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STRUCTURE AND PROPERTIES OF POROUS CEMENT
SYSTEMS AND THEIR MODIFICATION BY IMPREGNANTS

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SOMMAIRE

On mesure, à l'aide de disques d'une épaisseur de 1.3 mm,
la microdureté et le module de Young de plusieurs systèmes
de ciment portland / silice traité à l'autoclave, de ciment
portland hydraté normalement et de verre poreux, repré-
sentant un large éventail de porosité et de répartition des
pores suivant leur grosseur. Ensuite, ces échantillons sont
complètement imprégnés de soufre. Les résultats sont dé-
crits de façon adéquate en fonction de la règle de mélange
du modèle Reuss, si l'on suppose une bonne adhérence entre
le liant et l'imprégnant, et des propriétés semblables pour
l'imprégnant dans les pores comme à l'extérieur, en vrac.
On étudie également des systèmes auxquels une partie ou
l'ensemble des suppositions ne s'appliquent pas, comme le
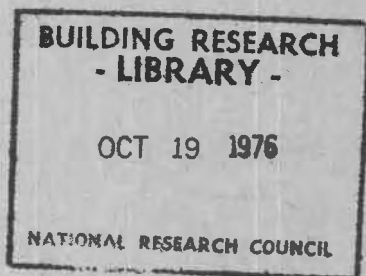verre poreux imprégné de soufre et le ciment portland hy-
draté imprégné de méthacrylate de méthyle.

STRUCTURE AND PROPERTIES OF POROUS CEMENT SYSTEMS
AND THEIR MODIFICATION BY IMPREGNANTS

ANALYZED

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SUMMARY - Microhardness and Young's modulus of discs 1.3 mm thick were
measured on several autoclaved portland cement/silica systems, normally hydrated
portland cement and porous glass, representing a wide range of porosity and
pore-size distributions. These samples subsequently were fully impregnated with
sulfur. It was found that the results could be adequately described by the
Reuss model mixing-rule, assuming that good bonding was achieved between the
matrix and the impregnant and that the impregnant had similar properties when
in the pores as when outside, as bulk. Systems were also studied for which
some or all the assumptions did not hold, e.g. porous glass impregnated with
sulfur, and hydrated portland cement impregnated with methyl methacrylate.

* * * * * * *

        Porosity is one of the major factors controlling the resistance to
chemical attack and the mechanical properties of portland cement mortars and
concrete. (1,2) In the case of hydrated portland cement materials it has been
difficult to define or measure porosity. (3) Pores in hydrated portland cement
have been defined as spaces that can be occupied by water that is evaporable at
the vapour pressure of ice at -79°C. This definition has the obvious disad-
vantage of including as pores some of the hydrate water that dissociates at
such low pressures. In addition it is now known that large structural changes
occur in this material on severe drying, i.e. there are large irreversible
dimensional changes and reduction in surface area. (4,5)

        Recently it has been shown that porosity at 11 per cent relative
humidity (R.H.) can be measured with appropriate corrections by methods using
helium, methanol or saturated solution of $Ca(OH)_2$; measurement at 11 per cent
R.H. avoids the problem of dissociation at lower vapour pressures. All these
techniques give similar results. (3) Subsequent work by Harris et al (6) using
inelastic neutron scattering, showed that the porosity determined by this
technique, although performed on undried samples, was similar to that obtained
by the others, (3) and that the discrepancy with the evaporable water technique

was due to the removal of interlayer water on drying.

Other factors related to the structure (besides porosity), such as the crystallinity and density of the products, the nature of the bonding between crystallites, and geometric characteristics of pores, perhaps affect mechanical properties.

This paper will attempt to contribute to the information on the effect of these other factors by examining results from two complementary studies:

1. A study of the relationship between porosity and mechanical properties for a variety of crystallites and pore distributions of related portland cement systems, for which a reliable method for porosity determination was used;

2. A study of these systems, when impregnated (as completely as possible), yielding information on the dependence of a mechanical property on the volume fraction of impregnant, from which further insight concerning the structures may be gained.

EXPERIMENTAL

Materials

The following materials were used:

Normal type I cement mixed with varying proportions of silica and hydrated at water-solids ratios from 0.26 to 0.45.

Silica prepared by grinding Ottawa silica sand, retaining that which passed through a 100-mesh sieve, and mixing with cement (5, 10, 20, 30, 50 and 65 per cent by weight) prior to autoclaving.

Sulfur of reagent grade containing 3 ppm of H_2S.

Hydrated portland cement paste cured at room temperature prepared at water-cement ratios of 0.25, 0.45, 0.70 and 1.1 and hydrated for eight years.

Two samples of porous glass obtained from Corning Glass Works. Porosities were 29.7 and 31.8 per cent with pores 60Å in diameter. (Specimens in this study were in the form of 3.2 cm diameter discs, 1.3 mm thick, to facilitate drying procedures and to enable complete and homogeneous impregnation.)

Methyl methacrylate - reagent grade.

Methods

1. Porosity determination

Porosity was determined before and after impregnation by measuring

solid volume by helium comparison pycnometry; this has been described previously. (3) The apparent volume was determined by weighing in methanol, samples saturated with methanol.

2. Mechanical properties

Young's modulus and microhardness of the samples were determined before and after impregnation. Techniques used for these measurements have been described. (1,2) Ten hardness measurements were made on each disc and three discs were tested for each preparation.

3. Impregnation

(a) Sulfur

Five discs of each preparation were impregnated. Prior to impregnation the samples were heated at 128 °C in vacuum for 24 h. The samples were impregnated under molten sulfur in a vacuum vessel. A full description will be presented in another paper.

After this treatment the residual porosity was measured by determining the new solid volume by the helium pycnometer.

(b) Methyl methacrylate

Samples conditioned at 11 per cent R.H. were vacuum saturated with methyl methacrylate monomer in a vacuum vessel; samples were contained in a metal basket. After saturation, the samples were raised above the excess monomer and, in the presence of its vapour, exposed to cobalt radiation, $\simeq$ 2,500 rad/min for 17 h. After the mechanical properties and porosity were measured, the samples were reimpregnated to reduce residual porosity due to shrinkage during polymerization, and re-exposed to the radiation.

4. Effect of water on dimensional stability of the composites

Samples, both impregnated and unimpregnated, were mounted on Tuckerman strain gauges. They were in the form of prisms 1 by 3 by 0.13 cm and were enclosed in vacuum vessels; samples from each preparation were immersed in liquid water and companion samples of each preparation were exposed to water vapour at 100 per cent R.H. Expansion was measured as a function of time.

RESULTS

1. Mechanical properties of unimpregnated systems

The logarithms of 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; Figure 1 shows the results for Young's modulus. (2) The results of linear regression analysis are recorded in Table I.

TABLE I

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

$$E = E_{01} \exp(-b_E p)$$

%Si	E_{01} (MPa x 10^{-2})	b_E *	$r^\dagger$
0	3200.0	0.0885 ± 0.0074	0.962
5	704.7	0.0509 ± 0.0078	0.960
10	887.2	0.0599 ± 0.0058	0.978
20	568.9	0.0405 ± 0.0021	0.998
30	387.3	0.0300 ± 0.0035	0.979
50	419.8	0.0380 ± 0.0023	0.995
65	477.5	0.0415 ± 0.0055	0.970
Rm. temp.	300.0		

$$H = H_{01} \exp(-b_H p)$$

%Si	H_{01} (MPa x 10^{-2})	b_H	r
0	-	-	
5	30.27	0.0667 ± 0.0072	0.989
10	33.96	0.0669 ± 0.0083	0.976
20	32.89	0.0629 ± 0.0065	0.970
30	18.16	0.0452 ± 0.0055	0.973
50	21.83	0.0521 ± 0.0086	0.957
65	39.45	0.0680 ± 0.0147	0.950
Rm. Temp.	14.50		

* gives 90 per cent confidence limits
† correlation coefficient

Microhardness and modulus of elasticity for the autoclaved and room temperature hydrated paste obey the general relationship,

$$E, H = (E_{01}, H_{01}) \quad \exp. \quad [\ (\ -b_{E,H}) \ p] \tag{1}$$

where E and H refer to modulus of elasticity and microhardness respectively, p represents porosity, and b is a constant. E_{01} and H_{01} are the modulus of elasticity and microhardness of the autoclaved and room-temperature hydrated paste at zero porosity.

2. Density of unimpregnated systems

The solid densities were determined at 11 per cent R.H. by helium displacement for all preparations studied. The specific volume for a given water/solid ratio increases to a maximum value as silica content increased and then decreased at large silica contents (Figure 2). Samples with low specific volume contained $\alpha C_2 S$ hydrate (determined by x-ray diffraction) and had relatively low values of Young's modulus and microhardness. Samples with the highest specific volume contained poorly crystallized hydro-silicate and had maximum values of Young's modulus and microhardness. (2)

3. Young's modulus and microhardness, at zero porosity

These values were obtained for all the preparations by extrapolating to zero porosity the general relationship referred to above; they are included in Table I. It can be seen that the highest values were obtained for the samples with the low silica content (containing the larger quantity of high density $\alpha C_2 S$), although these preparations had lower elastic modulus and microhardness values at higher porosities. This result suggests that the low values for the samples having high porosity may be due to low bond strength or small area of bond between inherently strong crystals. With decreasing porosity the area of bond increases, and the properties of the body should tend to those of the individual crystallites. The morphology of the crystals, their bonding and their inherent mechanical properties all appear to play a role in determining the mechanical properties of a porous body.

4. Mechanical properties of portland cement systems impregnated with sulfur

Figure 3 gives the observed dependence of Young's modulus on volume fraction of sulfur impregnant. These results show that the larger the sulfur volume fraction, the smaller the Young's modulus for each composition and that properties of the composite are not uniquely determined by the volume fraction of sulfur. The properties of the cement matrix are also important in determining the mechanical properties of the composite. The observed dependence of Young's modulus on the silica content before and after impregnation is presented in Figure 4, and the sulfur content dependence of the ratio of Young's modulus after to that before impregnation E_c/E is shown in Figure 5. Values of Young's modulus of the samples made with 5 and 10 per cent silica

were the lowest before impregnation and the highest after impregnation. These preparations, as stated previously, were composed of predominantly high density $\alpha C_2 S$.

The following equation (derived from Reuss' model (8)) for the modulus of elasticity of a two-phase composite material was found to be in good agreement with the results given in Figure 3:

$$E_c = 1 \left/ \left\{ \frac{V_1}{E_{01}} + \frac{V_2}{E_{02}} \right\} \right. \tag{2}$$

where V_1 and V_2 are the volume fractions of matrix and impregnant respectively and E_{01} and E_{02}, the zero porosity values for the matrix and impregnant materials. Young's modulus, E_c , for samples with the lowest volume fraction of sulfur, were used in Eq. (2) to calculate E_{01} for each preparation. (9) E_{02} for zero porosity sulfur, was taken at 13.9×10^3 MPa. (10) The values for E_{01} obtained in this way are tabulated in Table II along with the values obtained by the extrapolation technique. Relatively good agreement was obtained. (9)

The microhardness data fit a modified form of Reuss' equation, factors being added to account for stress concentrations. (7) The ratio of microhardness of impregnated samples to that of the unimpregnated samples varied from 1.5 to 6.0 depending on composition and volume fraction.

TABLE II

Modulus of Elasticity from Mixing-rule and Extrapolation

% Si	E mixt. x 10^{-3} MPa	E extrap x 10^{-3} MPa	$\left[\dfrac{E_{Mx} - E_{ext}}{E_{Mx}} \right]$ x 100
5	82.4	70.5	+17
10	71.0	88.7	-23
20	47.7	56.9	-19
30	41.1	38.7	+ 5.8
50	38.4	42.0	- 9.0
65	42.7	47.8	-11.7
Rm. Temp.	33.0	30.0	+ 9.1

5. Mechanical properties of portland cement systems impregnated with methyl methacrylate

Samples with compositions similar to those used for the sulfur impregnation study were also impregnated with methyl methacrylate monomer. Residual porosities after impregnation were in the order of 1 to 2 per cent. The observed dependence of Young's modulus on volume fractions of methyl methacrylate is shown in Figure 6. The correlation coefficients for the linear regression lines given in the figure were all better than 90 per cent. Details concerning this work are to be published later. A comparison of these results with those for sulfur impregnation shows that the curves for sulfur are displaced to higher values, for the same volume of material impregnated. Another observation is that the relative order of the compositions in each set of data is similar indicating that the matrix is influencing the properties of the composite in a similar way in both cases. Similar behaviour was observed in the measurements of microhardness.

The mixing-rule equation was also applied to this system; the values for E_c, E_{01} and the volume fractions of the components were substituted in Eq. (2) to obtain E_{02}, the modulus at zero porosity for polymethyl methacrylate. The value obtained was 2 to 4 times larger than the bulk value. A possible explanation for this is that as the polymer was actually formed in the pores (being placed there as the monomer), its behaviour may be different from that of the bulk material.

6. Porous glass impregnation

The original porosity of the sample impregnated with sulfur was 29.7 per cent. After impregnation the residual porosity was 4.4 per cent, similar in value to several of the portland cement preparations. The increase in Young's modulus was only 15 per cent; in the microhardness, it was 35 per cent. In the case of methyl methacrylate impregnation, the porosity of the sample was 31.8 per cent and after impregnation there was about 1 per cent residual porosity. The increase in Young's modulus was 84 per cent and in microhardness approximately 160 per cent. The results for the sulfur/glass systems were not in good agreement with the increase in modulus and hardness was much lower than would be predicted. In the case of methyl-methacrylate/glass system, the computed E_{02} was much higher than the bulk value, as was also found for the portland-cement/methyl-methacrylate system.

7. Dimensional stability of composites

Expansion as a function of time was measured for the glass/sulfur, room-temperature cured paste/sulfur, and methyl-methacrylate/paste systems. The sulfur/porous-glass composite expanded rapidly and broke into small pieces after about 2 h of exposure to water vapour at 100 per cent R.H. Expansion exceeded 1 per cent in length. The hydrated-cement/sulfur composite also expanded when exposed to the water vapour, but at a lower rate than the glass-sulfur composite. It disintegrated after 12 to 15 h. The sample became laminated and warped. The cement/methy-methacrylate system also expanded on exposure but at a much slower rate than the other composites.

The unimpregnated samples remained intact but expanded more rapidly when immersed in liquid or when exposed to water vapour at 100 per cent R.H.; the value expected from length change adsorption measurements was obtained. These values were much less than those observed for the impregnated samples.

DISCUSSION

1. Structure of portland cement systems

(a) Porosity, probably the most important parameter controlling mechanical properties of these systems, can be reduced by two methods: preparation initially of a body with a larger unhydrated cement product content, and impregnation with another material. It is considered that both techniques improve the bonding between individual crystallites. The mechanical properties of materials containing large amounts of $\alpha C_2 S$ are low at high porosities relative to the other preparations, probably due to poor bonding between the crystallites. (2,9)

Both of these techniques show that in the case of preparations low in silica, where the dense, more crystalline material, $\alpha C_2 S$, is predominately present, strong bodies are formed when the surfaces of the crystallites are in close proximity or bonded together by an impregnant. The fact that the values of the elastic modulus for zero porosity, E_{01}, for these preparations, were the greatest, indicates that the shape of the pores and the bonding between crystallites are very important in determining mechanical properties. It would appear that impregnation greatly increases bonding between crystallites and/or changes the shape of pores or flaws so as to reduce stress concentrations. The greater E_c/E ratios (Figure 5) for these materials can thus be

understood as well as the lower ratios for the room-temperature cured paste and the 20 and 30 per cent silica preparations. The latter materials are poorly crystalline, with larger surface areas, and chances for good interparticle bond at higher porosities are greater. Thus, despite their lower density, their mechanical properties are superior at high porosities.

(b) The fact that E_{01} values can be determined from two independent equations, Eqs. (1) and (2), both involving porosity, and further, that E_c/E ratios can be predicted with reasonable accuracy, lends credence to arguments for measuring porosity by helium pycnometer techniques.

2. Validity of assumptions in use of mixing-rule equations

(a) In using the simple Reuss model mixing-rule it is implicitly assumed that the contact between phases is such that the impregnant phase is in fact being fully subjected to the stress imposed on the system. The contact between surfaces in the cement/sulfur and cement/methyl-methacrylate systems appear to be adequate for satisfactory stress transfer although it is still not good enough to prevent re-entry of water vapour. The phenomenon of destruction observed here is complex and will be discussed in a future paper. The results from the porous glass/sulfur system, i.e. the low increase in mechanical properties and the rapidity of entry of water into the system, indicate that little or no bond occurs at the interface in this particular system.

(b) It is assumed that the properties of the impregnant, E_{02}, are similar to the bulk properties of the material. This assumption appears substantially correct in the case of sulfur where the material enters into the pores as molten sulfur and solidification occurs in the pores. However, in the case of methyl methacrylate, the chemical conversion from monomer to polymer takes place in the pores and, from the application of the mixing-rule, it would appear that this assumption does not hold.

CONCLUSIONS

1. Porosity is an important property defining the structure and mechanical properties of hydrated portland cement; it can be measured by the helium pycnometer method.

2. Other important properties influencing the mechanical behaviour of these systems are the nature of the bond between crystallites and the mechanical properties of the individual crystallites.

3. Impregnation of hydrated cement paste cured at room temperature and autoclaved cement-silica preparations with sulfur and methyl methacrylate improves mechanical properties.

4.   Interfacial bond between sulfur and hydrated cement paste and methyl methacrylate and the paste is adequate for improving mechanical properties, but does not prevent re-entry of water vapour and the consequent expansion resulting, in some cases, in destruction of the specimen.

5.   Paste cured at room temperature has relatively high mechanical properties at high porosities when compared to products high in $\alpha C_2 S$ because of the chance of good bonding between poorly crystallized high surface-area crystallites.

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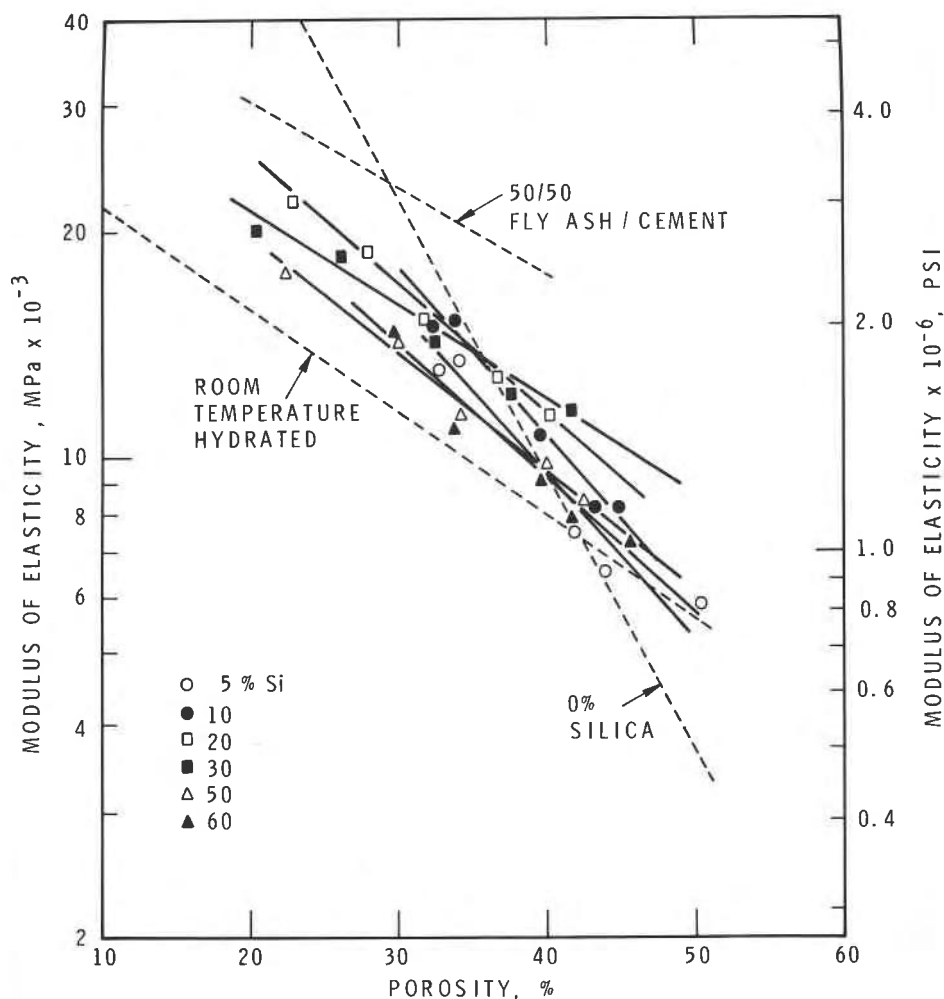
FIG. 1 - Modulus of elasticity versus porosity for various autoclaved and room temperature hydrated cement and cement-silica preparations
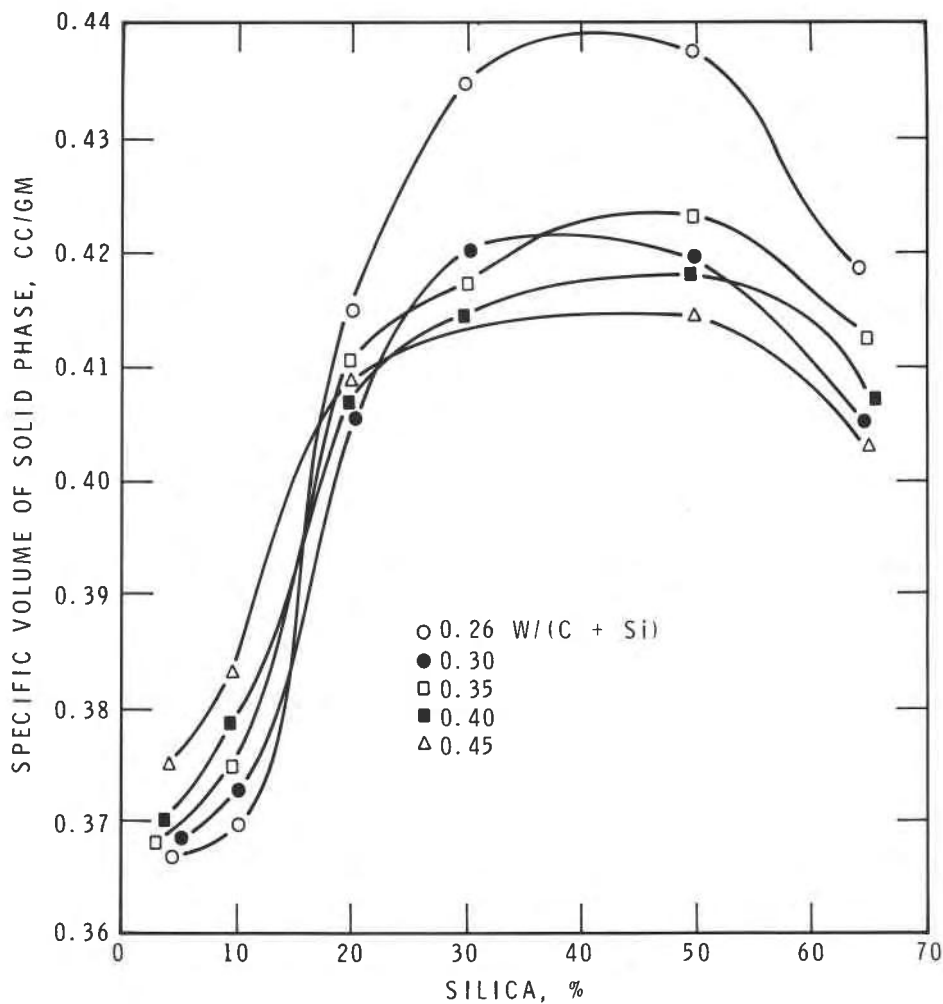
FIG. 2 - Specific volume of solid phase versus silica content for various autoclaved cement-silica preparations

FIG. 3 - Modulus of elasticity versus volume fraction of sulfur for different silica contents
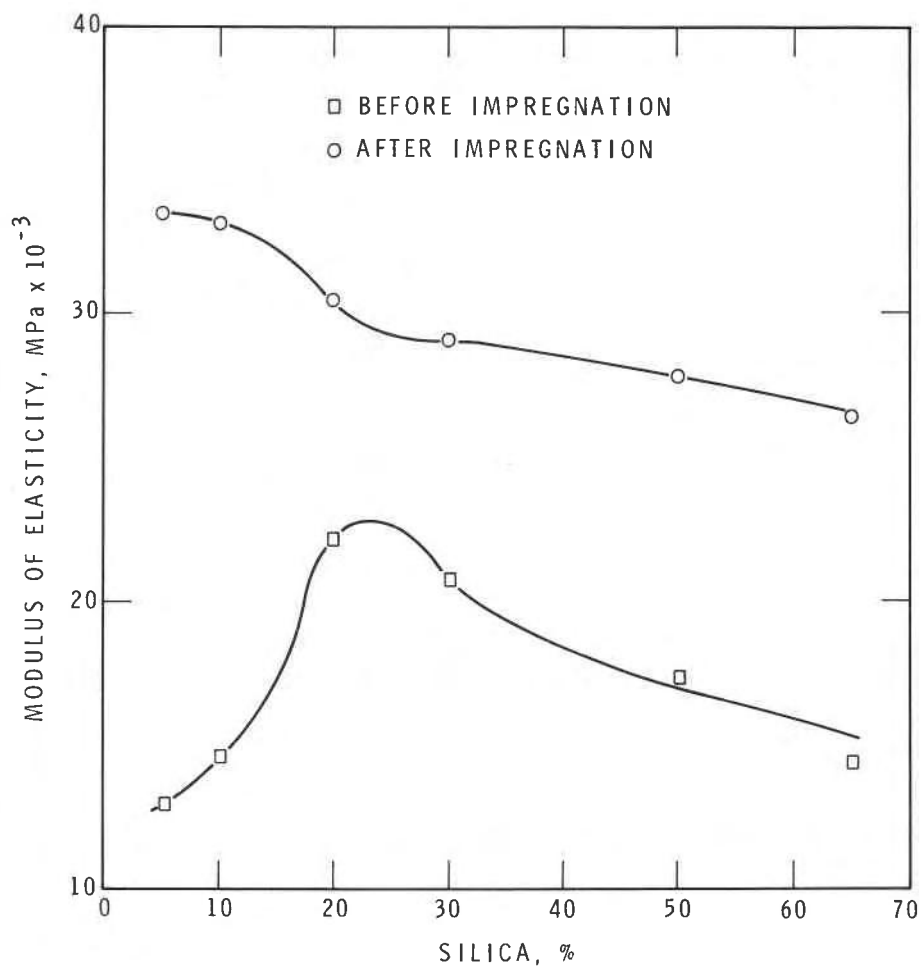
FIG. 4 - Modulus of elasticity versus silica content before and after impregnation (W/C = 0.26)
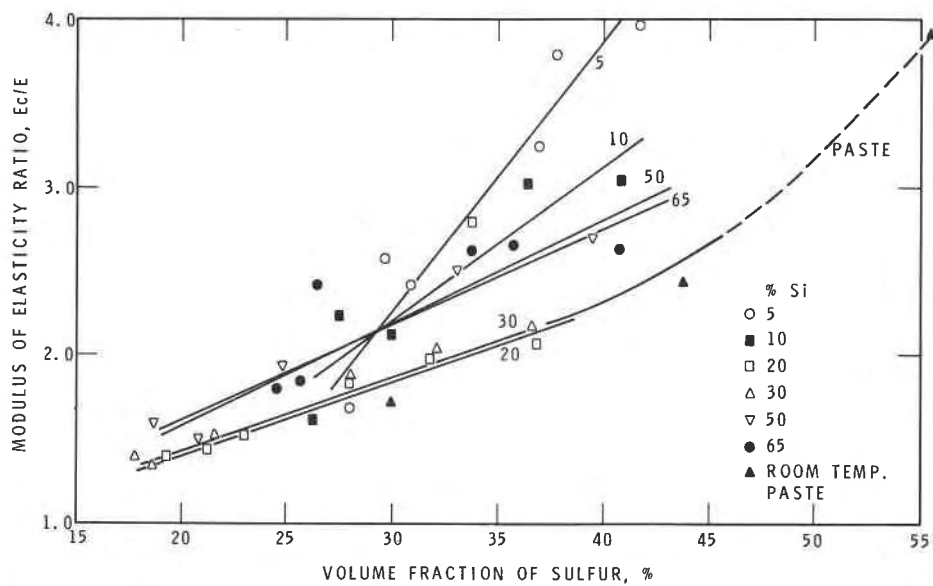
FIG. 5 - Ratio of modulus of elasticity after impregnation to modulus of elasticity before impregnation versus volume fraction of sulfur
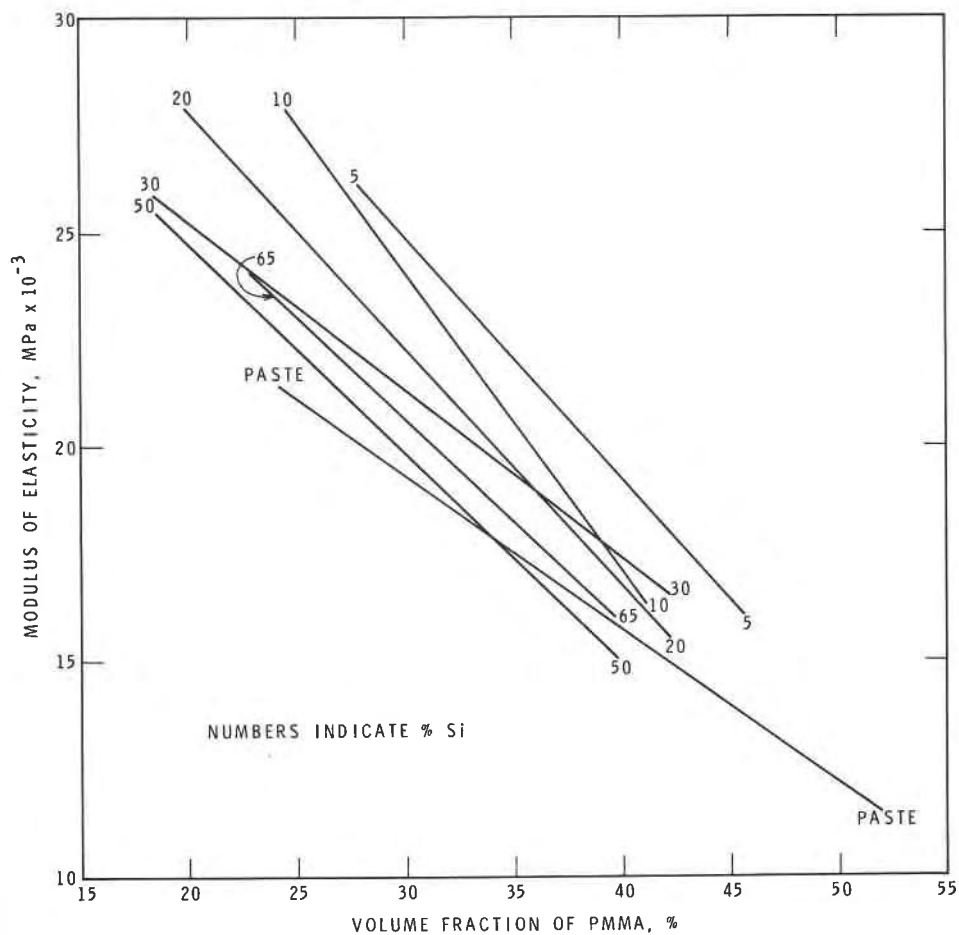
FIG. 6 - Modulus of elasticity versus volume fraction of poly-methyl
methacrylate for different silica contents

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