NRC Publications Archive Archives des publications du CNRC

Porosity measurements of some hydrated cementitious systems by high pressure mercury intrusion : microstructural limitations

Beaudoin, J. J.

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\(79\)90073-5](https://doi.org/10.1016/0008-8846(79)90073-5)

Cement and Concrete Research, 9, November 6, pp. 771-781, 1979-11-01

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=f2a125a1-a3ff-4251-af78-f7bd08d9c103>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=f2a125a1-a3ff-4251-af78-f7bd08d9c103>

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.

7589

National Research Council of Canada
Conseil national de recherches du Canada

Ser
TH1
N21d

no. 868
cop. 2

BLDG.

ANALYZED

POROSITY MEASUREMENTS OF SOME HYDRATED
CEMENTITIOUS SYSTEMS BY HIGH PRESSURE MERCURY
INTRUSION - MICROSTRUCTURAL LIMITATIONS

by J. J. Beaudoin

Reprinted from:

Cement and Concrete Research
Vol. 9, No. 6, November 1979
p. 771 - 781

DBR Paper No. 868
Division of Building Research

Price \$2.25

OTTAWA

NRCC 17860

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 00209 9882

POROSITY MEASUREMENT OF SOME HYDRATED CEMENTITIOUS SYSTEMS BY
HIGH PRESSURE MERCURY INTRUSION-MICROSTRUCTURAL LIMITATIONS

J.J. Beaudoin

Research Officer, Materials Section, Division of Building Research,
National Research Council of Canada, Ottawa, Canada K1A 0R6

(Communicated by J. Skalny)
(Received Sept. 11, 1979)

ABSTRACT

Porosity measurements using both mercury intrusion and helium pycnometric methods are reported for several different hydrated cementitious systems. Significant differences in porosity values, where they arise, are explained in terms of microstructural limitations of the matrix material. Several mechanisms that affect mercury intrusion results are discussed.

Les mesures de la porosité à l'aide de deux méthodes, la pénétration du mercure et la pycnométrie à l'hélium sont rapportées pour plusieurs systèmes de ciments hydratés différemment. Les différences significatives des valeurs de porosité, lorsqu'elles apparaissent, sont expliquées en termes de limites micro-structurales du matériau de la gangue. Plusieurs mécanismes qui influencent les résultats de la pénétration du mercure sont discutés.

Introduction

Opinion regarding meaningful techniques for porosity measurement of hydrated portland cement paste is varied (1,2). Some research demonstrated that portland cement paste is not a stable adsorbent when water is used as adsorbate; this led to the use of helium pycnometric method of porosity measurement (3). In the helium pycnometric method, samples are conditioned at 11 per cent RH to avoid dissociation of hydrates (due to further removal of water on drying) prior to volume displacement with helium.

Porosity values (for most cement pastes) as determined by helium pycnometry are similar to capillary porosity values - the remnants of water-filled space existing between cement grains at time of setting - as calculated by Helmuth (4); modulus of elasticity versus porosity curves for portland cement paste were identical when porosity was calculated as capillary porosity or was determined by helium pycnometry (5).

Previous work on the diffusion of helium into the microstructure of portland cement paste, which had been dried from 11 per cent RH, provided data

that supported the argument that hydrated portland cement paste was a layered material and that gel pores (internal porosity of hydration products themselves) and/or pores smaller than capillary pores did not exist (6). Thus organic fluids (e.g., methanol), capable of filling the capillary pore system, were considered suitable displacement media.

Winslow and Diamond, Young, Auskern and others used mercury porosimetry to study the evolution of porosity in portland cement and cited SEM work on hydrated cement to support their findings (7, 8, 9). These authors discussed the limitations of the governing relationship between pore size and intrusion pressure. However, possible effects such as compressibility of pore space and structural damage to the matrix material at high pressures have not been discussed in the cement literature.

The purpose of this study was to provide data to enable a reassessment of the mercury intrusion method as a technique for measuring total capillary porosity of several cement systems and to compare the porosity results with those obtained by helium pycnometry.

Experimental

Materials

A brief description of the materials used in preparing specimens for this study follows. Preparation details are given in Table I.

1. Normal Type I portland cement was mixed with water at various water-cement ratios to prepare paste samples.
2. Magnesium oxide and magnesium chloride solution (chemical and physical specifics are given in (10)) were used to prepare magnesium oxychloride cement paste at several solution-solid ratios.
3. Magnesium oxide and magnesium sulfate solutions (chemical and physical specifics are given in (11)) were used to prepare magnesium oxysulfate cement pastes at several solution-solid ratios.
4. Jet Set cement, supplied by Huron Cement Co., Alpena, Michigan, (chemical and physical specifics are given in (12)) was used to prepare cement pastes with and without CaCl_2 additions.
5. Vycor glass having pore volume 26 per cent, surface area $175 \text{ m}^2/\text{g}$ and pore radius about $25\text{\AA}$, was used.
6. A commercially available latex solution (polyacrylic latex solution containing approximately 50 per cent latex solids) was mixed with portland cement in varying concentration to produce latex based cement pastes having a wide range of latex-cement ratios and water-cement ratios.
7. Fly ash from nine different sources was used to prepare cement-fly ash (50/50 by weight) mixtures for autoclaving. Chemical composition and physical characteristics of fly ash are given elsewhere (13).

Methods

Helium comparison pycnometry

The application of this technique to the hydrated portland cement system is

TABLE I
Preparation Details for Various Cement Pastes Used in This Porosity Study

System	Preparation and Curing Conditions
Hydrated Portland Cement	Water-cement ratio = 0.25, 0.35, 0.40, 0.50, 0.60 Moist cured 2 - 7 years.
Magnesium Oxychloride Cement	Solution-solid ratio = 0.59, 0.64, 0.71, 0.77, 0.86 conditioned at 50% RH for several months Solution specific gravity = 1.18
Magnesium Oxysulfate Cement	Solution-solid ratio = 0.59, 0.72, 0.84, 0.96, 1.07, 1.43 conditioned at 50% RH for several months Solution specific gravity = 1.30
Jet Set Cement	Water-cement ratio = 0.53, 0.73, 0.88 Moist cured 3 - 7 days then at 11% RH for several weeks
Jet Set Cement + 1, 2, 5% CaCl ₂	Water-cement = 0.53, 0.57, 0.73, 0.88 Moist cured 3 - 7 days then at 11% RH for several weeks
Portland Cement-Latex Mixtures	
Series	
I 100% RH 1 mo → 11% RH	Solution 50% solids; water-cement .125 - .500; latex-cement .125 - .500
II 100% RH 1 mo → 11% RH	Solution 25% solids; water-cement .225 - .600; latex-cement .075 - .200
III 100% RH 1 d → 11% RH	Solution 25% solids; water-cement .150 - .450; latex-cement .050 - .150
IV 100% RH 1 d → 11% RH	Solution 50% solids; water-cement .150 - .350; latex-cement .150 - .350
V 57% RH 1 mo → 11% RH	Solution 12.5% solids; water-cement .220 - .440; latex-cement .031 - .062
VI 57% RH 1 mo → 11% RH	Solution 33.3% solids; water-cement .168 - .330; latex-cement .083 - .167
Autoclaved Portland Cement-Fly Ash Mixtures (50% Fly Ash by Weight)	Water-solid ratio = 0.22, 0.26, 0.30, 0.35, 0.40, 0.45 autoclaved at 216°C, 2.04 MPa

described elsewhere (1). Solid volume is measured enabling the determination of porosity when the apparent volume is calculated from sample geometry or measured by an alternate means. The solid volume is the instantaneous volume measured when helium is first admitted to the system and is not to be confused with any time-dependent helium diffusion which may subsequently occur.

Mercury Porosimetry

Porosity measurements for all samples were determined using an Aminco Porosimeter capable of intrusion pressures up to 407 MPa. Each hydrated portland cement sample was tested after conditioning to various moisture conditions from 11 per cent RH to D-dry. Samples conditioned at 11 per cent RH were pumped in the instrument until a vapor pressure of 50 μ m Hg was reached. Porous glass was tested in D-dry condition. Magnesium oxychloride and oxysulfate cement conditioned to 11 per cent RH were subjected to vacuum drying (10^{-4} mm Hg for 1-2 h) prior to test. Latex-cement mixtures and autoclaved cement-fly ash mixtures, previously conditioned to 11 per cent RH, were vacuum dried (10^{-4} mm Hg) for several hours prior to test. Many of these samples were also D-dried. Before every porosimeter test run a helium pycnometric test was performed with the same sample having the same moisture conditions.

Results

Porosity data are presented in three figures (Figures 1, 2, 3) wherein total porosity as measured by mercury porosimetry is plotted against total porosity measured by helium pycnometry.

In Figure 1 data from the following cement paste systems is plotted: hydrated portland cement, magnesium oxychloride cement, magnesium oxysulfate cement, Jet Set cement and Jet Set cement containing additions of CaCl_2 . A porous glass result is also plotted. Data for hydrated portland cement, Jet Set cement with CaCl_2 additions and the high porosity magnesium oxychloride sample lie on the line of equality for porosities greater than 21 per cent. At porosities less than 21 per cent (helium method) data for hydrated portland cement and magnesium oxychloride cement indicate lower porosity by mercury method than by the helium method. The largest difference for portland cement was 8 per cent mercury porosity* to 13 per cent helium porosity or 38.5 per cent. Largest difference for magnesium oxychloride cement was 6 per cent mercury porosity to 17 per cent helium porosity or 64.5 per cent of pore space accessible to helium but not available to mercury. The porous vycor glass sample had 18 per cent mercury porosity and 26 per cent helium porosity or 30.8 per cent helium pore space not available to mercury. Data for magnesium oxysulfate cement paste all lie above the line of equality; as helium porosity increases the difference between mercury and helium porosity increases, (at 32 per cent mercury porosity helium porosity is 13.5 per cent giving a difference of 137 per cent). Jet Set cement results all lie above the line of equality with maximum difference of approximately 20 per cent.

In Figure 2, porosity data from the portland-cement latex mixtures are plotted. Results are described as follows:

* Porosities measured by mercury porosimetry method will be referred to as mercury porosity; porosities measured by helium pycnometry will be referred to as helium porosity.

FIG. 2

Mercury porosity vs helium porosity
for several cement-latex mixtures

FIG. 3

Mercury porosity vs helium
porosity for autoclaved
cement-fly ash mixtures

Series I From latex-cement ratio 0.50 to 0.28 mercury porosity is approximately 8 to 10 per cent less than helium porosity, the difference between the methods being approximately 30 per cent at a helium porosity of 30 per cent. From latex-cement ratio 0.28 to 0.15 the change in mercury porosity is small whereas the helium porosity decreases to about 10 per cent. At helium porosities less than 20 per cent mercury porosities become larger than those measured by helium. At 3 per cent helium porosity (latex-cement ratio = 0.15) mercury porosity is 433 per cent larger than helium porosity.

Series II to IV Results for Series II to IV samples follow a similar trend to Series I results. There are some variations in the value of latex-cement ratio at which the region of small changes in mercury porosity with large changes in helium porosity begins.

In Figure 3, the cement-fly ash mixture data are plotted. Above 30 per cent helium porosity the data are generally clustered around the line of equality. Below 30 per cent helium porosity mercury porosity is greater than helium porosity; the difference between the two methods increases as porosity decreases. The largest difference was obtained at 8 per cent helium porosity when the mercury porosity was 21 per cent, i.e., 162.5 per cent difference.

Discussion

The results of this study indicate that porosity as measured by mercury intrusion method can be significantly different from porosity measured by helium pycnometry. Porosity (by mercury intrusion) can be significantly greater or less than helium porosity depending on the cementitious system studied.

Hydrated Portland Cement

As water-cement ratio decreases the properties of the hydrated solid change (14). There is experimental evidence to suggest that in low water-cement ratio pastes empty space - kinks - exists between the sheets of the layered silicates (3,6,15-18.) These observations are as follows:

(1) Significantly lower solid densities in spite of the presence of some high density unhydrated cement. Solid densities of the product decrease from approximately 2.30 g/cc for water-cement ratio 0.80 to 2.16 g/cc for water-cement ratio 0.25.

(2) Significantly larger hydraulic radius calculated by using $600-S_{N_2}$ and not $S_{H_2O}-S_{N_2}$ in the expression $\{V_{H_2O}-V_{N_2}/600-S_{N_2}\}$. S_{N_2} and S_{H_2O} are surface areas measured by nitrogen and

FIG. 4

Helium intake vs time for hydrated portland cement paste

water vapor adsorption; V_{H_2O} and V_{N_2} are the pore volumes measured with water and nitrogen respectively. Winslow and Diamond (19) have measured an internal surface area for hydrated cement paste of approximately 670 m²/g (on dry weight of paste basis).

(3) Significantly larger helium flow into interlayer space than can be accounted for by removal of water alone. The total helium inflow for specimens conditioned at 11 percent RH increases significantly when water-cement ratio is below 0.40 (Fig. 4). Analysis of the volume change parameter, ∇V - ∇D , versus weight loss curves (20) enables an accounting for the volume previously occupied by the water which has been removed. Water densities should be approximately 1.0-1.2 g/cc. When excess helium flow occurs calculations give values for water density which are too low indicating helium is flowing into space in excess of that which was occupied by water. In other words for low water-cement ratio pastes some helium is diffusing into empty space between the CSH sheets. It is this space which is referred to as 'kinked' space.

(4) Calculations by Feldman (portland cement paste, W/C equals 0.60) indicate the ratio of the total 'pore' volume to monolayer volume $\approx$ 1.32 (3,6). ratio for perfectly parallel, smooth (no kinks) plates would be 1.00. Assuming a hydraulic radius of 10Å for W/C equals 0.60 this ratio would be 3.7 for spheres and 3.6 for cylinders.

As the mercury porosity is less than helium porosity it is apparent that mercury cannot enter all the space available to helium. It is possible that there exists trapped micro space between aggregations of CSH sheets (extra layer space) which is accessible to helium but not mercury. This space possibly forms as a result of deposition and consolidation of aggregations of CSH layers in confined space such as would be found in low water-cement ratio paste. The geometrical constraints on the deposition of these products is such that they cannot be deposited in a regular manner. It is postulated that many surfaces would come together or 'mate' within distances of molecular dimension while other surfaces would provide the boundaries of 'trapped space'. This may be similar to what Daimon and Kondo (21) refer to as an 'inter-crystallite pore' but it appears to be specific to low water-cement ratio CSH material. This space is not to be confused with 'kinked' space which is interlayer space and not accessible to mercury. Alternatively, there may be a simple sieve effect - micropores which permit entry of helium but not mercury; this would not explain, however, why mercury and helium give comparable values at higher water-cement ratios when the volume concentration of fine pores (<200Å diameter) increases with water-cement ratio (7,8,9). This trapped space, if present, appears to be present for only low water-cement ratio pastes. The solid matrix apparently has sufficient strength to resist the hydrostatic stresses imposed on it by mercury at high pressure.

In order to determine if there was any significant error in helium porosity measurement for low water-cement ratio pastes due to any diffusion during the measurement period, porosity measurements for most samples were independently measured using methanol as a displacement fluid. The porosity values were similar to those determined by using helium and it is felt that possible errors due to diffusion processes are insignificant. Previous work (1) using methanol as a displacement medium for porosity measurement had indicated that porosity values were equivalent to those when helium was used as a displacement fluid.

It is noteworthy that mercury porosimetry experiments on hydrated portland cement paste were conducted on samples which had been dried to various stages from 11 per cent RH to D-dry. There was no significant difference in the pore size distribution or total pore volume intruded for samples subjected to different degrees of drying. This is in apparent conflict with the results of Winslow and Diamond (7) although their intrusion pressures were only to 102 MPa.

Magnesium Oxychloride Cement

With the exception of the sample having solution-solid ratio = 0.86 all oxychloride samples have significantly greater helium porosities than mercury porosities. As porosity decreases the volume concentration of micropores less than 0.005 μm increases for this system (in contrast to hydrated portland cement system). Also the oxychloride system has been shown to have higher strength than the portland cement system (10). The products of hydration are mainly $\text{Mg}(\text{OH})_2$ and crystalline oxychloride complexes. It is possible that micropores <30Å diameter (estimated minimum pore diameter mercury will enter at 408 MPa) exist and therefore mercury will not enter, whereas helium will completely fill the micropore system. There are also pores into which helium slowly diffuses until pore filling is complete. These pores may have entrances too narrow for mercury to enter.

Porous Vycor Glass

The porous glass has an average pore diameter of approximately 50Å. Helium penetrates all the pores and a correct value of density can be determined using the solid volume measured using helium as a displacement fluid. Mercury was able to penetrate approximately 69 per cent of the pore space, indicating that the remainder of the pores had diameters less than approximately 30Å. The strength of the glass is sufficient to prevent crushing of pore walls and entry of mercury into the finest pores.

Magnesium Oxysulfate Cement

Unlike oxychloride cement, the volume concentration of fine pores for oxysulfate cement increases as solution-solid ratio increases. Also the difference between mercury porosity and helium porosity - mercury porosity being significantly larger - increases as solution-solid ratio increases. It has been shown that the mercury porosity is equivalent to the sum of the initial helium porosity plus the extra pore volume due to presence of discrete empty pores which become accessible to helium upon heating the sample to 200°C (11). The oxysulfate cement matrix is relatively weak and it is apparent that mercury can rupture pore walls and enter fine pore space not immediately accessible to helium.

Jet Set Cement

Jet Set cement without CaCl_2 is relatively weak (12), the volume concentration of micropores increases with water-cement ratio. It appears that mercury can damage pore walls and enter fine pores. The addition of CaCl_2 to Jet Set cement increases the strength of the matrix and for the porosity range studied there is no significant difference in mercury porosity and helium porosity.

In general, for the systems in Fig. 1, strength is in the following order: oxychloride>portland cement>Jet Set cement+ CaCl_2 >Jet Set cement>oxysulfate

cement. Apparent structural damage to pore walls occurred for the two weakest matrices. Figure 5 is a plot of microhardness versus porosity (helium) for five systems illustrated in Fig. 1; the relative strengths of these matrices are shown. The curves presented in Fig. 5 are regression lines for the various cement systems; regression analysis data is presented in detail in other papers (22-24). At least ten microhardness measurements are made on each sample tested enabling a better statistical evaluation of results. Correlation coefficients for the microhardness-porosity curves presented are greater than 90%.

Cement-Latex Mixtures

Between 10 to 30 per cent helium porosity there is little change in mercury porosity. At porosities greater than 20 per cent helium, mercury porosity is less than helium porosity; at porosities less than 20 per cent helium, mercury porosities are greater than helium.

In general latex-cement ratio decreases as helium porosity decreases. It is suggested that latex film is plugging up pores making penetration by mercury more

difficult. At porosities greater than 30 per cent (mercury) a large percentage of pores are $>0.1 \mu\text{m}$ in diameter. At approximately 20 per cent mercury porosity a significant percentage of pores have diameters between 0.1 to $0.01 \mu\text{m}$. Samples having lowest value of mercury porosity have a large number of pores between 0.01 and $0.003 \mu\text{m}$ in diameter. In other words, as latex-cement ratio increases water-cement ratio increases and the number of fine pores detected by mercury decreases. (In the absence of latex, the number of fine pores increases with water-cement ratio.) The reason for the decrease may simply be that they are plugged or blocked off by latex film and are not detected by mercury. In the absence of latex - at low water-cement ratios - there appears to be trapped space not accessible to mercury. In the presence of latex at low water-cement ratios, two possibilities are suggested. Helium diffusion experiments on the latex film alone indicate that the polyacrylic latex film itself contains micropores which can be penetrated by slow diffusion of helium. Mercury may be entering some of this space. Penetration may also be into trapped space between agglomerates of CSH sheets or even into small discrete pores formed during mixing with latex. The latter possibility, however, does not explain why mercury porosity is significantly less than helium porosity at higher latex-cement ratios.

As latex-cement ratio changes there is a possibility that surface energy changes and there may be a change in contact angle of mercury against these surfaces. Any changes in contact angle may have a contributory effect on the volume of mercury intruded (7).

FIG. 5

Microhardness vs porosity for several inorganic cementitious systems

Autoclaved Cement-Fly Ash Mixtures

Mechanical properties and chemical composition of these systems have been reported elsewhere (13). At helium porosities less than 30 per cent differences with the larger mercury porosity values increase. The largest differences are observed for the four weakest matrices, preparations 2, 7, 8, 9. Data for the strongest matrix, preparation 3, are nested about the line of equality. In general, for these systems, a greater volume concentration of fine pores is observed for lower water-cement ratios. Only two preparations are significantly weaker than room-temperature cured portland cement paste - preparations 8 and 2 - yet mercury is able to enter space that helium does not.

One explanation is that it is possible that in these systems trapped space exists between agglomerations of silicate sheets and that mercury can force its way into these spaces; some microstructural damage is likely. It is suggested that the potential penetration of trapped space is greater for less dense, low C/S ratio products. High C/S ratio products have highest solid density and lowest total helium intake as observed in helium diffusion experiments.

Conclusions

Porosity of several common cementitious systems, as measured by high pressure mercury porosimetry, may be subject to microstructural limitations. Several mechanisms of pore filling by mercury intrusion are therefore possible:

- (1) Complete filling of pore space according to a pore size-intrusion pressure relationship as is conventionally assumed (7).
- (2) Structural damage of the relatively weak walls of discrete pores and subsequent entry of mercury into these spaces.
- (3) Exclusion or entry of mercury from or into trapped space between aggregations of layered silicates.
- (4) Exclusion of mercury from pores or pore entrances which are too small for mercury to penetrate at a maximum intrusion pressure of 408 MPa.
- (5) Blocked pore space due to the presence of an interfering phase, e.g., polymer latex film.
- (6) Changes in contact angle between mercury and surface.

Acknowledgements

The author wishes to thank J.J. Wood for his fine work in conducting all the experiments. Thanks are also due Drs. R.F. Feldman and V.S. Ramachandran 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

1. R.F. Feldman. Cement Technology 3, 5 (1972).
2. R.S.H. Mikhail, L.E. Copeland and S. Brunauer. Canadian Journal of Chemistry 42, 426 (1964).

3. R.F. Feldman. *Cem. Concr. Res.* 4, 1 (1974).
4. R.A. Helmuth and D.H. Turk. Highway Res. Board, Washington, Special Report 90, 135 (1966).
5. R.F. Feldman and J.J. Beaudoin. *Cem. Concr. Res.* 6, 389 (1976).
6. R.F. Feldman. Proc. RILEM/IUPAC Int. Symp. on Pore Structure and Properties of Materials, C101-C116, Prague (1973).
7. D.N. Winslow and S. Diamond. *Journal of Materials*, 5, 564 (1970).
8. J.F. Young. *Powder Technology* 9, 173 (1974).
9. A. Auskern and W. Horn. *Journal of Testing and Evaluation*, 1, 74 (1973).
10. J.J. Beaudoin and V.S. Ramachandran. *Cem. Concr. Res.* 5, 617 (1975).
11. J.J. Beaudoin and V.S. Ramachandran. *Cem. Concr. Res.* 8, 103 (1978).
12. J.J. Beaudoin. To be published.
13. J.J. Beaudoin and R.F. Feldman. *Journal of Materials Science*, 14, 1681 (1979).
14. R.F. Feldman. *Cem. Concr. Res.* 3, 777 (1973).
15. J.J. Beaudoin. Unpublished data.
16. R.F. Feldman. *Cem. Concr. Res.* 3, 107 (1973).
17. R.F. Feldman. Highway Res. Board Record No. 370, 8 (1971)
18. R.F. Feldman and P.J. Sereda. *Matériaux et Constructions*, 1, 509 (1968).
19. D.N. Winslow and S. Diamond. *Journal Amer. Ceram. Soc.* 57, 193 (1974).
20. J.J. Beaudoin and R.F. Feldman. *Cem. Concr. Res.* 8, 223 (1978).
21. M. Daimon and R. Kondo. *Journal Amer. Ceram. Soc.* 60, 110 (1976).
22. J.J. Beaudoin and V.S. Ramachandran. *Cem. Concr. Res.* 5, 617 (1975).
23. J.J. Beaudoin and V.S. Ramachandran. *Cem. Concr. Res.* 8, 103 (1978).
24. R.F. Feldman and J.J. Beaudoin. *Cem. Concr. Res.* 6, 389 (1976).