

Electrically conductive cement-based materials

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Electrically conductive cement-based materials are useful for electrical grounding, lightning protection, resistance heating, static charge dissipation, electromagnetic interference (EMI) shielding, cathodic protection, and thermoelectric energy generation. The science and applications of electrically conductive cement-based materials are reviewed. In addition, a comparative study of the effectiveness of various electrically conductive admixtures (discontinuous forms of steel and carbon) for lowering the electrical resistivity of cement shows that the effectiveness decreases in the order: steel fibre of diameter 8 μm , steel fibre of diameter 60 μm , carbon fibre of diameter 15 μm , carbon nanofibre of diameter 0.1 μm , coke powder (< 75 μm) and graphite powder (< 1 μm). For EMI shielding, the effectiveness decreases in the order: steel fibre of diameter 8 μm , coke powder (< 75 μm), carbon nanofibre of diameter 0.1 μm , graphite powder (< 1 μm), steel fibre of diameter 60 μm , carbon fibre of diameter 15 μm , and steel dust of size 0.55 mm. By using steel fibre (8 μm diameter) at 0.72 vol.%, a resistivity of 16 Ωcm and an EMI shielding effectiveness of 59 dB (1 GHz) were attained. The carbon admixtures cause the absolute thermoelectric power to be more positive, whereas the steel admixtures can cause the absolute thermoelectric power to be more positive or more negative. In particular, steel fibre of diameter 60 μm at 0.2 vol.% causes the absolute thermoelectric power to be strongly negative ($-63\ \mu\text{V}/^\circ\text{C}$). Moisture loss has no effect on the absolute thermoelectric power, but increases the resistivity.

Introduction

Cement-based materials have received much attention in relation to their mechanical properties, due to their importance as structural materials. However, the need for a structural material to be able to serve one or more non-structural functions while retaining good structural properties is increasingly recognised¹. This is because the use of a multifunctional structural material in place of a combination of a structural material and a non-structural functional material (e.g., a structural material with an embedded non-structural functional material) reduces cost, enhances durability and repairability, increases the functional volume, avoids degradation of the mechanical properties, and simplifies design. Non-structural functions include sensing, actuation, heating, corrosion protection, self-healing, thermal insulation, heat retention and electromagnetic interference (EMI) shielding.^{1,2}

Electrically conductive cement-based materials are one category of multifunctional cement-based materials.^{3,4} The conductivity is attractive for electrical

grounding, lightning protection, resistance heating (e.g., in de-icing and building heating), static charge dissipation, electromagnetic interference shielding, thermoelectric energy generation and for overlays (electrical contacts) used in the cathodic protection of steel reinforcing bars (rebars) in concrete.

Electrical conduction

The cement matrix is electrically attractive due to its electrical conductivity, which is in contrast to the non-conductive behaviour of most polymers. Due to the conductivity of the cement matrix, an electrically conductive admixture (i.e., a conductive filler) in a cement-matrix composite can enhance the conductivity of the composite even when the volume fraction of the admixture is below the percolation threshold, which refers to the volume fraction above which the admixture units touch to form a continuous conduction path. The percolation threshold is determined from the variation of the electrical resistivity with the volume fraction of the conductive admixture. The electrical resistivity abruptly decreases by orders of magnitude at the percolation threshold.³ In most cases, the percolation threshold decreases with increasing aspect ratio and with decreasing unit size of the admixture. In the

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case of short carbon fibres (7 μm diameter) in cement, the percolation threshold decreases with increasing fibre length from 1 to 10 mm.⁵ However, the percolation threshold also depends on the unit size of the non-conductive or less conductive components in the composite. Thus, the presence of sand (a non-conductive component) affects the percolation threshold.³ In the absence of sand, the percolation threshold is between 0.5 and 1.0 vol.% when the conductive admixture in cement is short carbon fibre (15 μm diameter, 5 mm long).³

The curing age has relatively minor influence on the electrical resistivity, although it has major influence on the mechanical properties. From a curing age of 1 to 28 days, the resistivity is increased by 63% for plain mortar, by 18% for latex mortar, by 18% for carbon fibre (0.53 vol.%) latex mortar, and by 4% for carbon fibre (1.1 vol.%) latex mortar.⁶ Since the resistivity is a quantity that can vary by orders of magnitude, the percentage increases mentioned above do not reflect a large effect. Nevertheless, the effect in the absence of conducting fibres, especially in terms of the impedance, is sufficient for use in studying the curing process.⁷⁻¹⁰ An increase in the carbon fibre content from 0.53 to 1.1 vol.% diminishes the effect of curing age significantly, because the fibres become more dominant in governing the resistivity as the fibre content increases. The addition of latex also diminishes the effect of curing age.

Cement paste is electrically conducting, with DC resistivity at 28 days of curing around $5 \times 10^5 \Omega \text{ cm}$ at room temperature. The resistivity is increased slightly (to $6 \times 10^5 \Omega \text{ cm}$) by the addition of silica fume (SiO_2 particles around 0.1 μm in size, in the amount of 15% by mass of cement), and is increased more (to $7 \times 10^5 \Omega \text{ cm}$) by addition of latex (20% by mass of cement), which is a styrene butadiene copolymer in the form of particles of size around 0.2 μm .¹¹ The higher the latex content, the higher is the resistivity.¹² In case of mortars (with fine aggregate, i.e., sand), the transition zone between the cement paste and the aggregate enhances the conductivity.¹³ Whether aggregates (sand and stones) are present or not, the AC impedance spectroscopy technique for characterising the frequency-dependent electrical behaviour is useful for studying the microstructure.¹³⁻¹⁶

The non-conductive admixture effects on the resistivity, as mentioned above, are small in comparison with the effect of adding short conductive fibres. Nevertheless, the non-conductive admixtures can help the fibre dispersion, thereby causing the resistivity of cement-based materials containing conductive short fibres to be lower. At a volume fraction below the percolation threshold, the electrical conductivity of a composite is highly dependent on the degree of fibre dispersion. The greater the degree of fibre dispersion, the higher is the conductivity of the composite. This is because of the relatively long length of conduction path within the

matrix in case of poor fibre dispersion, as illustrated in Fig. 1. At the same carbon fibre (15 μm diameter) volume fraction (0.35 vol.%, below the percolation threshold), the resistivity of cement mortar is lower when silica fume is present along with the fibres, due to the effectiveness of silica fume in helping the fibre dispersion;¹⁷ it is further lowered when both methylcellulose and silica fume are present along with the fibres.^{17,18} The use of acrylic, styrene acrylic or latex dispersions in place of the methylcellulose solution is less effective.¹⁷ At the same steel fibre (60 μm diameter) volume fraction (0.05 vol.%, much below the percolation threshold), the resistivity of cement mortar is lower when silane is present along with the fibres, due to the effectiveness of silane in helping the fibre dispersion.¹⁹

The electrical conductivity of a cement-based material containing a conductive admixture is governed by the conductivity of the admixture itself, the degree of dispersion of the admixture and the contact electrical resistivity of the interface between the admixture and the cement matrix. Due to the conductivity of the cement matrix, this contact resistivity is important, particularly when the admixture volume fraction is below the percolation threshold. The contact electrical resistivity between stainless steel fibre (60 μm diameter) and cement paste is around $6 \times 10^6 \Omega \text{ cm}^2$ and is smaller if the fibre has been acid washed.²⁰

The interface between steel fibre and cement matrix behaves similarly to that between steel rebar and concrete. The latter is more common in practice than the former. The contact resistivity of the latter interface is around $6 \times 10^7 \Omega \text{ cm}^2$.²¹

Applications

Electrical grounding is needed for buildings and other structures which involve electrical power. Lightning protection is needed for tall buildings. Metals such as steel are commonly used for these applications. However, the use of electrically conductive concrete to diminish the volume of metal required is attractive for cost reduction, durability improvement and installation simplification.

Static charge dissipation is needed for structures that come into contact with sensitive electronic devices.

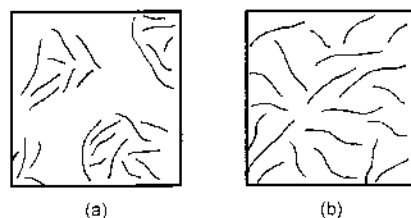


Fig. 1. Fibre dispersion below the percolation threshold. (a) Poor dispersion. (b) Good dispersion. From Ref. 19

Metals and conductor filled polymer-matrix composites are used for this purpose. However, the use of electrically conductive concrete for this application allows large volumes of structure to have the ability for static charge dissipation.

Due to the environmental problem associated with the use of fossil fuels and due to the high cost of solar heating, electrical heating is increasingly important. Although electric heat pumps are widely used for the electrical heating of buildings, resistance heating is a complementary method which is receiving increasing attention due to the low costs for its implementation and control, its adaptability to localised heating (e.g., the heating of a particular room of a building), its nearly 100% efficiency of conversion of electrical energy to heat energy, and the increasing demand of safety and the quality of life. Resistance heating is needed in buildings and for the de-icing of driveways, bridges, highways and airport runways. De-icing is valuable for hazard mitigation. The alternative technique of snow removal (shovelling) is labour intensive and takes time, in contrast to the automatic and continuous nature of de-icing by resistance heating.

Resistance heating involves passing an electric current through a resistor, which is the heating element. In relation to the heating of buildings and other structures, resistance heating typically involves the embedding of heating elements in the structural material, such as concrete. The materials of heating elements cannot be too low in electrical resistivity, as this would result in the resistance of the heating element being too low and a high current would be needed to reach a certain power. The materials of heating elements cannot be too high in resistivity either, as this would result in the current in the heating element being too low (unless the voltage is very high). The materials used for heating elements are commonly metal alloys such as nichrome. Thus metal wires are commonly embedded in a structural material in order to provide resistance heating. However, the embedding degrades the mechanical properties of the structural component and the repair of the embedded heating element is difficult. Furthermore, the embedding is limited to selected locations of a structural component, and consequently the heating is not uniform. The non-uniformity is worsened by the poor thermal conductivity of the structural materials. An electrically conductive cement-based material can be used as a resistance (Joule) heating element.^{22,23} There is no need to embed wires in the structural component, thereby alleviating the problems mentioned above in connection with the embedment. Conventional concrete is electrically conducting, but the resistivity is too high for resistance heating to be effective.

Cathodic protection is one of the most common and effective methods for corrosion control of steel-reinforced concrete.²⁴⁻²⁸ This method involves the application of a voltage so as to force electrons to go to the

steel rebar, thereby making the steel a cathode. For directing electrons to the steel-reinforced concrete to be cathodically protected, an electrical contact is needed on the concrete. The electrical contact is electrically connected to the voltage supply. One of the choices of an electrical contact material is zinc, which is a coating deposited on the concrete by thermal spraying. It has a very low volume resistivity (thus requiring no metal mesh embedment) and it can serve both as a sacrificial anode and as an electrical contact, but it suffers from poor wear and corrosion resistance, the tendency to oxidise, a high thermal expansion coefficient, and high material and processing costs. Another choice is a conductor filled polymer,²⁹ which can be applied as a coating without heating and can be used alone or as an adhesive between concrete and a zinc plate, but it suffers from poor wear resistance, high thermal expansion coefficient and high material cost. Yet another choice is a metal (e.g., titanium) strip or wire embedded at one end in cement mortar, which is in the form of a coating on the steel reinforced concrete. The use of electrically conductive mortar for this coating facilitates cathodic protection.³⁰

Electrically conductive cement-based materials are also attractive for EMI shielding,³¹⁻³⁵ which is in demand due to the interference of wireless (particularly radio frequency) devices with digital devices and the increasing sensitivity and importance of electronic devices. Shielding is particularly needed for underground vaults containing transformers and other electronics that are relevant to electric power and telecommunication. It is also needed for deterring electromagnetic forms of spying. Although a material that is effective for EMI shielding tends to be electrically conductive, a material that is superior in conductivity is not necessarily superior in EMI shielding also, as shown in this study.

The main mechanism for EMI shielding using conductive materials is reflection.³⁵ The loss (attenuation) due to reflection increases with decreasing frequency. However, another mechanism is absorption, as enhanced by electric and magnetic dipoles in the material. The loss due to absorption increases with increasing frequency. The third mechanism, multiple reflections off the external surfaces and internal surfaces and interfaces of the material, is only important when the specimen is very thin or when the specimen has a great deal of internal surfaces or interfaces.

The ability to reflect electromagnetic radiation (particularly radio wave) is useful for automatic lateral guidance of vehicles. Lateral guidance as attained by steering is limited in safety due to the tendency for human error. It is also limited in accuracy, as shown by the difficulty of steering a car through a narrow lane or parking a car very close to a curb.

Automatic lateral guidance is needed for automatic highways,³⁶ which refer to highways that provide fully automated control of vehicles, so that safety and

mobility are enhanced. In other words, a driver does not need to drive on an automatic highway, as the vehicle goes automatically, with both lateral control (steering to control position relative to the centre of the traffic lane) and longitudinal control (speed and headway).

Instead of human steering, lateral guidance can involve electromagnetic or magnetic interaction between a car and a lane, so that the reliance on human steering is reduced or removed, thereby enhancing safety and mobility, and facilitating parking a car very close to a curb (as needed by buses and by electric vehicles that require battery recharging).

This alternative form of lateral guidance currently involves the use of magnetic sensors in the cars together with magnetic highway marking. When a car deviates from its path, which is marked by magnets embedded along the length of the pavement, the magnetic sensor in the car detects the deviation. The signal from the sensor is then used to control the steering automatically in real time. In contrast, this chapter uses an electromagnetic form of lateral guidance, as made possible by a radio wave reflecting concrete.

Radio wave reflecting concrete is concrete which contains an electrically conductive admixture, which causes the concrete to be a strong reflector of radio waves. Conventional concrete is a poor reflector. By coating either the middle portion (Fig. 2(a)) or the edge portions (Fig. 2(b)) of a lane of a highway with radio wave reflecting concrete (or mortar) and by installing in each vehicle a transmitter and a detector of radio waves, a vehicle can sense its lateral position relative to the middle portion of the lane through the intensity of the radio wave bounced back by the pavement.

In comparison with the magnetic technology, the attractions of the electromagnetic technology are low material cost (reflecting concrete, although more ex-

pensive than conventional concrete, is much less expensive than concrete with embedded magnets or magnetic strips), low labour cost (same as conventional concrete, thus much less than concrete with embedded magnets or magnetic strips), low peripheral electronic cost (off-the-shelf oscillator and detector), good mechanical properties (reflecting concrete exhibits better mechanical properties and lower drying shrinkage than conventional concrete, whereas embedded magnets weaken concrete), good reliability (less affected by weather, as frequency, impedance and power selectivity provide tuning capability), and high durability (demagnetisation and marking detachment not being issues). Moreover, the magnetic field from a magnetic marking can be shielded by electrical conductors (such as steel) between the marking and the vehicle, whereas the electromagnetic field cannot be easily shielded.

Electrically conductive cement-based materials are also attractive for thermoelectric energy generation (i.e., conversion from thermal energy to electrical energy) and temperature sensing (i.e., cement-based thermocouples in the form of cement-based pn-junctions).^{37,38} Although a material that is effective thermoelectrically tends to be conductive, a material that is superior in conductivity is not necessarily superior in the thermoelectric behaviour, as shown in this study. The use of cement-based materials for thermoelectric functions is attractive as this allows the functions to be built-in to concrete structures.³⁹⁻⁴³ Due to the large volume of concrete structures and the low cost of concrete compared with conventional thermoelectric materials (e.g., bismuth), thermoelectric applications using concrete may be viable even if the efficiency is not high.

Materials

The cement matrix is only slightly conductive, with an electrical resistivity of 10^5 or $10^6 \Omega \text{ cm}$.¹⁻³ By the use of electrically conductive admixtures in the form of particles or short fibres, the resistivity of a cement-based material can be greatly decreased.³ Continuous fibres can also be used to reduce the resistivity,⁴⁴ but they cannot be incorporated in a cement mix and, as a consequence, the making of a continuous fibre cement-based material is much more complicated than that of a short fibre cement-based material. This paper only addresses the use of particles and short fibres as electrically conductive admixtures.

Due to the requirements of low material cost and long-term compatibility with the chemical environment in a cement-based material, the electrically conductive admixtures are mainly either steel or carbon. Steel is more conductive than carbon, but it is less available in the form of fine particles or fibres. It is desirable to attain a low resistivity at just a low volume fraction of an admixture, because the workability and compressive

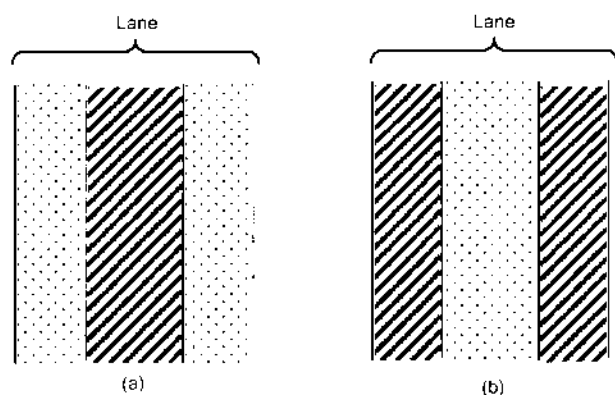


Fig. 2. Radio wave reflecting concrete (or mortar), as indicated by the shaded portion(s) of a lane and conventional concrete, as indicated by the dotted portion(s) of a lane, for attaining electromagnetic lateral guidance of vehicles

strength decrease with increasing volume fraction of the admixture (due to the increase in air void content)^{1,2} and the cost increases with the admixture volume fraction. As a consequence, a small particle size, a small fibre diameter and a large aspect ratio are usually attractive for the admixture. However, too small an admixture unit size can be a disadvantage for the conductivity, as shown in this study, due to the electrical contact resistance at the interface between the adjacent admixture units and the large number of such interfaces when the filler unit size is small.

Among the steel admixtures are steel fibres, shavings and dust. Steel shavings and dust are waste materials from the machining of steel components. Although they are less expensive than steel fibres, they are usually less pure and are available in much larger sizes. Steel fibres are available at diameter ranging from 8 μm to 2 mm. Steel fibres that are relatively fine are only available in the form of stainless steel. Stainless steel fibres of diameter 60 and 8 μm have received particular attention in relation to electrically conductive cement-based materials, although carbon steel fibres of much larger diameters are typically used in purely structural applications of cement-based materials. The steel fibres used in this study were all made of stainless steel.

Among the carbon admixtures are graphite powder, coke powder (i.e., coke breeze), carbon fibres (typically of diameter ranging from 7 to 15 μm and length around 5 mm) and carbon nanofibres (also known as carbon filaments, typically of diameter ranging from 0.01 to 1 μm and length 100 μm or more). In this paper, fibres refer to those of diameter 1 μm or above, whereas nanofibres refer to those of diameter below 1 μm .⁴⁵ Carbon fibres are typically made from pitch, polyacrylonitrile or other polymers.⁴⁶ Carbon nanofibres are typically made catalytically from carbonaceous gases.⁴⁶ Coke is less crystalline than graphite, so it is less conductive. However, coke is less expensive than graphite. Carbon fibres and nanofibres are even more expensive than graphite powder. However, their large values of the aspect ratio facilitate electrical connectivity among the conductive admixture units, thereby enhancing the conductivity of the composite. On the other hand, due to the large values of the aspect ratio, fibres and nanofibres have the tendency to cling together, thus making their dispersion more difficult than the powder counterpart. Dispersion is important for both electrical and mechanical properties of the composites. Very fine particles, such as silica (SiO_2) fume of mean particle size around 0.1 μm , are effective as an admixture for helping fibre dispersion.^{3,17,18,47}

The various forms of carbon also differ in their mechanical properties and reinforcing effectiveness, which are important for structural materials. Due to its high crystallinity and the consequent tendency to undergo shear between the carbon layers, graphite powder is mechanically weaker than coke powder. On the other hand, carbon fibres and nanofibres are more

effective than the powder for reinforcement, due to their large values of the aspect ratio. The strength is particularly high along the axis of a carbon fibre, due to the preferred orientation of the carbon layers along the fibre axis.⁴⁶ For the carbon nanofibres, the preferred orientation of the carbon layers is not necessarily along the nanofibre axis.⁴⁶ A common form of carbon nanofibre (the form used in cement-matrix composites⁴⁸) has the carbon layers preferably oriented at an angle to the nanofibre axis. This microstructure is referred to as a fishbone morphology. As a result of the off-axis orientation of the carbon layers in this form of carbon nanofibre, the strength of a nanofibre along its axis is expected to be low, although mechanical testing of a single nanofibre has not been reported.

The reinforcing effectiveness also depends on the bond between admixture and cement. This bond is weak compared to that between filler and polymer (e.g., epoxy) in a polymer-matrix composite. Admixture surface treatment can be used to improve this bond,^{47,49,51} but the improved bond is still not strong and the surface treatment adds considerably to the cost of the admixture. Thus, a large amount of interface between admixture and cement, as in the case of the admixture being small in unit size (e.g., carbon filaments⁴⁸), can be unattractive for the mechanical properties of the composites.

Intercalation is a chemical process (a reaction) that can increase the conductivity of graphite and crystalline types of carbon fibres or filaments. It involves the insertion of a foreign species (a reactant called an intercalate) between the carbon layers, thereby forming a layered compound called an intercalation compound.⁵² Intercalation requires the carbon host to be graphitic. Thus, it cannot occur in the common grades of carbon fibre. Due to the high cost of the crystalline types of carbon fibre, intercalated carbon fibres are expensive. The increase in conductivity is a consequence of the charge transfer between the carbon host and the intercalate. In general, the intercalate can be an electron donor or an electron acceptor. Bromine is an intercalate which is an electron acceptor.^{52,53} Intercalation of graphite (a semi-metal) with bromine results in a whole metal. Bromine is a particularly attractive intercalate, due to the stability of the intercalation compound in air after desorption of the part of the intercalate which is loosely held.⁵⁴

Graphite powder,^{55,57} coke powder,^{56,61} carbon fibres (with intercalation⁶² and without intercalation^{3,62,65}) and carbon nanofibre (0.1 μm diameter)⁴⁸ have all been used as electrically conductive admixtures in cement-based materials.

Comparative study

This article provides a comparative review of the effectiveness of carbon and steel admixtures for enhan-

cing the electrical conductivity of cement-based materials. The data used in the comparison were all obtained in the laboratory of the author using the same testing method (i.e., the four-probe method of electrical resistance measurement) and the same specimen configuration.⁴⁸ In contrast to the two-probe method, the four-probe method eliminates the resistance of the electrical contacts from the measured resistance and is thus more reliable. Furthermore, all data were obtained on similar materials, i.e., materials that involve Type I Portland cement at 28 days of curing without any aggregate. Data on the EMI shielding effectiveness were all obtained in the laboratory of the author using the same testing method (i.e., the coaxial cable method, also called the transfer impedance method, involving the use of a network analyser) and the same specimen configuration.⁴⁸ Please refer to the cited references for details on testing methods and specimen preparation methods.

Although the emphasis of this article is on the attaining of high electrical conductivity in cement-based materials, the EMI shielding effectiveness and the thermoelectric behaviour are also addressed, due to their relationship with electrical conductivity. On the other hand, this article does not cover the piezoresistive behaviour, which pertains to the effect of strain or stress on the electrical resistivity and is useful for strain/stress sensing¹ (relevant to structural vibration control, traffic monitoring and weighing). Although cement-based materials that are strongly piezoresistive are also electrically conductive, the relationship between piezoresistivity and conductivity is weak.^{1,66,67} Piezoresistivity, which pertains to the conductive behaviour, is distinct from piezoelectricity, which pertains to the dielectric behaviour.⁶⁸

Steel rebars used to reinforce concrete are electrically conductive. Consequently they increase the conductivity of concrete. However, they do not affect the EMI shielding effectiveness of concrete, due to their large dimensions and the high frequency of the electromagnetic radiation. The effect of steel rebars is beyond the scope of this paper. However, the effect of steel fibres is addressed in this paper.

Table 1 compares the effectiveness of various electrically conductive admixtures at similar volume fractions in cement paste (without aggregate, whether fine or coarse). Among the various carbon and steel admixtures, stainless steel fibres (8 μm diameter)⁶⁹ are most effective for decreasing the DC electrical resistivity and for providing EMI shielding. The lowest resistivity attained in Table 1 is 16 $\Omega\text{ cm}$; the highest shielding effectiveness attained in Table 1 is 59 dB.

The resistivity decreases monotonically and the EMI shielding effectiveness increases monotonically as the conductive admixture content increases for any given admixture, except that steel fibre (8 μm diameter) gives lower resistivity at 0.72 than 0.90 vol.%. This exception is presumably a consequence of the increase

in air void content with increasing fibre volume fraction.

Stainless steel fibre of diameter 60 μm ^{38,70,71} at essentially the same volume fraction as steel fibre of diameter 8 μm gives much higher resistivity. However, steel fibre of diameter 60 μm gives the highest magnitude of the absolute thermoelectric power, which reaches $-63\ \mu\text{V}/^\circ\text{C}$. The absolute thermoelectric power of steel fibre (60 μm diameter) cement does not vary monotonically with increasing fibre volume fraction (Fig. 3), although the resistivity decreases monotonically with increasing fibre volume fraction.⁷⁰ This suggests that carrier scattering at interfaces (e.g., interface between steel and cement) probably dominates the origin of the thermoelectric behaviour of steel-cement composites.⁷¹ This suggestion is supported by the difference in the absolute thermoelectric power of the steel fibre itself ($+9\ \mu\text{V}/^\circ\text{C}$)⁷⁰ and the cement matrix ($+3\ \mu\text{V}/^\circ\text{C}$).⁴¹

Among the three steel admixtures, the effectiveness for shielding decreases in the order: steel fibre (8 μm diameter),⁶⁹ steel fibre (60 μm diameter)⁴² and steel dust (0.55 mm) (Wen and Chung (unpublished result), as shown by comparing the shielding performance of steel fibre (8 μm diameter) at 0.36 vol.%, steel fibre (60 μm diameter) at 0.40 vol.%, and steel dust (0.55 mm) at 6.6 vol.%. Thus, the greater the unit size of the steel admixture, the less effective is the admixture for shielding. This is expected from the skin effect.

Among the carbon admixtures, carbon fibre (15 μm diameter) is most effective for decreasing the resistivity. Intercalation does not decrease the resistivity of the composite much, but it greatly enhances the thermoelectric behaviour.⁴² This is due to the role of carrier hopping across the fibre-cement interface in governing the electrical conduction below the percolation threshold and the increase in the activation energy of the hopping (as determined from the variation of the resistivity with temperature) upon intercalation.⁶²

Carbon nanofibre (0.1 μm diameter) is much less effective than carbon fibre (15 μm diameter) for lowering the resistivity, but is much more effective for providing EMI shielding. This is because of (a) the skin effect, which makes an admixture with a smaller unit size more effective for shielding at the same volume fraction, and (b) the contact resistance at the admixture-cement interface, which is large in area per unit volume when the admixture unit size is small.

Coke powder is less effective than carbon filament for lowering the resistivity, due to its particulate (non-fibrous) nature, but is more effective than carbon filament for providing shielding (presumably due to better dispersion). The low cost of coke adds to the attraction of coke-cement for EMI shielding.

Graphite powder (< 1 μm in particle size, the solid portion of a water-based colloid) is less effective than carbon fibre (whether amorphous or crystalline), carbon nanofibre or coke powder for lowering the resistivity.

Table 1. Electrical resistivity (DC), absolute thermoelectric power (20–65°C) and EMI shielding effectiveness (1 GHz, coaxial cable method) of cement pastes containing various electrically conductive admixtures

Conductive admixture	Vol. %	Resistivity: Ω cm	Absolute thermoelectric power: $\mu\text{V}/^\circ\text{C}^a$	EMI shielding effectiveness: dB
None	0	6.1×10^5	+3	4
None, but with graphite powder (< 1 μm) coating ⁷²			-	14
Steel fibre ⁶⁹ (8 μm diameter)	0.09	4.5×10^3		19
Steel fibre ⁴² (60 μm diameter)	0.10	5.6×10^4	-52	-
Steel fibre ⁶⁸ (8 μm diameter)	0.18	1.4×10^3	+10 ^b	28
Steel fibre ⁴² (60 μm diameter)	0.20	3.2×10^4	63	-
Steel fibre ⁶⁸ (8 μm diameter)	0.27	9.4×10^2	-	38
Steel fibre ⁴² (60 μm diameter)	0.28	8.7×10^3	-5	-
Carbon fibre ⁶² (10 μm diameter)	0.31	6.7×10^3	+17	-
(crystalline, intercalated)				
Steel fibre ⁶⁹ (8 μm diameter)	0.36	57		52
Steel fibre ⁴² (60 μm diameter)	0.40	1.7×10^3	+25	12 ^b
Carbon fibre ⁶² (10 μm diameter)	0.36	1.3×10^4	+5	-
(crystalline, pristine)				
Steel fibre ⁶⁹ (8 μm diameter)	0.54	23	-	-
Steel fibre ⁴² (60 μm diameter)	0.50	1.4×10^3	+31	-
Carbon fibre ⁴¹ (15 μm diameter)	0.48	1.5×10^4	-4	-
(amorphous, pristine)				
Carbon filament ⁴⁸ (0.1 μm diameter)	0.5	1.3×10^4	-	30
Graphite powder ⁷² (< 1 μm)	0.46	2.3×10^5	-	10
Coke powder ⁵⁸ (< 75 μm)	0.51	6.9×10^4	-	44
Steel fibre ⁶⁹ (8 μm diameter)	0.72	16		59
Steel fibre ⁶⁹ (8 μm diameter)	0.90	40		58
Carbon fibre ⁴¹ (15 μm diameter)	1.0	8.3×10^2	-6	15 ^c
(amorphous, pristine)				
Carbon fibre ⁶² (10 μm diameter)	1.0	7.1×10^2	+22	-
(crystalline, intercalated)				
Carbon filament ⁴⁸ (0.1 μm diameter)	1.0	1.2×10^4		35
Graphite powder ⁷² (< 1 μm)	0.92	1.6×10^5		22
Coke powder ⁵⁸ (< 75 μm)	1.0	3.8×10^4		47
Coke powder ⁵⁸ (< 75 μm)	6.1	2.9×10^4		49
Steel dust (0.55 mm)	6.6			5 ^b
Graphite powder ⁵⁵ (< 45 μm)	37	4.8×10^2	+25	-

^a Seebeck coefficient (with copper as the reference) plus the absolute thermoelectric power of copper.

^b Wen S. and Chung D. D. L., unpublished result.

^c 0.84 vol.% carbon fibre in cement mortar at 1.5 GHz.⁷³

ity. Its inferiority to carbon fibre and nanofibre is due to its particulate nature; its inferiority to coke powder is probably related to its small particle size and the fact that its volume fractions are below the percolation threshold. Graphite powder is inferior to carbon nanofibre and coke powder for shielding, but it is superior to carbon fibre. The inferiority of graphite powder to carbon nanofibre for shielding is due to its particulate nature but the origin of the inferiority to coke powder is presently not clear, as the larger particle size of coke is expected to be disadvantageous for shielding. The superiority of graphite powder to carbon fibre for shielding is due to its small particle size and the skin effect.

Graphite powder (< 45 μm) is less effective than carbon fibre (whether amorphous or crystalline) for lowering the resistivity, as 37 vol.% of the graphite powder and 1.0 vol.% of carbon fibre have similar effects. This is due to the particulate nature of the graphite.

In terms of thermoelectric behaviour, all the carbon and steel admixtures at all volume fractions investigated cause the absolute thermoelectric power to be less negative (more positive), except that steel fibre (60 μm diameter) up to 0.2 vol.% causes the absolute thermoelectric power to be more negative (as negative as $-63 \mu\text{V}/^\circ\text{C}$). The steel fibre (60 μm diameter) itself, without cement, has a positive value ($+9 \mu\text{V}/^\circ\text{C}$) of the absolute thermoelectric power,⁷⁰ but it can cause the absolute thermoelectric power of a cement paste to be more negative or more positive, depending on its volume fraction (Fig. 3). The fact that bromine intercalation of carbon fibre causes the absolute thermoelectric power to be much more positive⁴³ supports the notion that holes contribute to the thermoelectric behaviour of the carbon-cement composites. However, both electrons (from steel) and carrier scattering (at the steel-cement interface) probably contribute to the thermoelectric behaviour of the steel-cement composite.

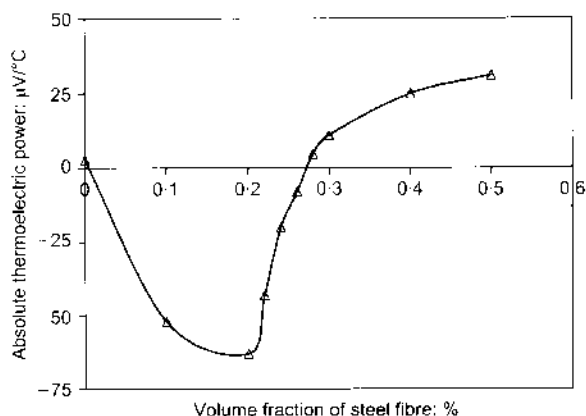


Fig. 3. Absolute thermoelectric power of cement pastes containing various volume fractions of steel fibre. All pastes with fibres contained silica fume

For providing a large magnitude of the absolute thermoelectric power, the effectiveness of steel fibre (60 μm diameter) is outstanding, if it is used up to 0.2 vol.% only. Beyond 0.2 vol.%, the absolute thermoelectric power becomes more positive as the fibre volume fraction increases. For thermoelectric energy generation, materials with opposite signs of absolute thermoelectric power are usually connected in series in order to have an additive effect on the voltage generated. Thus, materials that exhibit strongly positive and strongly negative values of the absolute thermoelectric power are both useful. Steel fibre (60 μm diameter) at 0.20 vol.% gives the most negative value ($-63 \mu\text{V}/^\circ\text{C}$), whereas the same fibre at 0.50 vol.% gives the most positive value ($+31 \mu\text{V}/^\circ\text{C}$). Graphite powder at 37 vol.% and steel fibre (60 μm diameter) at 0.40 vol.% give the same value of $+25 \mu\text{V}/^\circ\text{C}$, but the high volume fraction of graphite powder is unattractive due to its mechanical properties.

The following rank ordering of the effectiveness of various conductive admixtures was obtained from Table 1 by comparing the effectiveness at similar volume fractions of the admixtures. For lowering the resistivity, the effectiveness of the various admixtures decreases in the order: steel fibre (8 μm diameter), steel fibre (60 μm diameter), carbon fibre (15 μm diameter), carbon nanofibre (0.1 μm diameter), coke powder (< 75 μm) and graphite powder (< 1 μm). Steel fibre (8 μm diameter) is exceptionally effective compared with the other admixtures. Consistent with the exceptionally low resistivity of steel fibre (8 μm diameter) cement is the exceptionally high effectiveness of the material for use as a resistance heating element.²² In particular, the effectiveness is higher than that of carbon fibre (15 μm diameter) cement.²³ The steel fibre cement has not been evaluated for use as an overlay for cathodic protection, but carbon fibre mortar has been shown to be more effective than plain mortar (without fibre) for cathodic protection, as the required voltage is reduced.³⁰

For providing EMI shielding, the effectiveness of the various admixtures decreases in the order: steel fibre

(8 μm diameter), coke powder (< 75 μm), carbon nanofibre (0.1 μm diameter), graphite powder (< 1 μm), steel fibre (60 μm diameter), carbon fibre (15 μm diameter) and steel dust (0.55 mm). That steel fibre (60 μm diameter) is better than carbon fibre (15 μm diameter) is just suggested by the slightly lower shielding effectiveness attained by steel fibre (60 μm diameter, 0.40 vol.%) than carbon fibre (15 μm diameter, 1.0 vol.%). The relative shielding performance of graphite powder (< 1 μm) and steel fibre (60 μm diameter) has not been investigated, although both are included in the ranking above. The other parts of the rank ordering are well substantiated. Although steel fibre (8 μm diameter) is more effective than coke powder for shielding, it is much more expensive than coke powder. Thus, coke powder is preferred when both cost and performance are considered.

A material which is superior in conductivity is not necessarily superior in shielding also, as shown by comparing carbon nanofibre cement and coke cement. Carbon nanofibre (0.5 vol.%) cement is better than coke (0.5 vol.%) cement in conductivity, but is inferior in shielding. A material which is stronger in the thermoelectric behaviour is not necessarily better in conductivity, as shown by comparing steel fibre (8 μm diameter) cement and steel fibre (60 μm diameter) cement. Steel fibre (60 μm diameter, 0.2 vol.%) cement is stronger thermoelectrically, but is less conductive than steel fibre (8 μm diameter, 0.2 vol.%) cement. A material which is superior in shielding is not necessarily superior in conductivity also, as shown by comparing graphite powder (< 1 μm) cement and carbon fibre (15 μm diameter) cement. The former (0.92 vol.%) is better than the latter (1.0 vol.%) for shielding, but is much inferior in conductivity.

The use of graphite powder (< 1 μm) in the form of a water-based colloid to coat cement without admixture results in increase of the shielding effectiveness from 4 to 14 dB,⁷² as shown in Table 1. The coating thickness is 0.3 mm. When the substrate is Mylar (electromagnetically transparent) instead of cement, the shielding effectiveness is 11 dB.⁷² Although the coating method is effective to a limited degree for shielding and is convenient for implementation in existing structures, it suffers from the tendency to be damaged by abrasion and wear.

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.⁷⁴ In other words, ions do not readily respond to a temperature gradient, although they respond to a voltage gradient.

Conclusion

A comparative review of the effectiveness of various electrically conductive admixtures (steel fibres, steel

dust, carbon fibres, carbon nanofibre, coke powder and graphite powder) for cement-based materials has shown that steel fibre of diameter $8\ \mu\text{m}$ is most effective for lowering the electrical resistivity and providing EMI shielding. Carbon fibre ($15\ \mu\text{m}$ diameter) is more effective than carbon nanofibre ($0.1\ \mu\text{m}$ diameter), coke powder or graphite powder for lowering the resistivity. However, coke powder is better than carbon nanofibre, which is in turn better than graphite powder or carbon fibre in providing shielding. The greater the unit size of the steel admixture, the less effective is the admixture for shielding. All the steel and carbon admixtures investigated in terms of the thermoelectric behaviour cause the absolute thermoelectric power to be more positive, except for steel fibre ($60\ \mu\text{m}$ diameter) at up to 0.2 vol.%, which causes the absolute thermoelectric power to be more negative (as negative as $-68\ \mu\text{V}/^\circ\text{C}$). By using steel fibre ($8\ \mu\text{m}$ diameter) at 0.72 vol.%, a resistivity of $16\ \Omega\ \text{cm}$ and an EMI shielding effectiveness of 59 dB (1 GHz) were attained.

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