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SUGGESTIONS FOR PORE MODELS ON THE BASIS OF GRAVIMETRIC SORPTION EXPERIMENTS*

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ABSTRACT

Using a microgravimetric apparatus water vapour adsorption isotherms at room temperature were measured. The resulting isotherms were reproducible; however, a noticeable hysteresis was observed, closing only at the zero point. No clear relationship could be found between the creep behaviour, isotherm shape and the microstructure of the specimens investigated. Based on these results a discussion of hysteresis mechanisms is presented.

INTRODUCTION

As reported at the preceding Microbalance Techniques Conference at Dijon (ref. 1) water vapour sorption measurements on hydrated cement pastes resulted in isotherms of a surprising shape, all being strictly reversible but exhibiting noticeable hysteresis loops extending to the zero point of relative pressure. On the other hand, no clear relationship could be found between the creep behaviour, isotherm shape and the microstructure of the specimens investigated. In the present paper filling and depletion mechanisms in pore systems are discussed.

EXPERIMENTAL

The investigation, already described in detail (ref. 2) deals with the relationship between the creep behaviour and the microstructure of hardened Portland and Portland-blastfurnace

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Fig. 1. General view of equipment for water vapour sorption experiments including a Cahn 2000 microbalance

cement pastes. At several relative humidities shrinkage and creep experiments have been performed with thin-walled hollow cylindrical specimens. The pore structure was determined by means of physical desorption and adsorption of water vapour at room temperature using a microgravimetric apparatus (Fig. 1). The silicate structure has been studied by means of trimethylsilyl derivatives made from the silicates present in the hydrated cement pastes, which were analyzed by gas-liquid chromatography.

RESULTS

The isotherms obtained with water vapour sorption on hydrated cement paste were of type H3 of the IUPAC classification (ref. 3). They were reproducible and showed large hysteresis loops, closing only at the zero point (Figs. 2,3). The time needed to reach equilibrium at each stage varied between 1 and 5 days.

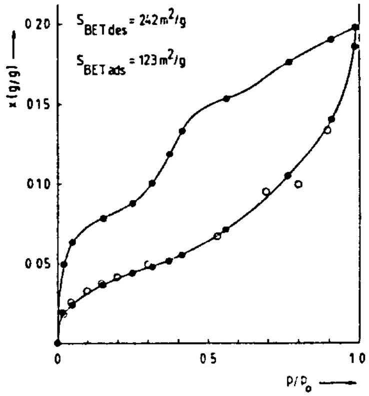


Fig. 2. Water vapour isotherm at 25°C of hydrated Portland cement paste after creep experiments at 75 % r.h.

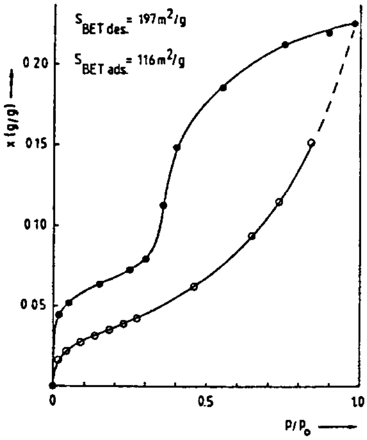


Fig. 3. Water vapour isotherm at 25°C of hydrated Portland blastfurnace cement paste after creep experiments at 75 % r.h.

Clear differences were found between both the pore structure (Fig. 4) and the silicate structure (ref. 2, p. 38) of hydrated Portland and Portland-blastfurnace cement pastes. The influence of relative humidity and pretreatment of the sample (shrinkage or creep) on the microstructure of the hydrated cement pastes appeared to be minor. No clear relation could be found between the creep behaviour, isotherm shape and microstructure of the specimens investigated.

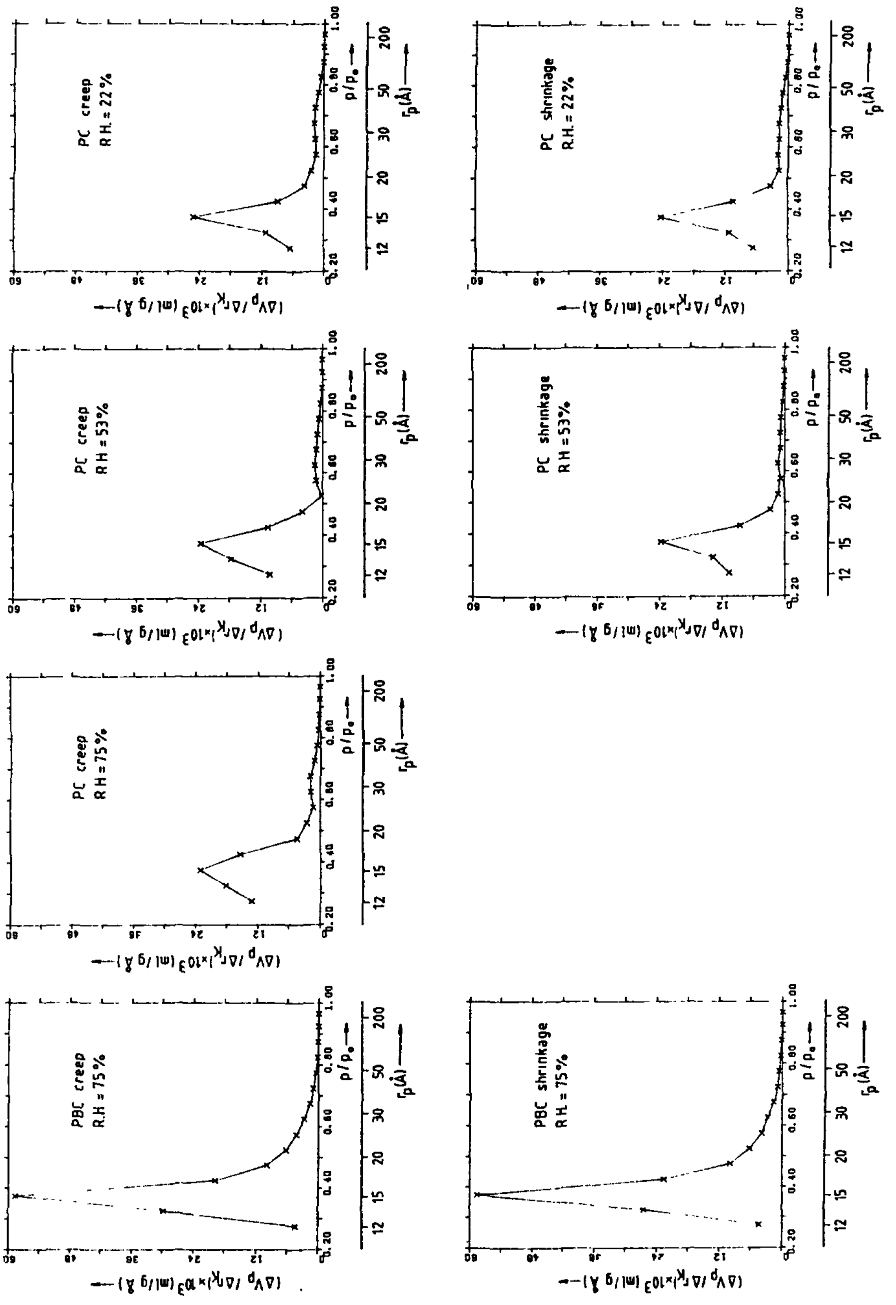


Fig. 4. Pore size distribution of hydrated PC and PBC specimens after shrinkage and creep experiments at 22, 53 and 75 % r.h.

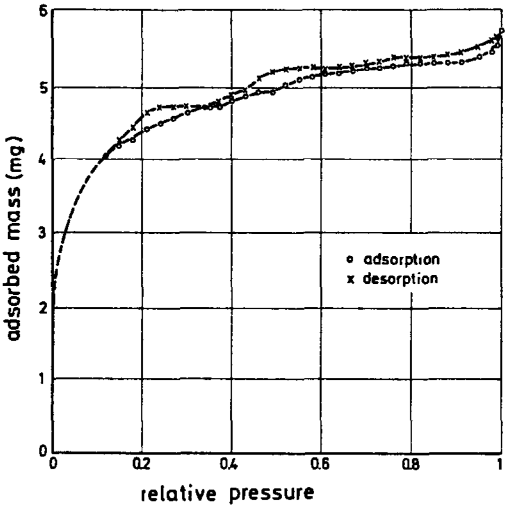


Fig. 5. Nitrogen isotherm at 77 K at polyacenoquinone pyrolysate

Hysteresis loops made up of the adsorption and the desorption branches of isotherms have been observed frequently with various adsorptives (ref. 4), also in the micropore region (Fig. 5, refs. 5,6). The occurrence of low pressure hysteresis in isotherms of hydrated cement pastes with several adsorptives, including water vapour, has also been reported before (refs. 7,8).

MODELS EXPLAINING HYSTERESIS

Two regions of the isotherm may be distinguished: the monolayer region and the multilayer region. Micropores can be defined as being able to contain up to three "layers" of molecules, one layer on each wall and one in between. These layers are bound more strongly than monolayers at the outer surface or in mesopores.

Monolayers in general exhibit a higher density than subsequent multilayers which can only be built up in meso- and macropores or at the outer surface. The phase of an adsorbed layer may deviate from that of the undisturbed bulk liquid (ref. 9). In the following discussion only wetting liquids or liquid-like adsorptives (contact angle < 90°) are considered.

Multilayer region

Within the multilayer region in macro- and micropores a meniscus is generated at the top of the liquid adsorbate. The radius of curvature is in equilibrium with the pressure of the adsorptive according to the Kelvin equation. This radius of

Fig. 6. Meniscus in a concave shaped pore

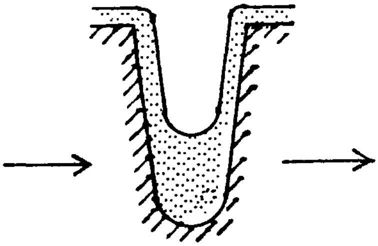


Fig. 7. Menisci in cylindric pores

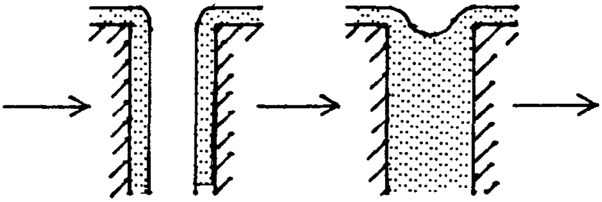
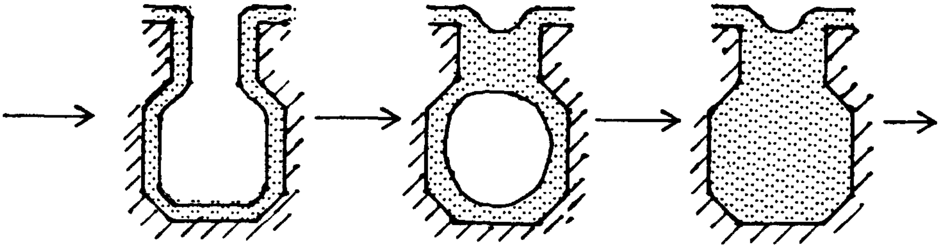


Fig. 8. Menisci in ink-bottle pores



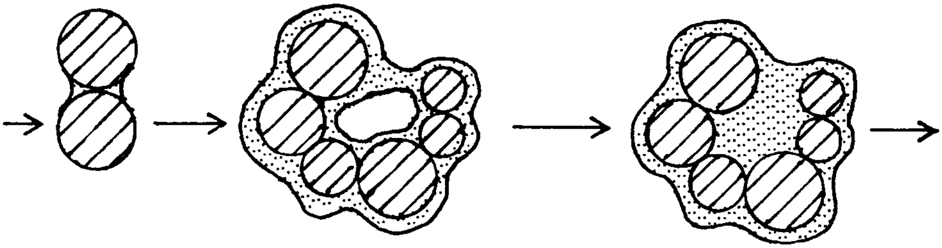


Fig. 9. Menisci in gussets between spheres and in sphere packing

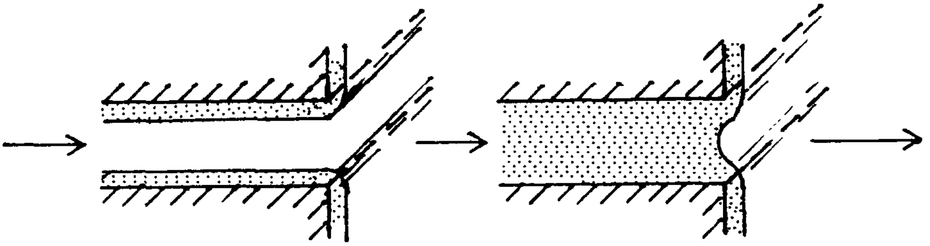


Fig. 10. Menisci in slit pores

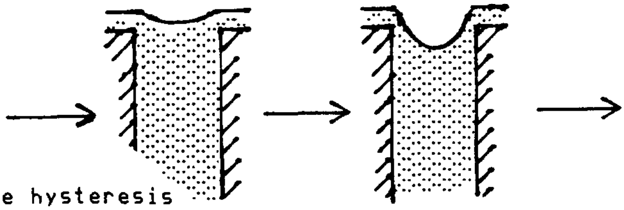


Fig. 11. Contact angle hysteresis

Fig. 12. Swelling

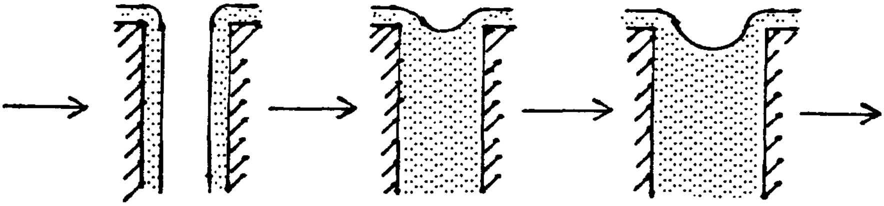


Fig. 6 - 12. Mesopore hysteresis effects.

curvature equals the core radius of the pore (radius measured to the adsorbate surface). The occurrence of hysteresis between adsorption and desorption branch of the isotherm may be due to the following effects:

a) In practically every pore the surface of the liquid adsorbate exhibits at least two stable radii of the meniscus at a given relative pressure, one connected to the adsorption process, the other to the desorption process, concave shaped pores excepted (Fig. 6). The situations with cylindrical pores and with ink-bottle pores are depicted in Figs. 7 and 8, respectively. Between adherent bodies a pore cannot be measured in this way, because there are two curvatures at the surface of the condensate, one of which is negative (ref. 10, Fig. 9). The packing of spheres, particles, fibres etc. itself exhibits a porous matrix which may behave like ink-bottle pores. With slit shaped pores between flat, parallel solid layers in the adsorption process the radius is infinite for an incomplete filled pore (Fig. 10).

b) In a filled pore a contact angle hysteresis takes place connected with a change of the curvature as a result of variations of the pressure of the adsorptive (Fig. 11). Receding and advancing contact angles may not represent equilibrium conditions.

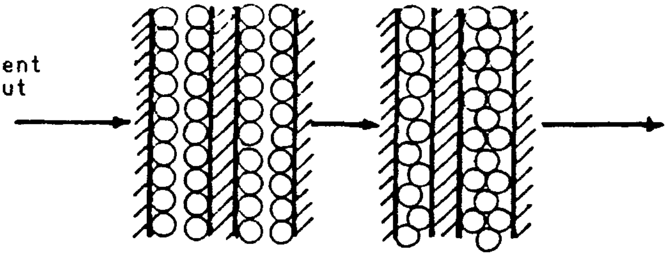


Fig. 13. Rearrangement of pore walls without swelling.

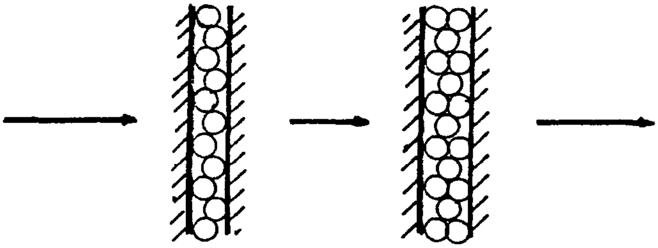


Fig. 14. Swelling.

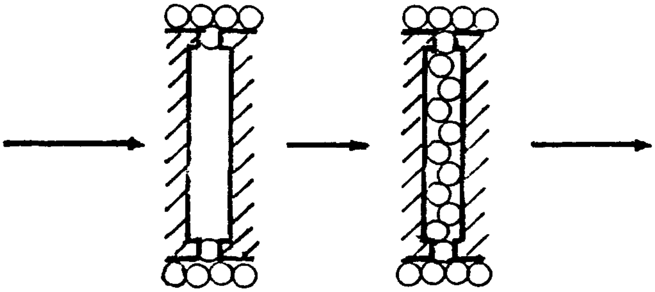


Fig. 15. Micropore blocking.

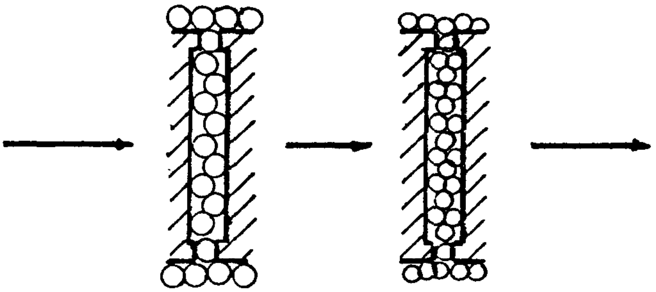


Fig. 16. Freezing of a "condensate".

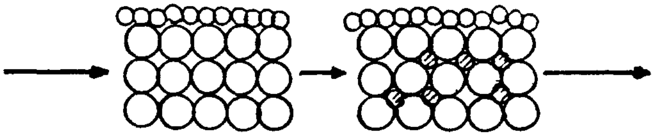


Fig. 17. Interstitial absorption.

Fig. 13 - 17. Micropore hysteresis effects.

c) Swelling of the matrix increases the pore volume (Fig. 12). Subsequently the pore width is altered.

Micropore region

In a micropore, a meniscus cannot be defined. With the exception of swelling, other mechanisms are responsible for the hysteresis effect. Therefore, mesopore hysteresis cannot extend to low relative pressures (for nitrogen p/p_0 <≈ 0.4), whereas a pronounced micropore hysteresis may cover the whole isotherm. The following processes in micropores can generate hysteresis:

d) Increase of the micropore volume due to rearrangement of pore walls within the micropore structure (Fig. 13) or to the detriment of the mesopore volume without increase of the sample volume.

e) Swelling to make space for a second or third interlayer (Fig. 14).

f) If at the entrance of a micropore an adsorption site of higher energy exists the pore may be blocked by the first molecule adsorbed (Fig. 15) and may be filled only at higher pressure, possibly in the mesopore range. By depleting the matrix by desorption leads to the reverse blocking effect taking place. Thus, in a network as exists e.g. in molecular sieves a pore blocking effect similar to that suggested by Doe and Haynes (ref. 11) for the mesopore region can occur.

g) As a result of phase transitions (e.g. freezing) or restoring processes a denser packing towards a lower energy level can be adjusted, e.g. in a zeolite structure (Fig. 16). The density of the adsorbate increases.

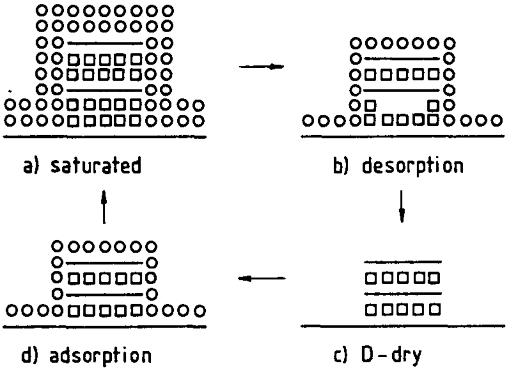
h) Interstitial absorption in the lattice (Fig. 17). This may be a slow diffusion process, and can give rise to the false impression of equilibrium in the adsorption measurement.

i) Weak chemisorption.

In the example of hydrated cement paste demonstrated at the last conference the penetration of water interlayers in the gel structure of calcium silicate hydrate, including a weak chemisorption process, was assumed (ref. 12, Fig. 18). Increase of the micropore volume can occur partly to the detriment of the mesopore volume. (In this case only small changes in the external dimensions of a sample will be observed).

As a consequence of the many possible reasons for the generation of a hysteresis loop made up of the adsorption and the desorption branch listed above, we hardly think that it will ever be possible to evaluate hysteresis effects quantitatively.

Fig. 18. Schematic representation of the CSH-gel structure at different stages during water sorption experiments.
ooo adsorbed water
□□□ interlayer water
—— layer of CSH



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