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by

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A STUDY OF MECHANICAL PROPERTIES OF AUTOCLAVED CALCIUM SILICATE SYSTEMS

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ABSTRACT:

Compressive strength, modulus of elasticity, and microhardness measurements were made on a variety of autoclaved cement-silica preparations covering a wide range of porosity. A spectrum of linear log mechanical property - porosity functions was observed. Analysis demonstrated that the slopes of these functions were dependent on the preparation silica content and density of the hydrated product. The slopes of the lines for each mechanical property bore a constant ratio with slopes calculated from the corresponding lines of the other two mechanical properties. This resulted in expressions interrelating mechanical properties which were independent of porosity and valid for all preparations studied. Compressive strength and microhardness for preparations studied were shown to be directly related.

La résistance à l'écrasement, le module d'élasticité et la microdureté d'un assortiment de préparations ciment-silice autoclave furent déterminés pour une grande gamme de porosité. Un spectre de fonctions linéaires à base logarithmique propriété mécanique-porosité fut constaté. Une analyse a démontré que les pentes de ces fonctions dépendaient de la teneur en silice de la préparation et de la densité du produit hydraté. Les pentes des courbes pour chaque propriété mécanique ont maintenu un rapport constant aux pentes calculées à partir des courbes correspondantes des deux autres propriétés mécaniques. Il en résulta des expressions reliant entre elles les propriétés mécaniques qui étaient indépendentes de la porosité et valables pour toutes les préparations étudiées. Il fut démontré que la résistance à l'écrasement et la microdureté des préparations étudiées étaient directement reliées l'une à l'autre.

Compressive strength, modulus of elasticity and microhardness are mechanical properties that have been shown to be porosity dependent for room temperature hydrated cement paste (1 to 5). Recent work (6, 7) cites porosity, morphology and crystal bonding as contributing to the mechanical behaviour of autoclaved and room temperature hydrated paste. It appears that although porosity is a major factor controlling mechanical behaviour of porous cement hydrates other factors also play a role.

The chemistry of autoclaved pastes with and without quartz (silica) additions has been studied by various investigators (8 to 14); the principal products, depending on initial proportions of cement and silica, are crystalline αC_2S hydrate, 11Å tobermorite, poorly crystallized tobermorite (CSH(I) and CSH(II)) and sometimes hillebrandite and xonotlite.

A systematic study of the mechanical properties of the cement-silica system under autoclaved conditions on a porosity basis may help in elucidating the contributory role of morphology, crystal bonding and chemistry of the hydration product as characterized by solid density; this system is especially good for this type of study because of the wide variation possible in pore distribution and morphology. Mindess (15) studied strength porosity relationships for autoclaved lime-silica mixtures but assumed a constant value for the solid density in calculating porosity making any assessment of results difficult.

To assess the cementing properties of various waste products such as fly ash it would be useful to base selectivity on factors affecting a universally recognized engineering property such as porosity. Previous work (6) clearly showed that compressive strength and modulus of elasticity curves for room temperature hydrated paste were significantly displaced from those representing autoclaved cement paste. It was thought that a better defined system (cement-silica) under autoclaved conditions would provide a spectrum of mechanical property vs porosity functions that would assist in characterizing the engineering properties of fly ashes from different sources. The relationships between microhardness, strength and modulus of elasticity and their dependence on porosity would be further elucidated.

Experimental

Materials

The following materials were used:

1. Normal Type I Cement was mixed with varying proportions of silica and hydrated at water-solids ratios from 0.26 to 0.45.

2. Silica, prepared by grinding Ottawa silica sand and retaining that which passed through a 100-mesh sieve, was mixed with cement (5, 10, 20, 30, 50 and 65 per cent by weight) prior to autoclaving. The particle size distribution was as follows: 150 μm - 75 μm (40 per cent); 75 μm - 45 μm (16 per cent); 45 μm - 25 μm (14 per cent); 25 μm - 12 μm (10 per cent); 12 μm - 6 μm (10 per cent); 6 μm - 1.5 μm (5 per cent); and finer than 1.5 μm (5 per cent).

3. Fly Ash composed as follows: 56 per cent silica, 23 per cent alumina, 4 per cent ferric oxide, 13 per cent CaO and 4 per cent miscellaneous oxides. It was used as a 50 per cent replacement for cement in the cement-fly ash mixtures. Eighty-five per cent of the particles were 45 μm - 12 μm.

Methods

Helium Comparison Pycnometry

The application of this technique to the hydrated portland cement system is described elsewhere (16). Solid volume is measured enabling the determination of porosity as the apparent volume is calculated from sample geometry. The problem of rehydration encountered when water is used as the displacement medium is avoided. Using 11 per cent R.H. as datum avoids excessive decomposition of the hydrates (17).

Compressive Strength; Young's Modulus and Microhardness

Strength was measured in compression on 2-in. (5.1-cm) cubes; two cubes were tested for each preparation. Young's modulus was measured on 3.2-cm diameter discs, 1.3 mm thick; ten discs for each preparation were used. The procedure involves measuring the deflection of a specimen when it is loaded at its centre and supported at three points located at the circumference of a circle 2.5 cm (1 in.) in diameter (3). A Leitz microhardness testing machine with a Vickers indenter was used for the microhardness measurements which were made on the discs used for modulus of elasticity measurements and were carried out at 11 per cent R.H. There were ten hardness measurements made on each disc and three discs were tested for each preparation.

Hydration

Samples for autoclaving were prepared at water-solid ratios 0.26, 0.30, 0.35, 0.40 and 0.45. Preparations at each water-solid ratio consisted of six sets of samples, each set having a different silica content. Silica contents expressed as per cent by weight of solid were 5, 10, 20, 30, 50 and 65 per cent; this provided a total of 30 different preparations. Mixes were cast in cube molds and moist cured for 24 hours; three cubes were

cast for each preparation. After demolding samples were autoclaved at 216°C, 21 kg/cm^2 pressure for 3 hours. Two cubes were retained for compressive strength measurement. A 1.25-in. (3.2-cm) core was taken from the third cube with a diamond tipped core drill. Ten discs, 0.050 in. (.127 cm) thick, were sliced from each core for measurements of modulus of elasticity and microhardness.

Results

Porosity

The logarithms of compressive strength, microhardness, and modulus of elasticity were plotted against porosity; the plots resulted in a family of straight lines (each silica content yielding a different line) with different slopes (Figures 1 - 3). The results of linear regression analysis are recorded in Table 1. For lines representing each silica content the slope ratios were determined. Table 2 gives values of the slope ratios for the semilogarithmic functions representing the three mechanical

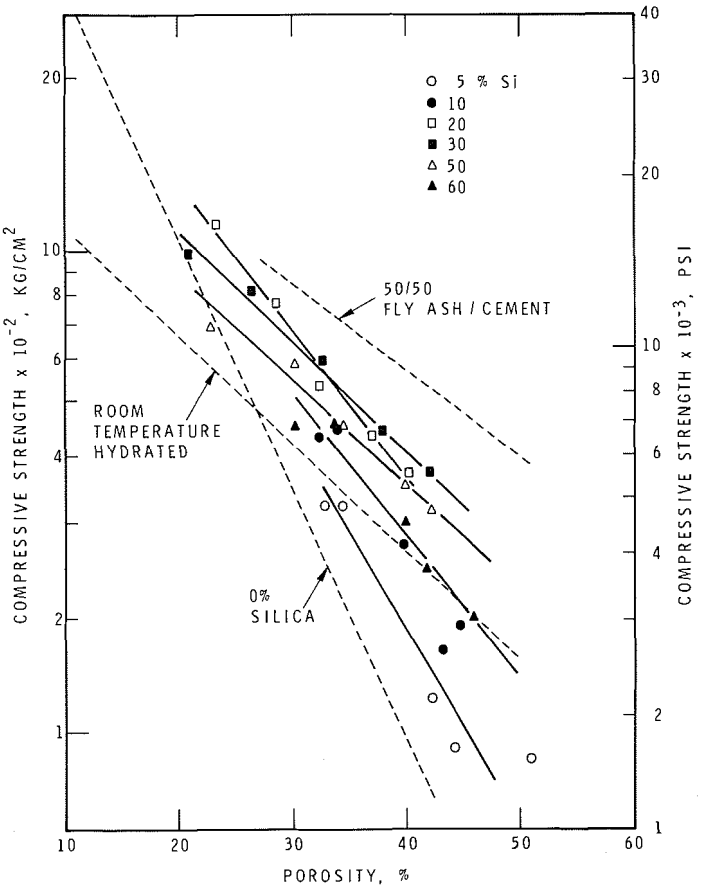

FIG. 1

Compressive strength vs porosity for various autoclaved and room temperature hydrated cement and cement-silica preparations

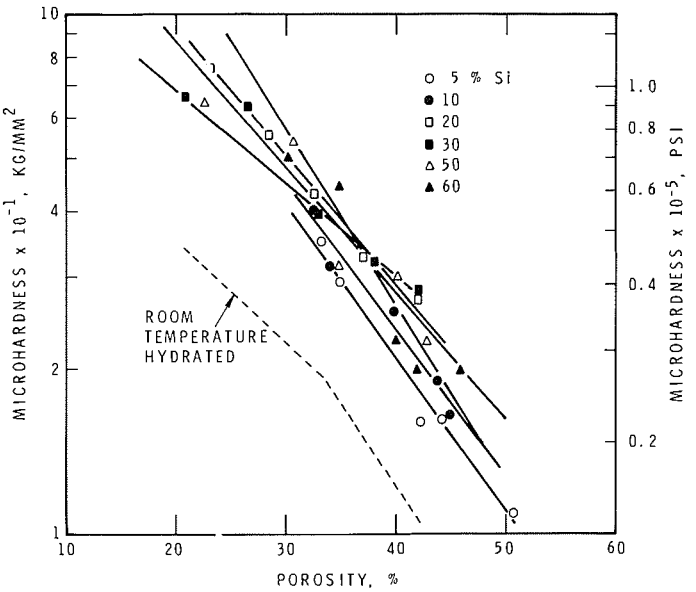

FIG. 2

Microhardness vs porosity for various autoclaved and room temperature hydrated cement and cement-silica preparations

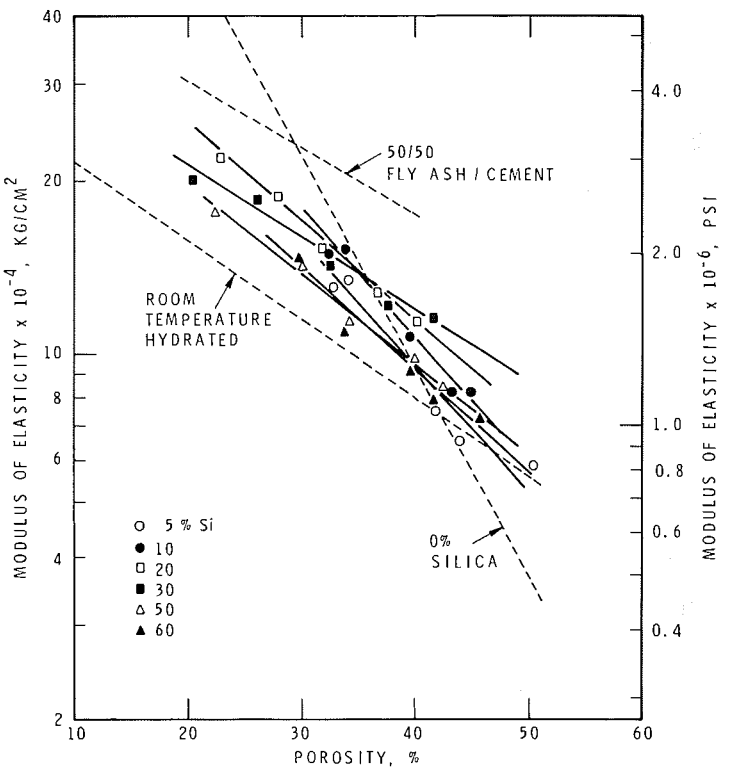

FIG. 3

Modulus of elasticity vs porosity for various autoclaved and room temperature hydrated cement and cement-silica preparations

Compressive strength, microhardness, and modulus of elasticity for room temperature hydrated paste obey the general relationship, $S, E, H = (S_o, E_o, H_o)\exp[(-b_{S,E,H})p]$ where S, E, H refer to strength modulus of elasticity and microhardness and p represents porosity. This appears to be true also for autoclaved cement-silica mixtures. The mean slope ratios for the range of silica contents studied are as follows:

a) $\frac{b_S}{b_E} = 1.429 \pm .183$

b) $\frac{b_H}{b_E} = 1.437 \pm .153$

c) $\frac{b_S}{b_H} = 0.991 \pm .126$

It can be easily shown that:

$$E = E_o \left(\frac{S}{S_o}\right)^{.70} \quad (1)$$

$$E = E_o \left(\frac{H}{H_o}\right)^{.70} \quad (2)$$

$$H = \frac{H_o}{S_o} S \quad (3)$$

TABLE 1

Regression Analysis of Modulus of Elasticity, Compressive Strength and Microhardness versus Porosity Data

$E = E_o \exp(-b_E p)$

%Si	E_o (kg/cm^{2}x10^{-3})	b_E*	r†
0	3200.0	.0885 ± .0074	.962
5	704.7	.0509 ± .0078	.960
10	887.2	.0599 ± .0058	.978
20	568.9	.0405 ± .0021	.998
30	387.3	.0300 ± .0035	.979
50	419.8	.0380 ± .0023	.995
65	477.5	.0415 ± .0055	.970

$S = S_o \exp(-b_S p)$

%Si	S_o (kg/cm^{2}x10^{-3})	b_S	r
0	9.500	.1085 ± .0142	.949
5	3.105	.0683 ± .0138	.945
10	6.223	.0767 ± .0138	.967
20	5.200	.0649 ± .0038	.995
30	2.952	.0479 ± .0018	.988
50	2.254	.0444 ± .0053	.977
65	2.838	.0560 ± .0067	.987

$H = H_o \exp(-b_H p)$

%Si	H_o (kg/cm^{2}x10^{-3})	b_H	r
0	-	-	
5	30.27	.0667 ± .0072	.989
10	33.96	.0669 ± .0083	.976
20	32.89	.0629 ± .0065	.970
30	18.16	.0452 ± .0055	.973
50	21.83	.0521 ± .0086	.957
65	39.45	.0680 ± .0147	.950

* gives 90 per cent confidence limits
† correlation coefficient

TABLE 2

Ratio of Slopes of Strength, Microhardness and Modulus of Elasticity vs Porosity Data

%Si	b_S/b_E	b_H/b_E	b_S/b_H
0	1.230	-	-
5	1.342	1.310	1.024
10	1.423	1.241	1.146
20	1.607	1.553	1.035
30	1.600	1.506	1.062
50	1.174	1.375	0.854
65	1.347	1.638	0.822

Equations 1, 2 and 3 apply within the statistical bounds of the ratios $\frac{b_S}{b_E}$, $\frac{b_H}{b_E}$ and $\frac{b_S}{b_H}$ and the validity of the general equation for S, E and H. They also imply that porosity generally influences the properties S, E and H in a similar way for range of compositions and morphologies. The constant of proportionality in Eq. (3) has a physical significance. It is the ratio of microhardness to compressive strength at zero porosity.

Density

Solid densities were determined at 11 per cent R.H. by helium displacement for all preparations studied. The specific volume increases to a maximum value as silica content increases and then decreases at large silica contents (Figure 4). The high density values correspond to the presence of αC_2S hydrate (determined by X-ray diffraction) and low values of compressive strength. Similarly the low density values correspond to the presence of poorly crystallized hydrosilicate and optimum strength. The above observations are also true for maximum and minimum values of modulus of elasticity and microhardness.

Interrelationship of Mechanical Properties

Figures 5 and 6 are plots of modulus of elasticity and microhardness vs compressive strength. Figure 7 plots modulus of elasticity vs microhardness. As expected from Equations (1) and (2), Figures 5 and 7 are nonlinear relations when the origin is included in the population of experimental points.

Equation (3) describes the relation between microhardness and strength as linear and passing through the origin. Regression analysis of the experimental data, which includes results from the 30 preparations as well as room temperature hydrated paste but does not include the origin in

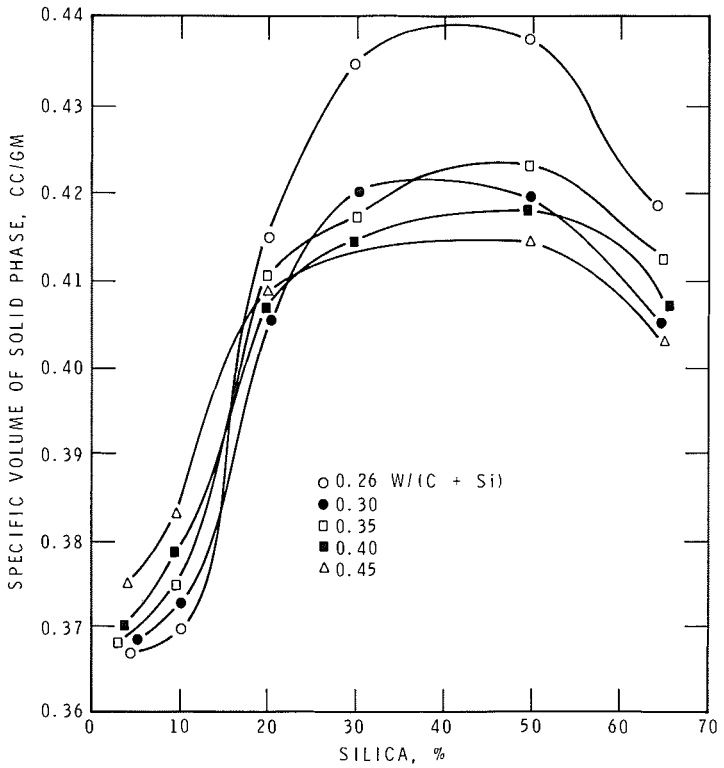

FIG. 4

Specific volume of solid phase vs silica content for various autoclaved cement-silica preparations

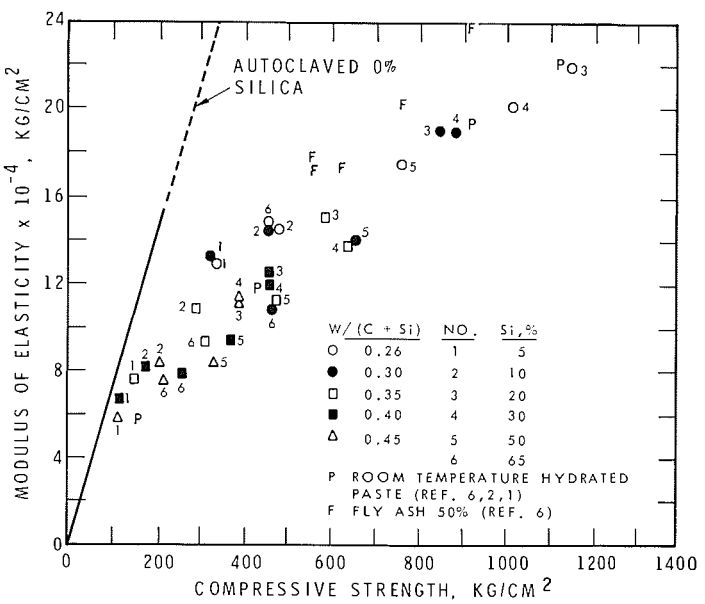

FIG. 5

Modulus of elasticity vs compressive strength for various autoclaved and room temperature hydrated cement and cement-silica preparations

the population of experimental points, gives the following relation:

$$H = 6.853 + .0615S \qquad (4)$$

The microhardness intercept 6.853 kg/mm^2 is small as the population of microhardness values covers the range $0 < H < 80$ kg/mm^2. The correla-

tion coefficient 0.960 indicates a good linear fit. Any disparity between Eqs. (3) and (4) is negligible and is probably inherent in errors associated with the third degree of freedom (porosity) on which the derivation of Eq. (3) is based. The data plotted in Figure 5 include: 30 preparations of autoclaved cement-silica mixtures; 5 preparations of autoclaved cement-fly ash mixtures; preparations representing room temperature hydrated paste; and, preparations of autoclaved paste without silica addition.

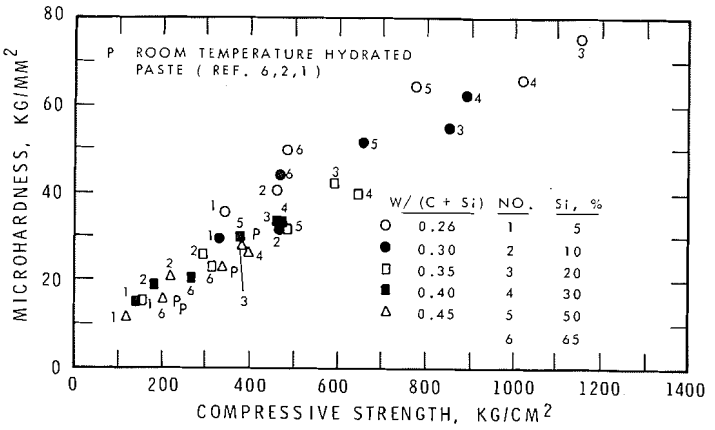

FIG. 6

Microhardness vs compressive strength for various autoclaved and room temperature hydrated cement and cement-silica preparations

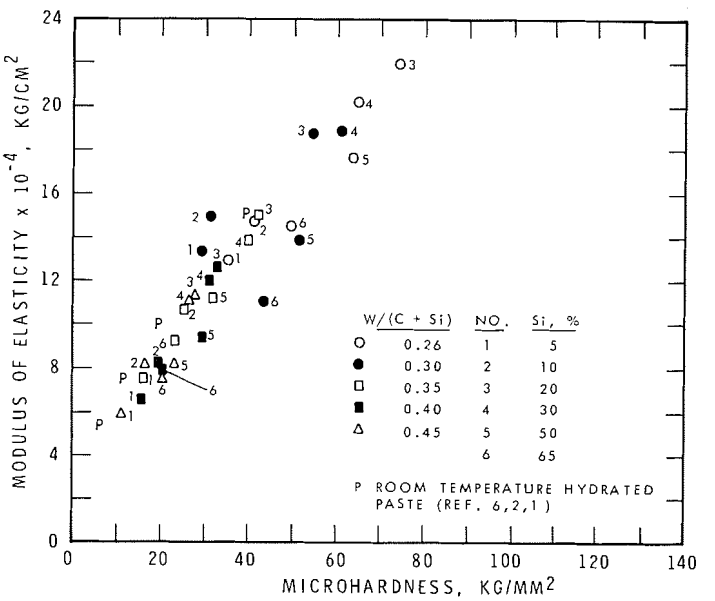

FIG. 7

Modulus of elasticity vs microhardness for various autoclaved and room temperature hydrated cement and cement-silica preparations

With the exception of autoclaved paste without silica the data are well described by a smooth curve representing Eq. (1). The data for autoclaved paste without silica lie on a line of constant slope; the data for autoclaved paste with silica lie below the line which represents samples with product densities between 2.75 and 2.88. It is noted that within the sample population described by Eq. (1) the locus

of points having low silica contents lies nearer the high density line than those having higher silica contents. An extension of the dashed segment of the high density line (Figure 5) likely includes data representing hot-pressed hydrated cement. Data on this line at strength levels less than 200 kg/cm^2 may be considered to be within the sample population described by Eq. (1).

Table 3 lists values of the ratio E_o/S_o (the ratio of modulus of elasticity at zero porosity to strength at zero porosity), calculated from data obtained by extrapolation of the mechanical property-porosity data. It will be noted that there is variation in the values of E_o/S_o and H_o/S_o for the different preparations; this is consistent with the distribution of data for varying sets of preparations in Figure 5.

TABLE 3
Ratio of Modulus of Elasticity and Microhardness at Zero Porosity to Strength at Zero Porosity

Preparation	E_o/S_o	H_o/S_o
Room Temperature Hydrated Paste	170.5	20.10
Autoclaved Paste Cement-Fly Ash 50/50	198.0	-
Autoclaved Paste 0% Silica	337	-
5% Silica	227	9.75
10% Silica	142	5.46
20% Silica	110	6.33
30% Silica	131	6.15
50% Silica	186	9.69
65% Silica	168	13.90

The high density line includes samples that represent the highest value of the ratio E_o/S_o. The 5 per cent silica preparation has the next highest value. The remaining cement-silica preparations have similar values. The accuracy of Eqs. (1), (2) and (3) in describing the data is also dependent on average values of H_o/S_o. These values are included in Table 3. It appears that a high density solid phase contributes to greater rates of change of modulus of elasticity with respect to compressive strength.

It is noteworthy that the data plotted in Figures 5, 6 and 7 include results representing preparations containing varying proportions of crystalline αC_2S hydrate, poorly crystallized hydrosilicate (CSH(I)) and tobermorite like calcium silicate hydrate.

The relation between modulus of elasticity and compressive strength

for several concretes (18) has the general form $E = aS^b$, where $0.45 < b < 0.78$. This relation, independent of porosity, was shown to be valid for hydration periods up to five years. For concrete, porosity seems to affect the mechanical properties of compressive strength and modulus of elasticity in a similar way.

Optimum Silica Content

The three mechanical properties investigated - compressive strength, microhardness and modulus of elasticity - had maximum values at silica contents between 20 and 30 per cent (see Figure 8 for compressive strength results; microhardness and modulus of elasticity showed similar dependence on silica content). X-ray diffraction results indicate that most of the silica has reacted at the maximum position. The characteristic shape for strength vs silica content observed by Menzel (19) was observed for each mechanical property.

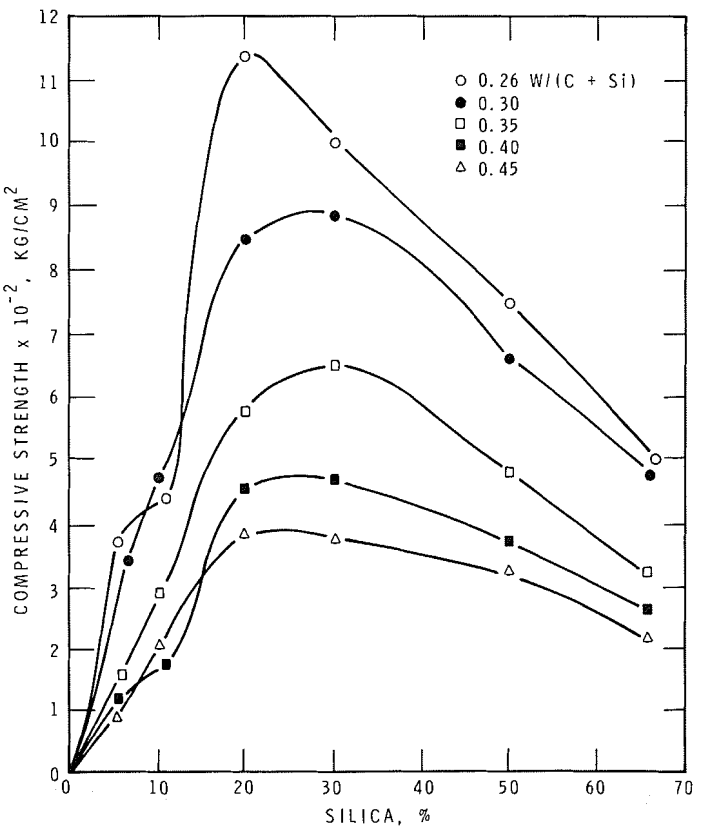

FIG. 8

Compressive strength vs silica content for various autoclaved cement-silica preparations

In addition it was also found that this type of characteristic occurred with two other parameters.

(a) The specific volume (as determined by helium displacement) yielded a maximum value at a silica content between 30 and 40 per cent (Figure 4).

(b) The inverse of the slopes of the logarithm of modulus of elasticity, strength and microhardness vs porosity functions (Figure 9) exhibit a maximum value at a silica content of approximately 30 per cent.

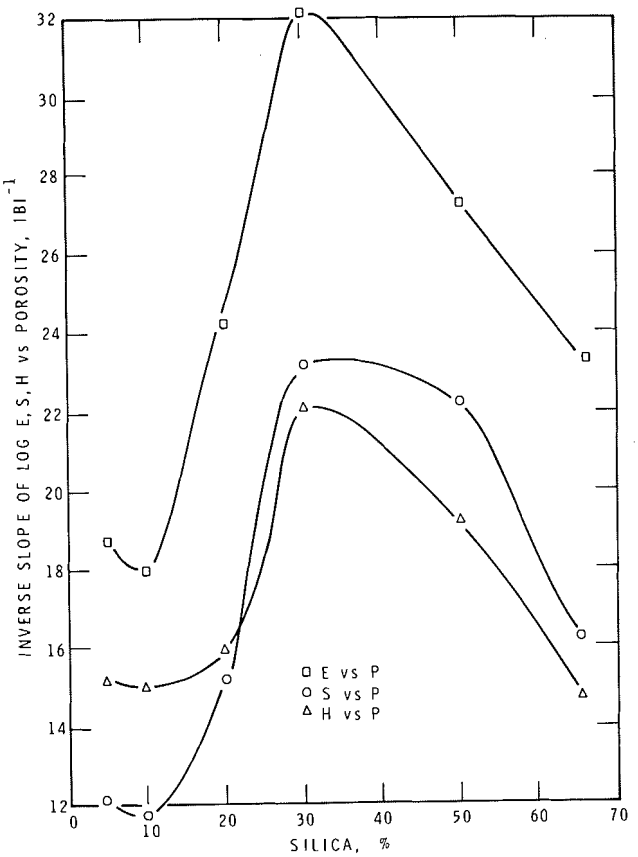

FIG. 9

Inverse slope of the log mechanical property-porosity relations as a function of silica content

Discussion

The compressive strength-porosity functions for room temperature hydrated paste and autoclaved paste are not colinear (6) but intersect at approximately 28 per cent porosity. Similarly the modulus of elasticity vs porosity functions intersect at approximately 40 per cent porosity. For autoclaved cement-silica mixtures a family of mechanical property-porosity

functions exist. As the silica content is varied the slope of the line changes; each line also reflects a change in product density and hence morphological and chemical change. These changes in slope and density at a given porosity support the view that an optimum amount of poorly crystallized hydrosilicate and well crystallized dense material provide maximum values of strength and modulus of elasticity. The line for autoclaved paste extrapolated to zero porosity included published values (20) for compressive strength of hot pressed paste up to 90,000 psi (6300 kg/cm^2). Divergence between lines in the low porosity region results from an intimate surface to surface bonding of high density units welded together with an optimum amount of poorly crystallized hydrosilicate. In the high porosity region poor bonding between the dense crystals and insufficient poorly crystallized hydrosilicate accounts for the divergence between lines and resulting low strength of the autoclaved product without silica. Porosity, crystal bonding and product density and morphology all play a role in determining values of compressive strength, microhardness, and modulus of elasticity. Additions of silica help preserve to some extent the poorly-crystallized structure. It has been observed (1) that the slope of the linear log mechanical property-porosity function for room temperature hydrated paste changes when the porosity exceeds 50 per cent; this is possibly due to a change in morphology with high water-cement ratios. It is possible that a similar change in slope would have been observed for autoclaved preparations had porosity exceeded 50 per cent. Purton (21) ascribes the 20 per cent decrease in solid volume upon formation of αC_2S hydrate and xonotlite as the major factor responsible for low compressive strength. Observed changes in compressive strength, modulus of elasticity and microhardness (when αC_2S hydrate is present) at a constant porosity suggest that these volume changes cannot alone account for observed changes in strength.

Purton (22) correlated drying shrinkage with the amount of hydrosilicate formed (defined as hydrate giving DTA exotherm at $820°C < T < 870°C$) but hypothesized that strength was more probably related to the degree to which the cementing material filled the voids. This seems in accord with the previous discussion of an optimum mixture of crystalline

and poorly crystalline material being responsible for optimum mechanical behaviour.

The linear correlation of microhardness and strength is interesting and significant. Obviously both processes involve the breaking of similar bonds. The result adds confidence to the cube crushing test and provides a way to estimate compressive strength when the making of cubes is inconvenient.

Conclusions

1. The observation that data representing measurements of modulus of elasticity, compressive strength, and microhardness for a variety of autoclaved preparations containing SiO_2 as well as room temperature hydrated cement paste, when plotted one against the other, lie on a single curve suggests that the relationships between these mechanical properties are not significantly influenced by the presence or absence of varying proportions of αC_2SH, CSH(I) or 11Å tobermorite. This also suggests that differences in the microstructure of the preparations studied do not significantly influence the interrelation of mechanical properties. The quantities of crystalline and poorly crystalline material are in such proportion as to impart to the hydrated paste composite similarities of mechanical behaviour, if 5 per cent or greater SiO_2 is added.

2. Porosity affects the mechanical properties of E, S and H qualitatively in a similar way. This follows from the previous statement as the relationships between E, S and H are independent of porosity.

3. To a first approximation, modulus of elasticity, E, can be expressed as an exponential function of strength or microhardness; i.e.,

$$E = \left(\frac{E_o}{S_o^{.70}}\right) S^{.70}; \quad E = \left(\frac{E_o}{H_o^{.70}}\right) H^{.70}$$

The constants subject to the accuracy of extrapolation have physical significance as E_o, S_o, H_o are modulus of elasticity, strength and microhardness at zero porosity respectively.

4. Compressive strength can be expressed as a linear function of micro-

hardness; $S = \frac{S_o}{H_o} H$. This gives a physical significance to the constant of proportionality which is the ratio of the compressive strength to microhardness at zero porosity. Conversely S_o/H_o can be determined from the slope of the S vs H plot without extrapolation.

5. For each mechanical property measured (modulus of elasticity, compressive strength, and microhardness), there is a family of straight lines when these properties are plotted as log mechanical property vs porosity; each line represents a different silica content.

6. The inverse slope of these lines when plotted as a function of silica content follows a bell-shaped curve similar to the Menzel compressive strength-silica content relationship.

7. Similarly the inverse of solid density (specific volume) when plotted as a function of silica content displays a bell-shaped curve. The curves for water-solid ratios 0.30, 0.35, 0.40, and 0.45 are well nested. The curve for water-solid ratio 0.26 has a significantly higher maximal value probably due to a lower degree of hydration.

8. Microhardness when plotted as a function of silica content also displayed a bell-shaped response akin to that for compressive strength and modulus of elasticity.

Acknowledgement

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