NRC Publications Archive Archives des publications du CNRC

Durability of porous systems impregnated with dicyclopentadiene modified sulphur

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

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.

Publisher's version / Version de l'éditeur:

International Journal of Cement Composites Lightweight Concrete, 6, 1, pp. 13-8, 1984-02

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

<https://nrc-publications.canada.ca/eng/view/object/?id=03d55828-5229-451a-85aa-26ff53050118>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=03d55828-5229-451a-85aa-26ff53050118>

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

no. 1218
c. 2
BLDG

National Research
Council Canada

Conseil national
de recherches Canada

11841

**DURABILITY OF POROUS SYSTEMS IMPREGNATED WITH
DICYCLOPENTADIENE—MODIFIED SULPHUR**

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

ANALYZED

Reprinted from
The International Journal of Cement Composites
and Lightweight Concrete
Volume 6, Number 1, February 1984
p. 13 - 18

DBR Paper No. 1218
Division of Building Research

Price \$1.00

OTTAWA

NRCC 23580

Canada

4745715

RÉSUMÉ

On évalue l'efficacité du soufre modifié au dicyclopentadiène (DCPD) à augmenter la durabilité des ciments Portland qui en sont imprégnés. Des échantillons de pâte de ciment Portland et de verre vycor poreux ont été imprégnés de soufre modifié et de soufre non modifié, et certains échantillons ont été chauffés à 180°C. En comparant la valeur mesurée du module d'élasticité avec des valeurs calculées à partir de formules de mélange, on a obtenu une mesure qualitative de l'adhérence entre la matrice et le produit d'imprégnation. Des variations de longueur et du module d'élasticité en fonction du temps d'exposition à 100% d'humidité relative ont été contrôlées; ces contrôles ont servi de base à l'évaluation de la durabilité. Les échantillons imprégnés de soufre modifié au DCPD et chauffés à 180°C se sont avérés les plus durables. On conclut que deux facteurs régissent la durabilité: l'interaction entre la matrice et l'agent d'imprégnation, qui influe sur la vitesse d'ingression de l'eau à l'interface, et l'interaction entre l'eau et les surfaces d'un solide à leur interface.

CISTI/ICIST

3 1809 00210 3874

Durability of porous systems impregnated with dicyclopentadiene-modified sulphur

J.J. Beaudoin and R. F. Feldman†*

*James J. Beaudoin is a senior research officer with the Division of Building Research, National Research Council Canada, Ottawa, Canada. He holds a B.A.Sc. and an M.A.Sc., and earned his Ph.D. in civil engineering from the University of Windsor in 1970. He was a postdoctorate fellow at the University of Toronto until he joined NRCC in 1972. His research at NRCC has been mainly concerned with the mechanical properties of inorganic cementitious systems.

†Rolf F. Feldman is a senior research officer at the National Research Council Canada. He holds B.Sc., M.A.Sc., Dip. Chem. Tech. and D.Sc. degrees and was made a fellow of the American Ceramic Society in 1983. His work at NRCC involves the physical structure of hydrated portland cement paste, its mechanical properties and other factors such as incorporation of waste materials pertinent to the strength and durability of portland cement concrete.

SYNOPSIS

The effectiveness of dicyclopentadiene (DCPD)-modified sulphur in improving the durability of impregnated portland cement systems is assessed. Portland cement paste and porous vycor glass samples were impregnated with modified and unmodified sulphur and some samples were heated to 180°C. Comparison of the measured modulus of elasticity with values calculated from mixture rules provided a qualitative measure of the adhesion between matrix and impregnant. Changes in length and modulus of elasticity with time of exposure at 100 per cent RH were monitored and formed the basis of durability assessment. Samples impregnated with DCPD-modified sulphur and heated at 180°C showed the least distress. It is concluded that two factors control durability: interaction of the matrix with the impregnant, which influences the rate of ingress of water to the interface, and interaction between water and solid surfaces at the interface.

KEYWORDS

Concrete durability, sulphur impregnation, cement paste, vycor glass, elastic modulus, expansion, fracture, moisture curing, composite materials, modified sulphur, wetting, additives, failure.

INTRODUCTION

Impregnation of porous cement systems with elemental sulphur produces composites with substantially increased strength and modulus of elasticity [1]. Durability studies have indicated, however, that in the presence of moisture there is a tendency for the sulphur impregnant to be extruded from the samples, resulting in cracking and deterioration [2, 3].

Molten sulphur generally reverts to the orthorhombic form when it cools to ambient temperatures, although some additives are effective in retarding crystallisation [4]. It was thought that porous bodies impregnated with modified sulphur, which may have surface interactive forces different from those of ordinary sulphur, might be less susceptible to damage from water. An olefin, dicyclopentadiene (DCPD), has been particularly effective in retarding the crystallisation of bulk sulphur to the orthorhombic form. DCPD reacts with elemental sulphur at 140°C (depending on concentration and reaction time) to give a mixture of unreacted sulphur and various polysulphides. The latter prevent the sulphur from crystallising to the orthorhombic form. The principal products of the initial reaction between DCPD and sulphur are a cyclic trisulphide and a pentasulphide. It was the object of this study to assess the effectiveness of DCPD-modified sulphur in improving the durability of porous cement paste and vycor glass.

EXPERIMENTAL PROGRAMME

Materials

Cement paste A cement paste having $w/c = 1.0$, made with normal type 10 portland cement and hydrated for 14 years was used. The high w/c ratio facilitates impregnation because of high porosity.

Vycor glass Typical porous vycor glass samples were used, with total porosity 28 per cent and a nominal N_2 surface area of $175 \text{ m}^2/\text{g}$. Samples in sheet and disc form were obtained from Corning Glass Co. They were heated in air at 500°C for 4 h to remove any organic impurities from the surface.

Sulphur Elemental sulphur, 99.99 per cent pure.

Dicyclopentadiene (DCPD) Reagent grade, supplied by Fisher Scientific.

Technique of impregnation and testing

Sample fabrication Discs 31.8 mm in diameter by 1.27 mm thick were used to determine modulus of elasticity for both cement paste and vycor glass [5]. Rectangular prisms approximately $30 \times 6.5 \times 1.27$ mm thick were used for length change measurements.

Impregnation The impregnation technique and apparatus have been described [1]. DCPD-modified sulphur was prepared by adding 5 per cent DCPD to elemental sulphur at 140°C and allowing it to react for 3 h. Concentration and reaction time were based on viscosity considerations as well as on the results of work on sulphur concrete (sulphur is the binder rather than portland cement) in which maximum values of compressive strength were achieved using a similar concentration and reaction time [6]. All samples were degassed at 110°C for 3 h prior to impregnation.

Modulus of elasticity Measurements were made on disc samples prior to impregnation, after impregnation, and at intervals during exposure to water vapour (100 per cent RH). The measurement technique, which involves centrally loading a disc supported at three points on the circumference, has been described [5].

Length change Measurements were made with impregnated prism samples exposed to water vapour (100 per cent RH). Samples were mounted on modified Tuckerman extensometers [7].

Test series

The composite test samples can be divided into two series: cement paste (Series I), and porous glass (Series II). Each was divided into four sets as follows:

- 1) composite impregnated with elemental sulphur,
- 2) composite as in 1) and subsequently heated at 180°C for 3 h,
- 3) composite impregnated with DCPD-modified sulphur,
- 4) composite as in 3) and subsequently heated at 180°C for 3 h.

Four samples from each set were used for length change and two for modulus of elasticity measurements.

TEST RESULTS

Modulus of elasticity changes on impregnation – Series I: Cement paste–sulphur systems

Results of modulus of elasticity measurements are given in Table 1. Large variations in E for very high-porosity, unimpregnated cement paste are similar to those previously reported [5]. The porosity range was 49.0 to 55.6 per cent. Impregnation modifies the effects of flaws and changes the nature of the interparticle contact in such a way that the range of E for impregnated samples is reduced significantly in comparison with that for unimpregnated samples.

Theoretical values for impregnated composites are computed from the mixture rule, $E_c = 1/[V_1/E_{01} + V_2/E_{02}]$, where E_c is the composite modulus, E_{01} and E_{02} are values of moduli for non-porous matrix and impregnant, respectively, and V_1 and V_2 are the corresponding volume fractions of the matrix and impregnant. Values of E_{01} for cement paste and glass are taken as 30×10^3 MPa and 75×10^3 MPa, respectively; the value of E_{02} for sulphur is 15.3×10^3 MPa [2].

The mixture rule calculation gives $E_c = 20 \times 10^3$ MPa. Mixture rule calculations assume that adhesion of matrix and impregnant at the interface is sufficient to allow both phases to contribute fully to composite stiffness.

Impregnated samples have E values varying from 66.7 to 84.5 per cent of the calculated value. Impregnation

Table 1 Arrangement of bond specimen

Series	Set	Modulus of Elasticity ($\text{MPa} \times 10^{-3}$)		
		Unimpregnated	Impregnated	Additional Heat Treatment (3 h at 180°C)
I cement paste	1	7.73	16.91	—
	2	5.00	13.34	18.48
	3	4.75	16.60	—
	4	6.27	14.50	16.41
II porous glass	1	19.20	27.35	—
	2	18.62	25.88	17.10
	3	14.54	14.93	—
	4	12.87	16.32	26.21

significantly increases E values for all sets; and heat treatment further increased them (sets 2 and 4), bringing them closer to the calculated values.

Modulus of elasticity changes on impregnation – Series II: Porous glass–sulphur system

Series II composite samples containing unmodified sulphur (sets 1 and 2) have significantly higher E values than unimpregnated samples (Table 1). The large range of E for unimpregnated samples is attributed to variations in effectiveness of leaching during the manufacturing process. The E values of composite samples containing modified sulphur, however, are not significantly different from those for the unimpregnated samples. The mixture rule calculation gives $E_c = 35 \times 10^3$ MPa. After brief exposure to water vapour, the E values of the impregnated samples (set 3) nearly doubled (14.93 to 29.39×10^3 MPa), approaching the calculated value. Heat treatment of set 2 samples results in a decrease in E to a value similar to that for unimpregnated glass. Heat treatment of set 4 samples, however, results in an increase in E to a value approaching that obtained by the mixture rule.

Exposure to 100 per cent RH – Series I: Cement paste–sulphur systems

Length change Length change versus time of exposure (100 per cent RH) curves are presented in Figure 1. It is convenient to divide the characteristics of the curves into two stages: expansion < 0.1 per cent and expansion > 0.1 per cent. In the expansion region < 0.1 per cent, expansion rate is high for sets 2 and 4, the samples that had additional heat treatment at 180°C . The expansion rate is considerably lower for sets 1 and 3. In addition, the time to reach 0.1 per cent expansion is 2, 2, 25 and 120 h for sets 2, 4, 1 and 3, respectively. In the expansion region > 0.1 per cent, the rate of expansion is large and fracture occurred for sets 1, 2 and 3. The rate of expansion for set 4 is greatly reduced and there are no visible signs of cracking.

Modulus of elasticity Figure 2 is a plot of modulus of elasticity versus square root of time of exposure at 100 per cent RH. Sets 2 and 4, which had additional heat treatment, underwent a rapid decrease in E after exposure for only $\frac{1}{4}$ h. The reduced E values approach those of samples prior to impregnation. Hence, additional heat results in an initial rapid decrease in E as well as the high initial rate of expansion. E values for sets 1 and 3 decrease at a much slower rate. It is only after 25 to 50 h that the modulus of elasticity is reduced to a value comparable to that of unimpregnated cement paste.

Exposure to 100 per cent RH – Series II: porous glass–sulphur system

Length change Length change versus time of exposure at 100 per cent RH curves are presented in Figure 3. The time required to reach 0.1 per cent expansion for sets 1, 2, 3 and 4 is 1.75, 0.5, 2.2 and 1 h, respectively. For both unmodified and DCPD-modified sulphur the initial rate of

Figure 1 Expansion of sulphur-impregnated cement paste exposed to 100 per cent RH

Figure 2 Modulus of elasticity values for sulphur-impregnated cement paste exposed to 100 per cent RH

Figure 3 Expansion of sulphur-impregnated porous glass exposed to 100 per cent RH

Figure 4 Modulus of elasticity values for sulphur-impregnated porous glass exposed to 100 per cent RH

expansion is faster with additional heat treatment. After reaching 0.1 per cent expansion, sets 1 and 2 samples expand rapidly and fracture in less than 8 h. Sets 3 and 4 samples expand at a reduced rate, the rate for set 4 being greater than that for set 3. At 30 h the rate of expansion for set 3 increases significantly and fracture ensues. The rate of expansion for set 4, however, is reduced and expansion continues for several hundred hours without fracture or visible cracking.

Modulus of elasticity Figure 4 is a plot of modulus of elasticity versus square root of exposure time at 100 per cent RH. E values for set 1 decrease rapidly on exposure to water, and prior to fracture reduce further to values lower than those of the unimpregnated samples owing to extensive cracking. E values for set 2 samples increase by 22 per cent after 0.7 h exposure, then decrease as for set 1 samples. Additional heat treatment in set 2 reduced E to a value similar to that of the unimpregnated sample. Set 1 samples had higher E values and took longer to expand to 0.1 per cent, but fractured rapidly thereafter. For DCPD-modified sulphur samples (set 3), impregnation had little effect on E values before exposure to 100 per cent RH; immediately after exposure to 100 per cent RH, however, E increased nearly 100 per cent. The set 3 samples then underwent a rapid decrease in E on exposure to water for 6½ h, reaching values similar to those for sets 1 and 2. Thus values for set 3 are similar to those for the unimpregnated case. E does not change significantly thereafter until, at about 25 h, it decreases rapidly as cracking, delamination, and fracture take place. In spite of the high initial E provided by heat treatment of set 4 samples, decrease in E to values approaching those of the unimpregnated condition is rapid (1 h). Subsequently, the modulus did not change significantly.

DISCUSSION

There appear to be at least two factors that affect E and control the rate of expansion of sulphur-impregnated porous bodies exposed to 100 per cent RH: 1) interaction of the impregnant with the matrix, and the influence of this interaction on the ingress of water to the interface; 2) interaction of water with matrix and impregnant surfaces at the interfaces.

Modulus of elasticity

Impregnation and heat treatment The increase in E of impregnated cement paste that has been heat treated may be due to increased adhesion of the impregnant to the matrix. In addition, if modified sulphur is used, increased reaction of DCPD with sulphur may improve adhesion. The increased adhesion provided by heat treatment of modified sulphur may be sufficient to give a high initial E value, but on exposure to 100 per cent RH it does not seem to prevent rapid ingress of water, interaction with solid surfaces, and associated decrease in E.

Porous glass has been used in previous studies to model performance and durability of cement paste [8]. In general, effects of moist environments on durability of impregnated systems are accelerated when porous glass is

the matrix material. The significant increase in E as a result of heat treatment of porous glass samples containing modified sulphur may also be due to increased adhesion between sulphur and glass. It is not clear, however, why heat treatment destroys the adhesion of the modified sulphur to glass but not to cement paste. It may be due to the much lower coefficient of thermal expansion of glass in comparison with that of cement paste. The coefficients for sulphur, cement paste, and glass are 55, 11–20, and $5 \times 10^{-6} \text{ }^\circ\text{C}$, respectively. The initial increase in E observed when the unmodified sulphur-glass system was exposed to 100 per cent RH might be explained as follows: water interacts with the sulphur surface to cause swelling and mechanical linking with the glass surface, resulting in an increase in stiffness of the system. The nature of the interaction, however, is not yet fully understood. Decrease in E following initial increase may be a result of a combination of loss of adhesion, extrusion of sulphur from the pores, and cracking.

Impregnation without heat treatment There is no significant increase in E for porous glass samples impregnated with modified sulphur, suggesting that adhesion between glass and modified sulphur is poor. The reason for the significant increase in E observed after brief exposure to 100 per cent RH and the subsequent decrease in E with increase in exposure time is similar to that for the heat-treated, unmodified sulphur system. Slower decreases in E after exposure to 100 per cent RH, observed for cement paste and glass systems without heat treatment, indicate slower loss of adhesion and ingress of water to the interfaces.

Length change

Impregnation and heat treatment A possible explanation of the higher initial rate of expansion of the modified sulphur systems is that heating permits more rapid access of water to the interface. Once water is available to the surfaces at the interface, the 'reactivity' of water with the impregnant and matrix controls the rate of expansion. Interaction of water with modified sulphur, which has been heated additionally, appears to be poor, so that in the cement paste system a reduced rate of expansion similar to that of the unimpregnated material occurs.

Impregnation without heat treatment Length change in the modified sulphur-cement paste system is small for the first 120 h indicating that adhesion is sufficient to prevent a significant amount of water from reaching the interface. After 120 h enough water may be present at the interface to interact with both sulphur and cement paste and cause the large observed expansion.

The rapid expansion and fracture of the unmodified sulphur-glass system (after a longer period to reach 0.1 per cent expansion) suggests that once ingress of water is sufficient the interaction with the sulphur and matrix surfaces is similar to that for the heat-treated system. Modification of sulphur with DCPD reduced the resulting expansion due to interaction with water, but the reduction was not enough to prevent fracture.

CONCLUSIONS

Two important factors control durability of sulphur-impregnated cement paste: interaction of the matrix with the impregnant, which influences the rate of ingress of water to the interface areas between matrix and impregnant, and effective interaction between water and the solid surfaces at the interface. Ideally, good durability would be achieved for cement paste when impregnation results in a significant increase in E , accompanied by good adhesion between matrix and impregnant, and when there is poor interaction between water and impregnant. Heat treatment of both DCPD-modified and unmodified sulphur-impregnated cement paste results in an increase in modulus of elasticity. The adhesion between matrix and impregnant, however, is quickly reduced on exposure to 100 per cent RH and the rate of ingress of water to the interfaces is rapid.

The effects of 100 per cent RH on durability are accelerated if porous glass is used as matrix material. Samples of both cement paste and porous glass that showed the least visible signs of distress were those impregnated with DCPD-modified sulphur followed by heat treatment. It is concluded that DCPD-modified sulphur is effective in increasing the durability of both these materials in a moist environment. Heat treatment contributes further to the reaction between DCPD and sulphur and should increase the concentration of polysulphides on the sulphur surfaces. Improved performance may be due to poor interaction between water and polysulphides.

ACKNOWLEDGEMENT

The authors wish to thank J. Wood and G. Chan for their assistance in conducting the experiments. This paper is a contribution from the Division of Building Research, National Research Council Canada, and is published with the approval of the Director of the Division.

REFERENCES

1. Feldman, R. F. and Beaudoin, J. J. 'Studies of composites made by impregnations of porous bodies. 1. Sulphur impregnant in portland cement systems', *Cement and Concrete Research*, Vol. 7, No. 19, January 1977, pp. 19–30.
2. Feldman, R. F. and Beaudoin, J. J. 'Some factors affecting durability of sulphur-impregnated porous bodies', *Cement and Concrete Research*, Vol. 8, No. 3, May 1978, pp. 273–82.
3. Litvan, G. G., Feldman, R. F. and Grattan-Bellew, P. G. 'Durability of cement and glass impregnated with sulphur and polymethylmethacrylate', *Cement and Concrete Research*, Vol. 12, September 1982, pp. 649–59.
4. Currell, B. R. 'The importance of using additives in the development of new applications for sulphur', *Symposium on New Uses For Sulphur and Pyrites*, Madrid, 1976, pp. 105–13.
5. Sereda, P. J., Feldman, R. F. and Swenson, E. G. 'Effect of sorbed water on some mechanical properties of hydrated portland cement pastes and compacts', *Highway Research Board*, Special Report 90, 1966, pp. 58–73.

6. Diehl, L. 'Dicyclopentadiene modified sulphur and its use as a binder, quoting sulphur concrete as an example', Symposium on New Uses for Sulphur and Pyrites, Madrid, 1976, pp. 202-14.
7. Feldman, R. F., Sereda, P. J. and Ramachandran, V. S. 'A study of length changes of compacts of portland cement on exposure to H₂O', Highway Research Board Record No. 62, 1964, pp. 106-18.
8. Ramachandran, V. S., Feldman, R. F. and Beaudoin J. J. 'Concrete science', Chap. 10, Heyden & Son, 1981, pp. 398.

This paper, while being distributed in reprint form by the Division of Building Research, remains the copyright of the original publisher. It should not be reproduced in whole or in part without the permission of the publisher.

A list of all publications available from the Division may be obtained by writing to the Publications Section, Division of Building Research, National Research Council of Canada, Ottawa, Ontario, K1A 0R6.