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Communication

Cement of high specific heat and high thermal conductivity, obtained by using silane and silica fume as admixtures

Yunsheng Xu, D.D.L. Chung*

Composite Materials Research Laboratory, Department of Mechanical and Aerospace Engineering, State University of New York at Buffalo, Buffalo, NY 14260-4400, USA

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Abstract

Cement paste of high specific heat and high thermal conductivity has been attained by using silane and silica fume as admixtures. These admixtures together cause the specific heat to increase by up to 50% and the thermal conductivity to increase by up to 38%. Silane acts to increase the specific heat and increase the thermal conductivity. Silica fume acts to increase the specific heat and decrease the thermal conductivity. Silane provides a network of covalent coupling among the silica fume particles. The network increases the compressive strength and modulus, decreases the compressive ductility, enhances heat conduction through phonons, and increases the specific heat through vibrations. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Concrete of low thermal conductivity is useful for the thermal insulation of buildings. On the other hand, concrete of high thermal conductivity is useful for reducing temperature gradients in structures. The thermal stresses that result from temperature gradients may cause mechanical property degradation and even warpage in the structure. Bridges are among structures that tend to encounter temperature differentials between their top and bottom surfaces. In contrast to buildings, which also encounter temperature differentials, bridges do not need thermal insulation. Therefore, concrete of high thermal conductivity is desirable for bridges and related structures.

Concrete of high specific heat is useful for increasing the temperature stability of a structure.

Cement paste exhibiting high specific heat and low thermal conductivity can be obtained by using polymeric admixtures such as latex (which is itself a thermal insulator), silica fume (which introduces thermal barrier in the form of the interface between silica fume particles and the cement matrix), short carbon fibers (which increase the air void content), and porous particles such as vermiculite and perlite [1]. Although carbon fibers are themselves thermally conducting, their addition cannot increase the thermal conductivity of cement, unless they are present in rather high concentrations. Thus, the intuitive thought that the addition of conducting fibers would give high thermal conductivity cement is not correct in general.

Previous work on increasing the thermal conductivity of concrete involved increasing the moisture content [2–4], the use of an aggregate of a higher thermal conductivity [2], and the use of steel fibers [5] or steel mesh [6]. Due to the mechanical property degradation resulting from an increase in the moisture content, the limited availability of special aggregates and the high concentration of steel fibers required, other methods of increasing the thermal conductivity are desirable. Due to the continuity of the steel in the mesh, the heat conduction path is essentially all in the steel and the concrete itself is essentially not involved in the heat conduction. Although the steel mesh is effective for increasing the thermal conductivity, it cannot be incorporated in the concrete mix as an admixture. This raises the processing cost as the placement of the steel mesh means extra labor cost. The objective of this paper is to provide cement paste

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* Corresponding author. Tel.: +1-716-645-2593 ext. 2243; fax: +1-716-645-3875.

E-mail address: ddlchung@acsu.buffalo.edu (D.D.L. Chung).

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of high specific heat and high thermal conductivity through the use of an admixture.

The thermal conductivity is the product of the thermal diffusivity, the specific heat, and the density. Hence, increases in all three quantities contribute to an increase in the thermal conductivity. In this paper, an increased thermal conductivity is attained mainly by increase in the specific heat. Increases in the specific heat by up to 12% has been previously attained through the use of admixtures, such as latex, silica fume, and carbon fibers [1,7]. This paper has attained a specific heat increase of up to 50%, in addition to a thermal conductivity increase of 38%.

The admixtures used in this paper are silica fume and silane together. Silane is molecular, but is not a polymer. Silane has been previously used as a coating on admixtures such as silica fume and on carbon fibers for enhancing the wettability of these admixtures by water [7–11]. However, silane has not been previously used as an admixture, which is added directly into the cement mix. Silane as an admixture was found in this work to increase the thermal diffusivity of cement containing silica fume by up to 27%, increase the specific heat of cement containing silica fume by up to 35%, as well as increasing the compressive strength and modulus, while essentially not affecting the density. These effects are attributed to the network resulting from the silane coupling of the silica fume particles.

2. Experimental methods

No aggregate (fine or coarse) was used. The water/cement ratio was 0.35. The cement used was portland cement (Type 1) from Lafarge (Southfield, MI). The silica fume (Elkem Materials, Pittsburgh, PA, EMS 965) was used in the amount of 15% by weight of cement.

The silane was aqueous amino vinyl silane (Hydrosil 2781, Sivento, Piscataway, NJ), chosen due to its stability in aqueous systems. In contrast, the silane used for coating silica fume [7–11] is not sufficiently stable in aqueous systems. Silane was used in the amount of 0%, 0.20%, 0.50%, 0.75%, 1.0%, 1.5%, and 2.0% by weight of cement. The corresponding amount of water-reducing agent was 1.0%, 0.10%, 0.10%, 0.05%, 0.05%, 0.025%, and 0.025% by weight of cement, respectively. The more the amount of silane used, the less was the amount of water-reducing agent needed to maintain workability. The water-reducing agent was TAMOL SN, Rohm and Haas, Philadelphia, PA, a sodium salt of a condensed naphthalenesulphonic acid. The surfactant, used in the amount of 1% by weight of cement to help distribute the silane, was polyoxyethylene lauryl ether, $C_{12}H_{25}(OCH_2CH_2)_nOH$, from Aldrich, Milwaukee, WI. The defoamer (Colloids, Marietta, GA, 1010) was used in the amount of 0.13 vol.%.

A rotary mixer with a flat beater was used for mixing. The cement, silica fume, and water-reducing agent were mixed at a low speed. Water, silane, surfactant, and defoamer were mixed and then the mixture was added to the cement mix and mixed for 10 min at high speed. 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, MA) and a computer with Labtech software and data acquisition board were used. The specimen was in the form of a disc with diameter 13 mm and thickness 2 mm. Sample preparation for laser diffusivity measurement involved (i) polishing both sides of the sample, (ii) coating both sides of the sample with gold for thermal contacts, and (iii) coating one of the sides (the side on which the laser beam would hit) with carbon (for avoiding 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. Four 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

Table 1
Thermal diffusivity, specific heat, density, and thermal conductivity of cement pastes

Silica fume (% by weight of cement)	Silane (% by weight of cement)	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, ±0.07)	Reference
0	0	0.37	0.703	1.99	0.52	[1]
15	0	0.260	0.782	1.98	0.403	This work
15	0.2	0.302	0.980	2.07	0.613	This work
15	0.5	0.314	1.003	2.06	0.649	This work
15	0.75	0.316	1.023	2.05	0.663	This work
15	1.0	0.321	1.030	2.08	0.688	This work
15	1.5	0.324	1.039	2.07	0.697	This work
15	2.0	0.329	1.057	2.07	0.719	This work

Table 2
Compressive properties of cement pastes

Silica fume (% by weight of cement)	Silane (% by weight of cement)	Strenght (MPa)	Modulus (GPa)	Ductility (%)	Reference
0	0	57.9 ± 1.8	2.92 ± 0.07	1.72 ± 0.04	[12]
15	0	65.0 ± 2.6	13.6 ± 1.4	0.614 ± 0.023	This work
15	0.2	77.4 ± 3.7	15.8 ± 1.6	0.474 ± 0.015	This work
15	0.5	78.1 ± 1.9	21.3 ± 0.9	0.427 ± 0.015	This work
15	0.75	82.2 ± 1.9	23.2 ± 1.2	0.387 ± 0.021	This work
15	1.0	82.3 ± 2.7	25.3 ± 1.3	0.373 ± 0.015	This work
15	1.5	81.0 ± 3.7	26.3 ± 1.4	0.366 ± 0.013	This work
15	2.0	82.7 ± 2.8	16.9 ± 1.6	0.344 ± 0.013	This work

material. The specimen was in the form of a disc of diameter 6 mm and thickness 1 mm. Four specimens of each type were tested.

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

For compressive testing according to ASTM C109-80, specimens were prepared by using a 2 × 2 × 2-in. (5.1 × 5.1 × 5.1-cm) mold. Compression testing was performed using a hydraulic material testing system (MTS). The cross-head speed was 1.27 mm/min. During compressive loading the strain was measured by using a mounted strain gage. Six specimens of each composition were tested.

3. Results and discussion

Table 1 shows the thermal diffusivity, specific heat, density, and thermal conductivity of cement pastes. The addition of silica fume decreases the thermal diffusivity, increases the specific heat and decreases the thermal conductivity, as previously reported and explained in terms of the interfaces associated with silica fume [1]. The further addition of silane increases the thermal diffusivity by up to 27%, further increases the specific heat by up to 35%, slightly increases the density, and increases the thermal conductivity by up to 78%. The overall effect of addition of both silane and silica fume is a decrease in thermal diffusivity by up to 18%, an increase in specific heat by up to 50%, and an increase in thermal conductivity by up to 38%.

Table 2 shows the compressive properties of cement pastes. The compressive strength is increased by 12% and the modulus is increased by 370% by silica fume addition, while the ductility is decreased. These effects of silica fume are consistent with previous reports [13–15]. Further addition of silane further increases the strength and modulus and further decreases the ductility. Addition of silane in the amount of 0.2% by weight of cement increases the strength by 19%. Addition of more silane causes the strength to increase further, but less significantly. Hence, a low silane content is effective.

The increases in compressive strength and modulus, and in thermal diffusivity, specific heat, density and thermal conductivity are all attributed to the network of covalent coupling among the silica fume particles, as provided by silane. The network strengthens, stiffens, enhances heat conduction through phonons, and increases the vibrational contribution to the specific heat. These effects of silane are most significant at a low silane content of 0.2% by weight of cement. The effects of additional amounts of silane are less significant. This means that the network formation does not require much silane. A further attraction for a low silane content is the low cost, as silane is expensive compared to cement.

The use of silane as an admixture which is added directly into the cement mix involves more silane material but less processing cost than the use of silane in the form of a coating on silica fume [7–11]. Both methods of silane introduction result in increases in the compressive strength and modulus. The former method causes the ductility of cement paste to decrease (Table 2), whereas the latter method causes the ductility of mortar to increase slightly [10].

The method of direct introduction of silane (this work) results in specific heat increases ranging from 25% to 35%. The method of coating silica fume with silane [7–11] results in a 0.8% increase in the specific heat. The former method (this work) results in thermal conductivity increases in the range from 52% to 78%, whereas the latter method (coating method) results in essentially no effect on the thermal conductivity. Thus, the method of direct introduction gives much larger effects on the thermal properties than the coating method. This suggests that the network attained by the method of direct introduction does not result from the coating method, due to the localization of the silane in the coating. The network also causes the ductility to decrease. It is formed from the hydrolysis and polymerization (condensation) reaction of silane during the hydration of cement.

4. Conclusion

Silane and silica fume together are effective admixtures for increasing significantly both the specific heat and the thermal conductivity of cement paste. Silica fume alone increases the specific heat but decreases the thermal conductivity. Silane provides a network of covalent coupling among the silica fume particles, thereby increasing both the specific heat and the thermal conductivity, in addition to increasing the compressive strength and modulus and decreasing the compressive ductility.

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