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SCIENCE DIRECT

Cement and Concrete Research 34 (2004) 481–485

CEMENT AND CONCRETE RESEARCH

Electric polarization and depolarization in cement-based materials, studied by apparent electrical resistance measurement

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Received 15 October 2001; accepted 2 September 2003

Abstract

Electric polarization in cement-based materials (without conductive admixture) under an applied DC electric field was found by apparent electrical resistance measurement to be faster than subsequent depolarization under a reverse field by a factor ranging from 5 to 8. The slow depolarization suggested a degree of ionic trapping. In contrast, depolarization was even faster than polarization in carbon fiber cement, due to the fast hole response. Sand addition slowed down polarization saturation, but enhanced the polarization. Silica fume addition did not slow down polarization saturation, but diminished the polarization slightly. An increase in temperature enhanced the polarization due to increase in ionic mobility.

Keywords: Electrical properties; Transport properties; Physical properties; Mortar; Polarization

1. Introduction

Electric polarization refers to the phenomenon in which the centers of positive and negative charges do not coincide. It commonly occurs in a dielectric material when it is exposed to an electric field. As an electric field is present during electrical resistivity measurement, polarization can occur in a material during electrical resistivity measurement. Because of the polarization-induced electric field in the material being opposite in direction from the applied electric field, polarization causes the measured resistivity (i.e., apparent resistivity, to be distinguished from the true resistivity) to increase with time during resistivity measurement.

Polarization can occur within cement as well as at the interface between cement and an electrical contact. The former dominates when the four-probe method is used, whereas the latter dominates when the two-probe method is used, as shown by observation of polarization reversal in carbon-fiber-reinforced cement [1].

Subsequent to polarization, reversal of the applied electric field causes depolarization, which can also be monitored by measurement of the apparent resistivity. This work is focused on study of the polarization and depolarization processes in cement-based materials, with emphasis on the effects of sand, silica fume and temperature. Previous related work addressed these processes in carbon-fiber-reinforced cement only [1]. The subject pertains to the movement of ions in response to an electric field and the reversibility of the movement under a reverse field. Ion movement is central to understanding the electrical and dielectric behavior of cement-based materials.

Temperature is known to affect the mechanical properties of cement-based materials. In particular, heating tends to cause moisture loss [6–11], porosity increase [6,7] and decreases in strength and modulus [6–14]. The effect of temperature on the electrical resistivity of cement pastes has been studied. The resistivity decreases with increasing temperature, due to the activation energy involved in electrical conduction [2–5]. This effect allows a cement-based material to function as a thermistor.

Both conduction and polarization of cement-based materials are thermally activated, as shown by impedance measurement of cement mortar [5]. The activation energy of polarization is about one-fourth of that of conduction [5]. In spite of the low activation energy of polarization, the effect of temperature on polarization is relevant to the use of a

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0008-8846/$ – see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.cemconres.2003.09.003

cement-based material as a thermistor. It is also relevant to studying the effect of temperature on the ionic mobility.

2. Experimental methods

The cement used was portland cement (Type I) from Lafarge (Southfield, MI). The sand used in the mortar was natural sand (100% passing 2.36-mm sieve, 99.9% SiO_2); the sand/cement ratio was 1.0. The water/cement ratio was 0.35. A water reducing agent (WR) was used in the amount of 1.0% by weight of cement. The WR was TAMOL SN (Rohm and Haas, Philadelphia, PA), which contained 93–96% sodium salt of a condensed naphthalene sulfonic acid. No coarse aggregate was used. For cement paste, silica fume (Elkem Materials, Pittsburgh, PA, EMS 965) was optionally used in the amount of 15% by mass of cement [15]. A Hobart mixer with a flat beater was used for mixing, which was conducted for 5 min. After that, the mix was poured into oiled molds. A vibrator was used to facilitate compaction and decrease the amount of air bubbles. Specimens were demolded after 1 day and then allowed to cure in a moist chamber at a relative humidity of 100% for 28 days.

Specimens were rectangular bars of size 75 × 15 × 15 mm. DC electrical resistance measurement was made along the length of a specimen, using the four-probe method, in which silver paint in conjunction with copper wires served as electrical contacts. Four contacts were made perimetrically around the specimen at four planes that were all perpendicular to the length of the specimen and that were symmetric with respect to the midpoint along the length of the specimen. The outer two contacts (50 mm apart) were for passing current. The inner two contacts (40 mm apart) were for measuring the voltage. A Keithley (Cleveland, OH) 2002 multimeter was used. For the resistance values encountered in this study (20-MΩ range), the resolution of the meter was 1 Ω and the current source in the meter gave a current of 70 nA. A resistance of 37 MΩ corresponded to a voltage of 2.6 V and an electric field of 0.65 V/cm between the voltage contacts.

Heating during resistance measurement was achieved by using resistance heating platens at the same temperature both above and below the specimen, such that the length of the specimen was parallel to the platen surfaces. The specimen was electrically insulated from both platens (steel) by using glass-fiber-reinforced Teflon films. The temperature was measured by using a T-type thermocouple near the center point of the rectangular specimen bar. Four specimens were tested at each temperature.

For the purpose of confirming the occurrence of polarization and studying the process of depolarization, the polarity of the resistivity measurement was switched after 200 s of resistivity measurement (i.e., 200 s of polarization). The resistivity measurement was performed continuously before and after the switching, which was conducted by controlling the voltage.

The resistivity (true or apparent) was obtained from the resistance (true or apparent) and the dimensions. The change in dimensions during temperature variation was neglected in considering the change in resistivity with temperature, due to its negligible effect on the resistivity.

The true resistivity of each specimen at a given temperature was indicated by the measured resistance in the initial 10-s period of resistivity measurement at the constant temperature, as polarization was negligible in 10 s. The true resistance was around 10^6–10^7 Ω for the specimens of this work. The fractional change in apparent resistance during polarization was essentially equal to the fractional change in apparent resistivity.

Weight loss at a constant elevated temperature (either 35 or 50 °C) was measured on mortar specimens in the form of disks of diameter 6 mm and thickness 1 mm by using a thermogravimetric analyzer (Perkin-Elmer, Norwalk, CT, TGA7). Three specimens were tested at each temperature.

3. Results and discussion

The true volume electrical resistivity of the cement-based materials of this work is shown in Table 1. It was increased by the addition of sand, as shown by comparing the mortar and paste, both without silica fume. It was essentially not affected by the addition of silica fume, as shown by comparing the pastes with and without silica fume. For a given material, the true resistivity decreased slightly with increasing temperature, as expected [2].

Fig. 1 shows the increase in the apparent resistivity with time of resistivity measurement for the mortar. The higher the temperature, the greater was the fractional change in apparent resistivity. In other words, the higher the temperature, the greater was the polarization for the same time of polarization, as shown in Table 2 for a time of 200 s.

The apparent resistivity of the mortar decreased abruptly upon polarity switching, such that the fractional change in apparent resistivity changed sign upon polarity switching. Shown in Fig. 2 is the behavior at 22 and 55 °C for mortar. This indicates the occurrence of electric polarization, which is the cause of the increase in apparent resistivity with the time of resistivity measurement before the polarity switching.

Table 1
True volume electrical resistivity (10^6 Ω cm) of the cement-based materials studied

Temperature (°C)	Mortar[a]	Paste[a]	Paste with silica fume
22	4.27 ± 0.01	0.820 ± 0.026	0.796 ± 0.013
35	3.22 ± 0.01	0.806 ± 0.018	0.793 ± 0.010
50	3.10 ± 0.01	0.801 ± 0.020	0.792 ± 0.011

The data were based on the measurement of three specimens for each type of specimen.

[a] Plain, without silica fume.

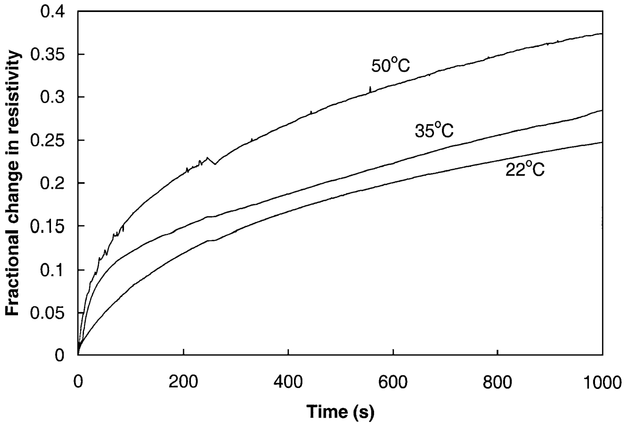

Fig. 1. Fractional change in apparent electrical resistivity of mortar vs. time at three different temperatures.

After the polarity switching, the apparent resistivity increased again, due to depolarization under the reverse electric field. However, the depolarization at 22 °C was not complete until 1100 s after the switching, as shown in Fig. 3 for the mortar. Hence, polarization was faster than depolarization by a factor of 5, indicating the tendency to retain the polarization. This tendency may be the consequence of electrostatic interaction between the mobile ions and the fixed charges in the material, i.e., a degree of ionic trapping.

The time for the completion of depolarization was similarly long (around 1000 s), whereas the time for polarization saturation was just 100 s for the cement pastes of this work. Thus, polarization was faster than depolarization by a factor of 8 for the cement pastes. In contrast, the time for depolarization was only 120 s (also after polarization for a period of 200 s) for carbon fiber (amorphous) cement paste [1], so that polarization was slightly slower than depolarization. The relatively fast depolarization for carbon fiber cement paste is due to the high electrical conductivity [2] imparted by the carbon fibers, which contributed holes to the electrical conduction [16–18]. Holes are expected to move more easily than ions due to their low mass.

After the completion of depolarization, polarization started to build up in the reverse direction as the reverse electric field was continuously applied (Fig. 3). However, this paper does not address the reverse polarization process.

Table 2
Fractional change in apparent resistivity at 200 s of polarization development

Temperature (°C)	Mortar[a]	Paste[a]	Paste with silica fume
22	0.1195 ± 0.0020	0.0923 ± 0.0025	0.0803 ± 0.0006
35	0.1561 ± 0.0022	0.1113 ± 0.0032	0.0872 ± 0.0010
50	0.2236 ± 0.0019	0.1317 ± 0.0029	0.0962 ± 0.0011

The data were based on the measurement of three specimens for each type of specimen.

[a] Plain, without silica fume.

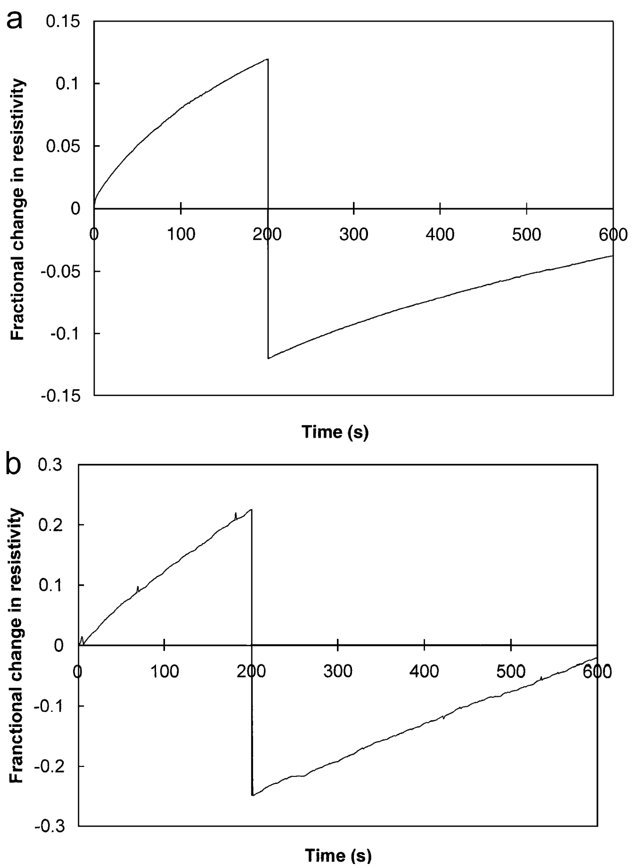

Fig. 2. Effect of polarity switching (at time = 200 s) on the apparent resistivity of mortar at (a) 22 °C and (b) 50 °C.

Fig. 4 shows the occurrence of weight loss (presumably due to moisture loss) at both 35 and 50 °C for the mortar. The weight loss was more significant at 50 °C than at 35 °C, as expected.

The true resistivity was lower at 50 °C than at 35 °C (Table 1). Polarization, a phenomenon that is associated with the dielectric behavior, is diminished by decreasing the resistivity, as previously shown by carbon fiber addition to

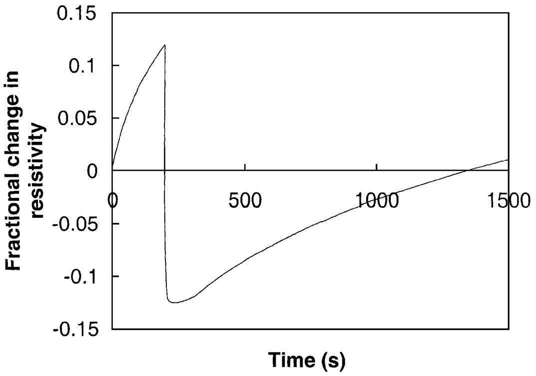

Fig. 3. Effect of polarity switching (at time = 200 s) on the apparent resistivity of mortar at 22 °C, showing the completion of depolarization at time = 1300 s.

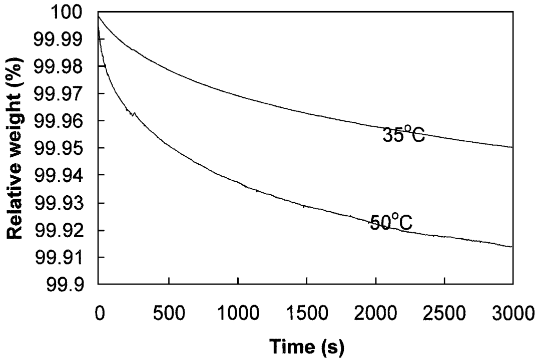

Fig. 4. Relative weight of mortar vs. time at 35 and 50 °C.

cement [1]. The loss in moisture was greater at 50 °C than at 35 °C; moisture contributes mobile ions to the polarization process [19,20]. In spite of this combination of facts, polarization was more significant at 50 °C than at 35 °C. This means that the observed increase in polarization with temperature is due to the increase in ionic mobility with temperature, rather than the change in ion quantity or electrical resistivity with temperature. In other words, an increase in temperature results in more thermal energy, which causes an increase in ionic mobility. This observation is consistent with the report that the polarization process is thermally activated [5]. The electric field involved with the resistance measurement was much too low (by orders of magnitude) for the occurrence of electric-field-induced strain (associated with the movement of ions in the diffuse double layer under an electric field and the transport of water by electroosmosis [21,22]) or electric-field-induced microstructural changes [23].

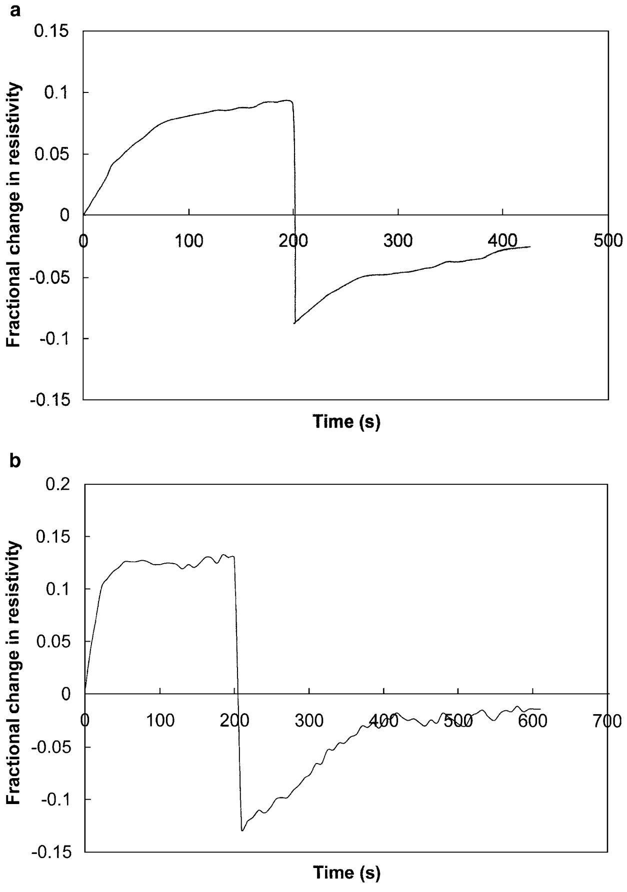

Fig. 5. Fractional change in apparent electrical resistivity of plain cement paste vs. time at (a) 22 and (b) 55 °C.

Because of the long time length of the observed depolarization (Figs. 2 and 3), the polarization is attributed to space charge polarization rather than orientation polarization, atomic polarization or electronic polarization. The space charges are associated with mobile charges within the cement-based material, rather than those at the electrical contacts, due to the use of the four-probe method rather than the two-probe method.

Fig. 5 shows the polarization behavior of plain cement paste at 22 and 55 °C. The polarization saturated after 100 s or less of resistivity measurement, as shown by the plateau reached by the resistivity. The higher the temperature, the shorter was the time needed to attain polarization saturation. This trend is consistent with the mortar case in Fig. 2, which shows that the polarization buildup was hastened by increasing the temperature. However, polarization saturation was not attained after 200 s of resistivity measurement in the mortar case, even at the highest temperature of 55 °C (Fig. 2(b)), whereas polarization saturation was attained after 30 s of resistivity measurement for the paste at 55 °C (Fig. 5(b)). Although polarization saturation was attained fast for the paste, the extent of polarization, as shown by the fractional change in apparent resistivity at 200 s of resistivity measurement (Table 2), was less for the paste (Fig. 5) than the mortar (Fig. 2). This means that the addition of sand (to form mortar) increased the extent of polarization and slowed down polarization saturation, respectively, due to the increase in true resistivity (Table 1) and the decrease in ionic mobility (both due to the presence of sand).

Fig. 6 shows the polarization behavior of the cement paste with silica fume at 22 °C. Comparison of Figs. 5(a)

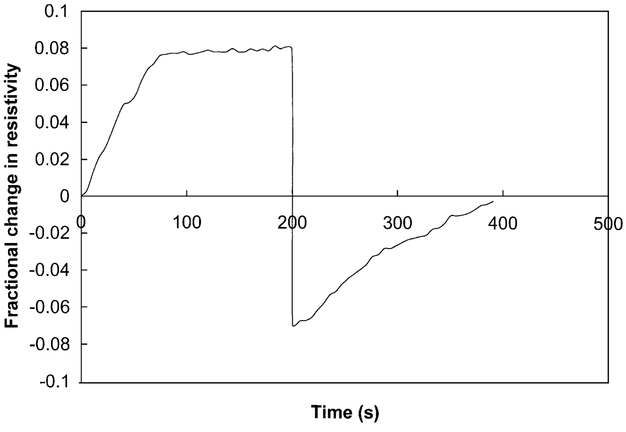

Fig. 6. Fractional change in apparent electrical resistivity of silica-fume cement paste vs. time at 22 °C.

and 6 show that the addition of silica fume decreased the extent of polarization, although the effect was small. This effect is also shown in Table 2.

Silica fume addition did not slow down polarization saturation, but sand addition did. This implies that silica fume did not decrease the ionic mobility, whereas sand did. This contrast between silica fume and sand is probably due to the pozzolanic nature of silica fume.

4. Conclusion

Electric polarization (space charge polarization) under a DC electric field and subsequent depolarization under a reverse field was monitored by apparent DC electrical resistance measurement for cement-based materials in the form of plain mortar, plain paste and silica fume paste. At 22 °C, polarization was faster than depolarization by a factor ranging from 5 to 8; polarization developed in mortar in 200 s took 1100 s to remove by depolarization. This is probably due to a degree of ionic trapping. (In contrast, polarization was slightly slower than depolarization in carbon fiber cement paste, which involved hole conduction.) An increase in temperature from 22 to 50 °C enhanced the polarization due to the increase in ionic mobility. Sand addition also enhanced the polarization, but it slowed down polarization saturation. Silica fume diminished the polarization slightly, but did not slow down polarization saturation.

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