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MICROGRAVIMETRIC MEASUREMENTS OF WATER VAPOUR SORPTION ON HYDRATED CEMENT PASTES

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ABSTRACT

To study the pore structure of hydrated cement pastes, differing in pretreatment and chemical composition, water vapour sorption experiments have been used. The experiments were carried out at 25.0°C in a pure water vapour atmosphere, up to relative vapour pressures of 0.98. The amount of water adsorbed or desorbed was determined gravimetrically using a Cahn 2000 microbalance. The set-up developed for this purpose and some experimental results are presented.

INTRODUCTION

It has been found (ref.1) that the shrinkage and creep behaviour of concrete, apart from the relative humidity, also depends on the type of cement that has been used. The shrinkage and creep behaviour of concrete largely depends on the mechanical properties of the hydrated cement paste which acts as the binding agent between the aggregate particles in the concrete.

Hydrated cement paste is a porous material mainly consisting of layered calcium silicate hydrates (CSH) of varying chemical composition. Because of the small dimensions of the hydrated products often the term CSH-gel is used. Under normal hygrical conditions the pores are more or less filled with water, depending on the relative humidity of the environment. It has also been found that the shrinkage and creep behaviour of hydrated cement pastes is affected by the presence and transport of water inside the pores (ref.2).

Therefore studies have been carried out to see if relations could be found between the microstructure and the mechanical behaviour of hydrated portland and portland-blastfurnace cement pastes. After performance of shrinkage and creep experiments at different relative humidities the pore structure of the various samples has been studied by means of water vapour sorption at 25.0°C. By using water as adsorbate, all the pores of importance in the shrinkage and creep processes were involved in the sorption measurements.

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EXPERIMENTAL SET-UP

The amount of adsorbed or desorbed water vapour was determined gravimetrically. Fig. 1 shows a schematic drawing of the set-up that has been developed for this purpose.

A Cahn 2000 microbalance is mounted in a glass vacuum bottle. The inside of the vacuum bottle and the hangdown tubes for sample and tare pans are coated with tinoxide. This transparent and conductive coating is electrically connected to the balance ground, to eliminate electrostatic charges.

The water vapour pressure inside the vacuum system is established by means of a small bulb, partially filled with bidistilled and outgassed water. By means of a programmable thermostat and a closed system in which ethanol is circulated, the temperature of the water in the bulb is varied between -24.8 and +24.7°C. In this way vapour pressures between 2 and 98% of the saturation vapour pressure of water at 25.0°C (3167 Pa) can be realized.

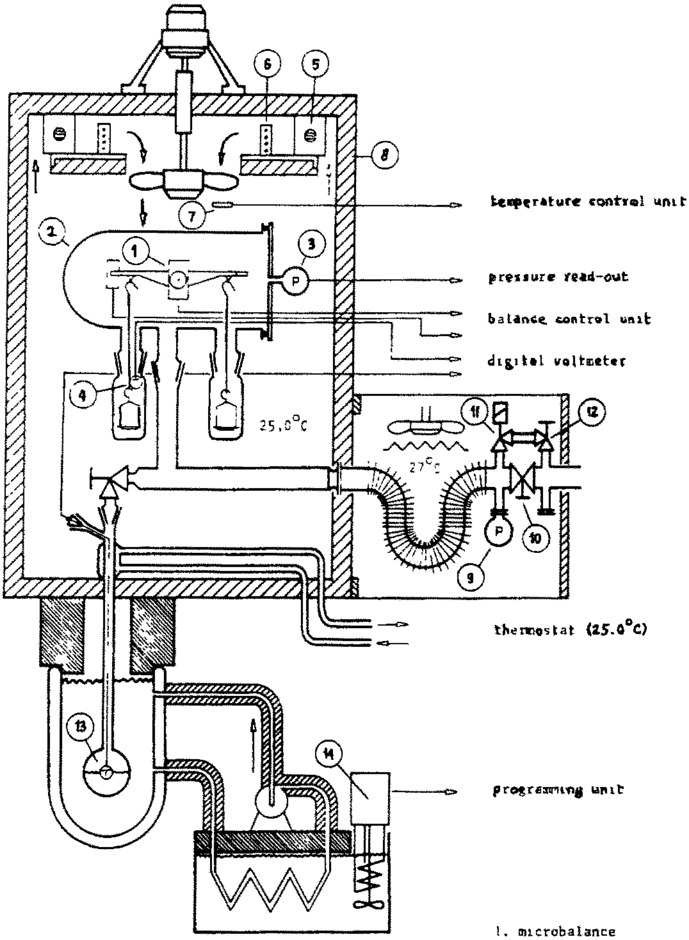
The samples were dried by immersing the bulb in a Dewar flask filled with dry ice and ethanol (-79°C). The saturation vapour pressure of water is then only 0.07 Pa. According to (ref.3) all the evaporable (not chemically combined) water is thus removed from the hydrated cement paste. In cement chemistry this procedure is known as D-drying. Saturation of a sample occurred at $p/p_0 = 0.98$, by keeping the temperature of the water in the bulb at 24.7°C.

Since no other vapours or gases are present, the total pressure in the vacuum system is identical to the saturation vapour pressure of the water in the bulb. It is measured with a Druck PDCR 110 W piezo-resistive pressure transducer, mounted in the lid of the vacuum bottle. This transducer is able to measure pressures up to 2×10^4 Pa with an accuracy of ± 2 Pa.

The temperature of the water in the bulb and the temperature near the sample are measured by means of thermocouples (iron-constantan) sealed in stainless steel housings.

The vacuum bottle and part of the vacuum system are housed in an isolated cabinet. The cabinet is thermostated at 25.0°C by means of an air-handling system fixed to the top. Because of the good temperature stability inside the cabinet, it was possible to achieve high relative vapour pressures (up to 0.99) without the appearance of condensation.

By means of a flexible metal tube the vacuum system is connected to a combination of an oil-diffusion pump and a rotary-vane vacuum pump. A set of valves is placed between the pumps and the system to control the pump rate.



1. microbalance
2. vacuum bottle
3. pressure transducer
4. thermocouple
5. cooler (water)
6. heater (kanthal wire)
7. temperature sensor
8. isolated cabinet
9. Pirani vacuum gauge
10. main valve
11. electromagnetic valve
12. variable leak valve
13. bulb for pressure control
14. programmable thermostat

Fig. 1: Schematic drawing of the sorption apparatus.

The part of the system outside the cabinet is surrounded by a plastic bag thermostated at 27°C. The whole experimental set-up was housed in a room, thermostated at 22°C. The experimental data like sample weight, water vapour pressure and the various temperatures were recorded with a data logging system and a multi- pen recorder.

EXPERIMENTAL RESULTS AND DISCUSSION

The isotherms obtained for one type of cement didnot show substantial differences due to the pretreatment of the samples (shrinkage or creep at three different relative humidities). Clear differences existed however in the course of the isotherms of portland cement samples (PC) and portland-blastfurnace samples (PBC). In the figures 2 and 3 representative examples of isotherms obtained with each type of hydrated cement paste, are shown.

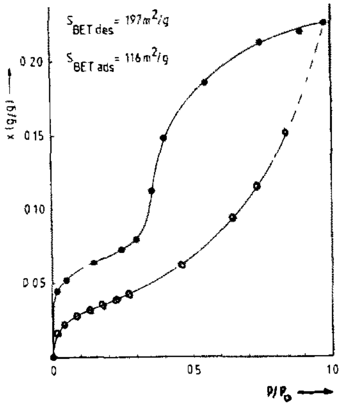


Fig.2 Water vapour sorption isotherm of hydrated PC paste after creep experiments at 75% R.H.

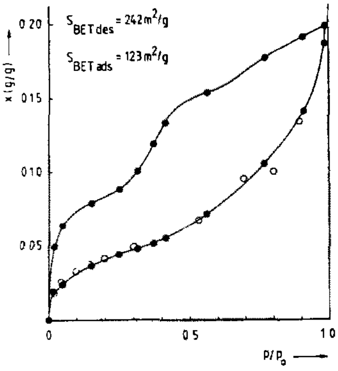


Fig.3 Water vapour sorption isotherm of hydrated PBC paste after creep experiments at 75%.

0: start = desorption

0: start = adsorption.

As can be seen the isotherms show remarkably large hysteresis loops, ranging down to $p/p_0 = 0$. This phenomenon was reported earlier by Krasilnikov (ref.4) and is caused by the different behaviour of the CSH-gel during adsorption and desorption experiments. Due to variations in the interlayer water content during water vapour sorption experiments, changes in the interlayer spacings of the cement gel occur (see Fig. 4).

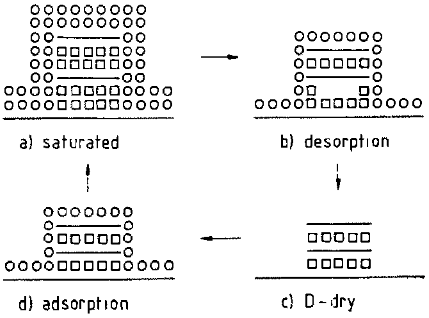


Fig. 4. Schematic representation of the CSH-gel structure at different stages during the water vapour sorption experiments.
0 = adsorbed water; ☐ = interlayer water; —— = layer of CSH.

During desorption experiments at first only capillary water will disappear from the pore structure. According to (ref.4) also part of the interlayer water will leave the CSH-structure for relative vapour pressures smaller than 0.35 (see Fig. 4b). When a sample is dried at a water vapour pressure of 0.07 Pa (D-dry), the situation presented in Fig. 4c may be obtained. Starting from this situation, increasing of the water vapour pressure will at first only result in the wetting of the outer surface of the gel (see Fig. 4d). Since the initial weights are recovered again (see Fig. 2 and 3) apparently at higher p/p_0 water is able to penetrate in the layered structure again. So during adsorption a kind of delayed reversible transport of water from the pores into the CSH-gel structure occurs. The large discrepancies in the BET surfaces when calculated from adsorption or the desorption branches (see Fig. 2 and 3) can also be explained by the phenomenon mentioned above.

Fig. 5 shows a general view of the pore size distributions of the various specimens examined. They have been obtained from the desorption branches down to $p/p_0 = 0.25$, using the Kelvin equation for cylindrical pores. Only minor differences exist in the pore size distributions of the various PC specimens. Obviously only small changes have occurred in the pore structure of the PC specimens due to the pretreatment. The same conclusion may be drawn for the PBC specimens tested at 75% R.H. However, clear differences exist between the pore size distributions of the PBC specimens and those of the PC specimens.

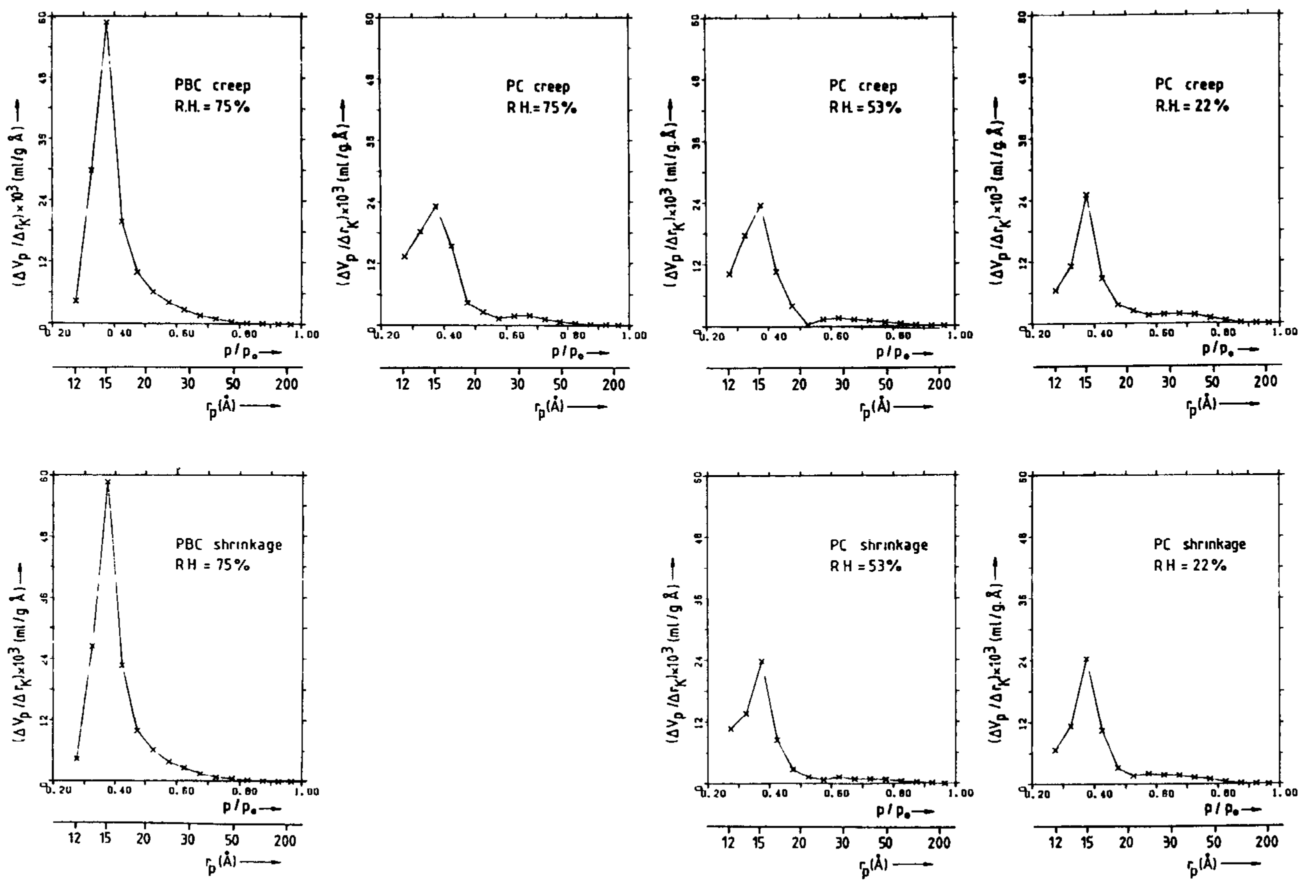


Fig. 5 Pore size distributions of the various samples.

The second much smaller peak at a pore radius of 35Å cannot be seen in the diagrams of the PBC specimens, while the peak at 15Å is much larger. Apparently in the PBC specimens a larger volume is present in the pores with radii between 12 and 20Å. This does not have to mean that also a larger surface area is present in this region. The great loss of water at p/p_o = 0.35 may also be caused by the presence of ink-bottle pores, having considerably smaller internal areas than cylindrical pores (with equal internal volumes).

The sharp knees in the desorption branches for $p/p_o < 0.1$ point to strong interaction between adsorbate and internal surface of the sample (large C_{BET} value) and may be attributed to the presence of micropores (ref.5). When micro- pores are present a plot of the volume adsorbed or desorbed against the layer thickness t usually shows a downward deviation for small t-values. This could not be observed for the specimens examined. However, a neat downward deviation of the V-t plot will only occur when no overlap occurs in the loss of mesopore and micropore water.

As already mentioned this is not the case for hydrated cement pastes.

Dubinin and Radushkevich (ref.6) developed a method to determine the micropore volume using the part of the isotherm at very low relative pressures ($p/p_o < 0.1$), where water is hardly present on the walls of the mesopores. According to them a plot of the logarithm of the weight adsorbed against $\log^2(p_o/p)$ should give a straight line (DR-plot) with intercept log W_o, where W_o is the weight adsorbed when the micropores are filled. From this the micropore volume can be calculated. In Fig. 6 the DR-plot of one PBC and one PC specimen are presented. The data for these plots have been taken from the desorption branches in the figures 2 and 3.

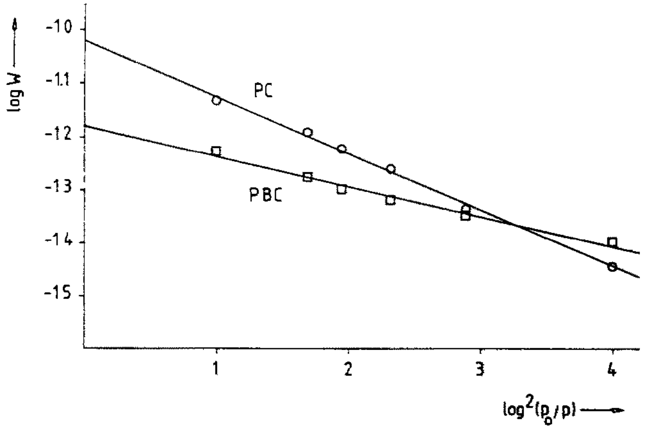


Fig. 6 DR-plots of specimens from Fig. 2 and 3.

As can be seen linear plots are obtained. The micropore volumes calculated from the intercepts on the log W axes are 0.096 ml/g for the PC and 0.066 ml/g for the PBC specimen. When these values are subtracted from the total water losses during the desorption experiments, the mesopore volumes are obtained. In this way a value of 0.103 ml/g is obtained for the PC and a value of 0.160 ml/g for the PBC mesopore volume.

It is unknown to what extend the above values are influenced by disturbing factors. In any case the values obtained for the micropore volumes are realistic, since the higher knee in the desorption isotherm of the PC specimen points to a larger micropore volume.

The mesopore volumes may also be calculated by addition of the volumes of the various groups of pores considered in the calculations of the pore size distributions. However, as already mentioned, at relative vapour pressures smaller than 0.35 capillary and interlayer water disappear simultaneously from the CSH-structure. Since in the calculations of the pore size distributions the volumes desorbed are exclusively attributed to capillary water, this will result in too large values calculated for the groups of pores considered. For the PBC specimens this even results in the fact that the total pore volume, calculated by addition of the volumes present in the various groups of pores, exceeds the total volume of water desorbed during an experiment. This, of course, is theoretically impossible. Although the effect will also play a part for the PC specimens the consequences there are less extreme, since a smaller volume is present in the pores that empty in the lower pressure region.

CONCLUSIONS

Although the use of water vapour sorption is the most obvious method to study the pore structure of hydrated cement pastes, in which during shrinkage and creep experiments transport of water occurs, this also causes some complications.

Due to the inhomogeneity of the hydration products and the different behaviour of the CSH-gel during adsorption and desorption experiments, current methods cannot always be used for interpretation of the isotherms. This prevents at this time, absolute judgements being given about the pore structures examined. However, with techniques, like for instance N.M.R. or I.R.-spectroscopy, it should be possible to study the amount and behaviour of the various types of water present in hydrated cement pastes during a sorption experiment. In that way more reliable data can be obtained about the pore structure.

For comparative studies of the pore systems of hydrated portland cement and portland-blastfurnace cement pastes water vapour sorption has proven to be an adequate method, simultaneously yielding additional information about the behaviour of the various types of water present in the samples.

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