NRC Publications Archive Archives des publications du CNRC

Some factors affecting durability of sulphur-impregnated porous bodies

Feldman, R. F.; Beaudoin, J. J.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

[https://doi.org/10.1016/0008-8846\(78\)90096-0](https://doi.org/10.1016/0008-8846(78)90096-0)

Cement and Concrete Research, 8, May 3, pp. 273-281, 1978-05-01

NRC Publications Archive Record / Notice des Archives des publications du CNRC :

<https://nrc-publications.canada.ca/eng/view/object/?id=8ff61622-1ea2-4d83-8f4b-160217312e71>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=8ff61622-1ea2-4d83-8f4b-160217312e71>

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.

H 1
121d
780
2

6711
c1

NATIONAL RESEARCH COUNCIL OF CANADA
CONSEIL NATIONAL DE RECHERCHES DU CANADA

**SOME FACTORS AFFECTING DURABILITY OF
SULPHUR-IMPREGNATED POROUS BODIES**

by
R. F. Feldman and J. J. Beaudoin

ANALYZED

Reprinted from
CEMENT AND CONCRETE RESEARCH
Vol. 8, No. 3, May 1978
pp. 273-282

**BUILDING RESEARCH
- LIBRARY -**

OCT 5 1978

NATIONAL RESEARCH COUNCIL

04664

DBR Paper No. 780
Division of Building Research

SOME FACTORS AFFECTING DURABILITY OF SULPHUR-IMPREGNATED POROUS BODIES

R.F. Feldman and J.J. Beaudoin
Division of Building Research, National Research Council of Canada,
Ottawa K1A 0R6

(Communicated by F. H. Wittmann)
(Received Feb. 6, 1978)

ABSTRACT

The effect of impregnation on long-term durability has been investigated by exposing 1.3-mm thick specimens of sulphur-impregnated, autoclaved, portland cement-silica mixtures, room-temperature-cured pastes and porous glass to various liquids including water.

All impregnated bodies were permeable to vapours, and matrices with specific surface areas in excess of $20 \text{ m}^2/\text{g}$ and impregnated with sulphur were subject to high internally-generated local stresses when exposed to water and other vapours, leading to possible failure.

RESUME

L'effet d'impregnation sur la durabilité à long terme a été étudié en exposant des spécimens de 1.3 mm d'épaisseur de mélanges ciment-silice Portland imprégnés de soufre et autoclavés, des pâtes à température de la pièce, et du verre poreux à divers liquides y compris l'eau.

Tous les corps imprégnés étaient perméables à la vapeur, et les matrices ayant une surface spécifique de plus de $20 \text{ m}^2/\text{g}$ et imprégnées de soufre ont été sujettes à de hautes contraintes internes lorsqu'elles ont été exposées à l'eau et à d'autres vapeurs, menant à une possibilité de rupture.

New types of composites have been formed by the technique of impregnation (1,2). Physical properties increased by several hundred per cent when porous bodies were impregnated with a variety of organic resins, and recently it has been shown that sulphur impregnation can achieve similar results (3-7). A theoretical study (6) showed that Young's modulus and the microhardness of a completely impregnated composite may be described by an equation similar to that derived from the Reuss model. It involves a knowledge of the properties of the matrix and impregnant as well as determination of the volume fraction of the two components.

Impermeability can also be improved by impregnation, which leads to an increase in corrosion resistance, but little is known about this property on a long-term basis. In fact, no reported work to date has adequately illustrated the effectiveness of an impregnant in improving long-term durability.

Samples already prepared for a previous study (6) - very thin, impregnated specimens - were used for the present investigation of the effects of impregnation on long-term durability. They were exposed to either liquid or vapour and any change in dimension or modulus of elasticity was noted. Autoclaved portland cement-silica mixtures of six different compositions, room-temperature-cured hydrated portland cement, and porous glass were impregnated with sulphur. The latter was exposed to methanol, carbon tetrachloride and water; the portland-cement systems were exposed only to water.

Experimental

Samples

Silica-portland cement mixtures having 5, 10, 20, 30, 50 and 65% by weight of silica were prepared and autoclaved at a water-to-cement ratio of 0.45, as was room-temperature cured paste at a water-to-cement ratio of 0.45.

The specimens were first prepared as 32-mm diameter discs, 1.3 mm thick. Prisms approximately $30 \times 10 \times 1.3$ mm were cut from these. The porous glass (supplied by Corning glass works) in the form of 25-mm diameter tubes of 2-mm wall thickness were also cut in the form of prisms $10 \times 30 \times 2$ mm.

Impregnant and solvents

Sulphur was of reagent grade, containing 3 ppm of H_2S .

Carbon tetrachloride was reagent grade (Anachemia).

Methanol also was reagent grade (Fisher). These solvents were dried with molecular sieves, Type 4A (Linde Co.)

Procedure

Impregnation

Prior to impregnation, which has been described (6), the samples were maintained at $128^\circ C$ in vacuum for 24 h. They were then weighed and placed with solid sulphur in another vacuum vessel and evacuated for 1 1/2 h. The vessel was heated to $128^\circ C$, allowing the sulphur to melt and the sample to become completely immersed. The amount of sulphur that was impregnated was determined by weighing and helium pycnometry. Porous glass samples were heated, prior to impregnation, to $160^\circ C$ for 40 h in vacuum.

Mercury porosimetry and nitrogen adsorption measurements

Measurements were made on samples heated for 24 h at $105^\circ C$ under vacuum conditions. Those for surface area determination by nitrogen adsorption were ground to pass 100 mesh. Mercury intrusion was performed to a pressure of 60,000 psi, using an American Instrument Co. porosimeter.

Young's modulus and length change measurements

Young's modulus was measured on 32-mm diameter discs, 1.3 mm thick; one disc was used for each preparation. The procedure involved exposing each disc to 100% RH in vacuum and measuring, with time, the deflection of the disc when loaded at its centre and supported at three points located at the circumference of a circle 25 mm in diameter. The 30- $\times$ 10-mm prisms were used for length change; they were mounted on 1-in. gauge length extensometers with sensitivity to 4×10^{-6} in./in. These systems were enclosed in vacuum chambers and exposed to 100% relative vapour pressure or immersed in liquid. The porous glass prisms were exposed to CCl_4 , CH_3OH and water in both liquid and vapour form. The cement systems were exposed to 100% water vapour pressure only.

Results

Porous glass

Samples of porous glass, 29.7% pore volume, were impregnated with molten sulphur. Residual porosity after cooling was 4.40% measured by the helium pycnometer. Young's modulus, measured on a disc, was 1.46×10^4 MPa before impregnation and 1.72×10^4 MPa afterwards, a 17.8% increase. Microhardness values were 13.14×10^2 and 17.73×10^2 MPa, respectively, representing an increase of 34.9%.

Length change on exposure to methanol. These results are presented on Fig. 1, exposure being in vapour phase. Expansion of the unimpregnated glass was approximately 0.25% and was close to the equilibrium state at the end of the test. The impregnated sample expanded slowly at first, but after 15 min surpassed the blank and in less than 1 h attained an expansion of 2.5%. Severe cracking of the specimen occurred just short of 2 h of exposure.

FIG. 1

Length change of porous glass on exposure to methanol in vapour phase versus time

Length change on exposure to carbon tetrachloride. Samples were exposed to both vapour and liquid (Fig. 2). Length change occurred immediately after exposure. For the unimpregnated sample it was relatively small, approximately 0.04%; for the impregnated body, it was about 1.5% for both vapour and liquid phases. Cracking of the sample was again observed, but was not of the same severity as had occurred with methanol.

Length change on exposure to water. The length change results for exposure to water in both vapour and liquid phases are presented on Fig. 3. The blank expanded about 0.3% and attained equilibrium by the end of the test. Although it expanded more slowly at first, the impregnated body surpassed the blank after less than 1 h of exposure. Exposure to water in the vapour phase produced an expansion of approximately 1.5% after 1.3 h, with very severe cracking. In the liquid phase, expansion slowed down after 1 h, but the sample cracked and broke between 8 and 23 h of exposure. The surface of the glass after exposure to water vapour is shown on Fig. 4. The sulphur is in an unknown

state and gives the impression of being extruded from the pores and subsequently agglomerated. Small pieces of glass broken off during exposure were examined; they had become completely transparent, indicating that the sulphur had been removed from them.

FIG. 2

Length change of porous glass on exposure to carbon tetrachloride versus time.
(A) liquid phase (B) vapour phase

FIG. 3

Length change of porous glass on exposure to water versus time.
(A) liquid phase (B) vapour phase

FIG. 4

SEM micrographs of fractured glass surface with extruded sulphur after exposure to water vapour

SEM photographs of the sample exposed to methanol also displayed an ill-defined form of sulphur, but for carbon tetrachloride well-crystallized orthorhombic forms were present.

Autoclaved portland cement-silica mixtures and room-temperature-cured paste

The length change of impregnated specimens of autoclaved cement-silica mixtures, silica content 5, 10, 20, 30, 50 and 65%, and room-temperature-cured paste on exposure to 100% water vapour are presented on Fig. 5. The results

for the unimpregnated specimens are shown on Fig. 6. For all impregnated specimens except the 5 and 10% silica, expansion increased in rate after a short period of exposure. For 5 and 10% silica content samples, expansion showed no rate increase up to 260 days. The 20% silica content specimen showed an increase in rate of expansion after 48 h; the 30% after 14 h; the 50% after 18 h; and the 65% and room-temperature-cured paste after 2 h. The blanks, on the other hand, showed a rapid initial rate of expansion, decreasing with time. In each case measured expansion was considerably less for the blanks than for the impregnated bodies. All the

FIG. 5

Length change of impregnated, autoclaved, cement-silica preparations on exposure to water vapour versus time

FIG. 6

Length change of unimpregnated, autoclaved, cement-silica preparations on exposure to water vapour versus time

FIG. 7

The change in Young's modulus on exposure to 100% relative humidity versus time

impregnated specimens disintegrated except those having 5 and 10% silica content.

The change in Young's modulus of the autoclaved samples with exposure to 100% relative humidity is presented on Fig. 7. The results are similar in character to the length change results. The 30, 50 and 65% silica content specimens show large decreases; the 5 and 10% specimens show negligible change. The 20% sample shows only a slight decrease, but after five days the disc warped and the readings are probably unreliable.

Surface area and pore size distribution

The surface areas measured by nitrogen adsorption of the specimens before impregnation are shown on Table I.

Both the 50 and 65% silica content specimens contained unreacted silica after autoclaving, and consequently the specific surface area of the actual reaction products was higher than the values tabulated, since the specimens include the relatively low surface area silica. These results conform approximately to the observation that the higher the surface area the greater the expansion on exposure (see Fig. 5).

TABLE I

Sample, % silica	m ² /g
5	13.8
10	19.3
20	26.5
30	31.8
50	20.1
65	20.6
Room-temperature-cured paste, w/c 0.5	50.0
porous glass	180.0

Pore size distribution of all specimens, plotted on a relative scale of intrusion pressure versus pore volume, is presented on Fig. 8; a pore size value calculated by the Kelvin equation is on the top scale. There is a clear difference between the three groups: 5 and 10% silica, 20 to 65% silica, and room-temperature paste and porous glass. On the basis of these results the samples are grouped as for the surface area results presented on Table I, although for porous glass the mercury penetrated only 60% of its pore volume.

FIG. 8

Pore size distribution of unimpregnated bodies

Discussion

Measurements made for this study show that all the impregnated matrices can be readily permeated by either liquid or vapour. There are several possible reasons for this:

- (a) The bond between the surface of the matrix and the sulphur may not be good; measurements of Young's modulus on impregnated porous glass indicate that this may indeed be so. A knowledge of the modulus of zero porosity glass and sulphur enables one to calculate the expected modulus of the fully impregnated porous glass by means of the Reuss equation (6,7). A value of approximately 3.2×10^4 MPa was calculated, compared to the measured value of 1.72×10^4 MPa. The same reasoning might, however, lead one to conclude that portland cement systems would yield composites resistant to exposure to water, because the modulus due to impregnation did increase according to the Reuss model. The resultant mechanical properties on impregnation were in accord with those predicted by the Reuss equation, which assumes good bonding.
- (b) Chemical interaction occurs at the interface, with subsequent chemical attack by the liquid; the possibility exists that sulphur may react with the silica surface, forming a compound that may in turn react with water. The expansion observed with both the relatively inert carbon tetrachloride and methanol, however, virtually rules out this possibility. When exposed to each of the fluids, including carbon tetrachloride, the impregnated specimens of porous glass expanded to a much greater extent than the respective unimpregnated specimens. It is concluded that expansion is due to a physical phenomenon.

The results of tests on specimens of the various portland cement mixtures also indicate this. All the specimens conformed approximately to the observation that the greater the specific surface area of the matrix material, the greater the expansion on exposure to water vapour. The 5 and 10% silica content specimens with specific surface areas below $20 \text{ m}^2/\text{g}$ were the only impregnated specimens to remain intact and show expansion with water or other liquids not greatly in excess of the unimpregnated material.

Although it appears that the cause of expansion is physical, there are several possible mechanisms by which stress might be imposed on the body:

- (a) During solidification, sulphur (within the pores) shrinks as much as 20% (this was verified by measuring porosity before and after impregnation (6)); this process may have imposed a stress on the body that was released when the body was exposed to vapour. The possibility was investigated by measuring sample dimensions before and after impregnation. They were also measured during melting and solidification of the impregnant with heating and cooling of the body; both measurements yielded negligible length changes.
- (b) During adsorption of vapour on the surface of unimpregnated glass, expansion occurred, as shown in Fig. 3, owing to the decrease of surface-free energy. If the decreased rate of permeation (owing to the impregnant) of vapours were to allow large stress gradients to develop, then failure might occur. The specimens tested were very thin, however, and the interaction and thus expansion produced by adsorption of carbon tetrachloride on unimpregnated porous glass was very small; it is therefore unlikely that large stress gradients would occur. Yet the expansion produced by exposing the impregnated body to carbon tetrachloride was 50 times as large. There must be some other mechanism to explain the very large expansion.
- (c) In order to fill the very small pores existing in some of the matrices studied (Fig. 8), the sulphur has to be in a very finely divided state. It may be calculated that the solidified sulphur in the impregnated porous glass would have a specific surface in excess of $500 \text{ m}^2/\text{g}$. If this surface could be reached by the vapour molecules and the interaction energies were of the normal adsorptive type, then the swelling forces created by the decrease in surface-free energy of the sulphur could be very high; owing to an irregular interfacial boundary, high local stresses acting at specific sites along the interface might exist, causing ultimate destruction of the matrix. This hypothesis is supported by the SEM micrographs (Fig. 4), which show apparent extrusion of the sulphur impregnant. Small pieces of broken sample examined after exposure, do in fact show that the sulphur had completely vacated the pores. The process requires access by the vapour to some of the impregnant surface, adsorption by the impregnant, and a high surface area of matrix.

Sulphur in the crystalline orthorhombic or monoclinic form is not readily wetted by water. Solidification in $50 \text{ \AA}$ diameter pores has left the sulphur in a finely divided, amorphous form (Fig. 4), however, and one would expect its surface energy to be quite different from that of a crystalline state.

Conclusion

1. All the sulphur-impregnated systems studied were permeable to water and other vapours, whether large increases in mechanical properties were achieved on impregnation or not.
2. Expansion of impregnated bodies on exposure to vapour is a physical phenomenon.
3. Expansion of impregnated bodies on exposure to vapours in excess of the expansion of unimpregnated bodies is due to swelling of the high specific

surface area impregnant within the pores owing to its adsorption of the vapour.

4. Matrices with specific surface areas in excess of $20 \text{ m}^2/\text{g}$ and impregnated with sulphur are subject to high internally-generated local stresses when exposed to water and other vapours, leading to possible failure.

Acknowledgement

The authors wish to thank G. Aarts for her very fine work in performing the experiments. 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. J. Gebauer, D.P.H. Hasselman and R.E. Long. Am. Ceram. Soc. Bull. 51, 471 (1972).
2. A. Auskern and W. Horne. J. Am. Ceram. Soc. 54, 282 (1971).
3. N. Thaulow. Cem. Concr. Res. 4, 269 (1974).
4. V.M. Malhotra, K.E. Painter and J.A. Soles. Proceedings, First Intern. Cong. on Polymers in Concrete, 1975. Construction Press Ltd., Hornby, Eng.
5. First Intern. Symposium on New Uses for Sulphur and Pyrites. Madrid 1976.
6. R.F. Feldman and J.J. Beaudoin. Cem. Concr. Res. 7, 19 (1977).
7. R.F. Feldman and J.J. Beaudoin. Cem. Concr. Res. 7, 143 (1977).