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Communication

Increasing the specific heat of cement paste by admixture surface treatments

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Abstract

The specific heat of cement paste was increased by 12% and the thermal conductivity was decreased by 40% by using as admixtures silane-treated silica fume and silane-treated carbon fibers. The specific heat was increased by the carbon fiber addition, due to fiber-matrix interface slippage. The increase was in the order: as-received fibers, ozone-treated fibers, dichromate-treated fibers, and silane-treated fibers, due to the increasing contribution of the movement of the fiber-matrix covalent coupling. The specific heat was increased by the silica fume addition, due to slippage at the interface between silica fume and cement. The increase was enhanced by silane treatment of the silica fume. Silane treatment of carbon fibers decreased the thermal conductivity.

Keywords: Physical properties; Fiber reinforcement; Cement paste; Silica fume; Silane

The specific heat of a material is the amount of heat required to heat up 1 g of the material by 1°C. A high specific heat means high ability for retaining heat—an ability that is desirable for energy conservation in buildings. It has been previously reported that admixtures (i.e., silica fume, latex, methylcellulose, or carbon fibers) increase the specific heat of cement paste [1]. For example, the addition of silica fume in the amount of 15% by weight of cement increases the specific heat by 9%; the addition of methylcellulose in the amount of 0.4% by weight of cement increases the specific heat by 4% [1]. The surface treatment of admixtures such as silica fume [2–5] and carbon fibers [4,5] has been reported to improve the mechanical properties, decrease the air void content, and improve the workability of cement paste. A particularly effective surface treatment involves the use of silane-coupling agent [3–5]. As the effect of admixture surface treatment on the specific heat has not been previously investigated, this paper is aimed at studying this effect. We found that admixture surface treatment increases the specific heat of cement paste.

In addition to a high specific heat, a low thermal conductivity is desired for the purpose of thermal insulation of buildings. It has been reported that admixtures (i.e., silica fume, latex, or methylcellulose) decreases the thermal diffusivity, thereby decreasing the thermal conductivity [1]. It has also been reported that the addition of carbon fibers in the amount of 0.5% by weight of cement increases the thermal diffusivity, thereby increasing the thermal conductivity [1]. The secondary objective of this study is to investigate the effect of admixture surface treatment on the thermal conductivity of cement paste.

The admixtures investigated in this work are silica fume, methylcellulose (used together with a defoamer), and short carbon fibers. The addition of silica fume to concrete is effective for increasing the compressive strength [6–9], decreasing the drying shrinkage [8,9], increasing the abrasion resistance [10], increasing the bond strength with the reinforcing steel [11,12], and decreasing the permeability [13]. Cement reinforced with short carbon fibers is attractive due to its high flexural strength, toughness, and low drying shrinkage, in addition to its strain sensing ability [10,14–24]. Silica fume and methylcellulose are used along with carbon fibers in order to help the dispersion of the fibers in the cement mix [18].

1. Methods

The carbon fibers were isotropic pitch-based, unsized, and of length ~5 mm, as obtained from Ashland Petroleum Co. (Ashland, Kentucky, USA). The fiber properties are shown in Table 1 of Ref. [4]. As-received and three types of surface-treated fibers were used. The fiber content was 0.5% by weight of cement. The surface treatments involved (a) ozone (O_3), (b) an aqueous solution of potassium dichromate ($K_2Cr_2O_7$, 30 wt%) and sulfuric acid (H_2SO_4, 40 wt%, which enhances the oxidation ability), and (c) silane. The

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ozone treatment for surface oxidation involved exposure of the fibers to O_3 gas (0.6 vol%, in O_2) at 160°C for 5 min. Prior to O_3 exposure, the fibers had been dried at 160°C in air for 30 min. The potassium dichromate treatment for surface oxidation involved immersion in the dichromate solution and heating to 60°C while stirring for 2 h, followed by filtration and washing with water and then drying at 110°C for 6 h. For the silane treatment, the silane coupling agent was a 1:1 (by weight) mixture of Z-6020 [$H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$] and Z-6040 [$OCH_2\ CHCH_2$-$OCH_2CH_2CH_2Si(OCH_3)_3$] from Dow Corning Corp. (Midland, MI, USA). Both silanes can react with active groups (such as -OH) on the surface of fibers and silica fume and form chemical bonds. The amine group in Z-6020 can help the epoxy end of the Z-6040 molecule react with the surface of fiber or silica fume. The other end of the silane molecule will react with cement during cement curing. In addition, the amine group in Z-6020 serves as the catalyst for the curing of epoxy and consequently allows the Z-6020 molecule to attach to the epoxy end of the Z-6040 molecule. The trimethylsiloxy ends of the Z-6020 and Z-6040 molecules then connect to the -OH functional group on the surface of silica fume or carbon fibers. The silane was dissolved in ethylacetate. Surface treatment was performed by immersion in the silane solution, heating to 75°C while stirring, and holding at 75°C for 1 h, followed by filtration, washing with ethylacetate, and drying. After this, heating was conducted in a furnace at 110°C for 12 h.

No aggregate (fine or coarse) was used. The water/cement ratio was 0.35. A water-reducing agent (TAMOL SN, Rohm and Haas Co., Philadelphia, PA, USA; sodium salt of a condensed naphthalenesulphonic acid) was used in the amount of 2% by weight of cement.

The cement used was portland cement (Type I) from Lafarge Corp. (Southfield, MI, USA). The silica fume (Elkem Materials, Inc., Pittsburgh, PA, USA, EMS 965) was used in the amount of 15% by weight of cement. The methylcellulose, used in the amount of 0.4% by weight of cement, was from Dow Chemical Co. (Midland, MI, USA, Methocel A15-LV). The defoamer (Colloids Inc., Marietta, GA, USA, 1010) was used whenever methylcellulose was used in the amount of 0.13 vol%.

A rotary mixer with a flat beater was used for mixing. Methylcellulose (if applicable) was dissolved in water and then the defoamer was added and stirred by hand for about 2 min. Then this mixture (if applicable), cement, water, water reducing agent, silica fume, and fibers (if applicable) were mixed in the mixer for 10 min. After pouring into molds, an external vibrator was used to facilitate compaction and decrease the amount of air bubbles. The samples were demolded after 24 h and then cured in air at room temperature and a relative humidity of 100% for 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., Sturbridge, MA, USA) 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 (a) polishing both sides of the sample, (b) coating both sides of the sample with gold for thermal contacts, and (c) coating one of the sides (the side the laser beam would hit) with carbon (to avoid reflection of the laser beam, since 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. Six specimens of each type were tested.

A Perkin-Elmer Differential Scanning Calorimeter (Perkin-Elmer Corp., Norwalk, CT, USA, 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 with a diameter of 6 mm and a thickness of 1 mm. Six specimens of each type were tested.

The density was measured by weight and volume (dimensions) measurements. Six specimens of each type were tested.

The air void content was measured by using ASTM method C185-95. Three specimens of each composition were tested.

Twelve compositions, as listed in Table 1, were studied. Six of the compositions had as-received silica fume; the other six had silane-treated silica fume. In addition to these 12 compositions, plain cement paste (with cement and water only, water/cement ratio = 0.45) was studied for the sake of comparison.

2. Results

Table 1 shows the specific heat of cement pastes. The specific heat is significantly increased by the addition of sil-

Table 1
Specific heat (J/g · K, ±0.001) of cement pastes

Formulation[a]	As-received silica fume	Silane-treated silica fume
A	0.782	0.788
A^+	0.793	0.803
A^+F	0.804	0.807
A^+O	0.809	0.813
A^+K	0.812	0.816
A^+S	0.819	0.823

The value for plain cement paste (with cement and water only) is 0.736 J/g · K.

[a] A = cement + water + water reducing agent + silica fume; A^+ = A + methylcellulose + defoamer; A^+F = A^+ + as-received fibers; A^+O = A^+ + O_3-treated fibers; A^+K = A^+ + dichromate-treated fibers; A^+S = A^+ + silane-treated fibers.

ica fume, as previously reported [1]. It is increased more by the further addition of methylcellulose and defoamer. It is increased even more by the further addition of carbon fibers. The effectiveness of the fibers in increasing the specific heat increases in the order: as-received fibers, O_3-treated fibers, dichromate-treated fibers, and silane-treated fibers. This trend applies whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives substantially higher specific heat than as-received silica fume. The highest specific heat is exhibited by the cement paste with silane-treated silica fume and silane-treated fibers. The specific heat is 12% higher than that of plain cement paste, 5% higher than that of the cement paste with as-received silica fume and as-received fibers, and 0.5% higher than that of the cement paste with as-received silica fume and silane-treated fibers. Hence, silane treatment of fibers is more valuable than that of silica fume for increasing the specific heat.

Table 2 shows the thermal diffusivity of cement pastes. The thermal diffusivity is significantly decreased by the addition of silica fume, as previously reported [1]. The further addition of methylcellulose and defoamer or the still further addition of fibers has relatively little effect on the thermal diffusivity. Surface treatment of the fibers by ozone or dichromate slightly increases the thermal diffusivity, whereas surface treatment of the fibers by silane slightly decreases the thermal diffusivity. These trends apply whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives slightly lower (or essentially the same) thermal diffusivity than as-received silica fume. Silane treatments of silica fume and of fibers are about equally effective for lowering the thermal diffusivity.

Table 3 shows the density of cement pastes. The density is significantly decreased by the addition of silica fume, as previously reported [1]. It is again decreased slightly by the further addition of methylcellulose and defoamer. It is decreased more by the still further addition of fibers. The effectiveness of the fibers in decreasing the density decreases in the order: as-received fibers, O_3-treated fibers, dichromate-treated fibers, and silane-treated fibers. This trend applies whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives slightly higher (or essentially the same) specific heat than as-received silica fume. Silane treatment of fibers is more valuable than that of silica fume for increasing the density.

Table 3
Density (g/cm^3, ±0.02) of cement pastes

Formulation[a]	As-received silica fume	Silane-treated silica fume
A	1.72	1.73
A^+	1.69	1.70
A^+F	1.62	1.64
A^+O	1.64	1.65
A^+K	1.65	1.66
A^+S	1.66	1.68

The value for plain cement paste (with cement and water only) is 2.01 g/cm^3.

[a] See Table 1 for abbreviations.

Table 4 shows the thermal conductivity. It is significantly decreased by the addition of silica fume, as previously reported [1]. The further addition of methylcellulose and defoamer or the still further addition of fibers has little effect on the density. Surface treatment of the fibers by ozone or dichromate slightly increases the thermal conductivity, whereas surface treatment of the fibers by silane has negligible effect. These trends apply whether the silica fume is as-received or silane-treated. For any of the formulations, silane-treated silica fume gives slightly lower (or essentially the same) thermal conductivity as as-received silica fume. Silane treatments of silica fume and of fibers contribute comparably to reducing the thermal conductivity.

Table 5 shows the air void content. It is significantly increased by the addition of silica fume, as previously reported [1]. It is decreased by the addition of methylcellulose and defoamer, but is increased by the further addition of fibers, whether the fibers have been surface treated or not. Among the formulations with fibers, the air void content decreases in the order: as-received fibers, O_3-treated fibers, dichromate-treated fibers, and silane-treated fibers. This trend applies whether the silica fume is as-received or silane-treated. For any of the formulations (including those without fibers), silane-treated silica fume gives lower air void content than as-received silica fume.

Table 2
Thermal diffusivity (mm^2/s, ±0.03) of cement pastes

Formulation[a]	As-received silica fume	Silane-treated silica fume
A	0.26	0.24
A^+	0.25	0.22
A^+F	0.27	0.26
A^+O	0.29	0.27
A^+K	0.29	0.27
A^+S	0.25	0.23

The value for plain cement paste (with cement and water only) is 0.36 mm^2/s.

[a] See Table 1 for abbreviations.

Table 4
Thermal conductivity (W/m · K, ±0.03) of cement pastes

Formulation[a]	As-received silica fume	Silane-treated silica fume
A	0.35	0.33
A^+	0.34	0.30
A^+F	0.35	0.34
A^+O	0.38	0.36
A^+K	0.39	0.37
A^+S	0.34	0.32

The value for plain cement paste (with cement and water only) is 0.53 W/m · K.

[a] See Table 1 for abbreviations.

3. Discussion

As explained previously [1], (a) silica fume increases the specific heat of cement paste because of the interface (however diffuse) between silica fume and cement, and the contribution of interfaces to the component of specific heat associated with vibrations; (b) methylcellulose increases the specific heat of cement paste because of the molecular nature of methylcellulose and the contribution of molecular movements to the specific heat; and (c) fibers increase the specific heat of cement paste because of the interface between fibers and the cement matrix. In this work, we found that silane treatment of silica fume or fibers increases the specific heat. This is due to the contribution of the movement of the covalent coupling between silica fume and cement matrix and between fiber and cement matrix. Surface treatment of fibers by ozone or dichromate also increases the specific heat (though the increase is not as great as that for silane treatment) due to the surface oxidation, the resulting active functional groups on the fiber surface, and the consequent fiber-matrix covalent coupling, the movement of which contributes to the specific heat. These explanations are supported by the following argument.

Correlation with the results on the effect of fiber surface condition on the loss tangent under dynamic flexural testing [5] shows that a higher specific heat is associated with a lower loss tangent. A lower loss tangent is associated with less fiber-matrix interface slippage (the main mechanism of vibration damping in a fiber composite without a viscoelastic component), which in turn is associated with less contribution of the interface to the component of specific heat due to vibrations. Thus, the effect of fiber surface condition on the specific heat (Table 1) cannot be explained in terms of the fiber-matrix interface slippage. Rather, it is explained in terms of the movement of the covalent coupling between fiber and matrix.

Correlation with the results on the effect of silica fume surface condition on the loss tangent of cement paste with silane-treated or dichromate-treated carbon fibers [5] shows that a higher specific heat is associated with a higher loss tangent at 0.2 Hz. Thus, the increase of specific heat due to the silane treatment of silica fume is probably related to enhanced slippage at the interface (however diffuse) between silica fume and cement. However, the movement of the silane molecules probably also contributes to this. As mentioned in the Results section, the effect of silane treatment of silica fume on the specific heat is small compared to that of silane treatment of carbon fibers on the specific heat.

Table 5
Air void content (%, ±0.12) of cement pastes

Formulation[a]	As-received silica fume	Silane-treated silica fume
A	3.73	3.26
A^+	3.42	3.01
A^+F	5.32	4.89
A^+O	5.07	4.65
A^+K	5.01	4.49
A^+S	4.85	4.16

The value for plain cement paste (just cement and water) is 2.87%.

[a] See Table 1 for abbreviations.

Silica fume decreases the thermal diffusivity of cement paste, partly because of the interface (however diffuse) between silica fume and cement, and the contribution of interface to the thermal resistance, and partly because of the low thermal diffusivity of silica fume. The addition of methylcellulose and defoamer slightly decreases the thermal diffusivity because of the low thermal conductivity of molecular materials. Silane treatment of silica fume or fibers slightly decreases the thermal diffusivity, due to the molecular nature of silane. Ozone and dichromate treatments of fibers slightly increase the thermal diffusivity, due to the surface oxidation and the resulting fiber-matrix covalent coupling, which probably strengthens the fiber-matrix interface [25] and probably decreases the thermal resistance of the interface. Another reason may be that the treatments enhance the wettability of fibers, thereby increasing the degree of fiber dispersion and decreasing the porosity.

Silica fume decreases the density of cement paste (Table 3) because of the increase in air void content (Table 5). The addition of methylcellulose and defoamer decreases the density slightly, in spite of the decrease in air void content. This is attributed to the low density of these molecular materials. The addition of fibers decreases the density, due to the increase in air void content. Among the pastes with different types of fiber surface condition, the higher the density is, the lower the air void content, whether the silica fume is as-received or silane-treated. Correlation with the results on the effect of fiber surface condition on the tensile strength and modulus [4] shows that the higher the density is, the higher the tensile strength and modulus. A higher modulus is probably due to a better bond between fiber and matrix. Hence, a better fiber-matrix bond results in a lower air void content, which in turn results in a higher density. Silane treatment of silica fume has negligible effect on the density, though the air void content is significantly decreased. This is attributed to the low density of silane.

Silica fume decreases the thermal conductivity of cement paste (Table 4) because of the decreases in thermal diffusivity (Table 2) and density (Table 3). The thermal conductivity is decreased in spite of the increase in the specific heat. Among the cement pastes with different fiber surface conditions, a higher thermal conductivity is associated with a higher thermal diffusivity. In other words, for carbon fiber cement pastes, the thermal diffusivity influences the thermal conductivity more than the density or the specific heat do.

Although the carbon fibers are quite conductive, their low concentration causes the thermal conductivity of cement paste to increase not very significantly. By using silane-treated carbon fibers, the thermal conductivity increase due to the fiber addition is even less.

For practical applications, a high specific heat and a low thermal conductivity are desired. By using silane-treated carbon fibers and silane-treated silica fume, both properties are attained. Relative to plain cement paste, the specific heat is 12% higher and the thermal conductivity is 40% lower.

4. Conclusion

The specific heat of cement paste was increased by 12% and the thermal conductivity was decreased by 40% by using as admixtures silane-treated silica fume and silane-treated carbon fibers. The effects were less when the silica fume was as-received or when the fibers were as-received, ozone-treated, or dichromate-treated.

The specific heat was increased by the carbon fiber addition, due to fiber-matrix interface slippage. The increase was in the order: as-received fibers, ozone-treated fibers, dichromate-treated fibers, and silane-treated fibers. The specific heat increase due to the silane treatment of the fibers is attributed to movement of the silane molecules. The specific heat increase due to the dichromate or ozone treatment of the fibers is attributed to movement of the functional groups on the fibers. The specific heat was increased by the silica fume addition, due to slippage at the interface between silica fume and cement. The increase was enhanced by silane treatment of the silica fume.

Silane treatment of carbon fibers decreased the thermal conductivity in spite of the increases in specific heat and density, due to the decrease in thermal diffusivity, which is attributed to the thermal resistance of the silane at the fiber-matrix interface. Dichromate and ozone treatments of carbon fibers gave higher thermal diffusivity than silane treatment of the fibers, due to the functional groups on the fiber surface strengthening the fiber-matrix interface.

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