



## NRC Publications Archive Archives des publications du CNRC

### **Durability of cement and glass impregnated with sulfur and polymethyl methacrylate**

Litvan, G. G.; Feldman, R. F.; Grattan-Bellew, P. E.

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\(82\)90027-8](https://doi.org/10.1016/0008-8846(82)90027-8)

*Cement and Concrete Research*, 12, September 5, pp. 649-659, 1982-09-01

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

<https://nrc-publications.canada.ca/eng/view/object/?id=53be8c9f-9529-48ca-a576-436536cc72e0>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=53be8c9f-9529-48ca-a576-436536cc72e0>

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.



National Research  
Council Canada

Conseil national de  
recherches Canada

Canada

Ser  
TH1  
N21d

National Research  
Council Canada

Conseil national  
de recherches Canada

10527

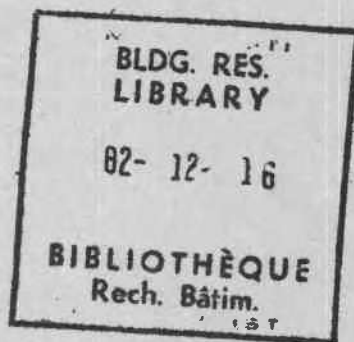
no. 1046  
c. 2  
BLDG

**DURABILITY OF CEMENT AND GLASS IMPREGNATED WITH  
SULFUR AND POLYMETHYL METHACRYLATE**

by G.G. Litvan, R.F. Feldman and P.E. Grattan-Bellew

ANALYZED

Reprinted from  
Cement and Concrete Research  
Vol. 12, 1982  
pp. 649 - 659



DBR Paper No. 1046  
Division of Building Research

Price \$1.25

OTTAWA

NRCC 20518

Canada

DURABILITY OF CEMENT AND GLASS IMPREGNATED WITH SULFUR AND POLYMETHYL  
METHACRYLATE

G.G. Litvan, R.F. Feldman and P.E. Grattan-Bellew  
Building Materials Section, Division of Building Research,  
National Research Council of Canada, Ottawa, Canada K1A 0R6

(Communicated by J. Skalny)  
(Received March 19, 1982)

ABSTRACT

Possible causes of instability of sulfur-impregnated bodies (porous glass and portland cement) have been investigated. As they are non-crystalline and have a large surface-to-volume ratio, impregnants in small pores are normally in a metastable state unless their free energy is lowered by meniscus effects or interaction with the matrix. Extrusion of sulfur on exposure to water or other adsorbing vapors occurs because of the weak interaction between impregnant and the siliceous surface and a lubricating effect created by the presence of the adsorbate on the surface of the impregnant. Non-isotropic expansion and impregnant-adsorbate interaction are suggested as the main causes of mechanical breakdown. Good interaction with the surface and resistance to flow due to cross-linking render polymethyl methacrylate a stable impregnant.

RÉSUMÉ

On a étudié les causes possibles de l'instabilité des corps imprégnés de soufre (verre poreux et ciment portland). Comme ils sont non cristallins et que le rapport surface/volume est élevé, les agents d'imprégnation contenus dans les petits pores sont normalement métastables, à moins que leur énergie potentielle libre ne soit diminuée en raison d'effets de ménisque ou de l'interaction avec la matrice. L'extrusion du soufre par suite de l'exposition à l'eau ou à d'autres vapeurs adsorbantes découle de la faible interaction de l'agent d'imprégnation et de la surface siliceuse, et de l'effet lubrifiant du produit d'adsorption à la surface de l'agent d'imprégnation. On croit que la dilatation non isotrope et l'interaction de l'agent d'imprégnation et du produit d'adsorption sont les causes principales de la dégradation mécanique. Une bonne interaction avec la surface et la résistance à l'écoulement que lui procure sa réticulation font du poly(méthacrylate de méthyle) un agent d'imprégnation stable.

### Introduction

The space in concrete resulting from porosity reduces strength, exposes the concrete to chemical attack and, if filled with water, leads to destructive frost action at low temperatures. Filling the pores permanently and completely with an inert solid appears to be an effective way to improve mechanical properties and durability. Laboratory studies of impregnation with polymers have indicated that this is beneficial (1). Recently, however, it has been observed that porous 96% silica glass and hydrated portland cement specimens impregnated with sulfur are highly unstable (2). For example, on adsorption of carbon tetrachloride or methanol, sulfur-impregnated porous glass expanded 40 to 50 times more than the control specimens.

Exposure of sulfur-impregnated porous glass to water vapor results in extremely large dimensional changes and extrusion of the sulfur. Normally, complete disintegration of the specimen occurs in hours. The potential significance of this observation with regard to impregnation of porous solids in general has prompted investigation of the causes of instability in sulfur-impregnated solids and the stability of solids impregnated with methyl methacrylate.

### Experimental

The fabrication of specimens, their impregnation and the materials used were similar to those described by Feldman and Beaudoin (2). Determination of length changes and pore size distribution also follow the same procedures. The surface area was measured by the continuous flow method in a Quantasorb Sorptometer. Water pick-up was determined gravimetrically with a quartz helical spring (sensitivity 30.68 cm/g).

### Results

#### Sulfur as Impregnant

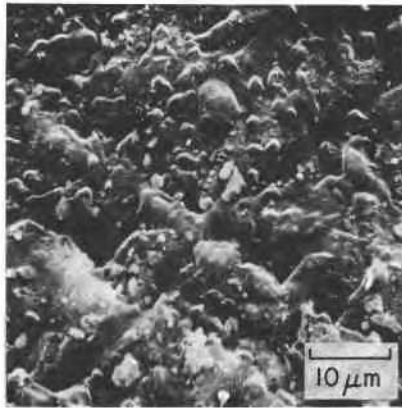
When sulfur-impregnated porous glass is stored over a desiccant its surface becomes coated with sulfur. Figure 1 shows photographs of the various phases of the sulfur exudation process in the presence of water vapor. On exposure for one hour to 41% RH, relatively large sulfur whiskers developed that combined into bundles after 3 hours. Five hours of exposure resulted in formation of a coalesced cover, with individual whiskers still discernible, but after 6 hours the sulfur coat became thick and continuous except for large shrinkage cracks.

Simultaneously, the rate of extrusion of sulfur was determined with electron probe analysis following the change in the S/Si ratio on the surface of the glass. As may be seen in Fig. 2, extrusion proceeds, after a short induction period, at a relatively high rate until the entire surface is covered with sulfur. This behaviour is in agreement with the SEM observations, according to which a dense coat is formed after 3 hours.

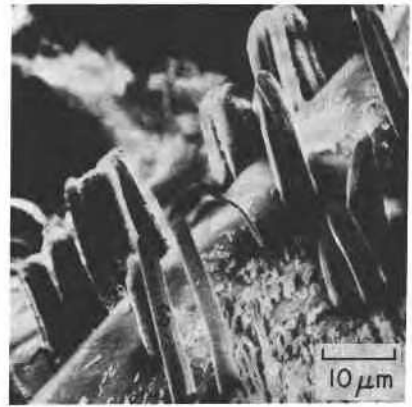
The X-ray intensity change of the (222) sulfur peak as a function of time (Fig. 3) confirms the results obtained with the electron probe analysis, but in addition it indicates continuous exudation, albeit at a slower rate, even after approximately 15 to 20% of the sulfur contained in the pores (determined by weighing) has been exuded.

#### Surface Area

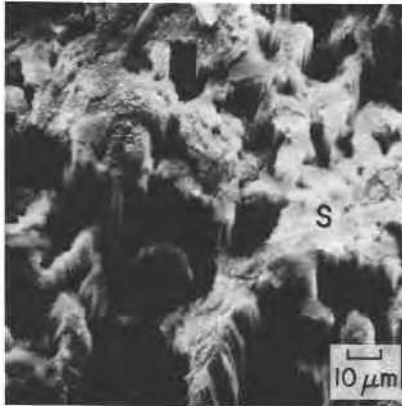
The BET  $N_2$  surface area of one porous glass specimen was reduced by impregnation from 180  $m^2/g$  to 1.50  $m^2 g^{-1}$  and that of another to 1.72  $m^2 g^{-1}$ . Such a large decrease indicates fairly complete filling or at least sealing of the pores.



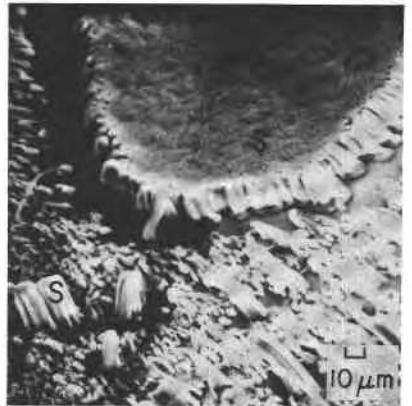
A



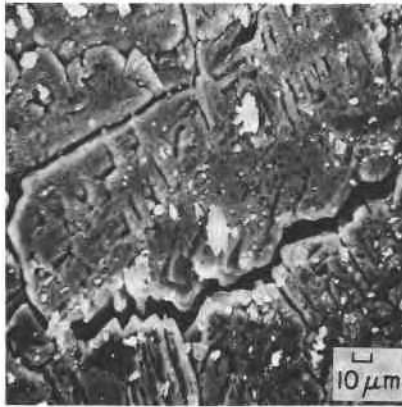
B



C



D



E

FIG. 1

Electron micrographs of sulfur-impregnated porous glass exposed to 41% RH for various lengths of time: A: 0 h, B: 1 h, C: 3 h, D: 5 h, E: 6 h.

On exposure to 45% RH the surface area value increased to  $5.19 \text{ m}^2\text{g}^{-1}$  in 10 days in one case and to  $4.1 \text{ m}^2\text{g}^{-1}$  in 14 days in another case (Fig. 4). The surface area against square root of time gives a linear plot suggesting that diffusion of water is the rate-controlling step.

A characteristic feature of the sulfur-impregnated glass specimens is the difficulty of removing adsorbed water by only purging with  $\text{N}_2$  gas. Normally, reproducible surface area values are obtained in consecutive experiments after 90 min of purging; for sulfur-impregnated glass the surface area increased even after 31 days (744 h) of drying, as may be seen in Table 1.

The effect of continuation of drying appears (according to the results) to reflect physical reality because in unimpregnated glass, specimen No. 2, no change in surface area could be detected when drying time was increased to 27 hours.

Disregarding the uncertainties with respect to absolute value, it may be concluded that the surface area of sulfur-impregnated porous silica glass increases on exposure to water vapor; as sulfur is extruded, more surface becomes accessible to nitrogen and the extended sulfur itself probably has a rather high specific surface. Sintering of the extruded sulfur does not seem to be significant because no decrease in area with time during storage at 0 or 51% RH has been observed (see Table 1). If the effect of sintering were compensated by the drying process, the latter should not be a linear function of  $t^{1/2}$  (Fig. 4).

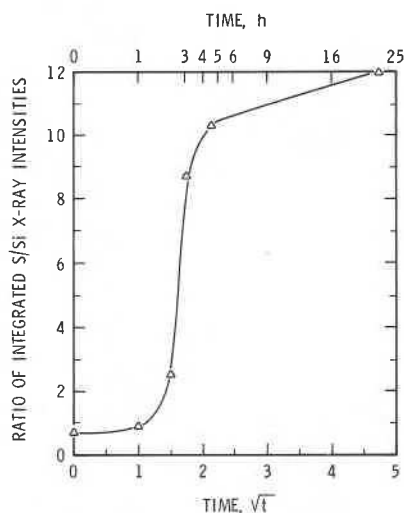


FIG. 2

Change of integrated S:Si X-ray intensity ratios of sulfur-impregnated porous silica glass on exposure to 41% RH.

#### Polymethyl Methacrylate as Impregnant

Changes in the modulus of elasticity ( $E_c$ ) of the specimens with length of storage in 100% RH and chloroform atmosphere, respectively, are shown in Fig. 5. Despite a fairly large scatter of values it can be stated that:

- 1)  $E_c$  increases rapidly at the very beginning of exposure;
- 2)  $E_c$  appears at all stages to be less in a chloroform than in a water atmosphere.

The absolute value of  $E_c$  is greater than that predicted by the Reuss equation (3):

$$E_c = \frac{1}{\frac{V_1}{E_{01}} + \frac{V_2}{E_{02}}}$$

where  $E_{01}$  and  $E_{02}$  are Young's moduli for zero porosity matrix and impregnant, respectively, and  $V_1$  and  $V_2$  are the volume fractions of the matrix and the impregnant, respectively. The values of  $3.63 \times 10^3$  MPa and  $66.19 \times 10^3$  MPa were used in the calculation for Young's moduli of polymethyl methacrylate (PMMA) and glass, respectively, and the volume fraction of the impregnant was taken as 0.25.

The calculated value of  $E_c$  was found to be  $12.46 \times 10^3$  MPa, while the measured value was approximately  $18.6 \times 10^3$  MPa - about 50% larger - suggesting good interaction between glass and polymethyl methacrylate.

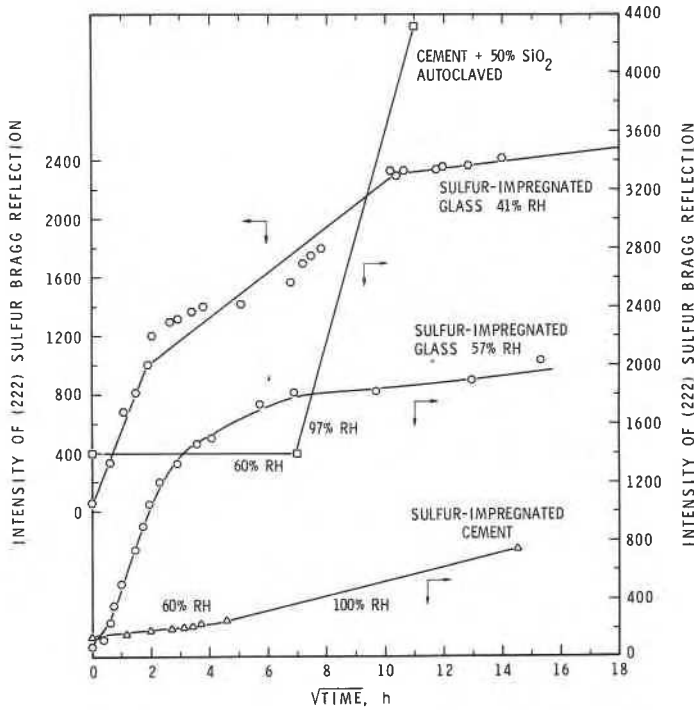


FIG. 3

Rate of change of (222) sulfur reflection of sulfur-impregnated porous glass and neat cement paste stored at humidities as indicated.

TABLE 1

Surface Area of Sulfur Impregnated Porous Glass Exposed to 41% RH and Dried Before Test for Various Lengths of Time

Expo- sure, days	Purg- ing Time, h	Area m <sup>2</sup> g <sup>-1</sup>	Purg- ing Time, h	Area m <sup>2</sup> g <sup>-1</sup>	Purg- ing Time, h	Area m <sup>2</sup> g <sup>-1</sup>	Purg- ing Time, h	Area m <sup>2</sup> g <sup>-1</sup>	Purg- ing Time, h	Area m <sup>2</sup> g <sup>-1</sup>
Specimen No. 1										
0	1.5	1.50								
0.25	1.5	1.71								
1.0	1.5	2.32	5	11.2	24	11.5				
2.0	1.5	3.29	1	3.9	4	3.2	6	3.9	24	5.7
3.0	1.5	3.60	3	5.6	48	10.6	96	12.4		
7.0	1.5	4.72	20	11.2	44	10.8	46	10.6	68	11.2
10.0	1.5	5.19	72	12.11						
Specimen No. 2										
0	1.5	1.72	4	1.75	27	1.74				
7	1.5	3.78	4	6.00	168	8.7				
14	1.5	4.10	44	9.3	90	10.8	168	12.5	744	15.4
44	1.5	6.80	168	10.3						

The amount of water adsorbed by the impregnated porous glass specimen stored in 100% RH and the concomitant length changes are shown in Figs. 6 and 7.

The following observations can be made:

- 1) Length changes, in the order of 0.5%, are more than twice the expansion that occurs on complete saturation of dry unimpregnated glass.
- 2) The plot of  $\Delta l/l$  versus  $\Delta W/W$  expressed as water uptake per gram glass matrix shows that the length increase on adsorption of 0.0154 g water per gram glass is  $50 \times 10^{-5}$ . For unimpregnated glass such expansion occurs only when 0.050 g/g water is adsorbed.
- 3) Although, with decreasing rates, expansion continues even after 498 days, no water uptake was detected after 200 days of exposure (Fig. 6).

4) When, after 88 days of storage in 100% RH, impregnated glass was subjected to drying in vacuo for 400 days, only 62% of the moisture expansion proved to be reversible (Fig. 7).

5) Considering its non-polar nature, expansion caused by adsorption of chloroform is surprisingly large. The shape of the expansion versus time of exposure plot is similar to that obtained with water as adsorbate. Expansion is still continuing after 498 days. The magnitude of expansion in the last 230 days for the specimens exposed to water and chloroform was similar.

#### Discussion

#### Instability of Highly Dispersed Impregnants

Porous silica glass has 26% total porosity, with approximately 58% consisting of small capillaries of less than 5.0 nm diameter (Fig. 8). (Cement paste shows more uniform distribution, while autoclaved cement-silica contains mainly large sized pores.) This results in very high surface-to-volume ratio and surface-free energy, not only for the glass but also for the impregnant filling the pores. Considerable work has therefore to be expended in the impregnation process itself and steps have to be taken to avoid the spontaneous reversal of the process. Bean, Doyle and Pincus (4) applied 320 MPa pressure to fill, with mercury, the pores of the same type of porous glass as was used in this study, and as soon as the pressure was reduced the mercury flowed out.

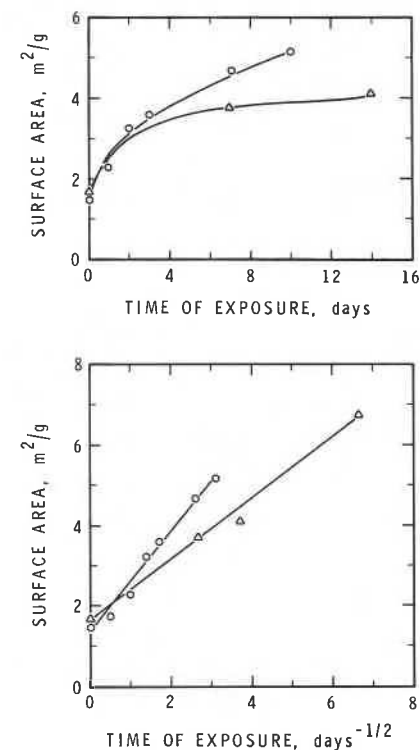


FIG. 4

$N_2$  surface area of sulfur-impregnated porous glass on exposure to 41% RH as a function of time and square root of time of exposure.

The impregnant will easily infiltrate and remain in the pores if attraction between it and the surface is greater than its surface tension.



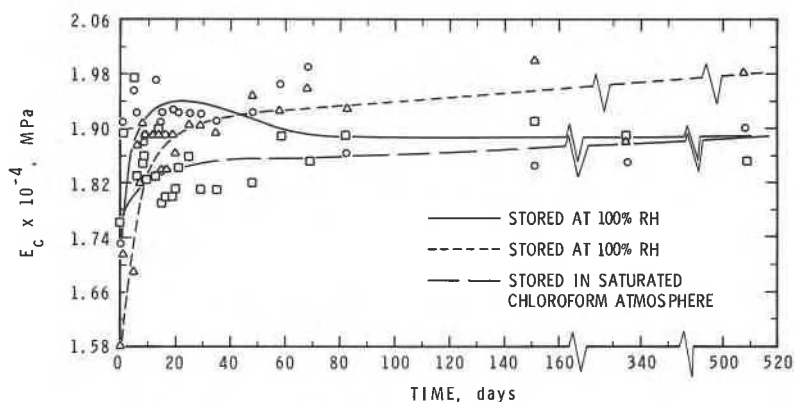


FIG. 5

Young's modulus of porous glass impregnated with PMMA.

Migration of the impregnant from the impregnated systems could thus have been caused by the alteration of the interaction between the impregnant and the matrix. The observed expansions could be a manifestation of a decreased interaction coupled with an interaction between vapor and impregnant. In this respect the difference between sulfur and PMMA as impregnant is largely related to the degree of interaction of the impregnant with the matrix.

The impregnant may remain in the pores under atmospheric pressure, even in the presence of adsorbates, if its resistance to flow is high. Schmidt and Charles (5) reported that impregnation of porous 96% silica glass with various metals having low melting points succeeded only with lead and bismuth; on solidification they developed a strong and coherent oxide coating that effectively capped the pores. Other metals such as indium, cadmium, and gallium exuded shortly after the 385 MPa pressure applied during impregnation was reduced.

Another possible cause of instability is the non-crystalline state of the impregnant. Molten sulfur is in the form of a puckered 8-member ring. Pore-

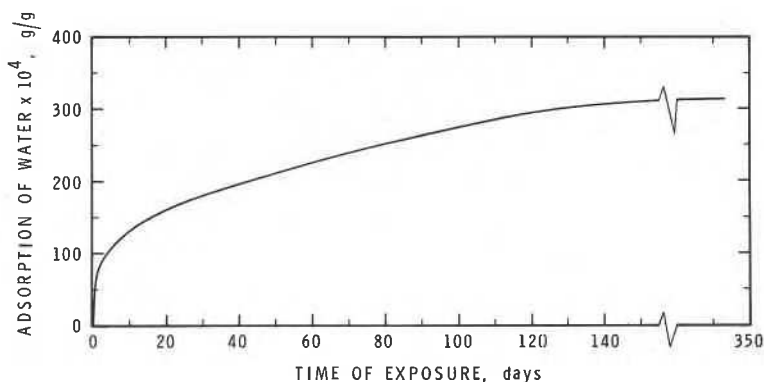


FIG. 6

Uptake of water by porous glass impregnated with PMMA in 100% RH atmosphere.

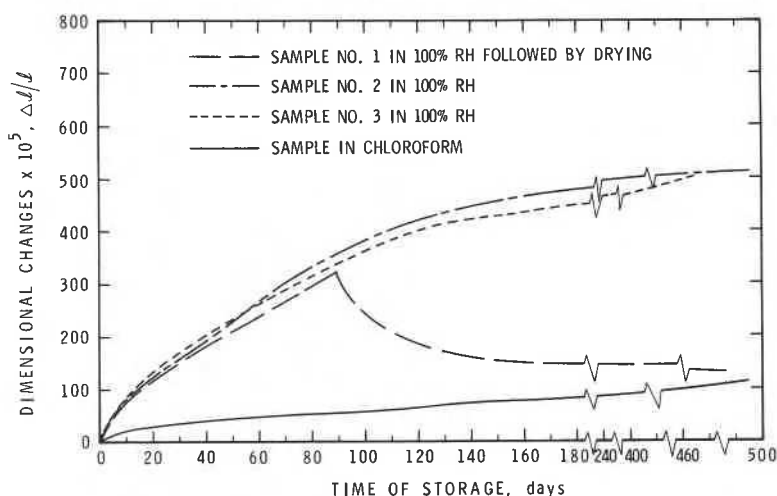


FIG. 7

Dimensional changes of porous glass impregnated with PMMA on exposure to water and chloroform vapors.

held sulfur, on solidification, forms orthorhombic crystals with dimensions of  $a = 10.47$ ,  $b = 12.87$ , and  $c = 24.5$  Å. The unit cell of sulfur normally contains sixteen 8-membered rings. Because, in the small pores of glass and cement paste, there is insufficient space to form crystals with regular habit, however, a spherulitic phase forms (6). Similarly, in apochlorotic bacteria sulfur globules were found also in the form of spherulites, which have an order intermediate between those of the liquid and crystalline phases. Owing to fewer nearest-neighbor interactions and more unsatisfied bonds than those existing in the crystalline state, the spherulitic phase has higher energy and is metastable. It tends to migrate from the pores to the exterior surface where the crystalline modification can be formed. This is, perhaps, the reason for the formation of a sulfur coating on the surface of sulfur-impregnated porous glass stored over a desiccant.

Water contained in porous solids shows similar behavior in many respects when exposed to temperatures below  $0^{\circ}\text{C}$  (7). Water solidified in the pores can be considered as an impregnant, which is also largely non-crystalline and therefore unstable in the presence of regular bulk ice in the environment. As a consequence, water leaves the pores and migrates to the external surface. It appears that the tendency for migration of some impregnants out of pores is a phenomenon of general validity and not one restricted to sulfur.

Quantitative differences in some properties may determine whether the impregnant will or will not exude and to what extent. For example, because the temperature region of interest for frozen water is in the vicinity of the melting point but over  $100^{\circ}\text{C}$  deg below that of sulfur, equilibrium by partial extrusion can be easily reached in the former and not in the latter case. With water, only an amount sufficient to equalize the free energy of the remaining unfrozen water (due to the formation of concave menisci) with that of bulk ice has to be removed. If no concave surface can form to reduce the free energy, as is presumably the case with mercury or sulfur at room temperature, equilibrium in a thermodynamic sense cannot be established without emptying the pores completely. Where concave menisci can form,

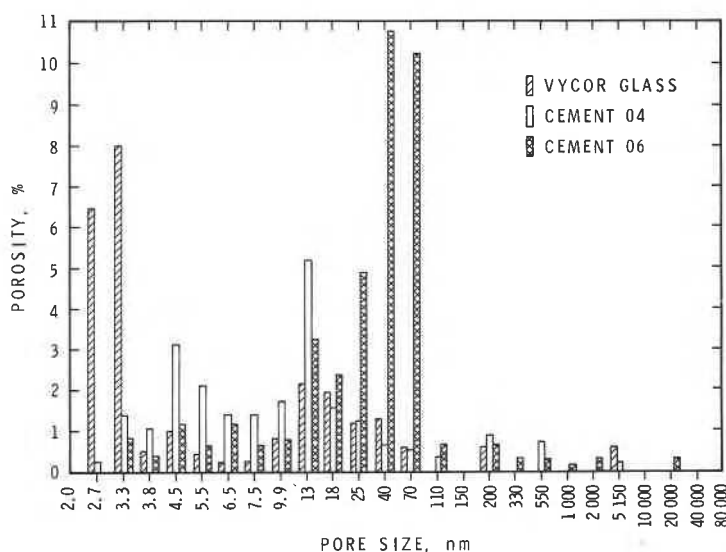


FIG. 8

Pore size distribution in porous silica glass (Vycor), neat cement paste (04) and autoclaved 50-50% cement-silica paste (06).

equilibrium under given conditions is possible only if the redistribution of the adsorbate can take place in the time available.

An important practical difference between sulfur and polymers as impregnant is the size and shape of the molecules. PMMA, for example, is a very long polymer that can easily become entangled and therefore has a very high flow resistance. Because of this solids are best impregnated by filling the pores with the monomer, followed by polymerization in situ. Although PMMA as an impregnant is perhaps inherently unstable, no migration or exudation takes place because of the hindered flow and apparently strong interaction with the siliceous surfaces.

#### Cause of Mechanical Failure

The most important aspect of the instability of sulfur-impregnated porous solids from an engineering point of view is the mechanical failure that occurs if they are exposed to water. Expansion before breakage is reported (2) to be above ten times larger than that occurring when only blank glass is saturated with water (0.25%). In contrast, PMMA-impregnated porous glass expands only 0.5%, with no apparent change in dimensions or loss of mechanical properties.

The difference in the behavior of the two systems must be ascribed to better bonding of PMMA to the glass. The low nitrogen surface area of 0.22 m<sup>2</sup>/g compared to 1.50 to 1.72 m<sup>2</sup> g<sup>-1</sup> for the sulfur-glass system indicates relatively good sealing of the pores and good contact between the impregnant and the substrate. The observation that porous glass impregnated with sulfur at 180°C instead of 150°C appears to be more stable, presumably due to improved contact, supports the weak sulfur-glass interaction hypothesis.

If bonding is incomplete and weak, then adsorption of the vapors on the glass substrate could also contribute to the observed strains. By creating

high relative strain at the interface of the substrate and impregnant, water or other vapors could conceivably further weaken the existing bond.

Weak interaction between impregnant and matrix is indicated by the experimentally determined Young's modulus of sulfur-impregnated glass, which is only 53% of the value predicted by the Reuss equation (2), while the measured value with PMMA is greater than that predicted.

A considerable strain manifested in the glass-sulfur composite on exposure to carbon tetrachloride and its minimal effect on blank glass suggests that in composite systems the vapor-glass interaction mechanism is less significant. If bonding is incomplete, the surface area of a gram of sulfur contained in the pores is estimated to be in excess of  $500 \text{ m}^2 \text{ g}^{-1}$  (2). The large surface energy associated with this highly disperse state can be lowered on interaction with water or other adsorbate. In contrast, PMMA interacts well with the surface of the matrix and through this protects the composite from destruction in several ways:

- 1) efficiently seals the pores against the permeation of vapors,
- 2) reduces the area of the matrix and impregnant available for interaction with vapors,
- 3) acts as a good stress modifier and reinforcer of the matrix.

PMMA, however, may absorb vapors, and the associated swelling could generate pressure against the walls. Swelling of PMMA-impregnated glass and the increase of Young's modulus, measured in flexure, is possibly due to vapor absorption. The continuing expansion after 498 days of exposure to water vapor, with no associated water uptake, may be explained by the static fatigue concept that is a common occurrence in glass under sustained load. Whatever the cause, if vapor can penetrate a fairly impervious system, a highly uneven distribution of stress will be created that can easily lead to failure.

The expansion of autoclaved, sulfur-impregnated porous cement-silica paste on exposure to water vapor was found to be directly proportional to surface area (2). Because surface area is inversely proportional to pore size, the results indicate instability of small pore systems. The stability of the cement-silica paste, which has small surface area and coarse porosity (Fig. 8), is due to the relatively large radius of curvature of the sulfur impregnant, which in turn results in smaller surface tension. On this basis the order of sensitivity in descending order is glass, neat cement paste, and autoclaved silica-cement paste. The results shown in Fig. 3 are consistent with this statement. For example, impregnated autoclaved silica-cement paste was unaffected by exposure to 57% RH; only with humidity raised to 100% did the X-ray diffraction intensity of extruded sulfur change.

#### Conclusions

1. Solidified adsorbates or impregnants in the small pores of solids are normally in metastable equilibrium. Spatial restrictions prohibit the formation of regular crystal habit; because of the formation of non-crystalline modifications the free energy is increased. In addition, owing to the large surface-to-volume ratio the surface-free energy is also large. In the absence of concave menisci or strong interaction with the matrix that would reduce the energy, the tendency for spontaneous exudation from the pores is increased.
2. Sulfur does not interact strongly with siliceous surfaces, so that water or other liquids can penetrate the porous network and adsorb on the substrate surface, weakening further the interaction between it and

- sulfur. Water adsorbs also on sulfur, creating a lubricating effect and high stresses due to surface energy decrease. Both effects facilitate extrusion and the latter causes destruction.
3. Because of the relatively slow penetration of water, non-isotropic expansion creates strains beyond the elastic limits.
  4. Although these aspects are applicable, in general, to impregnated solids having small pores, in some cases such as PMMA-impregnated glass apparent stability can exist owing to good interaction between the polymer and glass, the cross-linking in the polymer, and the spatial hindrance to flow.
  5. Some swelling of PMMA-impregnated glass occurs over a long period because of absorption of water in the polymer; long-term expansion is due to a static-fatigue phenomenon.
  6. Impregnated porous solids of small size can be successfully utilized for predicting the behavior of large sized systems.

#### Acknowledgement

The authors thank Messrs. A. Charron, P. Lefevre, E. Quinn and H. Schultz for carrying out the experimental work with great competence. 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.N. Swamy, Review, Polymer Reinforcement of Cement Systems, J. Mat. Sci. 14, 1521 (1979).
2. R.F. Feldman and J.J. Beaudoin, Some Factors Affecting Durability of Sulphur-Impregnated Porous Bodies, Cem. Concr. Res. 8, 273 (1978).
3. R.F. Feldman and J.J. Beaudoin, Studies of Composites made by Impregnation of Porous Bodies. 2. Polymethyl Methacrylate in Portland Cement Systems, Cem. Concr. Res. 8, 425 (1978).
4. C.P. Bean, M.V. Doyle, and A.G. Pincus, Synthetic High-Field, High-Current Superconductor, Phys. Rev. Letters 9, 93 (1962).
5. W.G. Schmidt and R.J. Charles, Metal Impregnation of Porous Glasses, J. Appl. Phys. 35, 2552 (1964).
6. G.J. Hageage, Jr., E.D. Eames, and R.L. Gherna, X-ray Diffraction Studies of the Sulfur Globules Accumulated by Aromatium Species, J. Bacteriology 101, 464 (1970).
7. G.G. Litvan, Adsorption Systems and Temperatures Below the Freezing Point of the Adsorptive, Adv. Colloid Interface Sci. 9, 253 (1978).