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Sorption of water on compacts of bottle-hydrated cement. I. The sorption and length-change isotherms.

Feldman, R. F.; Sereda, P. J.

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SORPTION OF WATER
ON COMPACTS OF BOTTLE-HYDRATED CEMENT
I. THE SORPTION AND LENGTH-CHANGE ISOTHERMS
II. THERMODYNAMIC CONSIDERATIONS AND THEORY OF
VOLUME CHANGE

BY

R. F. FELDMAN AND P. J. SEREDA

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SORPTION OF WATER ON COMPACTS OF BOTTLE-HYDRATED CEMENT. I. THE SORPTION AND LENGTH-CHANGE ISOTHERMS

By R. F. FELDMAN and P. J. SEREDA

To obtain information with regard to the porous structure of hydrated cement and the extent of its interaction with water, sorption and length-change isotherms were determined for this material.

Compacts of bottle-hydrated cement were brought to equilibrium in a high-vacuum system at various humidities, and measurements of the changes in length and weight during this process, were made to draw the isotherms.

Results showed that this system is basically similar to systems composed of other porous materials, although complicated by a discontinuity in the adsorption part of the cycle and a secondary hysteresis. It is considered that these characteristics are related and are the result of water associated with the system by a process other than physical adsorption.

It is also shown that menisci exist in the system on desorption to as low as 31% R.H. and cause considerable contraction. A surface-area calculation by a new method for estimating the zero adsorbed water yield a value of 80.6 m.²/g.

Introduction

In the past, sorption isotherms determined for a great variety of porous materials have yielded invaluable information about the physical state, surface area and pore sizes.¹ The usefulness of such isotherms needs no emphasis, especially when water is used as the adsorbate. Similarly length-change isotherms have been determined for a number of porous systems²⁻⁴ and these have been used to provide additional information concerning the interaction between adsorbent and adsorbate.

Although the shape of the isotherms gives some indication regarding the possible interaction between adsorbent and adsorbate, in cases such as the hydrated-cement-water system, the hydrates of cement begin to decompose as the water-vapour pressure is decreased to zero, so that it has not been possible by measuring weight loss alone to differentiate accurately between sorbed water and hydration water. Recently, however, it has been shown,⁵ that by incorporating length-change measurements with the sorption measurements at low vapour pressures, it is possible to locate the transition point between sorbed and hydration water.

Although a number of workers have reported results of sorption and length-change measurements on the hydrated-cement-water system,⁶⁻⁹ their results for the complete isotherm are difficult to interpret because of the rather arbitrary determination of the datum point (zero adsorbed water). Where length-change measurements were conducted, these usually involved only the first drying from the saturated state and seldom included the complete range of relative humidities for the adsorption and desorption cycle.

In the present work, results were obtained for the sorption and length-change isotherms by taking equilibrium points from relative vapour pressures (P/P_0) of 0.072 to 0.0982 on adsorption and 0.742 to 0.079 on desorption.

Experimental

Compacts formed at a load of 5000 lb. in a mould 1.25 in. dia. from bottle-hydrated cement paste were used to make the samples for these experiments. The procedure for making the compacts and the samples has been described previously.⁵ The sample of bottle-hydrated cement paste¹⁰ was obtained through the courtesy of the laboratories of the Portland Cement Association. The composition of the clinker is shown in Table I: it is a Type I cement. When hydrated in this way the cement paste remains as powder of less than 1 μ particle size; X-ray diffraction results on similar samples of bottle-hydrated cements indicated, within the accuracy possible, that after 90 days' hydration, the clinker was completely hydrated.¹¹

Previous work with compacts of different materials has shown that these can be made reproducible (void fraction) and as they are no more than $\frac{1}{16}$ in. thick they attain equilibrium quickly. It is these desirable characteristics that prompted the use of compacts in the study of the properties of hydrated Portland cement paste. Results obtained with compacts of other materials also confirm that compacts of hydrated cement will be reasonably representative of normal hydrated paste having the same void fraction and similar pore sizes.

Apparatus

The high-vacuum apparatus used for this work was designed to expose 12 samples simultaneously for long periods to the same vapour pressure conditions, with exclusion of air. Six of these samples were mounted in individual tubes on quartz spirals of the McBain-Bakr type

Table I

Composition of cement clinker

Chemical composition		Calculated mineralogical composition and minor constituents	
Oxide	% by wt.	Compound	% by wt.
SiO ₂	21.5	C ₃ S	44.5
CaO	64.0	C ₂ S	28.0
Al ₂ O ₃	6.4	C ₃ A	13.2
Fe ₂ O ₃	2.3	C ₄ AF	6.8
MgO	2.6	CaSO ₄	3.1
SO ₃	1.8	Free CaO	0.3
		MgO	2.6
		Na ₂ O	0.12
		K ₂ O	0.13
		CO ₂	1.8

and gave values of the weight changes to a sensitivity of 2.6×10^{-5} g. The remaining six samples were mounted on modified Tuckerman optical extensometers and placed in individual cells equipped with optical windows.¹² This determined the dimensional changes with changes in vapour pressure to a sensitivity of 2×10^{-6} in./in.

A three-stage oil diffusion pump backed by a rotary vacuum pump was used to obtain pressures of 10^{-6} mm. The adsorbate was introduced into the system from a bulb immersed in a bath that could be controlled at temperatures between 0° and 70°F within 0.1°F. The samples were maintained at 70°F by immersing the lower ends of the tubes and cells containing the samples to a depth of 12 in. in a controlled bath. Room temperature was controlled at $73 \pm 1^\circ\text{F}$.

Procedure

The samples measuring about $1\frac{1}{8} \times \frac{3}{8} \times \frac{1}{16}$ in. were cut from the compact and mounted, one on the extensometer and the other on the quartz spiral. Degassing of the samples was achieved by evacuating simultaneously through a manifold. A dry-ice trap was used together with the three-stage diffusion and rotary pumps and the degassing continued for 8 days.

Adsorption was effected by allowing the manifold to attain a R.H. of 7.2% by the control of the temperature of the bath in which the water source was immersed, and exposing the samples simultaneously to this humidity. This procedure was continued for equilibrium points up to 98.2% R.H. Three days were allowed for equilibrium to be attained between points below 25% R.H. and up to 7 days for points at higher humidities. Fifteen h. of constant weight always elapsed before the system was considered to be in equilibrium. The desorption procedure followed in the same manner, approximately 7 days being allowed for equilibrium between points. A total time of 4 months was taken for the determination of the whole isotherm.

Results

Adsorption

Fig. 1 shows the complete isotherm. Actual results are given in Table II. Point A represents the point to which the sample had been dried after 8 day's evacuation; point B

Table II

Length changes and moisture contents in calculation of adsorption isotherm

Adsorption			Desorption		
P/P ₀	Moisture, %	Length change, %	P/P ₀	Moisture, %	Length change, %
0.0723	1.42	0.0808	0.742	10.25	0.344
0.0882	1.60	0.0892	0.608	9.30	0.313
0.137	1.94	0.111	0.492	8.35	0.280
0.176	2.15	0.123	0.419	7.70	0.271
0.210	2.36	0.136	0.358	6.97	0.261
0.255	2.69	0.151	0.329	5.87	0.261
0.316	3.24	0.183	0.316	5.19	0.261
0.371	3.67	0.215	0.284	4.82	0.256
0.437	4.17	0.243	0.177	4.10	0.234
0.494	4.52	0.261	0.122	3.64	0.210
0.571	5.28	0.285	0.093	3.16	0.186
0.709	6.71	0.317	0.079	2.99	0.177
0.873	9.78	0.349	0	2.10	0.132
0.982	12.58	0.366			

represents the datum point,⁵ and is considered henceforth as the true point for zero adsorbed water. The adsorption curve is smooth and concave to the pressure axis until point C is reached; here a distinct discontinuity occurs, and this is at R.H. between 23 and 25%. The curve then becomes concave again until 50% R.H. is reached, when the isotherm behaves like a normal Type-II or Type-IV isotherm.¹

Fig. 2 presents the results for the dimensional change as a function of relative humidity. A, B, C, etc. represent the equivalent points as on Fig. 1. The curve is again concave to the pressure axis between B and C, and at C the discontinuity again occurs in an even more distinct form than is shown in the sorption curve. Above approximately 35% R.H., the curve continues concave to the pressure axis up to 98.2% R.H.

Fig. 1. Sorption isotherm for compact of hydrated cement
○ adsorption points ● desorption points

Fig. 2. Length change isotherm for compact of hydrated cement
○ adsorption points ● desorption points

Desorption

On Fig. 1, a gradual weight loss is shown from D to E for the desorption curve, a large primary hysteresis being apparent. Beyond E, however, at R.H. 35.8%, a large weight loss occurs; this continues until F is reached between 30 and 31% R.H. Desorption continues at lower humidities between F and G in a similar manner as the corresponding adsorption part of the loop BC. G is the datum point, the point for zero adsorbed water located for the desorption curve. A secondary hysteresis, the non-rejoining of the loop after primary hysteresis, is apparent. Continued degassing produces finally point J, which is slightly below B, the zero point for the adsorption part of the cycle. Length changes (Fig. 2) show a continual contraction between D and E, but between E and F where a large weight loss occurred, there was no change in length. From F to G contraction again occurred, producing a curve similar to the adsorption curve, concave to the pressure axis. Point J is considerably below point B. In this length-change isotherm then, the primary and secondary hysteresis are again exhibited and the points G and B are apart.

Once the length change and sorption equilibrium points with respect to vapour pressure are established, the most useful relationship in terms of interpreting data is the weight change ($\Delta W/W$) vs length change ($\Delta l/l$) plot, shown in Figs. 3(a) and 3(b). Again A, B and C represent the same points as on Figs. 1 and 2. Here AB is drawn linear, as discussed in a previous paper.⁵ Continuing from B, it is observed that the plot is linear beyond C. This linearity occurs up to approximately 30% R.H., after which an increase of slope occurs. This increase in slope is well illustrated in Fig. 3(b), which is an enlarged section of Fig. 3(a). It is observed that this region is where the discontinuity and change in slope occurred (Figs. 1 and 2). After approximately 50% R.H., the slope of the curve decreases continually as D is approached. The region DE, where weight loss occurs somewhat gradually with relative pressure, shows a very great contraction for unit weight loss. This is the region of primary hysteresis and is greatly emphasised by this plot. EF, the region where the primary hysteresis is completed, shows no length change. A careful study of the primary hysteresis in other materials^{2, 3, 13} has produced similar results. The large contraction in the primary hysteresis region DE is explained by the formation of menisci in the pores which imposes a compressive stress on the material. When these menisci

Fig. 3(a). Plot of length change arising from sorption on compact of hydrated cement (b). Enlarged section of plot in Figure 3(a)

- adsorption equilibrium points
- desorption equilibrium points
- desorption dynamic points

empty, the stress is released and the sharp rate of contraction halted. In some materials an expansion actually occurs.^{2, 3, 13} In this system there is a constant length as shown along EF. Along FG surface desorption continues; between 20% R.H. and zero adsorbed water at G, the curve is linear, the slope of the line being only slightly less than BC for adsorption. Thus in the region EF there is a balance of forces: contraction due to a reduction in spreading pressure of the adsorbed film and expansion due to the relief of the compressive stress of the menisci. The measurements of length change thus verify that the loss of water between EF is the emptying of pores and that this process finishes between 30 and 31% R.H.

Despite the large secondary hysteresis as observed in Figs. 1 and 2, the plot of $(\Delta l/l)$ vs $(\Delta W/W)$ in Figs. 3(a) and 3(b) might be misleading and taken to indicate that the loop is re-joined. This is not the case; the two zero points B and G, for the respective adsorption and desorption regions of the loop, are considerably displaced, as shown in Figs. 1 and 2. When the desorption is continued, however, until the $(\Delta W/W)$ is equal to that at B, approximately at point J, it is seen that the length is considerably below that at point B, by 0.094%. Thus, during this adsorption-desorption cycle, or first rewetting-second drying cycle, an irreversible shrinkage has taken place. The slope of the curve $(\Delta l/l)/(\Delta W/W)$ during desorption from G to J is greater than the slope from F to G and both curves have linear portions.⁵

Surface area calculation

Computation of the surface area by the B.E.T. method,¹ assuming the water molecule to occupy an area of $10.8 \text{ \AA}^2$, yields a value of $80.6 \text{ m}^2/\text{g}$. V_m , the weight of adsorbate required to complete one monolayer, was at R.H. 18.5%. To avoid using the part of the sorption isotherm in the region where the discontinuity occurred, the B.E.T. calculation was only applied in the R.H. range up to 21.0%.

Pore-size distribution calculation

Pore-size distribution was calculated by means of a modified form of the Kelvin equation,

$$R_i = \frac{2\sigma M}{RT \cdot \ln P_0/p} + t \dots\dots\dots (1)$$

where it is assumed that the adsorbate completely wets the solid and that on any point on the desorption isotherm all pores have an adsorbed film of thickness t , which may vary with pressure of adsorbate p . σ is the surface tension of water and M its molecular weight. All pores smaller than radius R_i are completely filled by adsorbed water, and for a filled pore with a radius of R_i , the meniscus is assumed to have a radius of $(R_i - t)$. The value of the thickness of the adsorbed layer t as a function of pressure was estimated from the adsorption isotherm and it was assumed that the thickness of the strongly adsorbed layer does not exceed two molecular diameters. Equation (1) was applied to the desorption curve from the isotherm for R.H. values between 30 and 95%. This distribution is shown in Fig. 4, a cumulative plot of pore volume vs pore radius. All pores smaller than radius R_i are completely filled by adsorbed water. This pore distribution extends down to a pore radius of 12.2 Å, with 65% of the pore volume being composed of pores smaller than 30 Å radius.

Fig. 4. Plot of pore-size distribution

Discussion

It should be emphasised that the results presented here apply to one sample of bottle-hydrated cement formed into rigid samples by compaction. Direct comparison of these results of other workers who have used normally hydrated cement paste is not possible because the two systems are different. It is considered, however, that any of the fundamental conclusions will apply to both systems.

The results of this work show that the sorption length change relationships are basically similar to those of other porous materials; a large proportion of the length changes occur in the low vapour-pressure region of the isotherm. The $(\Delta l/l)$ vs $(\Delta W/W)$ plot for adsorption is linear for 1–2 molecular layers and can be extrapolated through zero; a decrease in slope occurs at higher humidities. These results were also observed for the adsorption of water on Vycor glass,² 'Cab-O-Sil' silica and precipitated calcium carbonate,³ and calcium sulphate hemihydrate.⁴ This indicates that volume change in the system of hydrated cement is associated with the sorbed water and is not due solely to movement of water in to or out of the crystal lattice as has been suggested.⁹

The adsorption part of the loop is complicated by the discontinuity at C. Beyond C, which occurs at approximately 25% R.H., the increase in slope of the $(\Delta l/l)$ vs $(\Delta W/W)$ plot indicates that another process is taking place by which sorption has occurred, producing a different relationship between $(\Delta l/l)$ and $(\Delta W/W)$.

The points representing zero adsorbed water, G and B, (Figs. 1, 2 and 3a) for the desorption and adsorption parts of the loop do not coincide, although the $(\Delta l/l)$ vs $(\Delta W/W)$ plot for the desorption below 20% R.H. is again linear, and its slope is only slightly less steep than that for the corresponding adsorption region. The separation of G and B illustrates the secondary hysteresis, where the adsorption and desorption parts of the loop do not coincide in the region

below 30% R.H. where the primary hysteresis ends. In order that point B may again be attained to complete the cycle (Figs. 1 and 2) further degassing of the system is required. This is shown as GJ on Figs. 1, 2 and 3(a). The $(\Delta l/l)$ vs $(\Delta W/W)$ plot of GJ indicates a linear path but of steeper slope than that of BC or GF. Point G, the transition point between the two linear portions, has been considered as the point of zero adsorbed water for the desorption part of the cycle. Thus the water represented by GB (Fig. 1) has been irreversibly sorbed during the sorption cycle. It is considered that there is a relation between the water lost between GB and the sorbed water which resulted in the discontinuity at C. This will be discussed further in a later paper.

Desorption along DE (Figs. 1, 2 and 3a) gives evidence of contraction due to compressive menisci forces, where a large primary hysteresis is observed. Along EF these menisci are emptying; from Fig. 3, it is seen that all the capillaries have not emptied until approximately 30–31% R.H. has been reached. The pore-size distribution calculated from this desorption isotherm yields a result that places most of the pores between 12 and 14 Å radius. As yet it has not been observed that the primary hysteresis extends to such a low relative humidity for normally hydrated cement. Thus the computed pore radius for this system is somewhat smaller than has previously been reported for normally hydrated cement,¹⁴ where it was suggested that the primary hysteresis extended to 40–45% R.H. It was also considered that a water column under tension in a capillary cannot exist under a tension greater than approximately 1000 atmospheres. This condition is surpassed at 45% R.H. Work on the adsorption of water on other porous materials, however, has shown capillary condensation at even lower relative humidities.^{3,15}

Conclusions

(1) Surface area calculations by the B.E.T. method from results obtained with the new method for determining adsorbed water has yielded a figure of 80.6 m.²/g., but when the value for evaporable water determined by the conventional method of drying a powdered sample is used, a surface area of 141 m.²/g. was found. This difference is large and points out the significance of the new method for determining adsorbed water. It is evident that the bottle-hydrated cement used in this work is in fact different, from the standpoint of surface area at least, from normal hydrated paste for which other workers have given a surface area of about 220 m.²/g.

(2) A discontinuity in the adsorption part of the loop of the isotherm is observed at approximately 25% R.H. It is concluded that this is related to the secondary hysteresis, which is present in the adsorption-desorption cycle.

(3) A primary hysteresis exists down to approximately 30–31% R.H. and this produces a sharp contraction in the region where it exists due to compressive menisci forces.

(4) For both adsorption and desorption, a linear curve is obtained for the $(\Delta l/l)$ vs $(\Delta W/W)$ plot at low humidities, and can be extrapolated through zero. This is similar to results for other porous materials and is considered due to physical adsorption.

(5) A significant portion of the expansion during sorption takes place in the low relative pressure region. A total of approximately 0.36% occurs between R.H. 0 and 98.2%.

Summary

A compact of bottle-hydrated cement was fabricated at a load of 5000 lb. in a mould 1.250 in. dia., and sorption and length change isotherms were obtained by measuring equilibrium points between 7.2 and 98.2% R.H.

The results show that the sorption-length change relationship, i.e., the $(\Delta l/l)$ vs $(\Delta W/W)$ plot, is linear for one to two molecular layers and can be extrapolated through zero; at higher humidities a decrease in slope is observed. This is basically similar to the results for other porous materials and shows that volume change in the hydrated-cement-water system is associated with the sorbed water and not due solely to movement of water in to or out of the crystal lattice.

The adsorption part of the isotherm is complicated by a discontinuity at approx. 25% R.H. This discontinuity is considered to be the result of water associated with the system by a process other than physical adsorption. It is also thought to be related to the large secondary hysteresis observed on the desorption part of the isotherm. Supporting evidence for this is shown in the $(\Delta l/l)$ vs $(\Delta W/W)$ plot.

Evidence is shown in both the length change and sorption isotherms that a primary hysteresis exists to as low a humidity as 31%. Contraction in the region where this hysteresis is apparent is explained by compressive menisci forces.

A surface area calculation by the B.E.T. method using a datum point located from the $(\Delta l/l)$ vs $(\Delta W/W)$ plot as the point for zero adsorbed water yielded a figure of 80.6 m.²/g.

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National Research Council,
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Ottawa, 2,
Canada

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SORPTION OF WATER ON COMPACTS OF BOTTLE-HYDRATED CEMENT. II.* THERMODYNAMIC CONSIDERATIONS AND THEORY OF VOLUME CHANGE

By R. F. FELDMAN and P. J. SEREDA

In order that the hydrated-cement-water sorption may be adequately analysed, two thermodynamic processes connected with the material, encountered in adsorption, are discussed.

The B.E.T. surface area computed by the use of a modified form of the Gibbs adsorption equation, is found to be in close agreement with the value obtained by an experimental method of determining zero adsorbed water. The surface area calculated from the pore-size distribution is also in agreement with these values. It is found that over the range of vapour pressures from 0 to 25% the Gibbs adsorption and Bangham equations are obeyed.

Beyond 25% R.H. physical adsorption and the readmittance of the interlayer hydrate water of tricalcium silicate occur simultaneously. The secondary hysteresis observed in the sorption isotherm and other anomalies previously observed in the system are explained with these data.

Mechanisms of volume changes for the whole extent of the isotherm are presented; thermodynamic equations are applied to different regions of the isotherm to express the volume change and spreading force developed in the system during sorption. These are compared with those used in other volume-change mechanisms described for this system and the thermodynamic consistency of these is discussed. Calculations of Young's modulus from the above equations lead to the conclusion that the values obtained are for the individual elements of the body and that as such they will yield values larger than those obtained for the body as a whole.

* Part I: preceding paper.

Introduction

Sorption and length change isotherms for this system have been presented and discussed in the preceding paper.¹ Thermodynamically derived equations are now applied to these results and their significance discussed with respect to the fundamental theory.

In the interpretation of the results obtained it is recognised that cement gel as adsorbent is composed of very finely divided crystals. This finely divided system represents a state of unstable equilibrium, and it is apparent that the only thermodynamic stable state of the system is that of minimum surface energy in which the small particles have recrystallised to a single large unit. The thermodynamics of finely divided crystals is complicated by the fact that parts of even a single crystal are not, in general, in equilibrium with the whole; the rigidity of a crystal, which prevents the recrystallisation of the system, may also prevent internal adjustments essential to the equilibrium of the crystal.

In describing the thermodynamics of adsorption of a monodisperse liquid as adsorbent where the existence of complete equilibrium of the adsorbent in all parts of the system can be assumed, Copeland & Young² were able to ignore the non-equilibrium state inherent in a powdered adsorbent. A further work³ showed that an adequate understanding of a particular system involving a powdered adsorbent could be achieved when the thermodynamic functions for this system were defined as being equal to those in a process involving a monodisperse adsorbent in which true equilibrium could be achieved.

Analysis of the adsorption process

Two thermodynamic processes are considered:

The integral process

The differential process

In the integral process n_2 moles of adsorbate B are adsorbed on a finite amount n_1 of adsorbent A; the composition of the system is thus changing.

In the differential process, however, n_2 moles of B, the adsorbate, adsorb on an infinite amount of adsorbent A. The concentration is already n_2/n_1 moles of adsorbate for each n_1 mole of adsorbent. Thus the composition of B on A will remain constant.

If B is a nearly perfect gas, the free-energy change for the differential process is

$$\Delta G = n_2 RT \ln P/P_0 \dots\dots\dots(3)$$

where

P_0 is the saturated vapour pressure of the adsorbate B at the temperature T

and

P is the vapour pressure of the adsorbate B in the differential process.

In this differential process, it is noted that with constant composition of moles of B on A, P must also of course remain constant. This point will be brought up later.

For the integral process the Gibbs adsorption equation represents the decrease of surface free energy ($\Delta\gamma$) during the process. In this equation, where σ is the surface area of the adsorbent,

$$\Delta\gamma = \frac{RT}{\sigma} \int_0^P n_2/n_1 \cdot dP/P \dots\dots\dots(4)$$

It is assumed that the adsorbate is a perfect gas and that there is no alteration in surface area during the process, but the adsorbent-adsorbate surface energy changes during the process. Thus in the fundamental equation an extra term appears for the variation of the free energy of the "surface-phase" (that portion which comes under the influence of surface forces) compared with the equation for a homogeneous bulk phase. The concentration of adsorbate is given with respect to the surface area of the adsorbent.

Hydrated-cement-water system

The process of adsorption of water vapour on the surface of hydrated cement is an integral one and may be represented by the equation

Figs. 1 and 2 of an earlier paper¹ represent this process, showing sorbed water and length change as a function of the relative vapour pressure. By use of the Gibbs equation the decrease in free energy may be computed for the process as a function of coverage. For this calculation, however, the absolute values for the adsorbed water, i.e., the zero point for the adsorbed water versus relative vapour pressure plot, and the surface area are required. In another paper,⁴ an experimental method of determining the zero is described, and thus a surface area calculated by the B.E.T. method can be obtained.

The point for zero adsorbed water and the surface area can be predicted from the $\Delta W/W$ - $\Delta l/l$ relationships (Fig. 1) on primarily theoretical grounds. This method⁵ is based on the Gibbs equation and the Bangham equation.⁶ The latter considers the length change of an adsorbent during the adsorption process to be a measure of the surface free energy change.

$$\Delta l/l = k_1 \Delta \gamma \quad (6)$$

$\Delta \gamma$ is the surface energy change as determined by the Gibbs equation, $\Delta l/l$ the length change, and k is a constant related to the Young's modulus of a basic unit or crystal of the adsorbent. The relation is in effect an expression of Hooke's law as applied to tangential forces that have been imposed by the surface tension of the adsorbent. Because of the adsorption process the surface free energy is reduced and an expansion of the body that was subjected to the tangential stress occurs. When $\Delta \gamma$ is calculated by graphical integration for various points along the adsorption isotherm, and plotted against the corresponding length change, $\Delta l/l$, a straight line through the origin should result. The equation has been shown to apply for other adsorbent systems.^{5,7,8}

Fig. 1. Plot of length change versus water sorbed

The method of determining the zero point of hydrated cement for adsorbed water recognises the fact that at low humidities the processes of desorption and dehydration are likely to take place simultaneously. This makes it impossible on first consideration to estimate what portion of the water taken off is physically adsorbed; until this can be determined, the surface area of the hydrated cement cannot be calculated by the B.E.T. method.

Hydrated cement samples at approximately 7% R.H. may be considered as adsorbent with some adsorbed water present. If it were possible to remove this adsorbed water without decomposition of the hydrated cement, then the length change $\Delta l/l(A)$ resulting from the desorption of water $\Delta W/W(A)$ and the length change $\Delta l/l(H)$ from hydrated cement decomposition $\Delta W/W(H)$ would be known. Considering these length and weight changes as independent of one another we have the equations

* A mole of hydrated cement is a hypothetical quantity conceived mainly for use in the equations to achieve consistent use of units.

$$\Delta l/l(H) + \Delta l/l(A) = \Delta l/l(T) \dots\dots\dots(7)$$

$$\Delta W/W(H) + \Delta W/W(A) = \Delta W/W(T) \dots\dots\dots(8)$$

where $\Delta l/l(T)$ and $\Delta W/W(T)$ are the actual weight and length changes observed.

Since no decomposition of the hydrated cement takes place between approximately 7 and 25% R.H., this region, which is observed as linear on the $\Delta l/l$ vs $\Delta W/W$ plot (Fig. 1), is a relationship between $\Delta l/l(A)$ and $\Delta W/W(A)$. This same plot for other adsorbents, Vycor glass,⁷ precipitated CaCO_3 ,⁸ Cab-O-Sil silica,⁸ and calcium sulphate hemihydrate⁵ for low coverages from no adsorbed water to one or two molecular layers, shows a linear portion through the origin.

It may thus be concluded that if the linear portion is extrapolated backwards, this line will pass through the point where both $\Delta W/W(A)$ and $\Delta l/l(A)$ are zero. The residual $\Delta W/W(T)$ and $\Delta l/l(T)$ will be equal to $\Delta W/W(H)$ and $\Delta l/l(H)$ as may be seen from equations (7) and (8). Linearity may be expressed by the equation

$$\Delta l/l(A) = b \Delta W/W(A) \dots\dots\dots(9)$$

where b is a constant.

The zero point for $\Delta W/W(A)$ and $\Delta l/l(A)$ may then be found by a solution of equations (4), (6) and (9).

These equations result in

$$\left(\frac{b}{k_1}\right) \Delta W/W(A) = \frac{RT}{M\sigma} \int_0^P \Delta W/W(A) \cdot \frac{dP}{P} \dots\dots\dots(10)$$

Here σ ($\text{cm}^2/\text{g}.$), the surface area of the adsorbent, is also a function of $\Delta W/W(A)$ and thus of the pressure P of the adsorbate.

Equation (10) may be solved by a trial and error procedure; a point X on the extrapolated line (Fig. 1) is taken as zero and the B.E.T. area calculated. From this $\Delta\gamma$ can be calculated for several values of P and a plot against $\Delta l/l$ (or $\Delta W/W$) made; this did yield a straight line, but as shown in Figs. 2 and 3 it did not pass through the origin. The procedure was repeated until a straight line through the origin was obtained. Figs. 2 and 3 show plots of $\Delta l/l$ versus $\Delta\gamma$ and $\Delta W/W$ versus $\Delta\gamma$, respectively, for three cases in which the above calculation has been done. These three cases are located on Fig. 1 as X, Y and Z and are as follows:

Fig. 2. Plot of expansion as function of decrease in surface free energy

- plot with X as zero point (Fig. 1)
 - plot with Y as zero point (Fig. 1)
 - plot with Z as zero point (Fig. 1)
- (numerals on curves are P/P_0)

Fig. 3. Plot of decrease in surface free energy as function of coverage

- plot with X as zero point (Fig. 1)
 - plot with Y as zero point (Fig. 1)
 - plot with Z as zero point (Fig. 1)
- (numerals on curves are P/P_0)

Case (i) where the zero point, X, is taken such that the $\Delta W/W$ is greater than the practically obtained values by 1.54×10^{-2} g./g. This, as shown in Table I, results in a surface area of 118.8 m.²/g. and W_m is located at a P/P_0 ratio of 0.05. Figs. 2 and 3 show that a straight line up to P/P_0 0.25 is formed, but it cuts the $\Delta l/l$ and $\Delta W/W$ axes respectively at a considerable distance from zero.

Case (ii) where the zero point, Y, is taken at the experimentally obtained zero point. This results in a straight line that again cuts the axes, although much closer to the zero than in the last plot. The surface area value obtained is 80.6 m.²/g., W_m occurring at P/P_0 0.185.

Case (iii) where the zero point, Z, is taken such that $\Delta W/W$ is less by 0.46×10^{-2} g./g. than the experimentally obtained values. This results in a straight line through the origin, and the B.E.T. calculation yields a surface area of 73.1 m.²/g., W_m occurring at P/P_0 0.222.

Table I

Surface areas computed for different zero points

Zero point $\Delta W/W \times 100$ from transition point	W_m occurs at P/P_0	Surface area, m. ² /g.
-1.54	0.05	118.8
0	0.185	80.6
+0.46	0.222	73.1

Thus the theoretical zero point for adsorbed water is located at $+0.46 \times 10^{-2}$ g. of adsorbed water with respect to the experimentally obtained zero point and the surface area compares well with the experimentally obtained value. It may be observed that on moving the zero from X to Z (Fig. 1) the straight line plot in Figs. 2 and 3 tends to cut the axis with decreasing intercepts until at Z it passes through zero. If the zero had been taken even further along line XZ, the resultant line would cut the other axis. Point Z gives the unique solution for equation (10). It is true, however, that values for zero, determined both experimentally and theoretically, are not exactly the same; when the approximations in the whole procedure are considered, and as integration at low pressures cannot be too accurate unless adsorption data are obtained at very low pressure, the agreement must be considered excellent. The sorption curve between 0 and 7.2% R.H. was extrapolated and the value of $\Delta W/W$ for R.H. 2.5% taken from it, but the $\Delta l/l$ vs $\Delta \gamma$ plot was relatively insensitive to small changes in this extrapolation. It may thus be concluded that the behaviour of the hydrated-cement-water sorption system for the region of R.H. below 25% can be described by the Gibbs adsorption equation and equations (7), (8) and (10).

Sorption beyond the P/P_0 value of 0.25

When the plot of $\Delta l/l$ versus $\Delta \gamma$ (Fig. 2) is extended beyond 25% R.H. a surprising increase in slope may be observed. This coincides with the region where the discontinuity occurred in the sorption and length change isotherms,¹ and it is considered to be related to the secondary hysteresis observed in the desorption part of the loop. It has also been pointed out that if this water (sorbed beyond 25% R.H. and causing the discontinuity) is associated with the secondary hysteresis, then this water is sorbed irreversibly. It is also shown that on removal of this water a $\Delta l/l$ vs $\Delta W/W$ relationship shows a linear plot with a slope greater than that of the previously sorbed water.

If the B.E.T. parameter $[P/P_0]/[(\Delta W/W)(1-P/P_0)]$ is plotted beyond 25, to 33% R.H., it may be observed (Fig. 4) that the linear plot deviates sharply after 25% R.H. This indicates that the value of $\Delta W/W$ is too large to obey the B.E.T. equation, which usually applies up to 33% R.H. It is considered that beyond 25% R.H. two processes are occurring: (1) physical adsorption, and (2) a secondary process that yields a greater expansion per unit weight change than the physical adsorption.¹ This explains the increase in slope of the $\Delta l/l$ vs $\Delta \gamma$ curve. Two points remain unexplained: that this sorption is irreversible, and that the slope of the $\Delta l/l$ vs $\Delta W/W$ curve is greater for this secondary sorption. The existence of an activation step in chemi-sorption is well recognised,⁹ as is the fact that the activation energy required to surmount the barrier between the gas molecule and the surface is supplied entirely by the adsorbent. In this case, as the adsorbate takes a position on the surface, changes occur in the adsorbent. This

Fig. 4. B.E.T. parameter as function of relative vapour pressure

- plot with X as zero point (Fig. 1)
- plot with Y as zero point (Fig. 1)
- plot with Z as zero point (Fig. 1)

can be well understood as the adsorbent is by no means inert and there is considerable interaction between the adsorbent and adsorbate. In effect, an increase of the area available for adsorption is generated during coverage of the adsorbent by the adsorbate. It is uncertain whether this is achieved by modification of the lattice spacing, allowing greater penetration of the adsorbent, or by a change in interaction energies, making more sites available for sorption. This type of sorption, however, should not be of a reversible nature and will account for the secondary hysteresis in the isotherm. Water sorbed above 25% R.H. on new high-energy sites created by the modification in the adsorbent during sorption below 25% R.H., is likely to be removed at a considerably lower value.

Bernal¹⁰ viewed tobermorite gel as an orthosilicate with two hydrogens on two of the oxygen ions in the SiO_4 tetrahedra. According to his structural formula, $\text{Ca}_2[\text{SiO}_2(\text{OH})_2]_2, \text{Ca}(\text{OH})_2$, two of the water molecules, in hydroxylic forms are in the tobermorite layers—or in the $\text{H}_2\text{SiO}_4^{2-}$ chains, constituting parts of the layers. The third water molecule, likewise in hydroxylic form, is between the layers.

Brunauer¹¹ and his co-workers considered the interlayer water to be molecular, Bernal's formula being modified to $\text{Ca}_2[\text{SiO}_2(\text{OH})_2]_2, \text{CaO}, \text{H}_2\text{O}$ which includes the existence of O^{2-} and Ca^{2+} ions and H_2O in the same compound. However, with drying of increasing severity, the water is lost continuously until one molecule is removed; density measurements indicated that the c spacing is reduced during drying; they considered that when tobermorite gel was dried over the vapour pressure of ice at -78° , all the interlayer hydrate water was removed and the minimum distance between the layers was attained. When rewetted, the tobermorite did not readily swell.

If adsorption of water modifies the system in some way, allowing re-entry of water into the lattice at a specific relative humidity, a discontinuity in the isotherm is observed; as this water cannot be removed until low vapour pressure conditions occur, a secondary hysteresis should be expected.

The water, inside the lattice, interacts with the material as shown by the $\Delta l/l$ vs $\Delta W/W$ relationship³ in a way that is different from that of the water adsorbed. This difference provides a basis for differentiating between the two types of water.⁴

Once this explanation for the discontinuity and secondary hysteresis has been accepted some explanations for previous results can be made. Tomes *et al.*¹² found that, when specimens

of hydrated cement were dried for different periods of time, all of the water removed in the later stages of drying was not resorbed when samples were re-exposed to R.H. of up to 25%. Also, the greater the drying time, the greater was the computed surface area of the hydrated cement. This is here explained by the fact that a large portion of the water taken off during drying at the vapour pressure of ice at -78° is interlayer hydrate water and that only a portion of it returns to the original sites at R.H. below 25%. The longer the drying period, however, the greater is the absolute quantity of water resorbed. It is apparent that if this interlayer hydrate water is included as physically adsorbed water in a calculation of the surface area of the hydrated cement, an erroneous result will be obtained. Results for nitrogen sorption on hydrated cement have been reported;^{12,13} these show values for the surface area as low as 20% of the result computed from water adsorption. The value obtained by the experimental method of separating adsorbed and interlayer hydrate water yields a value approximately 60% of that computed for bottle-hydrated cement from water adsorption determined by the conventional method of drying.

It may now be seen that the B.E.T. plot, normally applicable between P/P_0 values of 0.05 and 0.33, may not be applied in this case beyond 0.25. Beyond this value, it is now considered that some admittance of interlayer hydrate water occurs. In Fig. 4 the plots of the B.E.T. parameter beyond 25% R.H. that show evidence of the interlayer hydrate water are presented for the three cases. When a large quantity of interlayer hydrate water is taken as adsorbed water, the deviation in the curve is not as great as for the other cases. For even greater degrees of dehydration, the deviation observed in the B.E.T. plot will become negligible. This may indicate why in previous work the deviation has not been observed.

Surface area from the pore-size distribution

This may be calculated by a numerical integration of the area of all the pores from the pore-size distribution curve shown in a previous paper.¹ Assuming cylindrical pores, then,

$$\Delta A_i = 2 \Delta V_i / R_i \dots\dots\dots (11)$$

where ΔA_i and ΔV_i are the area and volume per g. of sample for each group of capillaries taken to have R_i as a mean pore radius. Pierce's method¹⁴ was used in this calculation; a correction is made for desorption that occurs from the adsorbed film of larger pores which have already lost their menisci, as well as for the fact that the area obtained is that of the film and not of the pore walls. Fig. 5 shows a cumulative plot of pore radius versus surface area. At any point on the curve the surface area is provided by pores larger than R_i . Thus it can be seen that 95% of the surface area is provided by pores smaller than 50 Å in radius or 70% by pores smaller than 19 Å in radius. The total area is computed to be 101 m.²/g. Considering the approximations, this is in excellent agreement with the values obtained by the B.E.T. method, using the experimental and theoretical methods respectively for determining the zero for adsorbed water. It must be stressed that the pore-size distribution has been calculated by applying a modified form of the Kelvin equation to the desorption loop of the sorption isotherm. The close agreement of areas seems to indicate that menisci do exist down to R.H. of approximately 31%.

Fig. 5. Cumulative plot of surface area as function of capillary radius

Theory of volume change and calculations of Young's modulus

As has already been indicated, volume changes at different regions of the isotherm will be the result of different processes and should thus be described by different mechanisms. These regions will be treated separately here.

(1) *Region of physical adsorption only*

This region is considered to exist from a relative vapour pressure value of 0.25 to just short of zero vapour pressure. In this region it has been observed that the length change data obey the Bingham relation equation (6) where the change in surface free energy is represented by the Gibbs equation. Thus, the process of expansion is due to the release of the surface tension forces of the adsorbent which act tangentially. When the adsorption process takes place, interaction between the adsorbate and surface causes a decrease in surface free energy. The volume change of elements in contact with each other within the body is transmitted through each, and results approximately in the total volume change of the body. The magnitude of the effect, if any, of the porosity or packing of the sample on the transmission of the volume changes will be considered later. Thus, the change in surface free energy $\Delta\gamma$ is taken to represent the spreading pressure imposed on the system by the adsorbate and can be calculated by the Gibbs equation.

It is possible therefore, to calculate a value for Young's modulus of the hydrated cement. It is emphasised that this value is for the basic unit of the hydrated cement and will not necessarily be similar to the value obtained by mechanical means. From another relation derived by Bingham & Maggs⁶

$$E = \rho\sigma/k_1 \dots\dots\dots(12)$$

where

E is the Young's modulus of the material,

ρ (g./c.c.) the density,

σ the surface area (cm.²/g.)

and k_1 the constant obtained from equation (6).

This equation was derived for an infinitely long cylinder, where the surface area is taken to be composed only of the curved surface of the cylinder.

Assuming the density of the solid material in hydrated cement as 2.7 g./c.c., the surface area as 73.1×10^4 cm.²/g., and the value of k_1 taken from Fig. 2 as 1.96×10^{-5} cm./dyne, the value of E was computed as 1.01×10^{11} dynes/cm.² or 1.47×10^6 lb./in.²

(2) *Adsorption region beyond 25% R.H.*

In this region physical adsorption is complicated by water that enters between the layers of the crystal and alters the lattice spacing. From results discussed previously, it is now known that the length change for unit weight change is greater for this interlayer hydrate water than for physically adsorbed water. Length changes are affected by both processes, and it is not possible to differentiate between them.

The physical adsorption process, however, will continue to develop the spreading pressure according to the Gibbs equation. At some relative pressure, another factor, the formation of menisci within the pores, will tend to reduce observed expansions; but where this process first occurs is not possible to estimate accurately, although it is probably beyond R.H. 60%.

(3) *Desorption region down to 36% R.H.*

This region DE in Fig. 1 is within the area of primary hysteresis, and concave menisci forces are operative. The contraction of the adsorbent is due to the increased value of the negative pressure as the radii of the menisci decrease, as well as to the reduced spreading pressure of the film, which had adsorbed on the walls before filling of pores took place; both of these processes occur as the equilibrium pressure is reduced. The system under consideration can thus be divided into two parts, one consisting of that portion which comes under the influence of surface forces, and the other, the remainder of the adsorbate under the influence of menisci. Although these parts are considered separately it is not meant that any abrupt boundary between them exists, and the adsorbed film must always have the same chemical potential at equilibrium as the capillary liquid and the vapour in equilibrium with the system.

For the adsorbed film the Gibbs equation (4) may still be used to represent the change in surface free energy, but the surface concentration n_2/n_1 of the adsorbate on the adsorbent is considered a constant at approximately the value at 35% R.H. Thus the equation may be written

$$\Delta\gamma = \frac{RT}{\sigma} \frac{n_2}{n_1} \int_{P_1}^{P_2} \frac{dP}{P} \dots\dots\dots (13)$$

Integrating and combining with equation (6), we obtain

$$\Delta l/l_t = k_1 \frac{RT}{\sigma} \frac{n_2}{n_1} \cdot \ln \frac{P_2}{P_1} \dots\dots\dots (14)$$

where $\Delta l/l_t$ is the contraction caused by the adsorbed film due to the lowering of vapour pressure from P_2 to P_1 .

For the capillary water the process can be considered in some ways equivalent to the differential process; in effect a change in concentration with respect to the adsorbent is not taking place, since this water was defined as that not being influenced by surface forces. The capillary water maintains equilibrium with different vapour pressures by changing the radius of its meniscus. This in turn imposes a tension on the water. Thus the equation used to express the negative pressure in this water is similar to that derived for the pressure developed in the phenomenon of osmosis.¹⁵ Assuming that the length change, $\Delta l/l_c$, in this case contraction, is proportional to the pressure due to menisci ϕ , we obtain

$$\Delta l/l_c = k_2 \Delta\phi = k_2 \frac{RT}{\rho M} \cdot \ln \frac{P_2}{P_1} \dots\dots\dots (15)$$

Thus, the total length change $\Delta l/l_t$ between D and E (Fig. 1) may be represented by the equation

$$\Delta l/l_t = \left(k_1 \frac{RT}{\sigma} \cdot \frac{n_2}{n_1} + \frac{k_2 RT}{M\rho} \right) \cdot \ln \frac{P_2}{P_1} \dots\dots\dots (16)$$

where

ρ is the density of the capillary water and is taken equal to that of bulk water and M the molecular weight.

From equation (16) it may be seen that the contraction between D and E must be proportional to the logarithm of the relative vapour pressure. This is shown in Fig. 6 to be true for R.H. between 74 and 49%.

The calculation of Young's modulus from these data has been attempted before.^{7, 16} In one case, a cylindrical capillary was considered separately and subjected to a negative hydrostatic pressure from within; the theory for a thin walled tube, where the thickness of the wall t is small compared with the radius a , was used. This resulted in the equation

$$\Delta l/l_c = (0.25 a/t \cdot 1/E) \cdot \Delta\phi \dots\dots\dots (17)$$

where again $\Delta l/l_c$ is the contraction produced only by the negative stress $\Delta\phi$ produced by the change in radius of the menisci. It is not possible, however, to make an accurate estimate of the ratio (a/t) . It seems probable that the walls of the cylindrical capillary are rather thick for hydrated cement, which makes the theory inapplicable.

If the porous body of hydrated cement is considered to be under hydrostatic pressure due to the hydrostatic tension in the water, the bulk modulus of the material can be determined. Thus

$$3 \Delta l/l_c = \Delta\phi/K \dots\dots\dots (18)$$

where K is the bulk modulus of the hydrated cement.

$\Delta l/l_c$ is obtained from equations (14) and (16) using k_1 and σ as already determined from the 0–25% R.H. region of the curve and n_2/n_1 as the value obtained at approximately 35% R.H. on the sorption curve.¹ By assuming a Poisson's ratio of 0.25, the value obtained for Young's modulus was 1.54×10^{12} dynes/cm.² or 22.4×10^6 lb./in.²

(4) Desorption region of constant length

In the region EF (Fig. 1) the pores are emptying and the contractive force imposed upon the material is being removed. At the same time, the relative pressure has decreased from 35.8 to 31% and some desorption from adsorbed films may take place from pores that have already lost their menisci, these latter two effects causing contraction. The opposing effects balance in this case, giving a region of constant length.

(5) Desorption region below 31% R.H.

The region FG (Fig. 1) is similar to the region of 0–25% R.H. for the adsorption part of the

cycle, and the desorption process is accompanied by contraction due to an increase in the surface energy of the material. Contraction caused by removal of water in the region GJ is due to dehydration of the cement; the interlayer hydrate water is being withdrawn, giving a greater contraction per unit weight of water removed than for the adsorbed water.

It is observed that the sample at the completion of the cycle has suffered a permanent contraction. This is evident by the location of the point J (Fig. 1). Attention should be drawn again to the statement made earlier in this paper, where it was stressed that a finely divided system represents a state of unstable equilibrium. The predominance of the surface forces over the elastic forces becomes evident with time and is accelerated by a wetting and drying cycle. The reduction of the surface in this way will result in this form of irreversible shrinkage.

Fig. 7 is a simplified diagram for the $\Delta l/l$ vs $\Delta W/W$ relationship to illustrate clearly the different types of volume changes occurring in the hydrated-cement-water sorption system; it is not intended to show the precise mechanism or order in which processes occur. AB represents readmitting of interlayer hydrate water during sorption. BC represents physical adsorption and CK the readmittance of interlayer hydrate water that occurred between 25% R.H. and saturation, while KD represents the physical adsorption that occurred in that same region. It is noted that BC is drawn linear, as was observed for the first 1- to 2-molecular layers for other materials, while KD is of decreasing slope. DE' represents the region of hysteresis, E'F' the emptying of the pores, and F'G' is the desorption of the physical adsorbed water. G'B represents the dehydration of the sample, by the withdrawing of the interlayer hydrate water. This plot emphasises the similarity between CK and G'B, and how this causes the existence of the secondary hysteresis. Throughout the cycle, irreversible ageing or recrystallisation superimposes itself on the whole process; D, E', F', G' become line D, E, F, G, J, which is displaced by the amount E'E, representing irreversible shrinkage. Here the irreversible shrinkage is included with DE' only for convenience in the representation.

Fig. 6. Plot of length change against $\log_{10} P/P_0$ for desorption in the primary hysteresis region of the isotherm

Fig. 7. Diagrammatic representation of dimensional changes arising from sorption

Discussion

To describe the mechanism of volume change of hydrated cement for physical adsorption, previous authors^{17, 18} utilised an equation to compute swelling pressures similar to that derived for the potential pressure of an osmotic process, sometimes referred to as the Katz equation. In the derivation of the latter equation the fundamental thermodynamic equation of a bulk phase is utilised. Thus, for this and other reasons described previously, the use of the Katz equation for the integral process equation (1) is thermodynamically inconsistent.

The expansion of the hydrated cement due to physical adsorption was attributed to a process described in a series of papers^{16, 18, 19} and referred to as 'restricted adsorption'. Expansion due to the decrease in the surface tension force was held negligible. Results in this paper, however, show that the sorption-length change relationships obey the Gibbs and Bangham equations, and with their use a surface area is predicted very close to that found experimentally. The value of E calculated to be 1.47×10^6 lb./in.² from this region of the isotherm is less than that calculated from the capillary condensation region, which is 22.4×10^6 lb./in.² The former value, however, was calculated by an equation derived for rods of infinite length and circular cross-section. It is now recognised¹⁰ that hydrated cement is composed of rolled fibres and sheets.

Adsorption on to these rolled sheets should cause a larger expansion than that predicted for rods and will result in a larger value for E . The value for Young's modulus obtained from the capillary condensation region is much higher than that obtained by the sonic method.¹⁶ It must be stressed, however, that the values of Young's modulus obtained from the calculations in this paper are primarily for the basic material that makes up the porous body, and not the body as a whole. Further work on this aspect is in progress.

In examining the 'restricted adsorption' process, it seems necessary (in order to explain expansions observed from zero humidity upward, in accordance with equation 9) to postulate surface-to-surface distances about the size of the diameter of one molecule of water or less. In this case one would expect considerable solid-to-solid interactions to modify the adsorption forces, and where the pore sizes are slightly greater than the diameter of one molecule, molecular bridging can occur. This bridging, which has been observed in previous work,^{8,20} is due to the sharing of one molecule between two sites on opposing surfaces; the result of this is a contraction of the body on initial adsorption that has not been observed for hydrated cement. Further, when pores become filled and a continuation of adsorption is prevented, the restricted adsorption process explains the mechanism by which equilibrium is maintained with an increasing vapour pressure to the development of pressure in the adsorbed water which imposes a stress on the body, causing expansion. Evidence exists, however, for other porous bodies^{7, 8, 21} that equilibrium is maintained by the formation of a meniscus, which changes radius with relative vapour pressure according to the Kelvin equation. Results show that menisci can exist to as low as 31% R.H. for hydrated cement, possibly lower for some other materials, and that the formation of a meniscus results in a contractive force.

Conclusions

- (1) By using a modified form of the Gibbs adsorption equation

$$(b/k_1) \Delta W/W(A) = RT/M\sigma \int_0^P (\Delta W/W(A) \cdot dP/P)$$

it has been possible to calculate the point representing zero adsorbed water for the hydrated cement. The B.E.T. value for the surface area obtained through this equation is 73.1 m.²/g., which is in excellent agreement with the value of 80.6 m.²/g. obtained using the experimentally determined point for zero adsorbed water. Thus, the volume change and sorption characteristics of the hydrated cement due to physical adsorption for the region of R.H. below 25% can be described by the Gibbs adsorption and Bangham equations.

(2) Calculation of the surface area from the pore-size distribution of the hydrated cement assuming cylindrical pores, yields a value of 101 m.²/g. This agreement with the values obtained by the other methods indicates that menisci do exist down to R.H. of approximately 31%.

(3) The discontinuity and secondary hysteresis previously observed in the isotherm of hydrated cement is probably a result of the interlayer hydrate water of the tobermorite gel that has been irreversibly sorbed.

(4) Volume changes of the hydrated cement over the extent of the isotherm are due to both the volume change of the elements of the body by surface energy changes and menisci forces, and also to the movement of interlayer hydrate water into and out of the lattice. Recrystallisation of the hydrated cement also superimposes an irreversible shrinkage on the specimen.

(5) Calculations of Young's modulus from the results leads to the conclusion that the values obtained are for the individual elements of the body; as such they are much larger than the values that represent the Young's modulus of the body itself.

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