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**PORE STRUCTURE DAMAGE IN BLENDED CEMENTS CAUSED
BY MERCURY INTRUSION**

by R.F. Feldman

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RÉSUMÉ

Les ciments hydratés à base de laitier de haut fourneau et de cendres volantes se sont révélés très imperméables. Les mesures de porosité de ces matériaux par pycnométrie au méthanol et à l'hélium ont donné des valeurs moindres que celles obtenues par intrusion de mercure sous une pression de 410 MPa. Les résultats des trois techniques pour les ciments Portland hydratés ont été les mêmes.

Une des techniques employées consistait à récupérer le mercure par distillation après intrusion dans le matériau et à répéter l'intrusion. Cet essai a été effectué pour plusieurs ciments et mélanges de ciment.

La distribution dimensionnelle des pores du ciment hydraté a peu changé, alors que celle des mélanges a changé de façon marquée, révélant une distribution plus grossière. On en a conclu que les mélanges sont composés de pores discontinus relativement gros, dans lesquels le mercure pénètre en brisant la structure.

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Pore Structure Damage in Blended Cements Caused by Mercury Intrusion

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Hydrated blast furnace slag and fly-ash cement blends have been shown to be very impermeable. Porosity measurements of these materials by methanol and helium pycnometry have been less than the values obtained by Hg intrusion to 410 MPa. Results of the three techniques for hydrated portland cement were the same. A technique was used in which mercury could be removed by distillation after Hg intrusion, and intrusion was then repeated. This was performed on several cements and cement blends. Pore-size distribution for the hydrated cement changed marginally but both blended materials changed markedly, displaying a coarser pore distribution. It was concluded that the latter bodies are composed of relatively large, but discontinuous pores, into which Hg enters by breaking through the pore structure.

I. Introduction

The addition of blast-furnace slag and pozzolanas has been shown to improve the performance of concretes exposed to aggressive solutions.¹⁻⁴ Their greater resistance has been attributed to lower $\text{Ca}(\text{OH})_2$ content produced by the blended cements used in these concretes.⁵

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It was shown recently that hydrated blended cements have a pore-size distribution different from those of normal pastes⁶⁻⁸ and that their permeability is lower than these.⁸⁻¹⁰ Hence, the rate at which aggressive solutions enter the specimen is decreased. Their lower permeability has been attributed to a small volume of pores >90 nm in diameter⁸; but this property is also found in dense cement paste or mortar specimens that have exhibited low durability in tests.^{5,6}

The pore structure developed by hydrated cement blends may be relatively discontinuous, according to experiments in which methanol does not enter a portion of this pore structure but Hg does.¹¹ Porosities and solid densities of fly-ash and slag blends are consistently higher when measured by mercury intrusion than by helium or methanol, despite the fact that the methanol molecule has a diameter of ≈ 0.42 nm and mercury at the maximum pressure used can intrude pores ≈ 3 nm only in diameter. It was therefore suggested that mercury may be able to break through some structures with entrances <0.42 nm in diameter. Thus, mercury intrusion curves would not represent true pore-size distributions.¹¹

The mercury porosimetry technique consists of forcing mercury by pressure into the evacuated pores of a material. At the completion of an intrusion-extrusion cycle, some mercury is entrapped in most porous materials.¹² To investigate possible damage to the pore structure of hydrated portland cement and cement blends during mercury intrusion, a technique was devised to remove the mercury. A technique to achieve the same purpose was used previously on porous alumina.¹³ This paper addresses the problem and reports on pore structure measurements of cement subjected to an initial mercury intrusion.

II. Experimental Procedure

(1) Materials

Normal type I cement was mixed with two different waste materials, a fly-ash and a blast furnace slag, to give mixtures containing 35% by weight of fly-ash and 70% by weight of slag. Eighty-five percent of the fly-ash particles were between 45 and 12 μm in size. A reference mix containing no addition was also made. As shown

Table I. Chemical Composition of Cements and Additions

Oxide analysis	Fly ash	Slag	Type I cement
SiO_2	55.8	31.5	20.7
Al_2O_3	22.7	16.0	6.2
Fe_2O_3	4.3	1.0	2.2
CaO	13.3	36.0	64.5
MgO	2.4	13.0	1.3
Ign. loss	0.6		0.8
SO_3	0.2	2.8	3.0

Fig. 1. Hg intrusion of cement hydrated for 1 yr at 55°C for residual Hg contents indicated.

in Table I, the fly ash and slag contain much higher quantities of silica but lower quantities of CaO than the portland cement.

(2) Hydration

Cubes (50 by 50 mm) were made from the three mixes using a water/solid ratio of 0.45. The cubes were cored after curing for 24 h and sliced into disks 32 mm in diameter and 1.3 mm thick. Some cubes were cured for 2 years at 35°C, and others for 1 year at 55°C.

(3) Porosity and Pore-Size Distribution

American Instrument Company equipment was used. The pore-size distribution was obtained by mercury porosimetry, using a pressure of up to 414 MPa. A contact angle of 130° was used to calculate pore size from the pressure measurement. The volume of mercury intruded at the maximum pressure was considered to be the total porosity. Samples were prepared for intrusion by breaking disks into small pieces and drying them in vacuum; for the final drying, the samples were heated to 105°C under vacuum for 24 h. Residual mercury retained in the pores after a mercury intrusion

Fig. 2. Hg intrusion and derivative for cement paste hydrated for 1 yr at 55°C.

experiment was removed by heating at 105°C from 24 to 360 h depending on the time required for the sample to return to its original weight. Mercury intrusion was then performed on the resultant sample a second time, and a contact angle of 130° was again used to calculate pore sizes. It was felt that since most of the mercury was removed, there was no justification for using a different value.

III. Results

(1) Cement Paste

The influence of distillation time on the residual Hg content and on the second Hg intrusion curve of cement paste hydrated for one year at 55°C is shown in Figs. 1 and 2. Each sample is different for the four distillation times studied, but the four initial pore-size distribution curves are similar, both quantitatively and qualitatively. For the material hydrated at 55°C, as the period of distillation increases from 24 to 312 h, the residual Hg decreases from 65.4 to 4.8% by weight of sample (7.2 to 0.5% by volume of sample) and the second intrusion curve, which is similar in character for all the periods of distillation, becomes almost identical to the first intrusion curve. The results of the second intrusion show that the volume of pores between 90 and 50 nm in diameter increases slightly for the sample with 12.6% by weight residual Hg, but for pores >88 nm in diameter an increase of the volume to only 1.0% from 0.6% occurs. For the sample with residual Hg of 4.8% (Fig. 2) the volume of pores >88 nm in diameter increases from 1.2 to 2.4% (Table II). There is also a change in the threshold

Table II. Porosity and Residual Hg Content from Hg Intrusion Experiments

Material	Hydration period (yr)	Distillation time (h)	Residual Hg (% initial wt of sample)	Porosity >88 nm	
				intrusion	(vol%)
				1	2
35°C					
Cement	2	240	0.2	1.0	2.4
Fly ash blend	2	360	2.1	1.5	4.9
Slag blend	2	360	0.8	1.0	4.5
55°C					
Cement	1	216	12.6	0.6	1.0
Cement	1	312	4.8	1.2	2.4
Fly ash blend	1	72	12.7	3.2	9.5
Fly ash blend	1	120		1.5	7.0
Slag blend	1	157	12.9	2.5	10.0
Slag blend	1		4.5	2.5	9.5

Fig. 3. Hg intrusion and derivative for cement paste hydrated for 2 yr at 35°C.

diameter (the point where the initial rapid increase in $\Delta V/\Delta D$ occurs¹⁴) from about 70 to 130 nm. A major difference between the results obtained for the second and first intrusions is not observed in the change in derivative ($\Delta V/\Delta D$) of the pore-size distribution curves after distillation for 312 h, although it is evident that some pores were created between 100 and 40 nm in diameter at the expense of smaller pores between 40 and 20 nm in diameter.

According to the results for cement paste hydrated for 2 years at 35°C (Fig. 3), only 0.18% residual Hg remained following a distillation time of 240 h after the first Hg intrusion. Although the basic character of the curves for the first and second intrusions is similar, the second intrusion attained a higher volume of Hg, 23.5 to 21.5%, due to a higher volume of pores between 130 and 40 nm in diameter, but a lower volume of pores between 6 and 3 nm. This is shown clearly in the derivative plot and indicates that some breaking of structure probably occurred during the first mercury intrusion. Although threshold diameters change from about 40 to 100 nm after distillation, the volume of pores >88 nm in diameter increases to only 2.4% from 1.0%.

(2) Fly-Ash Cement Blend

The results for the fly-ash blend, hydrated at 55°C for one year, are presented in Fig. 4. The first Hg intrusion is very different from that for the hydrated cement paste; after about 102 MPa intrusion pressure (equivalent pore diameter of ≈ 12 nm), the slope of the curve increases greatly. The second Hg intrusion for both residual Hg levels changes markedly after distillation, the curve acquiring more of the characteristics of the hydrated cement, i.e. decreasing rate of intrusion (after 102 MPa) as the pore size decreases. However, the diameter where the intruded volume exceeds 2% increases from 70 to 170 nm (for the lowest residual Hg) and the volume of pores >88 nm increases from 3.2 to 9.5% for the sample with 12.7% residual Hg (distillation time 72 h) and from 1.5 to 7.0% for the sample distilled for 120 h (the residual Hg was not recorded) (Table II). The derivative plots display large differences between the first and second intrusions; a large portion of the small pores between 9 and 3 nm is eliminated and replaced by pores between 200 and 40 nm. These results indicate that, during the initial intrusion, a large portion of Hg enters the pores beyond 100 MPa due to breaking of the pore structures. These pores are probably larger pores with small entrances. This phenomenon appears to occur only on a small scale in the case of hydrated cement.*

* $\Delta V/\Delta(\log D)$ was also calculated for all results. These plots show the same trend as the $\Delta V/\Delta D$ plot but the difference in the pore distribution is emphasized in the region of the large pores.

Fig. 4. Hg intrusion and derivative for fly-ash cement blend hydrated for 1 yr at 55°C.

As shown in the results for the fly-ash blend hydrated at 35°C for 2 years (Fig. 5), a residual Hg level of 2.10% (0.23% by volume of sample) after 360 h distillation was attained. As with the other condition of hydration, the character of the intrusion curve changed completely; the rate of volume intrusion with pore diameter decreases from 5 to 3 nm in the second intrusion, compared with the increase in rate from 9 to 3 nm in the first intrusion. The decrease in intruded volume at high pressure for the second intrusion was replaced by an increase in the volume at low pressure. The diameter where the intruded volume exceeds 2% increases from 50 to 200 nm and the volume of pores >88 nm increases from 1.5 to 4.9% (see Table II). The derivative shows greater contrast in the two distributions, the second intrusion resulting in a reduced value of the derivative from 22 to 3 nm but an increase in value in the range of larger pores.

(3) Slag Cement Blend

Figure 6(A) and (B) shows the Hg intrusion curves for hydrated blast furnace slag-cement blend hydrated for 1 year at 55°C with 4.5% (0.5% by volume of sample) residual Hg. The change in character of the curve from first to second intrusion is similar to that for the fly-ash blend. The diameter where Hg intrusion exceeds 2% changes from 92 to 210 nm; this is similar for both residual Hg levels as well as for the volume of pores >88 nm, which changes from 2.5 to 10% (Table II).

Of all the preparations, the slag-cement blend hydrated for 2 years at 35°C shows the greatest difference between the first and second Hg intrusion. As shown in the results for the sample with 0.77% residual Hg (Fig. 6(C), (D)), the diameter when the intruded volume exceeds 2% increases from 30 to 310 nm, and the volume of pores >88 nm changes from 1.0 to 4.5%. The derivative for the first intrusions shows a much greater number of pores from 6.5 to 3.0 nm in diameter but a lower number in the range 6.5 to 100 nm.

IV. Discussion

Several studies have shown that the permeability of hydrated slag-cement and fly-ash cement blends is considerably lower than that of hydrated portland cement paste.⁸⁻¹⁰ Specifically, results have been obtained for the permeability of water and of ions such as Cl^- , Na^+ , and K^+ . It was found that, in all these cases, pastes or mortars formed from the blends are 10 to 100 times less permeable than ordinary portland cement paste or mortar. In addition, the blends are more resistant to salt attack.⁶ These results are difficult to explain because both maximum continuous pore size¹⁴ and pore-size distribution obtained from Hg intrusion porosimetry for the hydrated blends and portland cement in the range between 500 and 60 nm are not greatly different. However, pore volume mea-

Fig. 5. Hg intrusion and derivative for fly-ash cement blend hydrated for 2 yr at 35°C.

surements using methanol and helium indicate that there are substantial differences in the pore structures.^{6,11}

The repeat Hg intrusions after distillation, performed in this work, clearly indicate that in the hydrated blends, the pore distributions calculated from the initial intrusion are incorrect; damage to the pore structure during the application of pressure by the Hg occurs at ≈ 70 MPa due to a differential pressure across the pore walls. Damage may have occurred at even lower pressures but this cannot be proved by these intrusion curves because increased volume for the larger pores, due to structure destruction at lower pressures, will be masked. However, experiments in which a specimen is exposed to gradual increases of Hg pressure in steps, separated by distillations, may be feasible. These results show, furthermore, that many pores are of the ink-bottle variety and that, although the entrances of some of these pores were <0.42 nm in diameter, the main body of the pores was considerably larger; some are in the order of 200 to 300 nm. Damage to the pore structure also occurred to a minor extent in cement hydrated at 35°C; however, in contrast with the blends, the total porosity of hydrated portland cement whether measured by helium pycnometry, methanol pycnometry, or mercury porosimetry, generally remains the same.⁶

A pore structure composed of relatively large pores separated by very small entrances, such as in the hydrated blends, will result in very low permeability. This can be explained as follows: The two classes of materials differ in $\text{Ca}(\text{OH})_2$ content, which is $\approx 18\%$ for cement paste, 6% for fly-ash cement paste, and 2.5% for slag-cement paste. Scanning microscope investigations have revealed that, in cement paste, $\text{Ca}(\text{OH})_2$ is dispersed throughout the pore structure. When fly-ash cement has been hydrated for about 28 days, the $\text{Ca}(\text{OH})_2$ reacts with the SiO_2 and Al_2O_3 from the fly ash, reducing $\text{Ca}(\text{OH})_2$ from 14 to 6% at 21°C and from 8 to 5.5% at 35°C, and forming a silicate similar to C-S-H and possibly an aluminosilicate phase. In slag cement, $\text{Ca}(\text{OH})_2$ never exceeds 3.3% and a C-S-H phase is also formed. $\text{Ca}(\text{OH})_2$ may cause better continuity of the pores in hydrated cement paste because of either inhomogeneity of the composite and poor bonding at the C-S-H- $\text{Ca}(\text{OH})_2$ interface, or the inherent porosity of $\text{Ca}(\text{OH})_2$ crystals themselves.

Fig. 6. Hg intrusion and derivative for slag cement blend hydrated for (A), (B) 1 yr at 55°C and (C), (D) 2 yr at 35°C.

V. Conclusions

1. The Hg intrusion technique is acceptable for determining the pore-size distribution of most hardened portland cement pastes.
2. Pore-size distribution data of mature hydrated cement blends measured by mercury intrusion are incorrect owing to structural damage that occurs during the measurement.
3. Hydrated cement blends have lower permeabilities than hydrated portland cement owing to a discontinuous pore structure. Relatively large pores are connected by narrow entrances.

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