

Communication

# Role of moisture in the Seebeck effect in cement-based materials

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## Abstract

Moisture in the form of liquid water contributes little, if any, to the Seebeck effect in cement-based materials. Moisture loss has no effect on the absolute thermoelectric power, but increases the electrical resistivity.

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## 1. Introduction

The Seebeck effect is a thermoelectric effect in which charge carriers move in response to a temperature gradient, thereby resulting in a voltage. This effect results in the conversion of thermal energy to electrical energy. It is the basis for thermocouples. In addition, it provides a means of electrical energy generation.

It has been reported that the Seebeck effect in carbon fiber cement is due to the movement of holes [1,2]. This is supported by the positive sign of the absolute thermoelectric power ( $+5.5 \mu\text{V}/^\circ\text{C}$ ) [3] and the more positive value ( $+22 \mu\text{V}/^\circ\text{C}$ ) of this quantity when the carbon fiber has been rendered p type by bromine intercalation [4]. In contrast, the absolute thermoelectric power is low ( $+3 \mu\text{V}/^\circ\text{C}$ ) for plain cement paste [3].

It has been reported that the Seebeck effect in steel fiber (60  $\mu\text{m}$  diameter) cement becomes more negative (down to  $-63 \mu\text{V}/^\circ\text{C}$ ) as the fiber content is increased in the range from 0 to 0.20 vol% [5], but becomes more positive (up to  $+31 \mu\text{V}/^\circ\text{C}$ ) as the fiber content is increased in the range from 0.20 to 0.50 vol% [6]. The value for the steel fiber by itself is  $+9 \mu\text{V}/^\circ\text{C}$  [7]. The high magnitude of the absolute thermoelectric power compared to those of steel itself or to plain cement paste suggests that the Seebeck

effect in steel fiber cement is due to carrier scattering rather than conduction [6].

Moisture in cement contributes to electrical conduction by ionic conduction. Therefore, one tends to assume that moisture contributes to the Seebeck effect in a similar way. To shed more light on the origin of the Seebeck effect in cement-based materials, this paper investigates the role of moisture in this effect. Specifically, the effects of moisture loss (by heating at  $80^\circ\text{C}$  for up to 10 days) on the absolute thermoelectric power and the DC electrical resistivity are addressed.

## 2. Experimental methods

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

The carbon fibers were isotropic pitch-based, unsized, and of length  $\sim 5$  mm, as obtained from Ashland Petroleum (Ashland, KY). The fiber properties are shown in Table 1. No aggregate (fine or coarse) was used.

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 the methylcellulose mixture (if applicable),

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Table 1  
Properties of carbon fibers

Filament diameter	$15 \pm 3 \mu\text{m}$
Tensile strength	690 MPa
Tensile modulus	48 GPa
Elongation at break	1.4%
Electrical resistivity	$3.0 \times 10^{-3} \Omega \text{ cm}$
Specific gravity	$1.6 \text{ g cm}^{-3}$
Carbon content	98 wt.%

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.

Four types of cement paste were prepared, namely, (i) plain cement paste (consisting of just cement and water), (ii) silica-fume cement paste (consisting of cement, water and silica fume), (iii) 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., 0.49 vol%), and (iv) carbon-fiber silica-fume cement paste (same as (iii) except for having carbon fibers in the amount of 1.0% by mass of cement, i.e., 0.98 vol%). The water/cement ratio was 0.35.

Thermopower measurement was performed on rectangular samples of size  $75 \times 15 \times 15 \text{ mm}$ , such that heat (up to  $65^\circ$ ) was applied at one of the  $15 \times 15\text{-mm}$  ends of a sample by contacting this end with a resistance heated platen of size much larger than  $15 \times 15 \text{ mm}$ . 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  $15 \times 15\text{-mm}$  end surface of the sample as well as the four side surfaces for a length of  $\sim 4 \text{ mm}$  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 the copper foil was a copper wire that had been 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 2002 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 temperatures of the two ends. Voltage and temperature measurements were done simultaneously using the multimeter. The voltage difference (hot minus cold) divided by the temperature difference (hot minus cold) 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 ( $+2.34 \mu\text{V}/^\circ\text{C}$ ) [8] is the absolute thermoelectric power of the sample. Each sample was heated at one end at a rate of  $0.009^\circ\text{C/s}$  and then cooled with the power of the platen turned off. The heating rate was constant, but the cooling rate was not.

DC volume electrical resistivity was measured using the Keithley 2002 multimeter and the four-probe method [9]. 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 ( $75 \times 15 \times 15 \text{ mm}$ ). The four planes were symmetrical around the midpoint along the length of the specimen, such that the outer contacts (for passing current) were 65 mm apart and the inner contacts (for measuring the voltage in relation to resistivity determination) were 55 mm apart.

Three specimens of each composition were tested. Each specimen was tested in terms of both the thermopower and the resistivity.

The extent of moisture loss was assessed for each specimen by weight measurement before and after heating at  $80^\circ\text{C}$  for either 24 h or 10 days. No silver paint or electrical contact was present during heating or weight measurement.

### 3. Results

Table 2 shows that weight loss mostly occurred in the first 24 h of heating at  $80^\circ\text{C}$ . The additional weight loss up to 10 days of heating was relatively small. The fractional loss in weight was less when silica fume was added, but the further addition of carbon fiber increased the weight loss. The higher the fiber content, the greater was the weight loss. This effect of fiber content is consistent with the increase of air void content with increasing fiber content [10]. However, the effect of fibers on the weight loss was small compared to the effect of silica fume on the weight loss.

Table 2  
Effect of moisture loss (by heating at  $80^\circ\text{C}$  for 24 h or 10 days) on the electrical resistivity and absolute thermoelectric power of cement pastes

Cement paste designation	Weight loss (%)		Resistivity ( $10^5 \Omega \text{ cm}$ )			Absolute thermoelectric power ( $\mu\text{V}/^\circ\text{C}$ )		
	24 h	10 days	Initial <sup>a</sup>	24 h	10 days	Initial <sup>a</sup>	24 h	10 days
(i)	0.50	0.53	$8.2 \pm 0.6$	$10.7 \pm 0.6$	$11.2 \pm 0.6$	$+2.71 \pm 0.03$	$+2.72 \pm 0.05$	$+2.72 \pm 0.04$
(ii)	0.33	0.38	$3.7 \pm 0.7$	$4.2 \pm 0.5$	$4.8 \pm 0.2$	$+2.68 \pm 0.05$	$+2.70 \pm 0.06$	$+2.71 \pm 0.03$
(iii)	0.38	0.40	$0.68 \pm 0.03$	$0.81 \pm 0.07$	$0.86 \pm 0.06$	$+3.80 \pm 0.03$	$+3.82 \pm 0.04$	$+3.82 \pm 0.02$
(iv)	0.44	0.46	$0.40 \pm 0.06$	$0.50 \pm 0.03$	$0.53 \pm 0.05$	$+5.18 \pm 0.06$	$+5.17 \pm 0.05$	$+5.16 \pm 0.03$

<sup>a</sup> Prior to any heating.

Table 2 also shows that the resistivity was increased after heating, with the most effect occurring in the first 24 h of heating. This is consistent with the weight loss, which occurred also mostly in the first 24 h of heating. The resistivity was decreased by the addition of silica fume and was further decreased by the further addition of carbon fiber. The higher the fiber content, the lower was the resistivity, as expected. Hence, there was substantial correlation between resistivity and weight loss, indicating that moisture loss caused the resistivity to increase.

Table 2 also shows that the thermopower was not affected by heating. This means that moisture loss did not affect the thermopower. The absolute thermoelectric power was not affected by silica fume addition, but became less negative and more positive as the fiber content increased, as previously reported [3].

#### 4. Discussion

Moisture contributes ions, namely,  $H^+$  and  $OH^-$  ions. The ions as well as electrons/holes move in response to an electric field, thus contributing to electrical conduction. This notion is well known and is supported by the resistivity results of this work. However, a surprising finding of this work is that ion movement contributes in a minor way, if at all, to the Seebeck effect. This means that ions do not readily respond to a temperature gradient, although they do respond to a voltage gradient. On the other hand, electrons/holes readily respond to either a temperature gradient or a voltage gradient, due to their small size compared to the size of ions. The low value of the absolute thermoelectric power of plain cement paste is thus mainly due to electrons rather than ions, although both electrons and ions contribute to electrical conduction.

The moisture loss was related to the evaporation of liquid water rather than the dehydration of bound water, as indicated by the small fractional loss in weight. This paper shows that liquid water does not contribute much, if at all, to the Seebeck effect, whether the cement contains silica fume or not, and whether the cement contains fiber or not. On the other hand, liquid water contributes to the

electrical conduction, even in the presence of carbon fiber. However, the effect of moisture on the conduction is small compared to the effect of fiber or silica fume on the conduction.

#### 5. Conclusion

Moisture loss results in an increase in the electrical resistivity, but no change in the absolute thermoelectric power. Moisture in the form of liquid water contributes little, if any, to the Seebeck effect in cement-based materials, although it contributes to electrical conduction. In other words, ions do not readily respond to a temperature gradient, though they respond to a voltage gradient. The Seebeck effect of plain cement paste is mainly due to electrons.

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