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A NEW MODEL FOR HYDRATED PORTLAND CEMENT AND ITS PRACTICAL IMPLICATIONS

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UNE NOUVELLE REPRÉSENTATION POUR LE CIMENT PORTLAND HYDRATÉ. CONSÉQUENCES PRATIQUES

SOMMAIRE

Les concepts antérieurs et les représentations relatives au ciment portland hydraté sont étudiés et plusieurs observations expérimentales sui ne peuvent pas être expliquées par ces représentations sont énumérées.
Le progrès de la recherche est décrit et on indique comment certaines techniques passées n'étaient pas satisfaisantes dans l'étude du ciment portland hydraté.
Une nouvelle représentation est proposée pour expliquer certaines des anomalies présentes dans certains secteurs. Les données obtenues par l'absorption, par les phénomènes de changements de longueur et par les variations des propriétés mécaniques en fonction de l'humidité relative servent au développement de cette représentation.
En se fondant sur la nouvelle représentation, des conclusions et des prédictions sont avancées concernant des paramètres tels que la contraction et le fluage.

A New Model for Hydrated Portland Cement and its Practical Implications

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It is now recognized in this era of rapid development of materials science and engineering that a greater understanding of the nature of a material can lead to its wider and more efficient use. This is no less true of portland cement, the most common and the most extensively used of industrial chemicals, than of more sophisticated and costly materials. The setting property of portland cement determines its usefulness as a binding agent by which various aggregates can be formed into a stone-like material and is of such overriding importance that it outweighs any deficiencies or departures from ideal performance in other directions. Although these can be "diluted" by the relatively high proportion of aggregate to cement in concrete, significant and important characteristics of concrete are determined by the inherent characteristics of the hardened cement paste.

In recent years there has been considerable effort to understand the microstructure of hydrated cement paste and to explain its behavior. The Division of Building Research has been active in this area of work, devoting special attention to the properties of dimensional stability and durability of concrete and other building materials. This has led, inevitably, to work designed to answer certain basic questions and ultimately to new concepts of the character of hydrated portland cement paste, i.e., to a new model, as described in a recent paper.[1]

The term "model" is used frequently in connection with materials. It is, essentially, a hypothetical physical representation or structure that, like other hypotheses in science, should be compatible with all that is known about a material. A model for any material, therefore, shows its average chemical, physical, and mechanical properties and provides a concept of its microstructure. This model, if valid, can be used in predicting or explaining behavior under all conditions.

New hypotheses must be developed when new facts indicate that previous models are inadequate. Models exist for the atomic arrangement of many materials. They include concepts involving ordered arrays of atoms which led to theoretical predictions of strength far in excess of those practically attainable. Subsequently the Griffith flaw concept provided a new model to account for decreased failure stress and significant advances in the technology have resulted. Similarly, more advanced models for hydrated cement paste and concrete can be expected to generate advances.

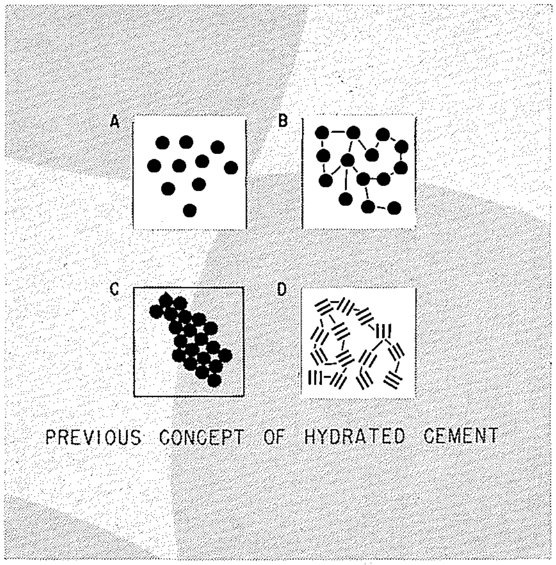


Figure 1
Previous concept of hydrated cement

A number of Canadian research laboratories engaged in the study of cement and concrete are now emphasizing the basic aspects of engineering materials and are concerned with microstructure and its relation to mechanical behavior. In view of this, it is useful to review new developments and ideas as reflected in any proposed new model. This paper, therefore, discusses the evolution of the older models and their weaknesses, the general direction research has taken in advancing knowledge, and the new model itself and how it sheds light on several unsolved problems.

Previous Models

Hydrated portland cement paste saturated with respect to water was first considered[2] to be an assemblage of spheres 100 Å in diameter, separated by films of water 6 A thick. To provide this body with strength and to keep it together the existence of solid bonds between the spheres was postulated. Figure 1 (a and b) depicts these stages. Where the hydrated cement is dried, the spheres are said to come together (Figure 1 (c)). Finally, when it was discovered through electron microscopy[3] that hydrated cement paste was composed of thin sheets and foils, the model was changed to that represented in Figure 1 (d). The explanations for expansion and shrinkage on wetting and drying (i.e., the separation and rejoining of units) were, however, retained.

Shortcomings of Previous Models

The original model introduced several concepts that must now be questioned. Several experimental observations have recently been made that it cannot explain. The main points are listed below:

(1) The nature of the solid links between units and the way the links transform from the water-saturated to the dry state are difficult to conceive.

(2) The mechanism on wetting by which the adsorbed water molecule is able to penetrate between units, overcoming the more powerful solid-to-solid forces, is not clear.

(3) Experimental observations concerning the variation of Young's modulus, flexural strength, length and weight change with relative humidity cannot be accounted for.

(4) The irreversibility and hysteresis effects observed in the length-and weight-change water isotherms cannot be explained; neither can porosity values determined by helium, nitrogen, methanol and water, and surface area values determined by nitrogen, methanol and water.

This model is largely the result of the pioneering work of Powers.[2] Closer examination reveals that it is, in fact, very similar to the model for wood or other cellulosic materials.[4] Because cement paste was considered a gel, it is not surprising that this comparison was made. With cellulosic material, the fibres are held together by hydrogen bonds from hydroxyl groups. These bonds are attenuated by sorbed water molecules and the fibres separate. On drying, the water molecules are removed and the hydrogen bonds are remade. A strength-versus-water-content plot[4] for these materials is very instructive and will be discussed to illustrate the difficulty of explaining the behavior of hydrated portland cement with Powers' model.

For cellulosic material there is a linear decrease in strength with the amount of water sorbed; the more that is sorbed, the greater the number of hydrogen bonds attenuated and the lower the strength.

If the Powers' model for hydrated cement is correct, the strength-sorption results should be similar to those for cellulosic materials. The strength or micro-hardness of hydrated portland cement, quartz, and porous glass[4-6] as a function of relative humidity is shown on Figure 2. There is a large decrease in strength up to 15% RH and little change after that. There is a great similarity in these results, but they are completely different from those of cellulosic materials.

Figure 2
Effect of humidity on microhardness and strength

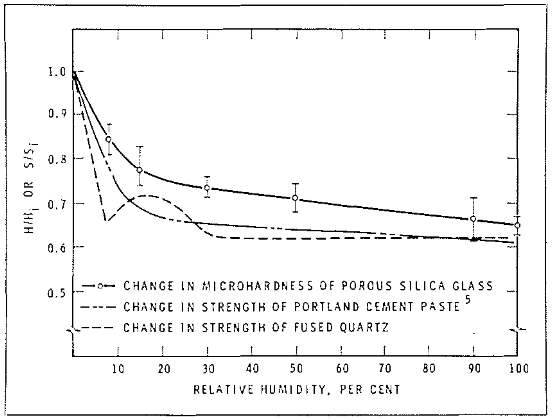


Figure 3
Observed forms of hysteresis

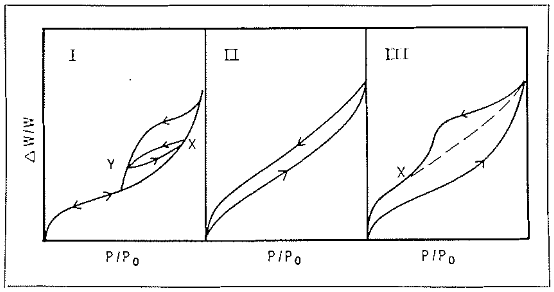
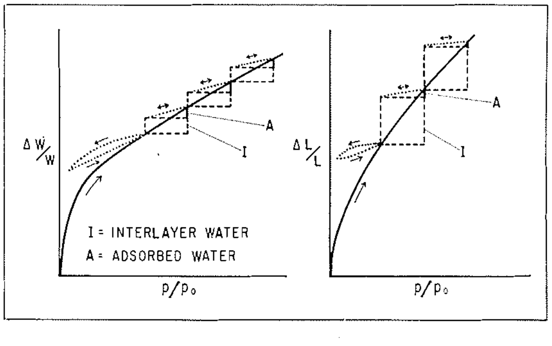


Figure 4
Method of separation of interlayer and adsorbed water



Despite the dissimilar nature of the materials referred to in Figure 2 (quartz is non-porous; porous glass, 97% silica, has a high porosity and surface area of 150 m^2/gm), the results can be explained. Breaking will be initiated at the apex of pointed cracks (Griffith cracks) where there are stress concentrations; $-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-$ bonds will be strained and this strain energy will contribute to a greater ease of formation of hydroxyl groups $(-\overset{|}{\underset{|}{Si}}-OH\ HO-\overset{|}{\underset{|}{Si}}-)$ in the presence of water vapor. Thus the breaking of the bonds will occur at a lower stress level in the presence of water vapor. When the concentration of water molecules is sufficient to maintain a rate of diffusion that will deliver a minimum amount of water into a spreading crack no further decrease in strength will occur.[4] In this view, the decrease in strength is not due to a change in state of the solid or to a modification of bonding between units, as with cellulosic materials, but to a change in the environment where the breaking process is occurring. This concept is recognized and incorporated in the new model.

Although Powers' model laid the foundation, the new experimental evidence strongly suggests that the model needs to be modified.

Problems in Research on Hydrated Cement

At first thought one might be surprised at how little is known of a material so long in use, but the difficulties of studying hydrated portland cement are great. Hydrated cement is a mixture of several compounds, all hydrates.[7] It is the process of formation of these hydrates from the anhydrous cement powder that yields a structure with strength.

The most important hydrates are the calcium silicate hydrates, but they are not well-developed crystals. Normal methods of investigation do not reveal much. X-ray diffraction and microscopy, for instance, could only reveal that the individual crystals were small and made up of flexible fibres and sheets bearing some similarity to a naturally occurring class of mineral called tobermorite. It is known that the crystals are a layered type[7] with water between the layers, called interlayer water, but it is not really known how many layers exist in the average crystal.

The layers are probably badly aligned and there are probably not very many of them. This would explain why there is no X-ray pattern for the c-axis.

Surface Area Determination and Stability of Hydrated Cement

During the evolution of the model, several workers used surface chemical techniques.[8] If one knows the total surface area, i.e., all the surface within the small pores in the material, then an estimate of the size of the crystal can be made and more will be known of its morphology and crystallography.

Surface areas are usually measured with gases or vapors, such as N_2, H_2O, and CH_3OH. One can calculate the surface area from:

(1) surface chemical theory;
(2) the knowledge of the cross-section of one molecule of the gas used;
(3) the number of molecules required to cover a surface completely.

Physically adsorbed water is attracted to the surface by a gravitational-type force (van der Waals forces) and is generally non-specific. There is a dynamic equilibrium, a reversible process of placement and removal of molecules. The state of the adsorbed gas is then considered to be compressed perpendicular to the surface, with a gaseous-type pressure tangentially (spreading pressure) along the surface. The solid is considered to be unperturbed.

Before surface areas can be measured, all the molecules have to be removed from the surface; this usually takes both heat and vacuum. Hydrated portland cement, however, is unstable both chemically and structurally, and cannot take this kind of treatment. An example of its structural instability is the shrinkage on first drying from a saturated state.[9] A fair portion of this shrinkage is irreversible and cannot be recovered on rewetting. This phenomenon, though known to exist, has not been given enough attention and should be recognized in considerations of creep and durability of concrete.

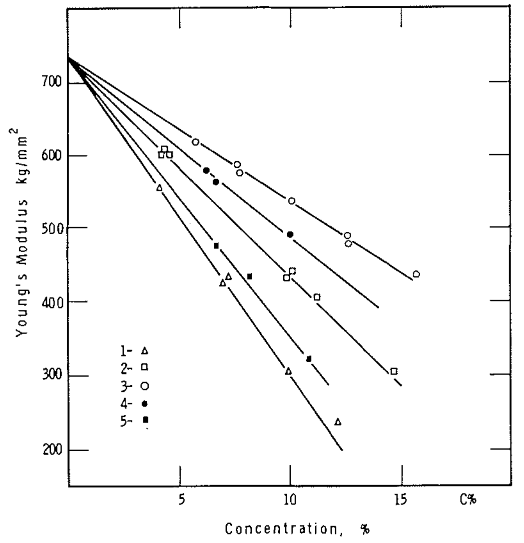
Chemical instability occurs when cement is dried below 30% RH or possibly even a higher humidity[10]; decomposition of the hydrates occurs. Of great importance is the decomposition of the silicates; the interlayer water is removed when a sample is "d-dried" (i.e., dried to the vapor pressure of ice at -79°C, about 0.5 micron). This decomposition involves a large shrinkage of the hydrated cement. It is clear that an important area of investigation is the stability of the silicate

Figure 5
Effect of various gases upon Young's modulus for acetate silk

Figure 6
Variation of modulus of elasticity with relative humidity

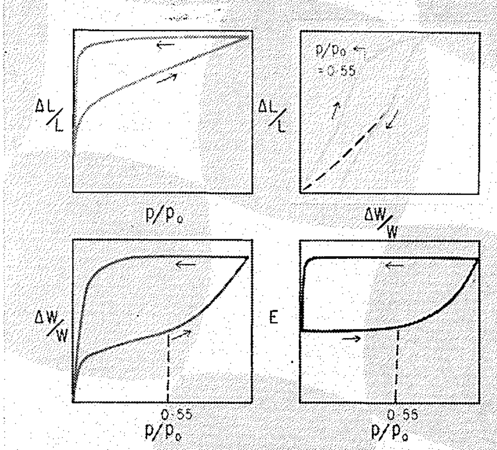
Figure 7
Interlayer water and modulus of elasticity

Figure 8
Model of entry and exit of interlayer water



EFFECT OF VARIOUS GASES UPON YOUNG'S MODULUS OF ACETATE SILK. (From Zhurkov)
1 - METHYL ALCOHOL, 2 - ETHYL ALCOHOL,
3 - BUTYL ALCOHOL, 4 - ACETONE,
5 - WATER; CONCENTRATION, %

5



INTERLAYER WATER AND MODULUS OF ELASTICITY

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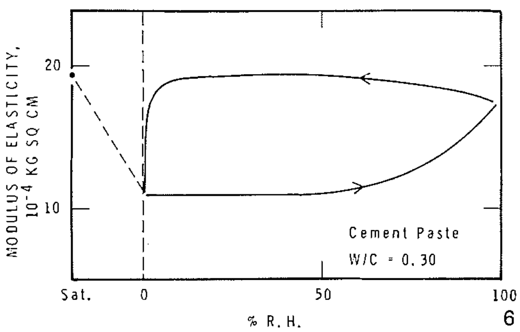

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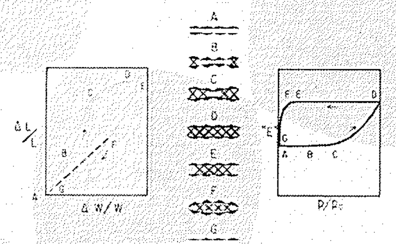

MODEL OF ENTRY AND EXIT OF INTERLAYER WATER

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hydrates under stress; this is another area that should provide some answers with regard to the creep mechanism.

The instability of hydrates has made it difficult to distinguish between adsorbed and interlayer or other hydrate water in surface chemical experiments,[11] and it is now clear that work in this area alone is not going to yield a complete answer. Investigations to date have made it clear, however, that the role of the various types of water is important in understanding the behavior, structure and chemistry, i.e. the nature, of hydrated portland cement.

Techniques and Experiments for Development of a New Model

The aim of experiments at the Division of Building Research of the National Research Council of Canada was threefold: to obtain information concerning the classification and role of water in hydrated portland cement, to find how water modifies its properties, and to gain information concerning the structure of the solid and its effect on various mechanical properties.

The experiments can be divided into two categories:

(1) measurement of the variation of adsorbed water, length (E), flexural strength, and microhardness with variation of relative humidity;

(2) measurement of the variation of E, flexural strength, and microhardness with method of fabrication and porosity at constant conditions of relative humidity.

Methods of fabrication involved:

(1) compaction of hydrated portland cement powder at different pressures to form rigid porous bodies of different porosities;

(2) cast samples at different water-cement ratios;

(3) recompacted cast samples.

All samples were made very small (30 mm diameter and 1 mm thick) to avoid stresses due to temperature gradients and to facilitate equilibrium. These methods of fabrication have provided insight into the nature of the bond between crystallites, i.e., the basis for strength development of hydrated portland cement. (Before some of the results derived from these experiments are discussed, however, a few pertinent points concerning adsorption hysteresis will be presented.)

Separation of Physically Adsorbed and Interlayer Water

Figure 3 shows the various types of isotherms and the associated hystereses obtained for different materials.[12] The first is reversible in the lower pressure region from which surface area may be calculated. The high pressure region exhibits a primary hysteresis generally explained by capillary effects. The second is the kind of isotherm obtained for cellulosic materials and some clays. As the vapor pressure increases, the adsorbate continually enters the structure of the solid, thus changing the structure. In this case it is difficult or even impossible to calculate the surface area of the material. The third is the isotherm obtained for layered crystals like clays, graphites and hydrated portland cement. The

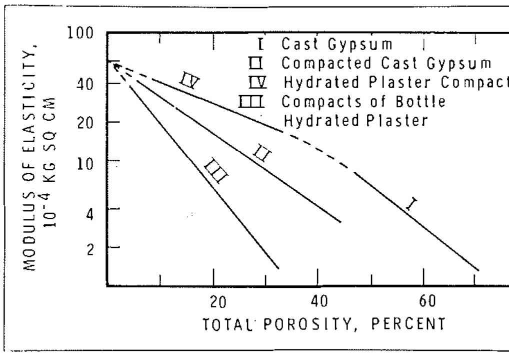

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Figure 9
Young's modulus vs porosity relations for various gypsum specimens

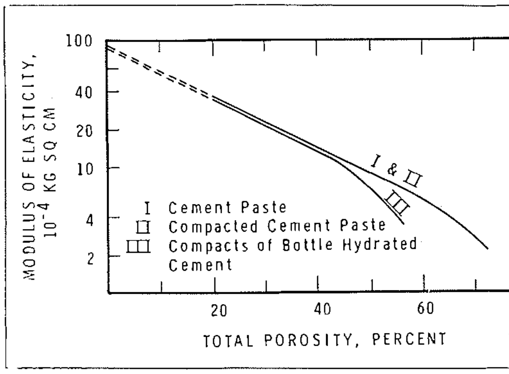

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Figure 10
Young's modulus vs porosity relations for various hydrated cement specimens

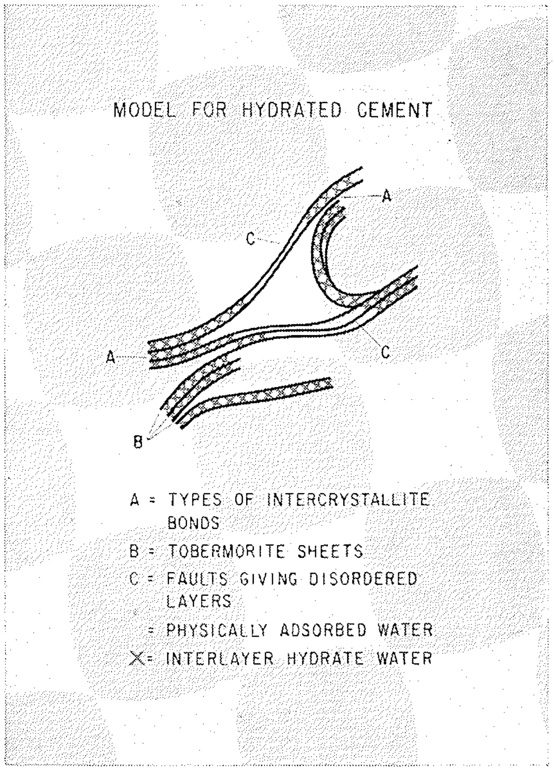

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Figure 11
Model for hydrated cement

hysteresis obtained at low pressures has been observed, by X-ray where possible, to be due to penetration between the layers (interlayer hydrated water for the cement system). If some of this penetration occurred for the cement-water system at the low pressure region where calculations for surface areas are made, then surface areas and many other conclusions made from this isotherm would be invalidated. (This includes conclusions made with regard to the morphology and size of the c-axis of the hydrated silicate crystals.) Figure 4 illustrates the irreversibility of the sorption and length change isotherms of water on hydrated portland cement. These experiments involved the interruption of sorption by intervals of desorption in order to test whether the isotherm is reversible. The main continuous line is the path followed when sorption occurs; the small lines are scanning loops and are the paths followed when desorption occurs. The isotherm is irreversible at all points.

Interlayer water, it was concluded,[10] enters while adsorption occurs up the isotherm. It was possible to separate the interlayer and physically adsorbed water and to construct isotherms for both.[10] This will be shown later, but Figure 4 illustrates how the interlayer and adsorbed water were separated. Generally, over small increments on the isotherm, the adsorbed water was considered to go on and off reversibly while the interlayer water was considered, once sorbed, not to come off over the small pressure increment. From these calculations it is possible to draw conclusions that completely support this approach and account for many of the properties of hydrated portland cement. The conclusions made from the isotherm of physically adsorbed water will be presented first. Figure 3 (I) shows the kind of isotherm obtained.

(1) Surface areas from N_2 and H_2O adsorption are very similar; one of the major discrepancies in adsorption work was that surface areas obtained by nitrogen were even less than 1/10 that of water.

(2) For many samples the total volume of interlayer water found by calculation from scanning isotherms was equal to the difference between the total volume of water sorbed and the total volume of nitrogen or methanol sorbed. This was previously ascribed to small-necked pores that prevented nitrogen, but not water, from entering, i.e.,

$$V_{H_2O} - V_{N_2 \text{ or methanol}} = v_{\text{interlayer water}}.$$

(3) A length-change versus weight-change plot for physically adsorbed water is similar to that observed for many relatively inert materials. The data also conform to thermodynamic equations that describe the length-change sorption process. From these equations calculations of E for the solid material could be made. This value was very similar to that obtained by direct measurement of E as a function of porosity and extrapolated to zero porosity.

(4) Porosity values obtained by helium pyknometry[13] were very similar to those obtained by methanol or water adsorption with correction for interlayer water (obtained from scanning isotherms).

Determination of Young's Modulus and Its Correlation with Interlayer Water

Before supporting evidence derived from the irreversible isotherm is presented, a short discussion of E of porous, high surface area materials is given.

Measurements of Young's modulus E as a function of relative humidity for high surface area materials have revealed two types of responses:

(1) no change for rigid porous bodies; this has been observed with porous glass;[6]

(2) a continuous decrease; this has been observed largely with cellulosic materials, and is shown on Figure 5. [4]

Hydrated portland cement gave results[5] that conform to the first type but, in addition, presented certain features that could not be explained. These results are presented on Figure 6, where it may be seen that there is no change in E from 100% RH to low humidities on drying. On 'd-drying,' a large decrease in E is obtained. On adsorption, an increase in E is observed only above 50% RH.

At this point the discussion of the evidence derived from the separation of interlayer and physically adsorbed water can be continued.

If one considers the irreversible (interlayer hydrate water) isotherms for length change, $\Delta l/l$, and weight change, $\Delta w/w$, vs relative humidity (Figure 7), one will note the similarity between them and the E vs relative humidity plot, also shown on Figure 7. Hysteresis and effects beyond 50% RH are the same, and the $\Delta l/l$ vs $\Delta w/w$ plot shows a sharp break beyond 50% RH. There is also a large hysteresis in the $\Delta l/l$ vs $\Delta w/w$ plot.

It was possible[1] to incorporate these results in a simplified model that gives a satisfactory explanation for most of the results. (Naturally it is tentative and modifications may have to be made.)

The New Model

Individual Units

Silicate hydrate crystallites are of a layered type, and the new model represents this simply, as in Figure 8. Two thin sheets are used to represent the layers; water between layers is interlayer water. The other diagrams are included in this figure to illustrate how the many parameters change simultaneously. A, B to G each represents the same state of the material on the three diagrams.

The main points are that water enters from the edges, causing expansion by the opening of the layers from A to B to C. The water acts as a web or cross-link; there will be no real increase in E until the middle starts to fill as for a sandwichtype construction, then increases markedly to D. The length-to-weight-change results indicate a rapid increase of interlayer water with a not-so-great length change beyond 50% relative humidity. The model shows that most of the expansion has already taken place from the edges. Emptying starts from the edges from D to G, but only at low vapor pressures; this explains the hysteresis obtained in the curves for $\Delta l/l$, $\Delta w/w$ and E versus relative humidity. E does not decrease until the middle part of the water has gone out and this does not take place until very low vapour pressures. In addition, because desorption starts from the edges, while the middle is still full, the whole configuration is different, the $\Delta l/l$ vs $\Delta w/w$ characteristics will be changed, and a hysteresis must be expected in this plot also.

Assemblage of Units—Hydrated Cement Paste

This part of the model is based mainly on the final area of experimental work, which was earlier placed in the second category, i.e., the measurement of mechanical properties as a function of porosity and method of fabrication.

Preliminary work involved using another material as a model: plaster of paris ($CaSO_4\ \frac{1}{2}H_2O$) water system,[14] which hydrates to give gypsum. One may observe that plaster moulded into bodies and allowed to hydrate produces a higher E at a given porosity than bodies made from compacted, prehydrated gypsum; the two methods of fabrication produce equal E at zero porosity. The gypsum system is known to develop strength by intergrowth of crystals, and it was concluded that these bonds are partly broken in compacted cast gypsum.

With hydrated portland cement,[15] there is no difference in result with method of fabrication; powder compacted into a rigid body, normal paste hydration and remoulding of paste give very similar characteristics. These results are shown on Figure 10.

One may thus conclude that the same type of solid-solid bonds in hydrated cement result from the different methods of preparation. It was concluded that tobermorite sheets, forced into proximity, may produce a connection composed of both short- and long-range bonds (van der Waals), the relative amount depending on the degree of matching of the lattice. The results from the variation of E and strength with relative humidity has led to the conclusion that these bonds are not, on the whole, affected by physically adsorbed water. More detailed calculations based on previous sorption experiments showed that, from 0 to 100% relative humidity, less than 18% of the length change (expansion) was due to physically adsorbed water and the rest to interlayer rehydration. This leads to the possible conclusion that tobermorite crystal containing interlayer water decomposes under stress and that this is a cause of the creep phenomenon.

Conclusions

A simplified diagram illustrating the conclusions is presented on Figure 11. It shows the various types of water and bonds discussed. In addition, the disorganized nature of the crystallites is illustrated by C.

Although much remains to be done and it is recognized that each development is but a step forward in the evolution of the final model of hydrated portland cement, it is believed that this model allows a greater physical understanding of the material (solid-water system) and some of the phenomena. Some speculation is inevitable:

(1.) First Drying Shrinkage.

Saturated, hardened portland cement paste, which has never been dried, will probably be in some form of equilibrium between water and ions in solution and the solid with the respective bonds formed between units. As water is removed during drying some surfaces will approach each other, into their mutual solid-solid force field, forming new bonds (A in Figure 11). This would account for the irreversible shrinkage observed on first drying, because many of these bonds will remain on rewetting.

(2.) Irreversible Creep.

This phenomenon may be associated with irreversible first-drying shrinkage, but induced mechanically. It may also be associated with displacement of one layer in relation to the other, forming situations like C in Figure 11, or involve a process of breaking and remaking interparticle bonds such as A. Experiments on compacting and remoulding seem to show that this is possible.

(3.) Reversible Creep.

This could be associated with a slow decomposition of the interlayer hydrate when under stress with the liberation of water. Some of the water should return to its original position after stress is removed.

(4.) Expansion and Contraction.

These phenomena are associated with capillary effects, surface-free energy changes and hydration-dehydration of some of the components present in hydrated paste. Even when these effects are considered separately, one still encounters irreversibilities in the hydration-dehydration phenomenon and in the capillary effects. In addition, 'aging,' a term that can include both decrease in surface area and slow chemical effects leading to changes in the chemical structure of the silicates, may contribute to the complexity of the length-change phenomenon in the high humidity region.

Generally, between 100 and 35% RH shrinkage on drying can be considered the result of capillary and surface-energy effects, with the possibility of some dehydration. Below 35% RH down to the d-dried state, dehydration provides the major cause of contraction. On rewetting to 100% RH over 80% of expansion is due to rehydration.

These explanations lead to the final conclusion that hydrates of portland cement paste cannot be regarded as inert, and that their chemical stability under various conditions plays an important role in many phenomena.

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