



A study of the water vapor sorption isotherms of hardened cement pastes: Possible pore structure changes at low relative humidity and the impact of temperature on isotherms



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ABSTRACT

Using water vapor sorption isotherms measured by the “dynamic vapor sorption” (DVS) method, a resaturation study was conducted to investigate possible pore structure changes of hardened cement paste samples caused by the drying at low relative humidity during desorption measurements. The results indicate that either the relatively short term drying does not cause any microstructure changes or the pore structure of the hardened cement paste samples can be restored during the absorption process. Additionally, the temperature dependency of sorption isotherms was investigated using both hardened cement paste samples and a model material MCM-41. The pronounced impact of temperature on desorption isotherms of cement based materials as reported in literature was not found in this investigation. The results suggest that the differences between the sorption isotherms measured at different temperatures are mainly caused by the temperature dependent properties of water.

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1. Introduction

Water vapor sorption isotherms of a porous material are the graphic representation of the water content against the relative humidity (RH) of the environment at equilibrium condition, i.e., the RH inside of the material is equal to that of the external. Based on the determined water vapor isotherms, it is possible to derive important properties of the material under study. For hardened cement pastes, the properties including, e.g., the bulk porosity accessible to water vapor, the porosity and the amount of the hydration products—calcium silicate hydrate (C-S-H) gel, the specific surface area, the pore size distribution as well as the connectivity of the pores, can be studied [1,2]. Moreover, the transport properties, such as the permeability and the diffusion coefficients of the hardened paste can also be obtained from studying the sorption isotherms [3]. Additionally, the derived properties from the water vapor sorption isotherms are quite essential in the modeling of some important processes, e.g., moisture transport [3,4], drying shrinkage [5] and carbonation [6,7]. A clarification is made here about the terminology “adsorption” and “absorption”. In many cases, e.g., see [8], “adsorption” is used in describing the process of the liquid uptake, including both the adsorbed and the capillary condensed liquid. While some other authors, e.g., see [9,10], use “absorption” to describe exactly the same content, i.e., including both types of liquid uptake. In this work, the word “absorption” will be used to describe the combined effect of

both the adsorption and the capillary condensation while “adsorption” simply refers to the liquid fixed due to multilayer adsorption.

It has been reported in some studies, e.g., see [1,11–15], that changes of the pore structure of hardened cement paste samples can be expected during desorption measurements when the RH decreases to low values, e.g., below the RH of about 0.4. It has been argued by Jennings et al. [12–14] that drying below the RH at about 0.4 results into the restructuring, or more precisely the collapse of the low density (LD) C-S-H products. Additionally, it is argued in [12–14] that the loose-packed C-S-H will be converted into LD C-S-H at very low RHs. Based on a colloid description of the C-S-H structure, an explanation was proposed by the same authors, which is that the drying enhances the chemical aging, i.e., the increase of the polymerization degree of the silicate chains in the C-S-H particles over time. This kind of irreversible chemical aging will change the C-S-H particles into stiffer, stronger and denser ones. Baroghel-Bouny [1] studied the first and second desorption isotherms of several different hardened cement paste samples and concluded that microstructure changes occurred in some of the studied samples, represented by higher water contents measured during the second desorption isotherm in the low RH range (especially for RH between 0.33–0.12). Some other studies, e.g., in [11], reported that the pore structure of hardened cement paste samples was coarsened by the so-called drying effect at low RHs. Thus, it should be mentioned that for the same behavior of pore structure changes in this context, contradictory results have been reported, e.g., the results in [1] demonstrate the increase of small pores while that in [11] indicate the coarsening of the pore structure. Due to the instability caused by the drying involved in the desorption process, the first and the second desorption isotherm

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cycles have been studied rather extensively. It has been suggested that the second desorption is more stable and thus it should be more representative for a pore structure analysis [15]. However, based on some experimental evidence, Baroghel-Bouny [1] also pointed out that the microstructure changes of cement pastes caused by the drying at low RHs are reversible, which is different from the permanent changes as reported and discussed by Jennings et al. [12–14].

The influence of temperature on the sorption isotherms of cement based materials has been reported, e.g., in [16–21]. The absorption isotherms measured by Daian [19] between 20 °C and 55 °C demonstrated that the higher the temperature, the less the amount of the absorbed water at a certain RH. However, the differences between the absorption isotherms measured under different temperatures were rather small. Similar results were also reported in the study conducted by Radjy et al. [20]. The authors measured the absorption isotherms between 0 °C and 60 °C and the desorption isotherms between 0 °C and 40 °C on mature hardened cement paste samples, and the results showed hardly any temperature dependent property. Ishida et al. [21] investigated the absorption and desorption isotherms for an 80-day water cured hardened cement paste samples under 20 °C, 40 °C and 60 °C. Very limited differences were found in the absorption isotherms in that study, however, the differences in the desorption isotherms were found to be more pronounced. As the temperature increases, not only the amount of water adsorbed decreased but the shape of the isotherms was also concluded to be modified [21]. Similar behavior, i.e., rather significant differences of the desorption isotherms under different temperatures, was reported in [16–18]. The temperature dependence of sorption isotherms of cement based materials can be attributed to two different mechanisms [22,23]: (1) the coarsening of pore structure, e.g., ettringite dissolution and C-S-H alteration; and (2) the temperature dependence of water properties. Poyet et al. [16,17] pointed out that yet another factor may be involved in influencing the sorption isotherms at different temperatures. They assumed that the isotherm evolution is purely due to the so-called “thermal desorption”, which is to say that the shift of the adsorbed water content on the desorption isotherms at different temperatures is induced only by the temperature effect while the potential microstructure changes are considered as negligible. Based on these assumptions and the Clausius–Clapeyron formula, they developed a method to predict the desorption isotherms under different temperatures using a desorption isotherm measured at one temperature as a reference state. If the rather pronounced differences between desorption isotherms measured at different temperatures are due to the thermal effect as argued by, e.g., Poyet et al. [16,17], similar differences should be observed also on absorption curves measured at different temperatures while little difference is reported [16,17]. Since the reported results regarding the temperature dependent isotherms are not consistent for cement based materials, further exploration in this aspect is needed.

In the present work, possible changes of the pore structure of hardened cement paste samples at low RHs will be investigated through a resaturation method. Following a first desorption–absorption cycle, where the desorption goes down to $RH = 0$, the tested samples will be resaturated with distilled water. After that, a second desorption–absorption cycle will be conducted on the resaturated samples. In this way, the changes of the pore structure of the studied hardened cement paste samples at low RHs are expected to be observed by comparing the sorption isotherms of the first and the second cycle, if there is any. Moreover, the sorption isotherms will be measured under different temperatures to study important influencing factors with respect to the temperature dependence of the sorption isotherms of hardened cement pastes.

2. Experimental

2.1. Materials preparation

Three materials were studied in this investigation: one model porous material named MCM-41 and hardened cement pastes prepared

by two types of cement. By including the model material MCM-41, whose pore structure is considered stable during the studied temperature range (25–40 °C), it can provide reference information in the study of the temperature dependent isotherms in which the factor of the changing of pore structure caused by temperature can be excluded.

MCM-41 is a silica based material whose pore structure is in the form of hexagonal arrays of uniform tubular channels of controlled width, which is often used as a model material in porosity studies. The MCM-41 used in this study is produced by Tianjin Chemist Scientific Ltd. The information provided by the producer concerning the pore diameter, the specific surface area and the total pore volume is 3.0 nm, $\geq 800 \text{ m}^2/\text{g}$ and $\geq 0.70 \text{ ml/g}$, respectively.

CEM I 32.5 R and CEM III/B 42.5 N were the two types of cement used to prepare the paste samples, see Table 1. The W/C ratio for all cement paste samples was 0.4. The paste samples were mixed using a paddle mixer. After mixing, the pastes were cast into plastic vials with a diameter of about 15 mm and a length of about 50 mm followed by proper compaction. After the sealed curing at room temperature (about 20 °C) in the plastic vials for about one day, the hardened paste samples were demoulded. Then, each paste sample was placed into a slightly bigger plastic flask filled with saturated limewater to cure at room temperature until the desired age for experiments was reached. In the following description, the hardened cement pastes will be denoted as CEM I and CEM III.

The cement paste samples were cured for about 6 months before testing. Before sorption measurements, the prepared cylinder samples of the hardened cement pastes were vacuum saturated with saturated limewater and then the crushing and grinding of the samples was conducted in a carbon dioxide free chamber since very small sample size was needed (Section 2.2). To avoid possible drying during the process, the RH inside of the chamber was set at 1 (the measured RH was about 0.90–0.95) and the sample crushing and grinding was conducted rather quickly (in 30–40 min) for each paste. Immediately after that, the ground powder was placed into plastic flasks containing saturated limewater with the amount just to cover the powders (for about a week) before the sorption experiments. This procedure was also conducted in a carbon dioxide free chamber.

One concern with respect to the sample preparation of cement pastes is that the powder samples might not be fully saturated by submerging in limewater, even though a vacuum saturation was performed before the sample crushing. To check the saturation situation, powder samples were subjected to reduced pressure ($\sim 40 \text{ mbar}$) for about 3 h followed by 24 h of standing still. After that, the total (lime) water contents were determined. Compared with the samples submerged in limewater, the relative difference of the total (lime) water content was less than about 5%. In this sense, we think it is acceptable to submerge the powder samples in limewater for the purpose of sorption measurements.

Another concern is that drying might have already taken place during the sample preparation of cement pastes, even if special care was

Table 1
Properties and the chemical composition of the two cements used in this study.

		CEM I (CEM I 32.5 R)	CEM III (CEM III/B 42.5 N)
Density	(g/cm^3)	3.06	2.90
Fineness	(cm^2/g)	2905	4635
Water demand	(%)	26.2	32.3
Initial setting time	(min)	185	270
Loss on ignition	(%)	2.1	1.4
SiO ₂	(%)	20.6	29.2
Al ₂ O ₃	(%)	5.6	8.9
Fe ₂ O ₃	(%)	2.4	1.2
CaO	(%)	63.4	48.0
MgO	(%)	1.6	4.8
SO ₃	(%)	2.9	2.6
K ₂ O	(%)	0.7	0.6
Na ₂ O	(%)	0.2	0.2
Cl	(%)	<0.1	<0.1

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