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RÉSUMÉ

L'auteur poursuit l'étude d'une méthode mise au point précédemment et permettant d'accroître la résistance du béton au gel et au dégel par l'addition de particules poreuses ayant une structure de pores définie. On a évalué l'aptitude de la vermiculite et de deux types de pierre ponce et de perlite à servir d'additifs, et comparé leur performance à celle d'une brique étudiée plus tôt. Parmi les minéraux testés, la vermiculite, un type de pierre ponce et un type de perlite assurent une excellente résistance au gel et au dégel pour les pâtes de ciment (rapports eau/ciment = 0,48 et 0,42), le mortier (rapport eau/ciment = 0,75) et le béton (rapport eau/ciment = 0,63).

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Further Study of Particulate Admixtures for Enhanced Freeze-Thaw Resistance of Concrete

by G. G. Litvan

Investigation of a previously developed method of increasing the resistance of concrete to freezing and thawing by the addition of porous particulates of specified pore structure is continued. Vermiculite and two grades of pumice and perlite were tested for suitability as additives, and their performance compared with that of a previously examined brick. Of the mineral tested, vermiculite, one pumice, and one perlite provide excellent resistance to freezing and thawing of cement pastes (water-cement ratios = 0.48 and 0.42), mortar (water-cement ratio = 0.75), and concrete (water-cement ratio = 0.63).

Keywords: admixtures; bricks; cement pastes; compressive strength; concretes; **freeze-thaw durability**; mortars (material); **perlite**; porosity; **pumice**; **vermiculite**.

The resistance of hydrated cement paste and concrete to freezing and thawing can be improved significantly by the addition of porous particulates with the pore characteristics of 30 percent total porosity and pore diameters mainly between 0.3 and 2 μ.[1] The potential benefits of replacing a conventional air-entraining agent by a particulate admixture are significant. It is extremely difficult to control air content when mixing and placing concrete under many conditions (Whiting and Stark[2] list 23 factors that affect air entrainment). Using a porous-particulates admixture would eliminate practically all such problems and permit good control of air content. Moreover, the use of particles would enable controlled air entrainment in two areas of growing importance: (1) concrete made with blended cements, particularly with fly ash; and (2) concrete formed or compacted by extrusion, dry-impaction, vacuum dewatering, or other similar techniques. The present inability to control air entrainment in fly-ash concrete is the major impediment to its use in northern countries.

Particulate admixtures commercially marketed for industrial use must be effective and inexpensive and must not react detrimentally with the constituents of concrete. Waste materials from manufacturing processes, such as clay or refractory brick wastes, are usually unsuitable because they are not uniform. Effective mixtures may be obtained by crushing and sieving good-quality bricks, but this is an expensive process. Diatomaceous earth must be excluded because certain types have a tendency to react with the alkali in concrete. A survey of potentially suitable minerals shows that the pore characteristics of perlite, vermiculite, and pumice meet the requirements in terms of both total porosity and pore size distributions (Table 1), are often available in the required grain size, and are quite inexpensive. For these reasons, their effectiveness as admixtures was investigated.

A previous work was concerned mainly with the effects of crushed brick, diatomaceous earth, and sintered fly ash on the freeze-thaw resistance of cement paste.[1] The present study assesses the performance of vermiculite, perlite, and pumice in protecting cement paste, mortar, and concrete from damage due to freezing and thawing. For comparison, a previously investigated crushed brick was included in the test program.

Table 1 — Properties of materials used as additives

Particulate samples	True density, g/ml	Porosity volume, percent	Pores with 0.3 to 2 μm diameter: Fraction of apparent volume, percent	Pores with 0.3 to 2 μm diameter: Fraction of porosity, percent
Brick A	2.830	38.4	33.3	86.7
Vermiculite	1.735	97.1	62.8	64.0
Pumice RH	2.218	69.3	18.3	34.4
Pumice LK	2.585	47.3	7.2	15.3
Perlite LW	1.010	97.4	20.0	20.5
Perlite HW	0.815	86.3	28.7	33.2

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RESEARCH SIGNIFICANCE

Materials with a particular pore structure when used as admixtures are capable of protecting cement paste, mortar, and concrete from the detrimental effects of freezing and thawing. Certain types of perlite, vermiculite, and pumice have been found to be well-suited as admixtures and are in good supply and inexpensive. This method of protection against freezing and thawing promises to be more reliable, and thus more effective, than air entrainment. In addition, fly ash, extruded, dry impacted, and vacuum concrete might also be protected, though this is not possible or practical at the present time.

EXPERIMENTAL

Materials

Brick — Commercially fired building brick, previously designated A.[1]

Vermiculite — U.S. origin, expanded, construction grade.

Perlite — U.S. origin, expanded in Canada, construction grade; the two types are designated HW and LW.

Pumice RH — Icelandic origin, brown.

Pumice LK — Icelandic origin, black.

Cement — Portland cement Type 10.

Aggregate — Crushed limestone of 16 mm maximum dimension.

The grain size of all the admixtures was between 1.2 and 0.3 mm (16 to 50 mesh).

Test methods

Porosity and pore size distribution were determined by a mercury intrusion porosimeter (420 MPa maximum pressure) and density by an air compression pycnometer using helium gas. Water absorption was measured by a vacuum electrobalance. Freezing and thawing resistance was determined in conformity with the requirements of ASTM Standard C 666-80.[3]

Mix design

Previous research[1] established that a 10 percent concentration of Brick A particles by weight of cement was necessary to render cement paste frost resistant. A 60 ml bulk volume of brick provides this concentration in 6000 g of cement in mortar or cement mix. This figure was adopted as the standard amount for all admixtures to achieve similar particle concentrations for all specimens.

Because the particle size of all the additives was the same, the number of particles in each mix was approximately equal, although deviations from the target value could be expected because of differences in particle size distribution and shape. As the primary objective of this work was to establish the effectiveness of the additives in absolute and not necessarily in relative terms, effort was made to maintain only approximately uniform concentration levels. Mixes were prepared with single (high concentration) and double (low concentration) doses.

Table 2 — Admixture concentration and spacing factor of cement paste and mortar specimens at low (L) and high (H) dosage levels

Particulate samples	Number of particles per mix, thousands		Concentration, weight percent		Spacing factor, mm	
	L	H	L	H	L	H
Brick A	205	410	10.0	20.0	0.62	0.49
Vermiculite	673	1345	1.2	2.5	0.41	0.32
Pumice RH	247	494	4.9	9.8	0.57	0.45
Pumice LK	248	496	4.9	9.8	0.57	0.45
Perlite	233	466	1.2	2.3	0.58	0.46

The number of particles in a single dose and the spacing in the hardened paste can be calculated as follows. As the true density of brick is 2.83 g/ml, the true volume of brick particles having 60 ml bulk volume is $V = 60/2.83 = 21.2$ ml. The brick particle has 36 percent porosity; thus, the apparent volume is $V_A = 21.2/0.64 = 33.13$ ml. With an average diameter of 0.067 cm, the volume of a single particle is $V_P = 1.61 \times 10^{-4}$ ml. The number of particles in a standard dose is thus $V_A/V_P = 33.13/1.61 \times 10^{-4} = 2.06 \times 10^5$. Similar calculations for the other additives result in the values given with weight concentrations in Table 2.

The maximum distance between particles at any point within the paste, or the spacing factor, can also be calculated. The volume of the hardened paste (in cube form) was 367.08 ml, and contained 1.96×10^5 brick particles when the single dose was added. If the volume of a cube surrounding the particle is 187×10^{-5} cm^3, the distance between particles is 1.23 mm, or the spacing factor is 0.62 mm. The values obtained for the other additives at the two concentration levels are also given in Table 2. The calculated spacing factor values could not be verified experimentally because attempts to determine them by microscopical examination[4] failed due to insufficient contrast between the particles and the matrix.

Twelve mixes containing each of the six additives, with water-cement ratios of 0.42 and 0.48, were prepared in addition to a plain cement which served as reference. Mortar specimens at water-cement ratio = 0.75 and cement-sand ratio = 2.75 were also fabricated.

Because of water adsorption, the addition of porous particles to the cement mix can alter the water-cement ratio. The extent of water gain depends on the adsorptive capacity of the porous particle, its water content at the time of mixing, the rates of hydration and adsorption, the water-cement ratio of the mix, and other factors. It is not possible to calculate accurately the

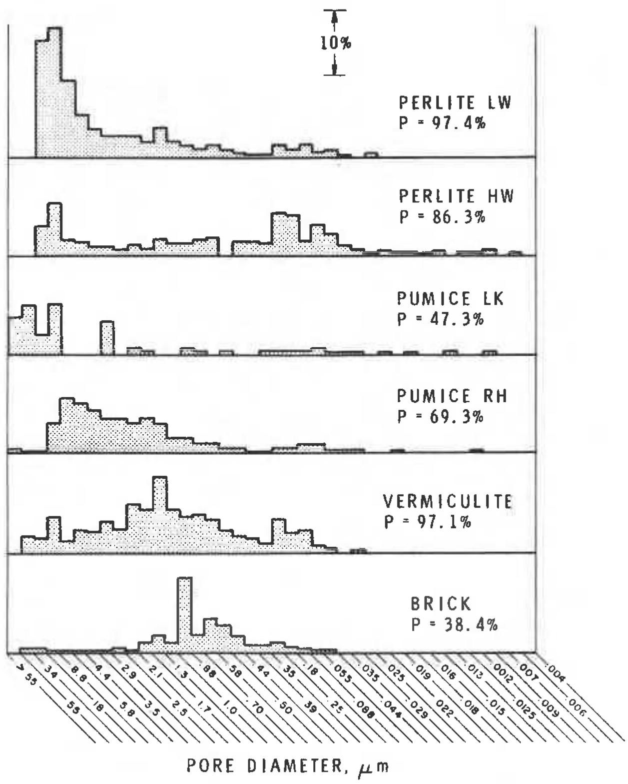

Fig. 1—Pore size distribution of particulates

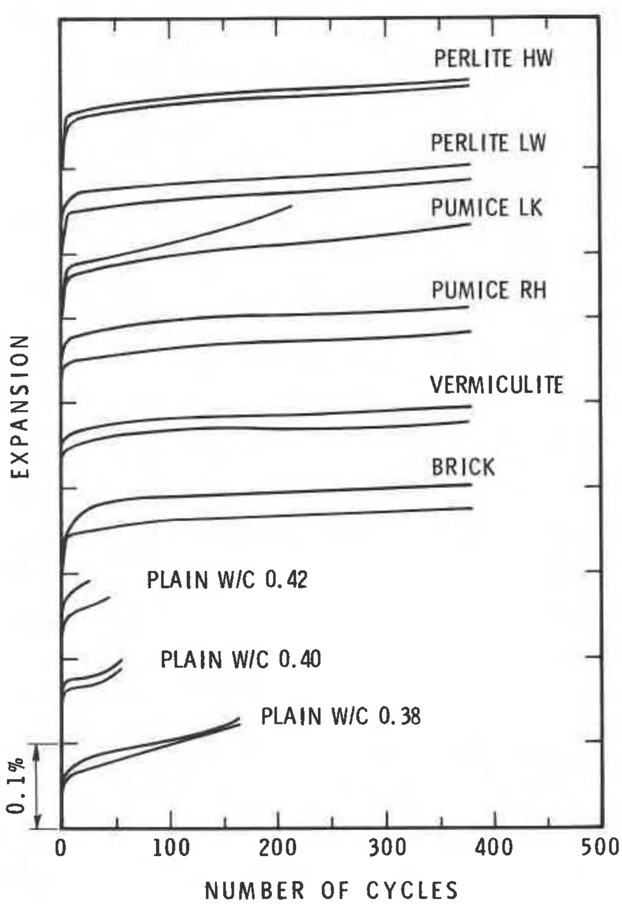

Fig. 2—Residual expansion as a function of number of freeze-thaw cycles of duplicate cement paste specimens with (water-cement ratio = 0.42) and without (water-cement ratios = 0.38, 0.40, and 0.42) particulate admixture in low concentration

Table 3 — Water-cement ratio, number, and concentration of particles, spacing factor, and compressive strength of concrete containing low (L) and high (H) concentration of additives

Particulate samples	Water cement ratio		Number per bar, thousands		Concentration as weight percent of cement		Spacing factor, mm		Compressive strength, MPa	
	L	H	L	H	L	H	L	H	L	H
Brick A	0.60	0.68	655	1310	26	52	0.58	0.29	31.3	30.2
Vermiculite	0.63	0.76	225	449	3.3	6.6	0.32	0.16	28.9	20.5
Pumice RH	0.63	0.69	83	165	12.9	25.9	0.43	0.21	29.4	25.1
Pumice LK	0.63	0.66	83	165	25.3	50.6	0.43	0.22	25.1	21.7
Perlite	0.63	0.64	78	155	3.1	6.1	0.43	0.20	25.2	24.4
Plain concrete	0.60								31.3	

amount of water withdrawn from the mix by the particles, and therefore not possible to determine the effective water-cement ratio. To evaluate more realistically the effectiveness of the admixtures relative to plain cement paste, standard mixes containing no admixture were prepared with lower water-cement ratios than the test mixes. For example, in the series with nominal 0.42 water-cement ratio, the standards with 0.40 and 0.38 water-cement ratio are also included.

The cement paste and mortar mixes were prepared according to the provisions of ASTM C 305.[5] The particulates were added with the dry cement. Bars 25 x 25 x 300 mm were fabricated and the change in their length measured according to ASTM C 490-77.[6]

Concrete mixes were prepared by hand mixing, with a cement:sand:aggregate ratio of 1:2.25:2.75. The water-cement ratios for the different mixes were chosen to maintain constant slump. The mixes, particle concentrations, and spacing factors are listed in Table 3. Two bars 75 x 75 x 300 mm were fabricated from each mix.

The specimens were cured in a fog room for 28 days before testing.

RESULTS AND DISCUSSION

Porosity

According to values given in Column 3 of Table 1, all six materials meet the previously formulated[1] requirement of porosity in excess of 30 percent volume.

Pore size distribution

As shown in Fig. 1, the pore volume in the 0.30 to 2.0 μm range varies substantially in terms of both the apparent volume of the solid (Column 4 of Table 1) and the fraction of the porosity (Column 5 of Table 1). Optimally, the particulate matter should have high porosity, all of it in the critical pore sizes (~ 0.3 – 2 μm). In such cases durability of the paste can be achieved with the minimum number of particles without introducing excessive porosity, which will decrease strength and may have other detrimental effects.

Brick A is the most efficient additive, with 87 percent of its porosity in the required size range, while

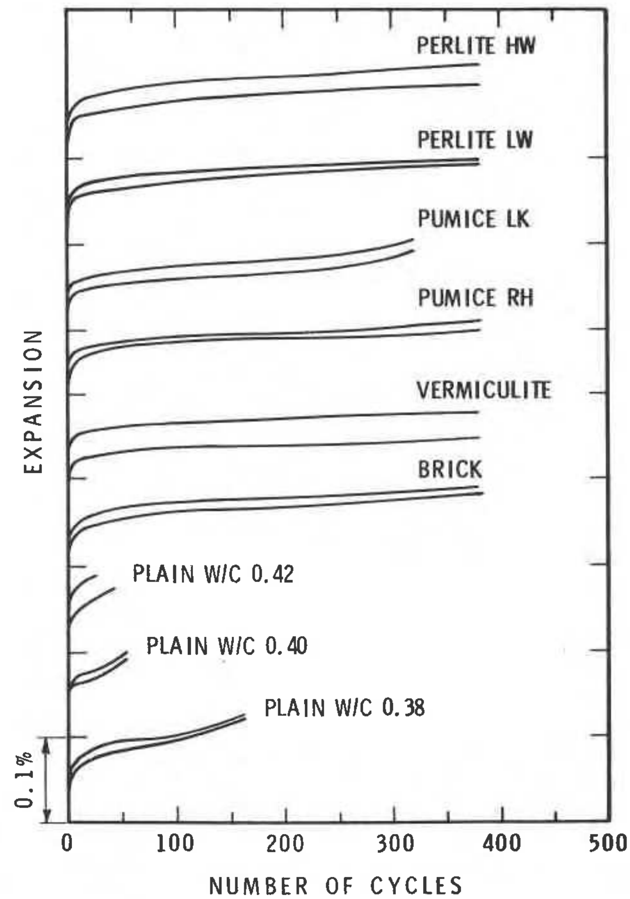

Fig. 3—Residual expansion as a function of number of freeze-thaw cycles of duplicate cement paste specimens with (water-cement ratio = 0.42) and without (water-cement ratios = 0.38, 0.40, and 0.42) particulate admixture in high concentration

Pumice LK has an overall low porosity with only 15 percent in pores of the required size.

Density

As shown in Table 1, Column 2, the true densities of the materials range from 2.83 to 0.81 g/ml. No difficulties were experienced in mixing, even with Perlite HW; the particles dispersed satisfactorily and showed no tendency to float to the surface.

Resistance to freezing and thawing

The length changes of hydrated cement paste specimens (water-cement ratio 0.42 and 0.48) as a function of a number of freeze-thaw cycles are shown in Fig. 2 through 5. Residual expansion is a reliable and sensitive indicator of freeze-thaw durability;[7] in susceptible solids, residual expansion significantly increases with the number of cycles. Plotted as a function of the number of cycles, the curve becomes exponential before failure.

The present experiments confirm that porous particles do provide protection against frost action. The plain, unprotected pastes survived fewer cycles than did those containing the particulate admixture, even though the reference pastes had lower water-cement ratios. It is possible that the water-cement ratio of the particle-pro-

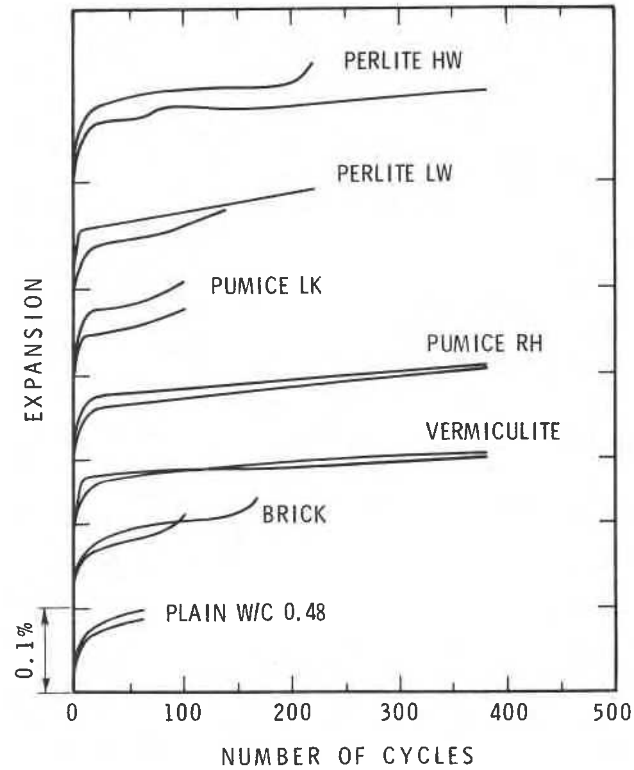

Fig. 4—Residual expansion as a function of the number of freeze-thaw cycles of duplicate cement paste specimens (water-cement ratio = 0.48) with and without particulate admixture in low concentration

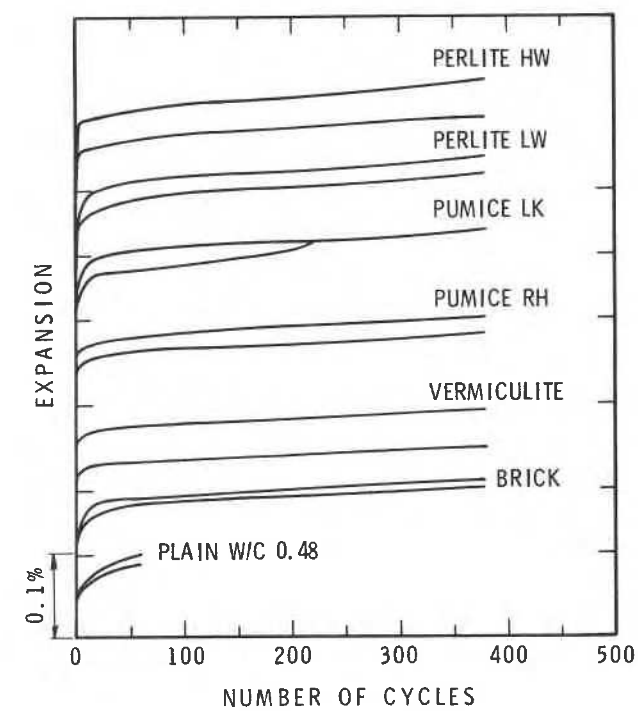

Fig. 5—Residual expansion as a function of the number of freeze-thaw cycles of duplicate cement paste specimens (water-cement ratio = 0.48) with an without particulate admixture in high concentration

tected paste was less than the nominal value. Based on the water adsorption values of the additives, it is estimated that due to the presence of the particles, the water-cement ratio of the mixes could have been lowered

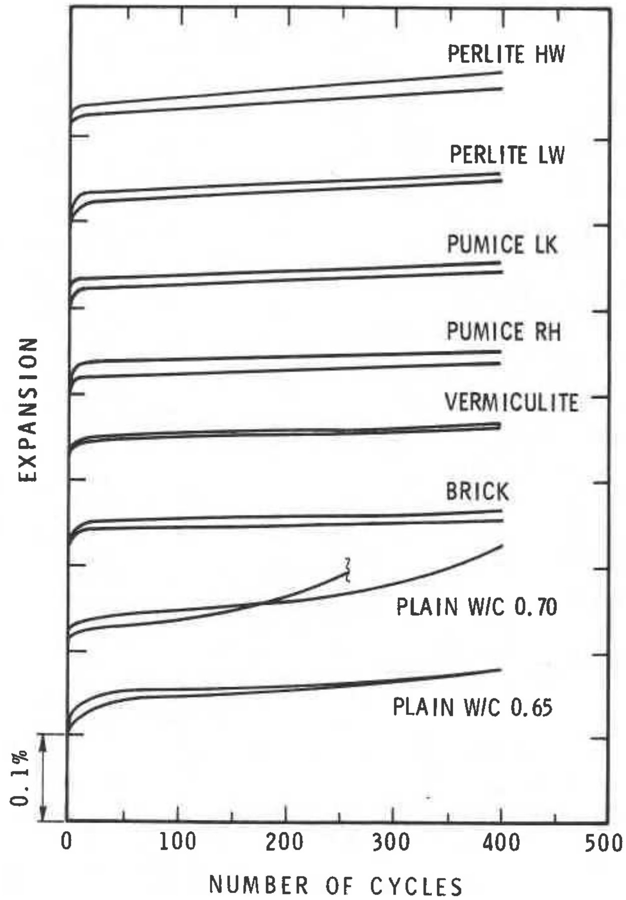

Fig. 6—Residual expansion as a function of number of freeze-thaw cycles of duplicate mortar specimens with (water-cement ratio = 0.75) and without (water-cement ratios = 0.70 and 0.65) particulate admixture in low concentration

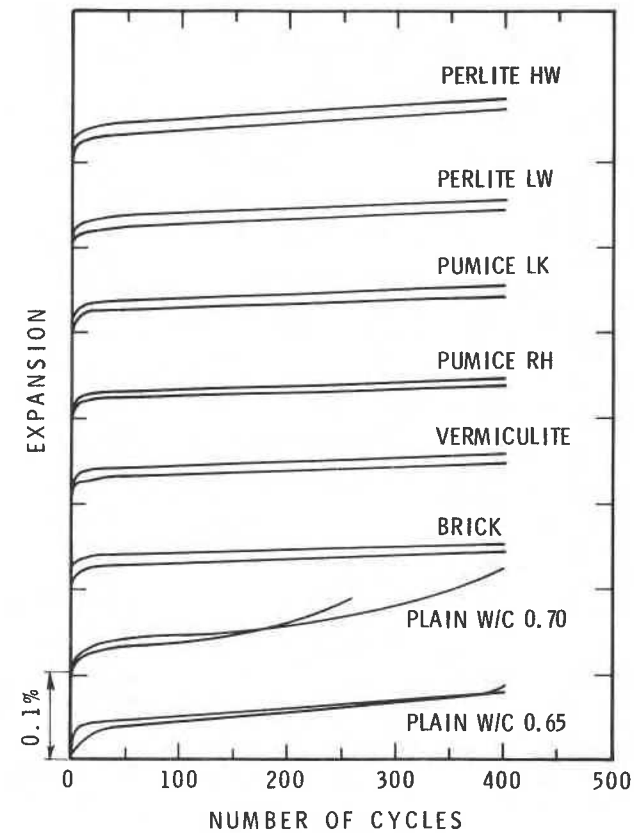

Fig. 7—Residual expansion as a function of number of freeze-thaw cycles of duplicate mortar specimens with (water-cement ratio = 0.75) and without (water-cement ratios = 0.70 and 0.65) particulate admixture in high concentration

to between 0.395 and 0.380 from the nominal 0.42 design value. Pick-up of a large quantity of water by the admixture is not probable; however, if substantial amounts of water had accumulated in the pores of the particles, this would have made them ineffective and susceptible to frost.

While the uncertainty of the true water-cement ratio water makes comparative evaluation somewhat difficult, whether due to the protective action of the particles or to the water-reducing effect, from a practical point of view only the de facto resistance to freezing and thawing matters. For example, sprinkling additional particles on surfaces where the water-cement ratio is usually increased by the finishing operation could be an effective method of providing extra protection for the top surface of sidewalks and roadways.

Of the six materials studied, vermiculite, Pumice RH, and Perlite LW showed consistently good results. Surprisingly, the specimens made of the high water-cement ratio paste containing brick in low concentration failed after 100 and 160 cycles (Fig. 4), a finding in need of further investigation. In every other instance (Fig. 2, 3, and 5) brick appeared to give excellent protection (indicated by the very low slope of the curves). The paste containing Pumice LK, on the other hand, showed consistently poor durability; thus this additive must be judged unsuitable.

The mortar specimens protected with any of the particulate admixtures showed good resistance to freezing and thawing (Fig. 6 and 7). No indication of susceptibility can be detected even with Pumice LK at low concentration. According to the residual expansion and relative dynamic modulus of elasticity results [Fig. 8(a) and (b)], concrete specimens containing particulate admixtures in high concentration showed no freeze-thaw susceptibility, except for Pumice LK. At low additive concentration, Pumice LK and Perlite LW proved to be nondurable [Fig. 9 (a) and (b)]. The plain reference concrete failed after 60 cycles despite its lower water-cement ratio (0.60 versus 0.65), and even at water cement ratio = 0.56 unprotected concrete was destroyed after 300 cycles. Vermiculite, Pumice RH, and brick and perlite additives provided very good protection against freezing and thawing.

Compressive strength

In general, the addition of particles (with the exception of brick) lowered compressive strength. Values for concrete cylinders cured for 28 days are given in the last column of Table 3. At the lower particle concentrations the reduction in compressive strength is 7.7 percent for vermiculite, 6.1 percent for Pumice RH, and

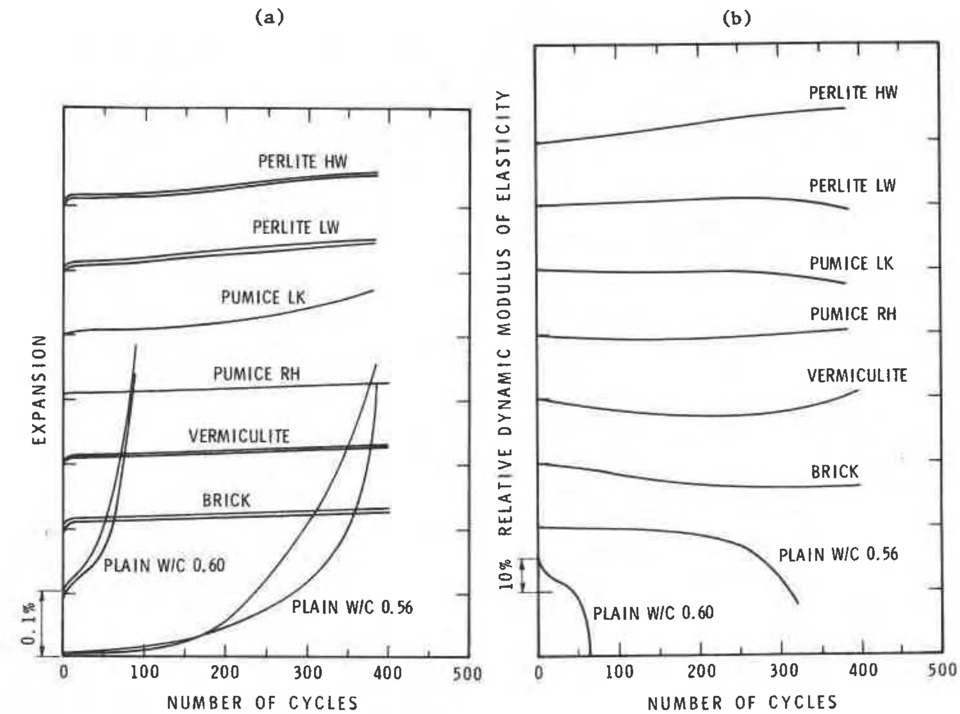

Fig. 8—Concrete without (water-cement ratios = 0.60 and 0.56) and with (water-cement ratio = 0.63) particulate admixture in high concentration: (a) residual expansion (duplicate specimens except for Pumices LK and RH), and (b) relative dynamic modulus of elasticity as a function of the number of freeze-thaw cycles

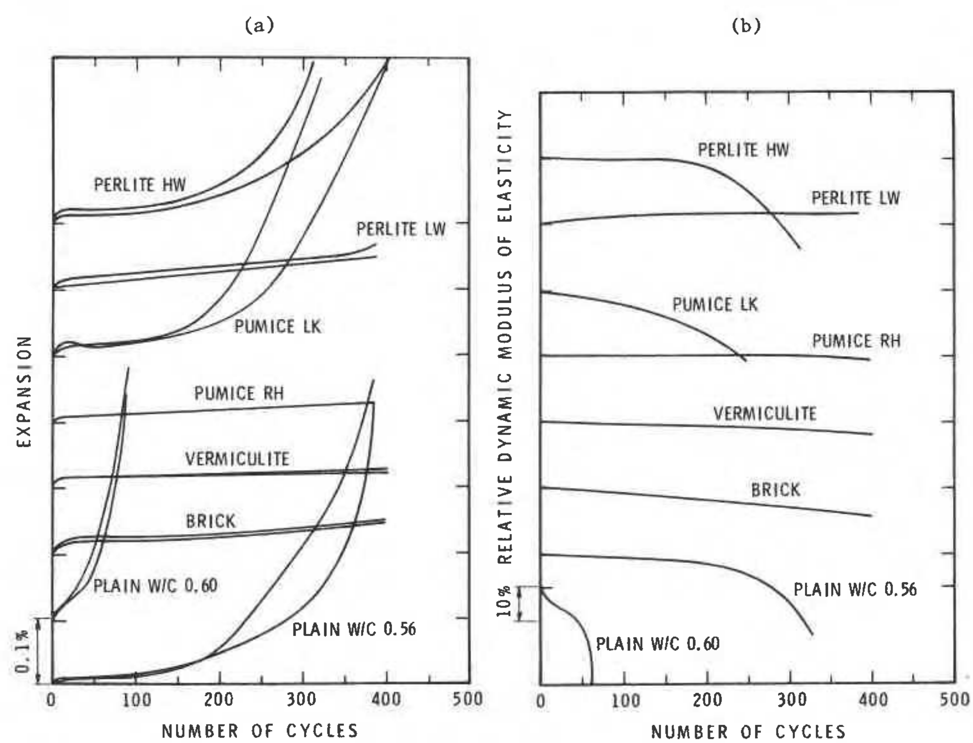

Fig. 9—Concrete without (water-cement ratios = 0.60 and 0.56) and with (water-cement ratio = 0.63) particulate admixture in low concentration: (a) residual expansion (duplicate specimens except for Pumice RH), and (b) relative dynamic modulus of elasticity as a function of the number of freeze-thaw cycles

19.5 percent for Perlite LW. Though undesirable, such a decrease is probably acceptable for many applications. For sidewalks, roadways, and other horizontal surfaces, strength is usually not critical and the compensation of better durability, which is a major concern, appears to be worthwhile. In applications for which high strength is essential brick particles can be used.

CONCLUSIONS

1. The general effectiveness of porous particulate admixtures in providing resistance to freezing and thawing is confirmed; specifically, the effectiveness of Brick A as an admixture designed to increase resistance to freezing and thawing of cement paste, mortar, and concrete is confirmed.

2. Vermiculite, Pumice RH, and Perlite LW admixtures, in the proper amounts, provide good frost resistance to cement, mortar, and concrete.

3. Pumice LK and, to a lesser degree, Perlite LW appear to be the least effective additives of those studied to provide resistance to freezing and thawing.

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