

NRC Publications Archive Archives des publications du CNRC

The flow of helium into the interlayer spaces of hydrated Portland cement paste Feldman, R. F.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below./ Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

https://doi.org/10.1016/0008-8846(71)90004-4 Cement and Concrete Research, 1, May 3, pp. 285-300, 1971-05-01

NRC Publications Archive Record / Notice des Archives des publications du CNRC :

https://nrc-publications.canada.ca/eng/view/object/?id=fc8098d6-3d66-4483-a3b0-8ef6036c4b7a https://publications-cnrc.canada.ca/fra/voir/objet/?id=fc8098d6-3d66-4483-a3b0-8ef6036c4b7a

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at https://nrc-publications.canada.ca/eng/copyright READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site <u>https://publications-cnrc.canada.ca/fra/droits</u> LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.





Ser TH1 N21r2 no. 476 c. 2 BLDG

ATIONAL RESEARCH COUNCIL OF CANADA EIL NATIONAL DE RECHERCHES DU CANADA

BUILDING RESEARCH - LIBRARY -MAY 25 1971

THE FLOW OF HELIUM INTO THE INTERLAYER SPACES OF HYDRATED PORTLAND CEMENT PASTE

> by R. F. Feldman

Reprinted from

CEMENT AND CONCRETE RESEARCH

An International Journal

Vol. 1, No. 3, May 1971 p. 285

Research Paper No. 476 of the Division of Building Research

OTTAWA MAY 1971

Price 25 cents

NRCC 11866

1253

ANALYZED

This publication is being distributed by the Division of Building Research of the National Research Council of Canada. It should not be reproduced in whole or in part without permission of the original publisher. The Division would be glad to be of assistance in obtaining such permission.

Publications of the Division may be obtained by mailing the appropriate remittance, (a Bank, Express, or Post Office Money Order, or a cheque made payable at par in Ottawa, to the Receiver General of Canada, credit NRC) to the National Research Council of Canada, Ottawa. Stamps are not acceptable.

A list of all publications of the Division is available and may be obtained from the Publications Section, Division of Building Research, National Research Council of Canada, Ottawa 7, Canada.



CEMENT and CONCRETE RESEARCH. Vol. 1, pp. 285-300, 1971. Pergamon Press, Inc. Printed in the United States.

ANALYZED

THE FLOW OF HELIUM INTO THE INTERLAYER SPACES OF HYDRATED PORTLAND CEMENT PASTE

R. F. Feldman

Division of Building Research, National Research Council of Canada Ottawa, 7, Ontario, Canada

(Communicated by G. L. Kalousek)

ABSTRACT

A helium flow technique has been worked out whereby the changes occurring to hydrated portland cement as a result of the removal of interlayer water can be measured. Results were obtained at water-cement ratios of 0.4, 0.6, 0.8 and 1.0. "Solid volume" measurements were also made. It was concluded that the spaces into which helium flowed were interlayer spaces and not fixed-dimension, narrow-necked pores. This work supported the mechanism discussed in the new model of hydrated portland cement on the sequence of water removal from the interlayer spaces and subsequent collapse of the spaces. An estimate of the density of the first 5.25% of the water removed from the 11% R.H. condition was made; this was 1.27 ± 0.08 gm/cc.

SOMMAIRE

On a élaboré une technique de flux d'hélium qui permet de mesurer les changements qui prennent place dans une pâte de ciment portland hydraté à la suite de l'enlèvement de l'eau dans les couches intermédiaires. Des résultats ont été obtenus pour des rapports eau:ciment de 0.4, 0.6, 0.8 et 1.0. Des mesures du "volume solide" ont aussi été faites. On a conclu que le passage de l'hélium se faisait dans les couches intermédiaires et non dans des pores étroites et de dimensions fixes. Cette étude appuie le mécanisme discuté du nouveau modèle de ciment portland hydraté sur la séquence de l'enlèvement de l'eau dans les couches intermédiaires et l'affaissement subséquent des espaces. Un estimé de la densité du premier 5.25% de l'eau enlevée aux conditions de 11% d'humidité relative a été fait; la valeur était de 1.27 ± 0.08 gm/cc.

Introduction

Scientific interest in experiments that provide information on the nature of hydrated portland cement paste is currently considerable, owing to a recently described new model for hydrated portland cement (1) and subsequent discussions (2, 3).

The new model recognizes that the hydrated calcium silicates in portland cement are layer-structured, and many of the properties of hydrated portland cement can be ascribed to this. Previous physical measurements such as density and water sorption determinations did not take into account the fact that the d-dried hydrates can rehydrate when re-exposed to water vapor; thus many accepted properties and parameters had to be reassessed or revised. In addition, it is now considered that the properties that led to the notion of "gel-pores" are in fact due to interlayer spaces.

Studies involving length and sorption scanning isotherms (4) have shown that up to 80% of the length change in the course of a sorption isotherm determination is due to interlayer hydration or dehydration. Seligmann (5) has analyzed NMR measurements of others and his own and has shown that a large portion of what was considered to be physically adsorbed water is interlayer water. Verbeck and Helmuth (6) have gone further and concluded that the water that was formerly considered to be gel water is interlayer water, and that gel pores are in fact interlayer spaces.

At this stage it was important to follow by some experimental technique the changes to the solid that result from the removal or replacement of the interlayer water in order to confirm its existence. The helium flow technique developed for this purpose and the results obtained with it are the subject of this paper.

Experimental

Materials

(a) Porous silica glass -- Porosity is approximately 50% by volume made up almost entirely of pores 25\AA radius; the surface area is $180 \text{ m}^2/\text{gm}$.

(b) Compacts of reagent grade NaCl -- Porosity varied from 18 to 0% by volume. Surface area was less than $0.5 \text{ m}^2/\text{gm}$.

(c) Compacts of reagent grade Ca(OH)₂ -- Porosity varied from 46 to 8% by volume. Surface area was $15 \text{ m}^2/\text{gm}$.

(d) A Type I portland cement was paste-hydrated at water-cement ratios 0.4, 0.6, 0.8 and 1.0, in cylinders 3.2 cm in diameter for 2.5 years. Discs 1.25 mm thick were cut from these and were used as the samples for helium flow measurements.

The compacts fabricated in (a), (b) and (c) were of the same dimensions. The analysis of the cement has been published previously(4).

Helium Comparison Pycnometer

As shown in Figure 1, the sample is placed in a cylinder which is then evacuated. Helium is allowed to fill the two cylinders at approximately 1 atm. The cylinders are then isolated and compressed to 2 atm by moving the reference piston to the forward fixed position (Figure 1); in doing this the volume is exactly halved and the pressure is doubled. The sample



piston is moved simultaneously with the reference piston, and by reference to the differential pressure indicator, the pressure in the two cylinders is kept the same.

In the actual experiment the sample is evacuated for 10 min and helium is then admitted to the sample for 15 sec. Pressure equalisation between the cylinders and compression take a further 1 min:45 sec. As soon as compression to 2 atm is complete, helium flow readings begin. The sample cylinder is always returned to 2 atm before a reading is taken by comparing with the reference cylinder through the differential manometer. Flow is plotted as milliliters of helium at 2 atm per 100 gm of sample and as a function of time.

General Procedure

The samples were heated under vacuum before a run, in a separate vacuum vessel. After a prescribed period of time dry air was allowed to enter the vessel and the sample was transferred to the pycnometer's sample cylinder in a gloved box dried with magnesium perchlorate. The sample, except in the case of porous glass, was in the form of several discs as already described, the total weight varying from 15 to 30 gm. Porous glass was in the form of broken tube, 2-mm wall thickness and 2.5 cm in diameter. The runs on the hydrated cement were done at different moisture contents. At first moisture was removed by evacuation alone and then by heating at increasing temperatures and for different periods of time. The sample was weighed after the helium flow run which extended over 40 hr, so the change in flow characteristics could be plotted as a function of weight change. Some runs were also performed using nitrogen as the fluid.

The instrument itself exhibited a small leak rate, but this was determined before the experiments. All runs were performed in a temperature-controlled laboratory at 22°C.

Results

NaCl and Ca(OH), Compacts

The standard procedure was followed with these materials using only helium as the fluid. It was found that the flow rate was of the same order as the blank run (<0.100 ml for 40 hr) and was independent of the porosity of the compact. Density calculations (from Boyle's law) were made by assuming that the value obtained directly after compression was

Vol. 1, No. 3

correct. Results corroborated this and indicated that the helium gas had completely entered the pores regardless of the porosity.

Porous Glass

The same result as above was obtained for porous glass when helium was used as a fluid, but when nitrogen was used, it was found that the "apparent volume" was very low, giving an abnormally high value for density. It was concluded that nitrogen was adsorbing on the clean porous glass surface during the compression from 1 to 2 atmospheres.

The lack of flow when helium was used was significant. The density value was realistic and it was apparent that helium very rapidly entered the pores even when these were 25Å radius.

Hydrated Portland Cement

Two sets of samples were used at the four water-cement ratios of 0.4, 0.6, 0.8 and 1.0. One set was dried to what had been previously determined by conventional techniques to be equivalent to the d-dried state (4); the other set was dried well beyond the d-dried state. All the samples had been initially equilibrated over concentrated NaOH solution (11% R.H.) in desiccators for a minimum of 6 months. The first helium flow run was done at this state and the samples were then dried in 10 to 12 steps, a helium flow run being done at each step. The first set lost a total of about 8.2% based on the weight at 11% R.H. and the second set about 10.8%. In general it took from 40 to 50 days until the final stage of drying.

Helium Flow as a Function of Time

Figure 2 presents the flow of helium versus time for the watercement ratio 0.4 (weight loss to 10.8%). The curves for all the watercement ratio samples are similar (water-cement ratios of 0.6, 0.8 and 1.0, not shown). The curves in Figure 2 can be divided into three types. The curve for the sample at 11% R.H. and the subsequent two curves up to a weight loss of 1.92% show a very rapid helium flow for approximately the first 50 min. From about 8 to 10 hr onward the rate is no greater than that of the blank run, and one can assume that helium is no longer flowing into the sample. This is the first type of curve, designated Type I. Further weight loss up to 4 or 5% yields curves which show even more rapid helium flow at the early periods and a less rapid decrease in rate, the rate at 10 hr still being significant, but insignificant at 40 hr. Beyond this point, up to a weight loss of 6 to 7%, one observes the second type of curve (Type II),



₿ △ 4, 794%

11 🔻

7.513%

16

10.822%



FIG. 2

where the rate in the first 50 min becomes less than in the previous condition, but there is a crossover of curves at a later period, with more helium penetrating ultimately. The rate at 40 hr at 6% weight loss now exceeds that of the blank run and it appears that at 40 hr helium has not yet fully penetrated. Beyond 6 to 7% weight loss is the third type of curve (Type III), which shows a loss in rate with weight loss before 1 hr and a net decrease in helium flow at 40 hr. Further weight loss before 1 hr and a net the rate decreasing at both the early and late periods. The rate at 10.82% weight loss after 40 hr is quite low even though little penetration has occurred.







Helium flow at 50 min and 40 hr, plotted as a function of weight loss for 0.4 water-cement ratio cement paste. Helium flow at 50 min and 40 hr, plotted as a function of weight loss for 0.6 water-cement ratio cement paste.

Effect of Weight Loss on the Volume of Helium Flow

To illustrate how the helium flow varies with moisture content, the volume that flowed into the sample at 50 min and at 40 hr was plotted as a function of moisture removed from the 11% condition. Figures 3 and 4 show the plots for water-cement ratios of 0.4 and 0.6, respectively. The only real difference in the curves is that for the water-cement ratio of 0.4 the maximum inflow was approximately 4.2 ml/100 gm, while for water-cement ratios of 0.6, 0.8 and 1.0 the maxima were 3.2 and 3.4 for 0.6, 3.2 and 3.6 for 0.8 and 3.1 and 3.6 for 1.0. This includes the two samples for the water-cement ratios 0.6, 0.8 and 1.0. The similarity between the curves for water-cement ratios 0.6, 0.8 and 1.0 and how they differ with 0.4 is not surprising when one considers their surface areas as determined by nitrogen adsorption. These are 30, 55, 51, and 57 m^2/gm for watercement ratios of 0.4, 0.6, 0.8 and 1.0, respectively. The plotted points show some scatter between the two samples for less than 2% water removed, especially for water-cement ratio of 0.8, but beyond 2% the agreement is quite good. They all show a decreasing amount of helium inflow after 50 min at approximately 4 to 4.5% weight loss, while the amount that flowed

in after 40 hr decreased very steeply after 6 to 6.5% weight loss. After 8 to 9% weight loss there is little further decrease in helium flow. This is just a little beyond the equivalent of the d-dried state.

Nitrogen Used as Fluid in Pycnometer

Nitrogen was also used as the fluid on hydrated portland cement; some of the results are shown in Figure 5 for the paste prepared at a watercement ratio of 1.0. Results indicated little flow of nitrogen into the small spaces of the sample. The curve for the sample equilibrated at 11% R.H. is little greater than a blank run. Since at 11% R.H. approximately a monolayer of adsorbed water exists, the surface will not be so active and adsorption of nitrogen will decrease relative to a bare surface. The other curves shown are for the sample in a fairly well dried state. In none of the cases does the nitrogen flow compare in amount with that for helium (Figure 2) and there is little change between 4 and 8% weight loss, the final curve being equivalent to the d-dried state. The latter curves can thus be explained by the fact that during drying the monolayer of water is removed, and increased adsorption of nitrogen will take place as a result of the compression of the gas from 1 to 2 atm. Examination of the curve representing a weight loss of 8.33% (approximately d-dried) reveals that in the first 20 minutes there is a high rate of nitrogen flow. This rate cannot be matched by the equivalent helium curve (Figure 2) and it is believed to be predominantly adsorption. The results from porous glass showed this even more clearly and also in the case of hydrated cement the density obtained by nitrogen was too high, approaching that of the unhydrated cement. This has been mentioned previously (7). It is clear then that in measuring the flow of helium into hydrated portland cement one is measuring flow into spaces which nitrogen cannot penetrate, whether these spaces contain some water or not. Studies, which will be reported in another paper, have shown that pore volumes computed by measuring solid volumes by this helium technique (the value is taken immediately after compression to 2 atm; flow is not taken into account) is the same as that obtained by methanol pycnometry. This in turn has been shown to give pore volumes similar to liquid nitrogen (8). Of interest in this paper are the nature of the spaces

that the nitrogen and methanol molecules do not enter, effect of removal of water from the spaces, and the role of water in them.

Total Space Vacated by Water Versus Degree of Drying (see Appendix for definitions)

Before a specific interpretation of the flow curves is made some further analysis will be helpful. In the helium pycnometric technique one may obtain a "solid volume" of the sample by using the value obtained by compressing the gas in the sample cylinder to 2 atm. No helium flow is taken into account. One may then plot a curve of change in "solid volume" (ΔV) with weight loss as shown on Figure 6 (this weight loss is due to the water removed in step-by-step drying from the 11% R.H. starting condition). Similarly on Figures 3 and 4 "total inflow" at 40 hours has been plotted against weight loss. This term "total inflow" now refers, of course, to the helium flow into the small pores into which nitrogen and methanol essentially cannot enter. Without discussing any interpretation of the curves it can be observed that removal of moisture leads to a change in "solid volume" and a change in helium flow (ΔD). Adding these together a parameter $\Delta V - \Delta D$ is obtained where the decrease in volume is a negative ΔV and increase in flow, ΔD , due to increased weight loss is regarded as positive. This can be regarded as the space vacated by the water, on the assumption that at the beginning of the flow experiments little helium entered into the small spaces vacated by the water for the short period at 1 atm and during compression. It is assumed that correction for this amount is made from the results of the first condition (the sample conditioned at 11% R.H.) which are subtracted from the others to obtain ΔV and ΔD . It is also assumed that the helium does not interact with the surface or other body forces and is at 2 atm within all the small spaces that water has vacated.

As water is removed from the sample one would expect a continual decrease in the parameter $\Delta V - \Delta D$. In Figure 6, $\Delta V - \Delta D$ is plotted for the two sets of samples from 0.4 to 1.0 and for C_3S paste hydrated at 0.5 and 0.8 water-cement ratio; for the C_3S pastes only up to a loss of 3.5% was plotted. The parameter $\Delta V - \Delta D$ appears linear up to about 5.5% weight loss (Figure 6). Consequently, a linear regression analysis was applied to





FIG. 6

Nitrogen flow into 1.0 water-cement ratio paste at different water contents, as a function of time. Plot of $\triangle V - \triangle D$ and $\triangle V$ as a function of weight loss for 10 different pastes.

the points (39 in all) below a weight loss of 5.3%. This straight line is $v = 0.31034 (\pm 0.15939) - 0.7886 (\pm 0.05052)x$, x being the weight loss. The correlation coefficient is 0.9823 giving a significance in the 0.99 level for the correlation. (The errors are estimated at the 99% confidence level.) If all the assumptions are correct and the helium filled all the space that the water vacated, the inverse of the slope gives the density of the water from 0 to 5.3% weight loss. This value comes to 1.27 ± 0.08 gm/cc. The parameter $\Delta V - \Delta D$ beyond 5.3% weight loss to approximately 11% (Figure 6) shows practically no further decrease; in fact over some regions there is an increase plotted on Figure 6 for the 0.4 water-cement ratio paste), despite the fact that a further 5.6% of water has been removed from the sample. It appears that removal of water beyond 5.3% does not conform to the mere removal of water from pores. The curve for ΔV (Figure 6) shows that between 5 to 6% weight loss an increase in the rate of change of $\Delta V \; occurs$ (i.e., an increased shrinkage per unit weight loss). In addition, on Figure 3 the helium flow at 40 hr shows that after 5.8% weight loss there is a very abrupt decrease in the amount that has flowed into the small spaces of the sample.

FIG. 7

Two different models to explain the helium flow characteristics of the cement pastes. (a) model with pores having narrow necks and fixed dimensions (b) interlayer model.

(a)			(b)
4	K Z.	0)	XXXXXXXX
		(ii)	
	Ē	(111)	
	¥.	(iv)	XX
- The second sec	l.	(v)	

Discussion

In the presentation of results it was suggested that a specific interpretation of these results could be made. It was concluded that the flow of helium which was being observed in these experiments was flow from the pores of ~20Å radius, which fill rapidly during compression, into spaces which have entrances too small for the entrance of nitrogen. There are two models for hydrated portland cement. One model has a microstructure with a small area accessible to nitrogen but a considerably larger area available to molecules like water; the large area is composed of pores of fixed dimensions with necks of such a size that nitrogen cannot enter (Figure 7(a)). The other, the "new model" for hydrated portland cement, does not recognize the existence of these pores with fixed dimensions, but postulates the presence of layered crystals with interlayer water between adjacent layers; the surface area determined by nitrogen adsorption is the external area of the layered crystals. As the water is withdrawn, interlayer space is made available at first for helium flow, but then collapse of the layers occurs in a manner not proportional to the loss of interlayer water (Figure 7(b)). It will be shown how the latter model is the one that best fits the data.

At 11% R.H. it is assumed that the samples possess approximately a monolayer of adsorbed water. Restricted flow into the sample at this stage can be described by either model, i.e., flow into narrow-necked pores or into partially dehydrated entrances of interlayer spaces. As more water is removed from the sample an increase in flow would be expected from both models. Volume change can be explained in the early stages for both models if one assumed that the monolayer of adsorbed water on the external surface was being removed. In either model, this can only be used to explain a small part of the volume change, however, because the complete monolayer would occupy less than 1 ml/100 gm of a sample (calculated from external area determined by nitrogen adsorption; the surface area is $30 \text{ m}^2/\text{gm}$ for 0.4 water-cement ratio paste). Model (b) (Figure 7) can explain this since one would expect a diminution in "solid volume" as dehydration proceeds further into the layers. Part of the volume vacated by the water from the interlayer spaces is taken up by a slight collapse of the layers which causes an external volume change; the rest of the volume vacated by water will result in increased flow of the Type I flow curves.

The sum of the external volume change (ΔV) and change in amount of inflow (ΔD) (same as parameter $\Delta V - \Delta D$) plotted against the loss in weight (ΔW) for the many samples (Figure 6) produced a straight line giving a density of 1.27 gm/cc for the water removed up to 5.2%. Although this result by itself is consistent with model (a), it provides evidence against it because, at this weight loss (5.2%), ΔV is too large to be explained by the fixed-dimension narrow-necked pores of model (a). The flow curves and the value of density for the water would be consistent with both models up to about 4% weight loss. Beyond this loss, however, the flow curves show a decrease in initial rate although more helium has flowed in at 40 hours. (These curves were labelled Type II earlier in this paper). This last fact cannot be explained by model (a). Indeed, there is no mechanism in this model to account for a decrease in flow rate or total flow. One would expect an increase in initial rate and quantity as the volume of empty space in the small pores increases. As more water is removed, i.e., beyond 6%weight loss where the Type III curves occur, initial flow rate decreases even further; at 40 hours the total quantity of helium that has entered the sample now also decreases.

These results can be completely explained by model (b): as water is removed from the interlayer spaces more space is vacated and some collapse occurs. At first, however, the collapse is not as great as the space created and helium flow increases in rate. As entrances to interlayer spaces get significantly smaller, rate of flow decreases even though a

larger volume of helium can ultimately flow in. Where the weight loss is between 5 and 6% the rate of volume change with weight loss increases significantly; this fits in well with the flow curves and model (b). This increased rate of shrinkage has been indicated in previous studies of length change (4) and was part of the evidence used for constructing this model. Figures 3 and 4 show how rapidly the rate of flow decreases over a very small weight loss range. It is believed that in this region the collapsing layers not only present "narrow necks" to the helium atoms but also long narrow slits which greatly restrict flow. This is illustrated further in Figure 6 which shows that beyond 5.5% weight loss there is no further decrease in $\Delta V - \Delta D$; in fact it sometimes increases. The increase in shrinkage ($-\Delta V$) in this region (Figure 6) does not compensate for the decrease in flow in the parameter $\Delta V - \Delta D$ (Figures 2-4).

Results from sorption and length-change isotherms (1), and measurement of Young's modulus as a function of sorbed water, led to the idea that the water between the layers of the hydrated silicates played an allimportant role, especially the water in the middle portion, which, it was thought, controlled the collapse and change in elastic properties. Significant closing of the layers did not occur until the interior portion of the water was expelled. This explains the great influence of a small weight loss on the rate of flow, and the failure of parameter ($\Delta V - \Delta D$) to continue to decrease linearly as a function of weight loss. In effect, the collapse of the layers has trapped space vacated by water, and helium cannot enter this space even after 40 hours of exposure. Thus the new model also explains the behavior of the $\Delta V - \Delta D$ versus ΔW plot; model (a) would predict this plot to continue in essentially a linear fashion.

Conclusions

(1) A technique is described which makes possible the measurement of flow of helium or nitrogen into hydrated portland cement.

(2) Helium flows rapidly into all pores except the interlayer spaces. The measurement of helium flow data is the measurement of the rate of penetration of helium into interlayer spaces. Nitrogen gas produces slight, if any, penetration into these spaces.

(3) By measuring this parameter for the same sample at different levels of water content it is possible to state conclusively that these "small pores" into which helium is flowing are interlayer spaces, not fixeddimension narrow-necked pores.

(4) These measurements provide corroboration to the "new" model for hydrated portland cement and support the mechanism on the sequence of water removal from the interlayer and how this effects volume change.

(5) This technique makes possible the study of the interlayer nature of hydrated portland cement and thus should be helpful in studying all properties that are dependent on the nature of the interlayer, such as firstdrying shrinkage.

(6) The density of the water considered predominantly interlayer came to 1.27 ± 0.08 gm/cc. This is in line with measurements made on expanding and non-expanding clays for water contents of less than one monolayer (9). Results for some adsorbates 30% above their bulk values are also recorded in the literature (10). Brunauer et al have reported the value for the apparent density of the molecule of water in excess of $Ca_3Si_2O_7.2H_2O$ as 1.39 gm/cc (11). The density result thus lends support to the conclusions made from the helium flow technique.

Acknowledgments

The valuable contribution of S.E. Dods in observing and recording the phenomena is recognized here. Thanks are also given to Drs. V.S. Ramachandran and H. Whitehead for helpful discussions.

This paper is a contribution from the Division of Building Research, National Research Council of Canada, and is published with the approval of the Director of the Division.

References

 R. F. Feldman and P. J. Sereda. A model for hydrated portland cement as deduced from sorption-length change and mechanical properties. Matér. Constr. 1, No. 6, 509 (1968).

- S. Brunauer, I. Odler and M. Yudenfreund. The new model of hardened portland cement paste. Highw. Res. Bd. (to be published).
- 3. R. F. Feldman and P. J. Sereda. Discussion of paper "The new model of hardened portland cement paste" by S. Brunauer, I. Odler and M. Yudenfreund. Highw. Res. Bd. (to be published).
- R. F. Feldman. Sorption and length change scanning isotherms of methanol and water on hydrated portland cement. Proc. Fifth Int. Symp. Chem. Cement, Tokyo, 1968, Part III, Vol. III, p. 53.
- P. Seligmann. Nuclear magnetic resonance studies of the water in hardened cement paste. J. Portland Cement Assoc. Res. Dev. Lab. 10, No. 1, 52 (1968).
- G. J. Verbeck and R. A. Helmuth. Structures and physical properties of cement pastes. Proc. Fifth Int. Symp. Chem.Cement, Tokyo, 1968, Vol. III, p. 1.
- T. C. Powers and T. L. Brownyard. Physical properties of hardened portland cement paste. Portland Cement Assoc. Res. Lab. Bull.22. Chicago (1947).
- 8. R. Sh. Mikhail and S. A. Selim. Adsorption of organic vapors in relation to the pore structure of hardened portland cement pastes. Highw. Res. Bd. Spec. Rep. 90, p. 123.
- 9. R. T. Martin. Adsorbed water on clay: A review. Proc. Ninth Nat. Conf. Clay Clay Minerals (1962), p. 28.
- S. Brunauer. The Adsorption of Gases and Vapors. p. 420. Princeton University Press (1943).
- S. Brunauer, D. L. Kantro and L. E. Copeland. The stoichiometry of the hydration of β-dicalcium silicate and tricalcium silicate at room temperature. J. Am. Chem. Soc. 80, 761 (1958).

Appendix

The following are definitions of terms used in the text.

Solid Volume

This is the value obtained for solid volume from the helium pycnometer immediately after the helium is compressed to 2 atm. The solid volume is considered to exclude all pores, but include interlayer spaces which may or may not be occupied by water.

External Volume Change or ΔV

 $\Delta \mathbf{D}$

This is the change, due to a removal of water from the 11% R.H. condition, in the helium inflow taken at 40 hr. An increase in inflow yields an increase in ΔD .

ΔV - ΔD

This refers to the net effect of the removal of interlayer water and physically is a volume. When helium can enter all the vacated interlayer space, this term represents the volume which the removed interlayer water had occupied.