Cement as a thermoelectric material

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Cement pastes containing short steel fibers, which contribute to electron conduction, exhibit positive values (up to 68 μV/°C) of the absolute thermoelectric power. Cement pastes containing short carbon fibers, which contribute to hole conduction while the cement matrix contributes to electron conduction, exhibit negative or slightly positive values of the absolute thermoelectric power. The hole and electron contributions in carbon fiber reinforced cement paste are equal at the percolation threshold. Addition of either steel or carbon fibers to cement paste yields more reversibility and linearity in the variation of the Seebeck voltage with temperature difference (up to 65 °C).

I. INTRODUCTION

Thermoelectricity refers to the phenomenon in which electricity (i.e., a voltage) is generated by a temperature gradient. This phenomenon is known as the Seebeck effect. It also refers to the reverse phenomenon (known as the Peltier effect), in which electricity (i.e., a current through a junction between two dissimilar materials) causes heating or cooling. The Seebeck effect is the basis of thermocouples for temperature sensing. The Peltier effect is used for heating and cooling. This paper is focused on the Seebeck effect, which is scientifically the most basic aspect of thermoelectricity, as its occurrence does not require the presence of a junction.

Thermoelectric materials are conventionally metals and semiconductors, as they cannot be electrical insulators. Cement, such as Portland cement, is conducting, although it is far less conducting than metals. Cement reacts with water through hydration (curing) and forms cement paste (a solid), which is the matrix material in concrete (with fine and coarse aggregates) and mortar (with fine aggregate only). Since concrete is a widely used material for buildings and construction, and energy saving and thermal control are important for most structures, it is desirable to exploit the thermoelectric behavior of concrete. Therefore, this paper addresses the thermoelectric behavior of cement paste.

The electrical resistivity of cement paste can be decreased by orders of magnitude by the addition of short conducting fibers (such as steel and carbon fibers) to the cement mix.[1–9] In the same vein, the thermoelectic power of cement paste can be greatly changed by the addition of short conducting fibers.[10,11] As shown in this paper, plain cement paste is *n*-type. The addition of carbon fibers contributes to hole conduction[10,11]; the addition of steel fibers contributes to electron conduction (this work). Hence, the addition of carbon fibers causes the thermoelectric power to be less positive or more negative (depending on the amount of carbon fibers added), whereas the addition of steel fibers causes the thermoelectric power to be more positive (as high as 68 μV/°C), as reported in this paper.

The high value of the thermoelectric power attained by adding steel fibers makes steel-fiber-reinforced cement paste an attractive thermoelectric material. It should be mentioned that fiber-reinforced cement is also attractive in its structural properties, as the fiber addition results in increased toughness, decreased drying shrinkage, and, in many cases, increased tensile and flexural strengths as well.[12,18] The thermoelectric behavior makes the structural material multifunctional, thereby lowering cost and enhancing durability.

Previous work on the thermoelectric behavior of cement was limited to plain cement paste and cement paste containing short carbon fibers.[10,11] It was reported that plain cement paste exhibited a thermoelectric power of zero and that carbon fiber addition resulted in hole conduction and a nonzero value of the thermoelectric power.[10,11] The zero value of the thermoelectric power is not expected from the nonzero conductivity of plain cement paste. We recognize that the values reported in Refs. 10 and 11 were all relative to copper as the reference, so that the absolute thermoelectric power of plain cement paste was actually nonzero, as clarified in this paper.

II. EXPERIMENTAL METHODS

The steel fibers were made of stainless steel No. 434, as obtained from International Steel Wool Corp. (Springfield, OH). The fibers were cut into pieces of length 5 mm prior to use in the cement paste. The properties of the steel fibers are shown in Table I. The mechanical properties of mortars containing these fibers are described in Ref. 19. However, no aggregate, whether coarse or fine, was used in this work.

The carbon fibers were isotropic pitch based, unsized, and of length approximately 5 mm, as obtained from Ashland Petroleum Co. (Ashland, KY). The fiber properties are shown in Table II. No aggregate (fine or coarse) was used.

The cement used was portland cement (Type I) from Lafarge Corp. (Southfield, MI). Silica fume (Elkem Materials, Inc., Pittsburgh, PA, EMS 965) was used in the amount of 15% by mass of cement. The latex, used in the amount of 20% by mass of cement, was a styrene butadiene copolymer (Dow Chemical Co., Midland, MI, 460NA) with the polymer making up about 48% for the dispersion and with the styrene and butadiene having a mass ratio of 66:34. The latex was used along with an antifoaming agent (Dow Corning Corp., Midland, MI, No. 2410, 0.5% by mass of latex).

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. Latex (if applicable) was mixed with the antifoam by hand for about 1 min. Then the methylcellulose mixture (if applicable), the latex mixutre (if applicable), cement, water, silica fume (if applicable), and fibers (if applicable) were mixed in the mixer for 5 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.

Fourteen types of cement paste (Table III) were prepared, namely (i) steel-fiber cement paste (consisting of cement, water, and steel fibers in the amount of 0.5% by mass of cement, i.e., 0.10 vol% of composite); (ii) steel-fiber cement paste [same as (i) except for having steel fibers in the amount of 1.0% by mass of cement, i.e., 0.20 vol% of composite]; (iii) steel-fiber silica-fume cement paste (consisting of cement, water, silica fume, and steel fibers in the amount of 0.5% by mass of cement, i.e., 0.10 vol% of composite); (iv) steel-fiber silica-fume cement paste [same as (iii) except for having steel fibers in the amount of 1.0% by mass of cement, i.e., 0.20 vol% of composite]; (v) steel-fiber latex cement paste (consisting of cement, water, latex, antifoam and steel fibers in the amount of 0.5% by mass of cement, i.e., 0.085 vol% of composite); (vi) steel-fiber latex cement paste [same as (v) except for having steel fibers in the amount of 1.0% by mass of cement, i.e., 0.17 vol% of composite); (vii) silica-fume cement paste (consisting of cement, water, and silica fume); (viii) carbon-fiber silica-fume cement paste (consisting of cement, water, silica fume, methylcellulose, defoamer, and carbon fibers in the amount of 0.5% by mass of cement, i.e., 0.48 vol% of composite); (ix) carbon-fiber silica-fume cement paste [same as (viii) except for having carbon fibers in the amount of 1.0% by mass of cement, i.e., 0.95 vol% of composite]; (x) carbon-fiber silica-fume cement paste [same as (viii) except for having carbon fibers in the amount of 1.5% by mass of cement, i.e., 1.44 vol% of composite]; (xi) latex cement paste (consisting of cement, water, latex, ad antifoam); (xii) carbon-fiber latex cement paste (consisting of cement, water, latex, antifoam, and carbon fibers in the amount of 0.5% by mass of cement, i.e., 0.41 vol% of composite); (xiii) carbon-fiber latex cement paste [same as (xii) except for having carbon fibers in the amount of 1.0% by mass of cement, i.e., 0.82 vol% of composite]; and (xiv) plain cement paste (consisting of just cement and water). The water/cement ratio was 0.35 for all pastes except that it was 0.23 for pastes containing latex.

Thermopower measurement was performed on rectangular samples of size 75 × 15 × 15 mm, such that heat (up to 85 °C) was applied at one of the 15 × 15 mm ends of a sample by contacting this end with a resistance

TABLE I. Properties of steel fibers.

Nominal diameter	60 μm
Tensile strength	970 MPa
Tensile modulus	200 GPa
Elongation at break	3.2%
Volume electrical resistivity	6×10^{-5} Ω cm
Specific gravity	7.7 g cm^{-3}

TABLE II. Properties of carbon fibers.

Filament diameter	15 ± 3 μm
Tensile strength	690 MPa
Tensile modulus	48 GPa
Elongation at break	1.4%
Electrical resistivity	3.0×10^{-3} Ω cm
Specific gravity	1.6 g cm^{-3}
Carbon content	98 wt%

TABLE III. Cement paste compositions (percent by mass of cement).

Paste no.	Steel fibers	Carbon fibers	Silica fume	Latex	Water
i	0.5	...	...	...	35
ii	1.0	...	...	...	35
iii	0.5	...	15	...	35
iv	1.0	...	15	...	35
v	0.5	...	...	20	23
vi	1.0	...	...	20	23
vii	...	...	15	...	35
viii	...	0.5	15	...	35
ix	...	1.0	15	...	35
x	...	1.5	15	...	35
xi	...	...	...	20	23
xii	...	0.5	...	20	23
xiii	...	1.0	...	20	23
xiv	...	...	...	...	35

heated platen of size much larger than 15 × 15 mm. The other end of the sample was near room temperature. The thermal contact between the platen and the sample end was enhanced by using a copper foil covering the 15 × 15 mm end surface of the sample as well as the four side surfaces for a length of approximately 4 mm from the end surface. Silver paint was applied between the foil and the sample surface covered by the foil to further enhance the thermal contact. Underneath to copper foil, a copper wire was wrapped around the perimeter of the sample for the purpose of voltage measurement. Silver paint was present between the copper wire and the sample surface under the wire. The other end of the rectangular sample was similarly wrapped with copper wire and then covered with copper foil. The copper wires from the two ends were fed to a Keithley 2001 (Cleveland, OH) multimeter for voltage measurement. A T-type thermocouple was attached to the copper foil at each of the two ends of the sample for measuring the temperature of each end. Voltage and temperature measurements were done simultaneously using the multimeter. The voltage difference divided by the temperature difference yielded the Seebeck coefficient with copper as the reference, since the copper wires at the two ends of a sample were at different temperatures. This Seebeck coefficient plus the absolute thermoelectric power of copper (+2.34 μV/°C)[20] is the absolute thermoelectric power of the sample. Samples were heated at one end at a rate of 0.009 °C/s for all pastes, except that the rate was 0.012 °C/s for pastes (ii), (iv), and (vi). This was followed by cooling with the power of the platen turned off. The heating rate was constant, but the cooling rate was not.

After conducting thermopower testing, the direct current volume electrical resistivity was measured using the Keithley 2001 multimeter and the four-probe method. In this method, four electrical contacts were applied by silver paint around the whole perimeter at four planes perpendicular to the length of the specimen. The four planes were symmetrical around the midpoint along the length of the specimen, such that the outer contacts (for passing current) were the same as the wires for Seebeck voltage and the inner contacts (for measuring the voltage in relation to resistivity determination) were 45 mm apart.

Six samples of each composition were tested. Each sample was tested in terms of both the thermopower and the resistivity.

III. RESULTS AND DISCUSSION

Table IV, as well as Figs. 1–4, show the thermopower results. The absolute thermoelectric power is much more positive for all the steel-fiber cement pastes compared to all the carbon-fiber cement pastes. An increase of the steel fiber content from 0.5% to 1.0% by mass of cement increases the absolute thermoelectric power, whether silica fume (or latex) is present or not. An increase of the steel fiber content also increases the reversibility and linearity of the change in Seebeck voltage with the temperature difference between the hot and cold ends, as shown by comparing Fig. 1 (steel fibers in the amount of 1.0% by mass of cement) and Fig. 2 (steel fibers in the amount of 0.5% by mass of cement), and by comparing the values of the Seebeck coefficient obtained during heating and cooling in Table IV. The values obtained

TABLE IV. Volume electrical resistivity, Seebeck coefficient (μV/°C) with copper as the reference, and the absolute thermoelectric power (μV/°C) of various cement pastes with steel fibers (S_f) or carbon fibers (C_f).

			Heating		Cooling	
Cement paste	Volume fraction fibers	Resistivity (Ω cm)	Seebeck coefficient	Absolute thermoelectric power	Seebeck coefficient	Absolute thermoelectric power
Plain	0	...	−0.35 ± 0.03	1.99 ± 0.03	−0.38 ± 0.05	1.96 ± 0.05
SF	0	...	−0.31 ± 0.02	2.03 ± 0.02	−0.36 ± 0.03	1.98 ± 0.03
L	0	...	−0.28 ± 0.02	2.06 ± 0.02	−0.30 ± 0.02	2.04 ± 0.02
S_f (0.5[a])	0.10%	(7.8 ± 0.5) × 10^4	51.0 ± 4.8	53.3 ± 4.8	45.3 ± 4.4	47.6 ± 4.4
S_f (1.0[a])	0.20%	(4.8 ± 0.4) × 10^4	56.8 ± 5.2	59.1 ± 5.2	53.7 ± 4.9	56.0 ± 4.9
S_f (0.5[a]) + SF	0.10%	(5.6 ± 0.5) × 10^4	54.8 ± 3.9	57.1 ± 3.9	52.9 ± 4.1	55.2 ± 4.1
S_f (1.0[a]) + SF	0.20%	(3.2 ± 0.3) × 10^4	66.2 ± 4.5	68.5 ± 4.5	65.6 ± 4.4	67.9 ± 4.4
S_f (0.5[a]) + L	0.085%	(1.4 ± 0.1) × 10^5	48.1 ± 3.2	50.4 ± 3.2	45.4 ± 2.9	47.7 ± 2.9
S_f (1.0[a]) + L	0.17%	(1.1 ± 0.1) × 10^5	55.4 ± 5.0	57.7 ± 5.0	54.2 ± 4.5	56.5 ± 4.5
C_f (0.5[a]) + SF	0.48%	(1.5 ± 0.1) × 10^4	−1.45 ± 0.09	0.89 ± 0.09	−1.45 ± 0.09	0.89 ± 0.09
C_f (1.0[a]) + SF	0.95%	(8.3 ± 0.5) × 10^2	−2.82 ± 0.11	−0.48 ± 0.11	−2.82 ± 0.11	−0.48 ± 0.11
C_f (1.5[a]) + SF	1.44%	...	−3.10 ± 0.14	−0.76 ± 0.14	−3.10 ± 0.14	−0.76 ± 0.14
C_f (0.5[a]) + L	0.41%	(9.7 ± 0.6) × 10^4	−1.20 ± 0.05	1.14 ± 0.05	−1.20 ± 0.05	1.14 ± 0.05
C_f (1.0[a]) + L	0.82%	(1.8 ± 0.2) × 10^3	−2.10 ± 0.08	0.24 ± 0.08	−2.10 ± 0.08	0.24 ± 0.08

[a]% by mass of cement.
SF: silica fume.
L: latex.

during heating and cooling are close for the pastes with the higher steel fiber content, but are not so close for the pastes with the lower steel fiber content. In contrast, for pastes with carbon fibers in place of steel fibers, the change in Seebeck voltage with the temperature difference is highly reversible for both carbon fiber contents of 0.5% and 1.0% by mass of cement, as shown in Table IV by comparing the values of the Seebeck coefficient obtained during heating and cooling.

Table IV shows that the volume electrical resistivity is much higher for the steel-fiber cement pastes than the corresponding carbon fiber cement pastes. This is attributed to the much lower volume fraction of fibers in the former (Table IV). An increase in the steel or carbon fiber content from 0.5% to 1.0% by mass of cement decreases the resistivity, though the decrease is more significant for the carbon fiber case than the steel fiber case. That the resistivity decrease is not large when the steel fiber content is increased from 0.5% to 1.0% by mass of cement and that the resistivity is still high at a steel fiber content of 1.0% by mass of cement suggest that a steel fiber content of 1.0% by mass of cement is below the percolation threshold.

Among the steel fiber cement pastes at the same fiber content in percentage by mass of cement, the absolute thermoelectric power increases in the following order: steel-fiber latex cement paste, steel-fiber cement paste (without latex or silica fume), and steel-fiber silica-fume cement paste. The resistivity decreases in the above order as well. The correlation between the absolute thermoelectric power and the resistivity is due to the fact that both thermopower and conductivity are enhanced by a higher degree of fiber dispersion. Silica fume is known to be particularly effective in enhancing the degree of fiber dispersion.[12]

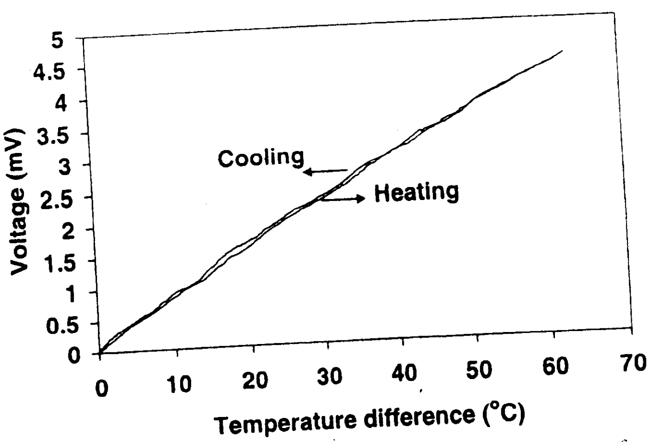

FIG. 1. Variation of the Seebeck voltage (with copper as the reference) versus the temperature difference during heating and cooling for steel-fiber silica fume cement paste containing steel fibers in the amount of 1.0% by mass of cement.

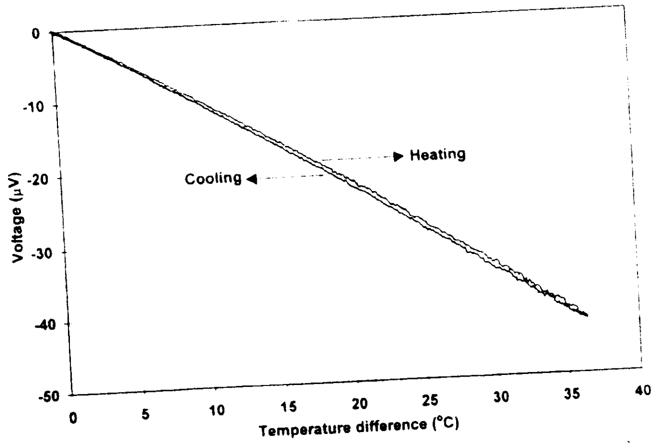

FIG. 3. Variation of the Seebeck voltage (with copper as the reference) versus the temperature difference during heating and cooling for carbon-fiber latex cement paste containing carbon fibers in the amount of 0.5% by mass of cement.

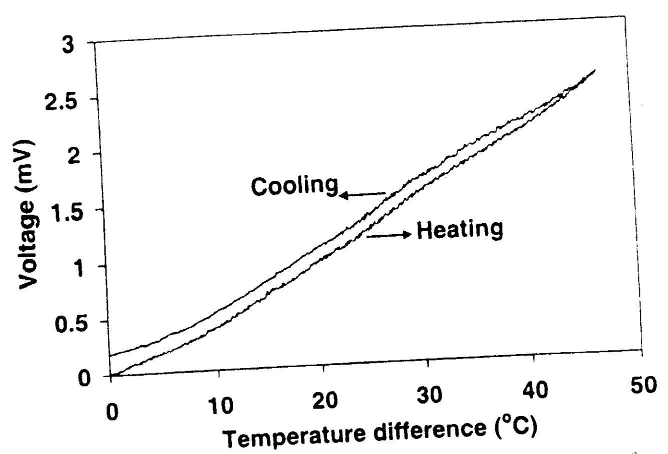

FIG. 2. Variation of the Seebeck voltage (with copper as the reference) versus the temperature difference during heating and cooling for steel-fiber silica fume cement paste containing steel fibers in the amount of 0.5% by mass of cement.

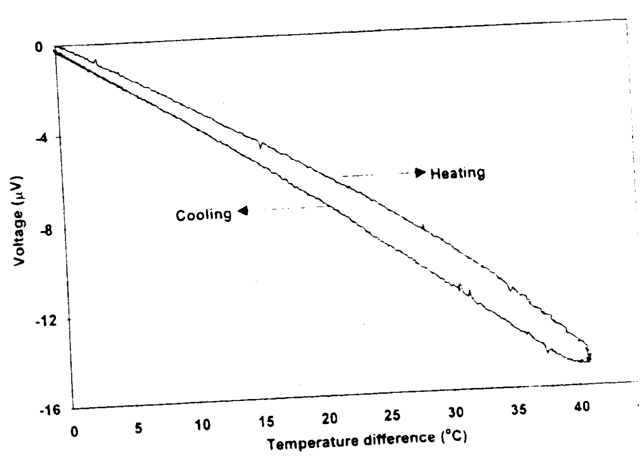

FIG. 4. Variation of the Seebeck voltage (with copper as the refe ence) versus the temeprature difference during heating and cooling f silica-fume cement paste.

Similarly for carbon-fiber cement pastes, silica fume yields a more negative value of the absolute thermoelectric power and a lower value of the resistivity than latex.

The highly positive values of the absolute thermoelectric power of steel-fiber cement pastes is attributed to the metallic nature of steel, which conducts by electron movement. In contrast, carbon fibers contribute to hole conduction. As a result, the absolute thermoelectric power of carbon-fiber cement pastes is either negative or slightly positive.

All types of cement paste studied were n-type (i.e., with negative carriers being the majority), except pastes (ix) and (x), which were p-type (i.e., with positive carriers being the majority). The higher the carbon fiber content, the less n-type (the more p-type) was the paste, whether silica fume or latex was present. Without fibers, the absolute thermoelectric power was 2 μV/°C, whether silica fume and latex were present or not. This is consistent with the similar values of the electrical conductivity for cement pastes with silica fume and with latex, but without fibers.[12] Thus, silica fume or latex addition did not have much influence on the thermoelectric power when fibers were absent, but it affected the degree of fiber dispersion, thereby influencing the thermoelectric power when fibers were present.

Whether with or without silica fume (or latex), the change of the Seebeck voltage with temperature difference is more reversible and linear at a steel fiber content of 1.0% by mass of cement than at a steel fiber content of 0.5% by mass of cement. This is attributed to the larger role of the cement matrix at the lower steel fiber content and the contribution of the cement matrix to the irreversibility and nonlinearity. Irreversibility and nonlinearity are particularly significant when the cement paste contains no fiber (Fig. 4).

From the practical point of view, the steel-fiber silica-fume cement paste containing steel fibers in the amount of 1.0% by mass of cement is particularly attractive for use in temperature sensing, as the absolute thermoelectric power is the highest (68 μV/°C) and the variation of the Seebeck voltage with the temperature difference between the hot and cold ends is reversible and linear. The absolute thermoelectric power is approaching those of commercial thermocouple materials. For example, the value for ZnSb at 200 °C is +220 μV/°C.[21]

IV. CONCLUSION

Steel-fiber cement pastes exhibit positive values (up to 68 μV/°C) of the absolute thermoelectric power. The use of silica fume in combination with steel fibers yields a particularly high value of the absolute thermoelectric power. The use of carbon fibers in place of steel fibers gives negative or slightly positive values of the absolute thermoelectric power, due to the contribution of carbon fibers to hole conduction. In constrast, steel fibers contribute to electron conduction. At the percolation threshold (a carbon fiber content between 0.5% and 1.0% by mass of cement), the absolute thermoelectric power changes from being positive to being negative, indicating compensation of the carriers, which are electrons (and/or ions) from the cement matrix and holes from the fibers. The Seebeck effect due to the holes becomes increasingly pronounced as the fiber content increases beyond the percolation threshold. The addition of steel or carbon fibers to cement paste increases the linearity and reversibility of the Seebeck effect. Admixtures such as silica fume and latex have minor influence on the Seebeck effect.

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