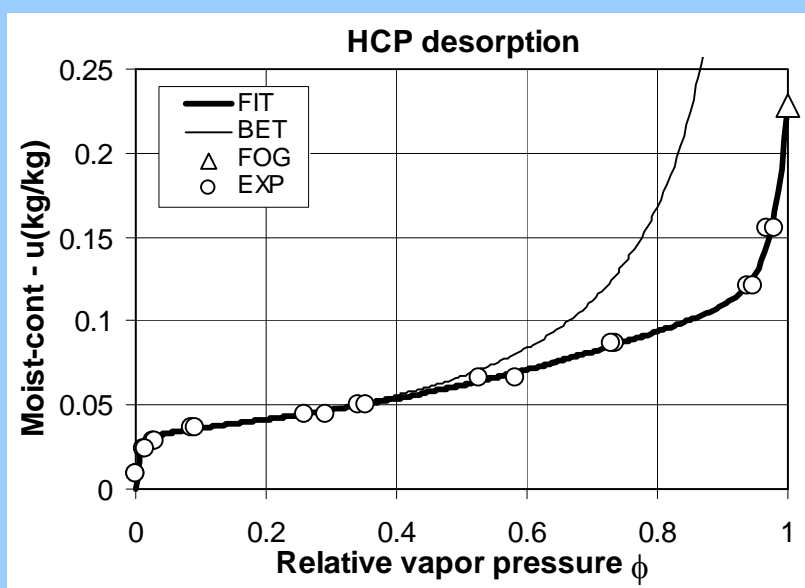# Moisture sorption in porous materials

a best-fit description from experimental data

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Contents

Abstract: Information on pore geometry is very important in any study of the mechanical and physical behavior of porous materials. Unfortunately pores are not very accessible for direct measurements. Indirect methods have to be used which involve impregnation (sorption) experiments from which pressure and weight data can be "translated" to pore geometry by known physical relationships. In this context, analytical descriptions are important which can relate moisture condensation in pore structures to ambient vapor pressure.

Such a description, the extended BET-relation, is presented in this paper. Contrary to the well-known original BET-relation (Brunauer, Emmett, Teller) the extended version applies at any vapor pressure.

Examples illustrate the capacity of the extended BET-relation to describe experimental data very well - and at the same time produce the best possible estimates of pore physical parameters, the so-called BET-parameters: The heat property factor, C, and the pore surface, S_{BET} (derived from the so-called uni-molecular moisture content u_{BET}).

A software 'SORP07' has been developed to handle any calculations made in the paper. For readers who have a special interest in the subject considered this software is available on request to the author.

Keywords: Porous materials, moisture, adsorption, desorption, BET-parameters.

1. Introduction

Information on pore size distribution is very important for any study of the mechanical and physical behavior of porous materials (1). Unfortunately pores are not very accessible for direct measurements. Indirect methods have to be used which involve impregnation experiments from which pressure and weight data can be "translated" to pore dimensions by known physical relationships.

One important experiment of this kind is the so-called sorption test, which considers the ability of a porous material to impregnate itself by liquefying an ambient gas atmosphere. The results of a sorption test are frequently presented in a sorption graph (moisture sorption isotherm) where weight at equilibrium of condensed gas (u [kg/kg dry solid]) is plotted against relative vapor pressure (φ).

Sorption graphs are the main topics of this paper. A rational method of sorption description, the extended BET-relation, is presented which includes the well-known original BET-relation (Equation 1) developed by Brunauer, Emmett and Teller at low vapor pressures. Three parameters (Q,P,M) are introduced which reflect the influence of pore geometry on moisture sorption at higher vapor pressures.

Examples illustrate the capacity of the extended BET-relation to describe experimental data very well, and at the same time produce the best possible estimates of the basic pore physical parameters: The heat property factor, C, and the weight, u_{UNI}, of a unimolecular moisture layer (proportional to pore surface, S_{BET}).

A software 'SORP07' has been developed to handle any calculations made in the paper. For readers who have a special interest in the subject considered this software is available on request to the author (2).

2. Basics

Two mechanisms are responsible for moisture 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 vapor-liquid interfaces.

The adsorption mechanism acts at any vapor pressure. The capillary mechanism acts only as long as the tensile stress produced does not approach the strength of the liquid. Practically this means (1) that no capillary condensation appears at low vapor pressures, $\varphi < 40 - 45 \%$

The phenomenon of adsorption has been studied by Brunauer, Emmett and Teller (3) who developed an expression - the so-called BET-relation (Equation 1) - which relates amount of adsorbed liquid to vapor pressure. The BET-equation is generally accepted to apply very well as a sorption description for porous materials at relative vapor pressures less than 40 - 45 %, where no capillary moisture is present.

$$u_{ADS} = \frac{C u_{UNI} \varphi}{(1-\varphi)(1+[C-1]\varphi)} \quad adsorbed\ moisture \quad (BET\text{-}relation) \qquad (1)$$

2.1 The BET-relation

The amount of liquid, u, being adsorbed on a surface exposed to gas at a relative vapor pressure, φ, is given by the BET-relation where u_{UNI} and C are physical constants applying to the solid/gas system considered.

u_{UNI} is weight of liquid when the surface is covered with a complete uni-molecular layer. The so-called BET-surface S_{BET} is related to this quantity as presented in Equation 2 where d_L is specific density of liquefied gas and D_{MOL} is molecule diameter. Heat properties of the system are considered by C as shown also in Equation 2 where adsorption heat of the first layer and of the next layers are denoted by W_A and W_L [J/Mol] respectively. T is absolute temperature and R is gas constant.

The BET-equation is developed considering a *plane surface* of a homogeneous solid, ignoring forces of gravity and assuming that heat of condensation does not vary from the second to higher molecule layers.

$$ S_{BET} = \frac{u_{UNI}}{D_{MOL}d_L} \quad with \quad D_{MOL}d_L = 3*10^{-7} \; kg/m^2 \; (water) \quad and \quad C = exp\left(\frac{W_A - W_L}{RT}\right) \qquad (2) $$

Remark: It is important to recognize these assumptions when BET-parameters (C and $u_{UNI} \Rightarrow S_{BET}$) are interpreted as they are deduced from tests on real porous materials. Such materials are very often composites with several components - and they have pores, which are not accessible for molecules of gas used in test method. Thus, in most practice experimentally obtained BET parameters must be considered as parameters quantifying some average behavior of the pore system considered. For example, the BET-surface obtained is a geometrical quantity, which depends on how it is measured, and also to some unknown degree on materials composition. These remarks are made only to emphasize that BET-parameters deduced from tests on real porous materials should not be explained too rigorously.

Keeping these remarks in mind we now proceed accepting the BET-relation to be the best possible fit of adsorbed moisture in porous materials at relative vapor pressures $\varphi <$ 40-45%.

3. Extended BET-relation

A rational method of describing experimental sorption data must predict results at low vapor pressures, which approach the results predicted by the BET-theory. In other words, a description must "start up" being the BET-expression at 0 vapor pressure (where there is no capillary liquid). Unfortunately a sorption description cannot be "tied up" physically at the other end of the vapor pressure scale. Today no relation exists between amount of capillary liquid and vapor pressure. Thus, as pressure increases we must presently accept that a description of total sorption in porous materials becomes more and more a question of mathematical fitting at higher vapor pressures (> 40-45 %). The process of fitting, however, may reveal information needed in future research on pore structures total moisture condensing capacity. It might be worthwhile exploring the possibility, that the parameters (Q,P,M) used in this paper can be given a geometrical/physical meaning.

It is indicated in Section 2 that a total sorption description must "degenerate" to a BET-relation as relative vapor pressure drops to low values. Such a description is developed by the author in (1,4,5). The result is presented in the following Equation 3 where $h(\varphi) = h[Q, P,M,\varphi]$ replaces $1/(1 - \varphi)$ in Equation 1.

$$ u(\varphi) = \frac{Cu_{UNI}\varphi \, h(\varphi)}{1+(C-1)\varphi} \quad with \quad h(\varphi) = \frac{1-\varphi^Q}{1-\varphi} + \frac{\varphi^{QP}}{1-\varphi^P}(1-\varphi^{PM}) \qquad (3) $$

The BET-parameters C and u_{UNI} are physical properties as previously explained. Also Q ≥ 1 is considered to be a physical constant applying to the solid/gas system considered.

The additional parameters $M \geq 1$ and $P \geq 1$ are thought to be pore specific quantities "controlling" the influence of pore geometry on total amount of moisture (adsorbed + capillary) attracted by a porous material at higher vapor pressures. All parameters can be determined from experimental data as subsequently demonstrated in Section 4.

3.1 Special moisture contents at $\varphi \approx 1$

Three special moisture contents are the following expressed by Equation 4: The so-called fog moisture content, u_{FOG}, is moisture condensed at the foggy state (extremely close to $\varphi = 1$) by adsorption and capillary forces. This quantity is easily obtained from Equation 3 for $\varphi \rightarrow 1$. The maximum moisture content, u_{MAX}, refers to the moisture, which can, at a maximum, be contained by the pores of the material considered. The fill-up moisture content, $u_{FILL-UP}$, is the difference between these two moisture contents.

$$u_{FOG} = u(\varphi \rightarrow 1) = (Q + M)\, u_{UNI} \qquad \text{(condensed moisture at foggy state)}$$

$$u_{MAX} = \frac{c_P}{1 - c_P} \frac{d_L}{d_S} \qquad \text{(moisture filled pores)} \qquad (4)$$

$$u_{FILL-UP} = u_{MAX} - u_{FOG} \geq 0 \qquad \text{(fill - up moisture)}$$

Remarks: The second moisture content, u_{MAX}, is only comparable with moisture contents described by Equation 3 if pore volumes considered in this expression is consistent with volumes detected (experimentally or analytically) for the determination of the porosity, c_P. For a number of porous materials we cannot be sure that such similarity exists. For cementitious materials, for example, with both gel- and capillary pores, methods of porosity determination are not too reliable in this context. The quantity of u_{MAX} is therefore of interest mainly in this paper for reasons of curiosity.

Strictly speaking, the two other moisture contents are also rather theoretical. They are reliable only if the true u_{MAX} can be determined - and if a sufficiently high number of experiments at vapor pressures close to $\varphi = 1$ allows u_{FOG} to be 'accurately' determined.

Thus, the three special moisture contents just considered at $\varphi \approx 1$ must be evaluated with some caution in the present analysis (and in any other sorption analysis know from the literature).

4. Deduction of sorption parameters

The parameters of the extended BET-relation in Equation 3 can be determined by linearization of experimental data as shown in Equation 5. Best parameters are obtained optimizing the quality of linear regression (r^2) with respect to Q, P, and M keeping C > 0.

$$Y = Y_o + \alpha * X \quad \text{linearization of Equation 3 with slope } \alpha \text{ and intercept } Y_o$$

$$X = \varphi \;\; ; \;\; Y = \frac{\varphi * h(\varphi)}{u(\varphi)} \text{ with for example} \left\{ \begin{array}{l} Q = 1, \dots\dots\dots 12 \\ M = 1, \dots\dots\dots 32 \\ P = 1, \dots\dots\dots 12 \end{array} \right. \Rightarrow \qquad (5)$$

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

5. Analysis and examples

A software (SORP07, 2) has been developed, which performs any calculations needed to determine the best fit parameters (Q,M,P), the BET parameters (C,u_{UNI},S_{BET}), and the special moisture contents (u_{MAX},u_{FOG}) from known (d_S,d_L,c_P,D_{MOL}) and experimental sorption data.

Examples are considered in this section, which illustrate the capacity of the software to describe moisture sorption in various porous materials. The materials data associated, and the experimental sorption data (water, 20°C) are presented in SORP07 (2). The immediate numerical results of the analysis are presented in the Appendix at the end of this paper.

Remark: A compilation by Hansen (6) of experimental sorption data for a great many materials can be recommended for exercises in using the software program.
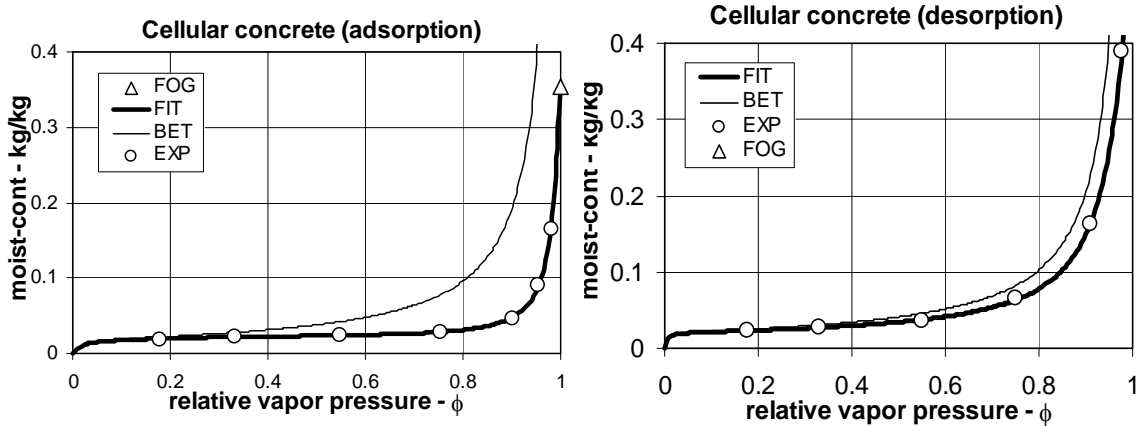

Figure 1. *Ad- and desorption graphs for Cellular concrete (500 kg /m³). Water moisture at 20°C.*
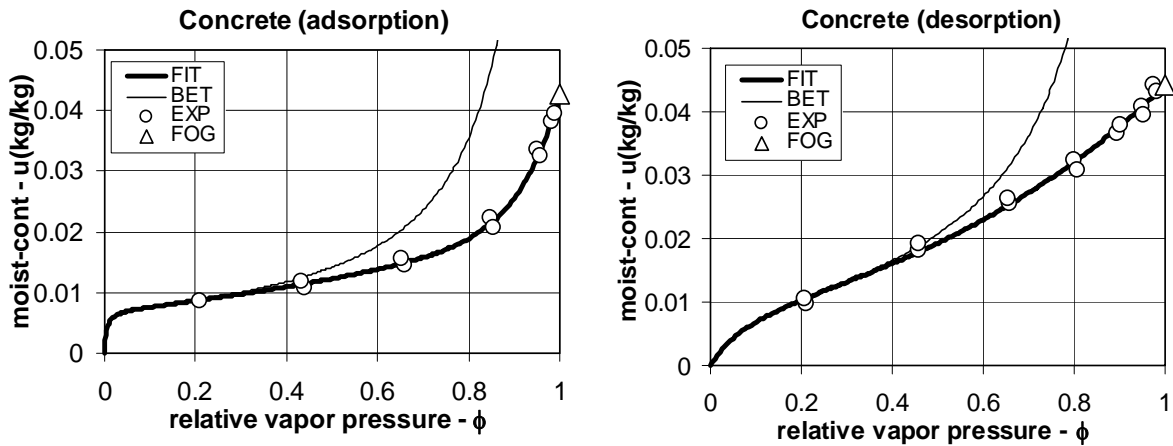

Figure 2. *Adsorption and desorption graphs for concrete (W/C = 0.66). Water moisture at 20°C.*
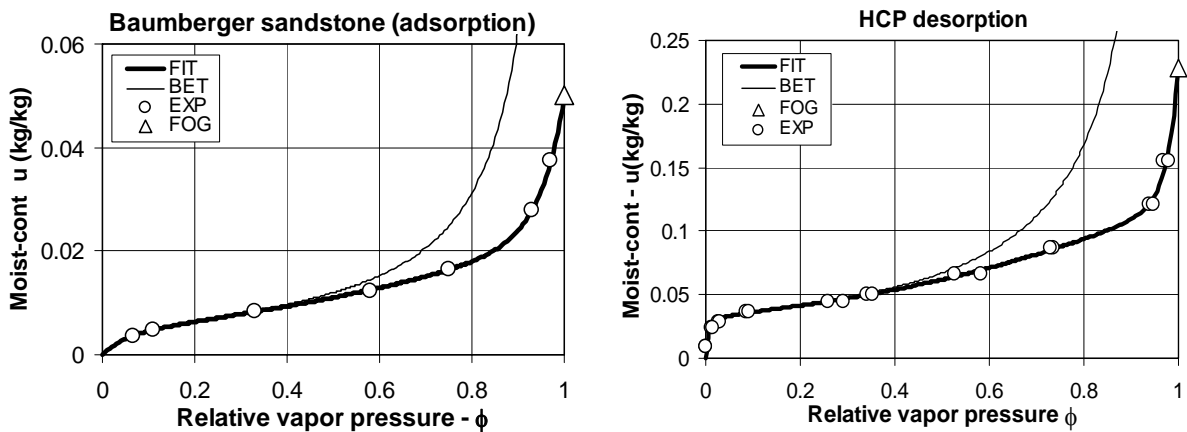

Figure 3. *Adsorption in sandstone and desorption in hardened cement paste (unknown W/C). Water moisture at 20°C.*

6. Final remarks

Excellent sorption descriptions by the method suggested in this paper are observed. The quality of physical properties obtained by regression increases with number of experimental data - especially at low vapor pressures.

Other sorption fit procedures are available in the literature; see (6,7,8,9,10,11) for example. The method presented in this paper, however, offers more than just an excellent fit of experimental sorption data. Of the five parameters involved C and u_{UNI} ($\Rightarrow$ pore surface S_{BET}) are the best possible estimates of the so-called BET-constants, which can be made from experimental data available.

As indicated in Section 1 and explained in (1) the high precision quality of the method to describe moisture sorption in porous materials is very useful in research on pore size distribution in such materials - and in the research on shrinkage of porous materials as related to ambient humidity. Application examples of such research are demonstrated in (12).

7. List of notations

Symbols frequently used in the analysis are summarized and briefly explained in the following list.

Liquid
d_L density (kg/m³)
D_{MOL} molecule diameter (m)
Solid and porous material
c_P porosity of porous material
d_S density of solid (kg/m³)
u_{MAX} weight of moisture which can at a maximum be filled into the pore system (kg/kg dry solid)
Sorption
φ relative vapor pressure
u total condensed moisture content, adsorbed and capillary, (kg/kg dry solid)
u_{ADS} moisture adsorbed by surface forces (kg/kg dry solid)
u_{FOG} moisture content just below $\varphi = 1$ (kg/kg dry solid)
$u_{FILL-UP}$ moisture which, literally, has to be 'poured' into pores at $\varphi = 1$ (kg/kg dry solid).
Q,P,M fit parameters for sorption descriptions
C BET parameter. Heat property factor.
u_{UNI} BET-parameter. Weight of uni-molecular layer on solid surface (kg/kg dry solid).
S_{BET} $= u_{UNI}/(D_{MOL}*d_L)$, Pore surface (m²/kg dry solid)

8. Appendix: Sorp07 analysis

Immediate results

The immediate numerical results of the sorption analysis (water, 20°C) referred to in Section 5 are as follows. The best BET-parameters and the fit-quality of the analysis are presented in shaded rows.

Cellular concrete

Cellular concrete	
Dmol(m)	3E-10
dl(kg/m3)	1000
ds(kg/m3)	2600
cp(porosity)	0.8
uMAX(kg/kg)	1.53846

Cell-concrete	Adsorption	Desorption
Q(fit)	1.37931	1.37931
M(fit)	17.0345	26.6552
P(fit)	5.17241	1.37931
C(BET)	54.6288	261.649
uUNI(BET)(kg/kg)	0.019255	0.020611
Sbet(m**2/kg)	64184.8	68702.8
r**2(fit)	0.991305	0.998035
uFOG(kg/kg)	0.354566	0.577814

Concrete

Concrete	
Dmol(m)	3E-10
dl(kg/m3)	1000
ds(kg/m3)	2300
cp(porosity)	0.15
uMAX(kg/kg)	0.076726

Concrete	Adsorption	Desorption
Q(fit)	2.89655	2.89655
M(fit)	3.13793	1
P(fit)	2.89655	1
C(BET)	219.183	10.7601
uUNI(BET)(kg/kg)	0.007103	0.011319
Sbet(m**2/kg)	23678.3	37730.2
r**2(fit)	0.989819	0.98987
uFOG(kg/kg)	0.042866	0.044105

Sandstone

Sandstone	
Dmol(m)	3E-10
dl(kg/m3)	1000
ds(kg/m3)	2700
cp(porosity)	0.255
uMAX(kg/kg)	0.126771

Sandstone	Adsorption
Q(fit)	3.65517
M(fit)	4.2069
P(fit)	3.65517
C(BET)	16.3166
uUNI(BET)(kg/kg)	0.006359
Sbet(m**2/kg)	21196.3
r**2(fit)	0.999855
uFOG(kg/kg)	0.049994

Hardened cement paste

Hardened cement paste	
Dmol(m)	3E-10
dl(kg/m3)	1.00E+03
ds(kg/m3)	2600
cp(porosity)	0.4
uMAX(kg/kg)	0.256

Hardened cement paste (HCP)	Desorption
Q(fit)	3.65517
M(fit)	3.13793
P(fit)	8.96552
C(BET)	284.718
uUNI(BET)(kg/kg)	0.033661
Sbet(m**2/kg)	112204
r**2(fit)	0.996312
uFOG(kg/kg)	0.228664

9. Literature

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