distribution ( $G$ ) can be determined theoretically from moisture content as shown by the latter two expressions in Equation 7. When  $G$  is determined pore volume distribution ( $H$ ) is given by the second expression in Equation 7.

#### MOISTURE CONTENT WHEN PORES $< \theta$ ARE FILLED

$$\begin{aligned}
 u &= H(\theta) V_{TOT} d_1 + (1 - G(\theta)) S_{TOT} N D d_1 \\
 &\quad \text{filled pores} \quad \text{surface bound} \quad \rightarrow \\
 U &= \theta_o H(\theta) + N(1 - G(\theta)) \quad \rightarrow \\
 \frac{dU}{d\theta} &= \theta_o h(\theta) + [1 - G(\theta)] \frac{dN}{d\theta} - N g(\theta) \quad \rightarrow \\
 \frac{dU}{d\theta} &= (\theta - N) \frac{dG}{d\theta} + (1 - G(\theta)) \frac{dN}{d\theta} \quad \rightarrow \\
 \frac{dG}{d\theta} &= \frac{dU/d\theta - [1 - G(\theta)] dN/d\theta}{\theta - N} \quad \text{when } \theta > N \\
 G(\theta) &= 1 - \frac{dU}{d\theta} = 1 - \frac{dU/d\theta}{dN/d\theta} \quad \text{when } \theta \equiv N
 \end{aligned} \tag{7}$$

It is obvious from concept C in Section 3.1 that pore size analysis based on sorption data can only be made in details for radii less than  $\theta \leq N(1) + \theta_c(\Phi_{CR})$  ( $\approx 10^{2-3}$ ). The amount of pores with greater radii are considered in total as described in Equation 9 which considers the so-called "fill-up" area where  $\Phi \equiv 1$ .

Algorithms for practical pore size analysis by computer are given in Equations 8 and 9. Some clarifying comments are given in the following list.

#### Preparation

- Experimental sorption data are given a continuous description by Equation 3 where the parameters  $Q, M, P$  and the BET-parameters  $C, u_{UNI}$  are deduced from experimental data as explained in Appendix A.
- $u_{TOT}$ ,  $\theta_{MAX} = r_{MAX}/D$  and  $\theta_o$  are calculated by simple rules based on elementary pore analysis (see list of notations).

#### Analysis

- Pore size distributions are calculated according to Equations 8 and 9 with vapour pressure  $\Phi$  as independent variable. Auxiliary relations are given in appendices A (rate of sorption) and B (numerical distribution increments).

N is given by Equation 2 with  $(Q_{AD}, P_{AD}) = (Q, 1)$  and  $M_{AD}$  considered as independent variable in the iteration process subsequently explained.  $\theta_c$  is given by Equation 5.

- Calculations are run such that  $G = 1$  is approached at  $\theta = \theta_{MAX}$ . A modified Newton's iteration principle,  $x_{NEW} = x - y/(\Delta y/\Delta x)$  (with if  $(x_{NEW} < 1)$  then  $x_{NEW} = (1+x)/2$ ), is very efficient for this purpose with independent variable  $x = M_{AD}$  (starting with  $x = 10 - Q$  f.ex.) and dependent variable  $y = G - 1$ .

$$\Phi < 1$$

When  $\theta(\Phi) = N(\Phi)$  (predicted  $G$  is monotonically increasing):

$$G = 1 - \frac{dU/d\Phi}{dN/d\Phi} ; H = \frac{U - N(1 - G)}{\theta_o} \quad (\text{derivatives: Append A})$$

When  $\theta > N$  with step from  $\theta_1 = N_1 + \theta_{c,1}$  to  $\theta_2 = N_2 + \theta_{c,2}$ :  
where indices 1 and 2 refer to  $\Phi_1$  and  $\Phi_2$  respectively. (\*\*)

$$\left. \begin{aligned} U_2 &= \theta_o * H_2 + (1 - G_2) * N_2 \\ U_1 &= \theta_o * H_1 + (1 - G_1) * N_1 \end{aligned} \right\} -$$

$$\Delta G = \frac{\Delta U - (1 - G_1)\Delta N}{\theta_o \frac{\Delta H}{\Delta G} - N_2} ; \begin{cases} \Delta U = U_2 - U_1 \\ \Delta G = G_2 - G_1 \\ \Delta H = H_2 - H_1 \\ \Delta H/\Delta G \text{ from Appendix B} \\ \Delta N = N_2 - N_1 \end{cases}$$

$$G_2 = G_1 + \Delta G ; H_2 = \frac{U_2 - N_2(1 - G_2)}{\theta_o}$$

Footnote \*\*: When  $\Phi_{CR} \leq \Phi < 1$ :  $\theta(\Phi) = N(\Phi) + \theta_c(\Phi_{CR})$

$$\Phi = 1$$

$$\begin{aligned} \theta_1 &= \theta_{FOG} ; \theta_2 = \theta_{MAX} \\ N_1 &= N_{FOG} ; N_2 = N_{FOG} \rightarrow \Delta N = 0 \\ U_1 &= U_{FOG} ; U_2 = U_{MAX} \rightarrow \Delta U = U_{MAX} - U_{FOG} = U_{FILL} \end{aligned} \quad (9)$$

$$\Delta G = \frac{U_{FILL}}{\frac{\Delta H}{\Delta G} - N_{MAX}} \quad \text{with } \frac{\Delta H}{\Delta G} \text{ from Appendix B}$$

**Comments:** The analysis has to be remade with a modified contact angle  $\alpha$  if the resulting distribution function does not increase monotonically with pore radius or if  $M_{AD}$  approaches a quantity where  $N(1) = M_{AD} + Q$  becomes greater

than approximately 10 – 12 (authors estimate). Generally an increasing  $K_a$  in Equation 5 will lower  $M_{AD}$ . In general: Keep both  $N(1)$  and  $K_a$  low.

### 3.3 Moisture distribution

The contents of micro pore moisture, surface moisture, and capillary moisture are related to pore size distributions as given in Equation 10. This is a consequence of the considerations made in Section 3.2

MOISTURE DISTRIBUTION		
$U_H = \theta_o * H(N)$	micro pores	(10)
$U_S = N[1 - G(N)]$	adsorbed moisture on non-micro pore related surface	
$U_C = U - (U_H + U_S)$	capillary moisture	

MEAN PORE STRESSES		
$\langle \sigma_H \rangle = \int_{\Phi_N=0}^{\Phi_N=\Phi} \sigma_H(\Phi, \Phi_N) dH(N(\Phi_N))$	micro pore pressure	
$\langle \sigma_C \rangle = \frac{U_C(\Phi)}{U_{TOT}} \sigma_C(\Phi)$	capillary pore tension	
$\langle \gamma \rangle = \int_{\Phi_N=0}^{\Phi_N=\Phi} \gamma(\Phi, \Phi_N) dG(N(\Phi_N)) + [1 - G(N(\Phi))] \Gamma(\Phi)$	film pressure	1 (
$\langle \sigma_1 \rangle = \frac{2\langle \gamma \rangle}{3r_S}$	pressure on solid phase surface (internal and external)	
$r_S$ is hydraulic radius of solid phase ( $r_S = V_{sol}/S_{TOT}$ )		
$r_S = \frac{1-c}{c} \frac{V_{TOT}}{S_{TOT}} = \frac{1-c}{c} D\theta_o$ ( $S_{TOT} \gg$ specimens external surface)		

### 3.4 Pore pressure and tension

The volume average of micro pore pressures from  $\Phi = 0$  to  $\Phi$  is calculated as shown in Equation 11 from the single micro pore solution in Equation 4 combined with pore volume distribution determined by the procedure described in Section 3.2.

The volume average of capillary moisture tension is calculated very easily by the second expression in Equation 11 with  $\sigma_C$  from Equation 5 and moisture contents as determined in Section 3.3.

The surface average ( $\langle \gamma \rangle$ ) of adsorbed film pressures in, and outside micropores is determined by the third expression in Equation 11 from the single micro pore and unhindered film pressure solutions in Equation 4. The

pressure effect of the adsorbed film pressure ( $\langle\sigma_v\rangle$ ) on pore walls can be calculated from the fourth expression in Equation 11 developed by the present author from a stress analysis made by Flood (15) on particles subjected to surface tension. It is noted that the pressure calculated acts hydrostatically on the total solid phase surface (pore surface and external surface).

#### IV. SHRINKAGE - SWELLING

There are two concepts of explaining ("hygroscopic") shrinkage/swelling of porous materials. Bangham et al. (16) suggested that the adsorption mechanism is the prime mechanism causing shrinkage. Powers (17), however, argued very convincingly that important cases cannot be explained without also considering the effects of micro pore pressures (disjoining pressure). The model suggested by Powers in (17) states that shrinkage of porous materials can only be explained in general by a combination of all three sorption mechanisms previously considered in this paper: Adsorption, disjoining pressure, and capillary tension.

The shrinkage analysis presented in Equation 12 quantifies the ideas of Powers that any three sorption mechanisms must be considered. In the present context this means that the present authors porous materials stiffness theory presented in (e.g. 18,19) and Appendix C of this paper is used to predict shrinkage/swelling as strain caused by the "hygroscopic loadings" given in Equation 11.

The shrinkage analysis presented in Equation 12 is straight forward. The simple result of strain caused by adsorbed moisture is due to the fact previously indicated that the equivalent surface pressure ( $\langle\sigma_v\rangle$ ) acts on the total solid phase surface producing a hydrostatic stress state in the solid involving  $\epsilon_{VOL}^* = \epsilon_{VOL}^S = \langle\sigma_v\rangle/K_S$ .

*Expansion of porous material  
(increasing moisture content)*

$$\epsilon_{LIN}^I = \langle\sigma_v\rangle (1 - 2\nu_s) \left( \frac{1}{E_o^*} - \frac{1}{E_s} \right) ; \quad (I = M, C) \quad (12)$$

$$\epsilon_{LIN}^r = \langle\sigma_v\rangle \frac{1 - 2\nu_s}{E_s}$$

$$\epsilon_{LIN}^* = \epsilon_{LIN}^M - \epsilon_{LIN}^C + \epsilon_{LIN}^r$$

#### V. EXAMPLES

Two examples are considered in this section which demonstrate the power of the theory developed to utilize experimentally obtained sorption data in pore size analysis of porous materials and prediction of shrinkage/swelling of

such materials. The examples are cellular concrete and hardened cement paste in damp atmosphere with experimental sorption data from (8) and (20, W/C = 0.35, steam cured) respectively. Basic materials data are given in Table 1. Sorption parameters are deduced from experimental data by the method explained in Appendix A at the end of this paper. Shape factors ( $\mu_0$ ) are estimated from the authors analysis in (18,19) of porous materials. Young's moduli ( $E_s$ ) have been given the values applying for solid silicate materials (which is certainly an upper bound quantity in the present context). The first estimate  $K_a$  quantities given in Table 1 reflect the authors experience using the pore size analysis described in Section 3.2 on a number of porous materials.

The results presented in Figures 2 - 13 are from calculations based on desorption data. Log-linear incremental variations of accumulated volume distributions with respect to pore radii are used.

TABLE I: GEOMETRY, STIFFNESS, AND SORPTION OF CELLULAR CONCRETE AND HARDENED CEMENT PASTE IN DAMP ATMOSPHERE

	CELLULAR CONCRETE		HARDENED CEMENT PASTE	
c	0.8		0.4	
$r_{MAX}$	0.003 m		0.001 m	
$d_s$	2500 kg/m <sup>3</sup>		2500 kg/m <sup>3</sup>	
$E_s$	$8 \cdot 10^4$ MPa		$8 \cdot 10^4$ MPa	
$\nu_s$	0.2		0.2	
$\mu_0$	0.4		0.3	
	ADS	DES	ADS	DES
C	26.4	25.4	65.9	139.1
$u_{UNI}$	.01705 kg/kg	.02170 kg/kg	.02390 kg/kg	.03459 kg/kg
Q	2.0	2.0	4.5	3.5
P	5.0	1.5	11.0	9.0
M	25.0	25.5	2.0	3.0
$\alpha_\infty$	0°	0°	0°	0°
$K_a$	50	50	100	50



## Example 1: Cellular Concrete in damp atmosphere

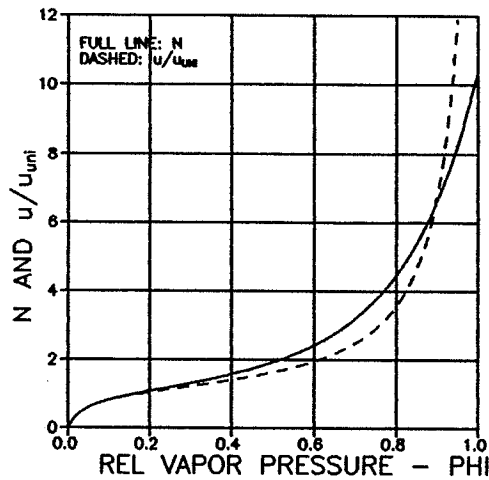


Figure 2. Number of adsorbed molecule layers (N) and normalized moisture content ( $u/u_{UNI}$ ).

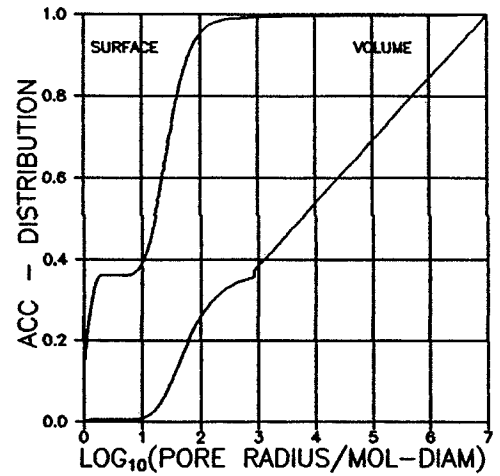


Figure 3. Distributions of pore volume and pore surface

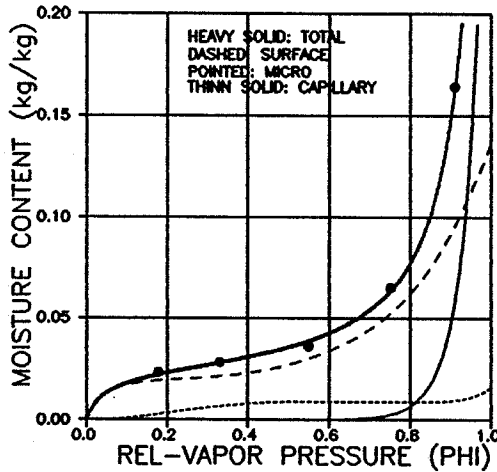


Figure 4. Moisture distribution. Dots are experimental desorption data.

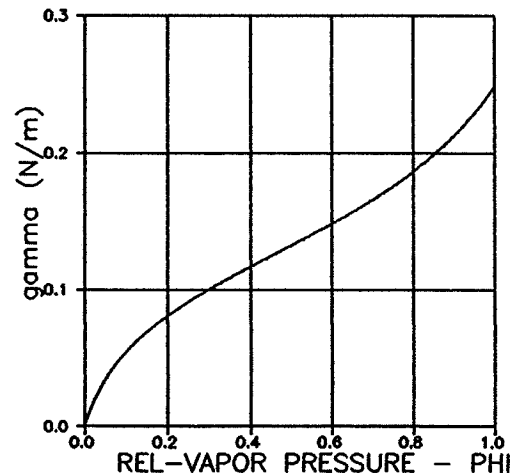


Figure 5. Film pressure in adsorbed moisture outside micro pores.

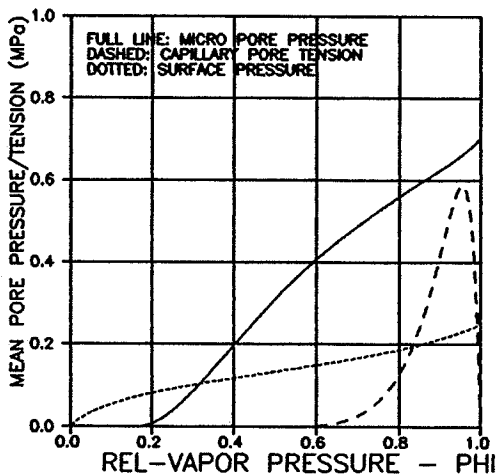


Figure 6. Micro pore pressure, capillary moisture tension and surface pressure (averages)

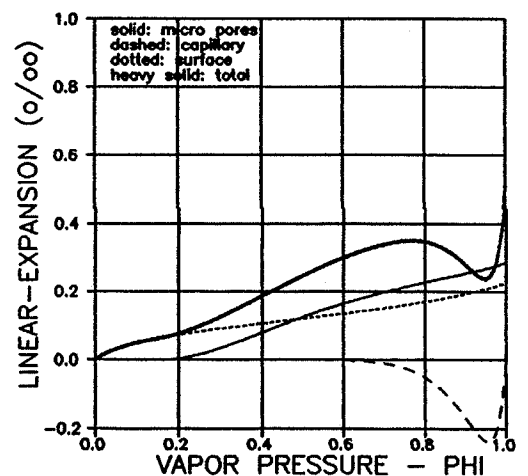


Figure 7. Shrinkage/swelling

## Example 2: Hardened cement paste in damp atmosphere

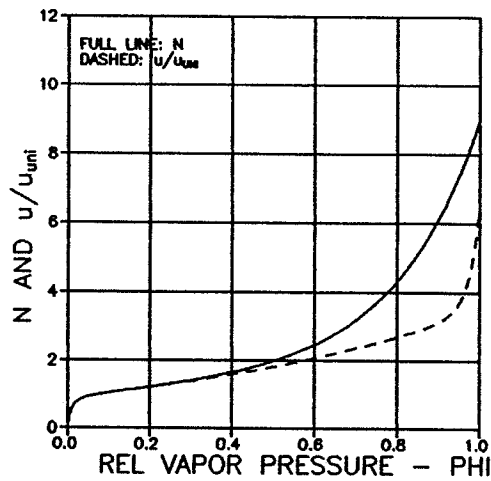


Figure 8. Number of adsorbed molecule layers ( $N$ ) and normalized moisture content ( $u/u_{UNI}$ ).

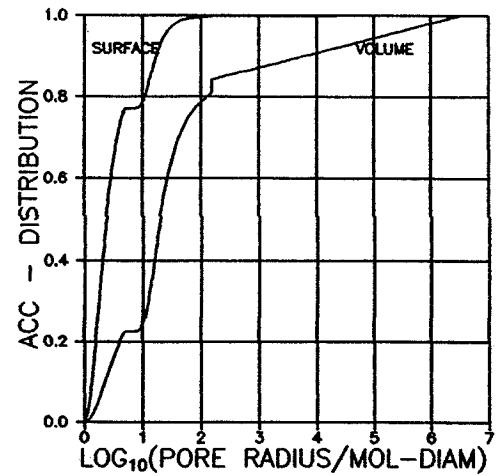


Figure 9. Distributions of pore volume and pore surface

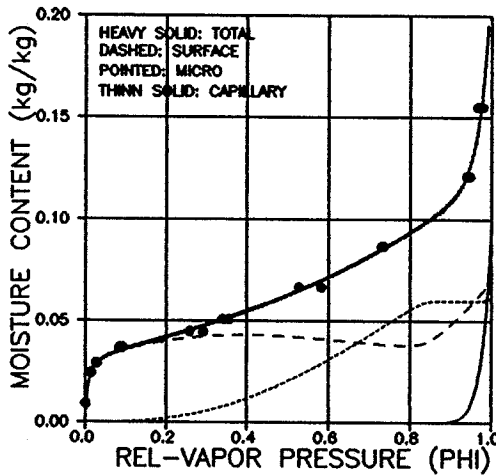


Figure 10. Moisture distribution. Dots are experimental desorption data.

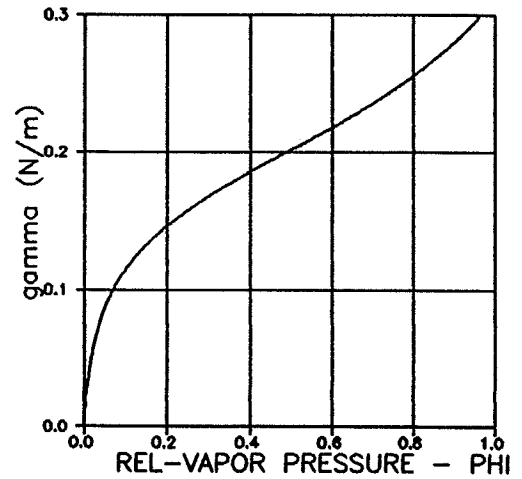


Figure 11. Film pressure in adsorbed moisture outside micro pores.

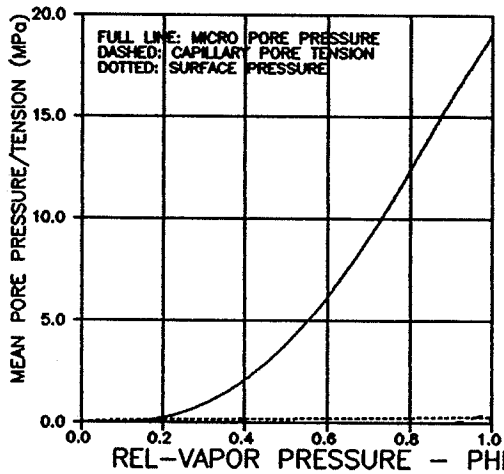


Figure 12. Micro pore pressure, capillary moisture tension and surface pressure (averages).

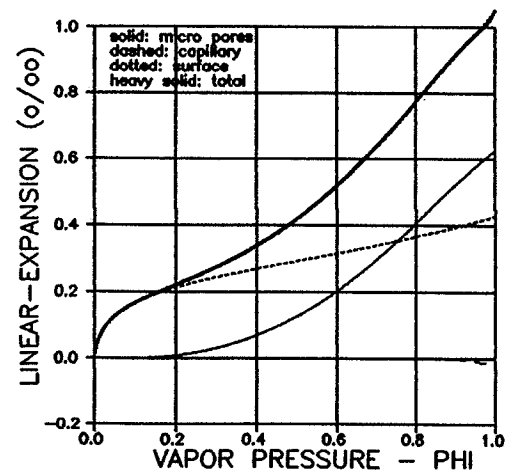


Figure 13. Shrinkage/swelling



## VI. CONCLUSIONS AND FINAL REMARKS

There are no deformation data following the sorption data referred to in Section V. There are also no information on Young's moduli of the solid phase. No direct check can therefore be made on the shrinkage/swelling strains predicted by Figures 7 and 13. The results, however, compare positively with orders of magnitudes generally observed in experiments: A shrinkage strain of approximately 0.25 ‰ of cellular concrete ( $d^* = 500 \text{ kg/m}^3$ ) for example was observed in (21) when drying from  $\Phi = 1$  to  $\Phi = 0.43$ . A swelling strain of approximately 1 ‰ was measured in (22) on normal hardened cement paste ( $W/C = 0.5$ ) increasing the relative vapor pressure from  $\Phi = 0.44$  to  $\Phi = 1$  - which agrees well with estimates of 0.7 - 1.2 ‰ made in (23, Fig. 227) for normal hardened cement pastes being dried from  $\Phi = 1$  to  $\Phi \approx 0.4$ . We recall that the solid phase Young's moduli estimated in Table 1 are upper bounds which might easily be 50 % too high (which will double the shrinkage/swelling strains predicted in Figures 7 and 13).

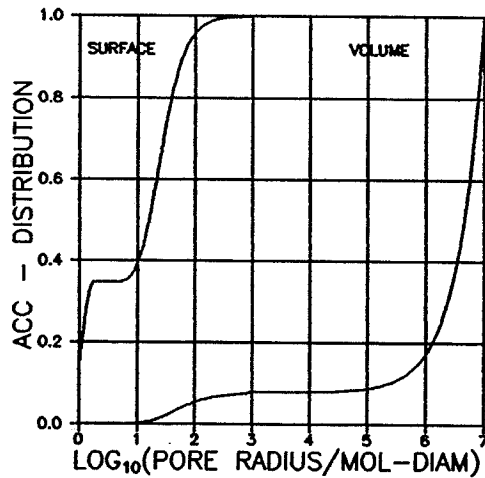


Figure 14. Cellular concrete as in Example 1 with porosity  $c = 0.95$ , however. Linear  $\Delta G/\Delta \log \theta$ .

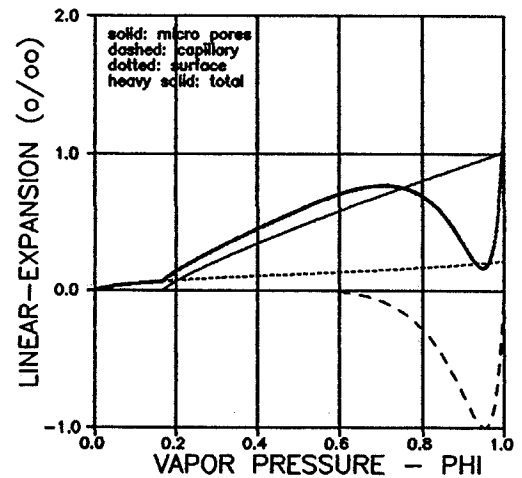


Figure 15. Cellular concrete as in Example 1 with porosity  $c = 0.95$ , however. Linear  $\Delta G/\Delta \log \theta$ .

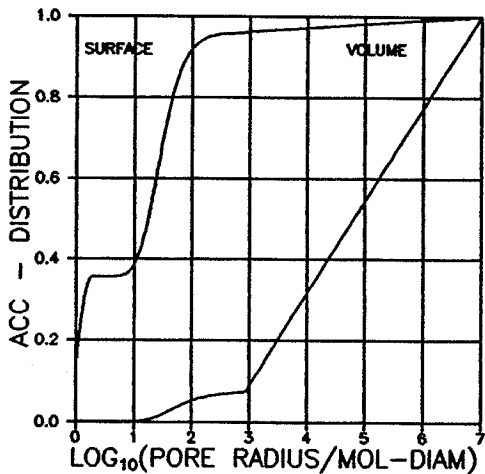


Figure 16. Cellular concrete as in Example 1 with porosity  $c = 0.95$ , however. Linear  $\Delta H/\Delta \log \theta$ .

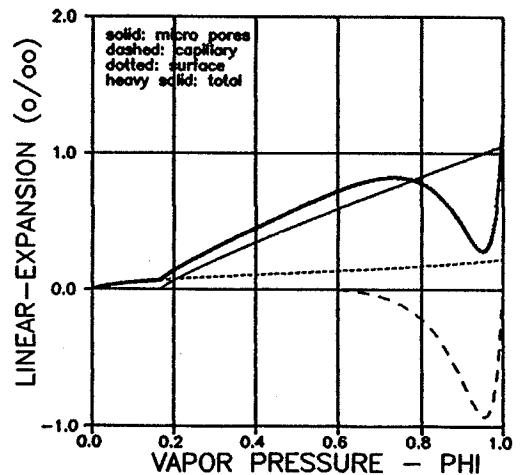


Figure 17. Cellular concrete as in Example 1 with porosity  $c = 0.95$ , however. Linear  $\Delta H/\Delta \log \theta$ .

The examples considered in Section V were analysed assuming log-linear incremental variations of accumulated pore volume distributions with respect to pore radius. A similar analysis based on log-linear variations of pore surface distributions did not reveal results significantly different from those illustrated in Figures 2 to 13 for relative vapour pressures between 0 and 1. In details the pore size distributions, of course, are influenced in the "fill-up" area where  $\Phi \equiv 1$  (and  $\log_{10}\theta$  varies between  $\approx 3$  and  $\approx 7$ ). However, the total fill-up variations in this area of pore size distributions are not influenced very much. This observation may justify the statement that the results obtained by the procedures presented in this paper are practically valid irrespective of how pore size distributions look in details beyond pore sizes detectable by sorption analysis. Figures 14 - 17 illustrate this point: An analysis has been made on the cellular concrete considered in Example 1 increasing the amount of (fill-up) voids such that porosity becomes  $c = 0.95$ .

The numerical pore size analysis presented is basically made by optimization of the parameters  $M_{AD}$  and  $K_a$  essential to quantify important sorption phenomenons like adsorbed layer thickness (Equation 2) and capillary contact angle (Equation 5) respectively. Further research in these areas is needed to establish more direct methods of quantifying modified BET-relations and capillary contact angles for porous materials. Further research is also needed where sorption experiments are made considering at the same time shrinkage/swelling and solid phase stiffness (Young's modulus).

## Appendix A

### Rate of sorption – Sorption parameters from experiments

Rate of number of adsorbed layers and rate of total sorption are determined by Equation A1 in this appendix together with Equations 2 and 3 respectively from the main text. Sorption parameters are deduced from experimental data by the procedure explained in Equation A2.

#### RATE OF SORPTION

$$\begin{aligned}
 U' &= \frac{dU}{d\Phi} \quad (\text{or } N' = \frac{dN}{d\Phi}) = C \frac{h + h'\Phi [1 + (C - 1)\Phi]}{[1 + (C - 1)\Phi]^2} \\
 h' &= \frac{dh}{d\Phi} = \frac{1 - Q\Phi^{Q-1} + (Q-1)\Phi^Q}{(1 - \Phi)^2} + \\
 &\quad + \frac{1 - M\Phi^{P(M-1)} + (M-1)\Phi^{PM}}{(1 - \Phi^P)^2} P\Phi^{P(Q+1)-1} + \\
 &\quad + \frac{1 - \Phi^{PM}}{1 - \Phi^P} Q P \Phi^{QP-1} \\
 h'(1) &= MQP + \frac{1}{2} [Q(Q-1) + PM(M-1)] \\
 U'(1) \text{ (or } N'(1)) &= MQP + \frac{1}{2} [Q(Q-1) + PM(M-1)] + \frac{M+Q}{C}
 \end{aligned} \tag{A1}$$

#### Sorption parameters – Deduction from exp. data

Moisture content  $u(\Phi)$  kg/kg at Rel-Vapor Pressure  $\Phi$

$Y = Y_o + \alpha * X$  linearization of Equation 3 with

$$X = \Phi \quad ; \quad Y = \frac{\Phi * h[\Phi, Q, P, M]}{u(\Phi)} \quad \begin{cases} Q = 1, Q_2, Q_3, \dots \\ P = 1, P_2, P_3, \dots \\ M = 1, M_2, M_3, \dots \end{cases} \tag{A2}$$

produces BET-parameters as follows from

$Y$ -intersection  $Y_o$  and slope  $\alpha$

$$C = 1 + \frac{\alpha}{Y_o} \quad u_{UNI} = \frac{1}{\alpha + Y_o}$$

Best BET-parameters (and  $Q, P, M$ ) are obtained optimizing the quality of linear regression ( $r^2$ ) with respect to  $Q, P$ , and  $M$  keeping  $C > 0$ .

## Appendix B

### Pore size distribution – Incremental G and H variations

Distribution variations consistent with Equation 6 in the main text are given in Equations B1 and B2 below.

*Linear variation of G between  $\theta_1$  and  $\theta_2$ :*

$$\left. \begin{aligned} \frac{G - G_1}{G_2 - G_1} &= \frac{\theta - \theta_1}{\theta_2 - \theta_1} \\ \frac{H - H_1}{G_2 - G_1} &= \frac{\theta^2 - \theta_1^2}{2\theta_o(\theta_2 - \theta_1)} \end{aligned} \right\} \quad \frac{H - H_1}{G - G_1} = \frac{\theta + \theta_1}{2\theta_o}$$

(B1)

*Log-linear variation of G between  $\theta_1$  and  $\theta_2$ :*

$$\left. \begin{aligned} \frac{G - G_1}{G_2 - G_1} &= \frac{\ln(\theta/\theta_1)}{\ln(\theta_2/\theta_1)} \\ \frac{H - H_1}{G_2 - G_1} &= \frac{\theta - \theta_1}{\theta_o \ln(\theta_2/\theta_1)} \end{aligned} \right\} \quad \frac{H - H_1}{G - G_1} = \frac{\theta - \theta_1}{\theta_o \ln(\theta/\theta_1)}$$

*Linear variation of H between  $\theta_1$  and  $\theta_2$ :*

$$\left. \begin{aligned} \frac{H - H_1}{H_2 - H_1} &= \frac{\theta - \theta_1}{\theta_2 - \theta_1} \\ \frac{G - G_1}{H_2 - H_1} &= \frac{\theta_o \ln(\theta/\theta_1)}{\theta_2 - \theta_1} \end{aligned} \right\} \quad \frac{H - H_1}{G - G_1} = \frac{\theta_2 - \theta_1}{\theta_o \ln(\theta/\theta_1)}$$

(B2)

*Log-linear variation of H between  $\theta_1$  and  $\theta_2$ :*

$$\left. \begin{aligned} \frac{H - H_1}{H_2 - H_1} &= \frac{\ln(\theta/\theta_1)}{\ln(\theta_2/\theta_1)} \\ \frac{G - G_1}{H_2 - H_1} &= \frac{\theta_o(\theta - \theta_1)}{\theta * \theta_1 \ln(\theta_2/\theta_1)} \end{aligned} \right\} \quad \frac{H - H_1}{G - G_1} = \frac{\theta * \theta_1 \ln(\theta/\theta_1)}{\theta_o(\theta - \theta_1)}$$

## Appendix C

### Stiffness of porous materials

Stiffness of porous materials can be predicted by Equation C1 reproduced from the authors work on such materials (e.g. 18,19). The reciprocal theorem from theory of elasticity is used in Equation C2 to obtain external strain of porous materials caused by pore pressure.

#### *YOUNG'S MODULUS OF POROUS MATERIAL*

$$\frac{E_o^*}{E_S} = \frac{(1 - c)^2}{1 + c(1/\mu_o - 1)}$$

with shape factor

(C1)

$$\mu_o \approx \begin{cases} 1 - 0.6 & \text{compact pocket pores} \\ 0.7 - 0.3 & \text{ribbons/channels/flat pockets} \\ 0.4 - 0 & \text{enveloping pore network} \end{cases}$$

#### *Strain of porous material caused by pore pressure (deduced by reciprocal theorem from theory of elasticity)*

**System 1:**

external load  $\sigma_{VOL}^*$  produces pore strain  $\epsilon_{VOL}^P = \frac{1 - k_o^*}{c} \frac{\sigma_{VOL}^*}{3K_o^*}$

**System 2:**

pore load  $\sigma_{VOL}^P$  produces external strain  $\epsilon_{VOL}^*$  (unknown) (C2)

**Reciprocal theorem:**

$$(\sigma_{VOL}^* \epsilon_{VOL}^*) * 1 = (\sigma_{VOL}^P \epsilon_{VOL}^P) * c \rightarrow \epsilon_{VOL}^* = (1 - k_o^*) \frac{\sigma_{VOL}^P}{3K_o^*} \quad \text{or}$$

$$\epsilon_{VOL}^* = \sigma_P \left( \frac{1}{K_o^*} - \frac{1}{K_S} \right) \quad \text{or} \quad \epsilon_{LIN}^* = \sigma_P (1 - 2\nu_S) \left( \frac{1}{E_o^*} - \frac{1}{E_S} \right)$$

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