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MICROSTRUCTURE AND STRENGTH
OF HYDRATED CEMENT

by

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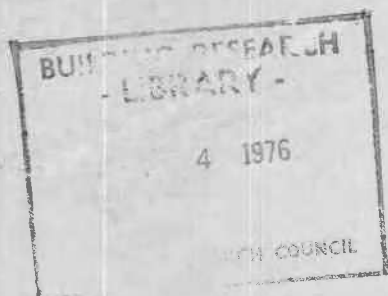# MICROSTRUCTURE AND STRENGTH OF HYDRATED CEMENT

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ABSTRACT

Several hydrated portland cement systems have been studied at DBR in
a wide range of porosities. These systems include room-temperature
hydrated paste, autoclaved paste, autoclaved with addition of sulfur
and silica, hot-pressed samples and compacts of synthetic 14Å
tobermorite. Measurements included compressive strength, Young's
modulus, product density, porosity and helium inflow, by which the
various systems were characterized. It was concluded that, at a
given porosity, an optimum proportion of higher density crystalline
material and poorly aligned and ill-crystallized material yields the
best strength but the quantity of poorly-crystallized material
required decreases with porosity.

A la Division des recherches sur le bâtiment, on a étudié plusieurs
systèmes de ciment portland hydraté de porosité très différente, y
comprise de la pâte hydratée à la température ambiante, de la pâte
mise en autoclave, de la pâte mise en autoclave avec addition de
soufre et de silice, des échantillons pressés à chaud et des
comprimés de tobermorite synthétique 14 Å. De nombreuses mesures ont
été effectuées, y compris la résistance à la compression, le module
de Young, la densité du produit, la porosité et le courant d'entrée
d'hélium, permettant de caractériser les divers systèmes. On conclut
qu'à une porosité donnée la résistance optimale est le résultat d'une
combinaison optimale de matériau cristallin à densité élevée et de
matériau peu cristallisé et de faible alignement. Toutefois, le
volume requis de matériau peu cristallisé diminue avec la porosité.

R. F. Feldman, J. J. Beaudoin

Strength is the property most sought-after during fabrication of hydrated portland cement products and much work (1,2) has been done in an effort to understand the various parameters governing it. Portland cement paste hydrated at room temperature has yielded fairly consistent porosity-strength plots, but extension of these data to very low porosities has revealed that porosity alone does not fully define the system (3,4).

Autoclaved cement pastes and pastes mixed with quartz have also been studied extensively by several investigators (1, 5-9) and the sequence of reactions has been fairly well worked out. It has been generally concluded that low strengths are associated with the formation of α-C_2S hydrate and high strengths with the formation of 11Å tobermorite together with poorly-crystallized tobermorite [C-S-H(I) and C-S-H(II)]. The high strength compounds are formed when a sufficient quantity of ground quartz is added to the cement. Bozhenov (8) concluded that there exists an optimum ratio of crystalline to poorly-crystallized products for a high strength product; Verbeck and Helmuth (2) considered that porosity alone could account for strength differences.

These approaches, although important in studies of strength, do not take into consideration other important factors, such as porosity of the various specimens, the crystallinity and density of the products, the nature of the bonding between crystallites or the significance of Young's modulus. A study by Mindess of the relationships between porosity and strength and porosity and Young's modulus in products formed by autoclaving mixtures of lime and silica of various ratios covered some of these areas but he assumed that the densities of the hydrated products were all the same, and thus was not able to compute a true porosity for all samples (7).

This present work considers, simultaneously, several of the parameters discussed. An accurate and well-tested method of measuring porosity and density in similar materials -- helium pycnometric technique -- was used (10); a technique for measuring the degree of disorder of hydrate product was also applied (11).

Strength and Young's modulus versus porosity were measured for several systems over a wide porosity range. Some of these were portland cement paste hydrated at room temperature, autoclaved cement paste with and without silica additions, and autoclaved cement paste with sulfur additions. These systems were compared and, knowing the density and type of product formed, conclusions made concerning the basis for their strength.

Experimental

Materials

The following materials were used:

1. <u>Normal type I hydrated cement</u> -- hydrated at water-cement ratios varying from 0.2 to 1.2. At the high water-cement ratio special techniques reported previously were used to avoid bleeding and non-uniformity (12). For strength, 5.1-cm (2-in.) cubes were made in the range of water-cement ratios up to 0.5.

2. <u>Flyash</u> composed as follows: 56% silica, 23% alumina, 4% ferric oxide,

13% CaO and 4% miscellaneous oxides. It was used as a 50% replacement
for cement in the cement-flyash mixtures.

3. Finely divided elemental sulfur was used in 2, 5 and 10% additions to
    cement before mixing; the surface area was 0.21 m^2/g as determined by N_2
    absorption.

4. 14Å tobermorite, prepared by precipitation from an aqueous solution, was
    obtained from N. Greening of the Portland Cement Association. Specimens
    for Young's modulus determination were prepared by compaction.

5. Hot-pressed hydrated portland cement, obtained from Professor D. Roy,
    Pennsylvania State University (3).

Methods

Helium comparison pycnometry and helium flow techniques

These techniques have already been described and applied to hydrated
portland cement systems (10, 11). Solid volume is obtained from these
measurements and, with the knowledge of the apparent volume, porosity can be
computed. Not using water to measure solid volume is considered important
because it avoids the problem of rehydration in many of the poorly-oriented
layered materials. It has also been found (10) that measurement of porosity
at 11% relative humidity (R.H.) eliminates most of the error because decom-
position of many hydrates below 11% R.H. can be largely avoided.

Helium flow has also been discussed (11). It is a measure of the flow
of helium with time usually into vacated interlayer spaces and may be
measured together with density.

Strength and Young's modulus

Strength was measured in compression on 2-in. (5.1-cm) cubes; Young's
modulus was measured on 3.2-cm diameter discs, 1.3 mm thick. The procedure
involves measuring the deflection of a specimen when it is loaded at its
center and supported at three points located at the circumference of a circle
2.5 cm (1 in.) in diameter (13).

Hydration

Samples for autoclaving were placed in molds and moist cured for 24 h.
Autoclaving at 216 °C, 21 kg/cm^2 pressure for 3 h was carried out after
demolding. Additions of sulfur or flyash were made during mixing with water
(14). Samples for measurements of Young's modulus were cut from 5.1-cm
(2-in.) cubes with a diamond tipped core drill. Paste samples were also
moist cured as cubes. The 0.25 water-cement ratio sample was cured for 2
years; the other water-cement ratio pastes were cured for only 90 days.

Length change

This was measured on samples in the shape of rectangular prisms 1 × 3 ×
0.1 cm using a Tuckerman optical extensometer (2×10^{-6} in sensitivity) (15).
Measurements were made from 100% to 11% R.H. and from 11% to the d-dry
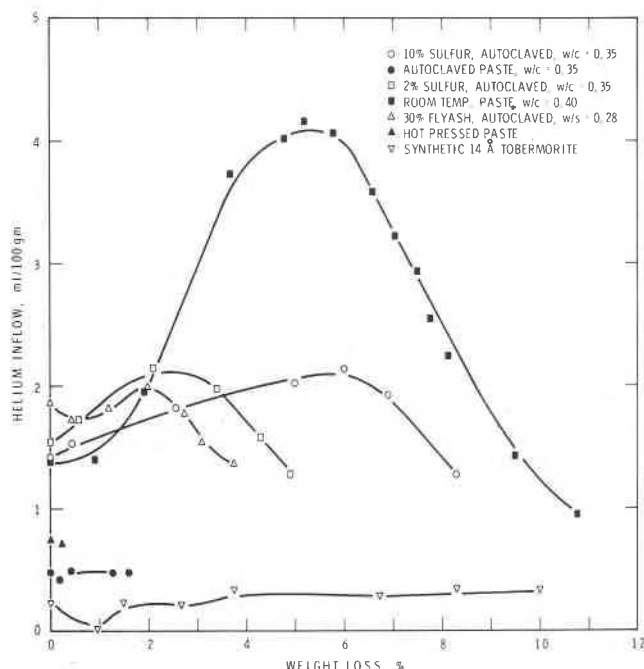position.

R. F. Feldman, J. J. Beaudoin

FIG. 1

Helium inflow versus weight
loss for various preparations

Results

1.   Helium Flow Measurements

Results for various preparations are presented in Fig. 1.   The 0.35 water-
cement ratio autoclaved paste shows little weight change or helium inflow.
The density of solid phase was 2.64 and probably consists of large quantities
of α-C_2S hydrate (16, 17).   The paste cured at room temperature shows the
maximum helium inflow as well as the characteristic decrease with weight loss.
This has been shown (11) to be due to partial removal of water from inter-
layer positions followed by collapse of the layers as the removal is complete.
The synthetic 14Å tobermorite is a layered material but shows little or no
helium inflow as the water is removed.   When water is removed from samples at
equilibrium with 11% R.H., however, weight change occurs linearly with solid
volume change; the slope of the curve is 1.48 gm/ml.   Thus most of the space
created by the removal of water is immediately taken up by the collapse of
the layers.   From this one must conclude that in a well-crystallized system,
the water molecules between the layers are thermodynamically similar, i.e.,
space between any two layers is either fully occupied by water molecules or
is empty.

In contrast, the solid volume of the sample hydrated at 0.4 water-cement
ratio at room temperature, when dried from 11% R.H., did not change linearly
with weight change but did so in the initial weight loss region at 2.98 gm/ml
and in the final region approaching d-dry at 1.59 gm/ml.   Thus in poorly-
crystallized, badly-aligned layered systems, water may be withdrawn incremen-
tally from between the layers.   The helium-inflow vs weight-loss characteris-
tic is an indication of a system having such a microstructure.   All the
pastes cured at room temperature exhibit this phenomenon.   In addition, the
samples autoclaved with additions of sulfur produced similar, although
reduced, characteristics.   Length change data from 100 to 11% R.H. and 11%

R.H. to d-dry conditions (Table I) confirm this. Length change in autoclaved
samples with 10% sulfur addition and a water-cement ratio of 0.35 is similar
to that for pastes. It must be concluded that additions of sulfur under auto-
clave conditions retard the conversion of C-S-H gel to α-C_2S hydrate and
tricalcium silicate hydrate and preserve some of the microstructure of C-S-H
gel. At higher water-cement ratios, preservation of structure becomes less
as it does with lower additions of sulfur. Examination of the densities also
confirms this. α-C_2S hydrate has a density of 2.80 (1) and, as more is
formed, the density of solid phase will increase. At water-cement ratios
below 0.35 the degree of hydration decreases and the density of solid phase
increases.

Additions of flyash preserve a microstructure in autoclaved products
similar to that of room-temperature pastes; shrinkage on drying is 2.5 times
greater than in autoclaved pastes but still much less than in room-
temperature pastes. Figure 1 shows helium inflow and Table I density and
shrinkage data. Finely-ground quartz in sufficient quantity leads to the
formation of 11Å tobermorite and poorly-crystallized tobermorite [CSH(I) and
CSH(II)] rather than α-C_2S hydrate (1, 17). CSH(I) and (II) probably cause
the helium inflow.

2.   Strength and Water-Cement Ratio

The results presented in Fig. 2 show the differences that are obtained in
strength at various water-cement ratios. The area representing room-
temperature paste was obtained from the results of many authors (2, 18-20).
The large increase obtained by the addition of sulfur at w/c ratio of 0.35 is
also only obtained below 0.4.

Values obtained with autoclaved mixtures of flyash are in the same zone
as the room-temperature paste and in an even higher zone at high water-cement
ratios.

FIG. 2

Strength versus water cement
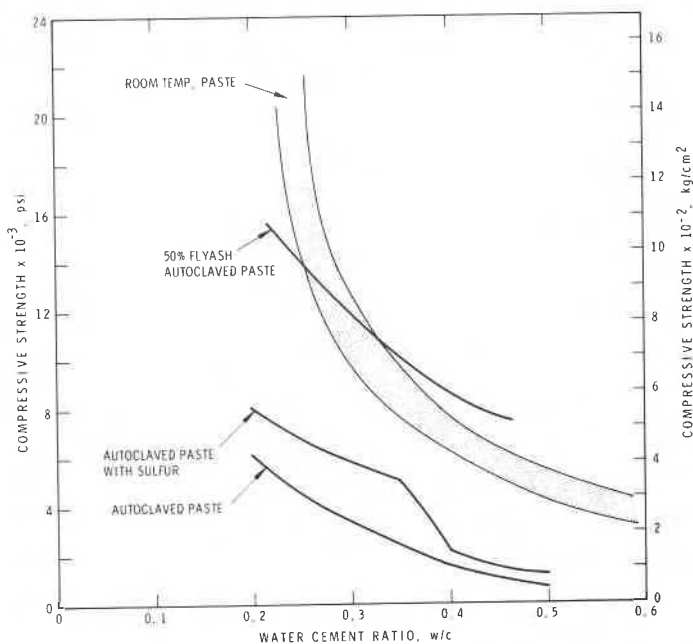ratio for autoclaved and
non-autoclaved mixes

R. F. Feldman, J. J. Beaudoin

TABLE I

PREPARATION AND PROPERTIES OF VARIOUS HYDRATED CEMENT MIXES

Composition	Water Cement Ratio	Helium Inflow	Density, gm/cc	Poros-ity, %	Strength kg/cm^2	E, kg/cm^2 $\times 10^{-4}$	Length 100 to 11%	Change, % 11% to d-dry
* (30% flyash (70% cement	0.28	fair	2.56	28.5	630	23	0.07	0.32
* (50% flyash (50% cement	0.23	fair	2.43	27.8	1,000	30.1		
* (50% flyash (50% cement	0.28	fair	2.42	27.8	945	25.2	0.07	0.25
* (50% flyash (50% cement	0.35	fair	2.39	33.0	725	19.9		
* (50% flyash (50% cement	0.40	fair	2.40	38.5	565	17.4		
* (50% flyash (50% cement	0.45	fair	2.39	44.0	555	18.1		
* 2% sulfur and cement	0.20	mod.	2.72	24.2	560			
* 5% sulfur and cement	0.25	mod.	2.68	28.5	455			
* 2% sulfur and cement	0.35	fair	2.47	31.5	370	20.3	0.16	0.29
* 10% sulfur and cement	0.35	fair	2.49	31.5	338	19.2	0.31	0.87
* 2% sulfur and cement	0.40	mod.	2.64	37.8	127			
* 2% sulfur and cement	0.45	mod.	2.65	43.2	90			
* 10% sulfur and cement	0.50	mod.	2.58	46.5	77			
* cement	0.20	low	2.75	25.2	427			
* cement	0.25	low	2.75	31.9	305			
* cement	0.35	low	2.64	36.7	206	12.2	0.03	0.10
* cement	0.50	low	2.75	49.8	43			
** room temp. cement	0.25	high	2.27	12.3	1,540	18.5	0.40	0.90
** room temp. cement	0.35	high		20.0	510			
** room temp. cement	0.40	high	2.24	22.0	420			
** room temp. cement	0.45	high		28.0	368			
** room temp. cement	0.50	high		36.0	286		0.40	0.90
** hot-pressed cement		mod.-low	2.88	6.0	5,250			

* - autoclaved   ** - not autoclaved

Little can be learned from this plot about the basic reasons for the strength of these materials except that there appears to be some relationship between strength and the amount of poorly-aligned ill-crystallized material present.

3. Density of Solid Phase

The density of pastes cured at room temperature varied between 2.24 and 2.27 (Table I). These are all well-hydrated except for the 0.25 w/c paste which was 60% hydrated. Two factors tend to increase the density of the solid phase above the values for the room-temperature paste. One is a low degree of hydration, which increases the amounts of unhydrated material (density 3.15); the other is a change in the products to some of the following: 11Å tobermorite (density 2.42 → 2.46) α-C_2S hydrate (density 2.80), xonotlite (density 2.71), tricalcium silicate hydrate (density 2.56). On the other hand CSH(I) has a density of 2.0 to 2.2 and CSH(II) is probably also low.

The change in the solid phase as reflected by density introduces a multiplicity of factors with regard to strength. As the density increases, the volume of solid decreases leading to an increase in porosity. If well-crystallized, large, dense crystals are formed the chances for good contact between them decrease. At the same time, strength of crystals of higher density and similar structure should be greater than ones of lower density.

The density of the autoclaved samples of cement paste shows large increases over samples hydrated at room-temperature. At a water-cement ratio of 0.35 (density 2.64), the density rises to 2.75 at w/c 0.50, probably because more of the α-C_2S hydrate product forms; at low water-cement ratios (0.20 and 0.25) it attains a density of 2.75. In the latter case, more unhydrated material is probably the reason. The addition of sulfur is very effective at a water-cement ratio of 0.35: densities are reduced to 2.47. But at a water-cement ratio of 0.5 density is 2.58; with less sulfur it is 2.65 and 2.64 at water-cement ratios of 0.45 and 0.4 respectively. The density increases further at water-cement ratios of 0.25 and 0.20 probably due, in part, to the presence of unhydrated material. Flyash additions of 50% reduce the density at all water-cement ratios (2.38 to 2.42 gm/cc) probably due to the formation of CSH(I) and (II) (1), although it is well in excess of the density of the room-temperature paste. Simultaneous formation of 11Å tobermorite is probably responsible for this (1).

Three preparations mentioned in the literature (3, 4) are of interest: the hot-pressed sample of density 2.88 gm/cc is mainly composed of unhydrated material; the other two are of very low porosity paste made at w/c of 0.20 with a cement of over 6000 cm^2/gm Blaine and have product densities in the order of 2.15 gm/cc.

4. Strength and Young's Modulus versus Porosity

(a) Strength versus porosity

In Fig. 3 the results for all the preparations are plotted as exponential functions as well as results for room temperature pastes obtained from several authors (2, 18-20). Considering the variety of data the agreement is fair; the best curve is shown for each set of data from each
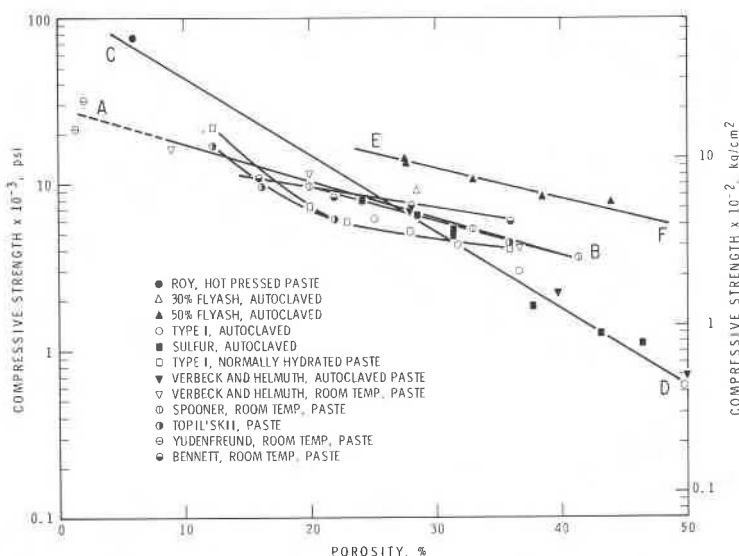
R. F. Feldman, J. J. Beaudoin

FIG. 3

Strength versus porosity for autoclaved and room-temperature preparations

author and the slopes are similar. The well-cured pastes of Verbeck and Helmuth (2) and the rotated cubes of Spooner (20) at high water-cement ratios produce a line, AB, around which the other data are scattered. The specimens of the present authors at intermediate porosities are of somewhat low strengths due to low hydration times. When extrapolated, the line AB (henceforth referred to as room-temperature paste line) meets the data of Yudenfreund et al (4) at porosities of 1.4 and 2%. The line thus covers data from 1.4 to 41.5% porosity.
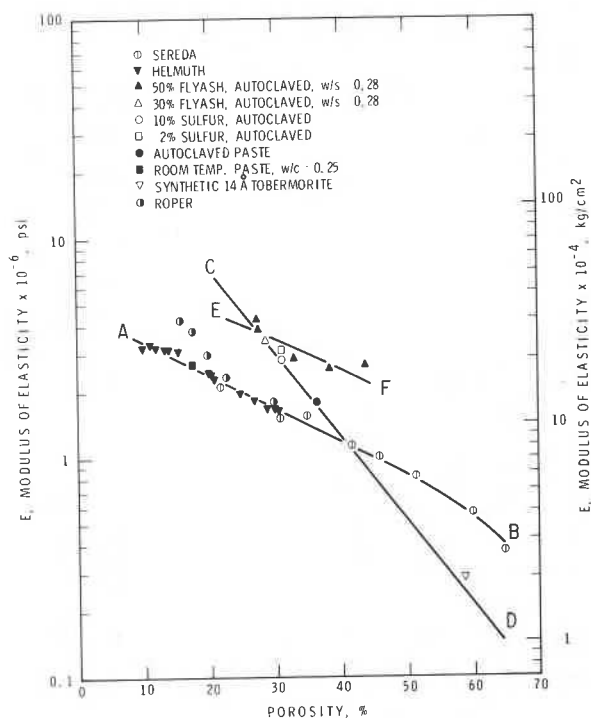
The second line, CD, represents the best fit for most of the autoclaved preparations exclusive of those made with flyash. This line, referred to as the high density line, intersects the room-temperature paste line at about 27% porosity, approximately at w/c 0.45 for a room-temperature paste. The line CD has a steeper slope than the room-temperature paste line and thus, for a given decrease of porosity, a greater increase of strength is obtained than for the room-temperature paste. Above 27% porosity, however, room-temperature paste is stronger at the same porosity than samples on the high density line despite their higher density products. This is evidence that porosity, although important, is not the sole factor governing strength as suggested by others, but bonding of individual crystallites plays a role. This was shown by Soroka and Sereda for the gypsum system (21). It is apparent that disorganized, poorly-crystallized material forms better bonds. Addition of sulfur always lowers the porosity of a preparation and thus improves strength along the high density line. This must also involve an improvement in bonding, however, since density has also decreased and some poorly-crystallized material has formed. As porosity decreases, the advantage of the superior bonding of the room-temperature paste diminishes. At lower porosities it seems apparent that better bonding exists between high density crystallites and the fact that the sample is composed of higher density and presumably higher strength material, manifests itself. Some authors (7) have ascribed this effect to pore-size distribution but this does not seem to be the case. The shape of pore and the area and proximity of contact between individual crystallites are of major importance concerning strength. When the line CD is extrapolated toward low porosities it meets the point for hot-pressed cement paste at 5250 kg/cm^2 (75,000 psi) and 6% porosity.

STRENGTH, POROSITY, HYDRATED CEMENTS

These two lines suggest that a correct balance between poorly-crystallized material and higher density material exists which will produce the strongest product at a specific porosity. This has been suggested by Bozhenov et al (8) and is found in line EF for the flyash and cement mixtures in the intermediate porosities where 11Å tobermorite and CSH(I) and (II) are probably formed. This line is approximately parallel to the room-temperature paste line but is composed of higher density material (approximately 2.40 gm/cc). At lower porosities, a relatively lower quantity of poorly-crystallized material will be required for ideal bonding and thus line EF also crosses the high density line. Work with the C_3A and CA systems has shown that, at low porosities, good strength could be obtained from the C_3AH_6 product because more bonds (increased area of contact) formed between crystallites than formed at higher porosities (22).

(b) Young's modulus versus porosity

The results of these tests are plotted as exponential functions in Fig. 4. Most of the data concerning the room-temperature paste samples have

FIG. 4

Young's modulus versus porosity for autoclaved and room temperature preparations

been taken from three papers (12, 23, 24) and again a "paste line", AB, is drawn. The high density line, CD, is again of higher slope than the "paste line" and the cross-over is at a higher porosity, 41%. The 14Å compact of tobermorite and the autoclaved paste without sulfur at w/c 0.35 fall on this line. The latter sample is above the paste line; in the strength data it is well below. The flyash preparations again have their separate line, parallel and above the paste line, but now cross the high density line. It appears as though the high density line has shifted to the right, relative to the strength plot.

R. F. Feldman, J. J. Beaudoin

Discussion

Strength and Young's modulus seem to be related through porosity for any one system when parameters, such as the composition morphology and bonds, are kept constant (25). Strength is also dependent on the ability of the material to resist crack propagation. A sample made up of high density crystals, if not stressed too highly, can give a high Young's modulus but it has a relatively low strength, a reflection of poor bonding. This is illustrated precisely in this work, once the porosity variable has been accounted for. Bonding is an important factor in Young's modulus behavior as shown by the work of Soroka and Sereda on the gypsum system (24) but the density of product plays a more prominent role in Young's modulus than in strength which is reflected in the values of the autoclaved samples with and without sulfur. The flyash samples, which were above the high density line in the strength plot, are again above this line for the Young's modulus plot but cross over at a porosity of 27.5%. This is again a compromise between characteristics of the solid phase, e.g., density, and bonding since the flyash samples have densities around 2.40 gm/cc.

A poor bond between two crystals can also be thought of as a crack. The bond between large crystals may be similar to longer cracks which, according to the Griffith criteria, will lead to higher stress concentrations. The role played by the low density high surface area paste then is to blunt and change the size of the crack and reduce the stress concentration.

Conclusions

1. Porosity is a major factor in controlling strength and modulus of elasticity of portland cement systems. Morphology, which involves crystal bonding, and product density are also important.

2. Poorly-aligned and ill-crystallized material has the best bonding properties.

3. At high porosities, bonding of well-crystallized material is very poor and strength is lower than for poorly-crystallized material of the same porosity.

4. Best strength is obtained by an optimum combination of dense, well-crystallized material and poorly-crystallized material. As porosity is decreased, a lower proportion of the latter is required for bonding the well-crystallized material.

5. Formation of low density products also improves strength because of an inherent reduction in porosity relative to high density products. An example of this is the formation of α-C_2S hydrate which usually results in weak bodies because of its high density and resultant high porosity and because of poor inter-crystal bonding.

6. Additions of sulfur and silica help preserve, to some extent, the poorly-crystallized structure.

Acknowledgments

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Appendix

Helium porosity values of the low porosity specimens of Yudenfreund et al, were estimated in two ways:

(a) The knowledge of the degree of hydration[26] and initial water-cement ratio together with an approximate helium density of hydration products enables a simple calculation of porosity to be made.

(b) The nitrogen pore volume per unit weight determined by Mikhail[27] and initial water-cement ratio, enable simple calculation of a porosity comparable to that of helium as calculated in (a).