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**APPLICATION OF THE HELIUM INFLOW TECHNIQUE
FOR MEASURING SURFACE AREA AND HYDRAULIC
RADIUS OF HYDRATED PORTLAND CEMENT**

by
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APPLICATION OF THE HELIUM INFLOW TECHNIQUE FOR MEASURING SURFACE AREA AND
HYDRAULIC RADIUS OF HYDRATED PORTLAND CEMENT

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ABSTRACT

The pore system of hydrated cement paste is very complex and changes with the type of drying. Solid volume, helium inflow, and length change measurements over different relative humidity conditions permit surface area and hydraulic radii to be measured. It is shown that the system is composed of (1) gross pores into which nitrogen methanol and other fluids can readily enter, and (2) interlayer spaces that separate layers and are only about the diameter of one water molecule apart.

Le système poreux de la pâte de ciment hydraté est fort complexe et varie selon le mode de séchage. La mesure du volume solide, de l'absorption d'hélium et des variations de longueur en fonction de différentes conditions d'humidité relative nous permet de déterminer la surface et le rayon hydraulique et de constater que ce système est composé (1) de pores grossières dans lesquelles l'azote, le méthanol et les autres fluides peuvent facilement pénétrer et (2) d'espaces intermédiaires, éloignés l'un de l'autre d'une distance correspondant au diamètre d'une molécule d'eau, qui séparent les différentes couches.

Introduction

Pore structure is one of the most important characteristics controlling the properties of porous materials. Many techniques, based largely on nitrogen or water vapour adsorption isotherms or mercury porosimetry, have been used to determine the pore structure of solids. Calculations based on these methods have been relatively successful for materials with pore structures that remain stable on removal or addition of water.

Hydrated portland cement, however, is a very unstable material requiring a knowledge of the relation between porosity and mechanical properties for engineering design. Used as a displacement fluid, water always gives a higher porosity for portland cement than other media such as nitrogen, methanol and helium (1). Many of the properties of hydrated portland cement are measured after drying, but this leads to decomposition of the hydrates. Changes in

porosity, surface area, and other physical properties will occur when this system is dried; if water is used for measurement, rehydration of the decomposed hydrates may make measurements difficult to interpret (2).

The helium flow technique has been used in studying hydrated tri-calcium and portland cement systems (3,4), permitting observation of the changes that occur during removal and re-entry of water, and of the pore structure as well. Interlayer spaces and other pores can also be distinguished.

An attempt has now been made to determine quantitatively the surface area and hydraulic radius of interlayer and capillary pore systems. Length change and determination of the solid volume change by helium pycnometry as the sample is exposed to different RH conditions was used to calculate the surface area of the material. The total surface area of hydrated portland cement paste (by low-angle scattering) (5) and the total volume of interlayer space (by the helium inflow technique) were determined in order to calculate the hydraulic radius of the interlayer space.

Theoretical Basis

Relation of Length and Volume Change

Previous work (1) has shown that the instantaneous pycnometric measurement with helium reveals the solid volume, which includes the interlayer space and any adsorbed water on the solid. Any change due to addition or removal of water can be detected by this measurement and will be referred to as $\Delta V/V$, the absolute volume change for a unit volume. A change in the volume of the adsorbed water registers in this measurement as a change in solid volume.

If changes in length of specimen are measured during removal or replacement of water, a more precise understanding of the process of drying or wetting may be obtained. Three times the fractional length change, $3\Delta l/l$, is approximately equal to the fractional volume change of the whole body for small changes in length. If the pore fraction of the body is assumed to remain constant during volume change resulting from changing conditions, then $3\Delta l/l$ is equal to that part of the fractional volume change of the solid phase that is transmitted through the body. It is also assumed that $\Delta l/l$ does not include the volume of adsorbed water.

The instantaneous solid volume change measured by helium is made up of four main components:

- (1) Bangham (6) volume change due to change in solid surface-free energy, depending on the quantity of adsorbed water;
- (2) volume change due to the attachment or removal of interlayer or structural water;
- (3) change in the solid volume due to aging effects, i.e., further alignment of sheets;
- (4) removal or attachment of adsorbed water on the solid surface.

Change in length should be due to components (1) and (2) if aging is not a factor; the difference between $\Delta V/V$ and $3\Delta l/l$ should then leave (4), the adsorbed water. Thus,

$$\Delta V/V - 3\Delta l/l = v/V \quad (1)$$

where v is the volume of the adsorbed layer and V is the volume of the d-dried sample.

If the experiments are carried out by exposing specimens equilibrated at 0 to 11% RH, or vice versa, assuming that an adsorbed monolayer exists at

11% RH, then v is the volume of an adsorbed water monolayer. Using the value of the density of the water as 1.20 g/ml (3), the mass of the monolayer of adsorbed water per unit mass of d-dried sample, W , is $v \times 1.20/W$. The surface area may thus be calculated, assuming that one water molecule covers $10.8 \text{ \AA}^2$.

Hydraulic Radius

This parameter is calculated by dividing the total pore volume of a pore system by its bounding surface area. For definite shapes the diameter is a fixed multiple of the radius and is useful for defining systems. For parallel plates the distance separating the plates is twice the hydraulic radius.

Experimental

Materials

The following materials were used: C_3S hydrated for 2.5 years at water-cement ratios of 0.5 and 0.8; type I portland cement hydrated for 2.5 years at water-cement ratios of 0.25, 0.4, 0.6 and 0.8; and a sample of the same cement hydrated with 0.75% calcium lignosulfonate at a water-cement ratio of 0.80.

Three samples of type I portland cement paste containing 0, 2 and 10% sulphur were autoclaved at 216°C , 21 kg/cm^2 pressure, for 3 h after 24 h of moist curing. Discs 1.25 mm thick and 32 mm in diameter were cut and used for helium flow measurements.

Procedure

Small prisms 5 mm wide and about 30 mm long were cut from some of the discs for length change measurements (6). Samples were conditioned in desiccators at 11% RH and then dried to the d-dried condition step-by-step. At each step of drying helium flow rate and solid volume were measured with the helium pycnometer and the length change from the optical extensometers. The samples were then exposed progressively to 11, 32, 42, 66, 84 and 100% RH; following this, each sample was re-exposed to 11% RH and the helium flow rates and solid volume were measured. Experimental details pertaining to this procedure and some results have already been reported (7). The d-dried samples were ground to 100 mesh and subjected to surface area measurement by nitrogen adsorption.

Results and Discussion

Volume and Length Change Measurements on Rewetting to 11% RH

The results are presented in Table 1. Columns 2, 3, 4 present, respectively, the per cent mass of water sorbed, the per cent solid volume change, and the relative length change, on the d-dried basis, following exposure of d-dried specimens to 11% RH. The actual values for the d-dried solid volume and its mass are tabulated in columns 5 and 6, respectively. Calculation of the term $(\Delta V/V - 3\Delta l/l) \times 1.2 V/100$ gives the mass of the monolayer of adsorbed water for volume, V (column 5), on the basis of the d-dried sample. The monolayer of adsorbed water per 100 g of d-dried sample is tabulated in column 7 and the surface area calculated from this, in column 8. Surface areas from nitrogen adsorption measurements are tabulated in column 9. A plot of the surface area determined by nitrogen adsorption versus surface area computed from equation (1) is presented in Fig. 1. The points vary somewhat from the line of equality, especially at low surface areas, but over-all agreement is considered good. It is possible that some of the assumptions may not be strictly valid at low surface areas.

Using the same method of calculation, surface areas are computed from data for drying the material from 11% RH to the D-dry condition. These results are tabulated in column 10, and it is clear that the surface areas

TABLE 1
Data for Calculation of Surface Area from Helium Pycnometry.

Sample	Rewetting							Drying	
	Per cent at 11% RH			V	W	w Per cent	m ² /g		m ² /g
	$\Delta W/W$ × 100	$\Delta V/V$ × 100	$\Delta \ell/\ell$ × 100				SA _{He}	SA _{N₂}	
1	2	3	4	5	6	7	8	9	10
Portland Cement									
w/c 0.25	3.78	1.706	0.332	40.16	91.30	0.38	13.6	5.2	236
" 0.4	4.74	2.827	0.362	41.98	91.83	0.96	34.8	30.1	65
" 0.6	4.96	3.567	0.342	40.59	91.71	1.35	49.0	52.0	110
" 0.8	5.36	3.420	0.359	38.72	89.38	1.22	44.4	52.0	188
C ₃ S									
w/c 0.5	4.81	4.033	0.304	41.31	92.82	1.67	60.4	56.5	83
" 0.8	5.01	4.137	0.278	40.95	92.87	1.74	63.5	67.3	138
Lignosol									
w/c 0.8	5.04	4.238	0.394	39.87	91.44	1.77	58.1	70.0	-
Sulphur Aut 0%									
w/c 0.35	1.23	1.197	0.057	37.17	98.45	0.47	16.9	8.9	-
Sulphur Aut 2%									
w/c 0.35	2.96	1.990	0.176	38.48	95.16	0.71	25.8	12.9	-
Sulphur Aut 10%									
w/c 0.35	3.30	2.54	0.306	35.46	91.87	0.75	27.3	24.0	179

Aut = Autoclaved

are much higher than those in columns 8 and 9. Previous results (8,9) have shown that under this condition aging occurs in the sample, and equation (1) does not take this factor into account. In addition, it is probable that the porosity of the specimen decreases with drying and that $3\Delta\ell/\ell$ is not equal to the volume change of the solid phase transmitted through the body. Surface area may, however, decrease, but the process is difficult to quantify through the simple analysis of equation (1).

Hydraulic Radius of Capillary Pore and Internal Space

Previously, hydraulic radius has been calculated by dividing the total volume of all the spaces by the total surface area. In the present work, an attempt has been made to differentiate the real capillary pore structure from the internal space.

FIG. 1

Relation between surface area by nitrogen adsorption and that by helium pycnometry

Pore structure

Table 2 shows the hydraulic radii for type I hydrated portland cement paste prepared at w/c = 0.4, 0.6 and 0.8 using the surface area value obtained by helium. The pore volumes used for this calculation have been reported (1). These results are consistent with results obtained by mercury intrusion techniques (10).

TABLE 2

Surface Area and Hydraulic Radius of Hydrated Portland Cement by Helium Pycnometry

Water/Cement Ratio	Surface Area, m^2/g	Hydraulic Radius, Å
0.4	35.0	39.4
0.6	49.0	64.2
0.8	44.0	107.0

Hydraulic radius of the internal space

Two methods are available for measuring the hydraulic radius of the internal space, both using the ratio of volume of the internal structure to internal surface area. Until recently this calculation could not be carried out without assuming a particular structure for the C-S-H gel. The low-angle scattering data of Winslow and Diamond (5), however, has provided the internal surface area.

Hydraulic radius from helium inflow and pycnometry: Previous work (7,8) has shown that the "internal structure" is re-opened by exposure (of d-dried specimens) to over 42% RH when more water enters the structure. Helium can, at this condition, fully enter the internal space within 40 h of flow time;

the volume of the internal structure (interlayer space) can thus be measured in the open, or partially open, state, depending on the relative humidity of exposure (using helium to measure the remaining internal volume).

Calculation of the surface area of the capillary pore structure showed that 1.35% of the water for the paste formed at 0.6 w/c was sorbed on the outer surface following exposure to 11% RH; after exposure to 100% RH and re-drying to 11% RH, 10.8% of the water was retained (7,8). This left 9.45% in the internal structure. In addition, 2.4 ml of space, unoccupied by water, was also measured in the structure by helium inflow. Using the density of water as 1.20 g/ml, the volume of the internal space amounted to 10.28 ml; and using the surface area of the internal space as $670 - 49 = 621 \text{ m}^2/\text{g}$, the hydraulic radius was equal to $1.65 \text{ \AA}$ (0.165 nm).

Assuming that the pores are bounded by two parallel plates, the average separation between the plates is $3.3 \text{ \AA}$ (0.33 nm) (twice the hydraulic radius). This model is consistent with the concept of the internal system, being composed of layers separated, on the average, by one water molecule. Validity of this calculation is verified further by the following calculation:

If 9.45% of water is held as a single layer between two sheets, it will cover twice the normal area per molecule, i.e., $10.8 \times 2 \text{ \AA}^2$ (0.216 nm^2). This will result in a surface area of $687.2 \text{ m}^2/\text{g}$, close to $621 \text{ m}^2/\text{g}$ given by low-angle X-ray scattering. The calculation assumes, however, that all the water is held as a single layer. There may be "kinks" in the alignment of the sheets, leaving room for more than one layer of water. On the other hand, the value of $10.8 \text{ \AA}^2$ (0.108 nm^2) for the coverage per molecule may be too high.

The hydraulic radius can also be calculated for the sample exposed to 42% RH, a state that corresponds to 5.15% water and 2 ml of space between the sheets. An average hydraulic radius of $1.0 \text{ \AA}$ (0.1 nm) is obtained because of a partial collapse of the interlayer space.

Hydraulic radius by measuring internal volume using water and nitrogen total porosities: Total porosities are determined by saturating the specimen in the two fluids. Results obtained by Brunauer et al (11) are presented in Table 3 together with the hydraulic radius calculation. This calculation was made by utilizing the low-angle X-ray scattering data of Winslow (5), giving the total surface area. The surface area values are shown in column 3 as S_T , the total surface area of completely hydrated d-dried portland cement paste. The average hydraulic radius for the pastes is $1.23 \text{ \AA}$, compared with $1.26 \text{ \AA}$ for montmorillonite. This comparison is considered to be significant, since montmorillonite is a layered material and, at the condition calculated, the layers are separated by one layer of water molecules. Figures for montmorillonite clay are also shown in Table 3.

Another set of data that may be used for a similar analysis was obtained by Mikhail and Abo-El-Enein (12). This was obtained for paste at the water-cement ratio of 0.2 for different degrees of hydration; results were corrected for this. The value of the total surface area was again obtained from the low-angle X-ray scattering data of Winslow and Diamond (5); it was the value for paste hydrated at a water-cement ratio of 0.3 and corrected for the degree of hydration. The average hydraulic radius for the samples is $2.51 \text{ \AA}$, or a sheet separation of $5.02 \text{ \AA}$ if a layered model is assumed. This is higher than the value of $2.46 \text{ \AA}$ for water-cement ratios of 0.35 to 0.57. Many kinked regions exist, however, in the sheet separation at low water-cement ratios, as evidenced by its low density (by helium pycnometer) (13) and this would yield higher average separation.

The evidence confirms that the microstructure of the hydrated silicates is

TABLE 3

Surface Areas, Porosities and Hydraulic Radii of Portland Cement Paste

Water/Cement Ratio	S_{N_2} m ² /g	$S_T - S_{N_2}$ m ² /g	$V_{H_2O} - V_{N_2}$ mL/g	$\frac{V_{H_2O} - V_{N_2} (\text{\AA})}{S_T - S_{N_2}}$	
0.35	56.7	580-56.7	0.0516	0.99	} Avg = 1.23
0.40	79.4	642-79.4	0.0717	1.28	
0.50	97.3	642-97.3	0.0823	1.51	
0.57	132.2	670-132.2	0.0617	1.14	
Montmorillonite	15	735	0.0964	1.26	

composed of two structures: 1) one made up of relatively coarse pores (whose size distribution can be measured by nitrogen adsorption and possibly by mercury porosimetry (1), and whose total porosity can be measured by helium and other fluids such as methanol (1)); 2) a layered structure composed of poorly aligned and poorly crystallized sheets separated by spaces approximately 3 Å wide. When water is removed these spaces partially collapse and have a limited swelling capability. Water that takes up position between the sheets has some order and limited mobility. In addition, the material has the ability to stabilize itself further when subjected to various treatments like wetting, drying and application of stress. The result of this ability is generally manifested in surface area decreases, large irreversible shrinkages, solid volume, and interlayer volume increases. The latter have been detected by the helium inflow technique, creep, and silica polymerization measurements. It is these changes and not the phenomenon of interlayer penetration alone that make the material difficult to define.

Conclusions

Hydraulic radii and surface area measurements with the helium inflow technique confirm the following:

- (1) Hydrated portland cement paste comprises
 - a gross pore structure accessible to nitrogen and other vapors;
 - a layer structure consisting of poorly aligned sheets (calcium silicate hydrate) incorporating highly oriented water.
- (2) At 11% RH, before d-drying, calcium silicate hydrate sheets are separated, on the average, by little more than one molecular layer of water.
- (3) Solid volume change and length change due to sorption from 0 to 11% RH can be related by a simple equation involving surface area without considering aging effects.
- (4) Large aging effects are manifested after samples have been exposed to 100% RH.

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References

1. Feldman, R.F., "Density and porosity studies of hydrated portland cement". Cem. Technol. 3 5-14 (1972).
2. Feldman, R.F., "Assessment of experimental evidence for models of hydrated portland cement". Highway Research Record 370, 8-24 (1971).
3. Feldman, R.F., "The flow of helium into the interlayer spaces of hydrated cement paste". Cem. Concr. Res. I (3), 285 (1971).
4. Feldman, R.F., "Helium flow and density measurement of the hydrated tricalcium silicate-water system". Cem. Concr. Res. 2 (1), 123 (1972).
5. Winslow, D.N. and Diamond, S., "Specific surface of hardened portland cement paste as determined by small-angle X-ray scattering". J. Amer. Ceram. Soc. 57 (5), 193-197 (1974).
6. Feldman, R.F., "Sorption and length change scanning isotherms of methanol and water on hydrated portland cement". Proc. Fifth Int. Symp. Chemistry Cement, Tokyo, Part III, Vol. III, 53-66 (1968).
7. Feldman, R.F., "Helium flow characteristics of rewetted specimens of dried portland cement paste". Cem. Concr. Res. 3 (6), 777 (1973).
8. Feldman, R.F., "Changes to structure of hydrated portland cement on drying and rewetting observed by helium flow techniques". Cem. Concr. Res. 4 (1), 1-11 (1974).
9. Feldman, R.F., "Mechanism of creep of hydrated portland cement paste". Cem. Concr. Res. 2 (5), 521-540 (1972).
10. Beaudoin, J.J., "Porosity measurement of some hydrated cementitious systems by high pressure mercury intrusion - microstructural limitations". Cem. Concr. Res. 9 (6) 771-781 (1979).
11. Brunauer, S., Oller, I. and Yudenfreund, M., "The new model of hardened portland cement paste". Highway Research Record 328, 89-107 (1970).
12. Mikhail, R. Sh. and Abo-El-Enein, S.A., "Studies on water and nitrogen adsorption on hardened cement pastes. I. Development of surface in low porosity pastes". Cem. Concr. Res. 2 401-414 (1972).
13. Feldman, R.F. and Beaudoin, J.J., "Micro-structure and strength of hydrated cement". Cem. Concr. Res. 6 (3), 389-400 (1976).