

Electrical percolation phenomena in cement composites containing conductive fibres

PING XIE, PING GU

Department of Civil Engineering, University of Ottawa, Ottawa, Ontario, Canada, K1N 6N5

J. J. BEAUDOIN

Materials Laboratory, Institute for Research in Construction, National Research Council, Ottawa, Ontario, Canada, K1A 0R6

Electrical conductivity measurements on cement composites containing carbon fibres or steel fibres were conducted. Percolation phenomena associated with electrical conductivity were observed. The conductivity of the systems studied increased by several orders of magnitude, at a specific concentration of conductive fibre, i.e. the percolation concentration. The percolation concentration is shown to be dependent on conductive fibre geometry instead of system composition. The results provide an important guide for the manufacture of conductive cement composites containing conductive fibres.

1. Introduction

Concrete, consisting primarily of Portland cement, fine and coarse aggregate, has been used as a primary construction material for many years owing to its excellent engineering properties and durability. Conventional concrete, however, is a poor electrical conductor, especially under dry conditions. The electrical resistivity of dried concrete usually ranges from 6.54×10^5 to $11.4 \times 10^5 \Omega \text{ cm}$ [1]. This indicates that concrete is a good insulator. Concrete with a combination of excellent mechanical properties and electrical conductivity may have important applications in the electrical and electronic, military and construction industries, for example electromagnetic interference shielding [2, 3], electrostatic discharge [3] and cathodic protection of reinforcing steel in concrete structures [4]. Electrically conductive concrete usually contains conductive phases, either conductive particles [3, 4] or conductive fibres [2, 4, 5]. It is apparent that conductive concrete composites containing conductive fibres have superior flexural strength and toughness due to the effect of fibre reinforcement.

A new conductive concrete with both superior electrical conductivity and mechanical properties has recently been developed at the Materials Laboratory, Institute for Research in Construction, National Research Council, Canada. In this paper, some scientific principles behind the development of this material are reported. These include the effect of content and size of conductive fibre, water/cement ratio and aggregate/cement ratio on the electrical conductivity of cement-based composite systems.

2. Experimental procedure

2.1. Materials and specimens

Type 10 Portland cement was used. The chemical composition (mass %) was as follows: CaO 61.85%, SiO₂ 20.35%, Al₂O₃ 6.20%, Fe₂O₃ 2.04%, MgO 2.38%, SO₃ 2.98%, K₂O 1.06%, Na₂O 0.19%. ASTM C-109 Ottawa sand was used as fine aggregate. The conductive fibres used were carbon fibre and steel fibre. The properties of the fibres are given in Table I. Water/cement ratios were 0.25, 0.30, 0.35, 0.40, 0.45 and 0.50. Sand/cement ratios were 1.0, 1.5 and 2.0.

Conventional mixing and casting procedures were employed. Cylindrical specimens, 3 cm diameter \times 5 cm long, were cast in Plexiglass moulds. The specimens were demoulded after curing at 23 °C and 100% RH for 24 h and cured under similar conditions until tested.

2.2. Electrical conductivity measurement

Generally, there are two basic types of electrical conduction in moist specimens: electronic and electrolytic. The former is through the motion of free electrons in the conductive phases, e.g. carbon or steel fibres, and the latter is through the motion of ions in the pore solution. In this investigation, the principal contribution to the electrical conduction is expected to be electronic. The conductivity measurement, therefore, requires the elimination of the effect of electrolytic conduction. Hence, the specimens were dried at 60 °C for 24 h at the designated ages before measurement.

The conductivity measurements in this study were carried out using a d.c. signal because polarization

TABLE I Properties of conductive fibres used

Fibre	Length (mm)	Diameter (µm)	Specific gravity	Tensile strength (MPa)	Modulus of elasticity (GPa)	Volume resistivity (µΩ m)
Carbon	3	18	1.65	590	30	150
Steel	3 (av.)	25 (av.)	7.85	> 600	200	—

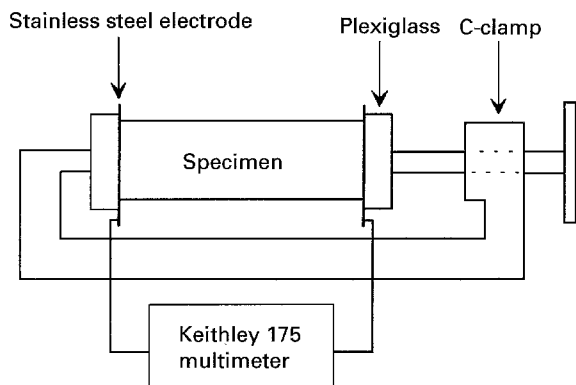


Figure 1 Experimental set-up for resistance measurement of concrete.

effects from electrochemical phenomena at specimen-electrode interfaces were not expected to occur for dried samples. These effects occur only when the specimen contains moisture.

The experimental set-up is illustrated in Fig. 1. The ends of the dried specimen were carefully polished and coated with a layer of graphite powder to eliminate possible errors resulting from poor contact between the sample and electrodes. The electrical conductivity of the specimen was calculated using the following equation

$$\sigma = \frac{1}{\rho} = \frac{L}{S R} \quad (1)$$

where σ and ρ are the electrical conductivity and resistivity, respectively; R is the resistance measured; L, S are the length and cross-sectional area of the specimen.

Effects of inter-electrode spacing on the conductivity value were reported by Banthia *et al.* [5]. It was demonstrated that the electrical conductivity of a conductive fibre-reinforced specimen increases with increasing spacing up to 6 cm after which the effect disappears. This effect was not found in this study with specimen length varying from 0.5–10 cm. Hence a 5 cm length was chosen for all the samples.

3. Results and discussion

3.1. Effect of conductive-fibre content on conductivity

The conductivity values versus volumetric fraction of carbon fibre for paste and mortar systems with different water/cement or sand/cement ratios at 1 day hydration are plotted in Figs 2 and 3, respectively. It can be seen that the electrical conductivity values of the composites increase with increasing carbon fibre content. The composite conductivity depends only on the

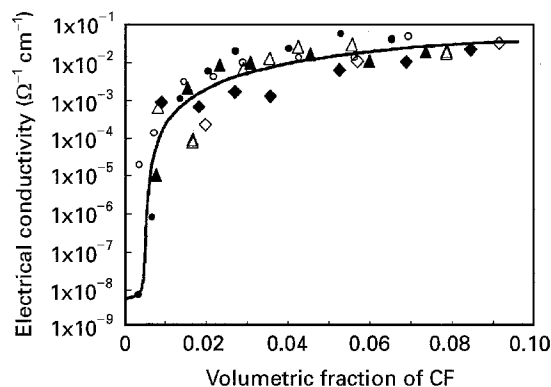


Figure 2 Conductivity versus carbon fibre content for paste systems. Water-cement ratio (w/c): (◇) 0.25, (◆) 0.30, (△) 0.35, (▲) 0.40, (○) 0.45, (●) 0.50. Carbon fibre length = 3 mm. 1 day hydration.

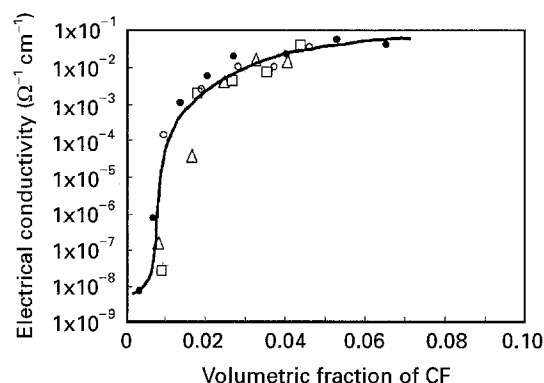


Figure 3 Conductivity versus carbon fibre content for mortar systems. Sand-cement ratio (s/c): (●) 0.0, (△) 1.0, (□) 1.5, (○) 2.0. Carbon fibre length = 3 mm. $w/c = 0.50$. 1 day hydration.

carbon fibre content for a given carbon fibre size and is approximately independent of water/cement and sand/cement ratio. It is apparent that in conductive fibre-reinforced cement-based composites, the properties and microstructure of the non-conductive components do not have much influence on composite conductivity. The conductive fibre content is the most important factor determining the conductivity of the system.

It appears that conductivity versus fibre volume fraction curves for conductive fibre-reinforced cement composite systems have typical features of percolation phenomena, Figs. 2 and 3. This is characterized as follows.

1. The conductivity changes by several orders of magnitude, when the concentration of carbon fibre reaches a critical value, referred to as the threshold.
2. The conductivity increases marginally with increasing content of conductive fibre in the post-threshold region.

These phenomena can be described by a percolation theory that deals with the effects of random variation on the number and quality of the interconnections present [6]. In fact, the conductivity change with fibre content reflects the connectivity change of the fibres distributed in a non-conductive matrix. In the region of very low fibre concentration the fibre is distributed homogeneously in the volume of the non-conductive matrix. There are no contacts between adjacent fibres. Agglomerates or clusters of the fibres form with increasing fibre concentration.

Fibres are in contact with each other within an individual cluster. The clusters are separate, however, until the threshold value of fibre concentration is reached. It is suggested that cluster size is not uniform but has a characteristic distribution in the low-concentration region. The characteristic size of a cluster can be represented by the spanning diameter or spanning length which is defined as the maximum separation of two sites in the cluster [6]

$$l \equiv \max \{ |r_i - r_j| \}_{i,j \text{ in cluster}} \quad (2)$$

where r_i and r_j are the position coordinates of two sites i and j in the cluster. The average spanning length for all clusters, l_{av} , obeys a power-law when the conductive fibre concentration approaches the percolation threshold value, i.e. as

$$\begin{aligned} (\varphi_c - \varphi) &\rightarrow 0 \\ l_{av} &\propto \frac{1}{(\varphi_c - \varphi)^v} \end{aligned} \quad (3)$$

where φ is the volumetric fraction of conductive fibre, φ_c is the threshold value of the volumetric fraction and the exponent v is a positive constant.

It can be seen that $l_{av} \rightarrow \infty$ when $\varphi \rightarrow \varphi_c$. This implies that the conductive fibre clusters are in contact with each other and hence form a network through the entire matrix. As a consequence of the first appearance of the network, the composite conductivity shows a dramatic increase. After the first conductive network is formed, the conductivity of the composite increases slowly with increasing fibre content because increasing fibre content in this region only slightly improves the connectivity of the conductive network. The above description can be illustrated by Fig. 4. Four different systems and the corresponding fibre connectivity situations are illustrated.

The conductivity of the composite can, according to the percolation theory, be expressed by the following equation [6, 7]

$$\sigma \propto (\varphi - \varphi_c)^t \quad (4a)$$

where σ is the conductivity of composite and t is a constant that is independent of the microstructure of the material.

Application of Equation 4a to the data taken from curves in Figs 2 and 3 where $\varphi_c \approx 0.01$ yields Fig. 5. Data in Fig. 5 cover specimens with a broad range of water/cement ratio and sand/cement ratio. Application of a least-square method to analyse the data in

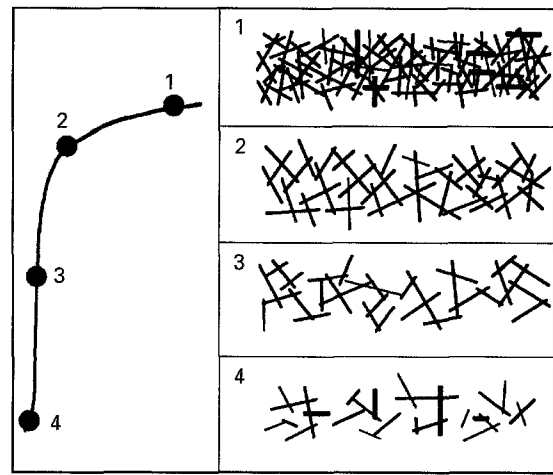


Figure 4 Relationship between conductivity and connectivity of conductive fibres.

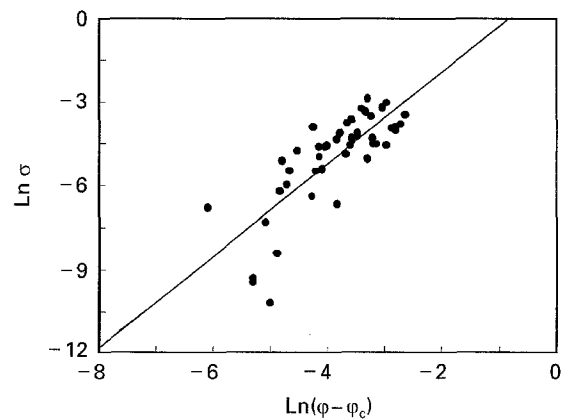


Figure 5 Experimental validation of power-law Equation 4a. $w/c = 0.25-0.50$; $s/c = 1.0-2.0$. 1 day hydration.

Fig. 5 leads to the following equation

$$\sigma = 4.10(\varphi - 0.01)^{1.65} \quad (4b)$$

The exponent t is 1.65 for the systems described in Figs 2 and 3. This is consistent with data on the physics of amorphous solids [6].

3.2. Effect of conductive-fibre size on percolation threshold

The percolation threshold is a fibre-size- and geometry-dependent parameter. It is mainly dependent on the fibre length and diameter. Different sizes of carbon and steel fibres were used to study this effect on threshold value. Shorter carbon fibres can be obtained by milling 3 mm long fibres. Fibres, 1 mm long on average, were screened from milled fibres for this study.

The effect of fibre size on the percolation threshold value is depicted in Figs 6 and 7 for carbon and steel fibre-cement systems, respectively. The results indicate that the percolation threshold value increases significantly with decreasing fibre length. Many more shorter fibres are needed to form a fibre network through the entire non-conductive matrix.

The above results indicate that the content and length of the conductive fibre are two principal factors

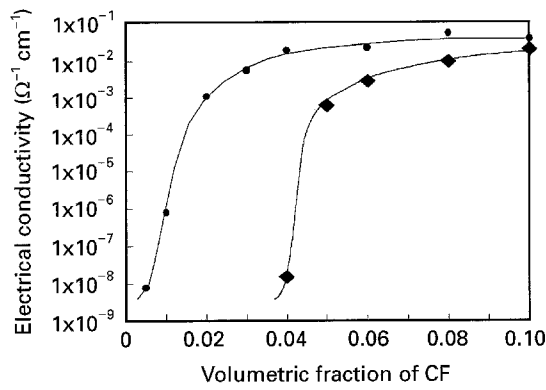


Figure 6 Effect of carbon fibre length on threshold content: (●) 3 mm, (◆) 1 mm. 1 day hydration, $w/c = 0.50$.

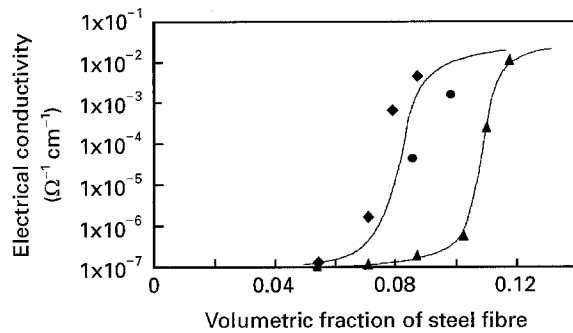


Figure 7 Effect of steel fibre length on threshold content: (▲) size 1, $w/c = 0.35$; (◆) size 2, $w/c = 0.35$; (●) size 2, $w/c = 0.50$. Steel fibre length: size 1, 1 mm; size 2, 3 mm. 1 day hydration.

that should be carefully examined when making conductive cement-based composites containing conductive fibres. Generally, excess fibres are not necessary if the fibre content is in the post-threshold region. Using longer fibres helps to reduce the minimum fibre content required to reach a certain conductivity value.

3.3. Effect of hydration time on percolation threshold and conductivity

In addition to the effect of conductive-fibre content and length, it might be expected that hydration time will influence the conductivity value of the system because microstructural change, e.g. the formation of new hydrates, with hydration can result in a change in connectivity of the conductive-fibre network. The fibre-fibre contact may be broken by the formation of new hydrates in areas close to the contact point.

The conductivity values at 28 days' hydration versus carbon fibre concentration are plotted in Fig. 8 for comparison with the 1 day hydration data presented in Figs 2 and 3. It is apparent that the percolation threshold value of carbon-fibre concentration does not change with hydration time, although the conductivity values show some change. The effect of hydration time on the composite conductivity value is depicted in Fig. 9 for the paste systems with $w/c = 0.35$. In Fig. 9, three typical fibre contents were chosen, as illustrated in the insert at the centre of Fig. 9. They represent different connectivity states of the carbon fibre network in the non-conductive matrix, as illustrated in Fig. 4. Point 1 represents the

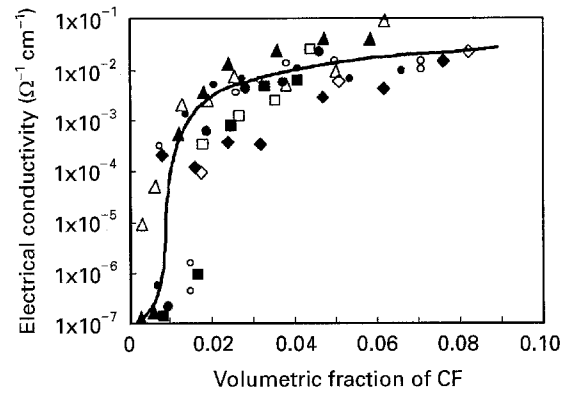


Figure 8 Effect of hydration time on percolation threshold content. Water-cement ratio (w/c): (▲) 0.50; (△) 0.45; (●) 0.40; (○) 0.35; (◆) 0.30; (◇) 0.25; (■) 0.5, $s/c = 1.0$; (□) 0.5, $s/c = 1.5$; (●) 0.5, $s/c = 2.0$. 28 days' hydration.

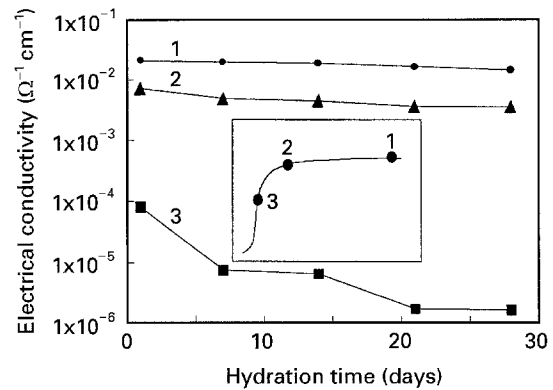


Figure 9 Effect of hydration time on composite conductivity. $w/c = 0.35$.

system in which the fibre network is well developed, point 2 the completed formation of a well-developed fibre network, and point 3 a system at the threshold point of incipient network formation. It is expected that the connectivity of the fibre network in the first two systems is not sensitive to the fibre-fibre contact point number, which may change due to microstructural changes resulting from cement hydration. It is expected, however, that the fibre connectivity and hence the composite conductivity in the third system will be very sensitive to the number of contact points. The conductivity of the third system is therefore expected to decrease with hydration time. The conductivity changes for systems 1 and 2 are marginal. The above analyses are consistent with the results depicted in Fig. 9 where the conductivity of the system 3 is reduced by almost two orders of magnitude from 1 day to 28 days' hydration.

4. Conclusions

1. Conductive fibres, e.g. carbon and steel fibre, are excellent conductive phases for the manufacture of cement-based conductive material.

2. The conductivity of cement-based composites reinforced with conductive fibre can be described by a percolation model. The conductivity changes significantly at a critical fibre content that is referred to as the threshold value.

3. A minimum amount of conductive fibre is required to obtain a conductive composite. This minimum content depends mainly on the fibre size.

4. Longer fibre can reduce the minimum content required.

5. Conductive fibre in excess of the threshold amount does not significantly increase composite conductivity.

Acknowledgement

Financial support by the Canadian Network of Centers of Excellence on High Performance Concrete is gratefully acknowledged.

References

1. H.W. WHITTINGTON, J. McCARTER and M.C. FORDE, *Mag. Concr. Res.* **33** (114) (1984) 48.
2. J. CHIOU, Q. ZHENG and D.D. CHUNG, *Composites* **20** (1989) 379.
3. J.R. FARRAR, *GEC J. Sci. Technol.* **45**(1) (1978) 45.
4. G.G. CLEMENA, *Mater. Performance*, March (1988) 19.
5. N. BANTHIA, S. DJERIDANE and M. PIGEON, *Cem. Concr. Res.* **22** (1992) 804.
6. R. ZALLEN, "The Physics of Amorphous Solids" (Wiley, New York, 1983) pp. 135-204.
7. F. LUX, *J. Mater. Sci.* **28** (1993) 285.

Received 1 December 1994

and accepted 13 February 1996