Title no. 107-M46

Triple Percolation in Concrete Reinforced with Carbon Fiber

by F. Javier Baeza, D. D. L. Chung, Emilio Zornoza, Luis G. Andión, and Pedro Garcés

The electrical resistivity of carbon fiber (CF) reinforced concrete with electrical continuity within the cement paste and sand-cement ratio (s/c) 0.75 depends on the CF content and gravel-sand ratio (g/s). For resistivity \leq 500 Ω .cm, the mortar must exceed 62 vol.% and the cement paste must exceed 44 vol.%. The minimum resistivities provided by double percolation (continuity provided by the cement paste in the mortar but no continuity of either paste or mortar), pseudo triple percolation (continuity provided by the cement paste of the mortar), and true triple percolation (continuity provided by the mortar) are 355, 36, and 7.6 Ω .cm, respectively. The true triple percolation threshold is 0.75% CF (by mass of cement) if g/s \leq 1.50 and 1.5% CF if g/s \leq 2.00. The pseudo triple percolation threshold is 1.5% CF if g/s = 2.50 to 3.00. The double percolation threshold is 0.75% CF if g/s = 2.00 to 3.00.

Keywords: carbon fiber; electrical conductivity; electrical resistivity; percolation.

INTRODUCTION

Cement-based materials reinforced by discontinuous carbon fibers that are dispersed in the cement are technologically important, due to their combination of good structural properties, ¹ durability, ² and exceptional functional properties. ^{3,4} The good structural properties pertain to the high flexural toughness and strength, high tensile ductility and strength, and low drying shrinkage. The exceptional functional properties pertain to the high electrical conductivity and the associated high effectiveness for electromagnetic interference shielding, ⁵ in addition to the piezoresistivity (change of the electrical resistivity with strain), which results in the ability to sense strain. ⁶ The high conductivity is attractive for applications including electrical grounding and resistance heating (as for deicing).

The attainment of high electrical conductivity in carbon fiber cement-based materials requires percolation, that is, the structure in which the adjacent fibers touch one another, thereby resulting in a continuous electrically conductive path. The fiber volume fraction above which percolation occurs is known as the percolation threshold. The electrical conductivity increases abruptly at the percolation threshold as the fiber volume fraction is increased. As a consequence, the curve of conductivity versus fiber volume fraction is S-shaped, that is, the conductivity varies only slightly with the fiber volume fraction in the regimes below and above the threshold, but it increases abruptly at the threshold. The observation of percolation in carbon fiber-reinforced cement was first made by Chen and Chung⁷ and confirmed by a number of other researchers.⁸⁻¹¹

A cement-based structural material such as concrete contains aggregates. In case of carbon fiber-reinforced mortar, which contains a fine aggregate but no coarse aggregate, double percolation has been observed. ¹² Double percolation refers to the structure in which there are two levels of

percolation in the same composite material, namely, percolation of the fibers in the cement paste and percolation of the cement paste in the mortar. The fibers are located in the cement (that is, cement paste) part of the composite material. The change of the conductivity with fiber volume fraction in the vicinity of the fiber percolation threshold is more gradual when an aggregate is present. The higher is the aggregate proportion (for example, the sand-cement ratio [s/c]), the lower is the conductivity for the same fiber volume fraction, 8,10,11 as expected due to the nonconductive nature of the aggregates. No S-shaped curve corresponding to cement percolation, however, (to be distinguished from fiber percolation) in the presence of an aggregate has been reported.

Triple percolation refers to the structure in which there are three levels of percolation in the same composite material. For the case of fibers in cement paste (without aggregate), there is only one type of percolation, which is associated with the electrical continuity of the fibers. For the case of fibers in cement mortar (which contains fine aggregate but no coarse aggregate), there can be two levels of percolation one associated with the electrical continuity of the fibers in the cement paste and the other associated with the electrical continuity of the cement paste among the fine aggregate particles. For the case of fibers in concrete, which contains fine and coarse aggregates, there can be also a third level of percolation, due to the electrical continuity of the cement mortar among the coarse aggregate particles. The second level of percolation is characterized by the conductivity decreasing abruptly as the volume fraction of the fine aggregate is decreased below a critical value, below which the cement paste starts to attain continuity. The third level of percolation is characterized by the conductivity decreasing abruptly as the volume fraction of the coarse aggregate is decreased below critical values, below which the mortar starts to attain continuity. To reach high electrical conductivity in a cementbased material that contains fine and coarse aggregates, all three levels of percolation are required. Thus, the characterization of the triple percolation behavior is important for the development of electrically conductive concrete.

Double percolation has been reported in carbon fiber-reinforced mortar¹² and in numerous polymer-matrix composites, particularly those involving polymer blends.¹³⁻¹⁵ Triple percolation has been previously reported for carbon-black glass-fiber polymer-matrix composites, with the triple percolation being attractive for decreasing the required loading of carbon black for achieving the desired level of

ACI Materials Journal, V. 107, No. 4, July-August 2010.

MS No. M-2009-288 received August 19, 2009, and reviewed under Institute publication policies. Copyright © 2010, American Concrete Institute. All rights reserved, including the making of copies unless permission is obtained from the copyright proprietors. Pertinent discussion including authors' closure, if any, will be published in the May-June 2011 ACI Materials Journal if the discussion is received by February 1, 2011.

F. Javier Baeza is working on his PhD thesis in multifunctional cement composites at the University of Alicante, Alicante, Spain. He received his BS in civil engineering from the University of Alicante in 2007.

D. D. L. Chung is a Professor at the University at Buffalo, State University of New York, Buffalo, NY, where she is also the Director of the Composite Materials Research Laboratory. She received her BS from the California Institute of Technology, Pasadena, CA, and her PhD in materials science from the Massachusetts Institute of Technology, Cambridge, MA. Her research interests include multifunctional structural materials.

Emilio Zornoza works at the University of Alicante. He received his PhD in chemistry from the Polytechnic University of Valencia, Valencia, Spain, in 2007. His research interests include the characterization of carbon/cement composites and the development of new nonstructural functions for these composites.

Luis G. Andión is a Professor at the University of Alicante. He received his MS in civil engineering from the State University of New York, and his PhD in CAC cements from the Polytechnic University of Madrid, Madrid, Spain, in 2006. His research interests include advanced concrete structures and durability problems.

Pedro Garcés is a Professor in the Department of Construction Engineering of the University of Alicante. He received his PhD in chemistry science from University of Alicante in 1987. His research interests include mechanical and durability properties of construction materials and on multifunctional conductive concrete.

electrical conductivity. ¹⁶ This paper provides the first report of triple percolation in cement-based materials. In particular, the transition from double percolation to triple percolation is studied through systematic decrease of the coarse aggregate proportion at various carbon fiber proportions.

The main objective of this paper is to observe and characterize the triple percolation behavior of carbon fiber-reinforced concrete that exhibits electrical continuity within the cement paste (due to the carbon fiber in the cement paste) and s/c 0.75. A related objective is to determine the appropriate proportions of carbon fiber and coarse aggregate for attaining high electrical conductivity in carbon fiber-reinforced concrete.

PERCOLATION CONCEPTS

True triple percolation involves electrical continuity provided by the mortar in the concrete. In other words, true triple percolation involves electrical continuity characterized by double percolation, in addition to electrical continuity of the mortar in the concrete. Pseudo triple percolation, which is a new concept introduced in this paper, involves electrical continuity provided by the cement paste part of the mortar in the concrete, that is, it involves electrical continuity characterized by double percolation in addition to electrical continuity of the cement paste part of the mortar in the concrete. Double percolation involves electrical continuity provided by the cement paste in the mortar, but no continuity of either paste or mortar in the concrete. In all three levels of percolation, there is electrical continuity of the carbon fiber in the cement paste.

RESEARCH SIGNIFICANCE

Concrete that exhibits high electrical conductivity is important for multifunctional behavior. For high conductivity, triple percolation is necessary. This paper provides the first observation of triple percolation in cement-based materials and gives information on the carbon fiber and aggregate proportions for achieving high electrical conductivity in concrete. In addition, it introduces the concept of pseudo triple percolation, which is to be distinguished from true triple percolation.

EXPERIMENTAL INVESTIGATION

Materials

Portland cement concretes with carbon fiber additions were fabricated. The components and proportions (relative to the cement mass) are as follows:

Cement, Type CEM I 52.5 R.

Table 1—Carbon fiber properties

| Type | PANEX 35 | | |
|------------------|--|--|--|
| Diameter | $7.2 \ \mu m \ (2.83 \times 10^{-4} \ in.)$ | | |
| Carbon content | 95% | | |
| Tensile strength | $3800 \text{ MPa} (551 \times 10^3 \text{ psi})$ | | |
| Elastic modulus | 242 GPa $(351 \times 10^5 \text{ psi})$ | | |
| Resistivity | $1.52 \times 10^{-3} \Omega \text{cm} (5.98 \times 10^{-4} \Omega \text{in.})$ | | |
| Density | 1.81 g/cm ³ (113 lb/ft ³) | | |

- Fine aggregate: sand, according to standard CEN UNE-EN 196-1:1996.
- Coarse aggregate: natural limestone aggregate (gravel), fraction 8/5, selected from aggregate 12.5/5, using 8/5 sieves series.
- Carbon fiber (CF), with 7.2 μ m (2.83 \times 10⁻⁴ in.) diameter and 3.5 mm (0.14 in.) length (Table 1) at 0.75, 1.0, 1.5, 1.7, and 2.0% by mass of cement.
- water-cement ratio (w/c) = 0.50.
- s/c = 0.75.
- Gravel-sand ratios (g/s) = 0.15, 0.25, 0.375, 0.75, 1.50, 2.00, 2.50, and 3.00.

The *s/c* is fixed at 0.75, which is an optimal proportion obtained as a compromise between cost and conductivity in prior work on double percolation. ¹² It is not possible to make a direct comparison of the results of this paper with those of Reference 12 because of the differences in formulation. Silica fume is not used in this paper but is used in Reference 12 for helping the fiber dispersion. In contrast, this paper uses sonication to enhance the fiber dispersion. Furthermore, the fiber aspect ratio is 500 in this paper, but it is 300 in Reference 12. The large aspect is expected to lower the double percolation threshold (that is, lower fiber content or higher sand content for double percolation). Due to the large aspect ratio, the *s/c* of 0.75 in this work guarantees double percolation.

To achieve a uniform dispersion of the CF in the mixture and to improve some of the specimen properties, fibers were subjected to two types of treatment prior to incorporation in the mixture. The first treatment was oxidation, as conducted by placing the fibers in air at 400°C (752°F), with a flow of 10 mL/min. (0.0003 gal./min.), for 4 hours. This treatment served: 1) to remove the fiber sizing to expose the carbon in the fiber; and 2) to form oxygen-containing functional groups on the surface of the carbon in the fiber to improve the wettability of the fiber by water and strengthen the fiber-matrix bonding. The second treatment involved sonication for 5 minutes, using a sonicator at maximum power (200 W), after the fibers had been dispersed in water.

Specimens

Prismatic specimens of size 160 x 40 x 40 mm (6.30 x 1.57 x 1.57 in.) were prepared. After casting and demolding, the concrete specimens were immersed in water at 20°C (68°F) for 28 days. Then they were externally dried.

Items of investigation

After curing and drying, silver electrically conductive paint was applied to the two opposite end faces of each specimen (1 and 2 in Fig. 1) and around the perimeter at two interior planes that were parallel to the end surfaces (3 and 4 in Fig. 1) to form four electrical contacts, as needed for the four-probe method of electrical resistance measurement. Then copper wire was wrapped around the perimeter at the

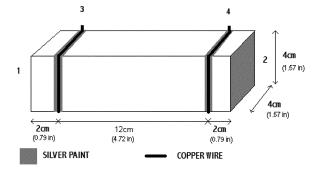


Fig. 1—Specimen configuration and electrical contact configuration. Contacts 1 and 2, located at two end surfaces of specimen, are for passing current. Contacts 3 and 4, located around the perimeter at two planes, are for voltage measurement.

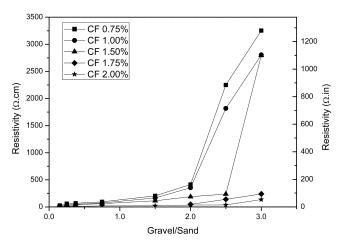


Fig. 2—Resistivity versus g/s for different CF proportions (by mass of cement, as shown in inset).

two interior planes. The electric current input was passed through contacts 1 and 2 (Fig. 1), while resistance measurement was made between contacts 3 and 4, using a digital multimeter.

Optical photographs of specimens were taken after small specimens of sizes suitable for microscopy had been cut from the original specimen at a plane near and parallel to the end surfaces of the original specimen, using a large-radius synthetic diamond blade lubricated with water. The surface of each specimen was not polished to avoid fiber pull-out from the cement matrix. Photographs were taken perpendicular to the plane of cutting. Photographs were taken using a digital camera, whether an optical microscope was used or not. The optical microscope was a zoom stereoscopic microscope.

EXPERIMENTAL RESULTS AND DISCUSSION Electrical resistivitY

Figure 2 shows the variation of volume resistivity as a function of *g/s* for different CF mass proportions. For a fixed CF proportion, the resistivity increases as the *g/s* increases, as expected.

For g/s equal to or greater than 2.00, the resistivity increases sharply with increasing g/s when the CF proportion is 1.5% (or below) by mass of cement. This means that triple percolation occurs when the g/s is sufficiently low, such that the critical g/s for triple percolation is higher at a CF proportion of 1.5% than at a CF proportion of 1.0 or 0.75%. In other words, a higher CF proportion facilitates triple percolation.

For a CF content of 1.75% or above (by mass of cement), the resistivity is influenced by the g/s to a limited degree. This means that low resistivity is obtained even at the highest g/s, if the CF proportion exceeds 1.5%.

The aforementioned results mean that, at a sufficiently high CF proportion, a cement paste bridge links electrically the mortar parts that are physically separated by a coarse aggregate. Due to the cement paste bridging, electrical continuity can occur in the absence of mortar continuity.

Figure 3 shows corresponding plots versus the CF proportion. For a given value of the g/s, a higher CF proportion results in

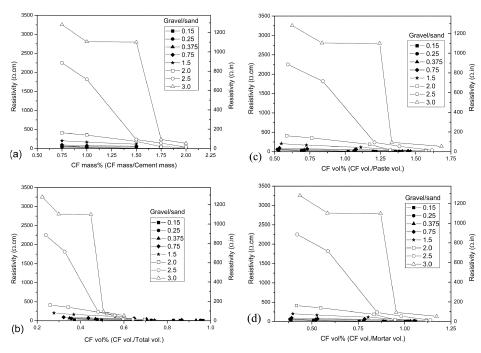


Fig. 3—Resistivity versus CF proportion for various values of g/s: (a) CF proportion indicated as CF mass by mass of cement; (b) CF volume fraction; (c) CF volume with respect to cement paste volume; and (d) CF volume with respect to mortar volume.

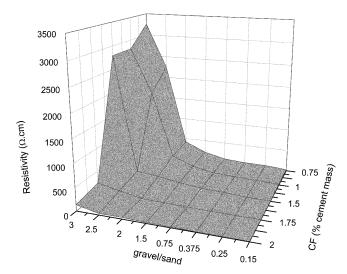


Fig. 4—Dependence of resistivity on CF proportion (by mass of cement) and g/s.

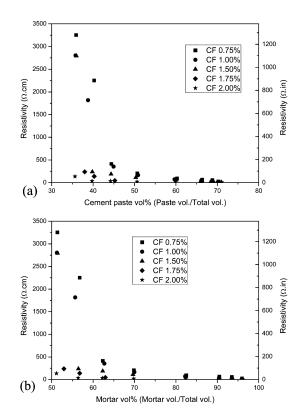


Fig. 5—(a) Resistivity versus cement paste content; and (b) resistivity versus mortar content.

a lower resistivity, as expected. For a given CF proportion, a higher g/s results in a higher resistivity, as expected. However, the effect of the g/s is small unless the g/s is 2.50 or above. When the CF proportion is at least 1.75% by mass of cement (0.5 vol.% of the concrete, 1.3 vol.% of cement paste, or 0.95 vol.% of mortar), the g/s (even up to the highest value of 3.0) has little effect on the resistivity. The CF proportion of 0.5 vol.% of the concrete is actually not very high. This indicates that high effectiveness of CF for providing triple percolation. On the other hand, when the CF proportion is only 0.3 vol.% of the concrete (0.53 vol.% of cement paste or 0.39 vol.% of mortar), the g/s should be 2.0 or less for the resistivity to be low.

Table 2—Resistivity data (mean ± standard deviation of data for three specimens of each type

| | | | | 71 |
|-------|---|---|--|---|
| g/s | CF% total | Resistivity | Percolation level | Relative standard deviation, % |
| 0.15 | 0.37 | 27.17 ± 0.29 | | 1.1 |
| 0.25 | 0.36 | 58.51 ± 1.45 | True triple | 2.5 |
| 0.375 | 0.35 | 66.67 ± 2.36 | True triple | 3.5 |
| 0.75 | 0.32 | 93.33 ± 5.94 | True triple | 6.4 |
| 1.50 | 0.28 | 205.32 ± 4.08 | True triple | 1.9 |
| 2.00 | 0.26 | 411.83 ± 8.90 | Double | 2.2 |
| 2.50 | 0.24 | 2250.18 ± 65.5 | Double | 2.9 |
| 3.00 | 0.22 | 3252.80 ± 45.9 | Double | 1.4 |
| 0.15 | 0.50 | 17.58 ± 0.22 | True triple | 1.3 |
| 0.25 | 0.48 | 32.63 ± 1.67 | True triple | 5.1 |
| 0.375 | 0.47 | 49.51 ± 1.90 | True triple | 3.8 |
| 0.75 | 0.44 | 73.33 ± 2.55 | True triple | 3.5 |
| 1.50 | 0.37 | 166.67 ± 5.19 | True triple | 3.1 |
| 2.00 | 0.34 | 354.50 ± 2.43 | Double | 0.7 |
| 2.50 | 0.33 | 1816.7 ± 29.3 | Double | 1.6 |
| 3.00 | 0.30 | 2803.5 ± 45.9 | Double | 1.6 |
| 0.15 | 0.73 | 8.76 ± 0.16 | True triple | 1.8 |
| 0.25 | 0.73 | 9.87 ± 0.03 | True triple | 0.3 |
| 0.375 | 0.70 | 40.00 ± 1.84 | True triple | 4.6 |
| 0.75 | 0.65 | 60.64 ± 2.54 | True triple | 4.2 |
| 1.50 | 0.56 | 113.33 ± 1.85 | True triple | 1.6 |
| 2.00 | 0.52 | 187.83 ± 4.31 | True triple | 2.3 |
| 2.50 | 0.48 | 237.61 ± 6.04 | Pseudo triple | 2.5 |
| 3.00 | 0.45 | 2795.00 ± 9.11 | Double | 0.3 |
| 0.15 | 0.86 | 8.22 ± 0.07 | True triple | 0.9 |
| 0.25 | 0.83 | 9.84 ± 0.01 | True triple | 0.1 |
| 2.00 | 0.60 | 46.77 ± 1.71 | True triple | 3.7 |
| 2.50 | 0.56 | 138.70 ± 2.86 | Pseudo triple | 2.1 |
| 3.00 | 0.51 | 238.47 ± 2.35 | Pseudo triple | 0.9 |
| 0.15 | 0.96 | 7.64 ± 0.07 | True triple | 0.8 |
| 0.25 | 0.95 | 7.92 ± 0.14 | True triple | 1.7 |
| 0.375 | 0.93 | 9.57 ± 0.04 | True triple | 0.4 |
| 0.75 | 0.87 | 17.57 ± 0.24 | True triple | 1.4 |
| 1.50 | 0.74 | 20.14 ± 1.13 | True triple | 5.6 |
| 2.00 | 0.70 | 35.20 ± 0.76 | True triple | 2.2 |
| 2.50 | 0.64 | 36.29 ± 0.06 | Pseudo triple | 0.2 |
| 3.00 | 0.60 | 135.84 ± 0.75 | Pseudo triple | 0.6 |
| | 0.25 0.375 0.75 1.50 2.00 0.15 0.25 0.375 0.75 1.50 2.00 0.15 0.25 0.375 0.75 1.50 2.00 0.15 0.25 0.375 0.75 1.50 2.00 0.15 0.25 0.375 0.75 1.50 2.00 0.15 0.25 0.375 0.25 0.375 0.25 0.300 0.15 0.25 0.375 0.25 0.300 0.15 0.25 0.375 0.25 0.375 0.25 0.375 0.25 0.375 | g/s volume 0.15 0.37 0.25 0.36 0.375 0.35 0.75 0.32 1.50 0.28 2.00 0.26 2.50 0.24 3.00 0.22 0.15 0.50 0.25 0.48 0.375 0.47 0.75 0.44 1.50 0.37 2.00 0.34 2.50 0.33 3.00 0.30 0.15 0.73 0.25 0.73 0.375 0.70 0.75 0.65 1.50 0.56 2.00 0.52 2.50 0.48 3.00 0.45 0.15 0.86 0.25 0.83 2.00 0.60 2.50 0.56 3.00 0.51 0.15 0.96 0.25 0.95 0.3 | g/s Cr b total volume (Ωcm)* 0.15 0.37 27.17 ± 0.29 0.25 0.36 58.51 ± 1.45 0.375 0.35 66.67 ± 2.36 0.75 0.32 93.33 ± 5.94 1.50 0.28 205.32 ± 4.08 2.00 0.26 411.83 ± 8.90 2.50 0.24 2250.18 ± 65.5 3.00 0.22 3252.80 ± 45.9 0.15 0.50 17.58 ± 0.22 0.25 0.48 32.63 ± 1.67 0.375 0.47 49.51 ± 1.90 0.75 0.44 73.33 ± 2.55 1.50 0.37 166.67 ± 5.19 2.00 0.34 354.50 ± 2.43 2.50 0.33 1816.7 ± 29.3 3.00 0.30 2803.5 ± 45.9 0.15 0.73 8.76 ± 0.16 0.25 0.73 9.87 ± 0.03 0.375 0.70 40.00 ± 1.84 0.75 0.65 60.64 ± 2.54 1.50 0.56 113 | g/sCl Notation volume $(\Omega \text{cm})^*$ True triple0.150.37 27.17 ± 0.29 True triple0.250.36 58.51 ± 1.45 True triple0.3750.35 66.67 ± 2.36 True triple0.750.32 93.33 ± 5.94 True triple1.500.28 205.32 ± 4.08 True triple2.000.26 411.83 ± 8.90 Double2.500.24 2250.18 ± 65.5 Double3.000.22 3252.80 ± 45.9 Double0.150.50 17.58 ± 0.22 True triple0.250.48 32.63 ± 1.67 True triple0.3750.47 49.51 ± 1.90 True triple0.750.44 73.33 ± 2.55 True triple1.500.37 166.67 ± 5.19 True triple2.000.34 354.50 ± 2.43 Double2.500.33 1816.7 ± 29.3 Double2.500.33 1816.7 ± 29.3 Double0.150.73 8.76 ± 0.16 True triple0.250.73 9.87 ± 0.03 True triple0.3750.70 40.00 ± 1.84 True triple0.3750.65 60.64 ± 2.54 True triple1.500.56 113.33 ± 1.85 True triple2.500.48 237.61 ± 6.04 Pseudo triple3.000.45 2795.00 ± 9.11 Double0.250.83 9.84 ± 0.01 True triple0.250.83 9.84 ± 0.01 True triple2.50 |

^{*}Resistivity conversion factor. 1 Ω cm = 0.39 Ω .in.

Figure 4 shows the combined effects of the CF proportion and the g/s on the resistivity. The sharp increase in resistivity occurs at the triple percolation threshold, which depends on the CF proportion and the g/s. When the CF proportion is low, the g/s at the threshold is low. When the CF proportion is high, the g/s at the threshold is high.

Table 2 shows the resistivity data obtained for every mixture in this work. The accuracy level reached is satisfactory because the relative standard deviation of three tested specimens of each mixture is under 7%.

Figure 5(a) shows that the same collection of data presented as a plot of the resistivity versus the cement paste volume fraction. The resistivity decreases with increasing cement paste volume fraction, such that the resistivity is low

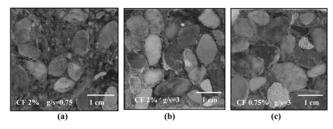


Fig. 6—Photographs of surface of specimens with various combinations of CF content (% by mass of cement) and g/s: (a) CF 2%, g/s = 0.75, ρ = 17.57 ± 0.24 Ω cm (6.85 ± 0.09 Ω in), with true triple percolation; (b) CF 2%, g/s = 3.00, ρ = 135.84 ± 0.75 Ω cm (52.98 ± 0.29 Ω in.), with pseudo triple percolation; and (c) CF 0.75%, g/s = 3.00, ρ = 3253 ± 46 Ω cm (1269 ± 18 Ω in.), with double percolation.

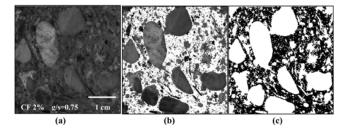


Fig. 7—Photographs of surface of different piece of specimen of Fig. 6(a), which has 2% CF content (by mass of cement), g/s = 0.75, and ρ = 17.57 ± 0.24 Ω cm (6.85 ± 0.09 Ω in.). Specimen exhibits true triple percolation: (a) image without digital processing; (b) image with digital processing to highlight aggregates (coarse and fine) as dark regions; and (c) image with digital processing to highlight cement paste as dark regions.

(less than 500 Ω .cm or 195 Ω .in.) when the cement paste volume fraction exceeds 0.44. When the CF proportion is 1.5% (or above) by mass of cement, the cement paste volume fraction only needs to be 0.40 for the resistivity to be low. When the CF proportion is 2.0% by mass of cement, the cement paste volume fraction only needs to be 0.35 for the resistivity to be low.

The corresponding plot for the resistivity versus the mortar volume fraction (Fig. 5(b)) shows that the mortar volume fraction needs to be at least 0.62 for the resistivity to be low (less than 500 Ω .cm or 195 Ω .in.). At the CF proportion of 1.5% (or above) by mass of cement, the mortar volume fraction needs to be at least 0.56 for the resistivity to be low. At the CF proportion of 2.0% (or above) by mass of cement, the mortar volume fraction needs to be at least 0.51 for the resistivity to be low. The higher is the CF proportion, the smaller is the minimum mortar volume fraction for achieving low resistivity in the concrete.

Microstructure

Zoom stereoscopic optical microscopy was used to distinguish among true triple percolation, pseudo triple percolation and double percolation, as indicated in Table 2. The results based on microscopy are consistent with those based on resistivity measurement, with double percolation giving higher resistivity than true or pseudo triple percolation.

Figures 6 to 8 show optical photographs of the surface of selected concrete specimens. Figures 6 and 7 were obtained using only a digital camera (in the absence of a microscope),

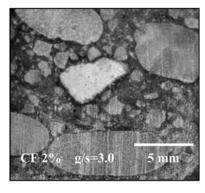


Fig. 8—Optical micrograph of surface of different piece of specimen of Fig. 6(b), which has 2% CF content (by mass of cement), g/s = 3.00, and ρ = 135.84 ± 0.75 Ω cm (52.98 ± 0.29 Ω in.). A phenolphthalein solution was applied to improve contrast among phases. The specimen exhibits pseudo triple percolation.

whereas Fig. 8 was obtained using a stereoscopic optical microscope in conjunction with a digital camera.

As the *g/s* is increased, the width of the mortar between coarse aggregate particles becomes narrower. When this width is too small, the fine aggregate cannot be present in the region, so only cement paste can be present. Nevertheless, due to the presence of carbon fiber in the cement paste, electrical continuity can be provided by the cement paste. This is not true triple percolation, however, because the mortar does not provide a continuous conductive path. Thus, we call this phenomenon pseudo triple percolation. The effect of *g/s* on the width of the region between coarse aggregate particles is shown by comparing Fig. 6(a) (which exhibits true triple percolation) and Fig. 6(b) (which exhibits pseudo triple percolation).

In relation to Fig. 6(b) and (c), both with a g/s of 3.00, the gravel content is so high that a continuous mortar conductive path does not exist. Due to the high fiber content, Fig. 6(b) exhibits pseudo triple percolation. The fiber content is low in Fig. 6(c), however, so only double percolation occurs in Fig. 6(c). In other words, double percolation is present in both Fig. 6(b) and (c), but pseudo triple percolation is present in Fig. 6(b). As a consequence, the resistivity is higher for Fig. 6(c) than Fig. 6(b).

The distribution of the mortar among the coarse aggregate particles and that of the cement paste among the fine aggregate particles is shown in Fig. 7 for the specimen of Fig. 6(a), with true triple percolation. Figures 7(b) and (c) were obtained from Fig. 7(a) by digital processing for the purpose of highlighting the aggregates. Figure 7(b) shows the aggregates as dark regions, whereas Fig. 7(c) shows the aggregates as bright regions and shows the cement paste as dark regions. Figure 7(b) shows the presence of mortar between adjacent particles of coarse aggregate. Figure 7(c) shows that the cement paste tends to line the surface of the large aggregate particles; this is reasonable because the cement paste is the part of the mortar that is able to penetrate a small gap.

Figure 8 was obtained using a stereoscopic zoom optical microscope for the specimen of Fig. 6(b). To enhance the contrast among phases, a phenolphthalein solution (with the phenolphthalein dissolved in a 1:1 water/ethanol solution) was sprayed over the sample prior to obtaining the micrograph of Fig. 8. Pink areas (darker areas) correspond to the cement paste regions. A very narrow pink band is present between

coarse aggregate particles that are almost in contact, thus providing support for the new concept of "pseudo triple percolation," that is, double percolation with cement paste rather than mortar that is electrically continuous in the presence of the coarse aggregate. In true triple percolation (or simply, triple percolation), mortar is at the interface between coarse aggregate particles, thereby providing an electrically continuous path. In contrast, in pseudo triple percolation, cement paste is at the interface between coarse aggregate particles, thereby providing an electrically continuous path. The presence of cement paste between coarse aggregate particles that are almost in contact is consistent with the observation (Fig. 7(c)) that cement paste tends to line the surface of the large aggregate particles.

Levels of percolation

Three levels of percolation in concrete are addressed in this paper, namely, double percolation, pseudo triple percolation, and true triple percolation, as distinguished by optical microscopy and supported by resistivity results.

Pseudo triple percolation is observed in this work only when the g/s is high (2.50 or 3.00) and the CF content is high (over 1.50% by mass of cement). When the g/s is lower than 2.50, either true triple percolation or double percolation occurs, depending on the combination of g/s and the CF content. For example, at a CF content of 2.0%, the decrease of the g/s from 3.00 to 2.00 causes the change from pseudo triple percolation to true triple percolation and hence the decrease of the resistivity from 136 to 35 Ω .cm (53 to 14 Ω .in.) (Table 2); at a g/s of 3.00, the decrease of the CF content from 2.0% to 1.5% causes change from pseudo triple percolation to double percolation and hence the increase of the resistivity from 136 to 2795 Ω .cm (53 to 1090 Ω .in.) (Table 2).

The state of double percolation is associated with a substantial range of resistivity due to the variation in the geometry of the continuous conductive path in the form of cement paste and in the conductivity of the cement paste. For example, for a CF content of 1.5%, double percolation occurs at a g/s of 3.00 (with resistivity 2795 Ω .cm [1090 Ω .in.]) (Table 2). Double percolation is observed for CF content of 1.5% (with g/s = 3.00), CF content of 1.0% (with g/s = 2.00 to 3.00), and CF content of 0.75% (with g/s = 2.00 to 3.00). In other words, with a lower CF content, the g/s can be lower to achieve double percolation. The lowest CF content for double percolation is 0.75% (possibly less, as the minimum has not been determined); the lowest g/s for double percolation is 2.00. The threshold for double percolation is at a CF content of 0.75% if the g/s is 3.00 or below. For each CF content, the lowest resistivity is achieved at the lowest g/s; this lowest resistivity decreases with increasing CF content, being 412 Ω .cm (161 Ω .in.) for a CF content of 0.75%, and 355 Ω .cm (138 Ω .in.) for a CF content of 1.0%. The lowest resistivity achieved by double percolation is thus 355 Ω .cm $(138 \Omega.in.)$.

The state of true triple percolation is associated with a range of resistivity, due to the variation in the geometry of the continuous conductive path in the form of mortar and in the conductivity of the mortar. For example, for a CF content of 0.75% and a g/s of 1.50, true triple percolation occurs with resistivity 205 Ω .cm (80 Ω .in.); for a CF content of 2.0% and a g/s of 2.00, true triple percolation occurs with resistivity 35 Ω .cm (14 Ω .in.) (Table 2). Among the numerous compositions studied, true triple percolation is observed for CF content of 2.0% (with g/s = 0.15 to 2.00), CF content of 1.75% (with g/s = 0.15 to 2.00), CF content of 1.75% (with g/s = 0.15

0.15 to 2.00), CF content of 1.5% (with g/s = 0.15 to 2.00), CF content of 1.0% (with g/s = 0.15 to 1.50), and CF content of 0.75% (with g/s = 0.15 to 1.50). With a lower CF content, the maximum g/s for achieving true triple percolation is decreased. The threshold for true triple percolation is at a CF content of 0.75% if the g/s is 1.50 or below, and is at a CF content of 1.5% if the g/s is 2.00 or below. With both cost and electrical performance taken into consideration, the CF content of 0.75% (by mass of cement) and a g/s below 1.5 are recommended. For each CF content, the lowest resistivity is achieved at the lowest g/s; this lowest resistivity decreases with increasing CF content, being 27 Ω .cm (11 Ω .in.) for a CF content of 0.75%, and 7.6 Ω .cm (3 Ω .in.) for a CF content of 2.0%. The lowest resistivity achieved by true triple percolation is thus 7.6 Ω .cm (3 Ω .in.).

The state of pseudo triple percolation is observed in this work for CF content of 2.0% (with g/s = 2.50 to 3.00), CF content of 1.75% (with g/s = 2.50 to 3.00), and CF content of 1.5% (with g/s = 2.50), and is associated with a range of resistivity from 36 Ω .cm (14 Ω .in.) (2.0% CF, with g/s = 2.50) to 238 Ω .cm (93 Ω .in.) (1.75% CF, with g/s = 3.00). This resistivity range is below that for double percolation. The resistivity can be above or below that of true triple percolation, however, due to the similarity in the effectiveness of the electrical path provided by the cement paste and by the mortar at the interface between adjacent coarse aggregate particles.

CONCLUSIONS

Based on the results of this experimental investigation, the following conclusions are drawn.

The electrical resistivity of CF reinforced concrete with electrical continuity within the cement paste and s/c 0.75 depends on both the CF content and the g/s. For a given g/s, increasing CF content results in decreasing resistivity. For a fixed CF content (by mass of cement), increasing g/s results in increasing resistivity. The effect of the g/s on the resistivity is not large, however, unless the g/s is 2.50 or above. When the CF proportion is at least 1.75% by mass of cement (0.5 volume % of the concrete, 1.3 volume % of cement paste, or 0.95 volume % of mortar), the g/s (even up to the highest value of 3.0) has minor effect on the resistivity. On the other hand, when the CF proportion is only 0.3 volume % of the concrete (0.53 volume % of cement paste or 0.39 volume % of mortar), the g/s should be 2.0 or less for the resistivity to be low. The mortar volume fraction needs to be at least 0.62 and the cement paste volume fraction needs to exceed 0.44 for the resistivity to be less than 500 Ω .cm (195 Ω .in.).

Triple percolation has been achieved in CF reinforced concrete. This includes true and pseudo forms of triple percolation. True triple percolation involves electrical continuity provided by the mortar in the concrete, whereas pseudo triple percolation involves electrical continuity provided by the cement paste part of the mortar in the concrete.

Pseudo triple percolation gives resistivity in the range from 36 to 238 Ω .cm (14 to 93 Ω .in.), which is below the resistivity range of 355 to 3253 Ω .cm (138 to 1269 Ω .in.) given by double percolation, and overlaps with the resistivity range of 7.6 to 205 Ω .cm (3 to 80 Ω .in.) given by true triple percolation. The minimum resistivity values provided by double percolation, pseudo triple percolation, and true triple percolation are 355, 36, and 7.6 Ω .cm (138, 14, and 3 Ω .in.), respectively. For each value of the CF content, the lowest resistivity is achieved for each level of percolation at the lowest g/s. With a lower CF content, the maximum g/s for

achieving either true triple percolation or pseudo triple percolation is decreased.

The threshold for true triple percolation is at a CF content of 0.75% (by mass of cement) if the g/s is 1.50 or below, and it is at a CF content of 1.5% (by mass of cement) if the g/s is 2.00 or below. The threshold for pseudo triple percolation is at a CF content of 1.5% (by mass of cement) if the g/s is 2.50, and it is 1.75% (by mass of cement) if the g/s is 2.50 to 3.00. The threshold for double percolation is at a CF content of 0.75% (by mass of cement) if the g/s is 2.00 to 3.00.

ACKNOWLEDGMENTS

The authors would like to acknowledge financial support received from Ministerio de Ciencia y Tecnologia (MAT 2003-06863), from Ministerio de Educación y Ciencia (BIA2006-10703), and from Ministerio de Fomento (9/2003 78110A03) (C63/2006) (Spain). E. Zornoza also thanks Ministerio de Ciencia y Tecnología (Spain) for its post-doctoral support by the Juan de la Cierva Programme.

REFERENCES

- 1. Garcés, P.; Fraile, J.; Vilaplana-Ortego, E.; Cazorla, D.; G. Alcocel, E.; and G^a Andión, L., "Effect of Carbon Fibres on the Mechanical Properties and Corrosion Levels of Reinforced Portland Cement Mortars," *Cement and Concrete Research*, V. 35, 2005, pp. 324-331.
- 2. Garcés, P.; G^a Andión, L.; Varga, I.; Catalá, G.; and Zornoza, E., "Corrosion of Steel Reinforcement in Structural Concrete with Carbon Material Addition," *Corrosion Science*, V. 49, 2007, pp. 2557-2566.
- 3. Chen, P.-W., and Chung, D. D. L., "Concrete as a New Strain/Stress Sensor," *Composites*, Part B, V. 27B, 1996, pp. 11-23.
- 4. Chung, D. D. L., "Piezoresistive Cement-Based Materials for Strain Sensing," *Journal of Intelligent Material Systems and Structures*, V. 13, No. 9, 2002, pp. 599-609.
- 5. Chung, D. D. L., "Electromagnetic Interference Shielding Effectiveness of Carbon Materials," *Carbon*, V. 39, No. 2, 2001, pp. 279-285.

- 6. Wen, S., and Chung, D. D. L., "Strain Sensing Characteristics of Carbon Fiber-Reinforced Cement," *ACI Materials Journal*, V. 102, No. 4, July-Aug. 2005, pp. 244-248.
- 7. Chen, P.-W., and Chung, D. D. L., "Improving the Electrical Conductivity of Composites Comprised of Short Conducting Fibers in a Non-Conducting Matrix: the Addition of a Non-Conducting Particulate Filler," *Journal of Electronic Materials*, V. 24, No. 1, 1995, pp. 47-51.
- 8. Chen, B.; Wu, K.; and Yao, W., "Conductivity of Carbon Fiber Reinforced Cement-Based Composites," *Cement and Concrete Composites*, V. 26, 2004, pp. 291-297.
- 9. Wang, X.; Wang, Y.; and Jin, Z., "Electrical Conductivity Characterization and Variation of Carbon Fiber Reinforced Cement Composite," *Journal of Materials Science*, V. 37, No. 1, 2002, pp. 223-227.
- 10. Reza, F.; Batson, G. B.; Yamamuro, J. A.; and Lee, J. S., "Volume Electrical Resistivity of Carbon Fiber Cement Composites," *ACI Materials Journal*, V. 98, No. 1, Jan.-Feb. 2001, pp. 25-35.
- 11. Chiarello, M., and Zinno, R., "Electrical Conductivity of Self-Monitoring CFRC," Cement and Concrete Composites, V. 27, 2005, pp. 463-469.
- 12. Wen, S., and Chung, D. D. L., "Double Percolation in the Electrical Conduction in Carbon Fiber Reinforced Cement-Based Materials," *Carbon*, V. 45, No. 2, 2007, pp. 263-267.
- 13. Potschke, P.; Bhattacharyya, A. R.; and Janke, A., "Carbon Nanotube-Filled Polycarbonate Composites Produced by Melt Mixing and their Use in Blends with Polyethylene," *Carbon*, V. 42, No. 5-6, 2004, pp. 965-969.
- 14. Ibarra-Gomez, R.; Marquez, A.; Ramos-de Valle, L. F.; and Rodriguez Fernandez, O. S., "Influence of the Blend Viscosity and Interface Energies on the Preferential Location of CB and Conductivity of BR/EPDM Blends," *Rubber Chemistry and Technology*, V. 76, No. 4, 2003, pp. 969-978.
- 15. Thongruang, W.; Spontak, R. J.; and Balik, C. M., "Bridged Double Percolation in Conductive Polymer Composites: an Electrical Conductivity, Morphology and Mechanical Property Study," *Polymer*, V. 43, No. 13, 2002, pp. 3717-3725.
- 16. Narkis, M.; Lidor, G.; and Vaxman, A., "New Injection Moldable ESD Thermoplastic Composites Containing Conducting Networks Formed Through Structuring in Melt Processing," 60th Annual Technical Conference, Society of Plastics Engineers, V. 2, 2002, pp. 1318-1322.
- 17. Fu, X.; Lu, W.; and Chung, D. D. L., "Ozone Treatment of Carbon Fiber for Reinforcing Cement," *Carbon*, V. 36, No. 9, 1998, pp. 1337-1345.