



# Decreasing the electric permittivity of cement by graphite particle incorporation



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## ABSTRACT

Cement containing graphite particles (admixture) was previously reported to exhibit attractive electromagnetic properties, which relate to the electric permittivity. The addition of graphite nanoplatelet (GNP, particles, 0.5% by mass of cement, ~0.5 vol %) to cement containing silica fume (particles, 15% by mass of cement) decreases the relative permittivity (10 Hz–1 MHz) by ~49% (unprecedentedly large fractional decrease among permittivity-affecting admixtures), decreasing from 33 to 17 (50 Hz), while affecting the resistivity negligibly. The decrease is attributed to the inhibition of the polarization-related charge carrier movement by the distributed GNP. The previously reported huge values of  $10^8$  at 10 Hz (Bhattacharya et al., 2008) and  $10^3$  at 50 Hz (Sachdev et al., 2015) of the relative permittivity of cement containing graphite particles are erroneous, due to the absence of an electrically insulating film between the specimen and either electrode during the capacitance measurement and the limitation of the impedance meter. The previously reported trend of the permittivity increasing with increasing graphite particle content (Bhattacharya et al., 2008) is opposite to the decreasing trend found in this work, and is also erroneous, as caused by the incorrectly high measured permittivity becoming even higher when the specimen is more conductive.

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## 1. Introduction

The electric permittivity (also known as the relative dielectric constant) is a dielectric property of a material. It relates to the tendency for the material to be polarized in the presence of an electric field. This behavior is relevant to the interaction of the material with electromagnetic radiation. A high value of the permittivity is attractive for electromagnetic interference (EMI) shielding, whereas a low value is attractive for low observability (Stealth) and electromagnetic transparency (as needed for radomes, for example).

Under an AC electric field, the AC polarization is associated with a capacitance. Under a DC electric field, the DC polarization gives rise to an opposing electric field, which increases the apparent (measured) resistance of the material [1,2]. The permittivity of cement is affected by the stress [3] and temperature [4], thereby providing a mechanism for monitoring these attributes. The

permittivity of cement is also affected by the admixtures, which enable the tailoring of the permittivity. This paper pertains to the admixture effect.

Cement is a dielectric material, mostly due to the water in it. Due to the water content, cement is an ionic conductor, though the addition of an electronic conductor such as carbon fiber causes the occurrence of electronic conduction as well [5]. Water has a high relative permittivity of 80 [6], which is high compared to the value of 3.9 for silica and the generalized value of 4.5 for concrete [6]. The addition of silica fume (nanoparticles) as an admixture decreases the permittivity [7], whereas the addition of either short carbon fibers (in the vicinity of the percolation threshold) or latex increases the permittivity [7]. Even though an increase in the latex/cement ratio decreases the air void content, it increases the electrical resistivity [8]. In contrast, the addition of short carbon fibers decreases the electrical resistivity [7,9]. Specifically, the relative permittivity at 10 kHz is  $29 \pm 3$  for plain cement paste,  $21 \pm 3$  for cement paste with silica fume,  $35 \pm 4$  for cement paste with latex,  $54 \pm 7$  for cement paste with silica fume and short carbon fibers (0.5 vol%),  $49 \pm 5$  for cement paste with silica fume and short carbon fibers (1.0 vol%), and  $63 \pm 5$  for cement paste with latex and

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carbon fibers (0.4 vol%) [7]. The decrease of the relative permittivity by silica fume addition is attributed to the volume occupied by the silica fume in place of cement and the inherent polarizability of cement paste, which is heterogeneous to a degree [7]. The increase of the relative permittivity by latex or carbon fiber addition is attributed to the interface between cement and these admixtures. This interface is between constituents with different electrical behavior. For example, the resistivity is higher for latex (without cement) than cement [8] and is lower for carbon fibers (without cement) than cement [7,9]. In general, the scientific origin of the effect of admixtures on the permittivity of cement has not been addressed adequately.

The addition of an electrically conductive filler to a matrix material (whether cement or polymer) commonly causes an increase in the permittivity, due to the interfacial polarization. This is discussed below in terms of graphite particles, carbon nanotubes and nickel nanoparticles as admixtures.

The addition of graphite particles (10–20  $\mu\text{m}$ ) to cement has been reported to cause the relative permittivity to increase, such that the value at 10 Hz is  $10^4$  at 2 wt% graphite and  $10^8$  for 5 wt% graphite (with these graphite contents being in the vicinity of the percolation threshold) [10]. The relative permittivity of cement containing graphite particles ( $\sim 1 \mu\text{m}$ ) at 3 wt% has been reported to be  $10^3$  at 50 Hz [11]. The relative permittivity values ranging from  $10^4$  to  $10^8$  at 10 Hz and the value of  $10^3$  at 50 Hz are larger than the values previously reported for cement pastes [7] by 3–7 orders of magnitude. Even though the prior work [7] does not involve graphite particles as the admixture, the values ranging from  $10^3$  to  $10^8$  [10,11] are unbelievably high. This calls for clarification.

The addition of carbon nanotubes (1 wt%, conductive) to a ceramic increases the relative permittivity from 1000 to 1100 under the condition of a fixed porosity [12]. The addition of nickel nanoparticles (conductive) to natural rubber increases the relative permittivity at 10 kHz from 2.8 to 4.7 [13].

On the other hand, the addition of ceramic nanoparticles (not conductive) to polyethylene decreases the permittivity. For example, the addition of either 12 nm silica nanoparticles (not conductive) [14] or 50 nm magnesia nanoparticles (not conductive) [15] to polyethylene decreases the relative permittivity at frequencies below 1 Hz from 4.6 to 2.5; the decrease is attributed to the charge carrier movement being inhibited by the presence of the nanoparticles.

Electrically conductive cement-based materials are useful for numerous applications, such as strain/damage sensing, deicing, electrical grounding, lightning protection, EMI shielding and anti-static structural components [16]. Cement containing graphite particles are attractive for EMI shielding [11,17], thermoelectric energy generation [18], electrically conductive coating for imposing electrochemical anti-corrosion treatment [19], the bipolar plate of the proton exchange membrane fuel cell [20,21], microbial fuel cell [22], and solar thermal storage [23].

Submicron graphite particles are an effective admixture for enhancing the EMI shielding effectiveness of cement paste, providing superior shielding than 15- $\mu\text{m}$ -diameter discontinuous carbon fibers, though inferior shielding than 0.1- $\mu\text{m}$ -diameter discontinuous carbon nanofibers [17]. For cement paste without silica fume, the shielding effectiveness at 1 GHz is 4.0, 10 and 22 dB for graphite contents of 0, 0.46 and 0.92 vol%, respectively [17]. However, the submicron graphite particles decrease the electrical resistivity only slightly, with the resistivity being  $8.2 \times 10^5$ ,  $2.3 \times 10^5$  and  $1.6 \times 10^5 \Omega \text{ cm}$  for graphite contents of 0, 0.46 and 0.92 vol%, respectively [17]. This implies that an increase in the shielding effectiveness is not necessarily accompanied by a substantial decrease in the resistivity, as expected from the fact that the shielding may stem from the dielectric behavior (such as the

permittivity) more than the conduction behavior.

In general, for applications that involve electrical conduction, the conductivity is obviously important. However, the permittivity should also be considered, since the capacitance associated with the permittivity becomes effectively one of the circuit elements and energy loss due to the conduction may occur. In case of EMI shielding, the permittivity is important, due to the interaction of the electric field with the electric dipoles in the material.

Graphite nanoplatelet (GNP), as obtained by the mechanical disintegration of exfoliated graphite [24], is an electrically conductive admixture that has been shown to render improvement to the mechanical properties of the cement-based material [25–28]. However, its effect on the permittivity of the cement-based material has not been previously reported.

This work is directed at (i) clarifying the value of the relative permittivity of cement paste containing graphite, in view of the abovementioned questionable results of prior work [10,11], and (ii) studying the effect of GNP incorporation on the electric permittivity of cement paste.

## 2. Experimental methods

### 2.1. Materials

The dispersion of admixtures that are small in size (in the micrometer scale or below) is not trivial. Silica fume as an admixture has been previously shown to be effective for enhancing the dispersion of short carbon fibers in cement, due to its submicron particle size and promotion of the degree of mixing during the mechanical mixing process [29]. The mechanism of the effectiveness of silica fume for helping the dispersion of short fibers is the same as that for the dispersion of particles. The mechanism involves the fine particles of silica fume breaking loose the fiber clumps or particle clumps as the cement slurry is being mixed. The mechanism has been discussed in Ref. [29]. Thus, silica fume is used in this work for helping the dispersion of GNP in cement, though it provides the additional benefit of reducing the pore size. The effect of silica fume is outside the scope of this paper. For the sake of studying the effect of the GNP addition, silica fume is used in this work whether GNP is present or not.

Portland cement (Type I, ASTM C150) is used. Silica fume (Elkem Materials Inc., Pittsburgh, PA, microsilica, EMS 965, USA), if applicable, is used at 15% by mass of cement, as in prior work [30]; it has particle size ranging from 0.03 to 0.5  $\mu\text{m}$ , with average size 0.2  $\mu\text{m}$ ; it contains >93 wt%  $\text{SiO}_2$ , <0.7 wt%  $\text{Al}_2\text{O}_3$ , <0.7 wt%  $\text{CaO}$ , <0.7 wt%  $\text{MgO}$ , <0.5 wt%  $\text{Fe}_2\text{O}_3$ , <0.4 wt%  $\text{Na}_2\text{O}$ , <0.9 wt%  $\text{K}_2\text{O}$ , and <6 wt% loss on ignition.

Due to the hydrophilicity of alkylsilane, the silica fume has been subjected to alkylsilane surface treatment. The alkylsilane treatment of silica fume has been previously shown to improve the workability and mechanical properties of silica fume cement-based materials, including those with and without short carbon fibers [31,32], so the effect of the treatment is not addressed in this work. As in the prior work [31,32], the alkylsilane coupling agent is a 1:1 (by mass) mixture of Z-6020 (3-(2-aminoethylamino)propyltrimethoxysilane,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ) and Z-6040 (3-glycidyloxypropyl)trimethoxysilane,  $\text{OCH}_2\text{—CH—CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ) from Dow Corning Corp. (Midland, MI). The amine group in Z-6020 serves as a catalyst for the curing of the epoxy and consequently allows the Z-6020 molecule to attach to the epoxy end of the Z-6040 molecule. The trimethylsiloxy ends of the Z-6020 and Z-6040 molecules then connect to the  $\text{—OH}$  functional group on the surface of the silica fume. The alkylsilane is dissolved in ethylacetate to form a solution with 2.0 wt% alkylsilane. Surface treatment of the silica fume is performed by

immersion in the alkylsilane solution, heating to 75 °C while stirring, and then holding at 75 °C for 1.0 h, followed by filtration and drying. After this, the silica fume is heated at 110 °C for 12 h.

No aggregate is used. Although cement paste (without aggregate) is far less effective as a structural material than concrete (which has aggregates), it is suitable and commonly used for scientific study of the effect of the cement paste formulation. The water/cement ratio is 0.42. A high-range water reducing agent (Glenium 3000NS, BASF Construction Chemicals) is used at 1.0% by mass of cement. The defoamer (Colloids Inc., Marietta, GA, 1010, USA) is used at 0.13% (% of specimen volume), as previously used in case of cement with short carbon fibers as an admixture [33]. All the ingredients are mixed in a rotary mixer with a flat beater.

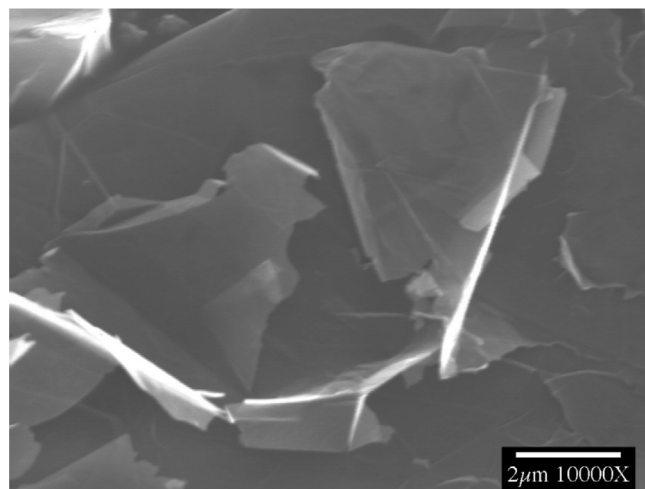
The GNP is prepared as described below. Exfoliated graphite (worms) are obtained by rapid heating of expandable graphite flakes (graphite flakes intercalated with sulfuric acid and nitric acid in the presence of catalysts, with a flake size of 300  $\mu\text{m}$ , as supplied by Asbury Graphite Mills, Asbury, NJ, USA, under the designation No. 3772) at 900 °C for 2 min with flowing nitrogen. The ratio of the volume of the worms to that of the corresponding flakes prior to exfoliation is 600, as obtained by measuring the bulk volume of the worms that result from the exfoliation of 5000 g of expandable graphite flakes. The worms are of length 2–4 mm. During exfoliation, the vast majority of the intercalate desorbs, so that the intercalate that remains after exfoliation is low in concentration and is strongly held to the graphite [24,34,35].

The exfoliated graphite obtained is then immersed in water and dispersed at a concentration of 2 mg/ml by repeatedly alternating between magnetic stirring for 24 h and sonication (using an ultrasonicator, Fisher Scientific International Inc, FS60H, Hampton, NH, at 100 W) for 24 h for a total time of approximately 16 days. Fig. 1 shows microscope photographs that indicate the thin flake morphology and micron size (typically around 3  $\mu\text{m}$ ) of the GNP particles. Based on specific surface area measurement, the number of carbon layers in the cell wall of the exfoliated graphite (which has a cellular structure) is about 60, i.e., the thickness of the cell wall is about 20 nm [36]. Thus, the thickness of a GNP particle is less than 20 nm. The GNP is used in the amount of 0.5% by mass of cement. This corresponds to about 0.5 vol% of the cement paste.

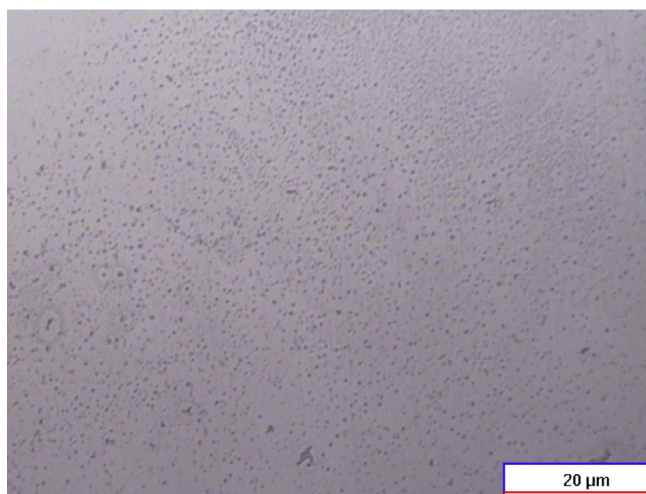
## 2.2. Permittivity measurement

For capacitance measurements, the mix is poured into silicone square molds of size 25.4  $\times$  25.4 mm and thicknesses 2.0, 3.0 and 4.0 mm to form square specimens of three different thicknesses. Actual specimen thicknesses differ slightly from these values due to mechanical polishing, and are separately measured for each specimen. For all specimens, after filling the mold, an external vibrator is used to facilitate compaction and diminish the amount of air bubbles. The specimens are demolded after 24 h and then cured at a relative humidity of essentially 100% for 28 days.

The relative permittivity is obtained by measuring the capacitance of a system comprising the specimen sandwiched between copper plate electrodes (35.0 mm thick), such that there is an electrically insulating tetrafluoroethylene (Teflon) sheet positioned between the specimen and each copper electrode (Fig. 2). For each specimen thickness, testing is conducted for three specimen areas, which correspond to the areas of 1, 2 and 3 squares that are in contact and lined up along an edge of the square in the same plane and the same direction (Fig. 3). This method of permittivity measurement is as previously reported and shown by detailed experimental and analytical work to be reliable [37]. A pressure of 4.96 kPa is applied to the specimen in the direction perpendicular to this plane. The electrodes are rectangular, with width (25.4 mm) equal to the specimen width and length equal to the length of the

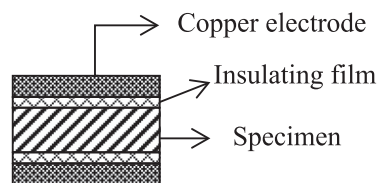


(a)



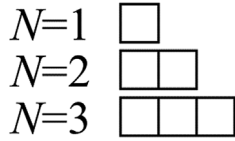
(b)

**Fig. 1.** Microscope photographs of graphite nanoplatelets. (a) An SEM photograph at a high magnification showing the flake morphology of the platelets. (b) An optical microscope photograph at a low magnification showing the submicron size of each particle. (A colour version of this figure can be viewed online.)



**Fig. 2.** Configuration for measuring the relative permittivity of cement. An electrically insulating film is positioned between the specimen and each of the two sandwiching copper electrodes. The drawing is not too scale, as the specimen dimension is much smaller in the vertical direction than the horizontal direction.

combined length of the 1–3 contacting lined-up square specimens (Fig. 3). The capacitance is measured using a precision RLC meter (QuadTech Model 7600), with the electric field across the thickness of the specimen fixed at 4.2 V/cm. The frequency ranges from 10 Hz to 1 MHz. The highest frequency is limited by the capability of the meter. These frequencies are much below those (typically in the GHz regime) that are relevant to EMI shielding.



**Fig. 3.** Specimen testing configuration in the form of 1, 2 or 3 square slabs lined up. The integer  $N$  refers to the number of square slabs lined up. The area of each square slab is  $A$ .

For each type of material tested, specimens at areas  $A$ ,  $2A$  and  $3A$  are tested, where  $A$  is the area of one square slab (Fig. 3). The measured capacitance  $C_m$  is for the specimen with inclusion of the effect of the two specimen-contact interfaces. The two interfaces and the specimen are in series electrically. Hence,

$$C_m = NC_s + C_o, \quad (1)$$

where  $N$  (equal to 1, 2 or 3) is the number of square specimens lined up (Fig. 3),  $C_m$  is the measured capacitance,  $C_s$  is the capacitance due to a single square specimen, and  $C_o$  is the capacitance related to the fringing electric field. Since

$$C_s = \epsilon_0 \kappa A / l, \quad (2)$$

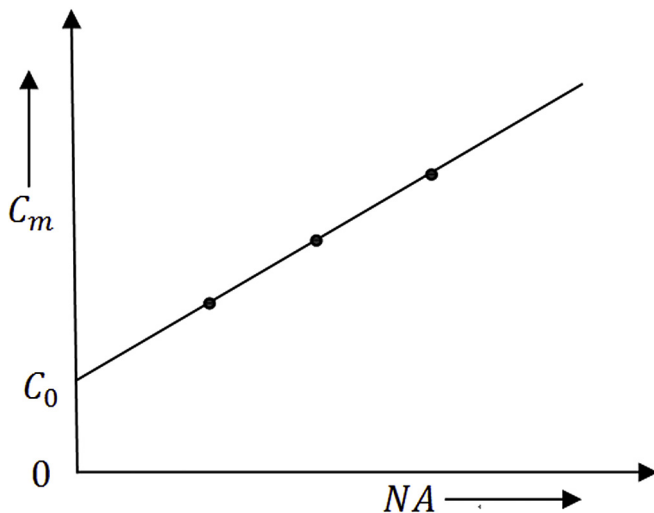
where  $\epsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12}$  F/m),  $\kappa$  is the relative permittivity of the specimen,  $A$  is the area of one square specimen ( $25.4 \times 25.4$  mm), and  $l$  is the thickness of the specimen. Combination of Eqs. (1) and (2) gives

$$C_m = \epsilon_0 \kappa NA / l + C_o. \quad (3)$$

By plotting  $C_m$  vs.  $NA$  (with  $N = 1, 2$  and  $3$ ), a straight line of slope  $\epsilon_0 \kappa / l$  is obtained (Fig. 4).

Based on the slope and the known value of  $l$ ,  $\kappa$  is determined. Since  $C_o$  corresponds to the intercept of the straight line on the  $C_m$  axis at  $N = 0$ , it does not influence the slope of the line. On the other hand, if only a single area is measured,  $C_o$  and  $C_s$  cannot be decoupled and hence the influence of  $C_o$  cannot be removed.

Prior work [10,11] in permittivity measurement of cement with graphite particles as an admixture did not involve the above-mentioned decoupling, as only a single area was used. Thus, the present work provides more accurate determination of the



**Fig. 4.** Schematic plot of  $C_m$  vs. the area  $NA$ . The area of each square slab is  $A$ .

permittivity.

Impedance spectroscopy, which measures the impedance as a function of frequency, does not allow the abovementioned decoupling of  $C_o$  and  $C_s$ . Furthermore, the use of an equivalent electrical circuit to analyze the Nyquist plot obtained by impedance spectroscopy for the purpose of determining the resistance and capacitance does not give a direct measurement of the resistance and capacitance and the results of the analysis are not unique, as they depend on the circuit model chosen.

### 2.3. Electrical resistivity measurement

For preparing specimens for DC resistivity measurement, the cement mix is poured into rectangular molds to form beam-shaped specimens of size  $25.0 \text{ mm} \times 8.0 \text{ mm} \times 3.0 \text{ mm}$ . The electrical resistivity along the longest dimension is measured by using the four-probe method, with the outer contacts ( $24.2 \text{ mm}$  apart) for passing current and the inner contacts ( $8.1 \text{ mm}$  apart) for voltage measurement. Each contact is in the form of a narrow strip of silver paint in conjunction with copper wire, such that the strip is along the entire  $8.0\text{-mm}$  width of the specimen in a direction perpendicular to the direction of resistance measurement.

## 3. Results

### 3.1. Density

The density (as obtained by measuring the mass and the specimen dimensions) is  $1.697 \pm 0.009$  and  $1.690 \pm 0.011 \text{ g/cm}^3$  for silica-fume cement without and with GNP, respectively. This means that the density is essentially unaffected by the GNP addition. It has been previously reported that the porosity increases with increasing graphite particle content beyond  $5 \text{ wt\%}$  [21]. The graphite content is only  $0.5\%$  by mass of cement in this work.

### 3.2. Electrical resistivity

In the presence of silica fume, the DC electrical resistivity is  $(5.77 \pm 0.36) \times 10^5 \Omega \text{ cm}$  and  $(9.71 \pm 0.40) \times 10^5 \Omega \text{ cm}$  for cement without and with GNP, respectively. Hence, the GNP addition increases the resistivity slightly. This is due to the resistance associated with the interface between GNP and cement and the fact the GNP content is below the percolation threshold.

The slight increase in resistivity upon the  $0.5 \text{ vol\%}$  GNP incorporation in the presence of silica fume (this work) is approximately consistent with the prior report of a slight decrease of the resistivity upon  $0.46 \text{ vol\%}$  submicron graphite particle incorporation in the absence of silica fume [17], since the effects are slight in both cases. The GNP is probably different in particle size and aspect ratio from the submicron graphite particles ( $0.7\text{--}0.8 \mu\text{m}$ ) of the prior work. Moreover, the presence of silica fume in this work is expected to help the dispersion of the graphite particles, thus affecting the tendency for the graphite particles to contact one another. Thus, quantitative comparison of this work and the prior work [17] in terms of the effect of the graphite incorporation on the resistivity is not appropriate.

### 3.3. Permittivity

Fig. 5 shows that the measured capacitance is linearly related to the area, as predicted by Eq. (3) and Fig. 4. For any of the frequencies studied, the addition of GNP decreases the relative permittivity by about  $49\%$ , as shown by comparing specimens with and without GNP at similar thicknesses ( $3.04 \text{ mm}$  without GNP and  $2.80 \text{ mm}$  with GNP) (Table 1 and Fig. 5). In general, a smaller thickness



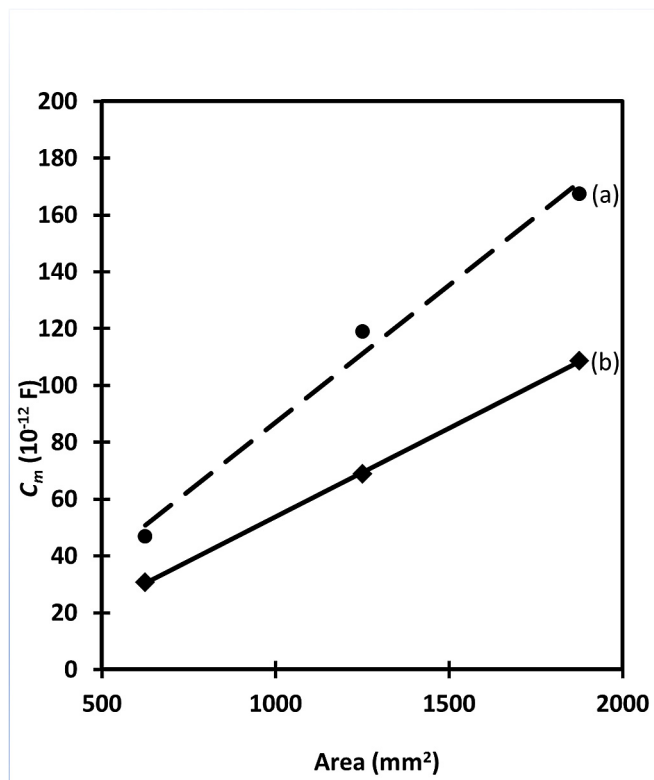


Fig. 5. Plots of  $C_m$  vs. area (NA) at 100 Hz. (a) Silica-fume cement of thickness 3.04 mm (b) GNP silica-fume cement of thickness 2.80 mm.

results in a higher capacitance, when all other factors are the same, as expected. In spite of the slightly smaller thickness for the specimens with GNP compared to those without GNP, the permittivity is lower for the former.

The largest fractional decrease in permittivity previously reported for cement paste due to admixture incorporation is 28%, as achieved by using silica fume (15% by mass of cement) as the admixture [7]. The large fractional decrease (49%) in permittivity obtained in this work by using GNP as an admixture is unprecedented. This large effect occurs in spite of the small content (0.5% by mass of cement) of GNP. The low permittivity is potentially attractive for concrete structures that exhibit low observability [38].

Prior work on the addition of submicron graphite particles to cement in the absence of silica fume shows that the EMI shielding effectiveness is increased by the graphite particle addition, while

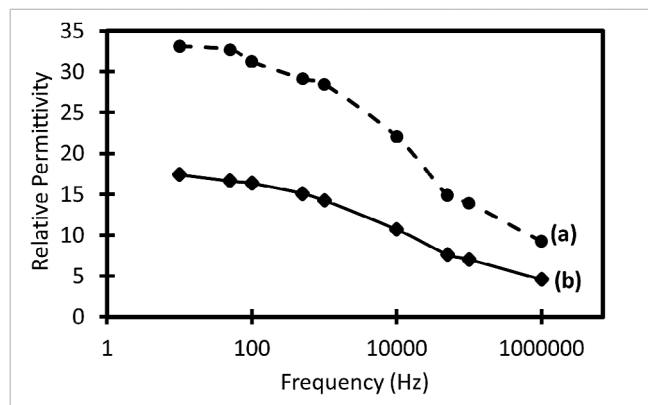


Fig. 6. Plot of the relative permittivity vs. frequency (log scale). (a) Silica-fume cement of thickness 3.04 mm (b) GNP silica-fume cement of thickness 2.80 mm.

the electrical resistivity is decreased slightly [17]. The permittivity was not reported in the prior work [17]. As explained in Sec. 3.2, quantitative comparison of this work and the prior work [17] in terms of the effect of the graphite incorporation is not appropriate.

The relative permittivity decreases with increasing frequency, as shown in Table 1 and Fig. 6. This trend is well-known for dielectric materials.

#### 4. Discussion

The GNP addition significantly decreases the permittivity while affecting the resistivity only slightly. This means that the GNP addition affects the dielectric (polarization) behavior in spite of the near absence of effect on the conduction behavior.

The decrease in permittivity due to the presence of GNP is in contrast to the increase previously reported for the addition of graphite particles [10], short carbon fibers [7], carbon nanotubes [12] or nickel nanoparticles [13] to cement. The decrease cannot be due to the effect of the GNP addition on the porosity, because the density is affected negligibly by the GNP addition (Sec. 3.1). The decrease also cannot be due to the interfacial polarization, which would increase the permittivity. Rather, it is attributed to the inhibition of the polarization-related charge carrier movement by the presence of the GNP. This mechanism has been previously reported to explain the decrease in relative permittivity due to the addition of silica or magnesia nanoparticles to polyethylene [14,15]. Although GNP is conductive, whereas the silica and magnesia nanoparticles are not conductive, the dispersion of the fine GNP particles (Fig. 2(b)) enables the GNP to inhibit the polarization-

Table 1

Measured values of the relative permittivity of cement pastes of thickness 2.8–3.0 mm and various frequencies. The measurement involves the presence of an electrically insulating film between the specimen and each of the two electrodes.

Frequency (Hz)	Relative permittivity		
	Silica fume	Silica fume + GNP	Fractional change due to GNP
	3.04 mm thick	2.80 mm thick	
10	33.2 ± 6.5	17.4 ± 2.4	–48%
50	32.7 ± 6.0	16.6 ± 2.8	–49%
100	31.3 ± 4.5	16.3 ± 2.7	–48%
500	29.1 ± 2.2	15.1 ± 2.4	–50%
1000	28.5 ± 1.0	14.3 ± 2.2	–50%
10,000	22.0 ± 0.9	10.7 ± 1.3	–49%
50,000	14.9 ± 0.8	7.7 ± 1.1	–48%
100,000	13.9 ± 2.4	7.1 ± 0.9	–49%
1,000,000	9.2 ± 0.2	4.6 ± 0.4	–50%

related charge carrier movement, as explained below.

Polarization is observed in this work by capacitance measurement, which must be conducted under AC (Alternating Current) condition. The capacitance relates to the permittivity. Another manifestation of polarization pertains to the gradual increase of the apparent (measured) DC (Direct Current) electrical resistivity as the resistivity measurement under a constant electric field continues. This manifestation of polarization has been previously reported in cement-based materials, including plain cement paste and silica fume cement paste, such that the effect is stronger for plain cement paste than silica fume cement paste [1,2], as consistent with the lower permittivity in the presence of silica fume [7]. The apparent DC resistivity increase upon polarization is due to the gradual build-up of a reverse electric field as the charge carrier movement associated with polarization occurs. The reverse field is against the current flow in the direction of the resistivity measurement, thereby causing the apparent resistivity to be higher than the true resistivity. An increase in temperature promotes the charge carrier movement, thereby causing the apparent resistivity increase to be greater [2]. The occurrence of the apparent resistivity increase is an indication that the mechanism of polarization involves charge carrier movement. For plain cement paste and silica fume cement paste, the charges are dominantly ions [5].

The decrease of the permittivity by the GNP addition is attributed to the inhibition of the polarization-related charge carrier movement by the distributed GNP particles. This interpretation is supported by numerous facts, as described below. Firstly, it is well-known that charge carriers in the form of ions exist in cement paste in connection with the silicate structure and water. Secondly, the polarization and the accompanying fractional increase in the apparent resistivity with increasing time of exposure to a DC electric field are both decreased by the addition of silica fume to cement paste, due to the silica particles (which are non-conductive in relation to both ionic and electronic conduction) serving as physical barriers against ion movement [2]. Thirdly, the resistivity is essentially unaffected by the GNP addition, so that conduction percolation does not occur, thereby causing the distributed GNP particles to be unable to provide a potential barrier against ion movement; rather the distributed GNP particles provide a physical barrier like that provided by the silica fume, which also decreases the permittivity (though less significantly). Fourthly, the density is essentially unaffected by the GNP addition, so the porosity (which would decrease the permittivity) is not increased by the GNP addition and thus cannot explain the observed permittivity decrease upon GNP addition.

The adequate dispersion of the GNP in the cement paste is supported by the reproducibility of the permittivity (Table 1), resistivity (Sec. 3.2) and density (Sec. 3.1) results among specimens of the same formulation, as shown by the  $\pm$  ranges. Poor dispersion would have caused different specimens of the same formulation to give quite different values of the same property.

The higher the frequency, the less is the time available for charge carrier movement in a cycle and hence the smaller is the excursion distance possible for the charge carriers. The adequate dispersion of the GNP is also supported by the observation of essentially the same fractional decrease in permittivity due to the GNP addition for all frequencies studied (Table 1).

The values of the relative permittivity reported in this work are in line with those of prior work on plain cement, silica-fume cement, latex cement, carbon-fiber silica-fume cement and carbon-fiber latex cement [7]. For example, the relative permittivity of silica-fume cement at 10 kHz is 21 in prior work [7], and 22 in this work.

The values of the relative permittivity reported in this work are lower by orders of magnitude than those previously reported for

graphite particle cement paste [10,11]. For example, the value at 10 Hz is  $10^4$  and  $10^8$  for graphite particle contents of 2 and 5 wt %, respectively [10]; the value at 50 Hz is  $10^3$  for the graphite particle content of 3 wt% [11]. In contrast, the value is only 17 at both 10 and 50 Hz for 0.5 wt% GNP in this work. The huge permittivity difference (by 3–7 orders of magnitude) cannot be explained by the difference in particle size or composition between the GNP cement of this work and the graphite particle cement of the prior work [10,11]. The huge permittivity was attributed in the prior work at least partly to the low porosity [11], but the porosity variability cannot account for the huge values of the permittivity. Rather, the huge permittivity is explained here by the fact that the prior work [10,11] did not use an electrically insulating film between the specimen and either of the two electrodes, whereas the present work does (Fig. 3). The importance of the insulating film is explained below and has been previously shown [39].

An impedance (RLC) meter allows meaningful measurement of the capacitance only when the resistance is high enough. The lowest resistance that a meter allows for capacitance measurement depends on the detailed specifications for the particular meter. Indeed, the prior work on cement with graphite particles reports that the capacitance cannot be measured by the meter when the graphite particle content exceeds 5 wt% [10]. In general, even if a meter shows a reading, the reading can be erroneous if the resistance is not high enough, as required for the particular meter. This problem can be circumvented by positioning an electrically insulating film between the specimen and at least one of the two electrodes, as performed in this work. The presence of the film is not suitable for resistance measurement, but is necessary for capacitance measurement when the specimen is conductive to a degree.

Recent work [39] on reduced graphite oxide by the same research group as this work has indeed shown experimentally that the removal of the insulating film increases the measured permittivity by six orders of magnitude, so that the permittivity result obtained without the film is erroneous [40]. In a similar way, the relative permittivity values reported in the prior work [10,11] for cement containing graphite particles are erroneous. Moreover, the reported trend of the permittivity increasing with increasing graphite particle content [10] is opposite to the decreasing trend found in this work, and is erroneous, due to the increasing graphite particle content causing a decrease in the resistivity [10] and hence a higher erroneous measured value of the permittivity when the measurement is performed without an insulating film. In general, the higher the conductivity, the more incorrectly high is the measured permittivity when the measurement does not involve an insulating film. The fact that the measured permittivity of reduced graphite oxide is increased by six orders of magnitude upon removal of the insulating film [39] reflects the relatively high conductivity of reduced graphite oxide.

In order to further confirm the abovementioned effect of the insulating film on the measured permittivity, measurement is conducted on the GNP cement of this work with and without the insulating film. For the GNP cement of thickness 2.80 mm, Fig. 7 compares the capacitance results obtained with and without the insulating film. For the same area, the capacitance is higher in the absence of the insulating film. From the slope of the curve of the capacitance vs. area, the relative permittivity is obtained as  $15.4 \pm 0.7$  and  $21.5 \pm 1.0$  for the cases with and without the insulating film, respectively. As expected, the permittivity is higher in the absence of the insulating film. The difference between these permittivity values is not by orders of magnitude. This is because of the low GNP content below the percolation threshold in this work and the consequent resistivity ( $1 \times 10^6 \Omega \text{ cm}$ ) that is comparable to that without the GNP. In contrast, the graphite particle content is

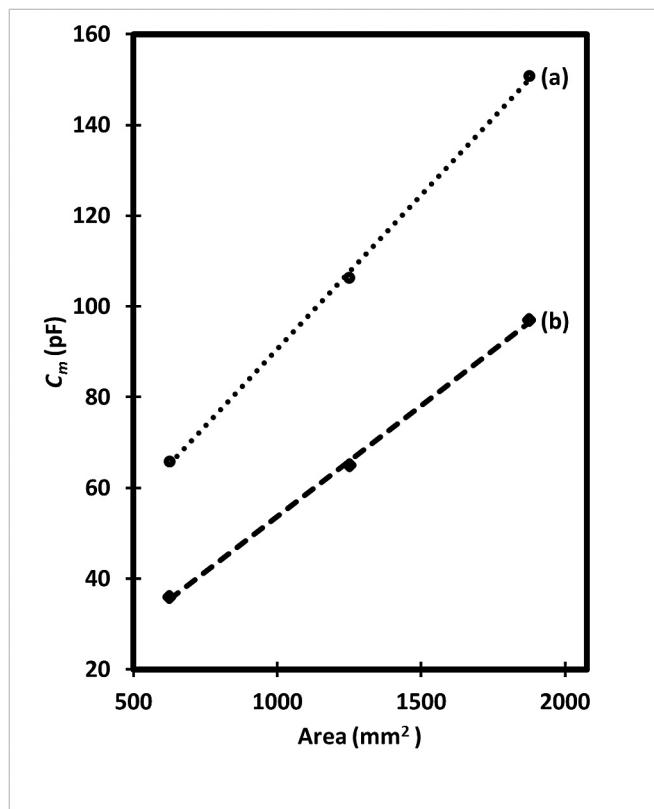


Fig. 7. Plots of the measured capacitance  $C_m$  vs. area (NA) at 100 Hz for GNP silica-fume cement. (a) Without insulating film. (b) With insulating film.

considerably higher in prior work (5 wt% [10] and 3 wt% [11]), being close to the percolation threshold ( $\sim 4$  wt% [11]), as shown by the resistivity ( $10^3 \Omega \text{ cm}$ , 5 wt% graphite) being lower by eight orders of magnitude than the corresponding cement without the graphite particles ( $10^{11} \Omega \text{ cm}$ ) [10].

The resistivity of  $10^{11} \Omega \text{ cm}$  [10] or  $10^8 \Omega \text{ cm}$  [11] reported for cement without the graphite particles (i.e., plain cement) is much higher than the previously reported values of plain cement. For example, a previously reported value for plain cement is  $5 \times 10^5 \Omega \text{ cm}$  [23], which is lower than the value of  $10^{11} \Omega \text{ cm}$  by 6 orders of magnitude. The unusually high value of  $10^{11} \Omega \text{ cm}$  [10] or  $10^8 \Omega \text{ cm}$  [11] is attributed to the unconventional method of cement-based material preparation [10,11]. The unconventional method involves dry mixing the cement powder and graphite particles, followed by compaction and then treatment with water [10,11]. This is in contrast to the conventional method that involves the wet mixing of the constituents. The unconventional method is expected to result in greater porosity than the conventional method. Porosity would increase the resistivity. Indeed, the occurrence of porosity is recognized [11]. Furthermore, the method of resistivity measurement is unclear [10,11]. If the method involved two probes rather than four probes, the measured resistance can be much above the true value, due to the inclusion of the contact resistance in the measured resistance.

The main scientific contribution of this paper is not a modification of a testing method, but the finding that the permittivity of cement is significantly decreased by GNP addition. In fact, the testing method modification has been reported in previous publications of the same research group, notably Ref. [39] on the permittivity of reduced graphite oxide. The finding of this paper is enabled by the modification of the testing method.

## 5. Conclusions

The addition of GNP (0.5% by mass of cement, i.e., about 0.5 vol %) to silica-fume (15% by mass of cement) cement decreases the relative permittivity (10 Hz–1 MHz) by about 49%, i.e., decreasing from 33 to 17 at 50 Hz and from 9.2 to 4.6 at 1 MHz. Such a large fractional decrease (49%) in permittivity has not been previously reported for any admixture in cement.

The GNP addition significantly decreases the permittivity while affecting the resistivity only slightly. This means that the GNP addition affects the dielectric (polarization) behavior in spite of the near absence of effect on the conduction behavior. The effect of the GNP on the permittivity is attributed to the inhibition of the polarization-related charge carrier movement by the distributed GNP. Whether the GNP is present or not, the permittivity decreases with increasing frequency, as expected.

The previously reported values of the relative permittivity (as high as  $10^8$  at 10 Hz) of cement containing graphite particles (10–20  $\mu\text{m}$ ) are erroneous, due to the absence of an electrically insulating film between the specimen and the electrodes and the limitation of the impedance meter. The previously reported trend of the permittivity increasing with increasing graphite particle content [10] is also erroneous, due to the incorrectly high measured permittivity becoming even higher when the specimen is more conductive (when the graphite content is higher). The correct trend is that the permittivity is decreased by the graphite addition.

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