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### Changes to structure of hydrated Portland cement on drying and rewetting observed by helium flow techniques

Feldman, R. F.

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

[https://doi.org/10.1016/0008-8846\(74\)90061-1](https://doi.org/10.1016/0008-8846(74)90061-1)

*Cement and Concrete Research*, 4, January 1, pp. 1-11, 1974-01-01

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**CHANGES TO STRUCTURE OF HYDRATED  
PORTLAND CEMENT ON DRYING AND REWETTING  
OBSERVED BY HELIUM FLOW TECHNIQUES**

by  
R. F. Feldman

REPRODUCED

Reprinted from

**CEMENT AND CONCRETE RESEARCH**  
*An International Journal*

Vol. 4, No. 1, January 1973-1974  
11 p.

Research Paper No. 580  
of the  
Division of Building Research

Price 25 cents

OTTAWA

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CISTI/ICIST



3 1809 00211 3659

CHANGES TO STRUCTURE OF HYDRATED  
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OBSERVED BY HELIUM FLOW TECHNIQUES

R.F. Feldman

Research officer, Materials Section,  
Division of Building Research, National Research Council of Canada

(Communicated by F. H. Wittmann)

(Received July 23, 1973)

ABSTRACT

Helium flow techniques are applied to the hydrated portland cement-water system during rewetting. Measurements of solid volume and density demonstrate irreversible changes to the structure. Measurement of changes in volume of interlayer space are made and are shown to be due to new alignment of layers and to the moving apart of layers as a result of water penetration. The density of the interlayer water is found by these techniques to be  $1.20 \pm 0.08 \text{ gm/ml}$ . Calculation of the parameter Total Volume/Monolayer Volume for the interlayer space yields a value of 1.32. This shows that the space approximates that bounded between two parallel plates.

On applique les techniques de flux d'hélium au système ciment portland hydraté - eau lorsque celui-ci est mouillé de nouveau. Les mesures du volume et de la densité du solide révèlent des changements de structure irréversibles. On mesure les changements de volume de l'espace intercouche et on montre que ces changements sont le résultat d'un nouvel alignement des couches et de la tendance de celles-ci à s'éloigner les unes des autres par suite de la pénétration de l'eau. D'après ces méthodes, la densité de l'eau intercouche est de  $1.20 \pm 0.08 \text{ mg/ml}$ . Le calcul du paramètre volume total/volume de la couche monomoléculaire pour l'espace intercouche donne une valeur de 1.32, ce qui indique que l'espace se rapproche de l'espace limité entre deux plaques parallèles.



### Introduction

The helium flow technique (1), has revealed that small spaces detected in hydrated portland cement and tricalcium silicate pastes were interlayer spaces which partially collapsed when water was removed. It has been further shown that on rewetting the collapsed spaces reopen (2) due to re-entrance of water at the lowest humidity attempted, 11 per cent R.H. There was evidence, however, that other phenomena occurred during rewetting. Some of this evidence has been presented and correlated with creep data obtained at different humidities (3).

This paper presents data obtained from helium flow techniques showing the variation of solid volume and density during drying and rewetting. Further evidence is also presented showing the interlayer nature of the "sorbed" water.

### Experimental

The samples were the same ones used previously, the results of which were presented in several previous papers (1 to 4). The two series of samples of water/cement ratios 0.4, 0.6, 0.8 and 1.0 were again used. Samples were dried in steps from the 11 per cent R.H. condition (1), some to d-dry, and some beyond. At each step of drying helium flow rate and solid volume were measured with the helium comparison pycnometer as a function of weight loss. These samples were then exposed to 11, 32, 42, 66, 84 and 100 per cent R.H. consecutively, but after exposure to each humidity the samples were re-exposed to 11 per cent R.H., after which helium flow rates and solid volume were measured. These parameters were also measured on second drying. Experimental details of the exact procedure have been published (1, 2).

### Results

The results of solid volume measurement as a function of sample weight for the four water-cement ratio d-dried pastes are presented on Figure 1. Measurements are plotted for first drying, rewetting and second drying; the rewetting points are all at 11 per cent R.H. while the drying points are from 11 per cent R.H. down.

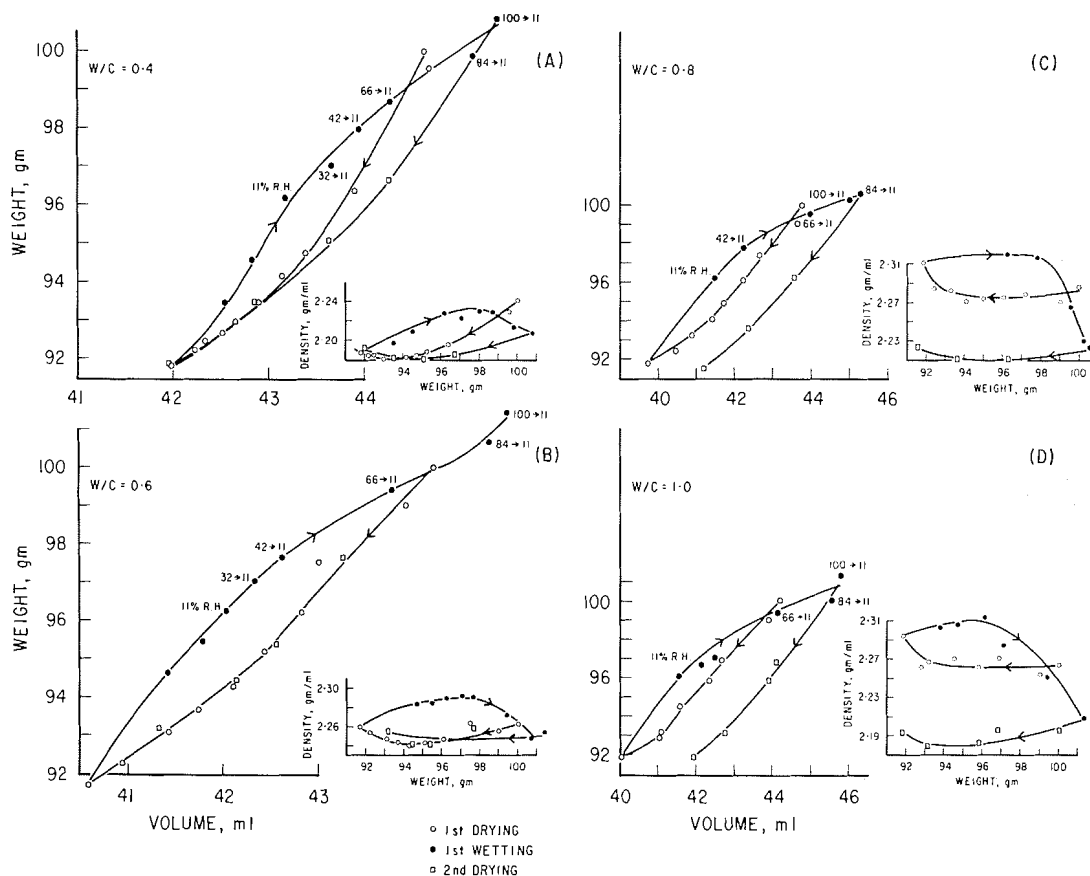


FIG. 1

Plot of volume and density versus weight change on drying and wetting cycles for samples d-dried.

The first drying and rewetting curves form a loop, the initial volume increase on rewetting not being as large as the volume decrease on drying. Above 42 per cent R.H., however, this ceases to be the case and the re-wetting curve subsequently crosses over the first drying curve. At the final point, after exposure to 100 per cent R.H. and then back to 11 per cent R.H., the solid volume of all four water/cement ratio samples are in excess of the solid volume of the sample at the original starting point of 11 per cent R.H. On second drying the curves for the 0.8 and 1.0 water/cement ratio samples are parallel but displaced to the first drying curve, so at the same weight loss they show a larger solid volume; the two drying curves for the

0.4 and 0.6 water/cement ratio pastes tend to merge, however, yielding a similar solid volume at the conclusion of the second drying as at the first. It was shown in a previous paper (2) that at the final point of rewetting (exposed to 100 per cent R.H. and dried to 11 per cent R.H.) there was a greater helium inflow than at the original 11 per cent R.H. position before drying.

Each solid volume vs. weight plot is accompanied by a density versus weight plot, calculated from the former. On first drying it may be observed that there is a slight decrease in density followed finally by a slight increase. This portion of the results has been discussed previously (4). On rewetting there is an increase in density up to the 42 per cent R.H. exposure level and then an abrupt decrease in density for exposure to 66 per cent R.H. and up. The increase in density might be considered unexpected as picking up a monolayer of adsorbed water externally should decrease the density. The d-dried sample, however, is in a partially collapsed state and helium can enter only very slowly into the enclosed interlayer spaces. As water re-enters and fills these spaces the weight and volume increases are not proportionate, the density will increase.

The large decrease in density is more difficult to explain. This occurs over the same region where there is a solid volume increase and there is an increase in helium inflow over the original sample at 11 per cent R.H. (2). It was also found that d-dried samples re-exposed to humidities above 50 per cent R.H. both increased their creep rate on loading and increased their irreversible shrinkage when subsequently dried (3). It was concluded that the wide entrances of interlayer spaces partially closed in during the period when the collapsed layers were pried apart by interlayer water re-entry (3). Further aggregation of layers was also postulated. These hypotheses can explain the increase in solid volume and decrease in density; the boundary between solid and helium gas defined as the "instantaneous solid volume measurement" would be increased by lengthening or aggregation of layers and this would include some space. Similarly, density would decrease if these layers were not as close together as the previous layers and helium inflow would increase.

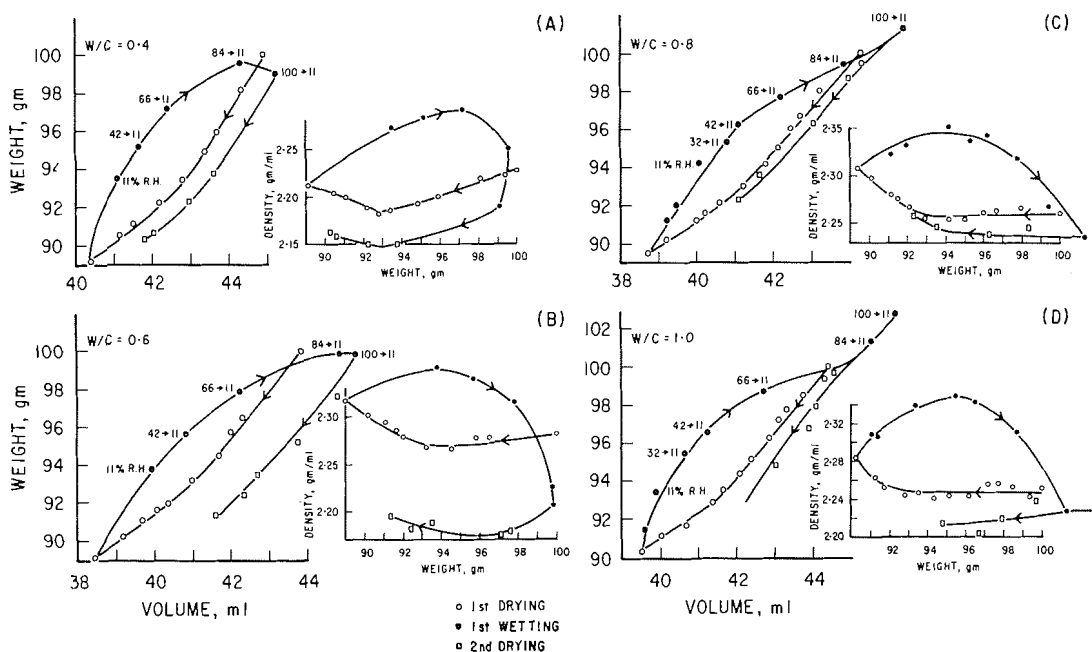


FIG. 2

Plot of volume and density versus weight change on drying and wetting cycles for samples strongly dried.

Second drying is similar to first drying except that in the cases of 0.8 and 1.0 water/cement ratio the densities are considerably displaced.

Figure 2 presents the results for the samples of the four water/cement ratios that were dried beyond d-dry. The volume increase on rewetting is not as large initially as the d-dried samples and this is reflected in a large density increase up to about 42 per cent R.H. In each case the final volume is increased over that of the original sample and this is also reflected in the large drop in density. The 0.4 and 0.6 samples show fairly large displacements from their original values even after second drying. Figure 3 shows the results when density is calculated, subtracting the volume of helium inflow from the solid volume; this naturally gives a larger density. Figures 3A and B are for d-dried samples, and C and D for strongly dried. Although they are not similar quantitatively, their general features are the same. The first drying curves have been explained in a previous paper (4), the increase



## DRYING, WETTING, HYDRATED CEMENT, HELIUM FLOW

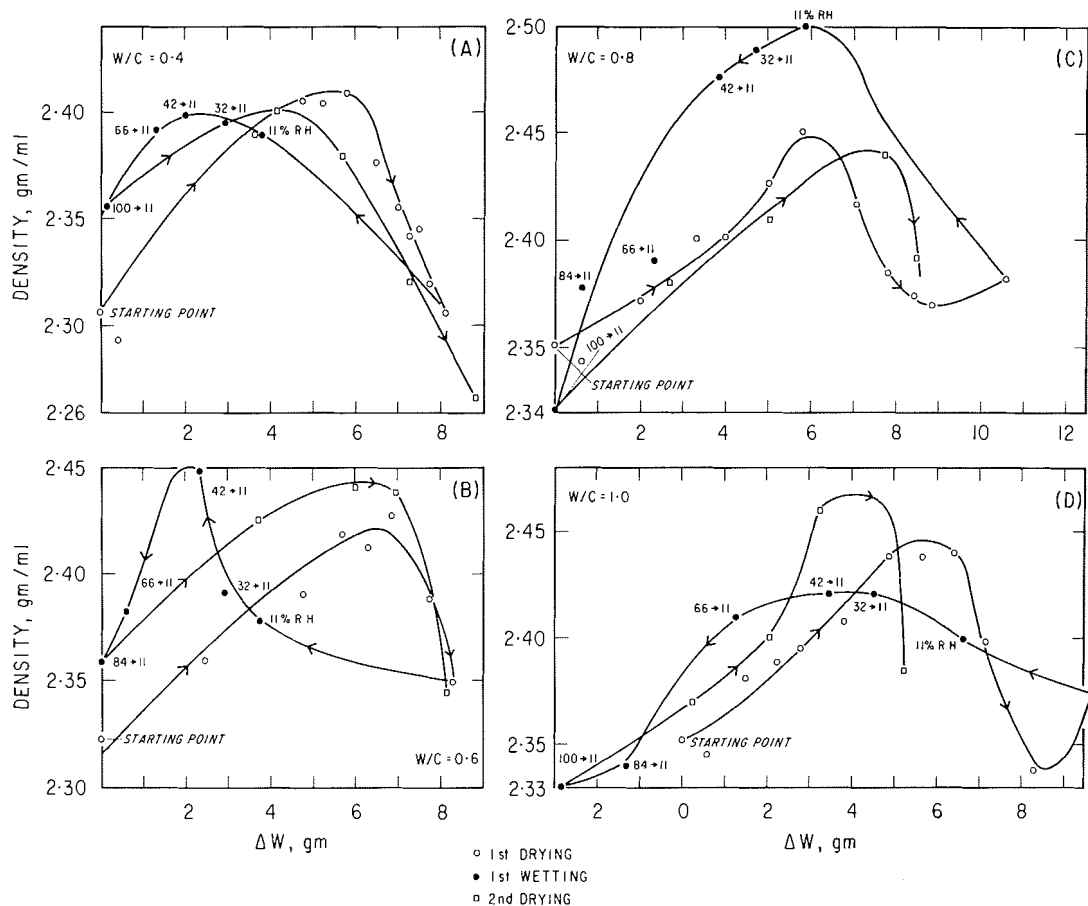


FIG. 3

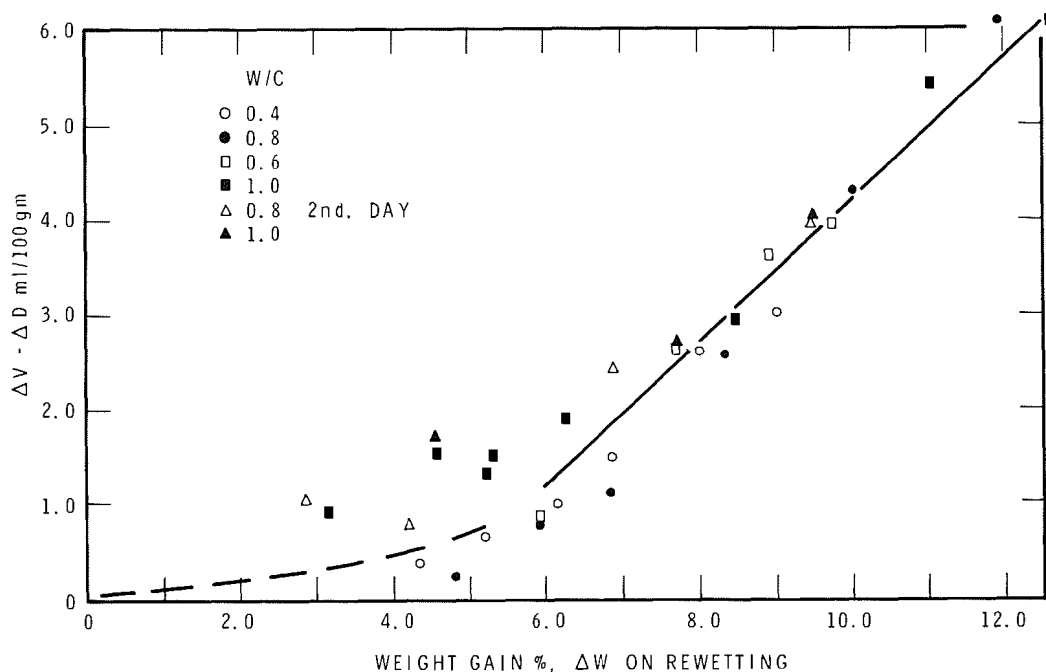
Plot of density (corrected for helium inflow) versus weight-change on drying and wetting cycles.

in density being due to the removal of water, the sharp decrease, to the collapse of layers not allowing helium to enter fully in 40 hr. The increase in density on rewetting then can only be explained by water returning to the interlayer structure without an equivalent re-expansion. The density decrease at the higher humidities is due to the large volume increase because of the swelling of the layers as more water is associated with the structure. Second drying again shows similar features as first drying.

The results obtained from the various helium flow techniques allow other calculations to be made. In a previous paper (1) it was possible to calculate the total space vacated on removal of water by calculating a para-

meter  $\Delta V - \Delta D$ . It was reasoned that removal of moisture leads to a change in solid volume ( $\Delta V$ ) and a change in helium inflow at 40 hr, ( $\Delta D$ ). In adding these together the above parameter was obtained where the decrease in volume is negative and increase in flow, due to increased weight loss, is regarded as positive.  $\Delta V - \Delta D$  was thus regarded as the total space vacated by the water on the assumption that, in the 40 hr that helium inflow measurements were taken, helium entered all the spaces. In this work the change in  $\Delta V$  on expansion is positive and a decrease in inflow ( $\Delta D$ ) is negative. Thus, again the parameter  $\Delta V - \Delta D$  should reflect the space occupied by the water molecules as they enter the structure or are adsorbed on the solid surface. Again one assumes that in 40 hr helium has entered all the small spaces available.

Figure 4 presents the  $\Delta V - \Delta D$  versus moisture gain plot for the four water/cement ratio samples of Series 2 where 30 - 35 gm samples were used (thus being 2 to 3 times more accurate than Series 1). The first 6.5 per cent weight gain resulted in a maximum value for  $\Delta V - \Delta D$  of under



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

2 ml per 100 gm of sample. This would imply an unreasonably high density of over 3 gm/ml for the water. The explanation is, as concluded from the results presented earlier for flow curves (2) and density calculations, that the water molecules are re-entering the interlayer structure that had partially collapsed on drying. Due to the "entrapped" space there, the  $\Delta V$  did not reflect the volume of the newly sorbed water. The increase in helium inflow (2) showed that the layers were partially re-opened but helium was still not able to occupy all the space in the 40 hr of measurement. Adsorption on the external surfaces would be a monolayer approximately since the samples for all the measurements were at 11 per cent R.H. This result indicates that the monolayer of adsorbed water on the surface is a relatively minor part of the 6.5 per cent sorbed. Beyond the 6.5 per cent water sorbed, the increase in  $\Delta V - \Delta D$  is much greater and correlates well to a linear relationship with amount of water sorbed, up to about 12.5 per cent. The equation for the line  $y = 0.8311 + 4.009x$  accounts for the data with a significance of better than 99 per cent 'y' is the parameter  $\Delta V - \Delta D$  and 'x' the change in sorbed water; the inverse of the slope gives the density of the water as 1.20 gm/ml. The points for second drying for water/cement ratios 0.8 and 1.0 are also plotted and fall back along the same line and the initial low slope part of the curve.

#### Discussion

Two main points are shown by the results, and both may be considered as a change in the structure of the hydrated silicates.

A. An irreversible change towards a higher degree of aggregation of the layered material, leading to an increase in solid volume or decrease in density during rewetting and drying cycles. This emphasizes the relative instability of the solid and explains many of the phenomena observed during typical strain-time experiments under load.

B. Water can reopen the partially collapsed structure when samples are exposed to low humidities even when these samples are severely dried.

$\Delta V - \Delta D$  of 2 ml/100 gm of specimen during addition of 6.5 per cent would yield a value of over 3 gm/ml for the density of the sorbed water if surface

adsorption were assumed. Only after exposure to 42 per cent R.H. is a linear portion of the curve obtained of slope yielding a density of  $1.20 \pm 0.08$  gm/ml, close enough to the value of  $1.27 \pm 0.08$  obtained on first drying (1). This portion of the curve is obtained after the structure has been opened enough to allow helium to measure the space within the layers unoccupied by water. Second drying reproduces this linear curve which is similar to the curve obtained on first drying and again shows how the layered structure partially collapses on drying. The fact that the linear portion is only obtained after exposure to 42 per cent R.H. (and returned to 11 per cent R.H.) is further evidence that it cannot be interpreted as being due to adsorbed water on open surfaces either on rewetting or on drying (5); thus most of the water sorbed after exposures to 100 per cent R.H. (and returned to 11 per cent R.H.) must occupy interlayer positions.

An approximation may be made of the monolayer of adsorbed water. Assuming that at 11 per cent R.H., all of the volume increase is due to the volume of the monolayer (this probably gives a value higher than the true monolayer) which is present after exposure at 11 per cent R.H., and gives a value of 1.5 ml (Figure 2B) for the water-to-cement ratio sample of 0.6. Using the density of 1.20 gm/ml leaves 1.8 gm of water as the monolayer. Subtracting 1.8 gm from the 6.5 gm of water sorbed after exposure to 42 per cent R.H. and return to 11 per cent R.H. results in the conclusion that 4.7 gm of the 6.5 gm of water sorbed up to 42 per cent R.H. is entering the layered structure.

As stated above at 42 per cent R.H. and over helium is now entering and measuring the volume of space within the layers. Results published previously, (Figure 2A of Ref. 2) show that after exposure of the same sample to 42 per cent R.H. (then redried to 11 per cent R.H.) 2 ml of space unoccupied by water exists in the structure which, as calculated above, also contains 4.7 gm of water per 100 gm sample; after exposure to 100 per cent R.H. and drying to 11 per cent R.H., the layered structure contains 9 gm of water (Figure 2B) and 2.4 ml (Figure 2A of Ref. 2) space. At 1.20 gm/ml the volume of water is 7.5 ml, and total space 9.9 ml; the ratio of total

volume to monolayer water volume (since sample is at 11 per cent R.H. all water is assumed monolayer) is  $9.9/7.5 = 1.32$ . Assuming an hydraulic radius of  $10 \text{ \AA}$  for water-cement ratio of 0.6, if the pore system was made up of spheres this ratio would be 3.7 and for cylinders 3.6. If the space was 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.

As water re-enters the layered structure, the total volume between the layers increases. At the 42 per cent R.H. level, using  $120 \text{ gm/ml}$  as density of water, the total volume is  $3.92 \text{ ml}$  occupied by  $4.7 \text{ gm}$  of water plus the  $2 \text{ ml}$  unoccupied space mentioned above for a total of  $5.92 \text{ ml}$ . After exposure to 100 per cent R.H. and redried to 11 per cent R.H. the total volume of interlayer space is  $9.9 \text{ ml}$ , an increase of  $3.98 \text{ ml}$ . This increase in interlayer space is 67.5 per cent of the total space at the 42 per cent R.H. exposure level.

The increase in total volume of interlayer space takes place as mentioned previously by two methods: a) separation of sheets as water re-enters, and b) sheets, formerly apart, come together either by further aggregation or by lengthening their alignment. Figure 2B shows that there is an increase of solid volume of  $1.45 \text{ ml}$  per  $100 \text{ gm}$  of sample over its original state. This increase can be accounted for by an increase in interlayer space, probably through method (b). Thus  $3.98 - 1.45 = 2.53 \text{ ml}$  is the increase in interlayer space due to method (a) if it is assumed that the solid volume increase of  $1.45 \text{ ml}$  occurs due to exposure to above 42 per cent R.H.

### Conclusion

1. Major changes occur to the layered structure of dried hydrated portland cement as it is re-exposed to above 42 per cent R.H. This involves a further aggregation of layers leading to an increase in solid volume and decrease in surface area. This phenomena regenerates specific sites responsible for creep and additional shrinkage of the material.

2. Conclusive evidence is obtained showing that a major part of water associated with dried hydrated portland cement when exposed to 100 per cent R.H. but re-equilibrated to 11 per cent R.H. has entered the structure and occupies interlayer positions. This water causes an increased separation of the sheets, and shows that the fine pore system cannot be considered as narrow-necked fixed-dimension pores. Calculations show that the spaces between the sheets approximate to the model of that between two parallel plates.

#### Acknowledgment

The author wishes to acknowledge the valuable assistance of Mr. S. Dods in performing experiments and gathering data.

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.

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