Dependence of frost resistance on the pore structure of mortar containing silica fume

Cheng-Yi, H.; Feldman, R. F.

Publisher’s version / Version de l'éditeur:

Journal of the American Concrete Institute, 82, 5, pp. 740-743, 1985-09

National Research Council Canada | Conseil national de recherches Canada

Institute for Research in Construction | Institut de recherche en construction

Dependence of Frost Resistance on the Pore Structure of Mortar Containing Silica Fume

by Huang Cheng-yi and R.F. Feldman

Reprinted from
ACI Journal
September-October 1985, No.5
Proceedings V. 82, p. 740-743
(IRC Paper No. 1404)

Price $2.00

NRCC 26361

Canada

RÉSUMÉ

Les auteurs ont évalué la résistance aux cycles gel-dégel de mortiers préparés suivant des rapports eau/ciment et silice fine [e/(c + sf)] (0, 10 et 30 % en poids) de 0,45 et 0,60. Ils ont déterminé, par injection de mercure, la répartition des pores selon le diamètre et, après distillation du mercure, ont procédé à des réinjections. Les résultats indiquent que l'ajout de silice fine modifie la structure des pores et que, dans les gammes de dimensions de pores 20 000 à 2 000 et 2 000 à 350 nm, le volume des pores augmente tandis que leur accessibilité diminue. La résistance au gel des mortiers ne contenant pas d'air entraîné et préparés suivant un rapport e/(c + sf) de 0,60 a augmenté considérablement avec l'addition de silice fine.

Title no. 82-68

Dependence of Frost Resistance on the Pore Structure of Mortar Containing Silica Fume

ACI JOURNAL TECHNICAL PAPER

Title no. 82-68

Dependence of Frost Resistance on the Pore Structure of Mortar Containing Silica Fume


by Huang Cheng-yi and R. F. Feldman

Mortars prepared at water to cement and silica fume [w/(c + sf)] (0, 10, and 30 percent by weight) ratios of 0.45 and 0.60 were assessed for resistance to freeze-thaw cycles. Pore size distribution was measured by mercury intrusion and reintrusion experiments were performed after distillation of mercury. Results indicate that addition of silica fume changes the pore structure, and that pore volume in the pore size ranges of 20,000 to 2000 and 2000 to 350 nm increases, whereas accessibility to the pores decreases. Frost resistance of mortars containing no entrained air and prepared at a w/(c + sf) ratio of 0.60 was improved greatly with the addition of silica fume.

Keywords: freeze-thaw durability; measuring instruments; microstructure; **mortars (material)**; porosity; **silica**; water-cement ratio.

The addition of condensed silica fume, a byproduct of the ferro-silicon industry, to cement mortars alters the microstructure of the product that forms on hydration.[1,*] The changes improve the compressive strength of the mortars, but their effect on the durability of the material is not fully known. Recent work on mortars[2,3] and on concrete[4-6] suggests that frost resistance is improved by the incorporation of silica fume into the mix, but there is little explanation given of the mechanism involved.

A technique has been devised whereby mercury can be removed from bodies into which it has been intruded by pressure during measurement of pore-size distribution, allowing study of a second intrusion to be made[7] and thus providing additional information about pore structure. The technique has been applied to mortars with silica fume replacements so that the results can be used to explain their resistance to frost action.

RESEARCH SIGNIFICANCE

A major cause of concrete deterioration is frost action. The main protective action usually taken is to entrain air in the concrete which, however, introduces other problems. This paper presents another method to provide frost resistance.

EXPERIMENTAL

Materials

Type I portland cement with a C_3A content of 11.82 percent and silica fume containing 95.2 percent SiO_2, 1.56 percent carbon, 0.27 percent K_2O, and 0.10 percent Na_2O (surface area = 21,000 m^2/kg) were used. Ottawa silica sand passing ASTM C 109 was used for mortar with a sand:binder ratio of 2.25:1. Binder in the mortar contained 0, 10, or 30 percent silica fume. Mixes were prepared at water to cement and silica fume ratios [w/(c + sf)] of 0.45 and 0.60. A sulfonated melamine formaldehyde admixture was used in the amount of 0.3 and 2 percent by weight of binder at w/(c + sf) of 0.45 for mixes containing 10 and 30 percent silica fume, respectively. No air-entraining admixtures were used.

Properties

Pore size distribution (Hg porosimetry to a pressure of 414 MPa) was determined on all six mixes after 28 and 90 days of curing time. Specimens were dried by vacuum and final heating for 24 hr at 100 C. Mercury was removed by heating specimens at 105 C in vacuum for three to four weeks until weight returned to the original value. Reintrusion was performed only on the same specimens intruded before on the six mixes cured for 90 days. Freeze-thaw resistance was determined in triplicate on all six mixes prepared in a laboratory type mixing machine in accordance with ASTM C 192 standard method. The mortars were made in the form of 25.4 x 25.4 x 127 mm prisms outfitted with steel studs. The freeze-thaw cycle consisted of freeze in air, thaw in water (-18 C to +5 C), and two cycles in 24 hr, according to ASTM standard test method C 666, Procedure B.

*Cheng-yi, Huang, and Feldman, R. F., "Influence of Silica Fume on the Microstructural Development in Cement Pastes," in press.

Received June 27, 1984, and reviewed under Institute publication policies.

Pertinent discussion will be published in the May-June 1986 ACI JOURNAL if received by Apr. 1, 1986.

Huang Cheng-yi is a research engineer at the Division of Cement Research, Institute of Building Materials, Beijing, China. A graduate of the Nanjing Institute of Chemistry, his research concerns the microstructure of hardened cement paste. From 1982 to 1984, he was a visiting scientist at the Division of Building Research, National Research Council of Canada.

ACI member R. F. Feldman is a senior research officer of the Division of Building Research, National Research Council of Canada. His research interests include durability of concrete and use of wastes and by-products in concrete. Dr. Feldman is a member of ACI Committee 209, Creep and Shrinkage in Concrete; of CSA, RILEM, and ASTM technical committees; and is President-Elect and Fellow of the Cements Division of the American Ceramic Society.

Table 1 — Summary of results of freezing and thawing test

Specimen number	Cycles producing 0.1 percent residual expansion	Cycles producing 0.1 percent residual expansion	Ultimate expansion, percent	Ultimate cycle	Expansion per 100 cycles, × 100
1	2	3	4	5	6
C^{ℓ}	>732	>732	0.012	733	0.16
B^{ℓ}_{10}	>722	>722	0.007	722	0.10
B^{ℓ}_{30}.1	79	92	0.658	123	53.6
B^{ℓ}_{30}.2	102	124	0.848	190	44.6
C^{H}	36	54	1.168	128	91.2
B^{H}_{10}	>696	>696	0.028	696	0.40
B^{H}_{30}	350	560	0.346	696	5.0

RESULTS

Freeze-thaw resistance

The freeze-thaw resistance results for mortars cured for 28 days are presented in Fig. 1, which includes nomenclature for the various mixes. A summary of results of the experiments is presented in Table 1. For mortars prepared at a w/(c + sf) = 0.45 the results are as follows: Specimens C^{ℓ} and B^{ℓ}_{10} showed very little expansion even after 722 cycles. Two different preparations were tested for specimen B^{ℓ}_{30}; both failed, as shown in Columns 2 through 6 of Table 1. Because Specimen B^{ℓ}_{30} displayed the greatest compressive strength and lowest permeability of the various specimens,[1] this result was not expected.

Mixes prepared at w/(c + sf) of 0.60 displayed a somewhat different trend. The plain mortar specimen C^{H} expanded after only a few cycles, failing at 128 cycles (about 1.16 percent expansion). Neither Specimen B^{H}_{10} nor B^{H}_{30} failed even after 700 cycles. Column 6 of Table 1 gives the average expansion per 100 cycles × 100 (freeze × thaw) for each. B^{H}_{10}, with a value of 0.40, ranks third after B^{ℓ}_{10} and C^{ℓ}, while B^{H}_{30}, B^{ℓ}_{30}, and C^{H} have values of 5.0, 53.6, and 91.2, respectively. The replacement of 10 percent cement by silica fume at a w/(c + sf) ratio of 0.60 without air entrainment provides considerable improvement in frost resistance of mortar exposed to freeze-thaw according to the procedure used here.

Pore size distribution

The mercury intrusion results (volume percent) for the specimens prepared at w/(c + sf) of 0.45 and cured for 90 days are presented in Fig. 2. Those for mortars with silica fume contents of 0, 10, and 30 percent are shown in Fig. 2(a) through (c). The curve for the second intrusion performed on the same specimen as previously intruded is included with each first intrusion curve and is labeled R. The first intrusion curves and Table 2 show that pore volume in the pore size range 97,000 to 875 nm increases considerably with addition of silica fume: 1.65, 5.06, and 5.63 percent by volume of sample for 0, 10, and 30 percent silica fume, respectively. If the volume of pores in the 875 to 175 nm range is also taken into account, the pore volume in the range 97,000 to 175 nm is 3.90, 7.0, and 6.38 percent for the same samples. Removing the mercury by distillation and repeating the intrusion experiments indicates that a significant portion of the pore volume of blends in the < 17.5 nm range now falls in the 97,000 to 875 nm range. Volumes for the latter range are 2.86, 8.28, and 8.44 for additions of 0, 10, and 30 percent silica fume. Pore volumes in the 875 to 175 nm range are 6.31, 9.48, and 9.40 percent, respectively.

The mercury intrusion results for specimens prepared at w/(c + sf) of 0.60 and cured for 90 days are presented in Fig. 3(a) through (c) for silica fume additions of 0, 10, and 30 percent, respectively. The results

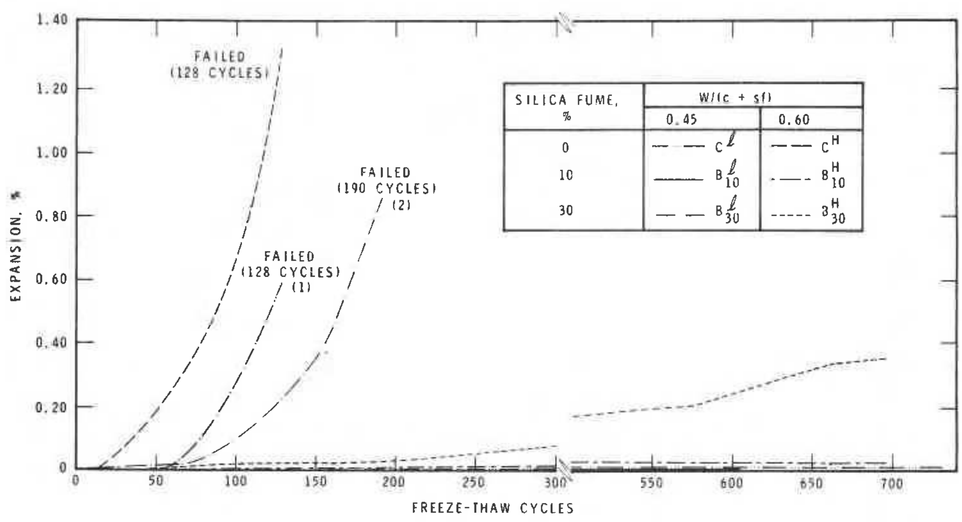

Fig. 1—Expansion of mortars with different silica fume contents as a result of freeze-thaw cycle exposure

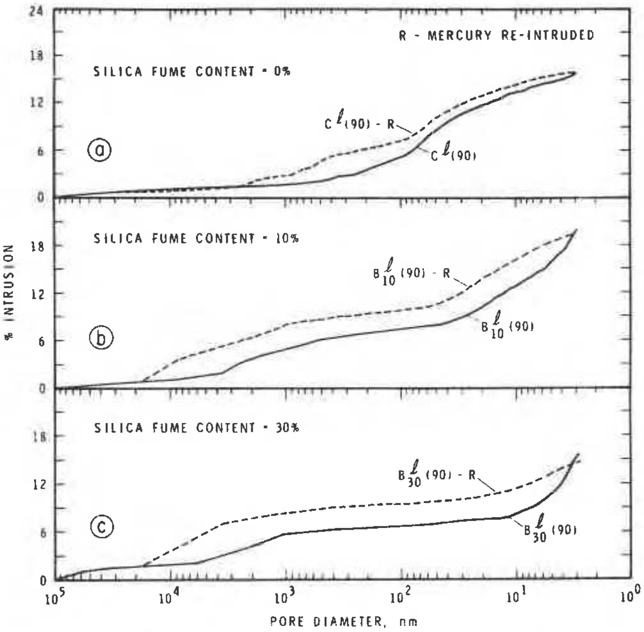

Fig. 2—Comparison of pore size distribution of cement mortar with different silica fume contents, first and second intrusions [w/(c + sf) = 0.45, 90 days curing]

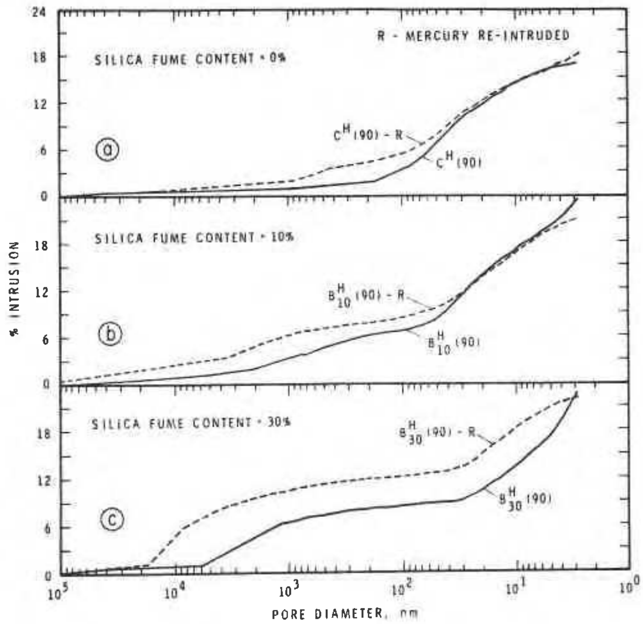

Fig. 3—Comparison of pore size distribution of cement mortar with different silica fume contents, first and second intrusions [w/(c + sf) = 0.60, 90 days curing]

Table 2 — Pore size distribution of mortars cured for 90 days before and after reintrusion, volume percent

Pore diameter, nm	$C^{\ell}(90)$	$C^{\ell}(90)R$	$B^{\ell}_{10}(90)$	$B^{\ell}_{10}(90)R$	$B^{\ell}_{30}(90)$	$B^{\ell}_{30}(90)R$	$C^{H}(90)$	$C^{H}(90)R$	$B^{H}_{10}(90)$	$B^{H}_{10}(90)R$	$B^{H}_{30}(90)$	$B^{H}_{30}(90)R$
97,000 to 875	1.65	2.86	5.06	8.28	5.63	8.44	0.94	1.91	3.61	6.48	6.75	10.95
875 to 175	2.25	3.45	1.94	1.20	0.75	0.96	0.93	2.39	2.76	0.86	1.47	1.20
175 to 17.5	8.11	6.92	3.72	4.67	0.94	1.15	10.29	8.12	8.28	6.48	3.02	3.76
17.5 to 2.9	3.90	2.55	9.23	5.42	8.26	4.22	5.61	4.30	8.70	6.70	11.58	6.51
Total	15.91	15.78	19.95	19.57	15.58	14.77	17.77	16.73	23.35	20.95	22.82	22.42

Table 3 — Pore volumes of mortars in pore size ranges beneficial for frost resistance

	Porosity, volume percent								
Pore diameter, nm	$C^{\ell}(90)$*	$C^{\ell}(90)R$†	$B^{\ell}_{10}(90)$	$B^{\ell}_{10}(90)R$	$B^{\ell}_{30}(90)$	$B^{\ell}_{30}(90)R$	$C^{H}(90)$	$C^{H}(90)R$	$B^{H}_{10}(90)$
20,000 to 2000	0.63	1.30	3.23	5.47	2.49	5.75	0.40	0.75	1.47
2000 to 350	1.22	4.11	2.61	2.71	2.06	1.48	0.52	1.70	3.40
	$B^{H}_{10}(90)R$	$B^{H}_{30}(90)$	$B^{H}_{30}(90)R$	$C^{\ell}(28)$*	$B^{\ell}_{10}(28)$	$B^{\ell}_{30}(28)$	$C^{H}(28)$	$B^{H}_{10}(28)$	$B^{H}_{30}(28)$
20,000 to 2000	2.85	4.00	8.45	0.25	0.96	2.20	0.30	0.78	4.58
2000 to 350	2.75	2.09	2.07	2.40	2.35	3.10	1.08	3.65	3.42

*(90) and (28) day curing.
†R — after reintrusion.

from the second intrusion experiments are also included. The pore volumes in the 97,000 to 875 nm range are 0.94, 3.61, and 6.75 percent for additions of 0, 10, and 30 percent silica fume; volumes including those in the 875 to 175 nm range are 1.87, 6.37, and 8.22 percent. Reintrusion experiments again indicate that a large portion of the pore volume formerly in the pore size range < 17.5 is shifted towards the 97,000 to 875 nm range. The value decreases from 11.58 to 6.51 percent for $B^{H}_{30}(90)$ in the smaller pore range. The sum of the pore volumes for the 97,000 to 875 nm range and 875 to 175 nm range is 4.30, 7.34, and 12.15 percent, respectively, for additions of 0, 10, and 30 percent. The total volume of Hg intruded for $B^{H}_{10}(90)R$ is less than that for $B^{H}_{10}(90)$ because the Hg was not completely removed from $B^{H}_{10}(90)$ during six weeks of distillation.

Results of pore-size distributions for specimens cured for 28 days have previously been reported.* The trends in pore-size distribution curves for specimens cured for 28 and 90 days are similar. In the freeze-thaw tests, the samples were initially cured for 28 days. Litvan[8] has suggested that pore volume in the size range 2000 to 350 nm, as well as pores > 10,000 nm, are effective in producing frost resistant mortar. Results for both 28- and 90-day cured specimens for pore size ranges of 20,000 to 2000 and 2000 to 350 nm are presented in Table 3. The pore volumes for both the 28- and 90-day cured specimens in these size ranges generally increase considerably with silica fume content, with the total volume (including both pore size ranges) for the 28-day

*See footnote, p. 740.

specimen being 2.65, 3.31, and 5.30 percent for Specimens C^ℓ, B^ℓ_{10}, and B^ℓ_{30}, and 1.38, 4.43, and 8.00 for C^H, B^H_{10}, and B^H_{30}, respectively.

DISCUSSION

Silica fume replacements to mortar cause significant changes in the pore structure of the hydrated product. Pore volumes in the 20,000 to 2000 and 2000 to 350 nm ranges are significantly greater for mortars with silica fume by first intrusion measurements, and with second intrusion measurements they appear to be even greater in the 20,000 to 2000 nm range. These results, which are in agreement with those of Litvan,[8] explain the greatly improved frost resistance of Specimens B^H_{10} and B^H_{30} over that of C^H. Previous work showed that $Ca(OH)_2$ is preferentially deposited in the interfacial zone around inclusions such as aggregates in mortar and concrete and fibers in paste.[9,10,*] The silica fume reacts with $Ca(OH)_2$, thereby affecting pore distribution in the mortar and creating further pores in the range 20,000 to 350 nm at the interfacial zone around sand grains. Assuming that pores of this size-range form around homogeneously distributed sand grains of uniform size (0.5 mm) in a mortar having a 2.25:1 sand-to-binder ratio, a simple calculation can demonstrate that spacing between these pores is less than 0.1 mm. This conforms to specification ASTM C 457-71 for frost durability. In addition, part of the pore volume in these pore-ranges is of the ink-bottle variety and relatively inaccessible. This property may be important to maintain a low level of saturation of these pores during the freeze-thaw cycles, and allow them to act as reservoirs; they may accommodate water migrating from small pores during the freezing process.

Specimen C^ℓ also performed well. Although this mix contained no silica fume, the pore volume in the range 20,000 to 350 nm increased from 1.85 to 5.41 percent by volume (Table 3) when mercury was reintruded, indicating that a large portion of these pores is relatively inaccessible. This compares with Mix C^H which had comparable values of 0.92 and 2.45 percent and which performed poorly. In addition, the lower w/c of C^ℓ would insure a lower general permeability and less capillary water than Specimen C^H.

The rapid deterioration of mortar Specimen $B_{30}{}^\ell$ with freeze-thaw cycles (although it exhibited the highest strength and salt solution resistance[1,*]) appears to be anomalous on first examination and is probably related to its low permeability and large (30 percent) silica fume content. The silica fume is in excess of that needed for complete reaction,[11] resulting in a higher effective water:binder ratio. In addition, previous results indicate that hydration is not complete, and at a w/(c + sf) ratio of 0.45 a relatively large amount of evaporable water still remains in the pores.* It is entrapped during the freeze-thaw cycles as a result of the low permeability of the specimen and results in damage. The greater permeability of Specimens B^H_{30} and B^H_{10} insures greater frost resistance.

CONCLUSIONS

1. Frost resistant mortars complying with ASTM C 666, Procedure B, at two freeze-thaw cycles a day can be made at a w/(c + sf) ratio of 0.60 by replacing 10 percent of cement with silica fume. No air-entraining agents or superplasticizers are required.

2. Frost resistance is improved by silica fume addition because of the increase in pore volume in pore sizes of 20,000 to 2000 and 2000 to 350 nm, and to the discontinuity of these pores.

3. The increased pore volume responsible for frost resistance occurs at the interfacial zone around sand grains.

4. Although they possess greater strength, mortars formed at a w/(c + sf) ratio of 0.45 and 30 percent silica fume content do not possess good frost resistance.

ACKNOWLEDGMENTS

The authors wish to thank G. Chan for his fine work in helping to perform the experiments. This paper is a contribution from the Division of Building Research, National Research Council of Canada.

REFERENCES

1. Feldman, R. F., and Cheng-Yi, Huang, "Microstructural Properties of Blended Cement Mortars and Their Relation to Durability," RILEM Seminar on Durability of Concrete Structures under Normal Outdoor Exposure, Hanover, Mar. 1984, pp. 1-9.

2. Mehta, P. K., and Gjørv, O. E., "Properties of Portland Cement Concrete Containing Fly Ash and Condensed Silica-Fume," *Cement and Concrete Research,* V. 12, No. 5, Sept. 1982, pp. 587-595.

3. Traetteberg, Aud, "Frost Action in Mortar of Blended Cement with Silica Dust," *Durability of Building Materials and Components,* STP-691, ASTM, Philadelphia, 1980, pp. 536-548.

4. Carette, G. G., and Malhotra, V. M., "Silica Fume in Concrete—Preliminary Investigation," *CANMET Report* No. M-38-82-1E, Energy, Mines and Resources Canada, Ottawa, Feb. 1982, 15 pp.

5. Virtanen, Jorma, "Freeze-Thaw Resistance of Concrete Containing Blast-Furnace Slag, Fly Ash or Condensed Silica Fume," *Fly Ash, Silica Fume, Slag and Other Mineral By-Products in Concrete,* SP-79, American Concrete Institute, Detroit, 1983, pp. 923-942.

6. Sorensen, Eigil V., "Freezing and Thawing Resistance of Condensed Silica Fume (Microsilica) Concrete Exposed to Deicing Chemicals," *Fly Ash, Silica Fume, Slag and Other Mineral By-Products in Concrete,* SP-79, American Concrete Institute, Detroit, 1983, pp. 709-718.

7. Feldman, R., "Pore Structure Damage in Blended Cements Caused by Mercury Intrusion," *Journal,* American Ceramic Society, V. 67, No. 1, Jan. 1984, pp. 30-33.

8. Litvan, G. G., "Air Entrainment in the Presence of Superplasticizers," ACI JOURNAL, *Proceedings* V. 80, No. 4, July-Aug. 1983, pp. 326-331.

9. Carles-Giberques, A.; Grandet, J.; and Olivier, J. P., "Contact Zone Between Cement Paste and Aggregate," *Bond in Concrete,* Applied Science Publishers, London, 1982, pp. 24-33.

10. Barnes, R. D.; Diamond, S.; and Dolch, W. L., "Micromorphology of the Interfacial Zone Around Aggregates in Portland Cement Mortar," *Journal,* American Ceramic Society, V. 61, No. 1-2, Jan.-Feb. 1979, pp. 21-24.

11. Sellevold, E. J.; Bager, D. M., Klitgard Jensen, E.; and Knudsen, T., "Silica Fume Cement Paste—Hydration and Pore Structure," *Condensed Silica Fume in Concrete,* BML 82610, Norwegian Institute of Technology, Trondheim, Feb. 1982, pp. 20-50.

*See footnote, p. 740.

This paper is being distributed in reprint form by the Institute for Research in Construction. A list of building practice and research publications available from the Institute may be obtained by writing to the Publications Section, Institute for Research in Construction, National Research Council of Canada, Ottawa, Ontario, K1A 0R6.

Ce document est distribué sous forme de tiré-à-part par l'Institut de recherche en construction. On peut obtenir une liste des publications de l'Institut portant sur les techniques ou les recherches en matière de bâtiment en écrivant à la Section des publications, Institut de recherche en construction, Conseil national de recherches du Canada, Ottawa (Ontario), K1A 0R6.