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3 **Mechanical, durability, depolluting and electrical properties of**
4 **multifunctional mortars prepared with commercial or waste carbon-based**
5 **fillers**
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23 **Highlights**

- 24 • Commercial and waste carbon-based fillers are compared in lime-based mixes
25 • Waste fillers increase the compressive strength of lime-based mixes
26 • Waste fillers decrease lime-based mixes water suction and increase VOCs adsorption
27 • Waste fillers increase electrical conductivity and EMI SE of lime-based mixes
28 • Waste fillers are a sustainable and cheap alternative for multifunctional mixes

30 **Abstract**

31 Carbon-based fillers from industrial wastes and commercial ones were compared to improve the
32 properties of lime-based mixes. As commercial fillers, graphene nanoplatelets and activated carbon
33 were used, whereas as industrial wastes a char obtained by the gasification of biomasses and a used
34 foundry sand were chosen. Carbon-based wastes were found to be a good cost-effective alternative
35 to commercial carbon based fillers to increase the compressive strength (of about 25%) and to reduce
36 water capillary absorption (of about 50%) thanks to the paste refinement; to enhance depollution
37 capacity (of about 25%) and increase both electrical conductivity (up to 65%) and electromagnetic
38 shielding effectiveness (of about 6%) of the hardened compounds thanks to the carbon content.

39

40 **Keywords**

41 Mortar, Multifunctionality, Carbon-based filler, Mechanical properties, Durability, Depollution,
42 Electrical properties.

43

44 **1. Introduction**

45 In the last two decades, carbon-based commercial fillers as carbon black, graphene and its derivatives
46 (carbon nanotubes, fullerenes, etc.), and carbon nanofibers have been studied as possible additions in
47 binder-based matrices in order to improve their multifunctionality. As a matter of fact, thanks to their
48 high mechanical strength, high specific surface area, porosity, lightness, and high electrical
49 conductivity [1,2] they can enhance the mechanical, durability, depolluting and especially electrical
50 and electromagnetic properties of mortars and concretes [3–7].

1 In particular, air pollution, related to the dispersion in atmosphere of particulate matters (PMs),
2 nitrogen oxides (NO_x), and volatile organic compounds (VOCs), is a serious problem not only for
3 outdoor but also for indoor environments where respiratory diseases and the so-called “Sick Building
4 Syndrome” can affect the health of occupants [8] since people spend about 90% of their time in



55 confined environments [9]. Also electromagnetic (EM) radiations generated by electronic devices
56 and communication systems, particularly at high frequencies, can be dangerous for humans [10,11],
57 besides interfering with other electronic devices [12–14].

58 A possible solution to these issues can be the development of multifunctional building materials that
59 can both decrease the concentration of air pollutants and reduce the spreading of EM signals in
60 confined environments. Indeed, considering air depollution, up to now, several indoor air cleaning
61 technologies have been improved; not only active technologies, which are energy consuming, as
62 filtration, non-thermal plasma and electrostatic precipitator [15] but also more sustainable passive
63 technologies, that can interact with the active technologies minimizing the energy consumption, using
64 construction materials as substrates for adsorption and photocatalysis have been developed. In
65 particular, adsorption can occur on highly porous materials, with high specific surface area (300-3000
66 m²/g) [16], and photocatalysis can mineralize pollutants into less harmful compounds by means of a
67 nano-catalyst, such as titanium dioxide (TiO₂) activated under UV-A radiation [17]. Construction
68 materials can also reduce passively the spreading of EM signals if, again, a high specific surface area
69 with porous materials is guaranteed since it enhances the electromagnetic shielding property [18] of
70 materials, that is the property to reflect and/or absorb electromagnetic radiations.

71 So far, carbonaceous fillers addition has been extensively studied in binder-based materials.

72 Activated carbon is one of the most efficient adsorptive materials for gases and vapours (VOCs or
73 NO_x) in air or pollutants in water both if used as it is [19,20] or if it is dispersed within a matrix
74 [21,22]. The effectiveness depends on its wide surface area, porosity and chemical functional group
75 that can act even in a binding matrix. Researchers have been also studied low-cost alternatives such
76 as from waste precursor [23]. Activated carbon, can also enhance the electromagnetic shielding
7 effectiveness of construction materials through the multiple reflections phenomenon [24].

8 Graphene and its derivatives, because of their high specific surface area, are suitable for gas sorption
9 materials [25]. Le et al. [2] proved that GNP is able to enhance the electrical conductivity of cement-
0 based composites and if GNP content exceeds the percolation value (the limit beyond which the



81 conductive particles touch each other), the moisture content does not influence the electrical
82 conductivity. Liu et al. [26] reported that GNP is better than graphene oxide nanoplatelets (GONP)
83 to manufacture electrically conductive cement-based materials. Moreover, GNP is reported to be
84 suitable also to produce mortars with piezoresistive behaviour [27,28], thus the material changes its
85 electrical resistivity if subjected to strain [29,30].

86 However, the essential prerequisite for the efficient use of carbon-based fillers to enhance multi-
87 functionality of binder-based composites is their good dispersion in the mix. Unfortunately, carbon-
88 based commercial fillers can be barely dispersible in polar liquids like water, since, due to their high
89 specific surface area, Van der Waals' forces create bundles and agglomerates. Moreover, many
90 commercial carbon-based materials as graphene nanoplatelets (GNP) and carbon nanotubes are
91 highly expensive and some of them, as carbon black or carbon nanotubes, are very toxic [31,32].

92 Cost can be saved by using carbon-based industrial by-products obtained by the thermal treatment of
93 biomasses that are much cheaper, being wastes, than commercial ones. Moreover, thanks to a
94 different chemical composition with the presence of functional groups formed by other elements than
95 carbon (as Mg, Al, Ca, Si, Na, K, Fe, O), they result more compatible with water and then easily
96 dispersible in polar liquids [33].

97 Char is an industrial by-product obtained by treating biomasses at high temperatures, as in the
98 gasification process. Gasification takes place at $T = 500-1400\text{ }^{\circ}\text{C}$ and the resulting char is a highly
99 porous material mainly composed by carbon [34]. A recent paper by Sirico et al. [35] reports that the
100 addition of char from gasification to mortars at 1 wt.% by cement maintains both the compressive
101 and flexural strengths similar to those of control specimens by slightly increasing the fracture energy.

102 Some studies have confirmed that thermal treated biomasses or waste biomass ashes can enhance the
3 absorption of VOCs [36,37] and can be a potential low-cost substitutes of activated carbon for air
4 depollution [34]. Moreover, the high carbon content makes char a good candidate also for enhancing
5 the electromagnetic shielding effectiveness and electrical properties of construction materials.



106 Used foundry sand is another industrial by-product obtained by the ferrous and non-ferrous metal
107 casting industries where it is used as a moulding casting material because of its great thermal
108 conductivity. The addition of used foundry sand has been already studied in cement-based
109 mortars/concretes; however, its use has been mainly focused as substitute of natural sand [38,39].
110 Used foundry sand has a high silica content, but contains also carbonaceous additions and several
111 metals [40]. Also in this case, the carbonaceous additions and the elevated metal content make this
112 by-product a good candidate to enhance the electromagnetic shielding effectiveness and electrical
113 properties of construction materials.

114 Therefore, in this paper, two commercial carbon-based fillers, graphene nanoplatelets and powdered
115 activated carbon, and two different low cost waste carbonaceous fillers, a char from gasification of
116 biomasses and the finest fraction of a used foundry sand, have been compared as addition to enhance
117 the mechanical, durability, depolluting, and electrical properties of pastes/mortars. As binder, a
118 hydraulic lime was chosen, since lime-based mortars are extensively used as renders/panels in indoor
119 applications. Moreover, hydraulic lime mortars are commonly used for rehabilitation of historical
120 buildings due to their compatibility with the substrate, where instead cement-based mortars are not
121 allowed, and lime is a more sustainable binder than ordinary Portland cement [41]. Literature reports
122 only few articles on the effect of carbon-based fillers on the properties of lime-based mortars:
123 graphene oxide added at 0.05 and 0.1 wt.% by lime [42] and the replacement of lime with waste
124 graphite powder up to 25 wt.% [43] are able to increase the mechanical performance of mortars by
125 decreasing their porosity. A recent paper published by some of the present authors has focused on the
126 use of gasification char and used foundry sand at 1.0% on the total volume as alternatives to graphene
127 nanoplatelets to decrease the electrical resistivity of cement-based mortars [44]. In the paper, it was
8 found that gasification char is better than used foundry sand to enhance some properties of cement
9 mortars since it decreases by 42% their electrical resistivity and by 17% their capillary water
0 absorption. However, to the best of authors' knowledge, there are no paper dealing with the use of
1 gasification char and used foundry sand as carbonaceous by-products for enhancing properties of



132 hydraulic lime-based mixes. Moreover, in the present paper lime-based pastes have been subjected to
133 investigation, to enhance the effect of additions on the matrix since, as reported in [45], aggregates
134 can act as an obstacle in the electric current path increasing the electrical resistivity of concrete.

135

136 2. Experimental

137 2.1 Materials

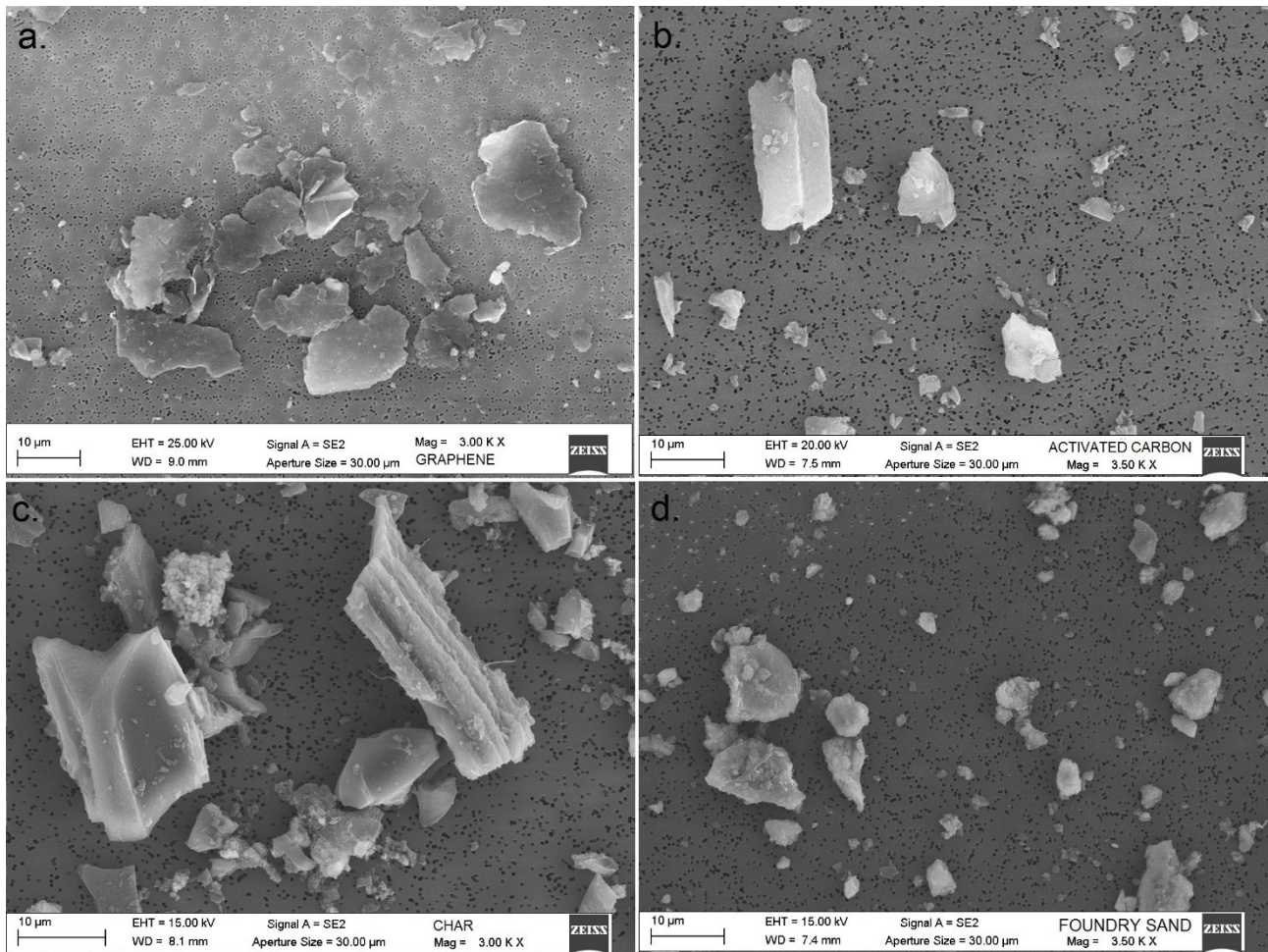
138 Natural hydraulic lime (NHL 5, according to UNI EN 459-1) was used as binder.

139 As commercial carbon-based fillers, graphene nanoplatelets (GNP) (Pentagraf, Pentachem S.r.l.),
140 with a thickness of 6 – 8 nm and a width lower than 5 μm and activated carbon (AC) (Norit® CAP
141 SUPER-WJ, Cabot Norit Nederland B.V.) with a mean particle size of 20 μm were used. GNP has a
142 BET surface area of 30 m^2/g , whereas AC has a BET surface area of 1800 m^2/g .

143 As waste fillers, a char (CH) from biomasses gasification, provided by a plant located in central Italy,
144 and the finest fraction of a used foundry sand (FS), provided by the Italian company LA.BO S.r.l.
145 were used. In particular, CH is obtained by the gasification (Holz-Kraft, Spanner Re² GmbH gasifier)
146 of natural wood chips, after to be dried to a moisture content lower than 13%. CH and FS were ground
147 and sieved in order to have a particle size distribution lower than 75 μm . CH and FS have a BET
148 surface area of 76 m^2/g and 341 m^2/g , respectively. The full characteristics of CH and FS are reported
149 in [44].

150 The morphology of the fillers analysed by Scanning Electron Microscopy (SEM) and the
151 corresponding elemental analysis obtained by EDX-Analysis are given in Fig. 1 and Table 1,
152 respectively. The SEM images highlight the flat shape of GNP (Fig. 1a), the spherical shape of FS
153 (Fig. 1d) and the more elongated aspect of both AC and CH fillers (Figs. 1b and 1c, respectively).





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Fig. 1. SEM of carbonaceous fillers: a. graphene nanoplatelets (GNP); b. activated carbon (AC); c. char (CH) from gasification minor of 75 µm; d. foundry sand (FS) minor of 75 µm.

Table 1. Elemental analysis of waste carbonaceous fillers (wt.%).

Filler	C	O	Ca	K	Mg	Si	Al	Na	Fe
GNP	99.50	0.50	-	-	-	-	-	-	-
AC	95.23	4.77	-	-	-	-	-	-	-
CH	76.72	14.93	5.39	2.04	0.57	0.36	-	-	-
FS	32.92	37.87	1.91	0.66	1.18	14.83	6.38	1.97	2.28

160

161

SEM and ImageJ processing software have been used to evaluate the morphology of the particles and to measure both the particle size and size distribution of AC and CH. An image analysis method was conducted, since indirect advanced methods (e.g. those involving scattered, diffracted light or laser) assume the particle being spherical, which was not the predominant case of AC and CH (Figs. 1b and 1c). In fact, for those particles that show an irregular shape, assuming them to be regular and



166 geometrical will result in an oversimplification. The irregular particles have been described by the
 167 diameter of a circle of equal projection area (d_{EC}), Feret's diameter (d_F) and minimal Feret's diameter
 168 ($Min d_F$), on the basis of previous researches carried out by the authors [46,47].

169

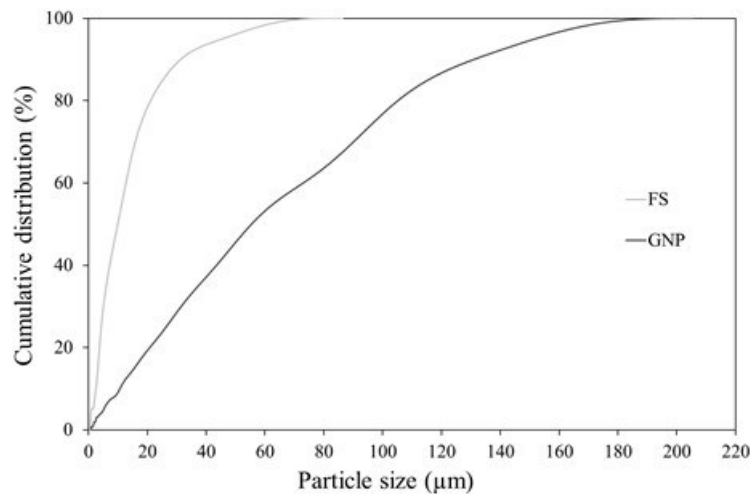
170 **Table 2.** Mean values and standard deviations of d_{EC} , d_F and $Min d_F$ for CH and AC samples.

Sample	d_{EC} (μm)	d_F (μm)	$Min d_F$ (μm)
CH	1.6 ± 2.5	2.5 ± 3.5	1.5 ± 2.3
AC	2.8 ± 3.2	4.7 ± 4.5	2.9 ± 3.0

171

172 In the case of GNP and FS, the particle size distribution was determined by laser diffraction analysis,
 173 since both showed a predominant spherical morphology (Figs. 1a and 1d). Results are showed in Fig.
 174 2: FS sieved at 75 μm is finer than GNP, which shows also a broader grain size distribution.

175



176

177 **Fig. 2.** Particle size distribution of graphene nanoplatelets (GNP) and foundry sand (FS) with particle
 178 size distribution lower than 75 μm .

179

0 *2.2 Preparation of the dispersion*

1 To better disperse each carbonaceous addition, fillers were put into different solutions, composed by
 2 water or by water and superplasticiser. Three different samples were prepared: one containing water
 3 and GNP and two containing water, superplasticiser and GNP. Two types of liquid superplasticiser

184 were compared: a naphthalene sulphonate superplasticiser (N200) (Mapefluid N200, Mapei S.p.A.)
185 and an acrylic superplasticiser (SP1) (Dynamon SP1, Mapei S.p.A.). N200 and SP1 were added in
186 two different amounts, namely 0.5 wt.% and 1.0 wt.% of the binder, whereas GNP was added at 0.5
187 wt.% of the binder. Initially, the compounds were manually stirred for 1 minute; then, they underwent
188 to sonication with an ultrasonicator for 10 minutes at 20 °C (the complete characteristics of the
189 ultrasonicator are reported below). The quality and stability of the dispersions were evaluated by
190 means of a portable turbidimeter (Orbeco-Hellige Model 966) after set periods of time, namely
191 immediately after sonication and after 5, 15, 30, 60 and 120 minutes. Also the amount and type of
192 superplasticiser for preparing the final mixtures were chosen after the evaluation of GNP dispersion
193 by means of the turbidimeter. The turbidimeter works with a light beam which passes through the
194 sample, if there are suspended particles the light is scattered. The dispersions were evaluated in terms
195 of turbidity, which describes the cloudiness of a fluid caused by large numbers of individual particles,
196 generally invisible to the naked eye. The turbidity is measured by Nephelometric Turbidity Units
197 (NTU); if a substance is completely dissolved in solution, light is nearly no scattered leading to a low
198 NTU value, whereas if the solubility limit is reached and the substance starts to precipitate, the light
199 is strongly scattered leading to a high NTU value.

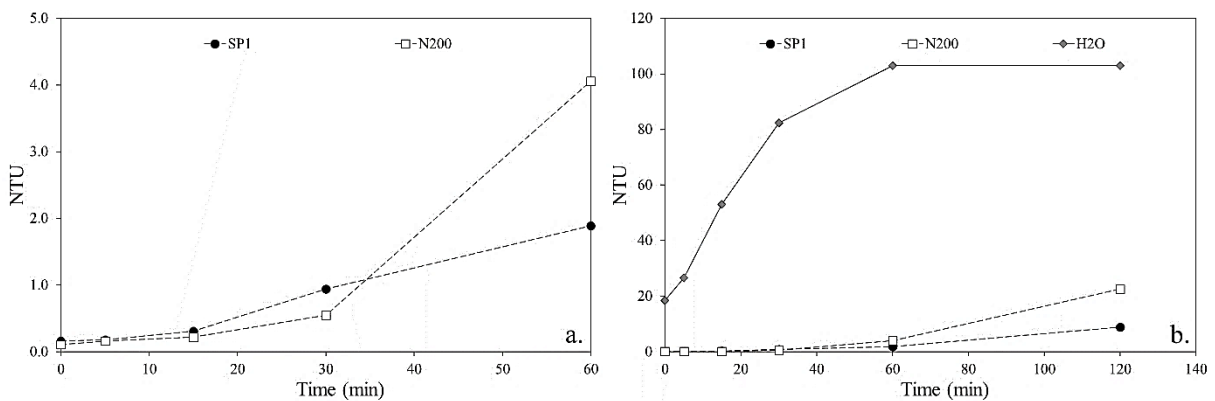
200 When SP1 and N200 were added to 0.5 wt.% of the binder, the NTU values after sonication were
201 1.30 and 1.00, whereas after 5 minutes 2.00 and 1.40, respectively. On the other hand, when SP1 and
202 N200 were added to 1.0 wt.% of the binder, after sonication the NTU values were 0.16 and 0.11,
203 whereas after 5 minutes 0.18 and 0.16, respectively. The slightly lower NTU values obtained by
204 samples prepared with N200 compared to those containing SP1 mean that N200 is better than SP1 to
205 disperse GNP. Moreover, when the superplasticiser is added at 1.0 wt.%, the dispersion is more
6 homogeneous than when added at 0.5 wt.%; for this reason, it was decided to use the superplasticiser
7 at 1.0 wt.% on the binder.

8 The turbidity levels of the dispersions prepared with the sole water and with 1.0 wt.% of
9 superplasticisers in time are reported in Fig. 3. Immediately after sonication, the dispersion of GNP



210 prepared with N200 obtained a lower NTU value compared to that prepared with SP1. This condition
 211 is maintained for the first 30 minutes after sonication, whereas later the two curves invert (Fig. 3a)
 212 and SP1 becomes the one which ensures the best dispersion up to 2 hours of sonication (Fig. 3b). On
 213 the other hand, when water alone is used as dispersant (H2O curve), the dispersion has a much higher
 214 NTU value, which is maintained for all the duration of the test (Fig. 3b), meaning that water alone is
 215 not effective neither to disperse GNP nor to maintain the dispersion stable after sonication.
 216 After a short period of time (30 minutes), the addition of N200 to water ensured a better dispersion
 217 of GNP compared to SP1. This is in agreement with other studies which suggest the use of
 218 naphthalene sulphonate superplasticiser as dispersing agent for carbonaceous fillers [2,48,49].

219



220

221 **Fig. 3.** Turbidity of the dispersion evaluated in terms of Nephelometric Turbidity Units (NTU) after
 222 a. 60 mins after sonication (enlargement) and b. 120 mins after sonication.

223

224 2.3 Preparation of specimens

225 The pastes were manufactured in order to reach a stiff consistency (flow value ≤ 140 mm, UNI EN
 226 1015:3), by using N200 and different amounts of carbonaceous fillers (0.25, 0.50 and 1.00 wt.% on
 7 lime). As reference (REF), a paste without filler addition was prepared. Mix proportions and
 8 workability of pastes are reported in Table 3.

9

230 **Table 3.** Mix proportions and flow values of pastes submitted to mechanical, microstructural,
 231 capillary water absorption, electrical conductivity and depolluting tests (flow and in batch tests).

Mixtures	NHL 5 (g/L)	Water (g/L)	N200 (g/L)	GNP (g/L)	AC (g/L)	CH (g/L)	FS (g/L)	w/b	Flow value (mm)
REF	1375	441	13.75	-	-	-	-	0.32	117
GNP 0.25	1375	441	13.75	3.44	-	-	-	0.32	112
GNP 0.50	1375	441	13.75	6.87	-	-	-	0.32	112
GNP 1.00	1375	441	13.75	13.75	-	-	-	0.32	107
AC 0.25	1375	441	13.75	-	3.44	-	-	0.32	112
AC 0.50	1375	441	13.75	-	6.87	-	-	0.32	107
AC 1.00	1375	456	13.75	-	13.75	-	-	0.33	107
CH 0.25	1375	441	13.75	-	-	3.44	-	0.32	109
CH 0.50	1375	441	13.75	-	-	6.87	-	0.32	113
CH 1.00	1375	441	13.75	-	-	13.75	-	0.32	110
FS 0.25	1375	441	13.75	-	-	-	3.44	0.32	112
FS 0.50	1375	441	13.75	-	-	-	6.87	0.32	115
FS 1.00	1375	441	13.75	-	-	-	13.75	0.32	112

232

233 In order to analyse the effect of carbonaceous fillers on the depolluting activity in terms of NO_x
 234 abatement, pastes were also prepared by adding 1 wt.% on lime of a titanium dioxide photocatalytic
 235 agent (TiO₂), AEROXIDE® TiO₂ P 25 (Evonik Resource Efficiency GmbH). In fact, its
 236 photocatalytic activity under UV radiation is a well-known issue [6]. Pastes compositions with TiO₂
 237 addition are reported in Table 4.

238

239 **Table 4.** Mix proportions of pastes with TiO₂ submitted to depolluting tests (flow test).

Mixtures	NHL 5 (g/L)	Water (g/L)	N200 (g/L)	GNP (g/L)	AC (g/L)	CH (g/L)	FS (g/L)	TiO ₂ (g/L)	w/b
REF T	1434	545	14.34	-	-	-	-	14.34	0.39
GNP 0.50 T	1434	545	14.34	7.17	-	-	-	14.34	0.39
AC 0.50 T	1434	545	14.34	-	7.17	-	-	14.34	0.39
CH 0.50 T	1434	545	14.34	-	-	7.17	-	14.34	0.39
FS 0.50 T	1434	545	14.34	-	-	-	7.17	14.34	0.39

0

1 The electromagnetic shielding effectiveness was evaluated on mortars prepared with a water/binder
 2 (w/b) ratio of 0.49 and a calcareous sand with a maximum grain size of 3 mm (sand/lime ratio = 3
 3 wt.%). In order to prevent detachment or cracking of mortars due to shrinkage from the sample holder

244 used in SE measurements, a shrinkage reducing admixture (SRA) (Mapecure SRA, Mapei S.p.A.)
 245 and a CaO expansive agent (Expancrete, Mapei S.p.A.) in amounts equal to 2 and 5 wt.% on lime,
 246 respectively, were added to mortars. Carbon-based fillers were added at the same dosage weight of
 247 dry materials used for pastes, namely 0.50 wt.% on lime for GNP and AC and 1.00 wt.% on lime for
 248 CH and FS, respectively. The fillers dispersion was carried out with the same procedure used for
 249 pastes. Mortars compositions are reported in Table 5.

250

251 **Table 5.** Mix proportions of mortars submitted to electromagnetic shielding property tests.

Mixtures	NHL 5 (g/L)	Water (g/L)	N200 (g/L)	GNP (g/L)	AC (g/L)	CH (g/L)	FS (g/L)	SAND (g/L)	CaO (g/L)	SRA (g/L)	w/b
M REF	524	256	13.75	-	-	-	-	1611	26.19	10.47	0.49
M GNP 0.50	524	256	13.75	6.87	-	-	-	1611	26.19	10.47	0.49
M AC 0.50	524	256	13.75	-	6.87	-	-	1611	26.19	10.47	0.49
M CH 1.00	524	256	13.75	-	-	13.75	-	1611	26.19	10.47	0.49
M FS 1.00	524	256	13.75	-	-	-	13.75	1611	26.19	10.47	0.49

252

253 Pastes were prepared by mixing the blend of water, N200 and filler with the lime (previously mixed
 254 with TiO₂, if necessary) until homogeneity for 3 minutes.

255 To manufacture mortars, lime was previously mixed with CaO and sand until homogeneity was
 256 reached, and then the blend of water, superplasticiser and filler was incorporated. Finally, SRA was
 257 added to the mortar and mixed for 3 minutes.

258 Superplasticiser was manually stirred together with the mixing water, later the carbonaceous fillers
 259 were added to the liquid. Fillers were dispersed for 10 minutes at 20 °C by means of an ultrasonicator
 260 Vibra Cell™ VCX 130 (Sonics & Materials, Inc.) equipped with a probe with a diameter of 13 mm
 261 that works with a frequency of 20 kHz by setting an amplitude of 70%. Since the stability of the
 2 dispersion with N200 is ensured during the first 30 minutes after sonication (Fig. 3a), the dispersion
 3 was immediately mixed with dry materials for the preparation of pastes and mortars in order to avoid
 4 a possible sedimentation of the carbon-based fillers.

265 After mixing, the workability of pastes was measured in accordance with the UNI EN 1015-3
266 standard.

267 Pastes and mortars were poured into different moulds according to the tests to be carried out and
268 cured at $T = 20 \pm 1$ °C and $RH = 95 \pm 5\%$ for 7 days and then maintained at $T = 20 \pm 1$ °C and $RH =$
269 $50 \pm 5\%$ until testing.

270

271 *2.3 Methods*

272 *2.3.1 Mechanical characterization*

273 In order to investigate the effect of the fillers on the mechanical properties of the pastes (Table 3),
274 **three specimens with 40x40x160 mm dimensions** were manufactured and submitted to both
275 compression and tensile splitting tests after 2, 7 and 28 days of curing according to UNI EN 1015-11
276 and UNI EN 12390-6, respectively.

277

278 *2.3.2 Microstructural characterization*

279 To establish the correlation of the obtained results with the microstructure, mercury intrusion
280 porosimetry (MIP) was performed using a Thermo Fisher Pascal 240 porosimeter to analyse the pore
281 size distribution and the total open porosity (V_p) of pastes. **One small fragment for each composition**
282 **(Table 3) of about 1 cm³** was tested after 28 days of curing. Moreover, SEM observations were
283 performed using a SEM PHILIPS XL20 equipment on small samples of graphite coated paste
284 specimens (Table 3) after 28 days of curing.

285

286 *2.3.3 Capillary water absorption*

7 Since water is the medium and the main carrier of aggressive ions (Cl^- , SO_4^{2-} , etc.) [50,51], the study
8 concerning the water absorption is of primary importance to give information on the durability of a
9 construction material. The durability of pastes (Table 3) was studied through capillary water
0 absorption tests by measuring the amount of water absorbed by a dried specimen through capillary



291 suction in time. For short contact periods (90 min), the capillary water absorption coefficient (C) was
292 calculated **on three 40x40x80 mm paste specimens per composition** according to UNI EN 1015-18
293 **and the average result was reported**. For long contact periods, the water absorbed per unit area (Q_i)
294 **by the same three specimens per compositions** was measured for 8 days according to UNI EN 15801.

295

296 2.3.4. Depolluting Tests

297 In order to investigate if the carbonaceous fillers additions used in this research could give a certain
298 depolluting activity to lime-based materials, the depolluting properties of different pastes were
299 evaluated after 28 days of curing. Two different experimental tests were performed: in-batch, in order
300 to explore the effect of different fillers on the adsorbent properties of pastes for VOCs; and in
301 continuous, by flow test method inside a reactor, to highlight the possible effect of the carbon-based
302 fillers on the photocatalytic ability of pastes. In flow test, pastes with and without TiO_2 were
303 characterized (Table 4 and Table 3, respectively).

304

305 2.3.4.1. In batch test

306 In batch test Gas Chromatography was used for monitoring the concentration of Methyl-ethyl-ketone
307 (MEK) against time injected in a 16.65 L sealed glass box containing the tested specimen [52]. Inside
308 the box a fan guaranteed a continuous air recirculation. The specimens were cylinders with an exposed
309 area of 5026 mm^2 . **For each composition, one specimen was tested**. Air samples inside the box were
310 collected by a micro-syringe every 8 min and analysed with a gas chromatograph (GC 8000 Top
311 Carlo Erba instruments®, injector split 1:15, carrier control by flow; capillary column characteristics:
312 length 25 m, thickness 0.52 μm , Ø 0.32 mm, crosslinked Methyl Siloxane, isotherm 50 °C, FID
3 Detector). The initial amount of MEK injected into the test box was 50 μL which corresponds to 2402
4 mg/m^3 (approximately four times the Threshold Limit Value – TLV). The monitoring over time of
5 data started after 20 min from the first injection to guarantee that all MEK was vaporised. Then, the
6 results were plotted as a percentage of the concentration detected (C_i) with respect to the initial



317 concentration (C_0). The tests were conducted in dark condition (absence of irradiation) for 110
318 minutes.

319

320 2.3.4.2. Flow test

321 The continuous flow test was performed according to UNI 11247 [8]. The specimens, with the same
322 dimensions of those used for the in batch test, were placed on a tripod inside a borosilicate glass
323 chamber of 3.58 L. An UVA metal-halogen quartz lamp (power 400 W), with mercury vapour peak
324 at 360 nm irradiated the specimen surface. The distance between the surface of the specimen and the
325 lamp guarantees a specimen radiance of about 20 W/m^2 , measured before each test [8]. The inlet gas
326 was a mixture of synthetic air and NO_x . The chamber was linked to an analyser Monitor Labs,
327 Nitrogen Oxides Analyser model 8841. The guaranteed inlet concentration of NO_x was 500 ppb and
328 the abatement coefficient A_c (the percentage of NO_x abated) was evaluated according to UNI 11247.

329

330 2.3.5. Electrical and electromagnetic shielding properties

331 Finally, the electrical and electromagnetic shielding properties of mortars were tested. It is well-
332 known that electrical and electromagnetic properties are related, and generally, at the lowest electrical
333 resistances, the best results for electromagnetic SE are found [53–55].

334

335 2.3.5.1. Electrical resistivity

336 The electrical resistivity of a material can be measured by using alternating current (AC) [56] or direct
337 current (DC) [28]. In this paper, electrical resistivity (ρ) was determined by means of a DC four-probe
338 approach (Fig. 4) **on three paste specimens per composition** (Table 3) at 7, 14, 21 and 28 days of
9 curing. The four-probe approach was used to determine the potential difference across the specimens,
0 after the application of a set constant current, and to remove the effects of electrodes polarization.
1 During casting, two AISI 304 stainless steel sheets (30x50x1 mm) were immersed in each specimen,
2 30 mm depth, leaving out the remaining 20 mm on the top of the surface and at a distance of 120 mm



343 each one (Fig. 4). At the same way, two AISI 304 stainless steel rods (\varnothing 3 mm) were immersed in
344 the specimens, 20 mm depth and placed at 100 mm each one, 10 mm far from the corresponding sheet
345 at the same specimen side, as showed in Fig. 4. A constant DC current was applied by an Amel Mod.
346 2059 potentiostat/galvanostat on the outer two stainless steel sheets, and the potential difference was
347 measured using a high impedance digital multimeter between the inner two stainless steel rods.
348 Since each electrolytic cell, as the lime pastes, is characterized by its own specific geometry, a cell-
349 constant K must be determined for it, considering that this particular conductor is conforming to the
350 second Ohm's Law:

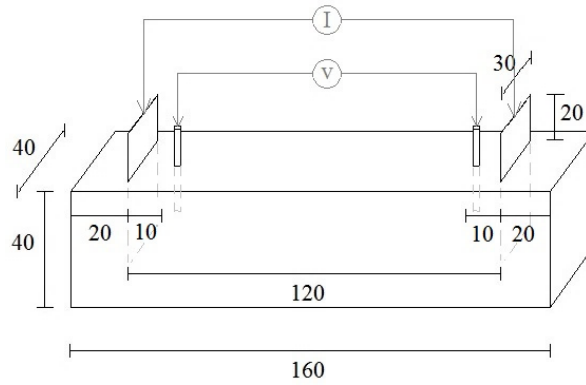
$$351 \quad R = \rho \frac{l}{A} \quad (1)$$

352 where R (Ω) is the resistance of the electrolytic conductor into the cell, measured between two
353 hypothetical metallic electrodes, placed at a distance of l cm and having a contact area A (cm^2). The
354 cell-constant K is given by the l/A ratio (cm^{-1}), whereas ρ ($\Omega \cdot \text{cm}$) is the resistivity of the electrolytic
355 conductor and the inverse ($1/\rho$) its conductivity κ ($\Omega^{-1} \cdot \text{cm}^{-1}$ or $\text{S} \cdot \text{cm}^{-1}$; S = siemens). Considering that
356 an ideal cell, with well-defined geometrical dimensions, does not exist, for real cells as showed in
357 Fig. 4, K was determined by the immersion of the four-probes in an aqueous solution having a known
358 K value, at the same configuration showed in Figure 4. Therefore, using the same equipment
359 described above, the resistance R was measured and κ was calculated using the Eq. (1). The solution
360 used for this purpose was KCl 0.01 M, having $\kappa = 1.408 \text{ mS} \cdot \text{cm}^{-1}$ at 25 °C [57]. Actually, the
361 conductivity of this solution was experimentally measured with an electrical conductivity meter
362 AMEL Mod. 160 and the value $\kappa = 1.442 \text{ mS} \cdot \text{cm}^{-1}$ was obtained.

363 In detail, in order to obtain the value of the resistance R of the cell with KCl solution for all the
4 specimens, firstly, the potential difference (ΔV_0) between the two rods was measured in absence of
5 current, then, a constant current I was applied between the two sheets in the range 5 – 10000 μA and
6 the new potential difference (ΔV_i) was measured. These measurements were plotted in a ($\Delta V_i - \Delta V_0$)
7 vs I diagram (Fig. 5). Interpolating the values that showed a linear trend, the value of the electrical

368 resistance R was obtained. From this R value, a cell-constant $K = 0.6849 \text{ cm}^{-1}$ was calculated. Using
 369 Eq. (1) and this K value, from R determinations, ρ values were calculated for all specimens as a
 370 function of the curing time.

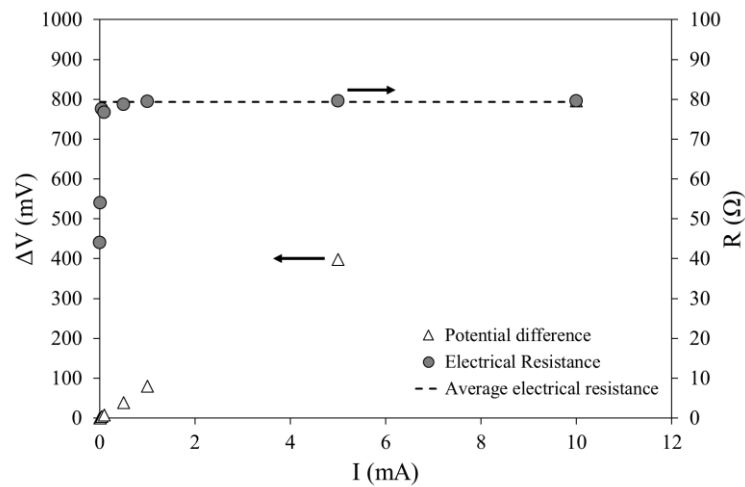
371



372

373 **Fig. 4.** Specimen scheme and electrodes configuration for DC electrical resistivity measurements.

374



375

376 **Fig. 5.** Example of the determination of the electrical resistance (R) through potential difference (ΔV_i
 377 - ΔV_0) and current (I) measurements.

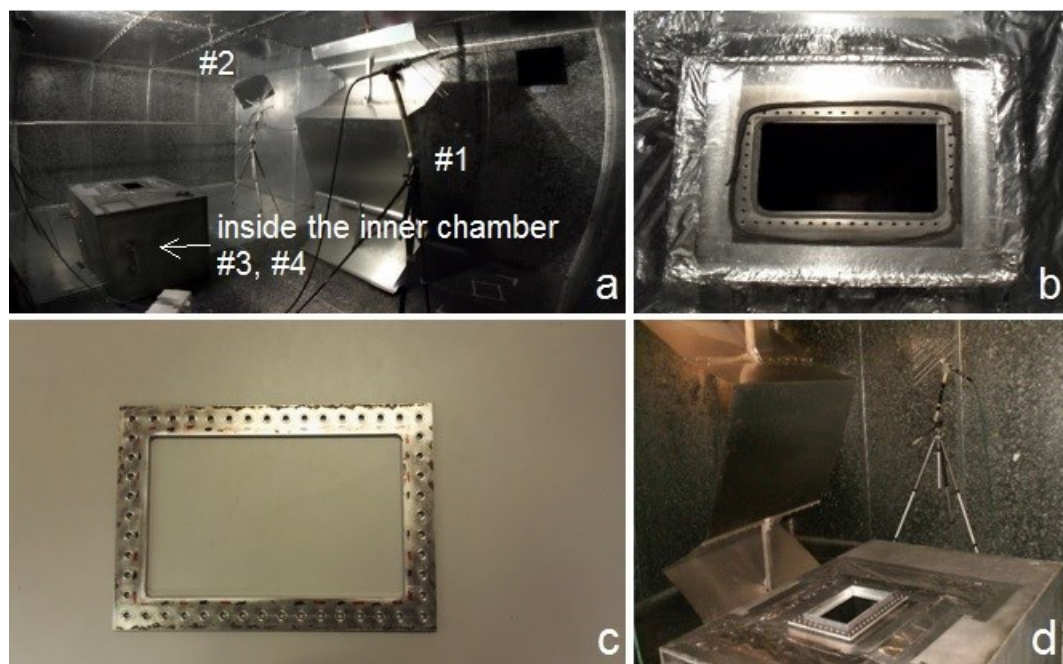
378

9 2.3.5.2. Electromagnetic shielding property

0 The electromagnetic shielding properties of the materials can be evaluated in diverse ways. In this
 1 paper the use of a reverberation chamber (RC) was proposed. The RC facility is able to reproduce a
 2 real environment, where the electromagnetic field is statistically uniform, isotropic and with random

383 polarization [58]. In this way, the sample was excited from all the possible directions (polarization
384 and incident angle), as a real-life scenario. In order to evaluate the SE, a smaller chamber with an
385 aperture, called nested chamber, was used. The sample under test (Table 5) was mounted on the
386 aperture [59,60]. Fig. 5a shows the adopted measurement setup. The outer RC which excites the
387 material under test had dimensions of $6 \times 4 \times 2.5 \text{ m}^3$, whereas the inner chamber of $1.2 \times 0.9 \times 0.8 \text{ m}^3$.
388 Within the outer RC, vertical and horizontal stirrers made of metallic rotating paddles provided the
389 field mixing. The sample was placed on the aperture (Fig. 5b). In order to have an optimal contact
390 between the sample edges and the aperture perimeter, avoiding field leakages [61], electromagnetic
391 gaskets was used (Fig. 5b). Moreover, in order to improve the contact between the sample and the
392 aperture, a multi-hole frame (Fig. 5c) with screws, pushing the sample towards the underlying
393 gaskets, was used (Fig. 5d).

394



395

6 **Fig. 5.** a) Measurement set-up: outer RC equipped by vertical and horizontal stirrers, two log-periodic
7 antennas and nested RC with the aperture on the top; b) aperture of the nested RC where both the
8 gaskets used to avoid field leakages and the holes, where the multi-hole frame was mounted with
9 screws to fasten the specimens and to provide a good contact, are visible; c) multi hole frame used to

400 improve the mechanical contact between the sample and the aperture; d) multi hole frame mounted
401 on the aperture.

402

403 The outer reverberation chamber was fed by a log-periodic antenna (#1) and the resulting energy
404 exciting the sample was monitored by a second antenna (#2) of the same type (Fig. 5a). The field
405 inside the nested chamber was picked up by two double ridge antennas, receiving (#3) and
406 transmitting (#4). A four port Vector Network Analyzer (VNA) was connected to the system to
407 measure the scattering parameters between the four antennas: (#1) and (#2) for the outer chamber and
408 (#3) and (#4) for the inner one. The power received was given by $|S_{ij}|^2$, where S is the complex
409 scattering coefficient measured by the VNA, i and j are the receiving and transmitting antennas,
410 respectively. In this case, the power received inside the outer and inside the inner reverberation
411 chamber and the power between the outer to inner chamber were $|S_{21}|^2$, $|S_{43}|^2$ and $|S_{31}|^2$, respectively.
412 In fact, the material exhibited also effective absorption of electromagnetic energy, thus reducing the
413 quality factor of both reverberation chambers [62]. The SE was evaluated by:

414

$$415 \quad SE = -10 \log \left(\frac{\langle |S_{21}|_{ns}^2 \rangle \langle |S_{41}|_s^2 \rangle \langle |S_{43}|_{ns}^2 \rangle}{\langle |S_{21}|_s^2 \rangle \langle |S_{41}|_{ns}^2 \rangle \langle |S_{43}|_s^2 \rangle} \right) \quad (2)$$

416

417 where $\langle \cdot \rangle$ is the ensemble averaged over the chamber realizations, the subscripts s means “the case
418 with the specimen” and ns means “the case without the specimen”. A single chamber realization of
419 the outer RC corresponded at each stirrer position. On the contrary, within the inner chamber, due to
420 the limited space, there was not a stirrer. In the inner chamber, a bandwidth with a frequency step of
421 250 kHz was considered, and the frequency stirring [63] was applied by using 400 frequency points,
422 each of them correspondent to a chamber realisation. The investigated band was from 0.8 to 8.4 GHz,
423 divided in several sub-bands of 400 MHz, where 1601 frequency points were acquired by the VNA,
424 sampled by steps of 250 kHz. The stirrers worked in synchronous way; they had the same angle step
425 and 9 stirrer positions were considered for both, 40 degrees shifted for each position.

426

427 **3. Results and discussions**

428 *3.1. Mechanical and microstructural characterisation*

429 The results of the tensile (f_{ct}) and compressive strength (R_c) of the pastes during the first 28 days of
430 curing are reported in Table 6.

431 As for regards the f_{ct} values, all the pastes show the same behaviour, with a gradual increase of tensile
432 strength during time; only FS 0.25 and FS 0.50 specimens reach approximately the maximum strength
433 after 7 days of curing. This effect is related to the presence of alkaline salts in the foundry sand [64]
434 (Table 1), which have operated as quick setting agents, contributing to a faster development of
435 mechanical strength during the first days after casting.

436 The maximal enhancement of f_{ct} is registered for the pastes manufactured with the two commercial
437 fillers since their strengths are 20% higher than REF if prepared with AC and more than 40% if
438 prepared with GNP at 1.00 wt.%. Gong et al. [65] found that the use of graphene oxide (GO) inside
439 Portland cement pastes increases the tensile strength more than the 40% when used at 0.03 wt.% on
440 the binder content. The great strength enhancement provided by the little amount of GO used by Gong
441 et al. is related to the great capacity of this material to be dispersed in water, being hydrophilic,
442 compared to graphene nanoplatelets, which conversely is hydrophobic. Instead, the addition of waste
443 carbon-based fillers (CH and FS) does not produce any effect on the tensile strength of pastes after
444 28 days of curing, since the results are comparable with those of REF.

445 Concerning compressive strength, the presence of carbonaceous fillers contributes to increase the R_c
446 values even after 2 days of curing, compared to the REF paste. Moreover, when CH and FS are added,
447 the values are two and three times higher, respectively. As for tensile strength, in FS pastes this
8 behaviour is related to the presence of alkaline salts inside this waste carbon-based filler (Table 1)
9 which act as quick setting agents. In the case of CH paste, this is probably due to the surface area of
0 CH particles ($76 \text{ m}^2/\text{g}$) that contributes to the growth of hydration products, giving again an
1 accelerating effect on the hydration kinetics at early ages, as reported by Gupta and Kua [66] for



452 cement-based mixtures. This behaviour was also detected in [67] where carbon-based fillers were
 453 added in hydraulic lime-based mortars. Furthermore, each addition at each percentage increases the
 454 final mechanical strength (R_c at 28 days) compared to the REF paste, except for AC 1.00 one, up to
 455 45%. This high content of AC decreases the workability of the paste much more than the other fillers,
 456 due to its very high specific surface area ($1800 \text{ m}^2/\text{g}$), so that additional water was necessary to reach
 457 a slump flow value comparable to that of the other pastes (Table 3). The additional water has changed
 458 the w/b ratio from 0.32 to 0.33 (Table 3), leading to a decrease in R_c after 28 days [68]. The ability
 459 of nano/micro fillers to increase the mechanical strength of cement-based materials already at early
 460 ages is known as “filler effect” [69]. Such materials, due to their high specific surface area [4,70],
 461 work as nucleation sites for C-S-H [71,72], accelerating the degree of hydration and therefore
 462 increasing the mechanical properties of hardened compounds. Moreover, it is well-known that the
 463 addition of fillers contributes to the refinement of the paste, lowering the total porosity (V_p) of the
 464 compound and shifting the critical pore radius (r_c) to smaller dimensions. Such effect is well visible
 465 in Table 6, where the REF paste shows a V_p of 41% whereas all other pastes have a lower total porosity
 466 value, which reaches the lowest value (36%) when FS is added. This effect is probably due to the best
 467 dispersion obtained by FS filler because of the small and spherical shape of its particles (Fig. 1d).
 468 Moreover, all the manufactured pastes are characterised by r_c smaller than the REF one, confirming
 469 the ability of all carbon-based fillers to refine the porosity of the matrix.

471 **Table 6.** Tensile strength (f_{ct}), compressive strength (R_c), total porosity (V_p) and critical pore radius
 472 (r_c) of pastes.

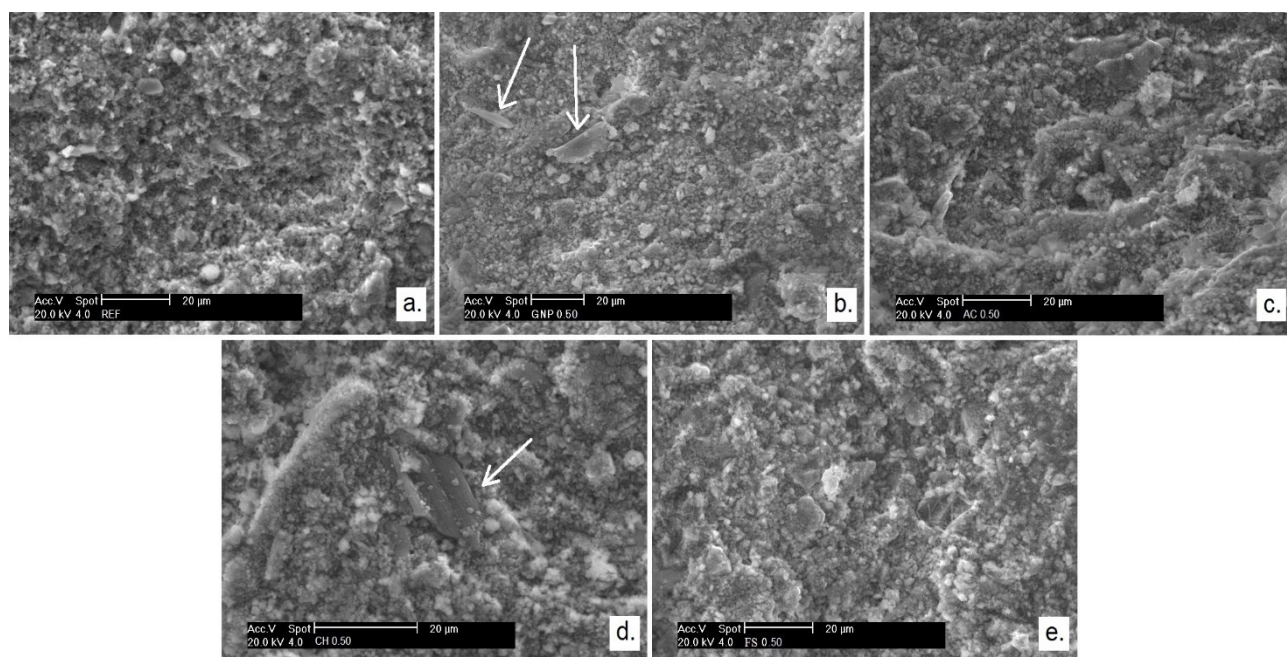
Mixtures	f_{ct} (MPa)			R_c (MPa)			V_p (%)	r_c (μm)
	2 days	7 days	28 days	2 days	7 days	28 days		
REF	0.20 ± 0.01	0.56 ± 0.00	0.82 ± 0.01	1.2 ± 0.0	4.2 ± 0.1	10.8 ± 0.3	41	0.116
GNP 0.25	0.30 ± 0.03	0.50 ± 0.04	0.92 ± 0.01	1.9 ± 0.0	4.8 ± 0.1	13.0 ± 0.5	37	0.082
GNP 0.50	0.30 ± 0.01	0.65 ± 0.00	0.88 ± 0.01	2.0 ± 0.1	3.5 ± 0.2	13.8 ± 0.1	39	0.103
GNP 1.00	0.40 ± 0.01	0.66 ± 0.01	1.17 ± 0.05	2.3 ± 0.2	3.7 ± 0.0	13.5 ± 0.1	39	0.104
AC 0.25	0.30 ± 0.03	0.48 ± 0.01	0.99 ± 0.00	1.2 ± 0.3	4.4 ± 0.0	12.8 ± 0.0	38	0.093

AC 0.50	0.30 ± 0.03	0.60 ± 0.01	0.97 ± 0.01	1.8 ± 0.0	4.3 ± 0.1	13.3 ± 0.1	38	0.096
AC 1.00	0.40 ± 0.01	0.58 ± 0.00	0.99 ± 0.01	1.7 ± 0.1	4.4 ± 0.1	11.1 ± 0.1	39	0.096
CH 0.25	0.34 ± 0.01	0.56 ± 0.03	0.69 ± 0.01	2.6 ± 0.1	4.2 ± 0.0	12.7 ± 0.2	38	0.111
CH 0.50	0.39 ± 0.00	0.47 ± 0.01	0.82 ± 0.02	2.7 ± 0.1	4.3 ± 0.3	12.1 ± 0.1	40	0.111
CH 1.00	0.39 ± 0.01	0.59 ± 0.03	0.82 ± 0.01	2.8 ± 0.0	5.1 ± 0.4	13.6 ± 0.1	39	0.110
FS 0.25	0.51 ± 0.01	0.85 ± 0.03	0.88 ± 0.03	3.7 ± 0.1	6.4 ± 0.2	15.8 ± 0.3	37	0.086
FS 0.50	0.57 ± 0.01	0.97 ± 0.04	0.82 ± 0.03	3.5 ± 0.2	7.5 ± 0.4	13.3 ± 0.0	36	0.084
FS 1.00	0.43 ± 0.00	0.58 ± 0.01	0.79 ± 0.01	3.0 ± 0.1	5.2 ± 0.1	13.1 ± 0.1	36	0.099

473

474 The SEM images of the REF paste and those manufactured with carbon-based fillers at 0.50 wt.% are
 475 given in Fig. 7. In AC 0.50 and FS 0.50 specimens (Figs. 7c and 7e), the presence of the carbonaceous
 476 addition is not visible, whereas in GNP 0.50 two agglomerates of graphene nanoplatelets partially
 477 embedded in the matrix can be noticed in the upper left side (Fig. 7b), confirming the higher
 478 difficulties in dispersing the GNP with respect to the other fillers. In CH 0.50 specimen, the presence
 479 of one particle of char perfectly adhered to the paste is visible in the middle area of Fig. 7d. The
 480 surface of CH particle is covered by the precipitation of hydration products, confirming again the
 481 capacity of CH to increase their growth [66].

482



3

484 **Fig. 7.** SEM of pastes: a. REF; b. GNP 0.50; c. AC 050; d. CH 0.50; e. FS 0.50. Arrows indicate the
485 carbonaceous particles.

486

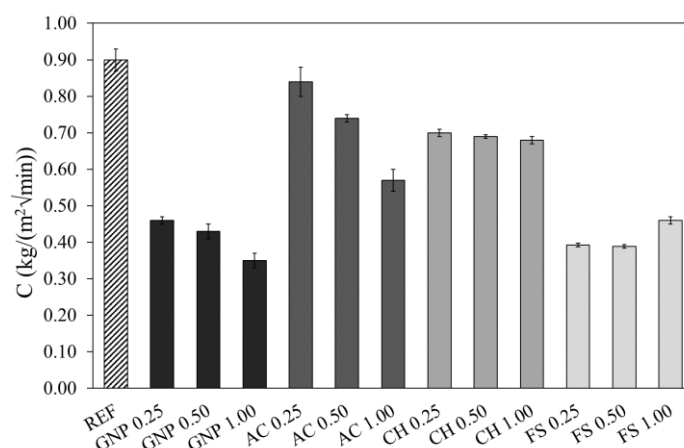
487 3.2. Capillary water absorption

488 As for regards the water absorption coefficient (C) (Fig. 8), carbonaceous fillers have a great influence
489 in decreasing the water uptake of pastes at short periods of contact with water (90 min). When GNP
490 and FS fillers are used, C coefficient reaches values lower than half of that of REF. In general,
491 increasing carbon-based fillers content, the water suction decreases, especially for pastes prepared
492 with the two commercial fillers, since both AC [73,74] and GNP [75–77] are hydrophobic materials.
493 This behaviour is less evident for pastes which contain CH, since their C values remain always around
494 76% of REF: this effect is related to their critical pore radii which are bigger than those of the pastes
495 manufactured with other fillers (Table 6). The results confirm that the saturation of the capillary pores
496 with higher dimensions occurs faster than for the smaller ones [78].

497 On the other hand, C value has a reversal trend when FS is used, seeing that it increases with the
498 amount of this filler, with absorption values equal to 43% and 54% of REF when 0.25% and 1.00%
499 of FS are added, respectively. The increased content of FS increases also the presence of clay
500 impurities [64,79]; it is well-known that clay is hydrophilic and thus it is much prone to water
501 absorption [68]. However, FS specimens show very low C coefficients thanks to their low total
502 porosities and small critical pore radii r_c (Table 6).

503





504

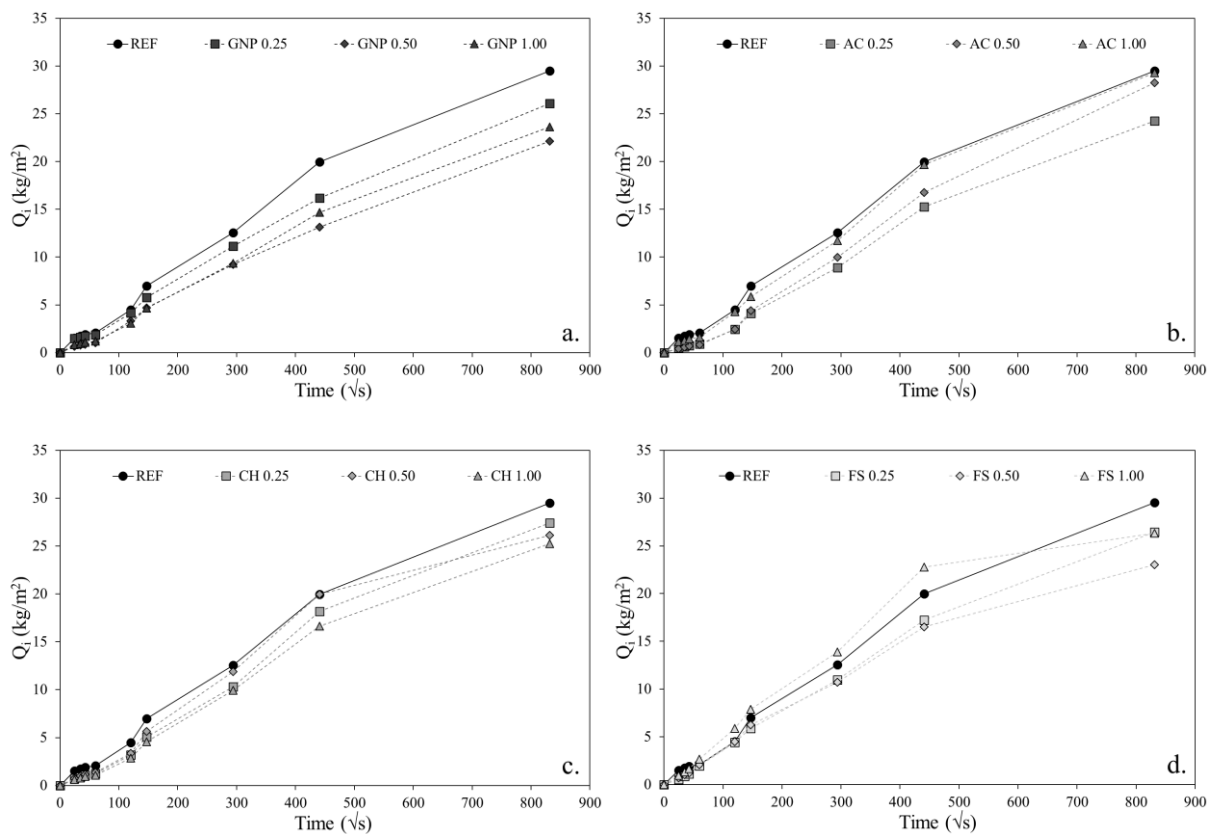
505 **Fig. 8.** Water absorption coefficient (C) of pastes after 28 days of curing.

506

507 The water absorbed per unit area (Q_i) by pastes after 28 days of curing is reported in Fig. 9. Also for
 508 a long time of contact with water (8 days), all specimens containing carbon-based fillers show a lower
 509 absorption compared to REF. In particular, the lowest absorptions are registered for GNP pastes (Fig.
 510 9a), confirming again the hydrophobic nature of GNP; GNP filler, acting as a barrier against the rise
 511 of capillary water, increases the winding of the water path [48]. Also the pastes containing FS exhibit
 512 very low water absorptions in time (Fig. 9d) thanks to their lowest total porosity (Table 6). In these
 513 cases, the lowest absorptions are obtained by the specimens manufactured with 0.50 wt.% of filler.
 514 For FS 0.50 paste this is due to the smallest dimensions of the critical pore radius (Table 6); for the
 515 GNP 0.50 paste this is due to the hydrophobicity of graphene particles, since neither the total porosity
 516 nor the critical pore radius of GNP pastes are the smallest (Table 6).

517 The Q_i values of the pastes manufactured with AC (Fig. 9b) show an opposite trend compared to the
 518 C coefficient (Fig. 8). In fact, whereas the C coefficient increases with the AC content, the absorption
 519 decreases. This effect is related to the AC behaviour: AC is hydrophobic only at early ages thanks to
 0 its non-polar surface characteristics [80], whereas it becomes hydrophilic for long contact time with
 1 water [73].

2



523

524

525 **Fig. 9.** Water absorbed per unit area (Q_i) of pastes after 28 days of curing. In each figure, the
 526 continuous line represents the REF paste.

527

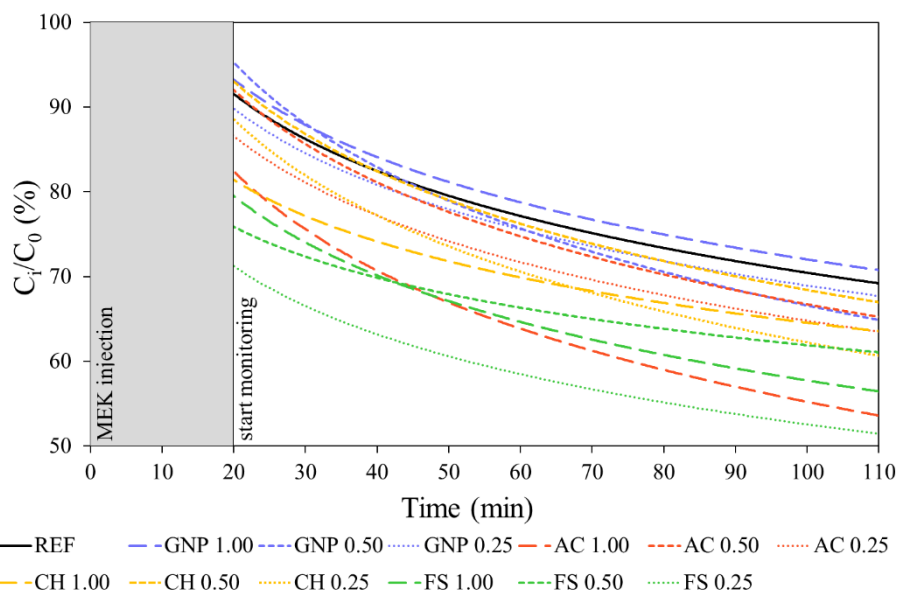
528 3.3. Depolluting tests

529 3.3.1. In batch test

530 The depolluting capacity of the pastes under dark condition is displayed in Fig. 10, where the residual
 531 percentage of MEK inside the box is plotted against time. The trendline starts at 20 minutes because
 532 this is the time necessary for vaporising MEK completely.

533





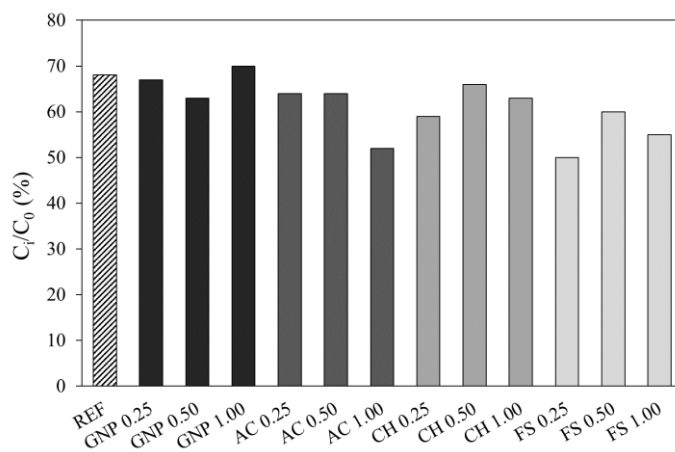
534

535 **Fig. 10.** Residual percentage of MEK inside the box during the in batch test carried out on pastes.

536

537 To better analyse and compare the results, in Fig. 11 the residual percentage concentration of MEK
 538 (C_i/C_0) inside the box after 110 min of test under dark condition is also reported.

539



540

541 **Fig. 11.** Residual percentage of MEK inside the box during the in batch test on pastes after 110 min.

542

3 Fig. 10 and Fig. 11 show that under dark condition the REF paste adsorbs approximately 30% of
 4 MEK at the end of test. Only pastes manufactured with some carbonaceous fillers improve this
 5 depolluting capacity. In particular, when GNP is added the depolluting efficiency remains around
 6 30%. AC, instead, when added at 1.00 wt.% of lime, increases the efficiency to 50%. Thanks to the

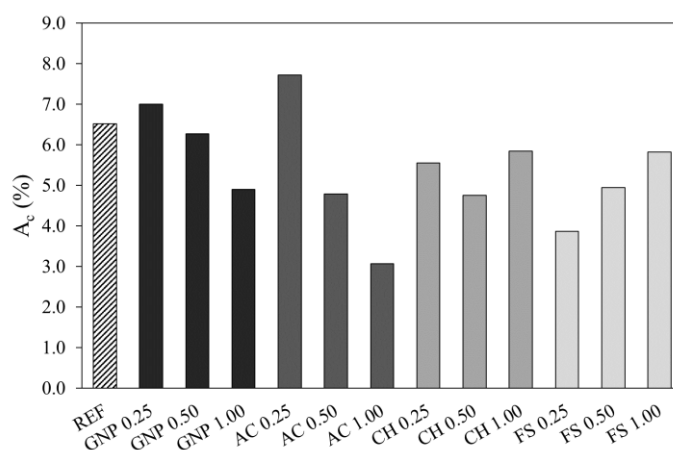
547 great ability of AC to reduce air pollutants by adsorption [81] because of its high specific surface area
548 (1800 m²/g), a minimum amount of 1.00 wt.%, as in this case, is enough to obtain a significant effect.
549 Referring to carbon waste fillers, the CH pastes show a poor effect on MEK removal, this can be
550 ascribed to its surface area which is not so high (76 m²/g). Even if CH is considered a potential
551 substitute of AC for VOCs removal [34], in this case it seems not compatible for adsorbing MEK. FS
552 appears the most effective filler to increase the depolluting capacity of pastes given that, by varying
553 its content, residual concentrations of MEK around 40 – 50% can be achieved, even if its specific
554 surface area (341 m²/g) is lower than AC.

555

556 3.3.2. Flow test

557 The photocatalytic efficiency of the pastes tested in terms of NO_x abatement under UVA radiation is
558 shown in Fig. 12.

559



560

561 **Fig. 12.** Photocatalytic efficiency under UVA radiation of pastes (NO_x abatement).

562

3 Both commercial and waste carbonaceous fillers do not modify the NO_x abatement of the REF paste
4 which is too low (6.5%) to be considered as a photocatalytic behaviour.

5 For the above-mentioned reason, it was decided to test some selected pastes with the addition of nano-
6 TiO₂, that is known to be an efficient photocatalytic agent [6], in order to evaluate if the carbon-based

567 fillers could affect the photocatalytic activity of TiO₂ improving the first stage of photoactivity
568 (adsorption of pollutants). In fact, carbonaceous fillers could interact with the photocatalyst; keeping
569 the surface chemistry unchanged, the increase of the specific surface area can create a high number
570 of active sites and e⁻-h⁺ pairs and high concentration of pollutants on the photocatalyst can be
571 expected [82]. For this reason, some pastes were manufactured using carbonaceous fillers at 0.50
572 wt.% and TiO₂ at 1.00 wt.% on hydraulic lime (Table 4).

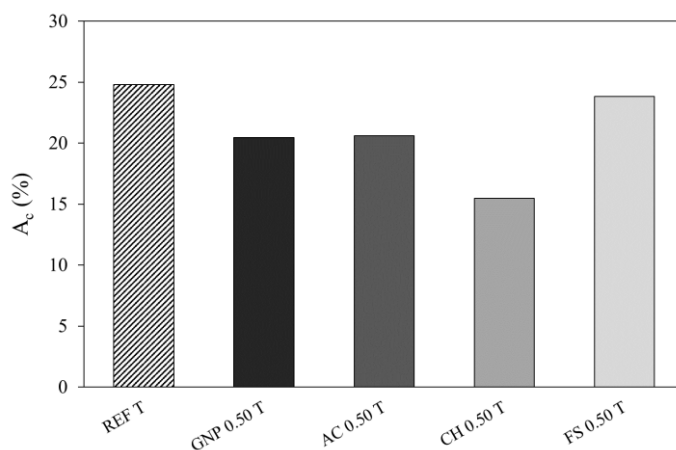
573 Results of the photocatalytic efficiency of the pastes with TiO₂ addition are reported in Fig. 13. When
574 TiO₂ is added to the paste (REF T), the NO_x abatement reaches values of 25%, four times higher than
575 that of the same paste without TiO₂ (REF specimen, Fig. 12). **This result was also reported by some
576 of the present authors in a recent paper [83], where the replacement of hydraulic lime with TiO₂ at 5
577 wt.% in a plain mortar contributes to enhance the photocatalytic efficiency from 5% to 35%. In**
578 general, also using carbonaceous fillers, all the pastes with TiO₂ show a great enhancement of the
579 photocatalytic action. In particular, GNP 0.50 T and AC 0.50 T show an A_c value around 20%, which
580 are four and three times higher than that of GNP 0.50 and AC 0.50, respectively (Fig. 12). As for
581 regards the waste carbon-based additions, the lowest NO_x abatement is found for CH 0.50 T with an
582 A_c value of 15%, which is three times higher than that registered for CH 0.50 specimen (Fig. 12). On
583 the contrary, the specimen manufactured with TiO₂ and foundry sand (FS 0.50 T) shows the same
584 photocatalytic efficiency of REF T, five times higher than that of the same paste without
585 photocatalytic agent (Fig. 12).

586 Observing the results of Fig. 12 and Fig. 13, it is evident that the addition of a photocatalytic agent is
587 necessary to obtain the photocatalytic abatement of NO_x under UVA irradiation. The results
588 demonstrate that the addition of carbonaceous fillers, without specific treatments, is not able to
9 increase the photocatalytic behaviour of TiO₂. For example, with GNP this effect can be only
0 achieved by using a functionalisation method [84], like hydrothermal [85] or sol-gel [86] treatments.
1 Moreover, the addition of carbonaceous fillers always worsens the depollution behaviour of pastes
2 compared to the reference one: only in the case of FS, the paste shows a result comparable to the



593 reference one, whereas the photocatalytic efficiency decreases by 20% in the case of GNP and AC
 594 addition, and even 40% in the case of CH addition. This effect could be related to the colouration that
 595 the specimens acquire because of the presence of the fillers, since their black colour has darkened the
 596 paste (Fig. 14). Only the one manufactured with FS shows a colour similar to that of REF T (Fig. 14a
 597 and 14c). It is reported that the addition of pigments, that provide a significant coloration on finishing
 598 products, can induce a moderate decrease of the photocatalytic activity in terms of NO_x abatement
 599 [87,88]. This result was also reported in [83], where the use of activated carbon in place of natural
 600 sand in TiO₂-rich hydraulic lime based mortars resulted in a decrease of the photocatalytic efficiency
 601 of about 40%, because the reduced reflectance of radiation of the darkened substrate has lowered the
 602 photocatalytic properties of the mortar [89].

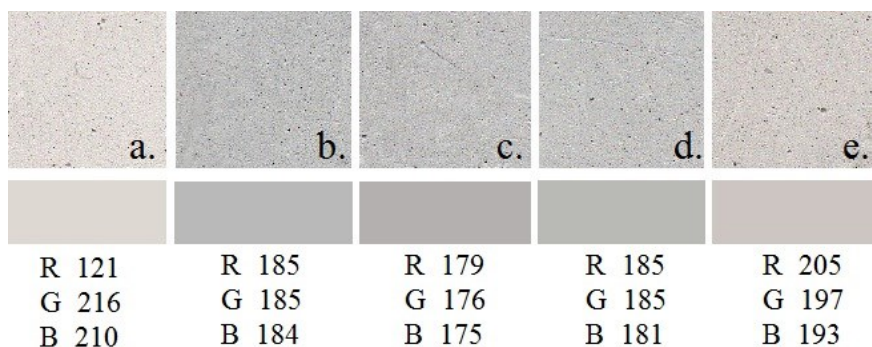
603



604

605 **Fig. 13.** Photocatalytic efficiency under UVA radiation of pastes (NO_x abatement) with TiO₂ addition.

606



7

608 **Fig. 14.** Scan images of the specimens' surface (up) and average RGB value measured in five different
609 points (down): a. REF T, b. GNP 0.50 T, c. AC 0.50 T, d. CH 0.50 T, e. FS 0.50 T.

610

611 3.4. Electromagnetic characterization

612 3.4.1. Electrical resistivity

613 The DC electrical resistivity (ρ) measurements conducted on the paste specimens at 7, 14, 21 and 28
614 days of curing are displayed in Fig. 15.

615 After the first week (Fig. 15a), the REF paste registers an electrical resistivity of 170 $\Omega\cdot\text{cm}$. All the
616 other pastes show similar ρ values ranging from 190 to 170 $\Omega\cdot\text{cm}$, unless that prepared with the FS
617 filler, which shows a higher electrical resistivity. Moving towards 0.25 to 0.50 and 1.00 percentages
618 of FS, the electrical resistivity decreases with values equal to 790, 360 and 210 $\Omega\cdot\text{cm}$, respectively.

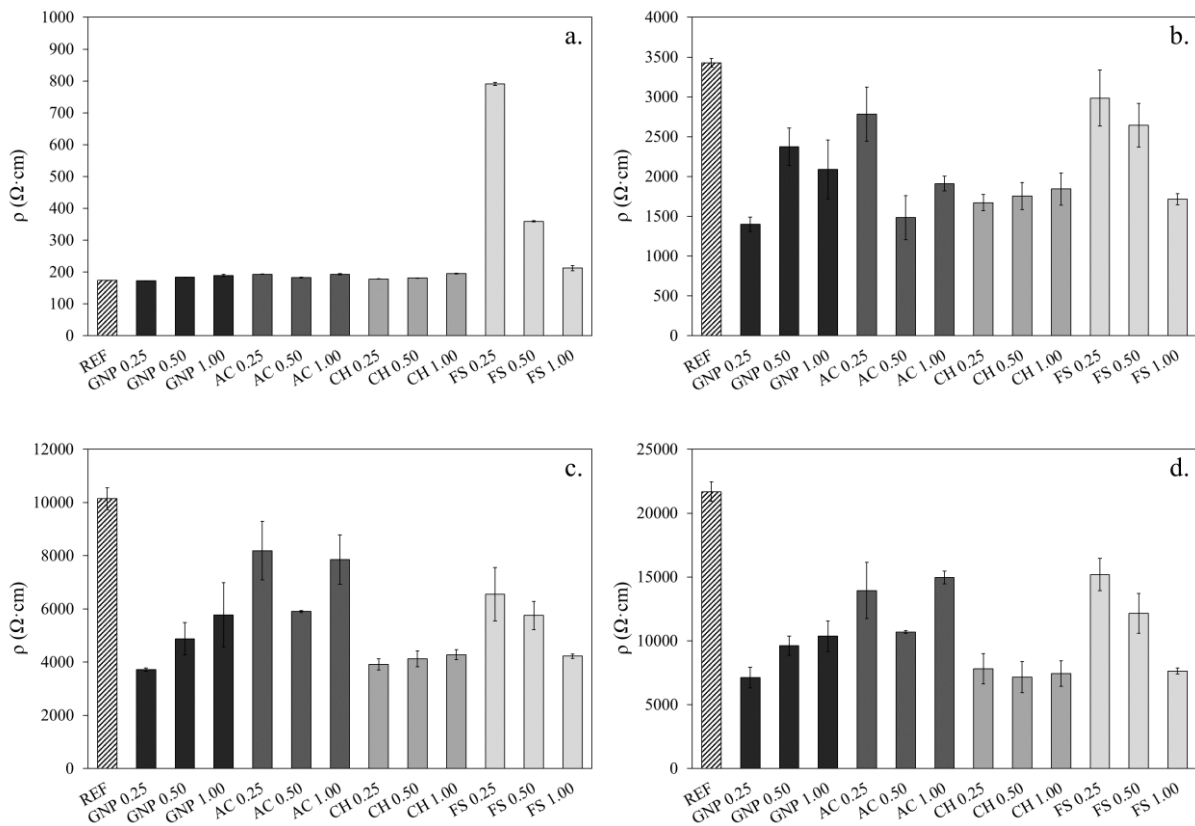
619 However, in these pastes the electrical resistivity decreases by increasing FS addition, as reported in
620 literature for GNP [2], carbon black [49,54], carbon coke [53] and graphite [14] additions.

621 After 14 days, the electrical resistivity of pastes increases of one order of magnitude (Fig. 15b). The
622 ρ measured in the REF paste is about 3400 $\Omega\cdot\text{cm}$, whereas all the other specimens with carbon-based
623 additions show a lower electrical resistivity. In general, a clear trend related to the different additions
624 of the same filler and electrical resistivity is not visible; in fact, only those with FS maintain the trend
625 observed at 7 days of curing.

626 After 21 days from casting (Fig. 15c), ρ values continue to increase, especially for REF paste,
627 achieving approximately 10000 $\Omega\cdot\text{cm}$. Also at this curing period, all pastes containing carbonaceous
628 fillers assume lower values of ρ than REF, even if those manufactured with GNP show an opposite
629 trend compared to that reported in literature since the higher the amount of the carbon-based fillers,
0 the higher the resistivity. This effect could be related to the agglomeration of GNP particles
1 [28,90,91], as observed in Fig. 7. It is reported that the decrease of electrical resistivity with the
2 increase of carbon-based fillers dosage is obtained only when the amount remains under the
3 percolation threshold and the particles are well dispersed or, above this value, a further decrease of



634 electrical resistivity occurs only if fillers segregate along the continuous conduction paths [92]. The
635 percolation threshold is the volume fraction above which the adjacent admixture units, whether fibres
636 or particles, touch the one to another forming a continuous conduction path [54]. For GNP, the
637 percolation threshold has been found to be between 10 and 15 wt.% by cement [2], much higher than
638 the amount of GNP used in the present paper. When AC is used, ρ shows a decrease from 0.25 to
639 0.50 wt.% AC addition and then ρ increases at 1.00 wt.% addition. It is possible that also for the AC
640 paste, the increase of ρ values is due to the agglomeration of particles which have discontinued the
641 available current paths. As for regards the waste carbon fillers, the electrical resistivity of CH
642 specimens, regardless the addition amount, is approximately 4000 $\Omega \cdot \text{cm}$ which is 60% lower than
643 REF, whereas FS specimens continue to maintain the same trend registered at previous ages.
644 After 28 days (Fig. 15d) the electrical resistivity increases again and, for REF paste it doubles the
645 value registered at 21 days reaching 22000 $\Omega \cdot \text{cm}$. For the specimens with carbonaceous additions,
646 the trend measured at 21 days is confirmed. In general, at 21 and 28 days of curing, the lowest ρ
647 values (approximately 65% lower than REF) are found for GNP 0.25, for all specimens manufactured
648 with CH, and for FS 1.00 paste.
649 The good electrical properties given by carbon-based addition are related to both their carbon content,
650 which is high especially for GNP and AC, and to their good dispersion within the matrix, as in the
651 case of waste CH and FS fillers.



653

654

655 **Fig. 15.** DC electrical resistivity (ρ) of pastes after: a. 7, b. 14, c. 21, d. 28 days of curing.

656

657 3.4.1. Electromagnetic shielding property

658 Generally, the electromagnetic shielding property increases with electrical conductivity. Since the
 659 lowest electrical resistivity values were found in pastes with waste carbonaceous fillers at the highest
 660 percentages (1.00 wt.%) and commercial fillers at 0.50 wt.%, the SE was determined only for these
 661 mixes. However, SE was measured not on pastes but on mortars (Table 5) since a perfect adhesion
 662 between the specimens and the mould used for the test shall be ensured and mortars shrink less than
 663 pastes.

664 The obtained results are given in Fig. 16. **It should be stressed that in literature, there is no paper**
 5 **considering the behaviour of carbonaceous additions on the SE of lime-based mortars.** In general, the
 6 SE of the present mortars is similar to that of cement-based mixes [33], as shown also by Samková
 7 et al. [93] who tested plasters manufactured with different binders and found that the SE of plain
 8 cement- and lime-based pastes was **comparable**. All mortars with carbonaceous additions register a

669 higher, or at least similar, SE compared to that of M REF; in particular, M GNP 0.50 mortar always
670 shows a SE 1 or 2 dB higher than the reference one. Only M AC 0.50 mortar shows a lower SE than
671 M REF at each investigated frequency value.

672 In order to analyse the obtained results in detail, Fig. 17 shows figures enlarged at 2 – 3 GHz, 4 – 5
673 GHz and 6 – 7 GHz, since in these frequency ranges the differences between mortars are more visible.

674 These frequencies are mostly familiar with wireless communication systems. Frequencies of 2.1 GHz
675 and 2.6 GHz are used for telecommunication mobile phones, Universal Mobile Telecommunications
676 System (UMTS) and fourth generation Long Term Evolution (4G-LTE), respectively. Moreover, 2.45

677 GHz for the Bluetooth standard, whereas 2.4 GHz and 5 GHz are used for wireless networks. The
678 frequency of 7 GHz is dedicated for point-to-point narrow band systems, as Plesiochronous Digital

679 Hierarchy/Synchronous Digital Hierarchy (PDH/SDH). In these frequency ranges, M GNP 0.50
680 increases SE of about 30% compared to M REF. Also the carbon-based waste fillers enhance the SE

681 at 2 – 3 GHz, 4 – 5 GHz and 6 – 7 GHz compared to the M REF mortar, even though the best
682 improvement is around 6% for M CH 1.00 mortar. These results confirm that the fillers giving the

683 lowest electrical resistivity to the pastes are also those giving the highest SE values. In general, the
684 high specific surface area, the high chemical stability and the high conductivity of graphene have

685 been reported to be the key parameters for its good EM wave absorption properties [94,95]. It has
686 been found that a low dosage of GNP equal to 0.1 wt.% is able to increase the electromagnetic wave

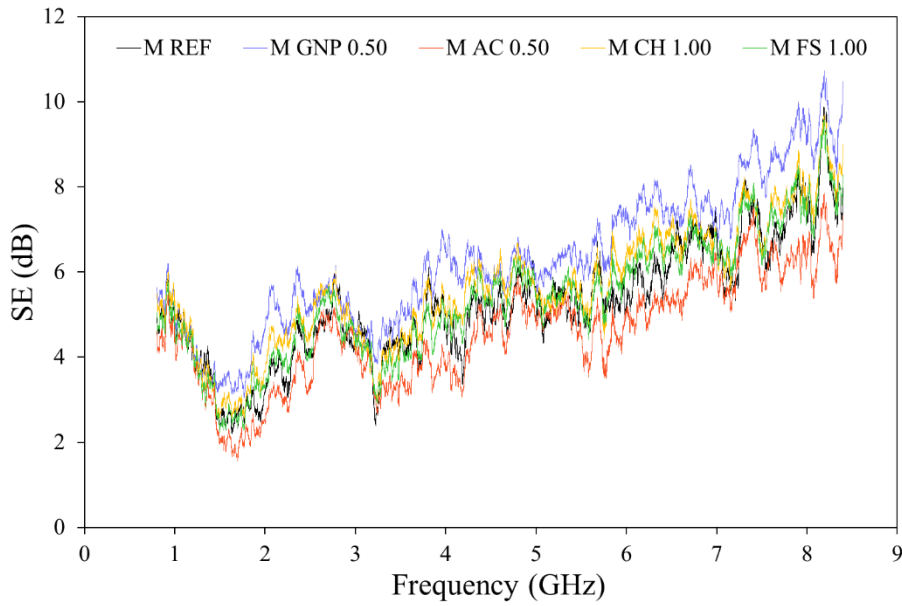
687 absorption of cement-based materials [94]. Therefore, even if GNP is surely the most effective filler
688 for enhancing the electromagnetic shielding properties of binder-based materials, in this study also

689 priceless waste carbonaceous fillers can improve this property [33]. The increased electromagnetic
690 SE of the mortar containing CH filler is due to its very good dispersion, which has formed a connected

1 and conductive network able to enhance the electrical conductivity of the material and to the enhanced
2 interfacial polarization of CH, as found by Mahmood et al. [96] who obtained the best SE by using

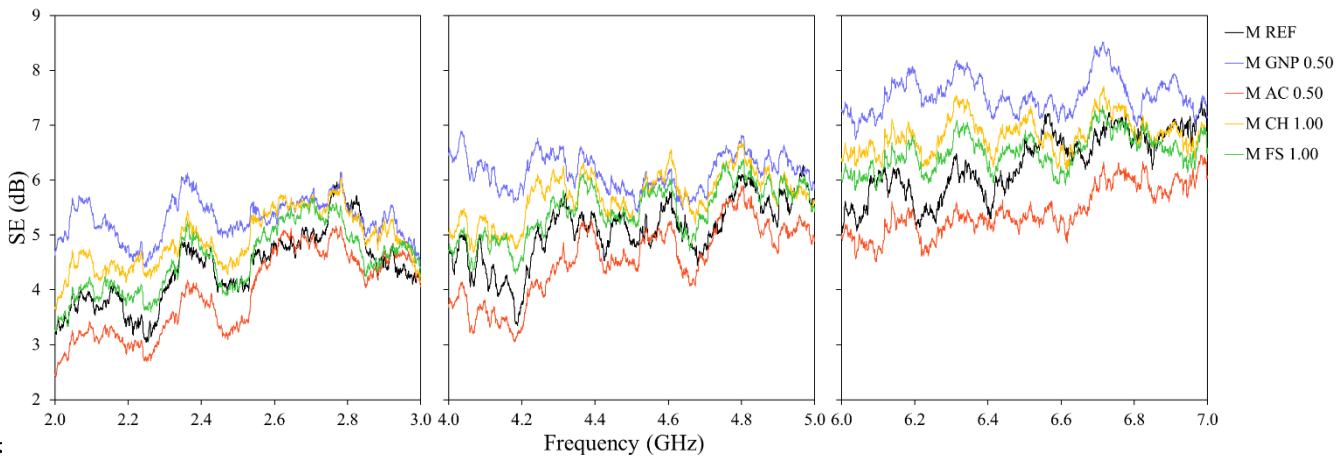
3 carbonized cotton stalk in mortars at 0.5 wt.% by cement.
4





695
696 **Fig. 16.** Shielding effectiveness (SE) of mortars after 21 days of curing.

697



698
699 **Fig. 17.** Shielding effectiveness (SE) of mortars after 21 days of curing in the ranges of frequencies
700 between 2 – 3, 4 – 5 and 6 – 7 GHz.

701

702 **4. Conclusions**

703 The use of commercial and waste carbon-based micro-fillers was investigated in order to improve the
704 mechanical, durability, depolluting, electrical and electromagnetic properties of hydraulic lime-based
705 pastes and mortars. As commercial fillers, graphene nanoplatelets (GNP) and powdered activated
706 carbon (AC) were used. As priceless wastes, a char (CH) obtained by the gasification process of

707 biomasses and the finest fraction of a used foundry sand (FS) were chosen. Fillers were added at 0.25,
708 0.50 and 1.00 % on lime weight.

709 The obtained results suggest the following conclusions:

- 710 • The addition of carbonaceous fillers, regardless of their nature and amount, is essential to
711 reduce the total porosity and the critical pore radius of pastes. The resulting “filler effect”
712 enhances the tensile strength of 40% and 20% when GNP and AC are added at 1.00 wt.% on
713 the lime, respectively. Particularly the compressive strength is increased for all the type of
714 additions, both commercial and waste up to 45%.
- 715 • The reduced porosity and the smaller critical pore radius lower the capillary water absorption
716 of pastes at each percentage and type of carbonaceous addition, both at short and long time
717 of contact with water. At early ages, the capillary water absorption is decreased more than
718 50% with GNP and FS.
- 719 • The depollution capacity of the pastes, in terms of MEK adsorption, enhances mostly by the
720 addition of AC at 1.00 wt.%. However, both the waste fillers, at all percentages, show very
721 good adsorption capacity, even equal to 50% when FS is added.
- 722 • No one of the carbonaceous fillers is effective to produce a photocatalytic activity to the
723 pastes when a photocatalytic agent is absent. Under UVA radiation and in the presence of
724 TiO₂, the carbonaceous fillers even decrease the photocatalytic behaviour because of the
725 darkening of the paste.
- 726 • Both the commercial and waste carbon-based fillers decrease the electrical resistivity of the
727 lime pastes; in particular, the use of CH decreases the electrical resistivity up to 65% as for
728 GNP at 0.25 wt.% and FS at 1.00 wt.%. This finding could be interesting for the development
9 of the so called “self-sensing” mortars/concretes.
- 0 • The highest EMI SE have been found for mortars containing GNP and CH; in particular, the
1 SE is enhanced by 6% in case of CH and even by 30% in case of GNP.



732 For the above-described results, it can be affirmed that addition of cheap waste carbon-based fillers,
733 such as gasification char and the finest fraction of a used foundry sand, can be a better alternative in
734 terms of cost/efficiency to more expensive and less sustainable commercial carbon based fillers, as
735 graphene nanoplatelets and activated carbon, to improve several properties of lime-based
736 pastes/mortars. In fact, the price of GNP is approximately 370 €/kg and the price of AC is around 260
737 €/kg, whereas CH and FS, being wastes, have no commercial value. In particular, in the present work
738 it has been found that waste carbonaceous fillers are able to increase the mechanical strength, the
739 durability in terms of capillary water absorption, the depolluting capacity in terms of VOCs
740 adsorption, the electrical conductivity and, even if slightly, the shielding effectiveness of lime-based
741 pastes/mortars that can be used for indoor renders and panels.

742

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748

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