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OF THE HYDRATED TRICALCIUM
SILICATE-WATER SYSTEM**

by
R. F. Feldman

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HELIUM FLOW AND DENSITY MEASUREMENT OF THE HYDRATED TRICALCIUM SILICATE - WATER SYSTEM

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(Communicated by P. J. Sereda)

ABSTRACT

Measurements were made on samples initially conditioned at 11% R. H. and dried in stages to the d-dry condition. Helium flow measurements, although less quantitatively, are qualitatively similar to those found for hydrated portland cement. It was concluded that the narrow spaces into which helium flowed are interlayer spaces, not fixed-dimension narrow-necked pores. In the measurement of density it was shown that if aqueous solution is used on d-dried samples, account will have to be made for the fact that re-entrance of interlayer water occurs. However, if the material is dried only to 11% R. H. density can be measured by helium, methanol or aqueous $\text{Ca}(\text{OH})_2$ solution. The value varies only from 2.35 to 2.37 gm/cc for the hydrated C_3S .

SOMMAIRE

On a mesuré des échantillons d'abord conditionnés à 11% d'humidité relative et séchés par étapes jusqu'à l'état "d-dry". Les mesures de flux d'hélium sont semblables, qualitativement - bien que moins quantitativement, à celles qui concernent le ciment portland hydraté. On a conclu que les minces espaces où pénètre l'hélium sont des espaces intercouches et non des pores de dimension fixe et à col étroit. Les mesures de densité ont montré que si l'on emploie une solution aqueuse pour des échantillons à l'état "d-dry", il faudra tenir compte du fait que l'eau pénètre de nouveau entre les couches. Toutefois, si l'on ne sèche le matériau qu'à une humidité relative de 11%, on peut recourir aux solutions d'hélium, de méthanol ou aqueuse de $\text{Ca}(\text{OH})_2$ pour mesurer la densité. La valeur ne varie que de 2.35 à 2.37 g/cc pour le C_3S .

Introduction

Density of the products of hydration of portland cement and its constituents is an important basic property which is used for determining the porosity, and therefore the durability and strength, of cement mortars and concrete. Defining porosity has always been a problem because of the presence of both physically adsorbed and hydrate water; the latter is unstable only under mild drying conditions making differentiation of the types of water difficult. Part of the water evolved during drying should be considered associated with the solid and part merely attached to the surface (1).

A new experimental technique has been recently devised (2) whereby the changes to the solid that result from the removal or replacement of the interlayer and physically adsorbed water can be followed. This is the helium flow technique and it was applied to hydrated portland cement pastes. The latter work supported and provided more details regarding the new model of hydrated portland cement and the sequence of water removal from the interlayer spaces and subsequent collapse of the spaces (1). The work (2) showed conclusively that the pores were not narrow-necked fixed-dimension pores (ink-bottle pores).

The helium flow technique involves the use of a helium comparison pycnometer by which density can be measured. The density values of hydrated portland cement obtained by this method have been compared with those obtained by normal pycnometry (3).

It was found that the density and porosity of d-dried hydrated cement cannot be measured with aqueous solutions because rehydration occurs and the density values become too high. At the 11% R. H. condition, however, the density and porosity can be measured by helium, methanol or aqueous Ca(OH)_2 solution if appropriate corrections are applied.

The purpose of this work was to apply the helium flow and density techniques to the hydrated C_3S -water system and to establish to what extent the properties found for hydrated portland cement may be attributed to calcium silicate hydrate.

Experimental

Materials

The C_3S used was prepared by calcination of $CaCO_3$ and SiO_2 , and was ground to a fineness of $3310 \text{ m}^2/\text{gm}$ Blaine. It contained 0.4% free CaO and was 99+% pure C_3S . This material was supplied by the Portland Cement Association, U.S.A.

Pastes were mixed in vacuum in glass tubes of 3.2 cm inside diameter; the tubes were placed horizontally on rotating rollers to prevent any segregation before set occurred. Specimens were prepared at water-cement ratios of 0.5 and 0.8 and were allowed to cure in the wet state in rubber membranes for 2.5 years. They were then cut in discs 3.2 cm in diameter and 1.25 mm thick for use as samples for helium flow and density measurements. The hydrated product contained 1% CO_2 by weight of the dried material.

Bottle-hydrated powder was prepared by rotating the C_3S in a bottle at a water-solid ratio of 5 for 18 months. The material was filtered, dried to 11% R.H. and screened through a 100-mesh sieve. Large $Ca(OH)_2$ crystals were separated, ground and remixed with the powder. CO_2 content of this material was 1.4%.

Surface areas were measured by nitrogen adsorption and found to be 56 and $67 \text{ m}^2/\text{gm}$ for pastes with water-solid ratios of 0.5 and 0.8 respectively. The surface area of the bottle-hydrated C_3S was $66 \text{ m}^2/\text{gm}$.

Procedures

Helium Comparison Pycnometry and Helium Flow

The apparatus and procedure for helium flow measurements are described in detail in previous papers (2, 3). At the end of 40 hr of helium flow, the density of the material is measured. The technique uses the gas laws and ideal gas assumption to calculate the solid volume of a sample. Small pores or interlayer spaces which cause a delayed flow of helium into the sample are in the first instance regarded as part of the solid.

General Procedure

The helium flow and density were measured at different moisture contents, starting from the 11% R.H. condition at which the samples were originally stored. Then moisture was removed by evacuation alone and finally by heating at increasing temperatures and for different periods of time. This was done in a separate vacuum vessel and the sample was then transferred to the pycnometer. Helium was allowed to flow into the sample for 40 hr at 2 atm. The pressure was reduced to 1 atm and recompressed to 2 atm. From this the "solid volume" was determined from the average of five readings.

Density Determinations by Welds Pycnometers

Measurements were made with both the aqueous saturated solution of Ca(OH)_2 and the methanol as fluids. The experiment was done at $24^\circ\text{C} \pm 0.1$, and the fluid was introduced into the bottle above the sample under vacuum conditions. This density measurement was made on bottle-hydrated C_3S at the 11% R.H. condition.

Results

Paste-Hydrated C_3S

(a) Helium Flow

Samples of C_3S hydrated at water-solid ratios of 0.5 and 0.8 were used in the helium flow experiments. In each case, as stated above, the first helium flow run was performed with the samples conditioned at 11% R.H. Subsequently, helium flow measurements were made at nine further moisture conditions for both the 0.5 and 0.8 water-solid ratio pastes. The samples lost in weight a total of 7.20 and 7.13% based on the weight at 11% R.H. The flow results for the 0.5 water-solid ratio paste are shown in Fig. 1; the curves are similar qualitatively to those found for hydrated portland cement (2), again showing three types of curves. The first, Type I, up to 2 or 3% weight loss, showed that most of the helium flow occurred in the first hour. In this type it can be assumed that helium was no longer flowing into the sample since the rate after 8-10 hr was no greater than that

FIG. 1

Helium flow into 0.5 water-solid ratio C₃S paste at different water contents, as a function of time.

of the blank run. Type II is represented by the curves up to about 5% weight loss where the rate in the first hour became less than in the previous condition, but there was an increase in helium penetration with weight loss

at 40 hr. With this type it appears that at 40 hr the helium had just penetrated fully. Beyond 5% weight loss, Type III, a loss in rate as well as in total helium flow occurred at 40 hr. Indications are that after 40 hr complete penetration had not occurred.

FIG. 2

Helium inflow at 50 min and 40 hr plotted as a function of weight loss for 0.8 and 0.5 water-solid ratio C_3S pastes.

Figure 2 illustrates how the helium flow varies with moisture content; the volume of helium that had flowed into the sample at 50 min and at 40 hr is plotted as a function of moisture content relative to the 11% R.H. condition. The results for the 0.5 and 0.8 water-solid ratio pastes are essentially the same. The maximum inflow after 50 min was at 3% weight loss and after 40 hr at 4.5% weight loss for both samples. The maximum amounts of helium to flow into the samples were 2.58 and 2.42 cc/100 gm for 0.5 and 0.8 water-solid ratios respectively. This contrasts with the average value of 3.3 cc/100 gm for hydrated portland cement at water-cement ratios of 0.6, 0.8 and 1.0. It agrees with the estimate that 80% of

normal d-dried hydrated portland cement is composed of layered material compared with 60% for hydrated C_3S (4). The maxima for these curves occur at lower weight losses than the previously reported results for hydrated portland cement, but the curves have the same characteristics, including the sharp decrease in helium flow observed after 5% weight loss. Therefore, these properties reported for hydrated portland cement are probably due to the properties of the silicate.

As discussed in the experimental section, solid volume was measured also by the helium comparison pycnometer at the different moisture content levels. One thus obtains a relationship between change in "solid volume" (ΔV) and weight loss (the weight loss is due to the water removed in the step-by-step drying from the 11% R.H. condition). Decrease in volume gives a negative ΔV . Similarly, one may obtain from the results in Fig. 2, the change in "total helium inflow," ΔD , at 40 hr relative to the 11% R.H. condition. An increase in helium inflow is regarded as a positive ΔD . The parameter $\Delta V - \Delta D$ is plotted against weight loss on Fig. 3 for the two C_3S pastes. This parameter, as discussed in a previous paper (2), can be regarded as the space vacated by the water. The straight line on Fig. 3, found by linear regression analysis, is the same as that presented in the previous paper for several portland cement pastes. In addition, beyond 4.5% weight loss there is only a small rate of change of $\Delta V - \Delta D$ and, in some cases, there is in fact an increase. From the inverse of the slope of the straight line, it was found previously (2) that the average density of the water removed was 1.27 ± 0.08 gm/cc.

It is apparent that for hydrated C_3S , as it was for hydrated cement paste (2), removal of water beyond a certain point does not indicate the mere removal of water from pores. The conclusions are the same as for cement paste by similar reasoning, i. e., helium is flowing into interlayer spaces, not fixed-dimension narrow-necked pores.

(b) Density by Helium Comparison Pycnometer

The densities of the two series of C_3S pastes are presented in Fig. 4. These are shown as a function of water loss from the 11% R.H. condition and do not include the volume of helium that may have flowed in after 40 hr.

FIG. 3

Plot of $\Delta V - \Delta D$ as a function of weight loss for 0.5 and 0.8 water-solid C_3S pastes.

Both curves show a slight decrease in density up to about 2 to 3% weight loss, then a slight increase. The values vary from 2.24 gm/cc at 11% R.H. to 2.27 gm/cc at 7.13% weight loss for the 0.8 paste, and 2.25 gm/cc at 11% R.H. to 2.25 gm/cc at 7.20% weight loss for the 0.5 paste. These are values not dissimilar to those found previously by the same technique for hydrated portland cement (3). The values are presented in Table I.

Table I also shows values obtained by calculations for the two extreme conditions. A correction is made on Model A for adsorbed water at the 11% R.H. condition by assuming the presence of a monolayer of water, the quantity of which is obtained from a knowledge of the surface area (determined by nitrogen adsorption). Values of 2.28 gm/cc were obtained for Model B for both the 0.5 and 0.8 pastes at the 11% R.H. condition. Also, assuming a Ca/Si ratio of 1:5, values for the C-S-H gel itself (presented as C-S-H(B)) were calculated to be 2.31 gm/cc for both the 0.5 and 0.8 pastes. Equivalent calculations at the dry state yielded values of 2.25 and 2.29 gm/cc respectively.

A recalculation of density was made by subtracting the volume of helium that had flowed in at 40 hr from the "solid volume" obtained in the den-

FIG. 4

Density vs weight loss for hydrated C_3S pastes with water-solid ratios 0.5 and 0.8.

sity determination; these results are presented in Fig. 5 and in Table I under Model C.

The density in general increases with water loss up to about 5% weight loss for the 0.5 and 0.8 pastes. Beyond 5% weight loss the density decreases abruptly to 2.32 and 2.35 gm/cc respectively at the d-dry condition. The decrease in density is a manifestation of the collapse of the layers, which encloses space vacated by water that cannot be penetrated by helium in the 40 hr. This phenomenon has been observed previously for hydrated portland cement paste (3) and the results here are qualitatively similar.

When a correction is made to the density measured at the 11% R. H. condition, values of 2.36 and 2.35 gm/cc are obtained for the C_3S paste Model C for the 0.5 and 0.8 water-solid ratios respectively, and 2.45 and 2.43 gm/cc for C-S-H(C) gel with the additional correction for the approximately 40% $Ca(OH)_2$ in hydrated C_3S paste.

The fact that the layers do not collapse completely and that space is trapped became evident from the data presented in Figs. 3 and 5. However, the point for the 0.8 water-solid ratio paste at a weight loss of 3.7% appears to be the last point where helium has fully entered at 40 hr. In Fig. 3, this point is prior to the deviation from the straight line plot and is near the point of maximum density in Fig. 5. Using this point of density, 2.38 gm/cc,

FIG. 5

Density calculated with helium flow included as pore volume vs weight loss.

it is possible to calculate the density excluding the interlayer spaces. Another 3.41% weight loss would give approximately d-dry conditions and, assuming the density of this water to be approximately 1.25 gm/cc, the density excluding interlayer spaces is 2.46 gm/cc. Correcting for $\text{Ca}(\text{OH})_2$, assuming a Ca/Si ratio of 1.5 for the C-S-H gel, gives a value of 2.63 gm/cc for this material. If one had assumed a value of only 1.0 gm/cc for the density of the water, a value of 2.74 gm/cc would have been obtained.

(c) Bottle-Hydrated C_3S - Density by Welds Type Pycnometers

Bottle-hydrated C_3S was used in these measurements at 11% R.H. Aqueous saturated solutions of $\text{Ca}(\text{OH})_2$ and dried methanol were used as fluids. With the aqueous solution the average density for C_3S was 2.38 ± 0.03 gm/cc. A correction for adsorbed water was applied here in the same manner as it was applied for the helium pycnometer results. Model C approximates this correction. A further correction which recognizes that water would have entered some partially vacated interlayer spaces with density 1.25 gm/cc brings this value to 2.37 ± 0.03 gm/cc; this corresponds to Model C in Table I and is illustrated in a previous paper on hydrated portland cement (3).

The above value is to be compared with the recalculated density obtained from helium pycnometry where helium flow was taken into account.

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TABLE I
Density Values for C_3S Pastes and Bottle-Hydrated C_3S (gm/cc)

Sample	Model * and Condition	Helium As Fluid	Sample	Model * and Condition	Methanol As Fluid	Saturated Aqueous $Ca(OH)_2$ As Fluid
	<u>11% R. H. :</u>			<u>11% R. H. :</u>		
Paste C_3S w/s 0.5	A	2.25				
" " " 0.8	A	2.24				
" " " 0.5	B	2.28	Bottle-hydrated C_3S	B	2.30	
" " " 0.8	B	2.28	" " "	C (approx)		2.38
" " " 0.5	C-S-H (B)	2.31				
" " " 0.8	C-S-H (B)	2.31				
" " " 0.5	C	2.36	" " "	C	2.37	2.37
" " " 0.8	C	2.35				
" " " 0.5	C-S-H (C)	2.45				
" " " 0.8	C-S-H (C)	2.43				
	<u>D-Dry:</u>					
" " " 0.5	B	2.25				
" " " 0.8	B	2.27				
" " " 0.5	C-S-H (B)	2.25				
" " " 0.8	C-S-H (B)	2.29				
" " " 0.5	C	2.32				
" " " 0.8	C	2.35				
" " " 0.8	C-S-H (C)	2.42				

* MODEL A - No correction is made to the results for adsorbed water or dehydrated interlayer space.

MODEL B - Correction is made only for adsorbed water. Dehydrated interlayer space is included as solid volume. C-S-H (B) signifies that $Ca(OH)_2$ correction to the value for C_3S paste has been made giving value for C-S-H gel.

MODEL C - Dehydrated interlayer space is no longer included as solid volume as in Model B. This space is taken as the helium inflow at 40 hr. C-S-H (C) signifies that $Ca(OH)_2$ correction to this value for C_3S paste has been made, giving value for C-S-H gel.

Values of 2.36 and 2.35 gm/cc were obtained for the 0.5 and 0.8 water-solid ratio C_3S pastes respectively, at the 11% R.H. condition (Model C in Table I).

The density obtained when methanol was used as the fluid was 2.295 ± 0.015 gm/cc and corresponds to Model B. An approximate correction for the fact that methanol does not flow into the partially dehydrated interlayer spaces can be made from the helium flow recorded at 11% R.H. for the 0.8 water-solid ratio paste; this yields a value of 2.37 gm/cc (shown as Model C in Table I).

The agreement among the three different results is striking as was also found for hydrated portland cement (3). It confirms the idea that the higher value given by water initially is due to interlayer spaces into which helium flows fairly rapidly at 11% R.H. but into which methanol cannot penetrate.

Discussion

The helium flow results show all the features that were reported for hydrated portland cement (2) which led to the conclusion that the helium flow

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technique enables one to observe the sequence of removal of water from the interlayer spaces and to what degree the collapse of these spaces occurs. Again of significance is the fact that although collapse occurs when interlayer water is removed, spaces remain between the layers into which helium enters very slowly. It is thus possible to state conclusively for hydrated C_3S (as was done for hydrated portland cement) that the spaces into which helium is flowing are interlayer spaces, not fixed-dimension, narrow-necked pores as has been suggested (5).

The importance of the above points becomes evident when such properties as adsorption, density, porosity, and surface area are determined by use of aqueous solutions. In much previous work (5-11) it was assumed that, on d-drying, layers completely collapse and do not reopen on re-exposure to water vapour or liquid water. However, recent work (3) has shown that if aqueous solution is used in measuring the density and porosity of d-dried hydrated portland cement one has to account for the fact that re-entrance of interlayer water occurs. This is also true for hydrated C_3S as stated in the results. The values of densities reported in Table I are much lower than the value of 2.86 gm/cc for the d-dried C-S-H gel reported by other workers (7). However, Taylor (12) reported a value of 2.38 gm/cc, calculated from refractive index measurements for C_3S paste, but it is not clear how the sample was dried. In another paper (13) values of several badly crystallized specimens of natural tobermorite minerals are given and none of these exceeds 2.35 gm/cc. The high value of 2.86 gm/cc mentioned above suggests that the method used gave the density of the layers themselves. This was substantiated in part by the results obtained where a correction for interlayer water was made to the density obtained by helium pycnometer by assuming an interlayer water density of 1.25 gm/cc and subtracting this water in the density calculation. In the situation where complete helium penetration occurred, a value of 2.63 gm/cc was obtained, and if the density of the interlayer water was taken as 1.0 gm/cc (assumed in previous work (7)) a value of 2.74 gm/cc was obtained. However, when dealing with d-dried material it is obvious that water causes changes to the material which are not completely accountable.

It has been shown (1) that interlayer water functions as part of the solid and that because it is present in the normal state in which hydrated portland cement is used, density and porosity should ideally be measured with it present. This was done by the three methods described using the three fluids with the sample at the 11% R.H. condition. The agreement for these three was excellent, varying only from 2.35 to 2.37 gm/cc for the C_3S pastes. However, even in these experiments, with the samples dried only to 11% R.H., it is believed that some of the interlayer water had already been removed (this was measured by helium flow). It is believed that it would be intact at higher humidities. This would change these "helium flow" modified values to the range 2.32 - 2.35 gm/cc. This point is well illustrated in a previous paper (3).

Conclusions

1. Helium flow measurements on C_3S pastes are qualitatively similar to those found for hydrated portland cement. The space into which helium is flowing is interlayer space, not fixed-dimension narrow-necked pores.
2. Helium flow and density values show that when interlayer water is removed from C_3S pastes, collapse occurs. This collapse, however, is not complete at d-dry conditions, leaving voids enclosed between the layers.
3. Density and porosity of C_3S pastes dried only to 11% R.H. can be measured with appropriate corrections by helium, methanol or aqueous $Ca(OH)_2$. Agreement is excellent.
4. Measurement of porosity for practical purposes should be done at 11% R.H. on samples that have never been dried to lower levels of humidity. The use of a saturated solution of $Ca(OH)_2$ as fluid is the simplest method.

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