Application of water vapor sorption measurements for porosity characterization of hardened cement pastes

CrossMark

Min Wu [a,*], Björn Johannesson [a], Mette Geiker [b]

[a] Department of Civil Engineering, Building 118, Technical University of Denmark, 2800 Lyngby, Denmark
[b] Department of Structural Engineering, Norwegian University of Science and Technology, Trondheim, Norway

HIGHLIGHTS

- Important factors influencing the sorption data analysis are reviewed.
- Water vapor sorption studies are applied to cement pastes and MCM-41.
- The specific surface area results depend on the considered adsorption equation.
- Pore size distribution curves derived from both sorption isotherms are compared.
- The network theory can be used to explain some of results.

ARTICLE INFO

ABSTRACT

Water vapor sorption can be used to study important properties of porous materials including specific surface area and pore size distribution (PSD). However, the data analysis is somewhat inconsistent in literature. In this work, the important factors influencing the analyzed results using sorption data were reviewed. Water vapor sorption measurements were then applied to two hardened cement pastes and one model porous material MCM-41. The specific surface area was calculated based on different equations accounting for multilayer adsorption and the PSD was analyzed from both the absorption and the desorption isotherms for comparison. The calculated specific surface area was quite dependent on which equation is considered for multilayer adsorption. For the studied hardened cement pastes, three characteristic peaks were found in the calculated PSD curves from the desorption isotherms with corresponding radii of 1.4, 1.8 and 3.0 nm while the peak at 1.4 nm was missing in the PSD curves calculated from the absorption isotherm. The network theory, suggesting desorption is controlled by the pore entry sizes while absorption is controlled by the interior pore sizes, can be used to explain some of the results.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Porosity is one of the most important characteristics of cement based materials. Vapor sorption measurement has been widely used to determine the specific surface area and the pore size distribution of porous materials [1,2]. The calculation of specific surface area is normally based on the classical BET theory [3]. With respect to the pore size distribution, the method proposed by Barret, Joyner and Halenda (the BJH model) [4] is widely adopted. The BJH model is based on the assumption that there are two types of liquid existing simultaneously in the pores of a material due to different binding mechanisms, i.e., adsorption and capillary condensation. This assumption allows the determination of the pore size distribution for pores in the meso-size and micro-size range (following the classification of International Union of Pure and Applied Chemistry (IUPAC) [2]). For clarification purpose, a note is made here about the terminology "adsorption" and "absorption". In many cases, e.g., see [2], "adsorption" is used in describing the process of the liquid uptake, including both the adsorbed and the capillary condensed liquid. Other authors, e.g., see [5,6], use "absorption" to describe exactly the same content, i.e., including both types of liquid uptake. Since the BJH model will be used throughout this study and to avoid any confusion, the expression "absorption" will be used to describe the combined effect of both multilayer adsorption and capillary condensation while "adsorption" simply refers to the liquid fixed due to multilayer adsorption.

Sorption measurement using nitrogen is perhaps the most common technique adopted in the context of porosity characterization, e.g., see [1,7,8]. However, a comparison study performed by

Hagymassy et al. [9] using both nitrogen and water vapor in characterizing hardened cement pasts demonstrated that both the total calculated pore volume and the calculated surface area using water vapor data are much larger than that using nitrogen data. The main reason was explained by the fact that nitrogen cannot penetrate into the entire pore system of hardened cement pastes due to the relatively big molecular size. It was, further, pointed out by the same authors that the use of nitrogen will result in that not only the smallest pores but also many big pores, the so-called ink-bottle pores with small entry (or neck) sizes but big interior sizes, are left out of consideration in the measurement using nitrogen. That is the smallest pore entries constraint the penetration of nitrogen molecules into the body of ink-bottle pores. Consequently, the pore structure analysis using nitrogen was concluded to be of little value in studying the hardened cement pastes. As the main purpose of this work is to study hardened cement pastes, water vapor is considered more suitable than nitrogen in the context of the porosity characterization. Another reason for using water vapor in studying cement based materials is that the pre-drying of the samples can be avoided compared with that using nitrogen since the drying process in some cases results in certain alteration of the pore structure of hardened cement pastes [10].

Sorption behavior of water vapor on porous materials can be used to study important characteristics of the materials, e.g., the specific surface area and the pore size distribution. As an indirect method, some important factors which influence the analyzed results using sorption data need to be considered.

1.1. Equations accounting for multilayer adsorption

The calculation of the specific surface area is based on the equation considered for multilayer adsorption. A number of equations have been developed and the most representative ones are discussed as follows.

The first sound theoretical development of the relation between the amount of adsorbed vapor and the relative pressure under equilibrium is attributed to Langmuir [11]. However, the limitation of the Langmuir model is that adsorption is restricted to the monolayer. A major step in the understanding of adsorption is the development of the BET multilayer adsorption theory [3]. After the development of the BET theory, a number of adsorption equations have been developed using the similar concepts. However, the standard BET equation remains the most important one. The standard BET equation is

$$\frac{v}{v_m} = \frac{cx}{(1-x)(1+cx-x)} \tag{1}$$

where v is the adsorbed moisture content (in the case of water vapor), v_m is the so-called monolayer capacity (the moisture content corresponding to that the first layer of the material surface is fully occupied), c is a constant related to the energy of adsorption and x is the relative pressure (humidity). To derive the standard BET equation, it is assumed that only the molecules in the first layer have a condensation heat that is different from that of the bulk water and that the heat of condensation in the second and higher adsorbed layers are equal, which is the same as the heat of liquefaction [3,12]. Johannesson [13] further studied the assumption regarding the heat of condensation, the assumption being modified so that both the condensation heat of the water molecules on the first layer and second layer are different from that of the normal bulk water while the water molecules on the third and higher layers have the same condensation heat as that of bulk water. By introducing this new assumption and combining other assumptions which are also made in obtaining the standard BET equation, a new equation, designated as the two-layer BET equation, can be obtained as

$$\frac{v}{v_m} = \frac{cx[1+(b-1)(2x-x^2)]}{(1-x)[cx^2(b-1)+(c-1)x+1]} \tag{2}$$

where there is one more constant parameter b accounting for the modified assumption concerning the condensation heat compared with the standard BET equation. With the help of a so-called sorption calorimeter [14,15], it is possible to study the assumptions regarding the heat of condensation of the water on different layers. Johannesson [13] conducted detailed studies by comparing the measured differential heat of adsorption and the predicted value based on the standard BET equation and the two-layer BET equation for different porous materials. The results showed a better agreement between the measured differential heat of adsorption and the value predicted based on two-layer BET equation compared with that obtained by using the standard BET equation. It was concluded that the assumptions about heat of condensation behind the two-layer BET equation is more adequate compared with that using the standard BET equation.

Guggenheim [16], Anderson [17] and de Boer [18] modified the standard BET equation by assuming that the heat of condensation of the water molecules on the second and all the higher layers are the same, but different from that of bulk water, and a good agreement was found between the experimental data and the modified equation on different tested adsorbates. The modified equation is the so called GAB equation [19], which is

$$\frac{v}{v_m} = \frac{ckx}{(1-kx)[1+(c-1)kx]} \tag{3}$$

Similar to the two-layer BET equation, there is one more constant, k, as compared to the standard BET equation. The property k is related to the modified assumption about the condensation heat compared with the standard BET equation.

Dent [20,21] conducted related studies and further discussed that the heat of condensation could actually differ for each layer, but the difference between the second and higher layers tends to be small. For simplicity, it was assumed that water molecules on the second and all the higher layers have the same condensation heat but different from that of bulk water. The Dent equation is based on the same principles as the GAB equation and also has the same mathematical form.

1.2. The thickness of the adsorbed layer

In order to calculate the pore size distribution according to the BJH model, it is necessary to know the thickness of the adsorbed layer. The BJH model assumes two types of water, i.e., the adsorbed water and the capillary condensed water [4]. However, the sorption measurement itself cannot distinguish the two types of water and only measures the total moisture content at a given relative humidity (RH). That is, the thickness of the adsorbed layer of water needs to be determined beforehand in the calculation of a pore size distribution.

It is often assumed that the statistical thickness of the adsorbed layer on a solid surface is a function of the relative humidity and this function is normally called the t-curve. The t-curve can be obtained by using the volume of the moisture adsorbed on the surface of an adsorbent divided by the surface area as

$$t = V_{ad}/S \tag{4}$$

where t is the statistical thickness of the adsorbed layer in m, V_{ad} is the adsorbed volume on the surface in m^3/g and S is the surface area in m^2/g. There is no direct means to obtain the exact surface area S of a studied material, and normally the BET specific surface area is used instead due to its wide application, e.g., see [22,23]. It should also be noted that there are some discussions on to which extent the BET specific surface area represents the true geometrical surface