

Article

Gasification Char and Used Foundry Sand as Alternative Fillers to Graphene Nanoplatelets for Electrically Conductive Mortars with and without Virgin/Recycled Carbon Fibres

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Featured Application: Electrically conductive low-cost fillers/fibres can be added to mortars/concretes to manufacture self-sensing structural elements.

Abstract: Structural health monitoring to assess the safety, durability and performance of structures can be performed by non-destructive methods such as the measurement of impedance in self-sensing cement-based elements. Cement-based materials, like mortars and concretes, generally have high electrical resistivity but the addition of carbon-based fillers and fibres decreases their electrical resistivity and thus enhances their self-sensing capabilities. In this study, two waste carbon-based fillers, namely, used foundry sand and gasification char were compared to commercial graphene nanoplatelets and used to produce self-sensing cement mortars, both with and without recycled or virgin carbon fibres. The mortars were tested in terms of their mechanical and electrical properties as well as their propensity to capillary water absorption. The results demonstrate that gasification char alone is the best carbonaceous waste for decreasing the electrical resistivity (−42%) and water absorption (−17%) of mortars, while their compressive strength remains unaltered. Moreover, although there is a slight reduction in compressive strength and an increase in water suction when gasification char is coupled with fibres, the combination of fillers and fibres has a synergistic effect in decreasing mortars' electrical resistivity, especially when recycled carbon fibres are used (−80%).

Keywords: self-sensing; carbon-based additions; fibres; fillers; gasification char; used foundry sand; graphene nanoplatelets; mechanical strength; electrical resistivity; capillary water absorption



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1. Introduction

Self-sensing is the ability of a structural material to perceive its own condition, which can include strain, stress, damage and temperature [1]. In this regard, the material does not need embedded sensors such as fibre-optic sensors or continuous carbon fibres to sense its own status because it becomes the sensor itself thanks to the inclusion of conductive additions, like carbon-based fillers and fibres [2].

In the last two decades, numerous studies have been carried out to investigate self-sensing cement-based materials containing carbon-based fillers or fibres to develop novel multifunctional structural materials [3]. These additions are able to improve the durability and mechanical, electrical and electromagnetic properties [3–5] because of their high mechanical strength, high aspect ratio (in the case of fibres), high specific surface area (in the case of fillers), lightness and high electrical conductivity [6–8].

With regard to carbon fibres, both long and short fibres can be used. However, the use of short fibres is preferable since they are cheaper and easier to disperse, even though they are less effective than long fibres as reinforcement in cement-based composites [9]. Being conductive, carbon fibres are able to improve cement-based composites' electrical properties [1] to create a conductive network that changes if the material is deformed or stressed [10]. Chiarello et al. [11] found that 6 mm-long fibres are better than 3 mm-long fibres for decreasing the electrical resistivity of mortars. This was also confirmed by Han et al. [12], who found that the electrical resistivity of cement mortars is highly reduced when carbon fibres are added at 1.1 wt% of cement. Moreover, a 15% increase in flexural strength and 18% increase in compressive strength was found when 6 mm-long fibres are added at 0.8 and 2.0 wt% of cement, respectively. Furthermore, Belli et al. [13] found that at the same length (6 mm) and volume dosage, carbon fibres are much more effective than steel fibres for decreasing the electrical resistivity of cement mortars.

Among carbon-based fillers, graphene and its derivatives are some of the most innovative materials studied in construction applications. Graphene is the basic structural unit of graphitic materials and it is composed of a single-layer sheet of carbon atoms closely packed into a two-dimensional (2D) honeycomb framework [14]. Graphene, thanks to its high mechanical resistance and electrical conductivity [4] is an interesting material for decreasing the electrical resistivity of cement-based materials [15–17]. A good dispersion of carbon additions in aqueous media is essential for their effectiveness in cement-based composites. Indeed, carbon-based commercial fillers such as graphene nanoplatelets (GNP) or carbon nanotubes (CNT) are difficult to disperse in polar liquids like water because of their hydrophobic nature and their high specific surface area, which are responsible for the formation of bundles and agglomerates [18,19]. In addition, the use of such materials at a large scale is unfeasible owing to their high costs.

It is reported that some carbon-based by-products that are obtained by thermal treatment of biomasses [20] or by other industrial processes exhibit comparable properties to those of commercial ones, and being wastes, are also much cheaper. Moreover, thanks to a less specific surface area and/or a different chemical composition (that is, the presence of functional groups containing elements other than carbon), they are more compatible with water and then easily dispersible [20].

Two interesting materials are gasification char (GCH) and used foundry sand (UFS), which have already been tested by the present authors as possible additions to manufacture lime-based pastes with multifunctional properties [21].

GCH is an industrial by-product produced by the thermal treatment of biomasses. One of these processes is gasification, which is carried out to produce energy at a temperature range of 500–1400 °C in the presence of oxygen (under stoichiometric conditions). As a result, it gives a gas (syngas), a liquid material (tar) and a solid material (GCH), which is highly porous and mainly composed of carbon [22]. To the best of the authors' knowledge, only two papers have already considered GCH in construction materials. In particular, Sirico et al. [23] found that when GCH is added to mortars at 1 wt% by cement, the compressive and flexural strengths remain comparable to those of control specimens, with a slight increase in fracture energy. Mobili et al. [21] found that GCH is able to decrease the electrical resistivity of pastes by 65%, regardless of the percentage added (0.25, 0.5, and 1.0 wt% on hydraulic lime).

On the other hand, UFS is an industrial waste obtained by the ferrous and non-ferrous metal casting industries. Its great thermal conductivity makes it a suitable material for mould casting. In the casting process, moulding sands are recycled multiple times, but, after many cycles the UFS becomes unsuitable for the manufacturing process, so it is removed and becomes a waste. Many studies exist on the use of UFS in cement mortars; however, it is mainly added to construction materials as a replacement for natural sand [24,25]. Even though UFS contains a high amount of silica, it also contains carbon-based additions and several metals [26], which makes it a good candidate for reducing the electrical resistivity of construction materials. In fact, as already found by the present

authors, even a small quantity, equal to 0.25 wt% of hydraulic lime, provides to pastes 27% lower electrical resistivity to pastes, which decreases up to 65% in the case of 1.0 wt% UFS addition [21].

Wen and Chung [27] have reported that the combined use of conductive fillers and fibres could be beneficial to composites since they may decrease the electrical resistivity of the material providing a synergistic effect. They found that the electrical conductivity and the electromagnetic shielding effectiveness of cement pastes are maintained unaltered by partially replacing carbon fibres with carbon black at 50 wt%. The present authors have found that the combined use of GNP at 1.0 vol% and recycled carbon fibres (RCF) at 0.2 vol% entails very low electrical resistivity and clear piezoresistive properties to cement mortars [17]. However, the combined use of carbon-based by-products and carbon fibres in mortars (as well as in concretes) has never been tested.

The aim of this work is to decrease the electrical resistivity of cement-based mortars manufactured with recycled carbon-based fillers and fibres as alternatives to more expensive commercial carbon fillers and virgin carbon fibres. In particular, GCH and UFS were used as fillers in place of GNP, whereas RCF was used as a substitute for virgin carbon fibres (VCF); also, the combined effect of fillers and fibres was investigated. Mortars were tested in terms of their flexural and compressive strength as well as electrical resistivity, which was measured by both direct current (DC) and alternating current (AC). Since water allows the ingress of Cl^- and SO_4^{2-} ions into construction materials, thus impairing their durability [28–31], the effect of carbon-based additions on the absorption of capillary water in mortars was also investigated.

2. Materials and Methods

2.1. Materials

A limestone cement CEM II A-LL 42.5R was used as a binder to manufacture mortars. A calcareous sand (0–8 mm diameter) with a density of 2650 kg/m^3 was used as aggregate in saturated surface dry (s.s.d.) condition, which is reached when sand absorbs 2 wt% of water. An acrylic ether superplasticizer (Dynamon SP1, Mapei) was used as an admixture.

A carbon-based commercial filler, graphene nanoplatelets (GNP) was used as a reference; it was supplied by Pentachem S.r.l. with the commercial name “Pentagraph 30” (CAS number 7440-44-0). GNP particles are mainly composed of carbon and have a thickness of 6–8 nm. The morphology of GNP was analysed by scanning electron microscopy (SEM) (Zeiss, Oberkochen, Germany) and its particle size distribution was investigated by laser diffraction analysis; the results are given in Figure 1.

The carbon-based wastes used to manufacture conductive mortars are a UFS and a char obtained by the gasification of natural wood chips (GCH). UFS was provided by the Italian company LA.BO S.r.l. whereas GCH was provided by a plant equipped with a gasifier located in central Italy (Holz-Kraft, Spanner Re² GmbH). Here, GCH are dried before being subjected to gasification to obtain a moisture content lower than 13%.

In Figures 2 and 3, the morphology and the particle size of UFS and GCH are reported, respectively. As shown in Figure 3, the D_{max} of UFS and GCH are 2.0 mm and 0.5 mm, respectively. In order to maximise the fineness and ensure the best dispersion inside the mortar mixes, UFS and GCH were ground in a ball mill for 60 min and then sieved at $75 \mu\text{m}$. It is reported that the smaller the filler particle size, probably the better the durability of the final material because better refinement of the pore structure can be attained [32].

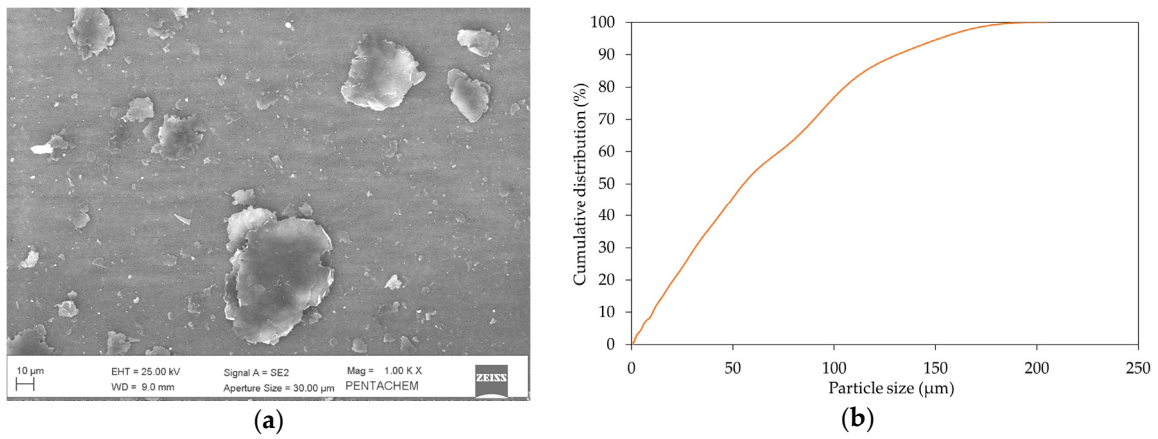


Figure 1. (a) SEM image and (b) particle size distribution of graphene nanoplatelets (GNP).

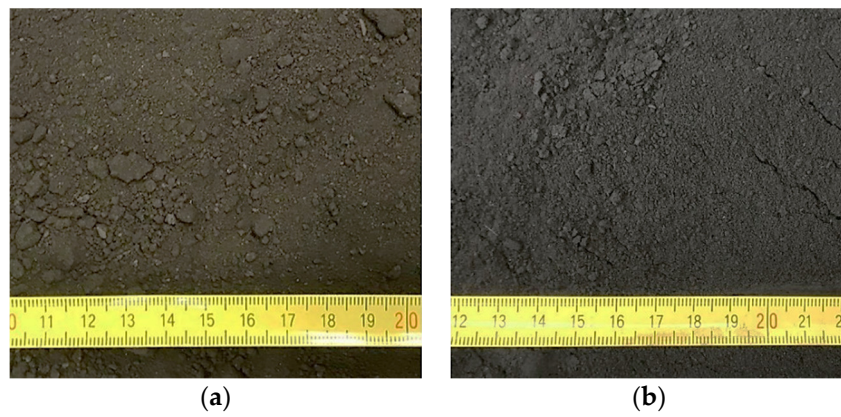


Figure 2. (a) Used foundry sand (UFS) and (b) gasification char (GCH) before grinding and sieving processes

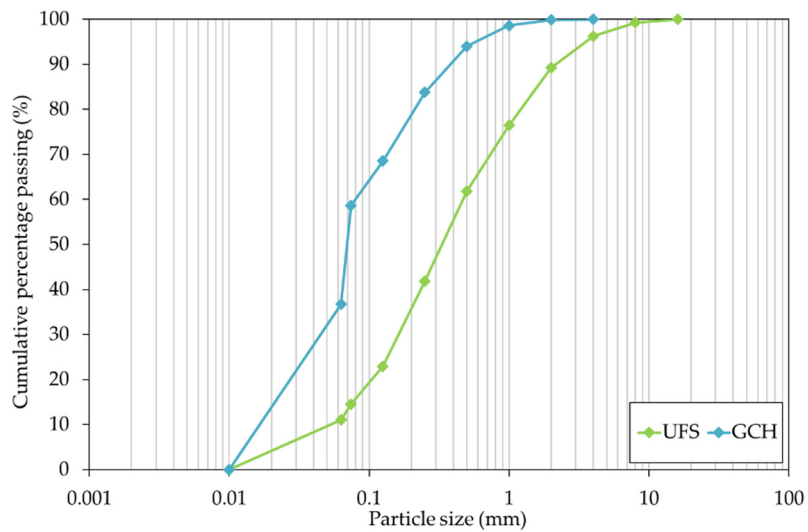


Figure 3. Particle size distribution of UFS and GCH before the grinding and sieving processes.

On the basis of Decision 2014/955/EU related to the list of waste pursuant to Directive 2008/98/EC, the UFS and the GCH used in this experimentation are classified as non-hazardous wastes; the former by the European Waste Code (EWC) 100912, which refers to “wastes from thermal processes—wastes from casting of ferrous pieces—other particulates

other than those mentioned in 100911" (code 100911 refers instead to waste containing hazardous substances), and the latter by the EWC 100103, which refers to "fly ash from peat and untreated wood".

Two types of commercial carbon fibres (CAS number 7440-44-0) were used, namely, virgin carbon fibres (VCF) and recycled carbon fibres (RCF). The VCF were supplied by Dolder Massara S.r.l. and RCF were supplied by Procotex Belgium SA. RCF are a mixture of all origins of carbon and graphite ex-polyacrylonitrile fibres obtained from spools of pure carbon fibres. The morphology of VCF and RCF, analysed by SEM, are reported in [13] whereas the technical properties of GNP, VCF and RCF are reported in [17].

2.2. Methods

2.2.1. Preparation of Mortars

In order to prepare mortars with self-sensing capabilities, carbon-based fillers (UFS, GCH and GNP) were added to each mixture at 1.0% of mortar volume. Carbon-based fibres (VCF and RCF) were added at two different percentages, namely, 0.05% and 0.2% of mortar volume.

In the first part of the experimentation, the two carbon-based by-product fillers, UFS and GCH, were tested in mortars in terms of their mechanical and electrical properties in order to evaluate which was the best one for improving the behaviour of the mortars. The mix design of these mortars is reported in Table 1.

Table 1. Mix design of mortars and slump value—the first part of the experimentation.

Mortar	Cement (g)	Sand (g)	Water (g)	SP ^a (g)	GNP ^b (g)	UFS ^c (g)	GCH ^d (g)	VCF ^e (g)	RCF ^f (g)	Slump (mm)
REF ^g	512	1535	256	2.8	-	-	-	-	-	188
UFS	512	1535	256	6.0	-	20.5	-	-	-	193
GCH	512	1535	256	6.0	-	-	20.5	-	-	182
GNP	512	1535	256	8.4	20.5	-	-	-	-	187
0.05VCF	512	1535	256	3.3	-	-	-	0.9	-	184
0.2VCF	512	1535	256	4.3	-	-	-	3.4	-	187
0.05RCF	512	1535	256	3.3	-	-	-	-	0.9	185
0.2RCF	512	1535	256	4.3	-	-	-	-	3.7	185

^a Superplasticizer; ^b graphene nanoplatelets; ^c used foundry sand; ^d gasification char; ^e virgin carbon fibres; ^f recycled carbon fibres; ^g reference mortar.

In the second part of the experimentation, the best performing filler was found to be GCH, therefore, it was added in combination with fibres in order to evaluate a possible further improvement in mortar properties as a result of the combined effect of the two types of materials. The mix design of these mortars is reported in Table 2.

Table 2. Mix design of mortars and slump value—the second part of the experimentation.

Mortar	CEM (g)	Sand (g)	Water (g)	SP (g)	GCH (g)	VCF (g)	RCF (g)	Slump (mm)
GCH-0.05VCF	512	1535	256	5.6	20.5	0.9	-	186
GCH-0.2VCF	512	1535	256	9.1	20.5	3.4	-	200
GCH-0.05RCF	512	1535	256	6.2	20.5	-	0.9	190
GCH-0.2RCF	512	1535	256	8.1	20.5	-	3.7	193

All mortars were prepared with the same water/cement (w/c) and sand/cement (s/c) ratios of 0.50 and 3 by weight, respectively. In order to better disperse each carbonaceous addition, fillers were put into a blend composed of the entire amount of mixing water and superplasticizer (SP). At first, the compound was manually stirred and then it underwent

sonication in an ultrasonic bath for 22 min. Also a reference mortar (REF) without fillers and fibres was manufactured.

The workability of mortars was maintained at a constant slump value between 140 mm and 200 mm by adding different amounts of SP in order to obtain plastic consistency according to the standard UNI EN 1015-6. The workability of mortars was measured by means of a flow table according to the UNI EN 1015-3 standard and the results are shown in Tables 1 and 2.

Mortars were poured into moulds with different geometries depending on the test to be carried out on them, as reported in the following sections, then, mortars were cured at a relative humidity (RH) of $95 \pm 5\%$ and a temperature (T) of 20 ± 1 °C for the first week and then at $RH = 50 \pm 5\%$ and $T = 20 \pm 1$ °C until testing.

2.2.2. Mechanical Tests

Mortars were tested under both flexure and compression on $40 \times 40 \times 160$ mm specimens after 28 days of curing. Mechanical tests were carried out on three specimens according to the UNI EN 1015-11 standard and the average results are reported. A Galdabini hydraulic press with a precision of 1% was used and mechanical testing were carried out at a loading speed of 0.3 (N·mm²)/s.

2.2.3. Electrical Resistivity Measurements

Direct Current (DC)

The electrical resistivity (ρ) of the mortars was determined by means of a DC four-probe approach on three $40 \times 40 \times 160$ mm specimens per mortar after 28 days of curing. The specimen configuration is reported in Figure 4 and the complete methodology used for the DC measurements is explained in [21]. However, in place of stainless-steel sheets, the outer electrodes were two AISI 304 stainless-steel meshes ($30 \times 50 \times 1$ mm dimensions), with a 3.5 mm aperture and 0.71 mm wire diameter. Obviously, since each electrolytic cell, thus the specimen is characterised by its own specific geometry, a specific cell-constant K value must be determined; in this specific case, it is equal to 0.493 cm⁻¹. Based on the second Ohm's law, knowing K and measuring the electrical resistance (R) as reported in [21], the resistivity ρ value of the specimens can be obtained.

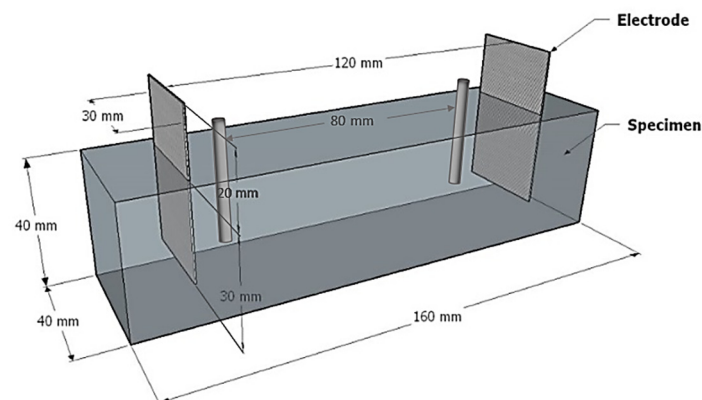


Figure 4. Specimen and electrode configuration for direct current (DC) and alternating current (AC) electrical resistivity measurements.

Alternating Current (AC)

AC measurements were carried out on the same three specimens per mortar used for DC measurements after 28 days of curing. The complete methodology used for the AC measurements is explained in [13]. Also, in this case, since the electrodes used for the measurements are just the two external meshes of Figure 5, a new value of K was determined to be 0.768 cm⁻¹. The ρ value was calculated as reported in [13] by considering the average values of $\log |Z|$, where Z is the electrochemical impedance, which corresponds

to a phase value close to 0° (encircled values in the blue line in Figure 5). These $\log |Z|$ values indicate the resistive electrical behaviour of the tested specimen. REF, UFS, and GCH specimens showed Bode's diagrams similar to Figure 5a, where the resistivity can be obtained at medium frequencies. On the other hand, specimens containing GNP, VCF and RCF showed different Bode's diagrams, where the phase shows two minimum values, one at low and another at high frequencies (Figure 5b). For these materials, the electrical resistivity ρ was determined through the average values of $\log |Z|$ where the phase reached values as close as possible to 0° .

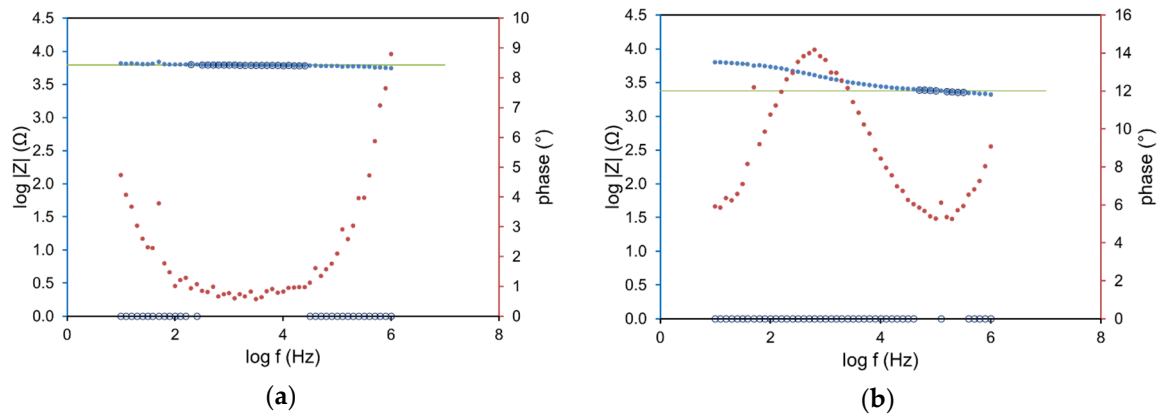


Figure 5. Curves of Bode- $|Z|$ and Bode-phase obtained as an example in (a) reference mortar (REF) mortar and (b) GNP mortar.

2.2.4. Capillary Water Absorption Test

Capillary water absorption was measured according to the UNI EN 15801 standard after 28 days of curing. Three specimens were obtained by $40 \times 40 \times 160$ mm prisms broken into two halves ($40 \times 40 \times 80$ mm). Before testing, the specimens were dried at $T = 60 \pm 2^\circ\text{C}$ until a constant weight (difference in weight after 24 h lower than 0.1%) was obtained and then tested. Specimens were placed in a box on a water-saturated filter paper. The box was kept closed to prevent water evaporation. Specimens were removed from the box after set periods of time (after 10 min, 20 min, 30 min, 60 min, 4 h, 6 h, and after a period of 24 h up to a total of 8 days), the surface was quickly dried with a moist cloth to remove the excess of water and then specimens were weighed and immediately placed back into the box. The obtained average values in terms of water absorbed per unit area (Q_i) were reported. The equation used is as follows:

$$Q_i = (m_i - m_0) / A \quad (1)$$

where m_i is the mass at time t_i , m_0 is the mass at time t_0 and A is the area of the specimen in contact with the water-saturated filter paper.

2.2.5. Morphological Analysis of Materials

The aspect of the materials, the microstructure of the mortars and the interface between the cement matrix and fibres were observed by using a SEM, FESEM ZEISS SUPRA 40 (Zeiss, Oberkochen, Germany). One mortar fragment of about 1 cm^3 was collected from each specimen and covered with a thin layer of gold to make it conductive.

3. Results and Discussion

3.1. Choice of the Best Performing Carbon-Based By-Product Filler

The results obtained for the REF mortar and those manufactured with UFS and GCH fillers after 28 days of curing are reported in Table 3.

Table 3. Mechanical and electrical results of REF, UFS and GCH mortars after 28 days of curing.

Mortar	R_f (MPa)	R_c (MPa)	DC ^a	AC ^b
			ρ ($\Omega \cdot \text{cm}$)	ρ ($\Omega \cdot \text{cm}$)
REF	8.0 ± 0.0	47.6 ± 0.9	7615 ± 334	8202 ± 214
UFS	7.0 ± 1.1	44.9 ± 1.3	10,863 ± 542	10,464 ± 371
GCH	7.4 ± 0.1	47.6 ± 0.5	5316 ± 159	4727 ± 29

^a Direct current; ^b alternating current.

It was observed that the addition of UFS filler decreases both the flexural and compressive strength of mortars compared to REF by about 13% and 6%, respectively. On the contrary, the use of GCH filler only slightly affects the R_f and does not modify the R_c values. This effect is probably related to the better interfacial transition zone (ITZ) between GCH particles and cement paste compared to that of UFS particles. Mrad and Chehab [33] reported that the ITZ between biochar particles and cement paste is more compact than that between natural sand and cement paste. This is related to the porous surface of biochar, which provides an interlocking mechanism caused by the migration of water from the internal reservoirs of the particles to the surrounding paste. This migration promotes hydration reactions and results in a denser and less porous ITZ. Probably, the pore structure of GCH, which is similar to that of biochar, generates the same effect [34]. On the contrary, UFS particles do not have a porous surface, therefore their ITZ with cement paste, even if still quite good, is weaker than that of GCH.

Results obtained for the electrical resistivity show that DC and AC measurements follow the same trend. However, the addition of UFS and GCH has a different effect on the mortars. In particular, UFS always causes an increase in the ρ values of mortars, which increase by 43% and 28% in DC and AC, respectively. Conversely, the use of GCH decreases the electrical resistivity of mortars by 31% and 42% in DC and AC, respectively. This is probably related to the higher carbon content of GCH compared to UFS, which is equal to 77% and 33%, respectively [21].

The results obtained for both the mechanical and electrical properties of mortars show that GCH gives a better performance than UFS as a conductive filler in mortars.

3.2. Effect of the Combined Use of Virgin and Recycled Fillers and Fibres on Mortars' Properties

3.2.1. Mechanical Strength

The second part of the experimentation was focused on the study of GCH added both alone, and together with VCF and RCF in cement mortars. The obtained results are also reported with those obtained for REF and GNP mortars, for comparison.

The flexural strength of mortars is shown in Figure 6.

As already explained, the GCH addition only slightly decreases the R_f of mortar, whereas the addition of commercial GNP increases the R_f value of about 10%. The enhancement of flexural strength in GNP up to 1.2 vol% has already been reported by Du and Pang [35]. The increase in flexural strength has been related to the capacity of almost 2D sheets, such as GNP, to behave as reinforcing materials that bridge cracks [4].

On the other hand, considering carbon fibres, the increase in flexural strength is higher the lower the amount of fibres addition. Moreover, RCF significantly increase the R_f of mortars compared to that of VCF. When GCH is added to mortars containing VCF, the flexural strength is similar to that of mortars containing GCH alone, whereas a slight increase in flexural strength compared to the REF mortar is registered when RCF are used.

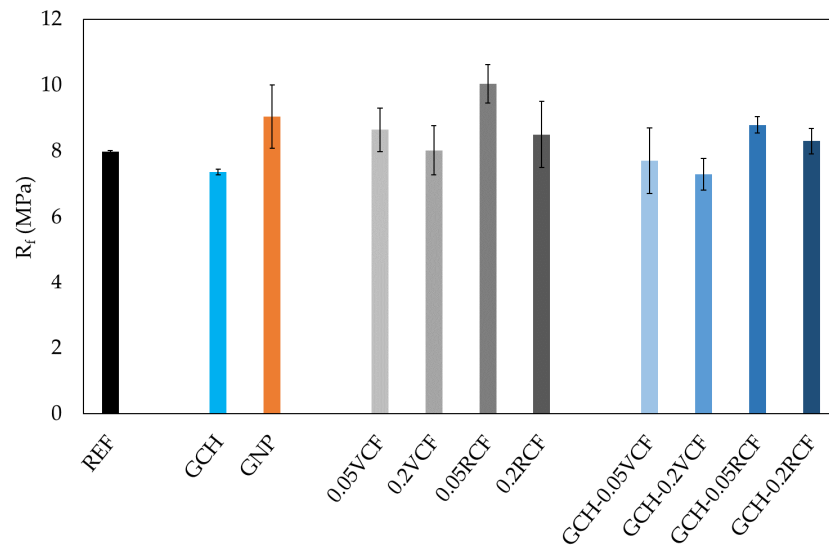


Figure 6. Flexural strength (R_f) of mortars after 28 days of curing.

The superior behaviour of mortars with 0.05 vol% of fibres compared to those containing 0.2 vol% is probably related to their better dispersion. It is known that an excessive content of carbon fibres causes both their agglomeration and the formation of air voids, which reduce the mechanical compressive strength of the material [12,13]. On the other hand, the higher flexural strength of mortars manufactured with RCF is related to the better interface of RCF with the cement paste compared to VCF. In fact, in the SEM images of broken mortars it is clear that the surface of VCF appears smooth (Figure 7a) whereas the surface of RCF is covered by the cement paste (Figure 7b).

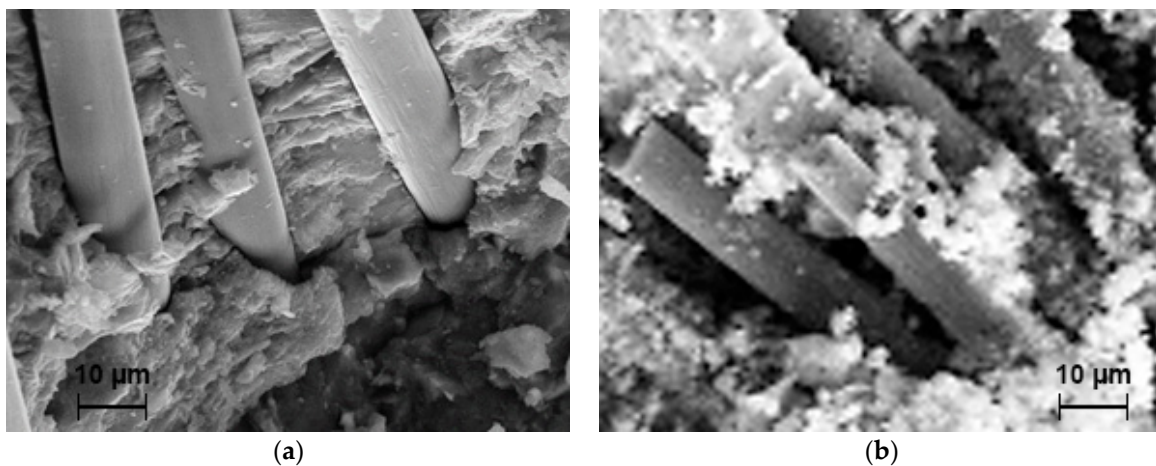


Figure 7. SEM images of mortars containing (a) VCF and (b) RCF.

Results for the compressive strength of the mortars are shown in Figure 8. GCH maintains the compressive strength of mortar, whereas GNP decreases the R_c value of mortar of by about 19%. The decrease in the mechanical properties of GNP mortar is related to the nature of GNP; the high specific surface area and the hydrophobicity of GNP [36] tend to create agglomerates that are barely dispersible in polar liquids like water. For this reason, GNP agglomeration results in the difficult compaction of mortar specimens [15] and a subsequent increase in the mortar's porosity [16,17,37].

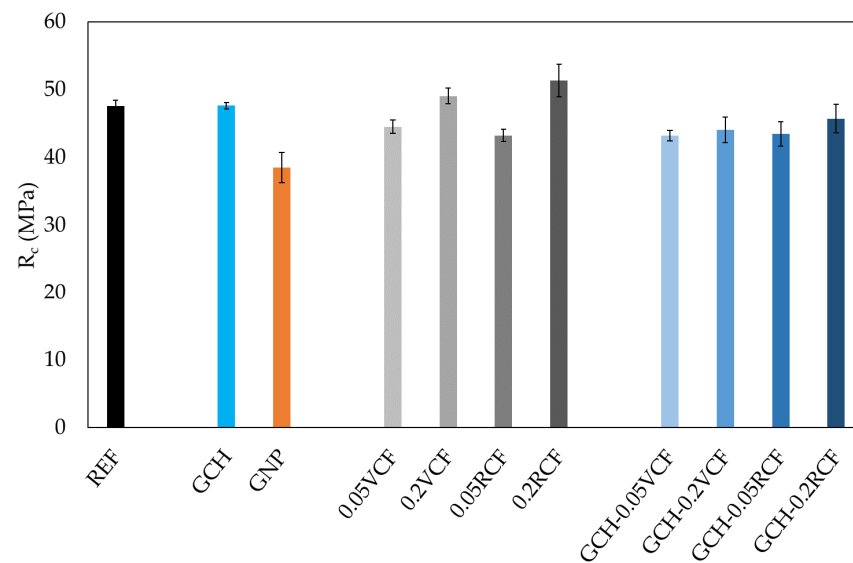


Figure 8. Compressive strength (R_c) of mortars after 28 days of curing.

The addition of carbon fibres generally does not significantly modify the compressive strength of mortars, which remains around 44 MPa, even if at high dosage they provide a slightly better behaviour than at low dosage.

The combined use of GCH and carbon fibres, regardless of their nature and amount, does not have any beneficial effect on the flexural and compressive strength of mortars, which instead suffer a slight decrease of mechanical performance.

3.2.2. Electrical Resistivity Measurements

Results obtained for the DC measurements are displayed in Figure 9. As already reported, GCH decreases the ρ value by 31% compared to REF mortar. On the contrary, the addition of GNP increases the electrical resistivity by 12%. Carbon fibres do not modify the electrical resistivity of mortars, which always remains similar to that of REF regardless of the type and amount of fibres. Finally, the combined use of GCH and fibres shows that when VCF are used the ρ value decreases by 21% and 12% at 0.05 and 0.2 vol%, respectively, whereas it increases by 15% and 23% when RCF are used at the same two dosages.

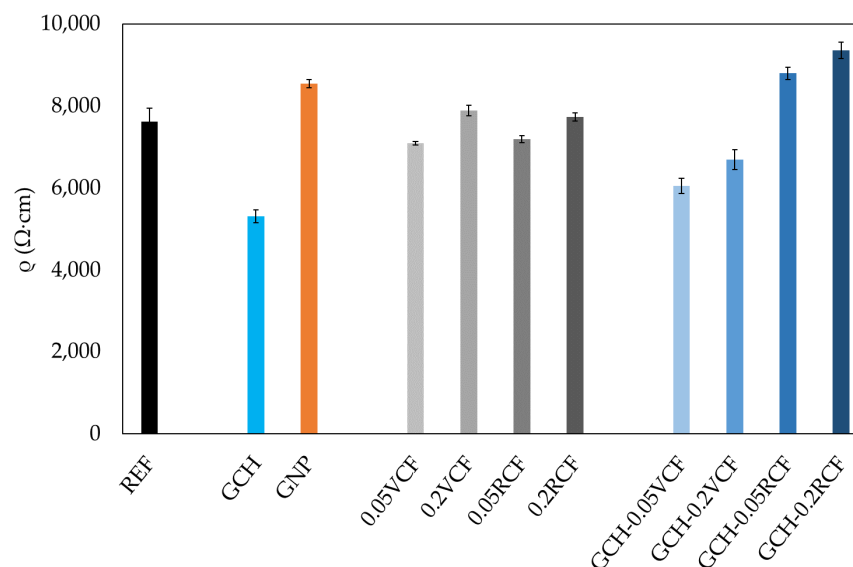


Figure 9. Electrical resistivity (ρ) of mortars after 28 days of curing measured in DC.

The electrical measurements carried out in AC are given in Figure 10. In the figure, the results are divided into three main ranges corresponding to the resistivity at $10 \div 50$ Hz, $50 \div 100$ Hz and $100 \div 10^6$ Hz, hereafter referred to as “low”, “medium” and “high” frequencies, respectively, in order to improve the readability and interpretation of the experimental data.

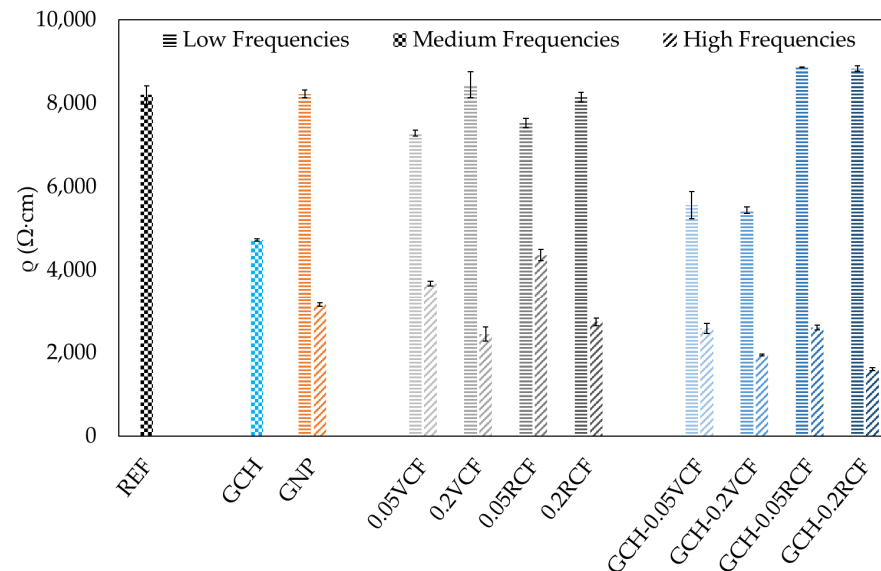


Figure 10. Electrical resistivity (ρ) of mortars after 28 days of curing measured in AC at low, medium and high frequencies.

As already reported, the REF mortar has a resistivity of $8202 \Omega \cdot \text{cm}$ and the addition of 1.0 vol% of GCH lowers the ρ value by 42% (both measurements are calculated in the range of medium frequencies). However, the addition of commercial GNP does not make possible to analyse the electrical resistivity at medium frequencies, but only at low and high frequencies (see “Alternating Current (AC)” in Section 2.2.3 for details). This filler at low frequencies gives a ρ value similar to that of REF, whereas at high frequencies it has a 62% lower ρ value.

The addition of fibres modifies the electrical resistivity of mortars both at low and high frequencies. In general, at low frequencies, mortars with fibres show ρ values slightly different from that of REF mortar whereas the electrical resistivity values are always lower than that of the reference when high frequencies are considered. In particular, in the high frequency range, the mortars manufactured with VCF show ρ values that are 55% and 70% lower than REF when fibres are added at 0.05 and 0.2 vol%, respectively. Mortars containing RCF, in the same frequency range, show ρ values that are 47% and 67% lower than that of REF mortar at the same two dosages, respectively. The obtained results show that VCF are slightly better than RCF in reducing the electrical resistivity of mortars at high frequencies, even if both behave as very good electrical conductors in cement-based mortars. Anyway, the higher the percentage of fibre addition, the lower the electrical resistivity of mortars, as was found by the present authors in [13] and also by others in [12,38].

The effect of the combined use of fibres and GCH filler in mortars is different in the case of VCF and RCF. In particular, when GCH is used with VCF, the electrical resistivity of mortars at low frequencies is around $5450 \Omega \cdot \text{cm}$ for both fibre dosages (33% lower than REF). At high frequencies, the resistivity becomes 68% and 76% lower than REF when fibres are added at 0.05 and 0.2 vol% amounts, respectively. On the contrary, at low frequencies, the addition of RCF to GCH causes an increase in electrical resistivity equal to 8% if compared to that of REF at any dosage. Instead, at high frequencies, RCF at a 0.05 vol% decrease the ρ value by 68% compared to REF at 0.2 vol%, which decrease it by around 80%.

The obtained results show that GCH is a good sustainable micro filler for decreasing the electrical resistivity of mortars in AC, since alone it provides a decrease of 42%. When carbon fibres are added, the electrical resistivity is not enhanced at low frequencies, whereas great enhancement is registered at high frequencies with both VCF and RCF at any dosage. The combination of fillers and fibres added to cement-based composites has been already studied by Wen and Chung, who substituted 50 wt% of carbon fibres with carbon black [27]. They reported that the filler particles interposing between adjacent fibres enhanced the electrical connectivity of the composite, thereby resulting in a synergistic effect.

In general, results in DC are confirmed by those obtained in AC at low and medium frequencies ranges for all the materials tested (Figure 11). This result can be expected considering that in these ranges, frequency goes toward the DC limit, where the effects of the only mortar matrix electrolytic conductivity is prevalent over the combined conductivity of the matrix (ionic conductivity), and in particular, of the fibres (electronic conductivity), which can be observed at high frequencies [39]. Therefore, such combined conductivity takes into account the contribution of both types of conductors with the corresponding and different conduction mechanisms, which cannot be revealed by DC or AC at low frequencies, and in some cases, AC at medium frequencies. Furthermore, when the AC measurements are performed at low frequencies, even the contribution of the polarisation of the interfaces between the electrodes and cement matrix cannot be negligible. This contribution is avoided in DC measurements, taking into account that the method uses a 4-electrode configuration (see “Direct Current (DC)” in Section 2.2.3 and Figure 5). On the other hand, the combined conductivity of the mortars’ matrix and fibres, with or without fillers, whose contribution is visible in any case (Figure 12), can be partially observed through DC measurements, at least in this work. However, the literature reports that GNP [8] is a good commercial filler and carbon fibres [3,17,27,40,41] are good reinforcing materials for decreasing the electrical resistivity of mortars through DC measurements.

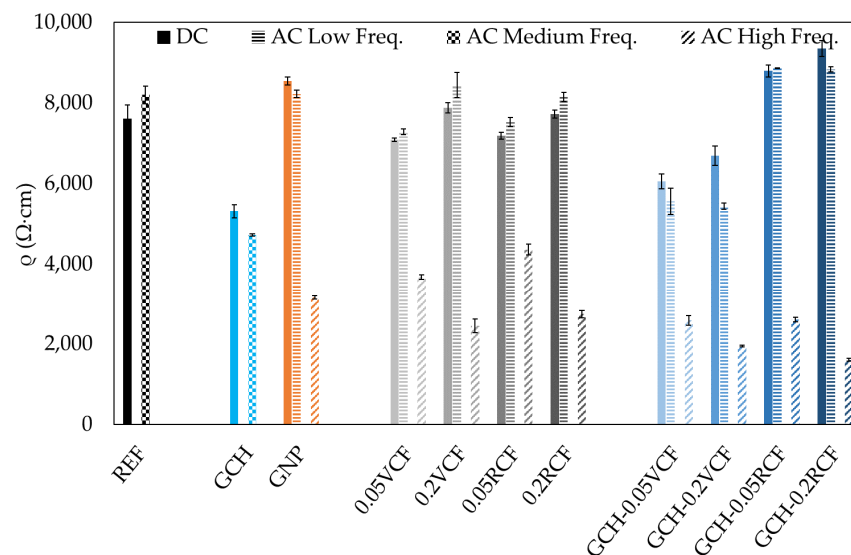


Figure 11. Electrical resistivity (ρ) of mortars after 28 days of curing measured in both DC and AC.

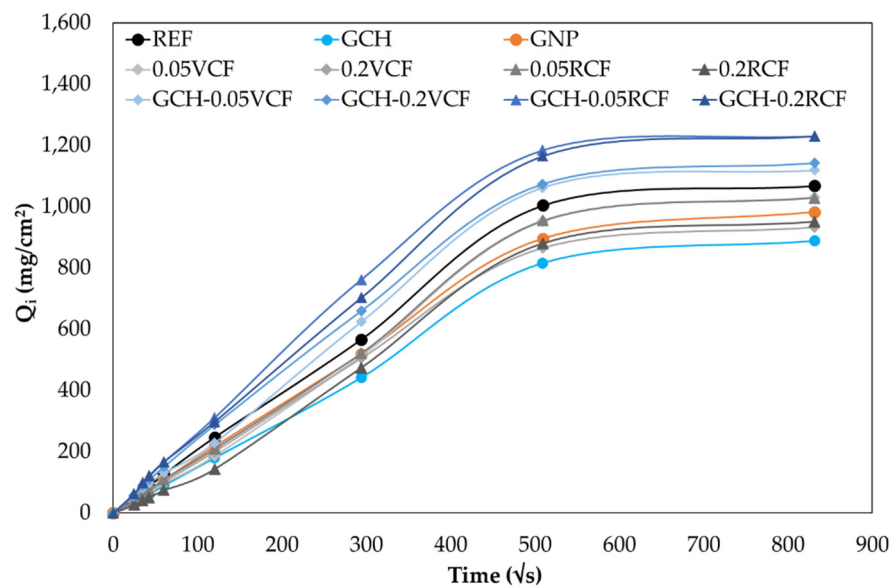


Figure 12. Water absorbed per unit area (Q_i) by mortars after 28 days of curing.

Therefore, the obtained results suggest that electrical impedance measurements should be performed in AC by using high frequency excitation signals in order to better analyse the behaviour of highly conductive cementitious composite materials like those containing GNP and carbon fibres. This avoids errors induced by polarisation of the electrodes or variation of the properties over time due to ion migration [42] and allows the measurement of only the properties of interest, that is, the resistivity of composite systems such as cement-based mortars containing conductive fibres [39] or fillers.

3.3. Capillary Water Absorption

The water absorbed per unit area (Q_i) by the mortars after 28 days of curing is reported in Figure 12. A flat trend in all the curves was observed at the end of the test, meaning that all specimens reached saturation.

Mortars manufactured with both GNP and GCH register a total water absorption, that is, about 8% and 17% lower than that of REF, respectively. GCH mortar is also the one that absorbs the least compared to all other mortars, confirming that GCH increases the durability of mortars by filling the mortars' pores [32]. Also, the addition of fibres slightly reduces the water absorption of mortars, regardless of whether they are VCF or RCF. On the other hand, the combined use of GCH with fibres increases the capillary water absorption of mortars, by about 15% in the case of RCF. Results obtained by capillary water absorption confirm those found by the mechanical tests, in fact, the addition of GCH [32], VCF and RCF alone [13] helps to refine the microstructure of mortars. On the contrary, the addition of GNP is useful to decrease the water absorption, since GNP (being hydrophobic) acts as a barrier for water ingress [18,35], even if it is slightly detrimental to the compressive strength. Finally, the combined addition of GCH and fibres in mortars increases the water absorption and decreases the mechanical resistance, probably because of the increased porosity generated by the high amount of superplasticizer, which produces excessive foam during the casting [35].

4. Conclusions

In this paper, we studied the use of a used foundry sand (UFS) and a gasification char (GCH) as possible low-cost green and alternative fillers to commercial graphene nanoplatelets (GNP) for manufacturing electrically conductive cement mortars. Since GCH provides mortars with the best performance in terms of both mechanical and electrical properties, it was also compared to virgin carbon fibres (VCF) and recycled carbon fibres (RCF)

used alone and coupled with GCH itself. Fillers were added at 1.0 vol%, whereas fibres were added at 0.05 and 0.2 vol%. The obtained results show that:

- GCH is a valid alternative to GNP because it decreases the electrical resistivity of mortars by maintaining their mechanical properties whereas GNP decrease their compressive strength.
- VCF and RCF have a similar effect on the compressive strength of mortars but RCF are better to improve their flexural behaviour, especially when the content of the fibres is low.
- GCH can be used alone to decrease the electrical resistivity of mortars; to further decrease the resistivity, VCF or RCF can also be added. The best performance can be obtained by adding RCF at 0.2 vol%.
- Fillers or fibres used alone reduce the capillary water absorption of mortars and the lowest absorption is provided by the addition of GCH.
- To measure the resistivity of composite systems, alternating current (AC) should be preferred to direct current (DC) in order to avoid polarisation of the electrodes or variation in properties over time due to ion migration (attributable to material polarisation).

Therefore, it can be concluded that it is possible to substitute commercial and expensive carbon-based fillers like GNP with more sustainable and low-cost industrial by-products, such as the GCH obtained by the gasification of wood chips to manufacture durable and electrically conductive cement mortars. Moreover, more sustainable and less expensive RCF can be used instead of VCF. Finally, the combined use of GCH filler and fibre by-products can have a synergistic effect on mortars in terms of decreased electrical resistivity, even though there is a slight reduction in compressive strength and water absorption.

In the future, it is planned to study how water penetration and other contaminants such as chlorides and CO₂ influence the electrical resistivity of mortars/concretes.

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