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A MODEL FOR HYDRATED PORTLAND CEMENT PASTE AS
DEDUCED FROM SORPTION - LENGTH CHANGE AND
MECHANICAL PROPERTIES

BY

R. F. FELDMAN AND P. J. SEREDA 10827

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UN MODELE MATHEMATIQUE DE LA PATE DE CIMENT
PORTLAND HYDRATE DEDUIT DE SES PROPRIETES
MECANIQUES ET DE SA COURBE ADSORPTION/MODIFICATIONS
DIMENSIONNELLES

SOMMAIRE

Les résultats obtenus récemment à la Division des recherches en bâtiment et dans d'autres laboratoires ont entraîné la révision du modèle mathématique couramment accepté pour la pâte de ciment portland hydraté. Les valeurs des superficies et des porosités obtenues par adsorption de N_2 paraissent les plus fiables pour l'élaboration du modèle, qui attribue de nombreux phénomènes observés au comportement de l'eau d'hydratation interstitielle. L'auteur définit clairement les liaisons entre cristallites et à l'intérieur des cristallites, et montre que les liaisons entre cristallites ne s'annulent pas quand l'ensemble adsorbe de l'eau. L'auteur décrit quelques-unes des équations thermodynamiques concernant les phénomènes d'adsorption, de variation de longueur et de fluage, et quelques-uns des principes fondamentaux régissant l'adsorption, ainsi que les types d'hystérésis. Les résultats proviennent de deux secteurs de travail: a) les expériences de chimisorption et b) les mesures des propriétés mécaniques des éprouvettes de ciment hydraté et de plâtre, comprimés et coulés.



SESSION I

A model for hydrated Portland cement paste as deduced from sorption-length change and mechanical properties

R. F. FELDMAN and P. J. SEREDA ⁽¹⁾

RÉSUMÉ

Des résultats obtenus récemment à la Division des Recherches sur le Bâtiment et dans d'autres laboratoires ont rendu nécessaire une révision du modèle jusqu'ici accepté pour représenter la pâte de ciment Portland hydraté. Ce modèle admet comme valeurs les plus sûres et les aires superficielles et les porosités déterminées par adsorption d'azote, et fait dépendre un grand nombre des phénomènes observés du comportement de l'inter-couche d'eau d'hydratation. La nature des liaisons dans les « cristallites », et entre elles, sont clairement définies ; on voit que les liaisons « inter-cristallites » ne sont pas affectées par adsorption d'eau.

Ce rapport expose quelques-unes des équations thermodynamiques relatives aux phénomènes de l'adsorption, variation de longueur et fluage, ainsi que quelques principes de base qui régissent l'adsorption et des types d'hystérésis.

Les résultats ont été fournis par deux séries de travaux : A. des expériences sur la chimie des surfaces ; B. la mesure des propriétés mécaniques des systèmes compactés et coulés de ciment hydraté et de plâtre.

Les expériences (A) intéressaient les phénomènes d'adsorption, et les modifications de longueur des réseaux d'isothermes ou de l'eau et du méthanol, et les résultats de ces expériences aboutissaient aux conclusions suivantes :

(i) L'isotherme de l'eau pour le ciment hydraté amené à siccité est irréversible en toute partie des courbes primaires, la cause étant la ré-introduction d'une intercouche d'eau d'hydratation.

(ii) Les calculs de Brunauer, Emmett et Teller de l'eau isotherme ne sont pas valables. Les aires superficielles et les porosités obtenues par l'adsorption d'azote sont des valeurs plus sûres.

(iii) A l'aide du réseau d'isothermes et du calcul, il est possible de séparer l'inter-couche et l'eau physique (adsorbée) ; les

SUMMARY

Recent findings in DBR and other laboratories has made it necessary here to revise the accepted model for hydrated portland cement paste. The model recognizes surface areas and porosities obtained by N₂ adsorption as the most reliable values, and attributes many of the phenomena observed, to the behaviour of interlayer hydrate water. The bonds between and within individual " crystallites " are clearly defined; it is shown that the " inter-crystallite " bonds do not separate when exposed to physically adsorbed water.

The paper describes some of the thermodynamic equations pertinent to the phenomena of adsorption, length change and creep, and some basic principles governing physical adsorption and types of hystereses.

The results were obtained from two areas of work : A. Surface chemical experiments. B. Measurement of mechanical properties of compacted and cast systems of hydrated cement and gypsum.

The experiments in (A) included sorption and length change scanning isotherms of water and methanol and led to the following conclusions :

(i) The water isotherm for " d-dried " hydrated cement is irreversible at all regions of the primary curves, due to the re-entry of inter-layer hydrate water.

(ii) B.E.T. calculations on the water isotherm are invalid. Surface areas and porosities obtained from N₂ adsorption are more reliable values.

(iii) By use of the scanning isotherms and calculation it is possible to separate interlayer and physical water; each of these were used to describe properties of the hydrated cement.

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deux méthodes ont été utilisées pour décrire les propriétés du ciment hydraté.

Les mesures (B) comprenaient celles du module et de la résistance en fonction de l'humidité relative et de la porosité; elles ont conduit aux conclusions suivantes :

(i) L'eau adsorbée ne se trouve pas aux limites « inter-cristallites ».

(ii) Les liaisons formées au cours de l'hydratation ne sont pas plus fortes que celles formées par compactage, contrairement à ce qui se passe avec le plâtre. Pourtant, les liaisons sont assez fortes et impliquent des proportions variables de forces agissant à long terme et à court terme. L'eau adsorbée normalement n'influence pas cette répartition.

(iii) Le fluage réversible et une partie du fluage irréversible sont probablement associés à la lente décomposition de l'inter-couche hydratée due à l'application d'une charge.

(iv) Le fluage irréversible est probablement le résultat de la rupture et de la reconstitution des liaisons « inter-cristallites » dans des conditions de contrainte contrariée.

The experiments in (B) included measurements of modulus and strength versus relative humidity, and porosity, and led to the following conclusions :

(i) Physically adsorbed water is not present at " inter-crystallite " boundaries.

(ii) The bonds formed during hydration are not stronger than those formed by compaction, in sharp contrast to the gypsum system. However, the bonds are fairly strong and involve a varying proportion of long-range and short-range forces. Physically adsorbed water does not normally influence these bands.

(iii) The reversible and part of the irreversible creep is probably associated with the slow decomposition of the interlayer hydrate due to application of stress.

(iv) The irreversible creep is probably the result of breaking and re-making of " inter-crystallite " bonds under confining stress conditions.

The development of the present model of hydrated portland cement has been largely based on surface chemical considerations; this involved the establishment of criteria for distinguishing between chemically combined and physically adsorbed water. The determination of the stoichiometry of the tobermorite gel, its water surface area and its porosity was based on the above criteria.

Recent findings in D.B.R. and other laboratories involved measurements of sorption and length-change relationships, and variations of mechanical properties with relative humidity and with porosity of compacts of bottle hydrated cement and small prisms of paste hydrated cement. This has provided new evidence, making it necessary to modify the accepted model for hydrated portland cement paste. This new model allows the possibility of new approaches to, and explanations for, some well-known phenomena.

1. THEORY

Some of the basic theories related to physical adsorption, adsorption hysteresis, and adsorption and length-change phenomena will first be discussed. The various experimental results and interpretations will then be presented with the aim of developing a new model. Final discussion will concern the relation of creep to this model.

a) Physical adsorption at lower humidities

Physical adsorption is associated with the attachment of the adsorbed molecule to the surface of the solid. The energy of the reaction for physical adsorption is usually similar to that of condensation of the particular gas, although it may be considerably higher on active points of the solid.

The amount of gas or vapour adsorbed when equilibrium is established at a given temperature and pressure is a function of the nature of the adsorbent and adsorbate.

The experimental observation most frequently made for sorption systems is of the adsorption isotherm; this is the measurement of the quantity of

adsorbed material as a function of its vapour pressure at constant temperature. This isotherm for a given solid-gas system should be reversible if there is no irreversible change in the nature of the solid and/or gas, since there thus can be only one state of equilibrium at a given vapour pressure. At lower pressures this is usually the case, but at higher pressures the problem of primary hysteresis arises. This is commonly related to the pore structure of the solid and a change in nature of the adsorbate. This change, it is postulated, manifests itself in the formation of a meniscus; the difference in the process of formation and recession of this meniscus causes the hysteresis.

Brunauer, Emmett and Teller [1] with some simplifications and assumptions derived their famous B.E.T. equation. This equation was generally applicable in the interval of partial pressures 0.05 to 0.35, and assumes reversibility and a constant surface area. From this equation the amount of adsorbate required to form a complete monolayer can be calculated; thus, from a knowledge of the size and packing of the adsorbate molecule, the surface area can be evaluated.

b) Adsorption hysteresis

Figure 1 illustrates three forms of hysteresis that have been observed on various materials [2]. A loop of type I is formed over a limited range of pressures and is generally considered (as stated above) to be associated with the formation of a meniscus. Scanning of the loop may be performed by desorbing after reaching X on the ascending boundary curve; thus, one reaches Y on the descending boundary curve and may return to X by re-adsorption. Type II hysteresis, where the loop extends over the whole pressure range, has been observed for water on cellulose or protein fibres and also for polar adsorbates on montmorillonite. In type III, which combines the characteristics of the other types, the ascending and descending branches only join at very low or zero pressure. The dotted lines show the pattern followed if adsorption recommences at X. Type III loops are found with some graphites, clay minerals and hydrated portland cement.

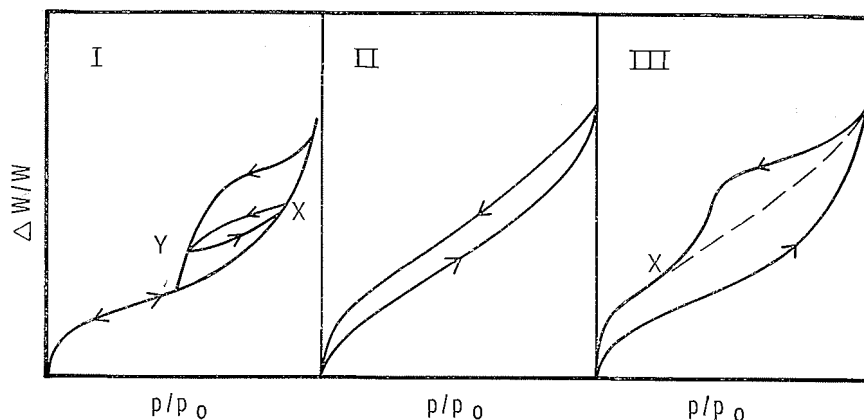


FIG. 1. — Types of sorption hysteresis.

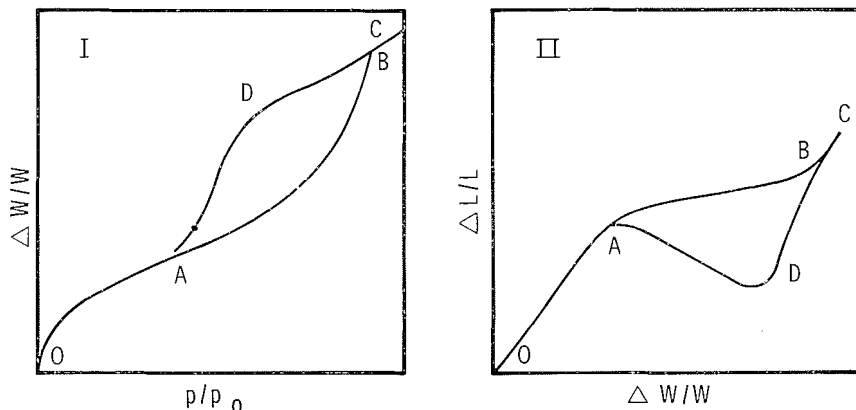


FIG. 2. — Basic length change - adsorption behaviour : I. Adsorption isotherm; II. Length change vs. weight change plot.

The low-pressure hysteresis phenomenon is usually attributed to irreversible intercalation of adsorbate within the structure of the solid. Quite often the solids have a layer structure and a change in the spacing of these layers has been observed.

c) **Adsorption length-change phenomenon**

Some of the basic considerations of this phenomenon are well illustrated by the work on porous glass by Amberg and MacIntosh [3].

In the region OA, shown on both graphs of figure 2 for $\Delta W/W$ vs. p/p_0 and $\Delta L/L$ vs. $\Delta W/W$, reversible adsorption occurs up to about two molecular layers at A.

In this region it was found that the Gibbs' adsorption equation held.

$$\Delta F = +RT \int_0^p n_1/p dp$$

n_1 is the concentration of adsorbate in gm moles/gm of solid and p is the vapour pressure of the adsorbate. ΔF is the decrease in free energy of pure adsorbent from its initial state under its own vapour pressure to its combining state, i.e. adsorbent plus adsorbate.

Gibbs' equation is extremely important in theories of length-change and adsorption but its application is apparently not completely understood [4]. Thermodynamic equations derived for dilute solutions in the "bulk state" have been erroneously used by some workers [11] to make calculations and analyse data. With the aim of presenting a clearer picture, an analysis of two thermodynamic processes and a simple derivation of Gibbs' equation, first presented by Flood [5], is given below. In (d) of this section, more detail of the thermodynamics will be given,

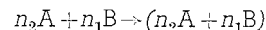
illustrating differences in the treatment of the homogeneous bulk and surface phases.

Consider the differential process n_1B (gas) \rightarrow n_1 moles of adsorbed B on A; n_3/n_2 is the concentration of B on A and is not affected by the addition of n_1 moles.

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

$$\Delta F = +n_1RT \ln p/p_0$$

p_0 is the saturated vapour pressure of the adsorbate B. The integral process



results in a system composed of n_1 moles of B adsorbed on n_2 moles of A.

Here the concentration is considered to be changing—thus n_1/n_2 is the new concentration. In this process Gibbs' adsorption equation represents the decrease of surface free energy.

The following is an outline of the derivation of Gibbs' equation as presented by Flood [5].

With the statement of the various thermodynamic restrictions necessary, and the basic assumption that "Assemblies of volumes of the pure adsorbent and adsorbate can each exist separately, in equilibrium with externally applied forces, in states that are thermodynamically identical with their states in the adsorbent-adsorbate system", the equation

$$dF_1 + dF_2 = dF_{12}$$

was presented as the condition for the process of

transformation of the separate systems 1 and 2 into the combined system 12 to be reversible at any point along a path of variation of the three systems.

At constant temperature, and making the customary assumptions, one can write

$$v_1 dp_1 + dF_2 = v_{12} dP_{12}$$

where v_1 is the volume of the pure gas at the equilibrium pressure p_1 , corresponding to the number of moles of gas n_1 adsorbed, and v_{12} and P_{12} are the volume and hydrostatic pressure of the combined system. Note that the combined system is not further defined here. It will be shown in (d) how conventional thermodynamics treats the combined system as a surface phase.

The above equation is integrated for a constant mass of solid n'_2 between appropriate limits:

$$\int_{p_1=0, n_1=0}^{F_1=p_1, n_1=n'_1} v_1 dp_1 + \int_{P_{2s}}^{P_2} dF_2 = \int_{P_{2s}(n_1=0, n_2=n'_2)}^{P_{12}(n_1=n'_1, n_2=n'_2)} v_{12} dP_{12}$$

P_{2s} , the pressure of the solid, is assumed to be very low and in the case of large adsorptions, v_1 will be much larger than v_{12} . In neglecting the third integral and integrating the following is obtained:

$$\Delta F_2 = - \int_0^p v_1 dp_1 = -RT \int_0^{p_1} n'_1 dp_1 / p_1$$

ΔF_2 is the change in free energy of pure adsorbent from its initial state under its own vapour pressure to its combining state, provided that this integral represents a path of thermodynamic reversibility. If it is assumed that the constant solid surface area σ m²/gm has undergone a change in surface tension, $\Delta\gamma$, we can write

$$\Delta F_2 = \sigma \Delta\gamma.$$

Thus

$$\Delta\gamma = -RT / \sigma \int_0^{p_1} n'_1 dp_1 / p_1.$$

$\Delta\gamma$ in fact measure changes in states of stress of the solid, brought about by an interaction of the adsorbed molecule with forces on the solid surface; these forces have placed the solid in a state of compressive stress.

The Bangham [6] equation provided a basis for testing Gibbs' equation on solids

$$\Delta L / L = k_1 \Delta\gamma.$$

A plot of the experimentally measured $\Delta L / L$ against $\Delta\gamma$ obtained from Gibbs' equation yielded a straight line through zero.

In summary, in region OA where the process is an integral one, Gibbs' equation must be used for evaluating changes in stress of the solid.

In region CD, which is reversible and is postulated as representing the changing of the radius of menisci without reversible desorption, one may consider, as an approximation, that this represents a differential process. In effect a change in concentration with respect to the adsorbent is not taking place, if the capillary water is defined as being remote from the 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 and a compression on the solid; thus the abrupt contraction CD in figure 2, II.

The equation easily derived is

$$\Delta L / L_c = k_2 \Delta P = k_2 RT / \rho M \ln p_2 / p_1$$

where $\Delta L / L_c$ is the contraction due to the pressure of the menisci (ΔP) changing radius as vapour pressure changes from p_1 to p_2 . ρ is the density of the adsorbate. The surface free energy must still change however, because the vapour pressure of the adsorbate changes. If we assume no change in concentration of adsorbed water which is within the field of force of the solid, Gibbs' equation becomes

$$\Delta\gamma = RT / \sigma \cdot n_1 \int_{p_1}^{p_2} dp / p$$

and the equation for total length change in CD is

$$\Delta L / L_T = (k_1 RT / \sigma \cdot n_1 + k_2 RT / M \rho) \ln p_2 / p_1.$$

Moderately successful attempts have been made to relate $\Delta\gamma$ and $\Delta L / L$ to the elastic constants of the material.

Calculations in regions AB and DA are generally not attempted because of the irreversible nature of the process.

d) Some aspects of homogeneous bulk and surface phase thermodynamics

Usually in thermodynamics it is assumed that every system consists of one or more completely homogeneous phases bounded by sharply defined geometrical surfaces. This is of course an oversimplification, for the interface between any two phases will rather be a thin layer across which the physical properties vary continuously from those of the interior of one phase to those of the interior of the other phase. In adsorption phenomena, it is necessary to consider the thermodynamic properties of these surface layers between two phases.

In any homogeneous bulk phase the force across any unit area is equal in all directions and is called pressure; but in the " surface phase " this is not so. The effective pressure will vary with its distance from the surface. In adsorption of vapours or gases on solids, the adsorbed phase is in fact in compression normal to the surfaces. There is a two dimensional pressure (much smaller than the above) tangential to the surface and equal in magnitude but opposite in sign to the change in surface energy of the solid.

In order to allow for this change in free energy resulting from an increase or decrease of surface energy, it is necessary to include a term ' $\gamma\sigma$ ' in the Gibbs-Duhem equation. Apart from the surface contribution, the free energy of a system of two components is given by

$$G = \mu_1 n_1 + \mu_2 n_2$$

where n_1, n_2 are the respective number of moles; μ_1, μ_2 are the respective chemical potentials, ' γ ' is the surface energy per sq. cm. and ' σ ' is the surface area (cm²); addition of the ' $\gamma\sigma$ ' term yields

$$G = \gamma\sigma + \mu_1 n_1 + \mu_2 n_2$$

for a constant temperature and pressure.

From this can be derived the surface-phase analogue for the Gibbs-Duhem equation:

$$\sigma d\gamma + n_1 d\mu_1 + n_2 d\mu_2 = 0,$$

the bulk phase equation is

$$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0$$

where n_1^0, n_2^0 are the respective number of moles for the bulk phases.

The fundamental differential equation for the total change in free energy of a homogeneous bulk phase is:

$$dG_{\text{bulk}} = VdP - SdT + \mu_1 dn_1 + \mu_2 dn_2.$$

The analogous differential equation for a surface phase is:

$$dG_{\text{surface phase}} = VdP - SdT + \sigma d\gamma + \mu_1 dn_1 + \mu_2 dn_2$$

'S' is as usual the entropy term.

Since the adsorbed phase is not a homogeneous bulk phase, but is part of the surface phase, the last differential equation is the one that describes the change in free energy due to the process of physical adsorption.

At constant temperature, and assuming that the amount of solid in the surface phase is constant, one obtains:

$$dG_{\text{surface phase}} = VdP - \sigma d\gamma + \mu_1 dn_1$$

where ' dn_1 ' is the change in number of moles of adsorbate per unit surface mole of adsorbent.

If one assumes that the adsorbed water is bulk water, and there is no surface energy term to be considered, one obtains:

$$dG_{\text{water}} = VdP + \mu_1 dn_1.$$

If there is no alteration in the number of moles of water or nearly so, then:

$$dG_{\text{water}} = VdP.$$

This is the equation used by one author [11] and others in dealing with adsorption, length change and creep phenomena in the system, hydrated portland cement and water. (This equation is in fact the one used in deriving the potential osmotic pressure of a solution.)

Looking again at the assumptions that were made implicitly on applying the above equation to the hydrated portland-water system:

- a) it was assumed that adsorbed water is not adsorbed, and there is no surface energy involved;
- b) there is no alteration in the number of moles of adsorbent or adsorbate.

Alternatively this last assumption may be restated — the original concentration of adsorbate to adsorbent is so high that any further addition of adsorbate is negligible; in other words, 100 gms of dried hydrated portland cement with 1 gm of adsorbed water on it, is equivalent to a *dilute solution* and that this 1 gm of adsorbed water can be considered as bulk water.

The above assumptions are of course untenable.

It may be stated here that the Kelvin equation, a form of which relates the tension in capillary water to the vapour pressure,

$$\Delta P = RT / \rho M \cdot \ln p_2 / p_1$$

is derived for a homogeneous bulk liquid. However, its use in surface chemistry has involved the assump-

tion that the water beyond some distance from the surface e.g. two molecular layers, is in essence bulk water. That this is an approximation is clear when one considers that water in pores as great as 100 Å U in diameter are influenced by surface forces.

2. EXPERIMENTAL EVIDENCE FOR THE MODEL, TAKEN FROM SURFACE CHEMISTRY CONSIDERATIONS

a) Adsorption, length-change and surface area

Water adsorption experiments have been used to measure the surface area of hydrated portland cement and computations have yielded values in excess of 200 m²/gm. The value was of great importance, and was used to estimate the number of layers in the tobermorite gel "crystallites"; it also provided the basis for calculating other physical parameters.

Kalousek [7] observed that the surface area using N₂ as adsorbate yielded very low values compared with those of water; the N₂ value was shown by Mikhail et al. [8] to decrease with the water cement (W/C) ratio to values below 30 m²/gm. Similar results were obtained when organic vapours such as CH₃OH were used as adsorbates [9].

It must be pointed out that the determination of surface area by adsorption of N₂, together with a calculation based on the B.E.T. equation, has become a standard method in the realm of surface chemistry. Carbons with very high surface areas and very small pores have yielded nitrogen surface areas that approach 1,000 m²/gm. Yet, in the case of hydrated portland cement, the "water area" has been the one generally held "true and valid". It was considered that the N₂ molecule could not enter small pores and adsorb on the whole surface because of its large size. The diameters of the water, nitrogen, and methanol molecules are approximately 3.25, 4.05 and 4.4 Å respectively; it seems difficult to allow for the situation where up to 90 % of the area is excluded to N₂ because of the small difference in diameters. If the holes were part of the crystal structure like certain "molecular sieves" which are cage-like molecules with small entrances, it would be realistic, but hydrated cement is not of this nature.

Several years ago it was found in this laboratory [10], during study of the length-change and sorption isotherms of water on bottle hydrated cement, that it was possible to detect characteristic differences in the type of water that was being removed on drying. These characteristics provided a means to study, and formulate an hypothesis on the expansion and contraction of hydrated portland cement on sorption and desorption of water. It must be emphasized that this theory did not relate to the phenomena that operate during first drying; this will be discussed in a later section.

The theory emphasized the role of the Gibbs and Bangham equations in the lower pressure regions and it was concluded that the expansion on sorption was due in the first instance to the decrease in surface energy of the solid. It was not necessary to introduce the concept that individual crystallites could not move back and forth with respect to each other in a reversible manner as a function of the vapour pressure. Once a solid-solid contact was made the large force realized from this proximity would make the bond difficult to break. Evidence for this is available from other adsorbent-water

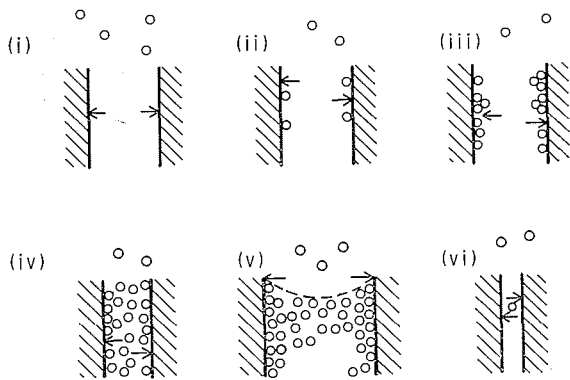


FIG. 3. — Simplified model for adsorption of molecules in cylindrical pores.

systems, and results, discussed in a later section on mechanical properties, have supported this concept. The idea of moving crystallites was conceived together with that of 'restricted adsorption' [11]. The latter is considered unrealistic. A surface attracts a molecule to it by forces emanating from it that fall off rapidly with distance. If this surface is in a pore (fig. 3 (i-vi)), the molecules diffuse gradually into the pore and are attracted to the surface. If small pores (3, iv) become full at low pressures, additional gas molecules will be prevented from coming into the region of the force field and being attracted by the surface. A larger pore (3, v), after becoming full, will form a meniscus whose radius of curvature will depend on the equilibrium vapour pressure. This less tightly held water in the middle of the pore comes under a tension. If the size of the pore is very close to the size of the molecule (3, vi), the molecule will be adsorbed from both surfaces. This has been termed 'molecular bridging' and at low vapour pressures, contractions have been observed (e.g. molecular sieves [12]).

At the intermediate and high pressure regions evidence for menisci forces influencing the length changes was obtained. Similarly, characteristics were observed similar to those discussed in Section 1 (c).

From the $\Delta L/L$ vs. $\Delta W/W$ characteristics it was recognized that the exit and entry of the interlayer hydrate water between the sheets of the tobermorite gel played an important role in expansion and contraction. This last point can be easily illustrated by the sketch of the isotherm shown for the type III isotherm discussed in Section 1 (b). Unfortunately, because of the nature of the tobermorite gel with regard to the c-axis, it has not been possible to confirm the interlamellar penetration by X-ray methods. It is clear that somewhere along the ascending branch of the isotherm, water is sorbed irreversibly. This would affect the over-all mechanism for the sorption-expansion phenomena, and the use of the ascending curve for B.E.T. calculations if interlayer water re-enters in the 0 to 35 % relative humidity range. It was concluded on the basis of length-change and sorption characteristics that water did enter the layers at both low and high humidities. As a result, part of the length-change throughout the isotherm is due to interlayer rehydration, and a B.E.T. area calculation from the water isotherm should yield a smaller value, if correction for interlayer hydration could be made.

b) Scanning loops on the isotherm

In the experiments outlined above, the samples were not dried completely to the "d-drying" point. It has been suggested [13] that the interlayer water will not re-enter if that point is attained because it is postulated that at this point, most of this water has been removed and the layers have closed tightly together, making re-entry impossible.

A detailed study of the length- and weight-change isotherms for water on hydrated cement dried to several conditions including the equivalent of 'd-drying' has been carried out recently [14], using bottle and paste hydrated cements, and re-entry of water has been shown to occur.

In essence, scanning loops have been obtained as low as 5 % relative humidity (R.H.) and to as high as 100 % R.H. (fig. 4.I). Here it is seen that the isotherm is irreversible at any point in the range of 5 to 100 % and probably lower. Also, plotting $\Delta L/L$ vs. $\Delta W/W$ (fig. 4. II) for OA on the ascending boundary curve and AB the descending scanning curve, it is observed that these characteristics are different. This implies that the mean location of the water sorbed is different to that desorbed.

The isotherm with the scanning loops enabled with some justifiable assumptions a complete separation of the reversible water (physically adsorbed) and irreversible water (interlayer-hydrate). This led to the construction of reversible and irreversible isotherms. Thermodynamic equations applied to the former led to $\Delta L/L$ vs. $\Delta W/W$, $\Delta L/L$ vs. $\Delta \gamma$ relationships and enabled an evaluation of Young's modulus which provided complete justification for this approach. The irreversible isotherm provided the basis for an hypothesis (to be described later) on the way interlayer water leaves and enters the crystal. Experiments to measure the variation of Young's modulus with vapour pressure, which will be described in a later section, provide firm support for the hypothesis.

These results then lead to the following conclusions:

a) The water isotherm for the drying conditions used is irreversible at all regions, and as such cannot be used for B.E.T. calculations.

b) Under these drying conditions, some interlayer water is entering at all regions of the isotherm.

c) Since a large but unknown portion of the "sorbed" water in the low pressure region is interlayer rehydration, the surface area must be considerably lower than the original value calculated for water.

d) The surface areas calculated from N_2 adsorption must be considered a more reliable figure. The N_2 measures mainly the "external" surface while the water in addition has gone between the layers.

e) Interlayer water can be separated from physical water and each of these separately can be used to evaluate and describe properties of the hydrated cement.

This thus leaves us with a considerably altered model of the *dried* hydrated portland cement. It has a much lower surface area which changes with the W/C ratio and the bonds between crystallites do not normally part. In addition, interlayer water plays an important role on the sorption and length-change phenomenon. This model will be further described when the different sections are discussed.

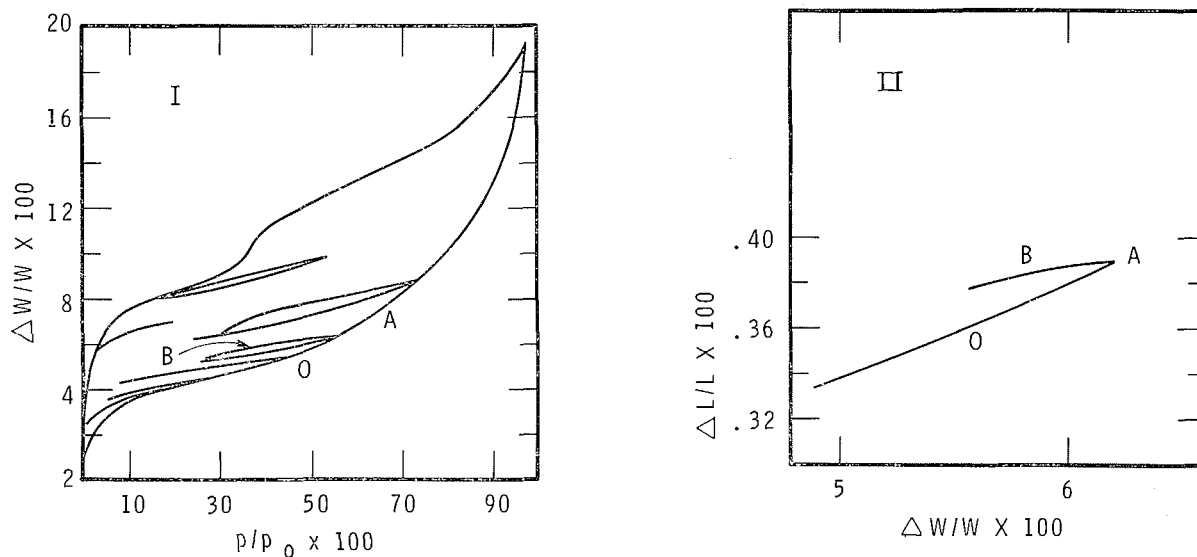


FIG. 4. — Sorption of water on hydrated Portland cement :
I. Isotherm with scanning loops; II. Length change vs. weight change plot over OAB.

c) Sorption and length-change of methanol

The sorption isotherm of methanol on hydrated portland cement was obtained by Mikhail [9]; this experiment was repeated in the D.B.R. laboratories in more detail, and also included measurements of the associated length-changes. The result shows similarities to the isotherms of both nitrogen and water. It resembled N_2 sorption in that the amount sorbed was low and the calculated surface area was similar to that obtained by N_2 . It yielded, however, a secondary hysteresis much larger than that for N_2 (which is relatively small but present) but not as large as for water; scanning loops were observed at low as well as high pressures. $\Delta L/L$ vs. $\Delta W/W$ characteristics of the ascending and descending portions of the loops again showed evidence of the CH_3OH being sorbed in different regions. CH_3OH has a dipole moment of magnitude comparable to water but, as already shown, is larger than water and nitrogen. Polar molecules, due to a mechanism discussed in ref. 14, tend to penetrate layered crystals more effectively than non-polar ones, but it becomes more difficult the larger the molecule becomes.

These results are discussed here as further evidence of the importance of the layered structure of tobermorite gel, and its low surface area. As would be expected, the expansion due to the adsorption of methanol is much less than that for water, since a much smaller amount has entered the layers.

d) First drying of hydrated portland cement

The discussion thus far has involved hydrated cement that has been dried from the original wet state formed from the hydration procedure. The first time that the hydrated paste is dried is rather a special case, and measurements taken at this time are very pertinent to problems encountered in the field. The high change in surface energy of the solid, and removal of water between crystallites for the first time might cause some permanent change.

Recent studies by Helmuth [15] have shown that the first drying does in fact yield a large irreversible shrinkage. On subsequent wetting, the original

length cannot be attained. This irreversible shrinkage is greater the higher the W/C ratio; this may be due to the fact that the degree of dispersion or surface area of the wet cement varies with W/C ratio and first drying is a manifestation of a major rearrangement of the layers or sheets of tobermorite gel. The removal of water between some individual sheets may bring about a layering of these sheets or further layering of others.

A further experimental result from this laboratory (unpublished data) may illustrate the importance of this rearrangement of layers or sheets of tobermorite gel on first drying.

Figure 5 shows the first drying (A) of a hydrated portland cement paste prepared at a W/C of 0.8

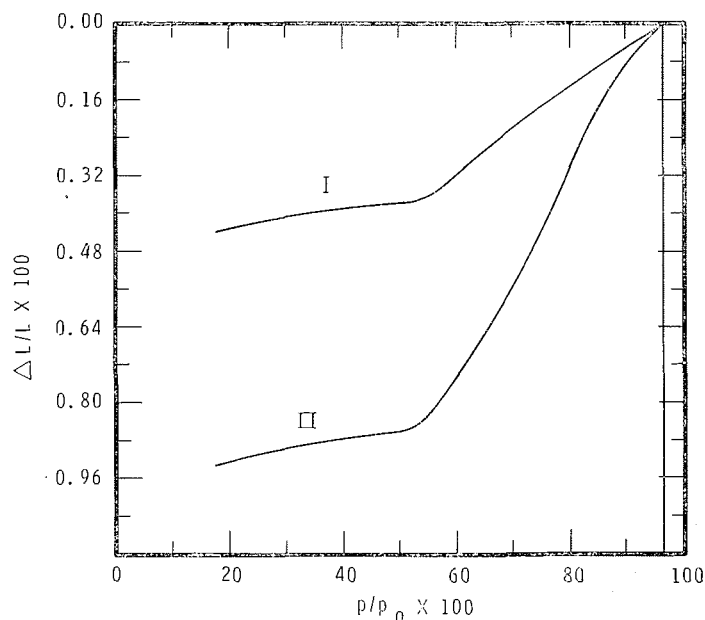


FIG. 5. — Contraction on first drying for paste hydrated Portland cement. Water cement ratio is 0.8: I. Without additive; II. With additive.

and (B) the same cement prepared at the same W/C with a dose of 0.0075 gms/gm of cement of a calcium lignosulphonate additive. This dose was three times larger than normal. It is believed that this effect can be explained by the influence of the additive on the initial degree of layering of the hydrate product; a more drastic change may then take place on the first drying involving the layering and rearrangement of the tobermorite gel sheet. This layering might not result in a well ordered product; orientation and spacing might be irregular and twisted and naturally the layers might vary in thickness.

There are, then, two different length change processes for which one might have to derive a model, or from which one might obtain information with regard to a model. It is also evident that in both processes the water between the layers of the tobermorite gel plays an important role. How these effects fit into this model of portland cement paste and the mechanism of creep will be discussed later after its mechanical properties are described in the next sections.

3. EXPERIMENTAL EVIDENCE FOR THE MODEL, TAKEN FROM MECHANICAL BEHAVIOUR

Mechanical behaviour of cement paste should further reveal what part water plays in the structural model. Before this is discussed, a closer look must be taken at the system of bonds which bind the layered structure of the particle and also the interparticle bonds.

a) Interparticle bonds

Philleo [16] discussed the various types of bonds and pointed out that the limited swelling in water of the cement paste has been considered evidence for the existence of some chemical (primary) bonds between the gel particles, but that the secondary bonds accounted for most of the strength of the cement paste.

It is recognized that the terms "chemical" and "secondary" bonds have been used in describing the structure of hydrated cement systems without a strict definition of their meaning. This has led to considerable misunderstanding. It is believed that what was meant by the "chemical" bond between the particles was a solid-to-solid contact similar to that of a grain boundary in a polycrystalline material where some atoms approach the spacing and arrangement in the crystal. Such "chemical" bonds could be formed during a crystallization process accompanying a chemical reaction where the mobility of atoms allows for a regular arrangement resulting in an intergrowth of crystals. It follows that these bonds would be strong and when broken would not be remade in normal circumstances.

It is believed that the term "secondary" bonds as applied to the hydrated cement system arose out of the assumption that physically adsorbed water was a constituent part of the interparticle bond; thus the general term of van der Waals forces was considered appropriate.

Previous work in this laboratory has indicated that neither of these definitions would adequately fit the interparticle bonds in the hydrated cement system. It is suggested, therefore, that a different interparticle

bond be postulated which would involve a solid-to-solid contact resulting from the bringing together of surfaces (by pressure externally or internally generated by the reaction), forming a particle boundary having little or no regular atomic arrangement or spacing. Atoms at such a boundary would engage a varying proportion of the long-range and short-range forces depending on the degree of disorder and the average spacing. It can be visualized that this interparticle bond can be broken and subsequently remade under appropriate loading conditions. This type of bond differs from the "chemical" bond just defined, which has a more regular atomic arrangement and the spacing of more of the atoms may approach that of the lattice spacing in the crystal. If water is involved in such a bond (it will be either chemisorbed or hydrated), it is considered a constituent part of the crystal.

Recent work at this laboratory (fig. 6 and 7) involving gypsum [17] and cement paste samples [18] has shown that both modulus of elasticity and hardness are related to porosity by a semi-logarithmic relation having the form:

$$E = E_0 e^{-bP}$$

where

E and E_0 are the moduli of elasticity at a given porosity and at zero porosity respectively, b is the empirical constant and P is the porosity.

When the above relation for modulus of elasticity was determined for samples of gypsum and cement paste representing three different structural systems, the following conclusions were made.

At 30 % porosity, the *in-situ* hydrated gypsum had a modulus about 10 times greater than compacted gypsum and about 5 times as great as samples of *in-situ* hydrated and later compacted samples, in contrast with the results for cement paste where the three different series of samples all gave virtually the same plot of modulus vs. porosity. These results suggest that the interparticle bonds are the same in all the series of samples of cement paste and are solid-to-solid contacts which are made by bringing the surfaces together with the appropriate pressure resulting either from the externally applied load as in compaction or internally generated during the hydration reaction.

The significant fact learned from these results is that the bonds formed during the hydration reaction are not stronger than those formed by compaction, in sharp contrast with what happens in the case of the gypsum system. In the latter case, the intergrowth of crystals seems to occur during hydration, forming "chemical" bonds which are very much stronger than those formed by compaction. Similarly, some recent work involving compacts of $\text{Ca}(\text{OH})_2$ during ageing [19] and during carbonation [20] shows how these interparticle bonds can be increased because of recrystallization of the material or because of new products formed as the result of the reaction.

Further evidence for the nature of the interparticle cement bond comes from the experiments where hydrated cement paste was compacted to lower porosities involving a reduction of porosity varying from as little as 5 % to as much as 45 %. In all cases the modulus values fitted the same relation as for the hydrated paste samples. If a "chemical" bond were to be formed during hydration, such a bond would be broken during subsequent compaction and would not be remade, resulting in a lower modulus

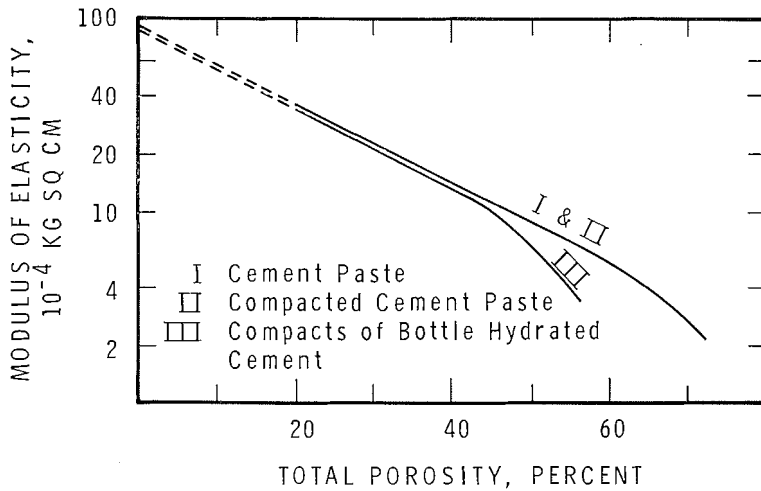


FIG. 6. — Modulus of elasticity as a function of total porosity for various hydrated cement samples.

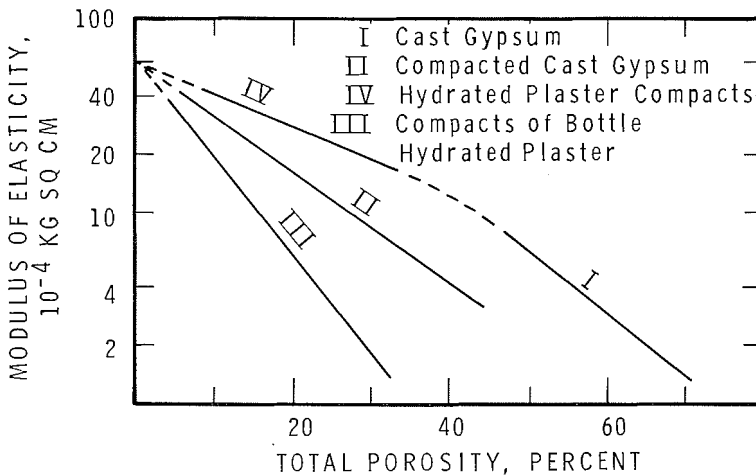


FIG. 7. — Modulus of elasticity as a function of total porosity for various gypsum samples.

for compacted paste. This was not the case, which is evidence of the absence of "chemical" bonds and leads to the conclusion that the interparticle bonds are solid-to-solid contacts which are responsible for the limited swelling of cement paste. These bonds appear to be of such a nature that they can be broken and remade without suffering permanent decrease in modulus.

The most important question relating to the interparticle bond is whether physically adsorbed water is a constituent part of the interparticle boundary, as has been postulated by many workers. It should be remembered that the area of actual contact between particles is probably no greater than 5% of the apparent cross-sectional area when the porosity is about 50%. If this is the case, it would result in great stress concentration at areas of contact during loading. For example, a load of 5,000 psi during compaction (about the lowest used to obtain a stable sample) would impose a load of approximately 100,000 psi on the bond area. It is unlikely that any adsorbed water would remain between the particles during the application of such high unit load. (Van Olphen [21] calculated that a pressure of 60,000 psi would remove a monolayer of water from between clay particles.)

Experimental evidence for the conclusion that adsorbed water is not present at an interparticle boundary is available from the work at DBR [22]. Bottle hydrated cement powder was compacted after conditioning to 0% R.H. as well as 30% R.H. The

compaction curves (fig. 8) where porosity was plotted against log compaction pressure are parallel and only slightly displaced. The displacement between these two curves could be explained on the basis of lower friction when a monolayer of water is present which allows far easier sliding and accommodation of particles. If water remained at the interparticle boundary in the one case and not in the other, then the compaction curves would be expected to be significantly different. The only

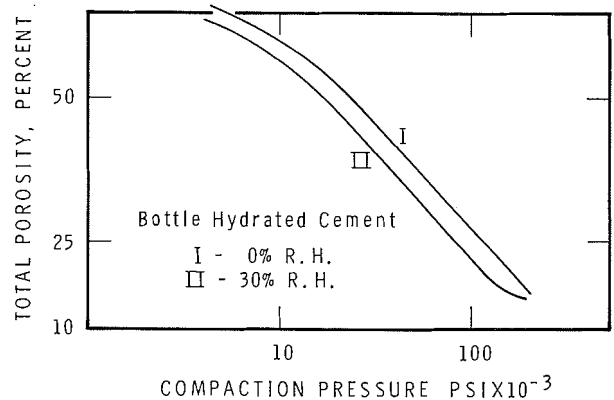


FIG. 8. — Total porosity as a function of compaction pressure for bottle hydrated cement: I. Dried to 0 per cent relative humidity; II. Dried to 30 per cent relative humidity.

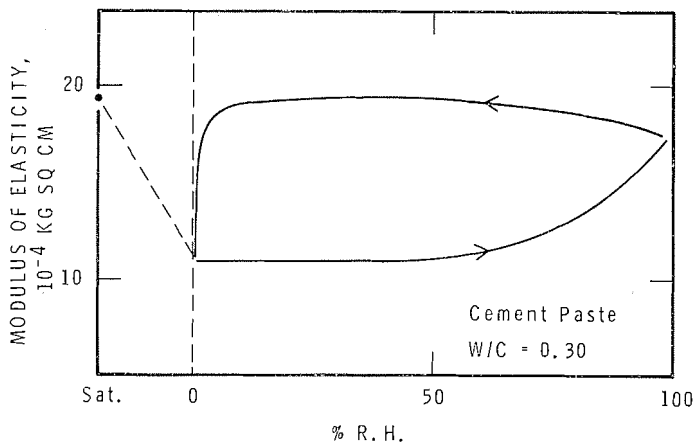


FIG. 9. — Modulus of elasticity as a function of relative humidity.

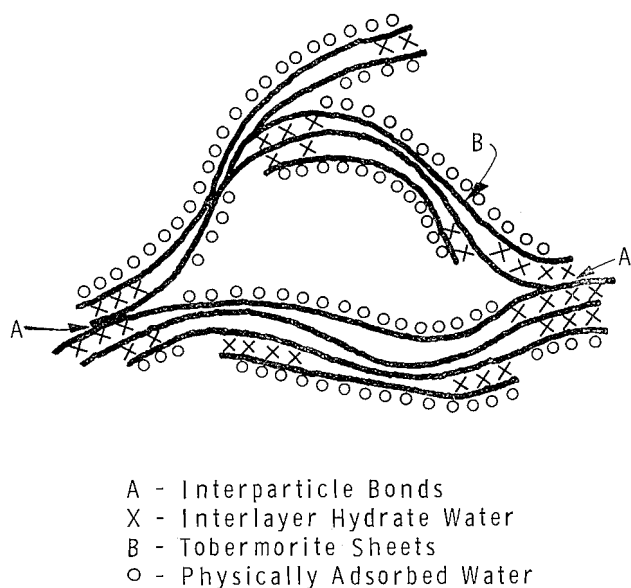


FIG. 10. — Simplified model for hydrated Portland cement.

difference is observed at very high pressure, however, where the curve for the cement conditioned to 30 % R.H. (containing about 6 % moisture content) flattens, possibly because this amount of water, which is large in relation to the low porosity, is trapped and prevents further compaction under rapid load application.

Perhaps the most conclusive evidence in support of the idea that interparticle bonds do not have adsorbed water at the boundary comes from the measurements of elastic modulus at different conditions of relative humidity [22] (fig. 9). It has been shown that the modulus remains unchanged while relative humidity is increased from 0 to 50 %. This is the region of high adsorption and correspondingly large dimensional change. If the adsorbed water were entering the interparticle bond area the net result should be a decrease in modulus, as occurs in the case of cellulosic material [23].

b) **Structure and bonds within the cement gel particle**

Adsorption studies have revealed that the gel particle of tobermorite is a layered structure into which

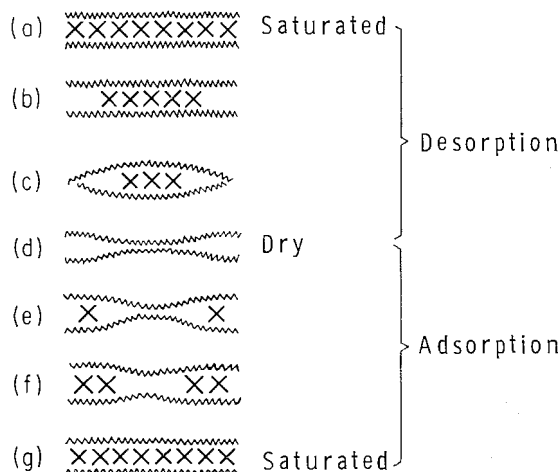


FIG. 11. — Simplified model for the exit and entry of water into the layers of tobermorite gel.

water enters, not as a physically adsorbed, but as a structural and " chemical " component that could be designated as an interlayer-hydrate water. If this is true, then the mechanical behaviour should exhibit certain peculiarities to suit this special model of the gel particle.

It has been found that the modulus of elasticity has the highest value when the paste is hydrated and tested in the saturated state (before first drying) (fig. 9). As the paste is dried the modulus decreases to a much lower value (depending on the initial W/C ratio). When water is adsorbed the modulus remains essentially constant until about 50 % R.H. condition is reached; after further adsorption the modulus then increases until at saturation the value is nearly the same as when the paste was saturated originally.

There is evidence that this interlayer water is removed progressively as the sample is dried, but mostly in the last part of the drying region. During sorption from the dry state the interlayer water goes into the crystallites progressively. The effect of this interlayer water on modulus, however, begins to be of significance only in the higher region of the isotherms. In this region the entry of interlayer water causes a much smaller length change

per unit of interlayer water gained. In Section 4 this will be shown to be consistent.

It is important to consider whether the interlayer water would be expelled during compaction of the hydrated cement particles as was suggested for the case of the interparticle bond area. First the area between layers must be large relative to the interparticle area and consequently unit pressure would not be high. Second, the interlayer water finds itself confined or blocked between the layers, and so would require considerable time to be expelled. Thus in the rapid application of pressure during compaction, very little of this water would be expelled, whereas during the sustained load application resulting in creep, a considerable amount of the interlayer water may be expelled. This possibility provides the link between drying shrinkage and creep deformation.

Thus the reversible part of creep is probably associated with the slow decomposition of the hydrate and liberation of water, which should return to its original position after the removal of the stress. The irreversible part of creep could be associated with the displacement of one layer relative to the other, but more likely involves a process of breaking and remaking the interparticle bonds. Just as compaction of paste is possible without any loss in strength when this is done under triaxial stress, so will sustained stress at a level considerably below the breaking stress, induce the breaking of certain highly stressed bonds and subsequent remaking after some reorientation of the particles. As long as there are as many bonds being remade as are being broken, no net loss in strength will be experienced.

4. MODEL FOR HYDRATED CEMENT PASTE

Evidence has been presented in support of the concept that the hydrated cement particle or crystallite is a layered structure of no definite number and of irregular configuration or arrangement.

It now appears certain that water constitutes a structural part (a crosslink or web) between layers and that this water is the irreversible water observed from the scanning isotherms, distinct from the rever-

sible physically held water. It is the outer surfaces that have been measured during N_2 adsorption, although at times during the structure formation some of these contacts may represent the interlayer situation existing inside the particle described above.

The reason for the N_2 area changes with W/C ratio is found in the concept that gel formed in more confined space (lower W/C ratio) is forced to be "pressed" together and that more of the spaces between particles become effectively interparticle spaces where water is preferentially admitted and becomes hydrate water.

The layered irregular structure is consistent with the various descriptions of electron micrographs of tobermorite as crumpled sheets. An attempt is made to represent diagrammatically a model of a tobermorite particle in figure 10, where the two types of water are differentiated. The interparticle bonding is represented as a solid-to-solid contact, although at times during the structure formation some of these contacts may represent the interlayer situation existing inside the particle described above.

The removal of the irreversible water during desorption is found to be different than its re-entry during sorption and this can account for the variation of Young's modulus and length change with vapour pressure (or irreversibly sorbed water) (fig. 11). This model shows in (a) and (b), the gradual removal of interlayer water from the edges. This probably occurs from 30 to 10 % R.H. and little change in modulus and length change occurs. Further removal, from (b) to (c), involves a larger length change, up to about 2 % R.H., but still no change in modulus. Only the final removal of the water in the middle shows a large decrease in modulus and again a large length change. On resorption large length changes occur up to about 50 % R.H. (states (e) and (f)) with no change in modulus; above 50 %, to 100 %, state (g) is reached, i.e., a filling of the middle of the layer, yielding an increase in modulus and lower rate of increase of length with interlayer water. This model explains the large hysteresis found for the variation of modulus, irreversible water, and length change of hydrated cement paste with relative pressure.

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