

## NRC Publications Archive Archives des publications du CNRC

### Volume change, porosity and helium flow studies of hydrated Portland cement

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.

#### Publisher's version / Version de l'éditeur:

*Proceedings RILEM/IUPAC 1973 International Symposium on Pore Structure and Properties of Materials: 18 September 1973, Prague, Czechoslovakia, pp. C-101-C-116, 1973*

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

<https://nrc-publications.canada.ca/eng/view/object/?id=f58d2afb-07fc-4d68-a737-003c28fd975e>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=f58d2afb-07fc-4d68-a737-003c28fd975e>

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

<https://publications-cnrc.canada.ca/fra/droits>

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.

Set.  
THI  
N21r2  
no 583

3572



National Research  
Council Canada

Conseil national  
de recherches Canada

# VOLUME CHANGE, POROSITY AND HELIUM FLOW STUDIES OF HYDRATED PORTLAND CEMENT

ANALYZED

BY

R. F. FELDMAN

52913

BUILDING RESEARCH  
- LIBRARY -

APR 30 1974

NATIONAL RESEARCH COUNCIL

REPRINTED FROM  
PROCEEDINGS, RILEM/IUPAC 1973 INTERNATIONAL SYMPOSIUM ON  
PORE STRUCTURE AND PROPERTIES OF MATERIALS  
HELD 18 - 21 SEPTEMBER 1973 IN PRAGUE

RESEARCH PAPER NO. 583  
OF THE  
DIVISION OF BUILDING RESEARCH

OTTAWA

PRICE 25 CENTS

NRC 13729

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 to the Receiver General of Canada, credit NRC) to the National Research Council of Canada, Ottawa. K1A 0R6. 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. K1A 0R6.

CISTI / ICIST



3 1809 00211 3691

VOLUME CHANGE, POROSITY AND HELIUM FLOW  
STUDIES OF HYDRATED PORTLAND CEMENT

R.F. Feldman

Division of Building Research

National Research Council of Canada, Ottawa, Canada

ABSTRACT

The mechanical properties of hydrated portland cement, are largely dependent on its pore structure. This paper describes these relationships and shows the difficulties in firmly establishing them because of (a) the instability of the material under any form of stress and drying and (b) the existence of interlayer spaces which play an important part in volume stability and elastic moduli of the material.

A new technique, the helium flow method, is described, where relative changes to the dimensions of very small pores, due to removal of sorbed water may be traced. This technique involves measuring the flow of helium as a function of time into the vacated spaces of the material as water is removed and returned. Simultaneously, volume change, porosity and density of the material are measured as a function of weight change.

Results obtained by this technique are presented showing the unique behaviour of this "porosity" and how density of the sorbed water can be computed. Results that show the effect of this "porosity" on Young's modulus are also presented.

Les propriétés mécaniques du ciment portland hydraté dépendent en grande partie de sa porosité. Le présent article décrit ces rapports et montre qu'il est difficile de les déterminer précisément à cause de a) l'instabilité du matériau vis-à-vis de toute forme de contrainte et de séchage, et b) l'existence d'espaces intercouches qui jouent un rôle important dans la stabilité du volume et les modules d'élasticité du matériau.

L'auteur décrit une nouvelle méthode, celle de l'écoulement d'hélium, qui permet de relever des changements relatifs de dimension de pores très petits par suite de l'enlèvement de l'eau sorbée. Cette méthode comporte la mesure de l'écoulement d'hélium, en fonction du temps, dans les espaces du matériau laissés vides par l'enlèvement de l'eau, qui est ensuite retournée. On mesure en même temps le changement de volume, la porosité et la densité du matériau en fonction du changement de poids.

L'auteur présente les résultats obtenus par cette méthode; il montre le comportement unique de cette "porosité" et indique la façon de calculer la densité de l'eau sorbée. Des résultats montrant l'effet de cette "porosité" sur le module de Young sont également présentés.

It is generally accepted that pore structure is an important parameter in determining the properties of porous materials. Many techniques to determine the pore structure of a solid have been used in the past. These were based largely on surface area, pore volume and pore-size distribution measurements calculated mainly from adsorption isotherms or mercury porosimetry. These calculations have been relatively successful on materials with a stable pore structure.

This ideal situation, however, does not exist for many materials used in every-day life. One such material is concrete made from portland cement, for which a knowledge of the relationships between porosity and mechanical properties are very important.

Twelve years ago a study was initiated by the Division of Building Research, National Research Council of Canada on the physical properties of hydrated portland cement and their dependence on surface chemical and pore structural considerations. Early work (1) soon showed that conventional techniques would not provide a full understanding and additional techniques were devised.

Several specific studies have been carried out including sorption with several adsorbates (2 - 4), and the associated length changes, porosity measurements by several techniques (5), and mechanical property - porosity relationships (6 - 9). These have been reported as separate works, including the additional technique of helium flow (10 - 13). The study is now complete and this paper incorporates the results from the several works and describes how the pore structure of hydrated portland cement has been elucidated.

Much is unknown about the physical properties of hydrated portland cement, due to its instability under any form of stress or humidity change and to the difficulty in distinguishing between forms of hydrates or structural water and purely pore water. It is possible to obtain different results with different fluids when measuring parameters such as porosity and surface area (2, 4, 5). This is particularly true when using water as adsorbate. Since in its practical function, hydrated portland cement has to be in contact with water, most measurements have been made with it. Figure 1 illustrates the difference in measuring porosity by different fluids, methanol, helium and water of compacts of hydrated portland cement (5). Water uniformly gives a higher porosity over the whole range of compaction pressures; the values for methanol and helium are similar. Nitrogen at liquid nitrogen temperatures gives similar values as with methanol and helium (3).

In order to measure the properties of hydrated portland cement it must be dried; this presents a major problem since decomposition

of hydrates will occur (14). One may also expect changes in porosity surface area and other physical properties. On exposing the material to water in determinations of porosity or surface area, rehydration of the decomposed hydrates may occur.

There are two main hypotheses with regard to the physical structure of hydrated portland cement (14, 15). Model (a) is designed mainly to account for the discrepancy between surface area and pore volume obtained as described above. It postulates that hydrated portland cement has a pore structure, a large portion of which is composed of pores with fixed narrow necks allowing water to enter but preventing nitrogen and other fluids from doing so. Model (b) postulates a layered structure for the material. Water resides between the layers, and when the water is removed the layers collapse. The water in this form contributes to the rigidity and stability of the system. Water may repenetrate into the system, but inert molecules do not, or only to a limited extent. This second explanation attempts to use evidence from several types of properties to provide a scheme for the structure.

#### Sorption - Length Change - Mechanical Property Relationship

Figures 2 and 3 show respectively sorption and length-change isotherms with scanning loops (2). It was postulated that on re-exposure to water vapour, water re-entered the layered structure of the dried hydrated portland cement in increments. The scanning loop, a path involving lowering and raising of vapour pressure to the original point, involved mainly water adsorbed on the external surface. Indeed a change in mechanical properties is observed during an isotherm. This is shown in Figure 4, where Young's modulus is shown to increase above 50 per cent R.H. to 100 per cent and decrease on desorption only at low humidities (6).

Other forms of instability exist. If the dried material is rewetted to various humidities and redried, its length at the dry state is shorter than before. Exposure above 50 per cent R.H. yields a greatly increased shrinkage, as shown in Figure 5 (16). This increased shrinkage is not regained on rewetting. It was also found that the material responded to stress in a similar way. If the material is placed under compressive stress, and strain rate at any time is plotted against R.H., a curve similar to Figure 5 is produced.

The helium flow technique (10 - 13) was developed in order to confirm some of the theories on structure. The feature of this technique is to indicate or follow the changes to the structure that result from the removal or replacement of water. It is also able to show quantitatively the space occupied by the solid and the degree of collapse.

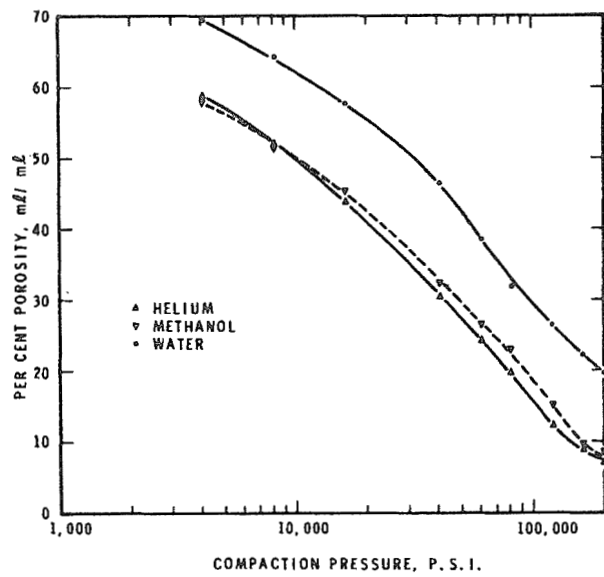


Figure 1: Relationship between porosity and compaction pressure for bottle-hydrated cement.

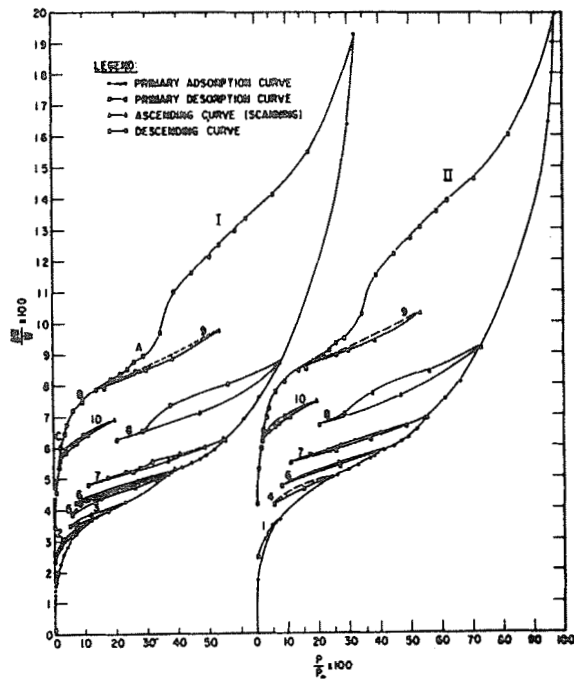


Figure 2: Weight change isotherms for bottle-hydrated portland cement compacts: I--de-gassed at 80°C; II--de-gassed at 96°C (scanning loops marked 1 to 10).

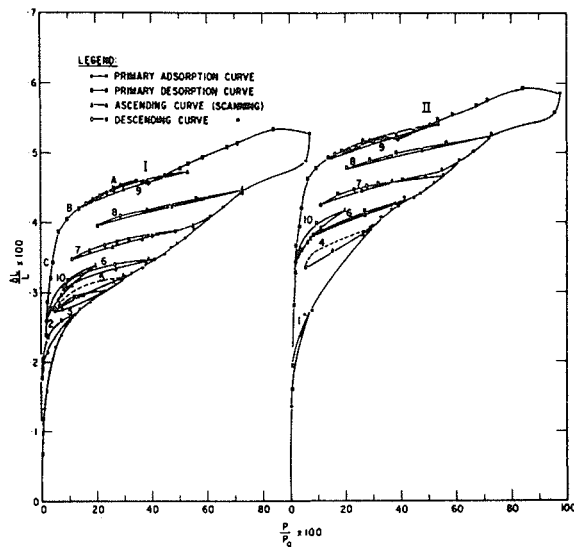


Figure 3: Length change isotherms for bottle-hydrated portland cement compacts: I--degassed at 80°C; II--degassed at 96°C (scanning loops marked 1 to 10).

Figure 4: Modulus of elasticity as a function of relative humidity.

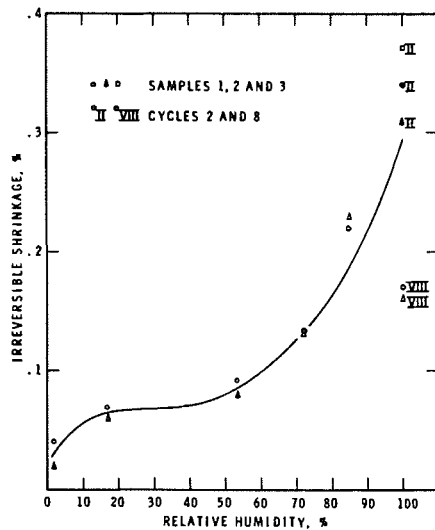
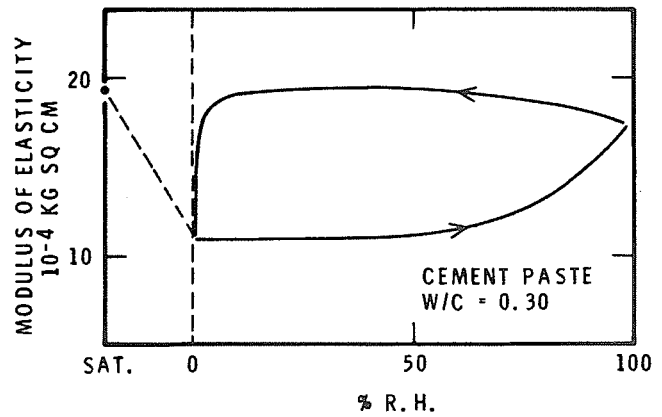


Figure 5: Irreversible shrinkage versus re-exposure relative humidity for cement paste.



Helium flow technique (10)

The apparatus used is a helium Comparison Pycnometer. The sample is placed in a cylinder which is then evacuated. Helium is allowed to fill the two cylinders at approximately 1 atmosphere. The cylinders are then isolated and compressed to 2 atmospheres by moving the reference piston to a fixed point; 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 experiments the sample is evacuated for 10 min. and helium is then admitted to the sample for 15 sec. Pressure equalization between the cylinders and compression takes a further 1 min. 45 sec. As soon as this period is complete a reading is taken which gives the "instantaneous solid volume." Subsequent to this helium flow readings begin. The sample cylinder is always returned to 2 atmospheres before a reading is taken. Flow is plotted as milliliters of helium at 2 atmospheres per 100 gm. of sample as a function of time, usually up to 40 hours.

Samples are treated under vacuum before a run in a separate vacuum vessel. After a prescribed period of time dry air is allowed to enter the vessel and the sample is transferred to the pycnometer's sample cylinder in a gloved box dried with magnesium perchlorate. The sample is usually in the form of thin discs about 1 mm. thick and weighing about 35 gm. Runs were performed on hydrated portland cement at 11 per cent R.H. and then dried by increments first by vacuum alone and then by heat and vacuum to the driest state. The samples were then re-exposed to various relative humidities up to 100 per cent R.H., but measurements were always made at 11 per cent R.H. so that the quantity of adsorbed water, approximately a monolayer at 11 per cent R.H., might remain constant. As shown by the scanning loops in Fig. 2, weight always increased after each exposure cycle to a higher humidity and back to 11 per cent R.H. 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. The instrument itself exhibited a small leak rate, which had been determined before the experiments.

Porosity measurements (Fig. 1), and helium flow and density measurements on other materials show that during the initial period of helium immersion, the gas enters rapidly into all but the smallest pores or spaces. It enters rapidly into the 25 Å radius pores of porous glass but more slowly into the small spaces of materials such as hydrated portland cement into which nitrogen or methanol molecules cannot enter. Helium flow then measures the rate at which this gas enters the spaces with entrances of size 4 Å or smaller. The "instantaneous solid volume" includes these spaces as solid volume.

## Results

### Drying

#### a) Helium flow as a function of time

Figure 6 (10) shows typical helium flow curves for a hydrated portland cement dried from the initial 11 per cent R.H. condition to a condition obtained by heating finally at 140°C for 6 hr under vacuum. Weight losses are recorded from the 11 per cent R.H. condition. The curve for the sample at 11 per cent R.H. and the subsequent two curves up to a weight loss of 1.92 per cent show rapid flow in the first 50 min. and very low flow subsequently. As water is removed, more helium can enter the sample rapidly but by 5 per cent weight loss the rate at 40 hr is still significant; further weight loss shows a cross-over of the curves as the initial rate decreases but more helium enters by 40 hr. The curves from 6 to 11 per cent weight loss show the rate decreasing over the previous curve at both early and late periods.

The effect of the withdrawal of water may be more clearly observed on Fig. 7 (10). Total helium inflows at 40 hr and at 50 min. are plotted against weight loss. The helium inflow at 50 min. decreases at approximately 4 to 4.5 per cent weight loss, while the amount of inflow after 40 hr decreased very steeply after 6 to 6.5 per cent weight loss. The total inflow after all the moisture is withdrawn is less than that at the beginning 11 per cent R.H. condition.

#### b) Solid volume and total space vacated by water on drying

A plot of the change of solid volume  $\Delta V$  with weight loss is plotted on Figure 8 (10); on Figure 7 "total inflow" at 40 hr against moisture loss has been plotted. Without discussing any interpretation of the curves it can be observed that removal of moisture leads to a change in "solid volume" ( $\Delta V$ ) and to a change in total helium inflow  $\Delta D$ . Combining these, a parameter  $\Delta V - \Delta D$  is obtained where the decrease in volume is a negative  $\Delta V$  and increase inflow,  $\Delta D$ , due to increased weight loss is regarded as positive. This then accounts for the space vacated by the water if helium enters all the space in 40 hr. It is again emphasized that the space referred to is that with entrances so small that nitrogen or methanol cannot enter.

As water is removed from the sample one would expect a continual decrease in the  $\Delta V - \Delta D$  vs. weight loss curve. In Figure 8,  $\Delta V - \Delta D$  is plotted against weight loss for 10 different samples. It appears linear up to about 5.5 per cent weight loss yielding a straight line of slope 0.7886, the inverse of which yields a value for the density of the water as  $1.27 \pm 0.08$  gm/ml. The parameter  $\Delta V - \Delta D$  beyond

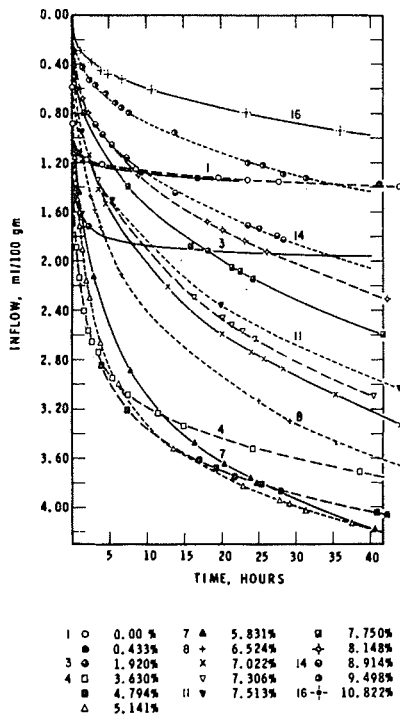


Figure 6: Helium flow into 0.4 water-cement ratio cement paste at different water contents, as a function of time.

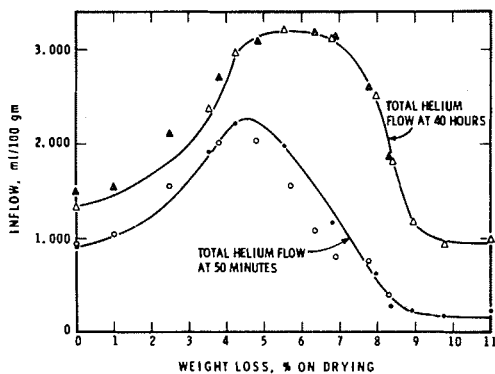


Figure 7: Helium flow at 50 min and 40 hr, plotted as a function of weight loss for 0.6 water-cement ratio cement paste.

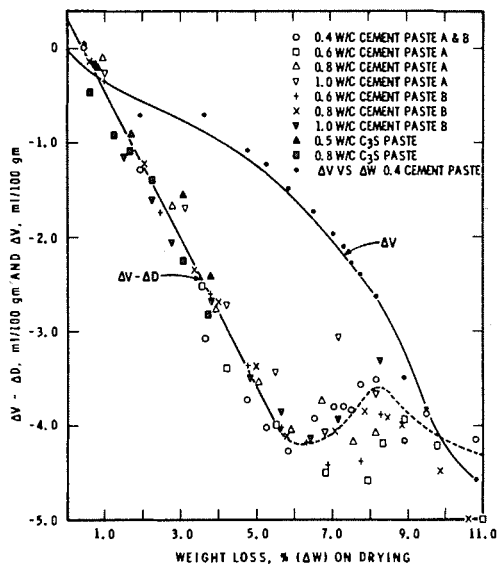


Figure 8: Plot of  $\Delta V - \Delta D$  and  $\Delta V$  as a function of weight loss for 10 different pastes.

5.5 per cent weight loss to approximately 11 per cent shows practically no further decrease and perhaps an increase even though the rate of change of  $\Delta V$  increases in this region (i.e. an increased shrinkage per unit weight loss). In addition, in Figure 7, the helium flow at 40 hr shows that after 5.5 per cent weight loss there is a very abrupt decrease in the amount that has flowed into the small spaces ( $\Delta D$ ). Thus the departure from linearity of the plot in Figure 8 is due to the sudden reduction in helium inflow.

#### c) Density calculations (5, 11)

Two forms of density can be calculated from the helium flow data. Using the instantaneous solid volume one obtains a value for density similar to that obtained by methanol. In this case the changes are not major with weight loss, an increase in 10 to 15 per cent being recorded over the full range of weight loss.

In the second calculation, the total volume of helium inflow at 40 hr is subtracted from the instantaneous solid volume, before computation. The results for 4 different samples are plotted in Figure 9 (5). The density increases monotonically and, at 5 to 6 per cent weight loss, starts to decrease. For some samples the final density is lower than at the initial 11 per cent R.H. condition.

#### Re-exposure to Water Vapour (12)

##### a) Helium inflow

Figure 10 (12) illustrates the scanning isotherms that are obtained from dried hydrated portland cement; in this portion of the work, the underlying reason for the scanning loops was investigated. Dried samples were exposed to 11, 32, 42, 66, 84 and 100 per cent R.H. After each exposure, samples were returned to 11 per cent R.H. (for reasons discussed previously) where helium flow measurements were made. Figure 10 also shows the weight gain of the samples, and the length of time at each condition. After the samples were exposed to 11 per cent R.H., they showed an increase in total helium inflow. This increased with humidity and then decreased, as shown in Fig. 11 (12), for several samples; total helium flow is plotted against weight change (Fig. 11) and in three of the four cases there was a further increase after exposure to 100 per cent R.H. This final point has a higher total helium inflow than the initial condition. The initial drying and a second drying are also plotted on these curves.

##### b) Solid volume and density measurements (13)

The variation of volume and density (calculated directly from the instantaneous solid volume) for drying, re-exposure to water vapour and final drying is presented in Fig. 12 (13). The first drying

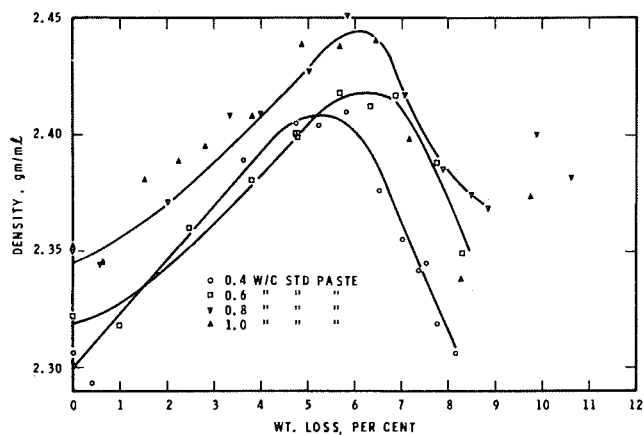


Figure 9: Relationship between density (corrected for helium inflow) and weight loss for cement pastes with w:c ratios of 0.4, 0.6, 0.8 and 1.0.

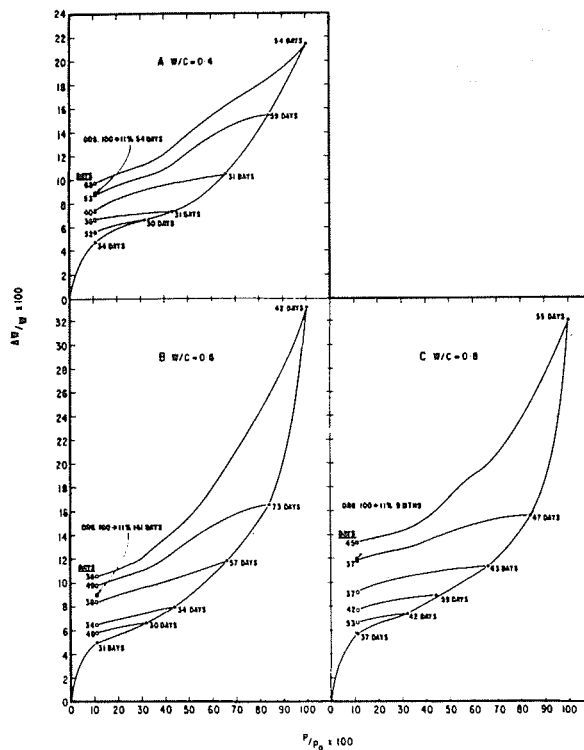


Figure 10: sorption isotherms for hydrated portland cement paste.

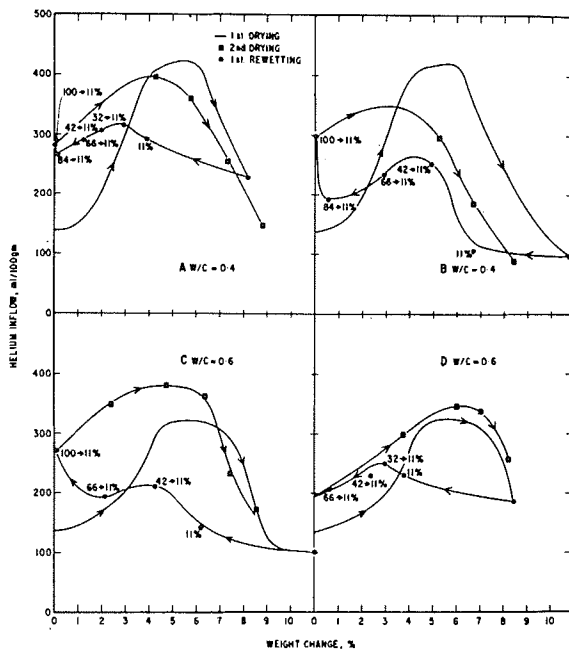
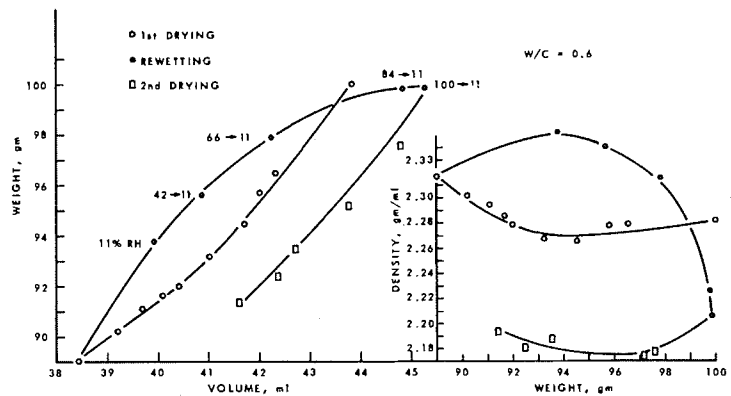


Figure 11: Helium inflow at 40 hours vs weight change.

Figure 12: Plot of volume and density versus weight change on drying and wetting cycles for sample strongly dried.



and re-exposure curves form a loop; above 42 per cent R.H., however, this ceases to be the case and there is a cross-over and the final volume is significantly larger than the starting point of the same condition. The density plot also forms a loop; when the dry hydrated cement is exposed to water vapour an increase in density occurs. This is followed by a decrease which results in a final density lower than the initial material.

A plot of  $\Delta V - \Delta D$  vs. weight change can also be made for re-exposure and this is shown in Figure 13 (13) for several samples. Up to exposure to 42 per cent R.H., where about 6.5 per cent weight gain is recorded, an increase in  $\Delta V - \Delta D$  of a maximum of 2 ml/100 gm is recorded. Beyond this point a good linear correlation is obtained for the data, which yield a density of 1.20 gm/ml for the water.

### Discussion

The two conflicting hypotheses for hydrated portland cement structure can be expressed as shown in Fig. 14 (12): (a) the narrow-necked fixed dimension pore and (b) the collapsing layer model (14, 15).

At the 11 per cent R.H. condition at the start, it is assumed that the sample possesses approximately a monolayer of adsorbed water. Restricted flow into the sample at this stage can be described by either model as more water is removed. Beyond 4 per cent weight loss, however, the flow curves show a decrease in initial rate although more helium has flowed in at 40 hr. 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. However the total helium inflow is less at the final point than it was at the start (Figs. 6 and 7). Density calculations (Fig. 9) corrected for helium inflow also show that the final density is less than that at the initial point.

Model (b) does not suffer from this difficulty in explaining results: 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 inflow 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 per cent, the rate of volume change with weight loss increases significantly. Figure 7 shows 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 Fig. 8 which shows that beyond 5.5 per cent weight loss

there is no further decrease in  $\Delta V - \Delta D$ , the increase in shrinkage ( $-\Delta V$ ) in this region does not compensate for the decrease in flow in the parameter  $\Delta V - \Delta D$ , thus some space must be encapsulated.

Helium inflow on re-exposure to water vapour further enhances model (b) for the structure of hydrated portland cement. Figure 11 shows how re-exposure to various humidities (measured at 11 per cent R.H.) increases helium flow into the sample. Fixed narrow-necked pores would predict only a decrease in helium flow but, if water molecules are reopening the layers and returning to the entrapped space, helium inflow would increase. The reentry of water into the collapsed structure explains the increase of density (Fig. 12), calculated on an instantaneous solid volume basis. The density calculated by subtracting the volume of helium inflow from the solid volume also increases sharply on re-exposure to water vapour. This also can only be explained by water returning to the interlayer structure without an equivalent re-expansion.

The  $\Delta V - \Delta D$  vs.  $\Delta W$  plot (Fig. 13) for re-exposure yields much information. If the fixed dimension narrow-necked pore exists, the volume of the monolayer would be (taken from the first part of the curve) a maximum of about 1.75 ml/100 gm or an area of less than 80 m<sup>2</sup>/gm assuming a density for adsorbed water of 1.20 gm/ml. This means that a considerable portion of the water sorbed at 11 per cent R.H. on re-exposure has gone into the structure (Fig. 10). In the other case if we accept the interlayer model, the first weight gain of 6.5 per cent would imply an impossibly high density of over 3 gm/ml for the water. The only explanation then can be that the water molecules are mainly entering the interlayer structure that had partially collapsed on drying, the helium in 40 hr is as yet not entering fully and is not measuring the volume occupied by the water. This also indicates that the monolayer of adsorbed water on the open surface (at 11 per cent R.H.) is a relatively minor part of the 6.5 per cent sorbed.

Beyond the 6.5 per cent sorbed, the water is completely interlayer since a monolayer was sorbed onto the material by 11 per cent R.H. The linear plot in this region indicates that helium now enters fully and measures the volume of space within the layers. The value of 1.20 gm/ml as density of interlayer water is significant since it is a realistic value and shows that most of the assumptions are approximately correct.

Values for pastes prepared at water-cement ratios of 0.6, obtained from Figs. 11 to 13, enable quantitative assessments to be made. For example, using the value of hydraulic radius of the pore system to be 10 Å (15), the ratio of total volume of pore to monolayer volume is 3.7 for a pore system of spheres and 3.6 for



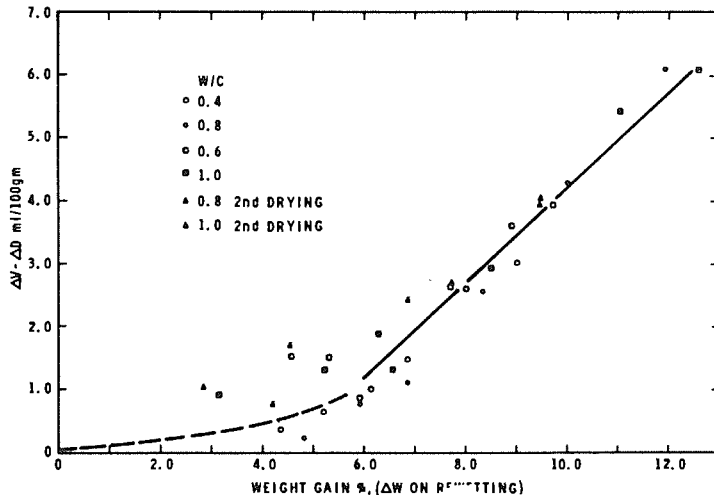


Figure 13: Plot  $\Delta V - \Delta D$  as a function of weight change for 4 different pastes on rewetting.

Figure 14: Two different models to explain the helium flow characteristics of the cement pastes. (a) model with pores having narrow necks and fixed dimensions (b) inter-layer model.

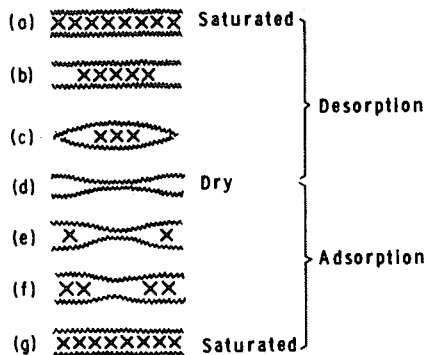
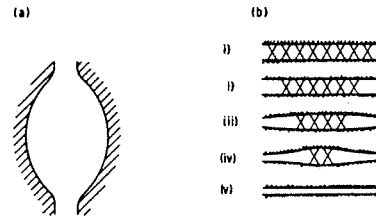


Figure 15: Simplified model for the exit and entry of water into the layers of tobermorite gel.

cylinders. The actual ratio for this system is 1.35. If the space were made up of perfectly parallel smooth plates with a monolayer between, the ratio would be 1.0. For corrugated plates, or lack of perfectly parallel alignment with kinks, it would be greater than one. This shows that the space approaches that between two approximately parallel plates.

Based on results of variation of Young's modulus with relative humidity (Fig. 4 (6)) and length change vs. weight change along the sorption isotherm a simplified scheme (Fig. 15 (2)) was proposed for the exit and entry of interlayer water. This accounts for the hysteresis in both these plots.

### Conclusions

The pore structure of hydrated portland cement has presented a difficult problem to elucidate, due to its instability and the presence of several types of water within the structure. Many techniques have been used, which, together with the helium flow techniques, show that the spaces in hydrated portland cement approximate the interlayer spaces as in some clays and not small-necked fixed-dimension pores. As water is removed they partially collapse. They re-open on re-exposure to water, and the water occupying these interlayer positions possess the property of being able to stiffen the material and to increase Young's modulus. During exposure to higher humidities, interlayer volume is increased leading to dimensional instability and such phenomena as creep.

### References

1. R.F. Feldman and P.J. Sereda. The sorption of water on compacts of bottle-hydrated cement, *Journal of Applied Chemistry*, Vol. 14, No. 2, Feb. 1964, p. 87 - 93.
2. R.F. Feldman. Sorption and length change isotherms of methanol and water on hydrated portland cement, *Fifth Intern. Symp. on Chem. of Cement*, Tokyo, 1968.
3. R. Sh. Mikhail, L.E. Copeland and S. Brunauer. Pore structures and surface areas of hardened portland cement pastes by nitrogen adsorption. *Can. Journal of Chemistry*, 42, 426 - 438 (1964).
4. R. Sh. Mikhail and S.A. Selim. Adsorption of organic vapors in relation to the pore structure of hardened portland cement pastes. Highway Research Board, Special Report No. 90, 123 - 134 (1966).
5. R.F. Feldman. Density and porosity studies of hydrated portland cement. *Cement Technology*, Vol. 3, No. 1, p. 5 - 14 (1972).

6. P.J. Sereda, R.F. Feldman, E.G. Swenson. Effect of sorbed water on some mechanical properties of hydrated cement pastes and compacts. Highway Research Board Special Report No. 90, p. 58 - 73 (1966).
7. R.A. Helmuth and D.M. Turk. Elastic moduli of hardened portland cement and tricalcium silicate pastes: effect of porosity. Highway Research Board Special Report No. 90, p. 135 - 144 (1966).
8. R.F. Feldman. Some factors affecting Young's modulus porosity relationships of hydrated portland cement. Cement and Concrete Research, Vol. 2 No. 4, 375 (1972).
9. I. Soroka and P.J. Sereda. The structure of cement-stone and the use of compacts as structural models. 5th Intern. Symp. on Cement Chemistry, Tokyo, 1968.
10. R.F. Feldman. The flow of helium into the interlayer spaces of hydrated Portland cement paste. Cement and Concrete Research, Vol. 1, No. 3, 285 (1971).
11. R.F. Feldman. Helium flow and density measurements on the hydrated  $C_3S$  - water system. Cement and Concrete Research, Vol. 2, No. 1, 123 (1972).
12. R.F. Feldman. Helium flow characteristics of rewetted specimens of dried hydrated portland cement paste. To be published.
13. R.F. Feldman. Observation of changes to structure of hydrated portland cement on drying and rewetting by helium flow techniques. to be published.
14. R.F. Feldman. Assessment of experimental evidence for models of hydrated portland cement. Highway Research Board Record No. 370, 8 - 24 (1971).
15. S. Brunauer, I. Odler, and M. Yudenfreund. The new model of hardened portland cement paste. Highway Research Board Record No. 328, p. 89 - 107 (1970).
16. R.F. Feldman. Mechanism of creep of hydrated portland cement paste. Cement and Concrete Research, Vol. 2, No. 5, p. 521, (1972).