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EFFECTS OF SILICA FUME, LATEX, METHYLCELLULOSE, AND CARBON FIBERS ON THE THERMAL CONDUCTIVITY AND SPECIFIC HEAT OF CEMENT PASTE

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ABSTRACT

Due to their poor conductivity, latex (20–30% by weight of cement), methylcellulose (0.4–0.8% by weight of cement), and silica fume (15% by weight of cement) decreased the thermal conductivity of cement paste by up to 46%. In addition, these admixtures increased the specific heat of cement paste by up to 10%. The thermal conductivity decreased and the specific heat increased with increasing latex or methylcellulose content. Short carbon fibers (0.5–1.0% by weight of cement) either did not change or decreased the thermal conductivity of cement paste, such that the thermal conductivity decreased with increasing fiber content due to the increase in air void content. The fibers increased the specific heat due to the contribution of the fiber-matrix interface to vibration. © *1997 Elsevier Science Ltd*

Introduction

The thermal conductivity and specific heat are properties that are relevant to numerous applications of concrete. A low thermal conductivity is desirable for structures, such as buildings, that need thermal insulation. A high thermal conductivity is desirable for floors and driveways with embedded heaters. A high specific heat is desired for heat retention in a building. Therefore, it is valuable to be able to design a concrete mix so as to have desired values of the thermal conductivity and specific heat (1,2).

The thermal conductivity of concrete increases with increasing moisture content (3–5). It is also increased by using aggregate of a higher thermal conductivity (5). With the exception of lightweight aggregates, the cement paste has a lower thermal conductivity than the aggregate, so lean mixes tend to give higher conductivity; in case of lightweight aggregates, the opposite holds (5). Steel fibers (50 mm long) increase the thermal conductivity of concrete at 30°C from 1.4 to 2.0 W/m·K (6). Welded wire mesh placed along the direction of heat flow increases the thermal conductivity of mortar from 1.0 to 1.5 W/m·K for the case

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TABLE 1
Amounts of Water and Water Reducing Agent (WR) for Each Mix

	Water/cement ratio	WR/cement ratio
Plain	0.45	0
+M	0.32	1%
+L	0.23	0
+SF	0.35	3%
+SF + M	0.35	3%
+M + fibers	0.35	3%
+SF + M + fibers	0.35	3%

Note: L = latex; M = methylcellulose; SF = silica fume.

of 5 mesh layers and to 6.9 W/m·K for the case of 15 mesh layers (7). Both thermal diffusivity and specific heat decrease during the curing of concrete (8).

Carbon fibers decrease the electrical resistivity of concrete (9–15), whereas latex (16) and silica fume (9) increase the electrical resistivity. However, the effect of these admixtures on the thermal conductivity has not been previously reported. In this work, we found that latex and silica fume are effective in decreasing the thermal conductivity, but carbon fibers are not effective in increasing the thermal conductivity. Methylcellulose is an admixture that increases the tensile strength and tensile ductility of cement paste (17) and increases the bond strength with steel rebar/fiber and with carbon fiber (18–20). It was found in this work to be also effective for decreasing the thermal conductivity.

Experimental Methods

Cement paste made from Portland cement (Type I) from Lafarge Corp. (Southfield, MI) was used for the cementitious material. The admixtures used include: 1) latex, a styrene butadiene polymer (Dow Chemical Co., Midland, MI, 460NA) with the polymer making up about 48% of the emulsion and with styrene butadiene in the weight ratio 66:34, such that the latex (20%, 25%, or 30% by weight of cement) was used along with an antifoam (Dow Corning Corp., Midland, MI, #2210, 0.5% by weight of latex); 2) methylcellulose (Dow Chemical Corp., A15-LV, 0.4% by weight of cement), which was used along with a defoamer (Colloids Inc., Marietta, GA, Colloids 1010, 0.13 vol.%); 3) silica fume (Elkem Materials Inc., Pittsburgh, PA, #965, 15% by weight of cement); and 4) carbon fibers, which were isotropic pitch-based and unsized, as obtained from Ashland Petroleum Co. (Ashland, KY), with length = 5 mm and diameter = 10 μm, used in the amount of 0.5% or 1.0% by weight of cement (corresponding to a fiber volume fraction of 0.53% or 1.1%, respectively). The water reducing agent was a sodium salt of a condensed naphthalenesulfonic acid (TAMOL SN, Rohm and Haas Company, Philadelphia, PA) used in amounts as shown in Table 1 for the various mixes. Table 1 also shows the water/cement ratio for each mix. The amounts in Table 1 were chosen in order to maintain the slump at around 170 mm. No aggregate (whether fine or coarse) was used.

A Hobart mixer with a flat beater was used for mixing. For the case of cement pastes containing latex, the latex and antifoam were first mixed by hand for about 1 min. Then this mixture, cement, and water were mixed in the Hobart mixer for 5 min. For the case of pastes containing methylcellulose, methylcellulose was dissolved in water and then fibers (if applicable) and the defoamer were added and stirred by hand for about 2 min. Then this mixture, cement, water, and the water reducing agent (and silica fume, if applicable) were mixed in the Hobart mixer for 5 min. After pouring the mix into oiled molds, an external vibrator was used to decrease the amount of air bubbles. The specimens were demolded after 1 day and then allowed to cure at room temperature in air (relative humidity = 40%) for 28 days. Testing was performed at 28 days.

The thermal conductivity (in W/m·K) was given by the product of the thermal diffusivity (in cm^2/s), specific heat (in J/g·K), and density (in g/cm^3). For measuring the thermal diffusivity, the laser flash method was used. In this method, a pulsed laser (Coherent General Co., Massachusetts) and a computer with Labtech software and data acquisition board were used. The specimen was in the form of a disc with a diameter of 13 mm and a thickness of 2 mm. Sample preparation for laser diffusivity measurement involved: 1) polishing both sides of the sample, 2) coating both sides of the sample with gold for thermal contacts, and 3) coating one of the sides (the side on which the laser beam would hit) with carbon (to avoid reflection of the laser beam, because carbon is black). The temperature of the specimen at the side without carbon coating was measured after the laser flash as a function of time by using a thermocouple. From the temperature vs. time curve, the thermal diffusivity was calculated by using an equation from Ref. 21. Six specimens of each type were tested. A Perkin-Elmer Differential Scanning Calorimeter (DSC-7) with UNIX Specific Heat Software was used for measuring the specific heat. A three-curve analysis method was used; it involved obtaining DSC sample, baseline, and reference material data. Sapphire was selected as a reference material. The specimen was in the form of a disc of diameter 6 mm and thickness 1 mm. Six specimens of each type were tested.

Results and Discussion

Table 2 shows the thermal diffusivity, specific heat, density, thermal conductivity, and air void content of various cement pastes at room temperature. The thermal conductivity decreased significantly and monotonically with increasing latex content, even though the air void content decreased monotonically and the specific heat increased monotonically. This is because both the thermal diffusivity and the density decreased with increasing latex content. That the thermal diffusivity decreased with increasing latex content is due to the insulating nature of latex. That the specific heat increased with latex content is due to the high specific heat of the latex and the decrease in air void content.

Methylcellulose (0.6% by weight of cement) was as effective as latex (20% by weight of cement) for decreasing the thermal conductivity, mainly because the former gave lower thermal diffusivity (but higher specific heat) than the latter. For the same reason, methylcellulose (0.8% by weight of cement) was as effective as latex (25% by weight of cement) for decreasing the thermal conductivity. The air void content was higher for the former than the latter (in each comparison), but the density was about the same.

Silica fume (15% by weight of cement) was as effective as latex (between 20% and 25% by weight of cement) and methylcellulose (between 0.6% and 0.8% by weight of cement) for decreasing the thermal conductivity, mainly because the former gave lower density (but

TABLE 2
Thermal diffusivity, specific heat, density, and thermal conductivity of cement pastes at room temperature

Cement paste	Thermal diffusivity (mm^2/s) (±0.03)	Specific heat (J/g.K) (±0.001)	Density (g/cm^3) (±0.02)	Thermal conductivity (W/m.K) (±0.03)	Air void content (%) (±0.02)
Plain	0.37	0.703	1.99	0.52	2.32
+latex (20% by weight of cement)	0.29	0.712	1.83	0.38	1.53
+latex (25% by weight of cement)	0.25	0.723	1.79	0.32	1.25
+latex (30% by weight of cement)	0.22	0.736	1.76	0.28	1.10
+methylcellulose (0.4% by weight of cement)	0.31	0.732	1.86	0.42	2.12
+methylcellulose (0.6% by weight of cement)	0.28	0.737	1.84	0.38	2.10
+methylcellulose (0.8% by weight of cement)	0.24	0.742	1.81	0.32	2.07
+silica fume	0.27	0.765	1.72	0.36	3.14
+silica fume + methylcellulose*	0.25	0.771	1.69	0.33	2.97
+methylcellulose* + fibers (0.5% by weight of cement)	0.33	0.761	1.73	0.44	3.33
+methylcellulose* + fibers (1.0% by weight of cement)	0.26	0.792	1.66	0.34	3.97
+silica fume + methylcellulose* + fibers (0.5% by weight of cement)	0.22	0.789	1.62	0.28	4.36

*0.4% by weight of cement.

higher specific heat) than the latter. The low density of the cement paste with silica fume is related to the high air void content.

The combined use of silica fume (15% by weight of cement) and methylcellulose (0.4% by weight of cement) gave lower thermal conductivity than the use of silica fume alone, mainly because the former gave lower thermal diffusivity (but higher specific heat) and lower density than the latter. In spite of the low density for the former, the air void content was lower for the former.

Silica fume (15% by weight of cement) was more effective than methylcellulose (0.4–0.8% by weight of cement) in increasing the specific heat. Methylcellulose (0.6–0.8% by weight of cement) was more effective than latex (20–30% by weight of cement) in increasing the specific heat. The high effectiveness of silica fume is due to the interface between silica fume and the cement matrix, as silica fume itself is not high in specific heat. The high effectiveness of methylcellulose, even at a low concentration, is probably due to the liquid solution form of methylcellulose added to the mix, in contrast to the solid dispersion form of latex added to the mix. The solution probably allowed more uniform distribution in the mix than the dispersion. Due to the high effectiveness of both silica fume and methylcellulose, their combined use resulted in a particularly large specific heat.

In spite of the relatively high thermal conductivity of carbon fibers, the addition of carbon fibers to cement paste with methylcellulose (whether with or without silica fume) was not effective for increasing the thermal conductivity. This is because of the increase in air void content (decrease in density) with increasing fiber content. In the absence of silica fume, with fibers at 0.5% by weight of cement, the thermal conductivity was essentially the same as that without fibers (but with methylcellulose); with fibers at 1.0% by weight of cement, the thermal conductivity was lower than that without fibers. In contrast, the electrical resistivity decreases monotonically with increasing carbon fiber content, even beyond a fiber content of 1% by weight of cement (22). The apparent contradiction between the electrical resistivity and thermal conductivity in their variation with fiber content is because carbon fibers are more electrically conductive than concrete by 10 orders of magnitude, whereas they are more thermally conductive than concrete by 1–2 orders only. As a result, voids are more detrimental to the thermal conductivity than to the electrical conductivity.

Whether with or without silica fume, the specific heat was increased by fiber addition. The specific heat also increased with increasing fiber content. This effect is due to the vibration in the form of slippage at the fiber-matrix interface because the specific heat of graphite is not high. In spite of the specific heat increase, the thermal conductivity failed to increase upon fiber addition.

In the presence of silica fume, the thermal conductivity was decreased by fibers in the amount of just 0.5% by weight of cement because the air void content was higher when silica fume was present. The cement paste with silica fume, methylcellulose (0.4% by weight of cement), and fibers (0.5% by weight of cement) gave: 1) one of the lowest thermal diffusivity and one of the lowest thermal conductivity (same as the paste with latex in the amount of 30% by weight of cement) among all the pastes investigated, 2) the second highest specific heat (just lower than that of the paste with methylcellulose and fibers in the amount of 1.0% by weight of cement) among all the pastes investigated, and 3) the lowest density (the highest air void content) among all the pastes investigated. Because latex (20–30% by weight of cement) is more expensive than fibers (0.5% by weight of cement), methylcellulose (0.4–0.8% by weight of cement), or silica fume (15% by weight of cement), the paste with silica fume, methylcellulose, and fibers is less expensive than that with latex (30% by weight of cement) and thus it is recommended for use in attaining low thermal conductivity or low thermal diffusivity. Because fibers are more expensive than silica fume, the paste with silica fume, methylcellulose, and fibers (0.5% by weight of cement) is less expensive than that with methylcellulose and fibers (1.0% by weight of cement) and thus it is recommended for use in attaining high specific heat. This paste also exhibited high tensile strength (1.88 MPa, compared to 0.88 MPa for plain cement paste), high tensile ductility (0.0173%, compared to 0.004% for plain cement paste), and high tensile modulus (14 GPa, compared to 10.9 GPa for plain cement paste); the high tensile strength and tensile ductility are mainly due to the fibers, whereas the high tensile modulus is mainly due to the silica fume (22).

Conclusion

Silica fume (15% by weight of cement), latex (20–30% by weight of cement), and methylcellulose (0.4–0.8% by weight of cement) were effective for decreasing the thermal conductivity of cement paste by up to 46%, due mainly to the relatively low conductivity of these admixtures and also due to the low density provided to the paste by these admixtures.

The specific heat was increased by addition of silica fume, latex, methylcellulose, or carbon fibers, such that silica fume was most effective for increasing the specific heat, which was increased by 9%.

The thermal conductivity of cement paste decreased and the specific heat increased with increasing latex or methylcellulose content. Methylcellulose (0.6–0.8% by weight of cement) was as effective as latex (20–25% by weight of cement) for decreasing the thermal conductivity. Methylcellulose (0.6–0.8% by weight of cement) was more effective than latex (20–30% by weight of cement) for increasing the specific heat.

The addition of short carbon fibers failed to increase the thermal conductivity of cement paste, due to the increase in air void content. The thermal conductivity was either not changed or decreased by addition of carbon fibers. The greater the fiber content, the lower the conductivity.

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