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Sulphuric acid sensing by single-walled carbon nanotubes incorporated alkali activated materials

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Abstract

Concrete infrastructures are susceptible to corrosion in acidic environments; therefore, the constituent material should be engineered to sense the onset of ion penetration and propagation into the critical sites of the structure. Based on this concept, an intelligent alkali activated chemiresistor has been designed to sense the presence and concentration of sulphuric acid (H_2SO_4), considering the prerequisites of the structural health monitoring of durable cementitious structures. The proposed nanocomposite developed out of SWCNTs, fly ash, ground-granulated blast-furnace-slag (GGBS), and sodium silicate, is a built-in, low-powered, and ambience-operating structural element. H_2SO_4 was introduced on the surface of the highly alkaline, porous, and fractured sensor. The chemiresistor responses were distinguishable as the consequence of H_2SO_4 neutralization and speciation into sulphate (SO_4^{2-}) and hydrogen sulphate (HSO_4^-) species. This fundamental study can facilitate the future real-time aggressive ion interrogation potential of the SWCNT alkali activated nanocomposites in the construction industry.

Keywords

Chemiresistors; smart alkali activated nanocomposites; single-walled carbon nanotubes; conductive network; sensor microstructure; acid sensing; concrete corrosion.

39 **1. Introduction**

40 Sensors are intelligent functional materials with an aptitude to alter their normal
41 characteristics in response to any ambient or desired introduced stimulus in the form of energy
42 or matter. The outcome of those interactions should be a detectable signal. SWCNTs are one of
43 these emerging sensors, which exhibit a tuneable electronic structure to be factionalized by
44 elements, and a substantial surface area to be absorbed by stimulant substances. The sensing
45 character of pristine SWCNTs (p-type) is mainly governed by the ballistic charge transport of the
46 lattice holes located in the valence band of the carbons. Thus, an increase in the concentration of
47 the hole carriers upon analyte exposure yields a rise in the conductance of the network [1–6].
48 SWCNT-based sensors can operate at ambient temperatures, and they are adaptable to sense a
49 broad spectrum of analytes. Considering their mechanical and chemical resistance and resilience,
50 they are multifunctional devices. Modified SWCNT-based devices can detect hazardous
51 environmental contaminants on the scale of down to ultra-small in concentration (e.g., 0.010 ppt
52 in [7]) and up to ultra-high in resolution (e.g., 0.370%·ppb⁻¹ in [8]) [3,7–13]. Generally, the smart
53 nanostructure of these sensing devices assists them to be sufficiently miniaturised, stable,
54 sensitive and robust to be deployed for inspection and interrogation in operational sites with
55 human-restricted access.

56 There are many hazardous and contaminated operational sites in the structure sector of
57 the construction industry requiring real-time monitoring, namely, foundations, waste disposal
58 systems, and marine or offshore infrastructures. They are remote and surrounded by aggressive
59 acids, salts, and gases, causing severe damage to the structures, which are mainly constructed out
60 of concrete. Because of the exposure to destructive environments, concrete experiences a
61 deterioration of its constituent binder (cement) and loses functionality. The mentioned
62 degradations are associated with the term “concrete corrosion” [14–17].

63 Concrete corrosion originating from sulphates (SO_4^{2-}) is one of the most prevalent
64 concrete corrosion classes, since sulphates are naturally and abundantly available in the
65 surrounding media or within the constituent raw material. Sulphate deterioration can occur
66 because of chemical or biogenic reactions. In chemical corrosion, water influx into the concrete
67 pore system introduces external SO_4^{2-} ions or liberates SO_4^{2-} from internal sources, which both
68 result in the initiation of the material decomposition. However, in the biogenic class or “microbial
69 induced concrete corrosion” (MICC), a chain of biological reactions driven by the metabolism of
70 microorganisms produces gases and acids, particularly H_2SO_4 that eventually release SO_4^{2-}
71 anions. The synchronous abovementioned intrusions, including the exposure to extreme acidic
72 pH, lead to material destabilisation. Generally, corrosion is triggered by leaching of the
73 cementitious framework and precipitation of weak and expansive monosulphoaluminate ($3CaO \cdot$
74 $Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$), ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), and

75 thaumasite ($2CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$). The mechanism of sulphate corrosion and the
76 damage imposed by H_2SO_4 are discussed intensively in the scientific community [16,18–25].

77 Many measures have been put forward for the modification of the cement to be more
78 durable and resistant to corrosive conditions. Novel types of cements such as calcium aluminate
79 or calcium sulphoaluminate, adding cementitious supplementary materials, and incorporation of
80 heavy metals as antimicrobial agents are amongst the proposed solutions [16,17,26,27]. In
81 parallel, alkali activated materials, especially modified geopolymers, have demonstrated the
82 capability to withstand the chemicals and contaminants. The more stable geopolymeric
83 framework and the absence of reactive portlandite ($Ca(OH)_2$) delay the dissolution of the
84 microstructure and postpone the crystallisation of unfavourable aggregates [14,28,29].

85 Notwithstanding those countermeasures, monitoring should be done consistently and
86 precisely to retain the integrity of the structures over their planned life span, as explained initially,
87 by the sensors. Monitoring of concrete corrosion, hitherto, has been done by introducing external
88 commercial sensors, mostly expensive and complicated, to measure the influencing parameters
89 [30]. To achieve a higher degree of compatibility, certainty, and reliability, the sensors can be
90 fabricated from the same or similar substances as the construction materials. This possibility
91 results in a device, which may additionally be an integral load bearing and chemical resistant
92 element, i.e., a multifunctional built-in sensor. According to the previous arguments, alkali
93 activated materials have already displayed such features and recently applied for novel,
94 unconventional applications. A sodium-based fly ash geopolymer coating was introduced for
95 temperature and moisture sensing [31]. The developed sensor was additionally investigated for
96 chloride-induced concrete corrosion [32]. Similarly, an automated deposition of sodium-based
97 metakaolin geopolymers, 3D printed [33], and robot-sprayed [34], were used for temperature and
98 strain sensing. Potassium-based fly ash geopolymers were developed as a capacitor for electrical
99 energy storage and a piezoresistor for stress sensing [35]. Similar smart and multifunctional
100 performances comparably have been reported for cementitious materials [36–41].

101 These innovative multifunctional sensors are electrolytic conductors, dependent on the
102 pore solution content and charge balancing cations' degree of freedom for charge transport. To
103 convert alkali activated materials to electronic conductors, SWCNTs can be embedded into their
104 nano and microstructures. This involves the SWCNTs electronic network being fully generated
105 and tightly percolated. So far, this strategy is not precisely applied to the alkali activated materials.
106 However, an example of a similar approach can be the piezoresistivity study of reduced graphene
107 oxide geopolymeric nanocomposites assessed by electrical impedance spectroscopy (EIS). The
108 sodium-based fly ash geopolymer had an inherent ionic conductivity of $0.77 \text{ S}\cdot\text{m}^{-1}$ at 25 kHz and
109 the 0.35 wt.% reduced graphene oxide nanocomposite exhibited an ionic plus electronic
110 conductivity of $2.38 \text{ S}\cdot\text{m}^{-1}$ at 25 kHz. The nanocomposite accomplished tension and compression
111 gauge factors of approximately double the composite, 20.70 and 43.87, respectively [42]. In

112 another relevant research, graphene was used as an electrode for an ionic conductor film made of
113 sodium-based fly ash geopolymer for temperature and tensile strain sensing. The highest
114 temperature sensitivity and gauge factor of the sensor, with an ionic conductivity of $1.72\text{E-}2\text{ S}\cdot\text{m}^{-1}$
115 at 5 kHz, were $21.50\text{ k}\Omega\cdot\text{C}^{-1}$ and 358, respectively [43].

116 The abovementioned horizons about SWCNT electronic sensors and alkali activated
117 electrolytic sensors were the main reasons for initiating this research on the SWCNT alkali
118 activated chemiresistors. Herein, a smart sodium-based fly-ash-GGBS alkali activated
119 nanocomposite is introduced for $\text{H}_2\text{SO}_4/\text{H}_3\text{O}^+/\text{SO}_4^{2-}$ sensing regarding the sulphuric acid
120 induced corrosion of concrete. To-date-reported sensors were validated by strain, temperature,
121 moisture, and chloride ions, and a similar study of sulphuric acid sensing of SWCNTs embedded
122 in alkali activated material was not found in the literature. The sensor can distinguish between
123 the presence and concentration of sulphate anions and hydronium cations. It is a confined
124 structural element, i.e., a built-in sensor, without the need for special architecture and substrate.
125 Overall, the introduced sensor is comparatively multifunctional, sustainable, and discriminative,
126 offering an operation in a very simplified and low-powered modality. Herein, the sensor
127 fundamentals are elucidated and the conceptual design is presented. The nanostructure of the
128 percolated network of SWCNTs in the alkali activated matrix is depicted by HRTEM for the first
129 time. Furthermore, the nanocomposites' electrical properties, sensing behaviours, and
130 microstructure are comprehensively characterised.

131

132 **2. Materials and methods**

133 **2.1. Materials**

134 The one-part blended alkali activated nanocomposites were fabricated by mixing
135 nanofluids, and solid precursors and activator materials. The nanofluids were composed of
136 conductive nanomaterial (SWCNTs), dispersant (sodium dodecylbenzenesulfonate (SDBS)), and
137 ultrapure water as dispersion medium. SWCNTs, commercially known as TUBALL™, were
138 provided from OCSIAL Europe, Leudelange, Luxembourg, and technical grade SDBS ($\text{MW } 348.480$
139 $\text{g}\cdot\text{mol}^{-1}$) from Merck KGaA, Darmstadt, Germany. The ultrapure water (conductivity of 0.055
140 $\mu\text{S}\cdot\text{cm}^{-1}$) was supplied from a dispenser device (Stakpure GmbH, Niederahr, Germany). Precursors
141 were made of a combination of fly ash (Steament® H-4 FA) and ground granulated blast-furnace
142 slag (GGBS), supplied from Steag Power Minerals GmbH, Dinslaken, Germany and Opterra GmbH,
143 Leipzig, Germany, respectively. The activator was Sikalon® A (sodium disilicate powder) obtained
144 from Wöllner GmbH, Ludwigshafen, Germany, with a molar ratio ($\text{SiO}_2/\text{Na}_2\text{O}$) of ≈ 2.1 and water
145 content of $\approx 16\text{ wt.}\%$. The SWCNTs' specifications were elaborated in reference [44] and the
146 chemical and physical properties of the precursors in reference [45].

147

148 **2.2. Methods**

149 **2.2.1. Preparation**

150 **2.2.1.1. Nanofluids**

151 Nanofluids were prepared according to the previously published papers on the synthesis of CNT
152 alkali activated nanocomposites in the references [44,45]. In particular herein, the one-part
153 methodology from the reference [44] was adapted. The modifications are described in the
154 followings. SWCNTs were incorporated in the percentage of total nanocomposite oxides mass
155 (wt.% of precursors plus activator oxides). The nanofluids and accordingly nanocomposites were
156 fabricated with the SWCNT concentration of 0.100 wt.%, respecting the preliminary percolation
157 study results. The mass and composition of nanofluids and nanocomposites were maintained
158 constant in the total research.

159 The nanofluids were synthesised by dispersion of SWCNTs in SDBS [44,46,47] and
160 ultrapure water with a Sonopuls HD 2200 ultrasonic homogenizer (Bandelin Electronic GmbH &
161 Co. KG, Berlin, Germany) using a KE 76 probe. The ultrasonication was carried out for a total of
162 600 seconds per sample, applying a 50% cycle with 70% amplitude in a stepwise order,
163 considering a total of 48 hrs intervening rest. Therefore, SWCNT, SDBS, and water were added
164 into a glass vial and kept isolated in a fridge with a temperature of 1°C for 24 hrs. Afterwards, in-
165 rest nanofluid was sonicated for 300 s and returned to the fridge for another 24 hrs. Finally, the
166 second round of ultrasonication (300 s) was carried out, and the nanofluid was immediately
167 shear-mixed with the solids. Therefore, SWCNTs obtained enough time to interact with SDBS, and
168 be more efficiently individualised by the ultrasonication and shear mixer probe energies. The
169 shear mixing of nanofluids and solid components was conducted for 600 s at 1000 rpm.

170

171 **2.2.1.2. Nanocomposites**

172 The nanocomposites were fabricated by casting shear-mixed nanofluids and solid components
173 according to the reference [44] and cured in ambient environment conditions for 7 days and 28
174 days. The scheme of the synthesis process of the nanocomposites can be seen in the reference
175 [44]. Before characterisation, the nanocomposites were heat treated for 24 hrs at 105°C in a
176 Heraeus LUT 6050 drying oven (Kendro Laboratory Products GmbH, Langenselbold, Germany) to
177 eliminate any potential residual entrapped water in the pore system of the nanocomposites.
178 Regarding the results obtained in preliminary percolation study, the SWCNT alkali activated
179 nanocomposites were percolated with the incorporation of 0.100 wt.% of SWCNTs, i.e., the
180 SWCNTs' conductive network has been generated. Therefore, SWCNTs concentration of 0.100
181 wt.%, is considered for the chemiresistors fabrications and analysis in this research. The
182 fabricated 7 and 28 days chemiresistors with 0.100 wt.% SWCNT incorporation accomplished
183 rather similar mechanical performance because of the ambient curing methodology. The
184 compressive and flexural strengths were 40 ± 2.48 MPa and 7 ± 0.21 MPa, respectively, measured

185 by Zwick 1445 universal testing system, ZwickRoell GmbH & Co. KG, Ulm, Germany.

186
187

188 **2.2.1.3. Analytes**

189 Sulphuric acid solutions in different concentrations and ultrapure water were utilised for
190 the sensing experiments. The sulphuric acid stock solution (98% ACS reagent from Merck KGaA,
191 Darmstadt, Germany) was diluted to reach the required concentration (calculated pH), $1.00\text{E-}05$
192 $\text{mol}\cdot\text{L}^{-1}$ (4.70), $1.00\text{E-}03$ $\text{mol}\cdot\text{L}^{-1}$ (2.73), $1.00\text{E-}01$ $\text{mol}\cdot\text{L}^{-1}$ (0.97), and $1.00\text{E+}00$ $\text{mol}\cdot\text{L}^{-1}$ (0.00). The
193 SI unit of concentration “ $\text{mol}\cdot\text{L}^{-1}$ ” will be shown in a simple form of “M” in the rest of the
194 manuscript. The specifications of sulphuric acid dilutions can be seen in Table 3 in the pH
195 influence section. The pH of dilutions after preparation were measured by a VWR pH phenomenal®
196 pH 1100 L showing a $\leq 5\%$ difference between calculated and measured values after equilibrium.
197 For the sensing characterizations, $30\ \mu\text{L}\cdot(180\ \text{s})^{-1}$ of the analyte was directly dropped on the
198 marked centre-point of the back surface of specimens. The analyte was dropped by an Eppendorf
199 Research adjustable volume pipette (10-100 μL) and the tip was renewed for each upcoming
200 cycle.

201

202 **2.2.2. Characterisations**

203 **2.2.2.1. Sensing and discriminating acquisition**

204 The measurements were conducted by a laboratory-scale programmed sensing setup
205 (Figure 1) according to the routine measurement procedures of the CNT-based sensing devices
206 [8,13,48–51]. A KEYSIGHT B2912A Precision Source/Measure Unit (SMU) applied a 100 mV DC
207 potential on the sensor electrodes (silver-coated parts of the nanocomposites) and accordingly
208 captured the generated current. A Raspberry Pi computer board recorded the current at a
209 frequency of 1 Hz and conveyed the data to a time-series database (InfluxDB) for visualization and
210 further processing (Grafana). The received data in the form of the resistance, R , were converted
211 to the resistivity/conductivity by applying the sensor geometry and normalized by means of
212 relative resistance in percentage, i.e., $100 \cdot ((R_1 - R_0) \cdot R_0^{-1})$, for the sensing analyses. The prism
213 sensor and sensing geometries were $60 \times 10 \times 10\ \text{mm}^3$, and $40 \times 10 \times 10\ \text{mm}^3$, respectively. This
214 means, all surfaces at both ends of the prism were covered by silver paint in a 10 mm length across
215 the edges to yield built-in electrodes. To calculate the standard error for each point of the data
216 (shown by grey highlights around the sensing curves), the measurements were repeated on three
217 pieces of newly-produced set of individual specimens.

218

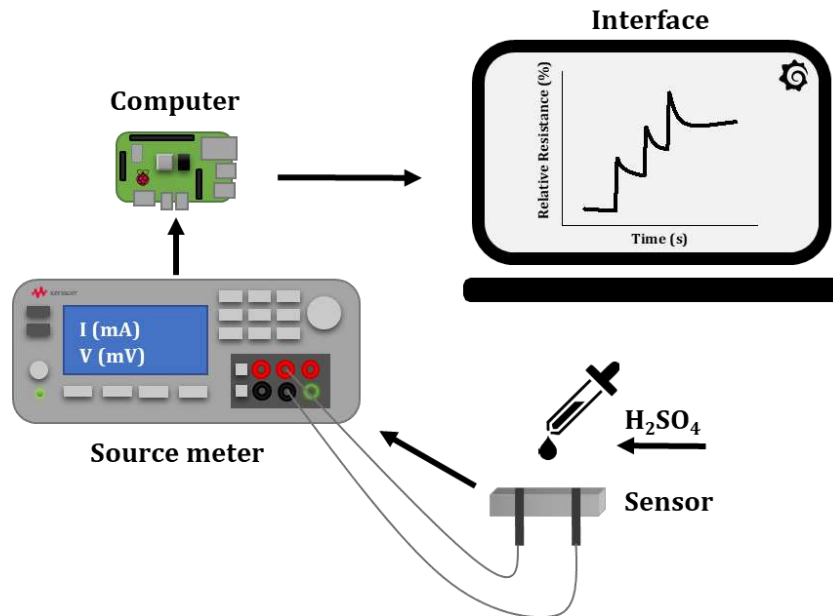


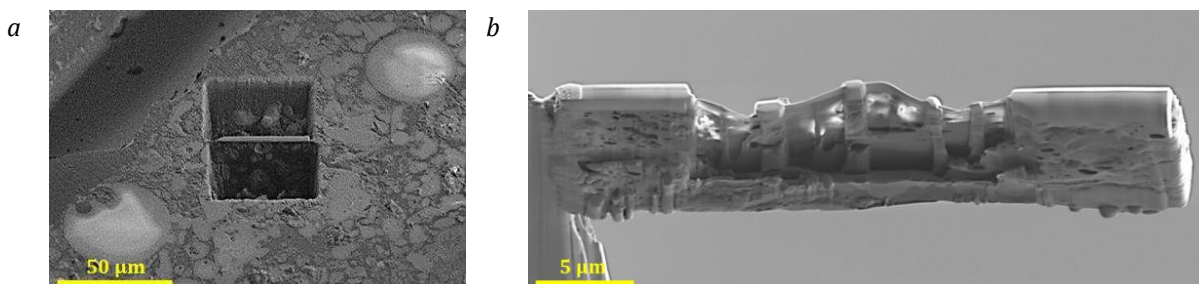
Figure 1. The laboratory-scale programmed sensing setup.

219
220
221

2.2.2.2. Transmission electron microscopy (TEM)

In order to visualize the network of individual SWCNTs within the blended alkali activated nanocomposite matrix, high-resolution transmission electron microscopy (HRTEM) was performed on an FEI Tecnai F30 (ThermoFisher Scientific company). This instrument was operated at a 300 kV acceleration voltage, providing a point resolution of 0.19 nm. Since HRTEM requires electron-transparent specimens with thicknesses of a few tens of nanometre, a TEM lamella was prepared by Focussed ion beam (FIB) using an FEI Helios 5 CX, ThermoFisher Scientific company. To this end, a cleaved piece of specimen was embedded in a mixture of G1 epoxy resin and carbon nanoparticles, to improve the material ductility and conductivity for FIB cuttings. The reinforced specimen was kept in vacuum condition for 24 hrs. Subsequently, the specimen was mounted on a stub, and ground by diamond foil and tripod polisher to a thickness of $\approx 1 \mu\text{m}$. The sample was cleaned several times in an ultrasonic bath between these steps. The entire process was repeated several times until all surfaces and pores of the nanocomposite were infiltrated by the epoxy resin. Next, some layers of platinum were deposited on the specimen to protect the surface from beam damage during cutting a cross-section using the FIB. In the final stage, a lamella was cut by the FIB and fixed on a Mo TEM omniprobe lift-out grid (Figure 2).

238



239 Figure 2. The TEM specimen prepared by epoxy embedding and FIB cutting; a- SEM image of platinum

covered cross-section; b- SEM image of the TEM-lamella.

240
241

242 **2.2.2.3. Scanning electron microscopy (SEM)**

243 SEM was performed by a GeminiSEM 500 (Carl Zeiss QEC GmbH, Jena, Germany) in a high
244 vacuum condition ($\approx 10^{-5}$ mbar) and at a landing energy (also EHT) of 3.00 kV on the surface and
245 ruptured cross-sections of the specimens. The specimens were kept in vacuum condition 24 hrs
246 before the microscopy without doing any additional treatment.

247

248 **2.2.2.4. Fourier-transform infrared spectroscopy (FTIR)**

249 FTIR was done by a Bruker FTIR spectrometer Vertex 80v (Bruker Optics GmbH & Co. KG,
250 Germany) with a Global radiation source, KBr beam splitter, and DTGS detector. The
251 measurement resolution was 4 cm^{-1} from 400 to 4000 cm^{-1} at the ambient laboratory conditions.
252 The samples were prepared by the KBr pellet method. The KBr powder (200 mg) was mixed with
253 the nanocomposite powder (10 mg) and pressed for 120 s at 7 tonnes by using a hydraulic press.
254 The nanocomposite powder was obtained by scraping the sulphuric acid exposed ($1.00\text{E-}01\text{ M}$)
255 and the non-exposed surface of the specimens with a scalpel.

256

257 **2.2.2.5. Mercury intrusion porosimetry (MIP) and roughness measurements**

258 The porosity of the nanocomposites was measured by Porotec mercury intrusion
259 porosimeters, Pascal 140, and Pascal 440 to obtain broad span spectra. The measurements were
260 conducted on cubes of the nanocomposites with a ≈ 10 mm edge. Roughness, scan resolution of
261 $0.\overline{33}\text{ }\mu\text{m}$, was evaluated by a Bruker stylus profilometer, Dektak XTL™ on the untreated full-size
262 samples.

263

264 **2.2.2.6. pH measurements**

265 As mentioned in section 2.2.1.3. Analyte, pH values were measured by a VWR
266 pHenomenal® pH 1100 L. Before any pH recording, the probe was washed with ultrapure water
267 and calibrated afterwards. For the simulation of the pH variation of sulphuric acid solutions after
268 contact with the nanocomposite, 6 mL of $1.00\text{E-}01\text{ M}$ (pH 0.97) sulphuric acid was diluted with 9
269 mL of ultrapure water, hence reaching a hydronium concentration of $5.45\text{E-}02\text{ M}$ and pH of 1.21.
270 Subsequently, a piece of nanocomposite (ca. 7850 mg) was broken into coarse-grained particles
271 and added to the sulphuric acid diluted solution.

272

273 **3. Results and discussion**

274 **3.1. Electrical properties**

275 The measured resistance of percolated alkali activated nanocomposites with
276 incorporation of 0.100 wt. % of SWCNT are approximately $90\text{ }\Omega$ and $70\text{ }\Omega$ respectively for 7-day

277 and 28-day nanocomposites. These magnitudes of electrical resistance, considering the geometry
 278 of nanocomposites ($60 \times 10 \times 10 \text{ mm}^3$), grant the 7-day and 28-day nanocomposites a resistivity of
 279 $0.22 \Omega \cdot \text{m}$ and $0.18 \Omega \cdot \text{m}$, and correspondingly a conductivity of $4.80 \text{ S} \cdot \text{m}^{-1}$ and $6.02 \text{ S} \cdot \text{m}^{-1}$ (Table 1).
 280 Table 1 shows the electrical properties of nanocomposites are age-dependent and vary over the
 281 curing period. The higher conductivity of 28-day nanocomposites (approximately 25% higher)
 282 can be attributed to a more developed nano-framework of the matrix causing SWCNTs to generate
 283 a rigid and compressed conductive network. The observed trend, furthermore, is consolidated
 284 with another study of SWCNT incorporation (the same nano-additive product from OCSIAL) in the
 285 cementitious nanocomposites [52]. Compared to the similar alkali activated nanocomposites,
 286 lower magnitudes of conductivity were reported for those incorporating higher quantities of CNT.
 287 Selected examples are summarized in Table 2, for comparison. The applied CNT nano-electrical
 288 structures (chirality) and the status of CNTs' dispersion and distribution have the most significant
 289 effects on the reported differences in the nanocomposites' electrical properties. In addition,
 290 operational parameters such as fabrication and curing methodologies might be influential,
 291 however to a lower degree.

292

293 *Table 1. Electrical properties of SWCNT alkali activated nanocomposites (specimen geometry: $60 \times 10 \times 10$*
 294 *mm^3 ; SWCNT conc. 0.100 wt.%).*

Property	Symbol	Unit	7-day	28-day
Resistance	R	Ω	88.33 ± 6.17	70.32 ± 4.23
Resistivity	ρ	$\Omega \cdot \text{m}$	0.22 ± 0.02	0.18 ± 0.01
Conductivity	$\kappa (\sigma)$	$\text{S} \cdot \text{m}^{-1}$	4.83 ± 0.32	6.02 ± 0.39

295

296 *Table 2. Reported conductivities of alkali activated nanocomposites.*

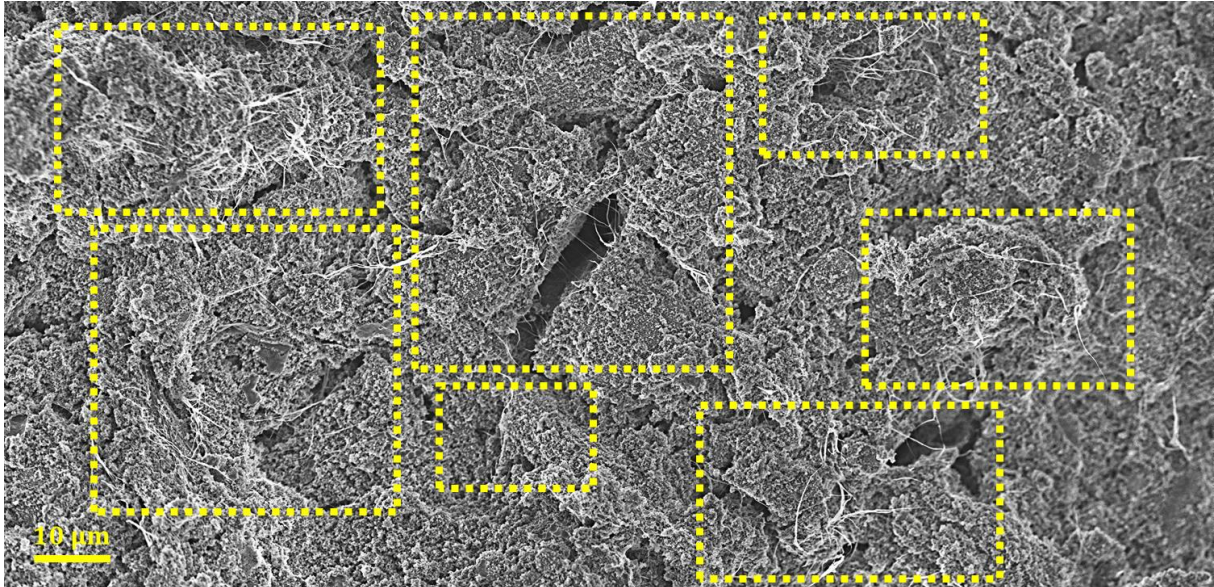
Reference	Matrix material	Conductive additive	Concentration (wt. %)	Conductivity ($\text{S} \cdot \text{m}^{-1}$)	Ref conductivity ($\text{S} \cdot \text{m}^{-1}$)
[53]	Clay	SWCNT	0.20	1.90E-03	9.80E-04
[54]	Slag	MWCNT	2.50	45E-03	15E-03
[55]	Fly ash	MWCNT	1.00	3.00	1.50

297

298 3.2. Morphology of the SWCNTs' network

299 The spatial distribution of SWCNTs in the matrix microstructure is displayed in Figure 3
 300 and the areas with the high content of SWCNTs are indicated by the yellow dashed boxes. The
 301 modified ultrasonication and shear mixing could detangle SWCNTs' bundles to a much higher
 302 degree compared to the previous practices of CNT incorporations into the identical two-part and
 303 one-part alkali activated matrices [44,45]. This inner-matrix distribution of SWCNTs was the
 304 prerequisite for nanocomposites percolated character and obtained conductivities in Table 1.
 305 Considering the bulk mass of the nanocomposites, a significant localization or segregation of CNTs

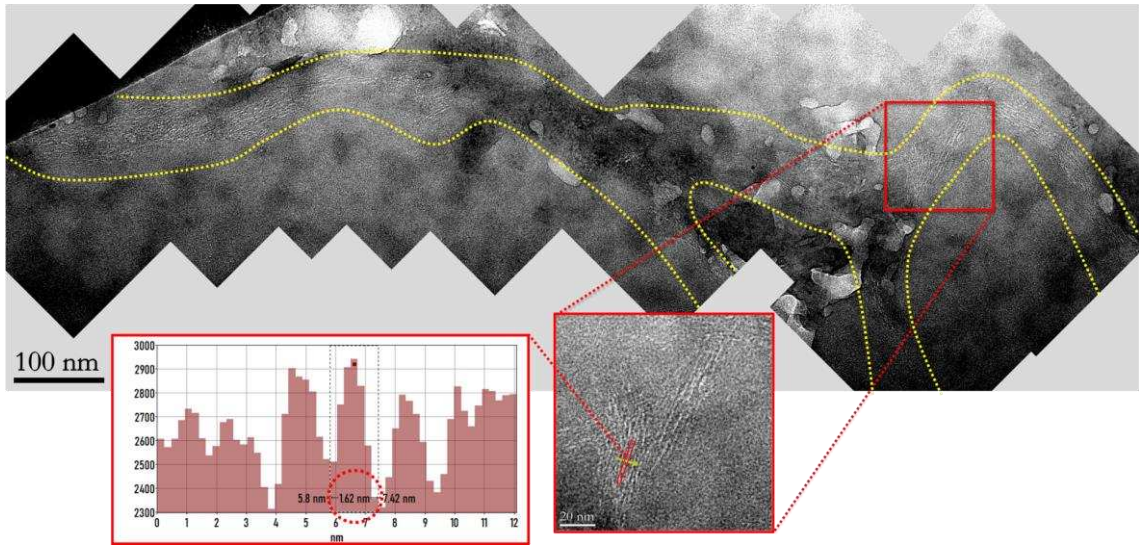
306 is not observed, and SWCNTs have a random and stochastic fractal distribution pattern through
307 all the entire mass of the alkali activated material, highlighted by the yellow dashed boxes in
308 Figure 3. The localized or segregated networks are mostly common in polymeric nanocomposites,
309 where CNTs are distributed in one phase of the blend or at the interface of copolymers [56].
310



311
312 *Figure 3. The spatial morphology and distribution of SWCNTs (conc. 0.100 wt.%) in the intentionally*
313 *fractured inner-matrix cross-section.*
314

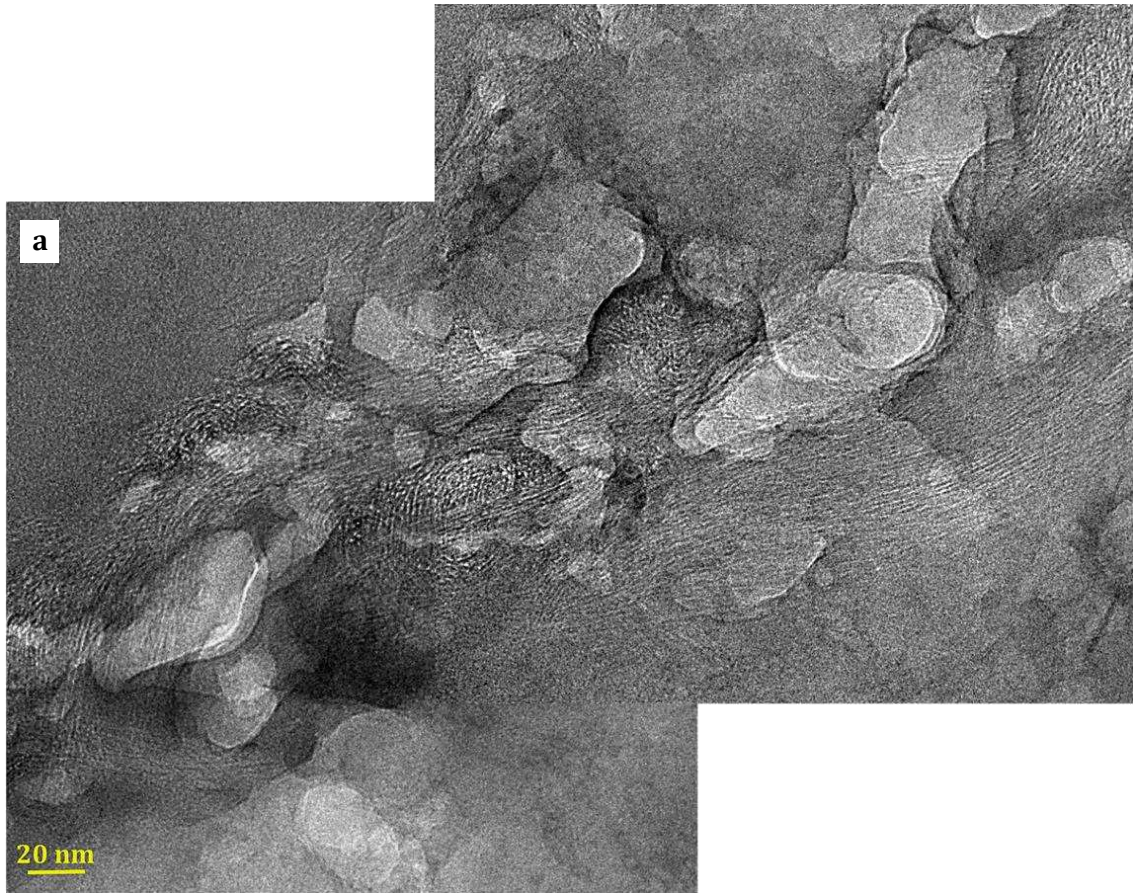
315 The percolated conductive network of embedded SWCNTs in the alkali activated matrix is
316 imaged with the atomic-scale HRTEM and depicted in Figure 4. The observed parallel patterns
317 with approximately 16 Å spacing are the SWCNTs' nanostructures (adjacent tubes/shells). The
318 well-distributed SWCNTs (shown in Figure 3) have established a dense interconnected grid made
319 of thick agglomerations spreading in all directions of the matrix. This state of SWCNTs' connection
320 is attributed to the percolated conductive network, which is highlighted in Figure 4 by the yellow
321 dashed continuous pathways. These continuous distributions and pathways of SWCNTs in the
322 matrix nanostructure are the main reasons of observed nanocomposites' low resistivity or high
323 conductivity.

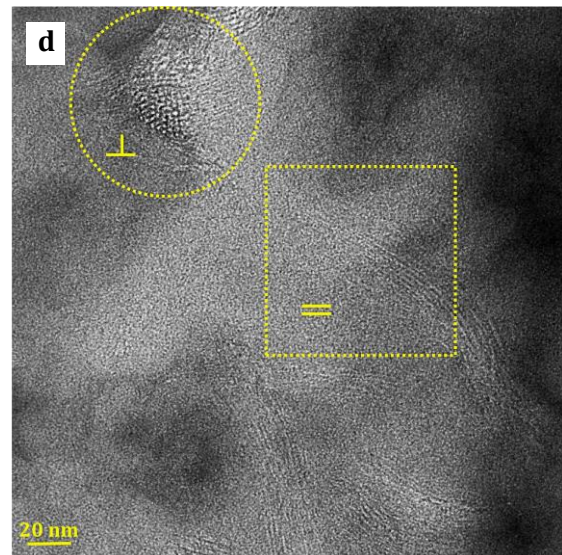
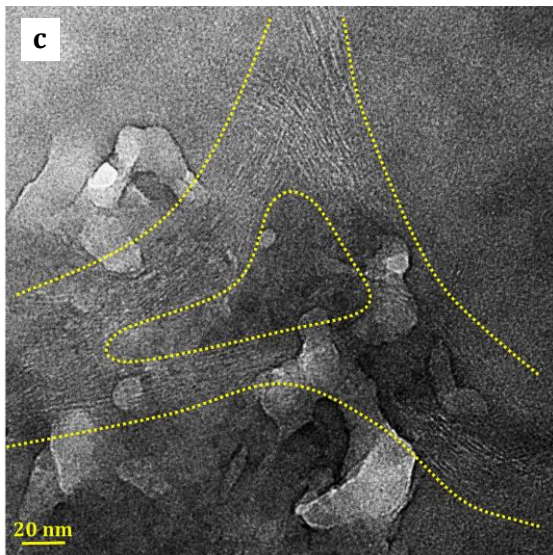
324 Such SWCNTs' intra-network configurations and layouts are shown with more detail in
325 Figure 5. According to these HRTEM micrographs, SWCNTs-nanostructures are constituted out of
326 at least ≈10 individual shells, which construct many alignments and conjunctions as depicted in
327 Figure 5 a, and magnified in Figure 5 b. These dense nanostructures are composed of SWCNTs'
328 crosslines (yellow dashed pathways in Figure 5 c), or perpendicular and horizontal orientations
329 of SWCNTs (yellow dashed circle and box in Figure 5 d).



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332
333

Figure 4. HRTEM image of SWCNTs' conductive network topology, embedded in the alkali activated matrix (SWCNT conc. 0.100 wt.%).





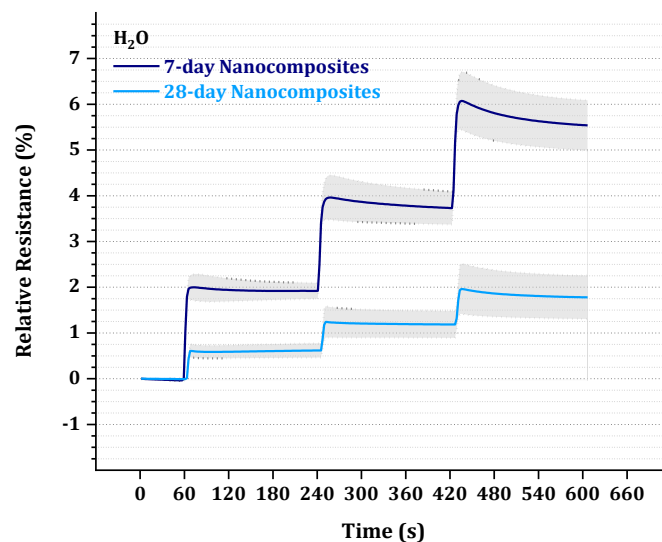
334 *Figure 5. HRTEM images of SWCNTs' intra-network alignments throughout the alkali activated matrix*
 335 *(SWCNT conc. 0.100 wt.%); a- SWCNTs' alignments and conjunctions; b- higher-resolution image of the*
 336 *centre of a; c- SWCNTs' cross lines; d- SWCNTs' perpendicular vs. horizontal orientations.*
 337

338 3.3. Sensing properties

339 3.3.1. Exposure to ultrapure water

340 The signal configuration of nanocomposites upon exposure to the ultrapure water is
 341 displayed in Figure 6. The start of each cycle, water introduction, is distinguished by an abrupt
 342 increase in the relative resistance. The first cycle is from 60 s to 240 s, the second from 240 s to
 343 480 s and the third from 480 s to 600 s, i.e., every 180 s. The 7-day sensors exhibit three times
 344 greater magnitudes of relative resistance compared to the 28 days. The maximum change of
 345 relative resistance is around 6% for 7-day nanocomposites, and 2% for 28-day nanocomposites.
 346 It is not expected SWCNTs' network to be recovered to the initial state in the short-term, i.e., the
 347 resistance of the sensor does not switch back to the original point within the investigation period.
 348 There are studies, which reported similar phenomena in sensing behaviour of the CNT-based

349 sensor devices, both pristine and doped [48,50,57–60]. Herein, it can be ascribed to the fact that
 350 in each cycle, the water is penetrating into the pore network and fracture system of the matrix
 351 and diffusing deeper with the onset of the next cycle, not evaporating off. Therefore, more
 352 SWCNTs will be involved in the sensing and the resistance will continue to increase. In addition
 353 to the direct interaction of water-species and the SWCNT network, the introduction of water may
 354 cause the connected tubes of adjacent CNTs to separate and relocate in the tunnelling gap or even
 355 beyond. As a consequence, the contact resistance of CNTs rose dramatically [6]. Furthermore, the
 356 water exposure may result in the leaching and mobilization of matrix alkaline cations, which were
 357 pre-suppressed by the drying process. These may additionally influence the SWCNTs' network
 358 and sensor resistance. However, this cannot yet be clarified completely in this work and will be
 359 part of a future study.



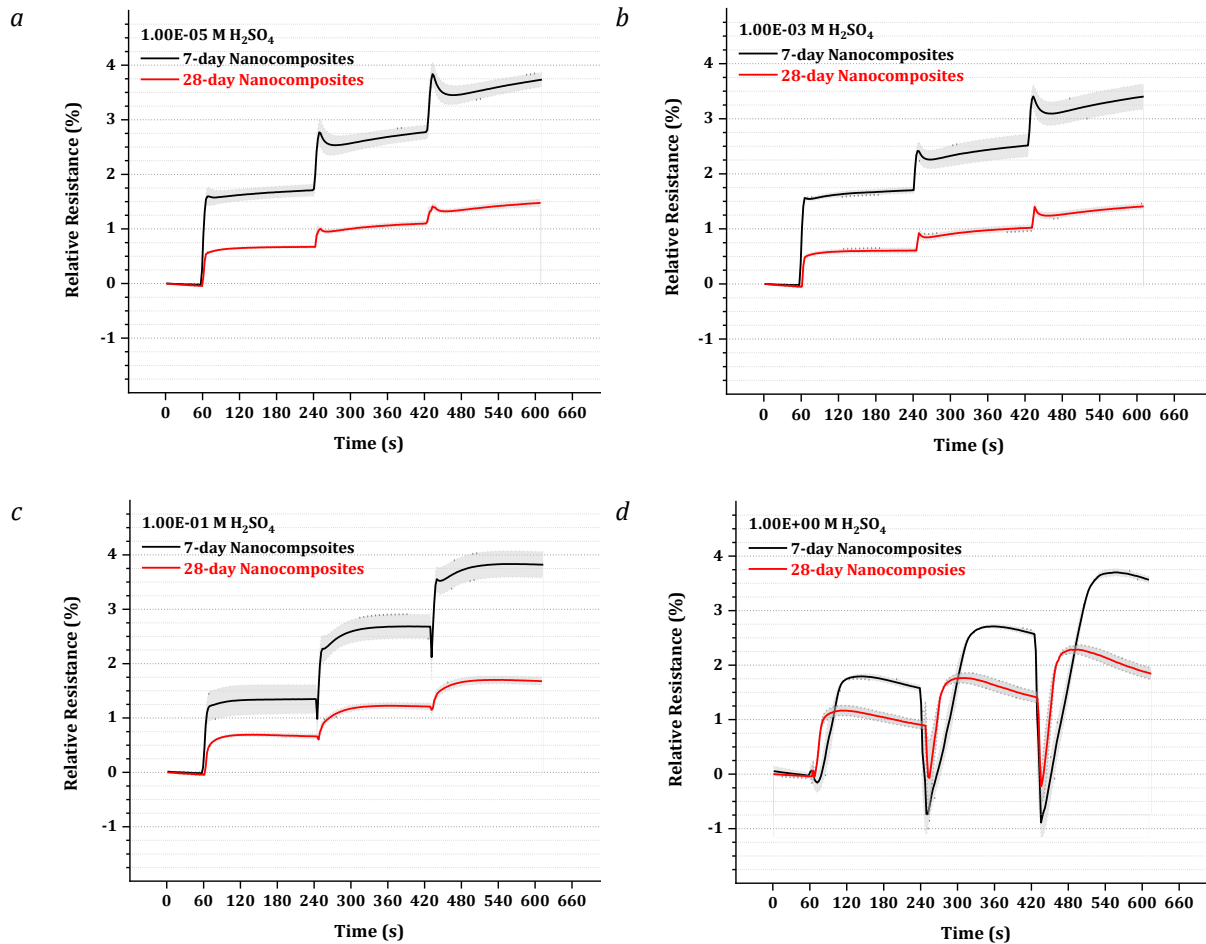
360
 361 *Figure 6. Sensing response of SWCNT alkali activated chemiresistors (SWCNT conc. 0.100 wt.%) after cyclic*
 362 *exposure to ultrapure water.*
 363

364 3.3.2. Exposure to sulphuric acid

365 The signal configurations with the variation of sulphuric acid concentration are shown in Figure
 366 7. The sensing behaviours of the sensors by the introduction of H_2SO_4 are very different compared
 367 to the ultrapure water exposure (Figure 6). The first distinct observation is the differentiation in
 368 the shape and appearance of signals, not only in comparison to water but also in comparison to
 369 each concentration of H_2SO_4 . This nonconformity puts a distinguishing boundary between high
 370 and low concentration regimes of sulphuric acid, in addition to the presence and absence of the
 371 sulphuric acid species, i.e., HSO_4^- & SO_4^{2-} , in comparison to the ultrapure water.

372 At the low H_2SO_4 concentration exposures, $1.00E-05$ M & $1.00E-03$ M, there is an almost
 373 perpendicular rise of the sensor relative resistance immediately after exposure, at the beginning
 374 of each cycle (Figure 7 a & b). This fact is valid just for the first cycle of high concentration regimes
 375 of H_2SO_4 ($1.00E-01$ M & $1.00E+00$ M). From the second cycle, there is an initial steep reduction of
 376 the measured signals, which is accompanied by a signal rise (Figure 7 c & d). This behaviour of the

377 sensor is very significant in $1.00\text{E}+00$ M H_2SO_4 , where the amplitude of oscillations reaches
 378 approximately 5% in the last cycle (relative resistance alteration between -1% and 4%) in 7-day
 379 nanocomposites and circa 2.50% in 28-day nanocomposites (Figure 7 c & d).
 380



381 *Figure 7. Sensing response of SWCNT alkali activated chemiresistors (SWCNT Conc. 0.100 wt.%) after cyclic*
 382 *exposure to different concentrations of sulphuric acid; a- H_2SO_4 conc. $1.00\text{E}-05$ M (pH 4.70); b- H_2SO_4 conc.*
 383 *$1.00\text{E}-03$ M (pH 2.73); c- H_2SO_4 conc. $1.00\text{E}-01$ M (pH 0.97); d- H_2SO_4 conc. $1.00\text{E}+00$ M (pH 0.00).*
 384

385 In an overall view, 7-day sensors demonstrate higher relative resistance values, as seen
 386 before in water exposure. The reasons will be elucidated in the successive section (3.4.
 387 Microstructure dependency). The maximum observed values of relative resistance in 28-day
 388 nanocomposites are $\approx 1.50\%$ for H_2SO_4 low concentration regimes ($1.00\text{E}-05$ M & $1.00\text{E}-03$ M),
 389 $>1.50\%$ for $1.00\text{E}-01$ M H_2SO_4 , and $>2\%$ for $1.00\text{E}+00$ M H_2SO_4 . The trend for 7-day sensors
 390 reaches a magnitude of around 3.50% for all H_2SO_4 concentrations. Moreover, recovery sections
 391 in the comparison of low and high concentration regimes of H_2SO_4 represent disparate and
 392 complex trends (Figure 7).

393 3.3.2.1. pH influence

394 Sulphuric acid in aqueous solutions dissociates into hydrogen sulphate (HSO_4^-), sulphate
 395 (SO_4^{2-}), and hydronium (H_3O^+) species (Equation 1 & Equation 2), which are highly

396 pH/concentration dependent interactions. Based on that, investigated sulphuric acid solutions
 397 with the pre-determined concentrations and pH are composed of different concentrations of
 398 HSO_4^- and SO_4^{2-} , provided in Table 3. Therefore, in H_2SO_4 low concentration regimes (1.00E-05
 399 M & 1.00E-03 M) the dominant species is SO_4^{2-} , while in H_2SO_4 high concentration regimes (1.00E-
 400 01 M & 1.00E+00 M), HSO_4^- is the prevalent species [61].



401

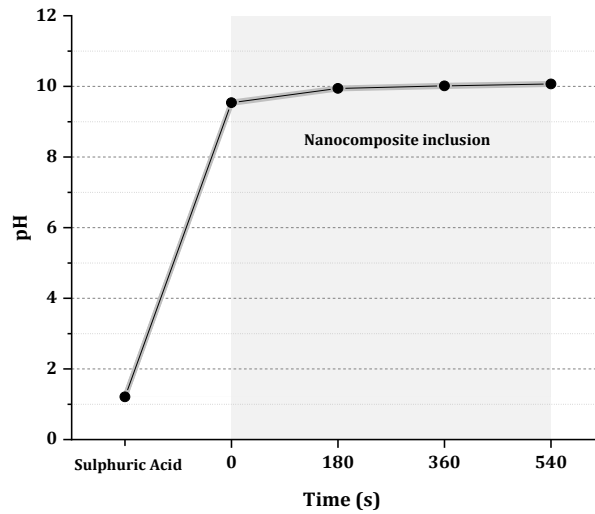
402 Table 3. Speciation of investigated concentrations of sulphuric acid (from the results in the reference [61]).

Concentration (M)	pH	HSO_4^- (%)	SO_4^{2-} (%)
1.00E-05	4.70	0	100
1.00E-03	2.73	10	90
1.00E-01	0.97	75	25
1.00E+00	0.00	80	20

403 As mentioned above, sensors showed very distinct responses based on the concentration
 404 of introduced sulphuric acid (Figure 7). The upward trends at the beginning of each cycle can be
 405 attributed to the interaction of H_3O^+ with SWCNTs. It might be possible that H_3O^+ cations can
 406 penetrate much faster into the pores and diffuse with accelerated kinetics in the internal cracks
 407 of the matrix than HSO_4^- and SO_4^{2-} . This penetration may additionally facilitate the intake of HSO_4^-
 408 and SO_4^{2-} anions in the upcoming cycles. Regarding H_2SO_4 in low concentration regimes (Figure
 409 7 a & b), from the second cycle, SO_4^{2-} additionally penetrates and diffuses into the pores and
 410 cracks. SWCNTs transmit the same sensing signal for both H_3O^+ and SO_4^{2-} , i.e., an ascent in sensor
 411 resistance leading to an increase of relative resistance. However, in H_2SO_4 high concentration
 412 regimes (Figure 7 c & d), SWCNTs exhibit a reduction of resistance, which can be interpreted as a
 413 steep descent of relative resistance due to the HSO_4^- contact. This can be obviously seen at the
 414 beginning of the second and third cycles. This behaviour can be ascribed to the acid-base reactions
 415 of the HSO_4^- anions and the alkaline matrix of the nanocomposites, eventually yielding the SO_4^{2-}
 416 species (Equation 1 & Equation 2). Thereafter, with the increase of sulphate concentration, the
 417 upward trend of relative resistance again appears.

418 The pH variation resulting from the interaction of HSO_4^- and the alkali activated matrix is
 419 demonstrated in Figure 8. For these measurements, coarse-grained particles of alkaline
 420 nanocomposite were added to a sulphuric acid solution with concentration of 5.45E-02 M and pH
 421 of 1.21. Hence, in this solution, 70% of the species are HSO_4^- and the remaining 30% are SO_4^{2-}
 422 [61]. Immediately after exposure, the pH ascends dramatically to 9.54 and reaches an equilibrium
 423 at pH 10, meaning that SO_4^{2-} anions are the only species in the solution. The pH alteration has no
 424 great influence on 1.00E-05 M and 1.00E-03 M speciation because they are inherently composed

425 of more than 90% SO_4^{2-} species. Nonetheless, the pH of 1.00E-01 M and 1.00E+00 M H_2SO_4
426 undergoes acid-base neutralization, i.e., shifting the pH from acidic to basic values (Figure 8).



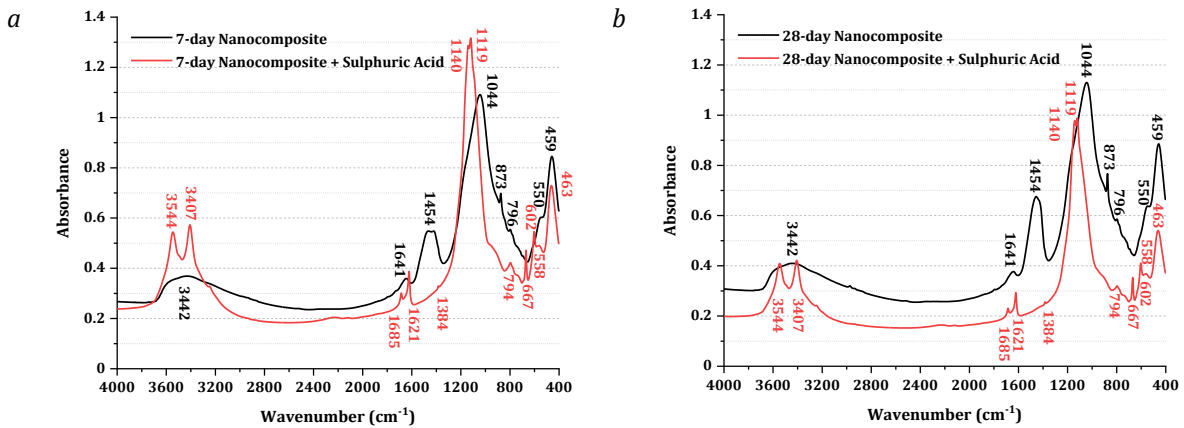
427
428 *Figure 8. pH measurements of SWCNT alkali activated nanocomposites (SWCNT conc. 0.100 wt.%) and*
429 *sulphuric acid 5.45E-02 M (exposure simulation experiment).*
430

431 This dual response of SWCNTs in the exposure to an analyte, an initial descent followed by
432 a secondary ascent, has never been reported in the literature. As explained above, the reason is
433 the synergistic interactions of the alkali activated matrix and SWCNTs. According to the published
434 literature, SWCNTs experience an increase in conductivity in exposure to an oxidising dopant, e.g.,
435 NO_2 & Cl_2 and a decrease, in the presence of a reducing dopant, e.g., NH_3 & H_2 [6,8,62-64]. H_2SO_4
436 is a strong electron acceptor and oxidative dopant (p-dopant) of SWCNTs and it can enrich the
437 hole concentration of SWCNTs by the protonation of the tubes (due to the presence of HSO_4^-)
438 [57,65]. Furthermore, HSO_4^- consumption as a consequence of the acid-base neutralization effect
439 of the alkaline matrix, and production of SO_4^{2-} species generates a scenario, which simulates the
440 addition of an electron donor and reducing dopant (n-dopant) to the SWCNTs. Hence, herein, two
441 consecutive mechanisms of charge transport between sulphuric acid species and SWCNTs are
442 implemented.

443 3.3.2.2. Surface composition change

444 The FTIR-spectra and correlation peak assignments of the sensors before (pristine) and
445 after exposure to sulphuric acid are shown in Figure 9 and Table 4. In an overall view, both 7 and
446 28 days pristine nanocomposites share the most features of FTIR-spectra; hence, there is not any
447 significant age-dependency of the nanocomposites surface composition. Nevertheless, the
448 significant differences between pristine (black spectra in Figure 9) and sulphuric acid exposed
449 (red spectra in Figure 9) sensors are present in i) the $Si - O - R$ stretching region, ii) the $R - OH$
450 stretching and bending regions, and iii) the $O - C - O$ stretching region. Moreover, the bands

451 ascribable to the SWCNTs and SDBS are mostly indiscernible because of the high intensity of the
 452 alkali activated core framework bands ($Si - O - R$ & $R - OH$).
 453



454 Figure 9. FTIR spectra of SWCNT alkali activated nanocomposites (SWCNT conc. 0.100 wt.%) before (black
 455 line) and after sulphuric acid exposure (red line); a- 7-day nanocomposites; b- 28-day nanocomposites.
 456

457 Considering the acid exposed red spectra in Figure 9 a & b, SO_4^{2-} (probably adsorbed on
 458 the surface pores) are detectable in 700 cm⁻¹-580 cm⁻¹ with two peaks, which are not present in
 459 the pristine specimens (black spectra in Figure 9 a & b). The peaks at 667 cm⁻¹ and 602 cm⁻¹
 460 correspond to the bending vibrations of $S = O$ and $S - O$ bonds of SO_4^{2-} species. The stretching
 461 vibrations of these species appear in an overlapped state (combined with $Si - O - R$ bands of core
 462 material) at 1140 cm⁻¹ and 1119 cm⁻¹ of the acid exposed red spectra. Furthermore, the
 463 characteristic bond vibrations of SO_3^- groups of SDBS should appear at $\approx 550+$ cm⁻¹ (bending),
 464 $\approx 1000+$ cm⁻¹ (symmetric stretching), and $\approx 1100+$ cm⁻¹ (asymmetric stretching) are not detectable
 465 due to the low concentration of SDBS in the matrix. Likewise, the aromatic carbon ring vibrations
 466 of SDBS, for instance, the stretching vibrations at ≈ 1600 cm⁻¹ ($C=C$ ring quadrant) and
 467 $\approx 1400/1500$ cm⁻¹ ($C=C$ ring semicircle), are not detectable [66–69].

468 The most intense absorbance band of the framework (1340 cm⁻¹ - 650 cm⁻¹) is positioned
 469 at 1044 cm⁻¹, which is attributed to the asymmetric stretching of the tetrahedral $Si - O - R$ bonds
 470 (R represents Si or Al) of the alkali activated ($N - (C) - A - S - H$) and geopolymeric ($N - A -$
 471 $S - H$) phases of the material core. The related symmetric stretching vibration of the material
 472 core is located at 796 cm⁻¹ in the form of a weak sharp shoulder structure. The bending vibrations
 473 of the core $Si - O - R$ tetrahedra, a strong absorbance band, is observed at 459 cm⁻¹ due to the
 474 $Si - O$ vibrations including $Al - O$ shoulder (overlapped) at 550 cm⁻¹ [28,29,70–72].

475 Sulphuric acid exposed material exhibits a shift of the core band toward higher
 476 frequencies, between 1570 cm⁻¹- 840 cm⁻¹ centering at 1140 cm⁻¹ & 1119 cm⁻¹, which is due to the
 477 SO_4^{2-} coverage [29]. The stretching shoulder of $Si - O - Si$ or $Si - O - Al$ bonds is detectable
 478 with a slight shift to 794 cm⁻¹. A broad weak band at 558 cm⁻¹ can be ascribed to the $Al - O$
 479 shoulder [70]. The bending vibration mode of the core at 463 cm⁻¹ is not affected strongly by the

480 acid exposure. The core band shift, accompanied by the appearance of a new band at 670 cm⁻¹,
 481 were additionally assigned to the presence of gypsum ($CaSO_4 \cdot 2H_2O$) in the references [28,70] for
 482 long-term immersions. Herein, the introduced quantity of sulphuric acid was 30 μL per cycle (a
 483 total of 90 μL of concentrated acid). Hence, during the short-term exposure to the extreme acidic
 484 environment, the core material could not be highly destroyed. Nonetheless, the aforementioned
 485 band shifts represent a potential deterioration of the material bonds, perhaps a slight core
 486 dealumination or decalcification [28,29].

487

488 *Table 4. FTIR correlation band data of nanocomposites (SWCNT conc. 0.100 wt.%); 7 and 28 days*
 489 *nanocomposites represent the same values; R corresponds to the tetrahedral Si or Al.*

Nanocomposite			Nanocomposite + Sulphuric Acid		
Range (cm ⁻¹)	Center (cm ⁻¹)	Vibration	Range (cm ⁻¹)	Center (cm ⁻¹)	Vibration
2500-3700	3442	<i>R – OH (str.)</i>	2700-3700	3544 & 3407	<i>R – OH (str.) & O – H (str.)</i>
1600-1700	1641	<i>R – OH (bend.)</i>	1570-1720	1621 & 1685	<i>R – OH (bend.) & O – H (bend.)</i>
1600-1350	1454	<i>O – C – O (asym.str.)</i>	1391-1376	1384	<i>O – C – O (sh.)</i>
1340-650	1044	<i>Si – O – R (asym.str.)</i> <i>(SO₃⁻ str.)</i>	1570-840	1140 & 1119	<i>Si – O – R (asym.str.)</i> <i>S = O & S – O</i> <i>(SO₄²⁻ /SO₃⁻ str.)</i>
885-864	873	<i>O – C – O (bend.)</i>	disappeared		
814-764	796	<i>Si – O – R (sh.)</i> <i>(sym.str.)</i>	840-700	794	<i>Si – O – R (sh.)</i> <i>(sym.str.)</i>
not detected			700-651	667	<i>S = O (SO₄²⁻ bend.)</i>
			651-580	602	<i>S – O (SO₄²⁻ bend.)</i>
579-527	550	<i>Al – O (sh.)</i> <i>(SO₃⁻ bend.)</i>	580-527	558	<i>Al – O (sh.)</i> <i>(SO₃⁻ bend.)</i>
650-400	459	<i>Si – O (bend.)</i>	527-400	463	<i>Si – O (bend.)</i>

490

491 The sharp band at 1454 cm⁻¹ and the 873 cm⁻¹ shoulder of the pristine samples (black
 492 spectra in Figure 9 a & b) are attributable to the vibrations of carbonate species (CO_3^{2-}). CO_3^{2-}
 493 species undergo acid-base neutralization reactions in the presence of sulphuric acid.
 494 Consequently, the 1454 cm⁻¹ band was converted to a weak shoulder at 1384 cm⁻¹, while the 873
 495 cm⁻¹ shoulder disappeared in the acidified specimens. The *O – C – O* band at 1454 cm⁻¹ is
 496 relatively strong because of the ambient curing of nanocomposites and the potential availability
 497 of the coordinating Ca^{2+} in the alkali activated framework, which can result in the fast formation
 498 of polymorphs of $CaCO_3$ [73,74].

499 Regarding the strong vibrations of the *Si – O – R* at 1340 cm⁻¹ - 650 cm⁻¹, the
 500 polycondensated core displays two other distinct *R – OH* absorbance bands in the pristine
 501 nanocomposites (black spectra in Figure 9 a & b). The stretching of *R – OH* appears in a very

502 broad band (from 2500 cm⁻¹ to 3700 cm⁻¹) centred at 3442 cm⁻¹. The much narrower and weaker
 503 bending mode is located in between 1600 cm⁻¹ and 1700 cm⁻¹ with the centre at 1641 cm⁻¹. Upon
 504 exposure to sulphuric acid, both of these bands split into two sharp bands with stretching poles
 505 at 3544 cm⁻¹ and 3407 cm⁻¹ and bending peaks at 1621 cm⁻¹ and 1685 cm⁻¹ [28,29,70,71,75,76].
 506 The appearance of these double peaks can be ascribed to the formation of *CaSO₄·2H₂O*, as
 507 reported in reference [28] for long-term immersions and in reference [77].

508 3.3.3. Sensor sensitivity

509 The correlation between the cumulative relative resistance and sulphuric acid
 510 concentration, and correspondingly the sensitivity of chemiresistors are represented in Table 5,
 511 Table 6, & Figure 10. The 7-day chemiresistors are superior in comparison to the 28 days with
 512 higher fractional changes and sensitivities. Furthermore, the fractional changes and sensitivities
 513 have a direct relationship with the sulphuric acid concentrations. The highest values are obtained
 514 for concentrated sulphuric acid regimes, i.e., 1.00E-01 M and 1.00E+00 M, and on the contrary,
 515 sensors do not exhibit significant sensitivity differences in low concentration regimes of sulphuric
 516 acid, i.e., 1.00E-05 M and 1.00E-03 M.

517

518 *Table 5. Cumulative relative resistance changes in SWCNT alkali activated chemiresistors (SWCNT conc.*
 519 *0.100 wt.%).*

H ₂ SO ₄ Concentration (M)	Sensitivity (%)	
	7-day nanocomposites	28-day nanocomposites
H ₂ O	6.10 ± 0.63	1.96 ± 0.45
1.00E-05	3.85 ± 0.21	1.53 ± 0.06
1.00E-03	3.44 ± 0.22	1.43 ± 0.07
1.00E-01	5.71 ± 0.42	1.99 ± 0.27
1.00E+00	15.99 ± 1.53	7.57 ± 0.68

520

521 *Table 6. Sensitivity of SWCNT alkali activated chemiresistors (SWCNT conc. 0.100 wt.%).*

H ₂ SO ₄ Concentration (M)	Sensitivity (absolute value)			
	7-day nanocomposites		28-day nanocomposites	
1.00E-05	0.0042	0.0229	0.0009	0.0056
1.00E-03				
1.00E-01	1.1426	0.6194		
1.00E+00				

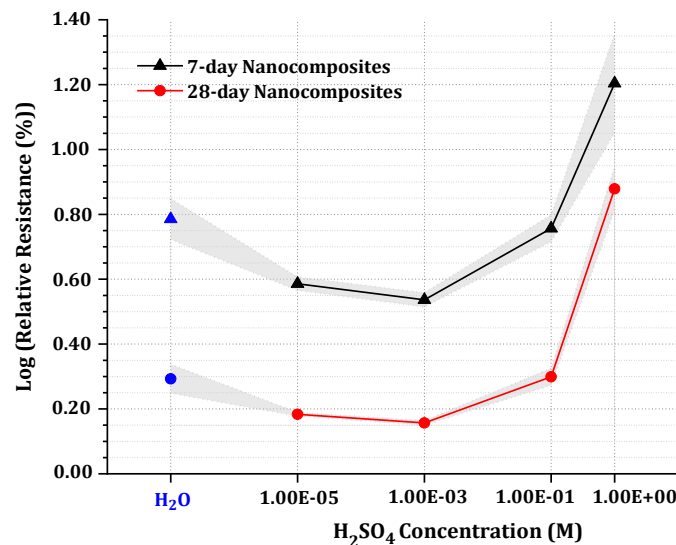
522

523 The chemiresistors have a relative resistance/resistance surge in both 7-day and 28-day
 524 nanocomposites due to the exposure to the 1.00E+00 M sulphuric acid, of ca. 16% and 8%,
 525 respectively (Figure 10). The presence of potential leaching matrix material anions and cations
 526 might restrain the newly introduced ions penetration and diffusion into the pore-crack system of

527 the alkali activated microstructure. Consequently, the SWCNTs might not encounter sufficient
 528 quantities of analyte to generate and transmit a significant signal, but the observations indicate
 529 contradictory results, possibly indicating a non-significant ion leaching. In this respect, it appears
 530 that the alkali activated sensors have no limitation in the high detection threshold.

531 The relative resistance function of alkali activated chemiresistors shows a curvilinear
 532 outline with a stationary point at 1.00E-03 M, which can be the sensor's lower detection threshold
 533 (Table 5 & Figure 10). From the curve stationary point toward higher concentrations, the relative
 534 resistance change and sensitivity of the sensors with an increase in sulphuric acid concentration
 535 is exponentially rising. The 7- day sensitivity is ≈ 0.02 for concentration range of 1.00E-03 M -
 536 1.00E-01 M, and ≈ 1.1 for the range of 1.00E-01 M - 1.00E+00 M (Table 6). This means that the
 537 sensor is able to discriminate more accurately between medium to high sulphuric acid
 538 concentrations than low concentrations. Moreover, this pH/concentration range is of interest to
 539 the researchers working on concrete durability due to the sulphuric acid exposure. The pH of
 540 0.800 [29], 1 [78-80], and 2 [78,79,81], and the concentration of 0.001 [82] have been studied in
 541 the relevant literature.

542



543

544

545 *Figure 10. Correlation of cumulative relative resistance of SWCNT alkali activated chemiresistors and*
 546 *introduced H₂SO₄ concentrations (SWCNT conc. 0.100 wt.%).*

546

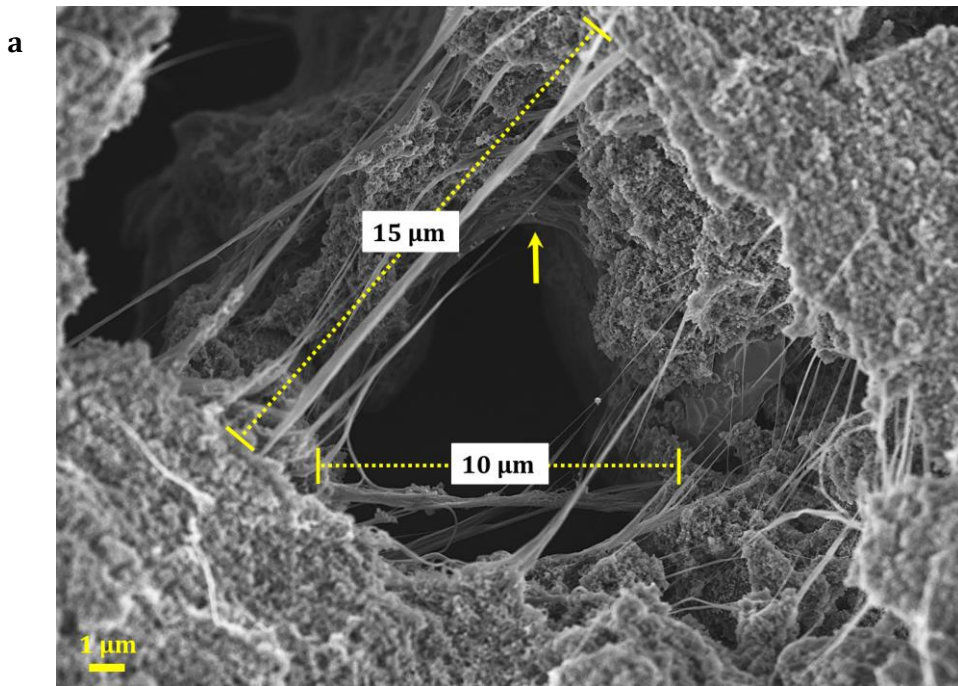
547 Notwithstanding that discrimination capability, because of the convex shape of the
 548 function, the relative resistance change of high-concentrated sulphuric acids may correspond to
 549 very low-concentrated ones, i.e., attributable to water or moisture. For instance, the change
 550 percentage of 1.00E-01 M sulphuric acid and ultrapure water is approximately the same.
 551 However, their response signal shapes still are obviously recognizable (Figure 7 c & Figure 6).
 552 Therefore, assessing a combination of original resistance signals and normalized values can be an
 553 asset for a more precise analyte discrimination.

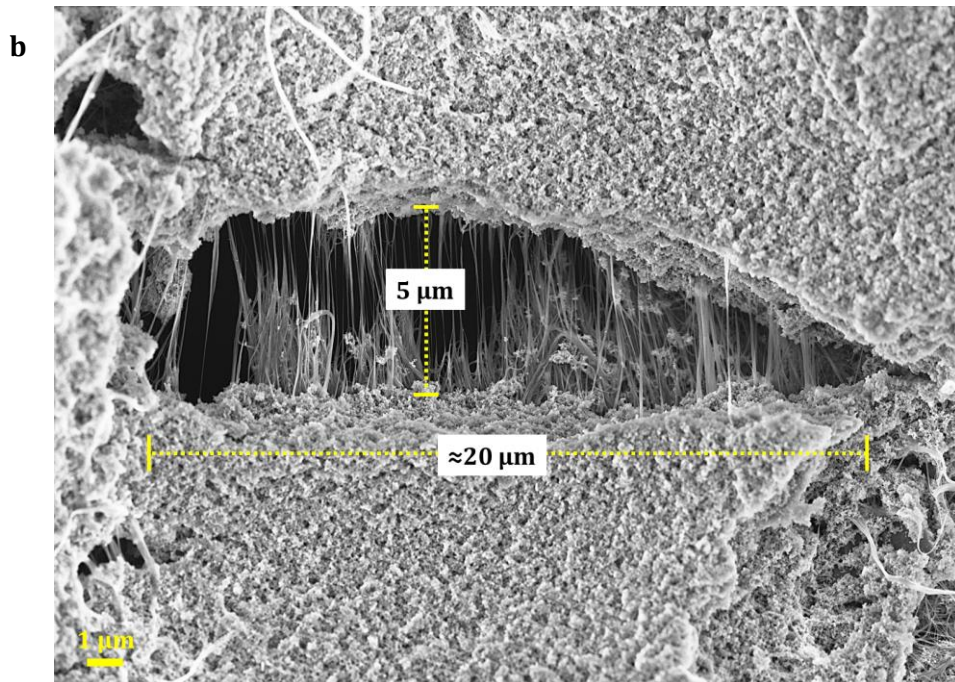
554 **3.4. Microstructure dependency**

555 **3.4.1. SWCNTs and matrix interactions**

556 The sensing properties of the SWCNT alkali activated chemiresistors are significantly
557 influenced by the physical interactions between SWCNTs and the matrix, considering the
558 microstructure characteristics of the alkali activated materials. SWCNTs' fractal and three-
559 dimensional propagation in the matrix, hole lining and coverage, cavities and fractures bridging,
560 agglomeration geometry, and embedment degree can be counted as dominant factors regarding
561 sensing behaviour of the chemiresistors. The SWCNTs' propagation, the fractal spread and
562 escalation of SWCNTs were depicted previously in Figure 3.

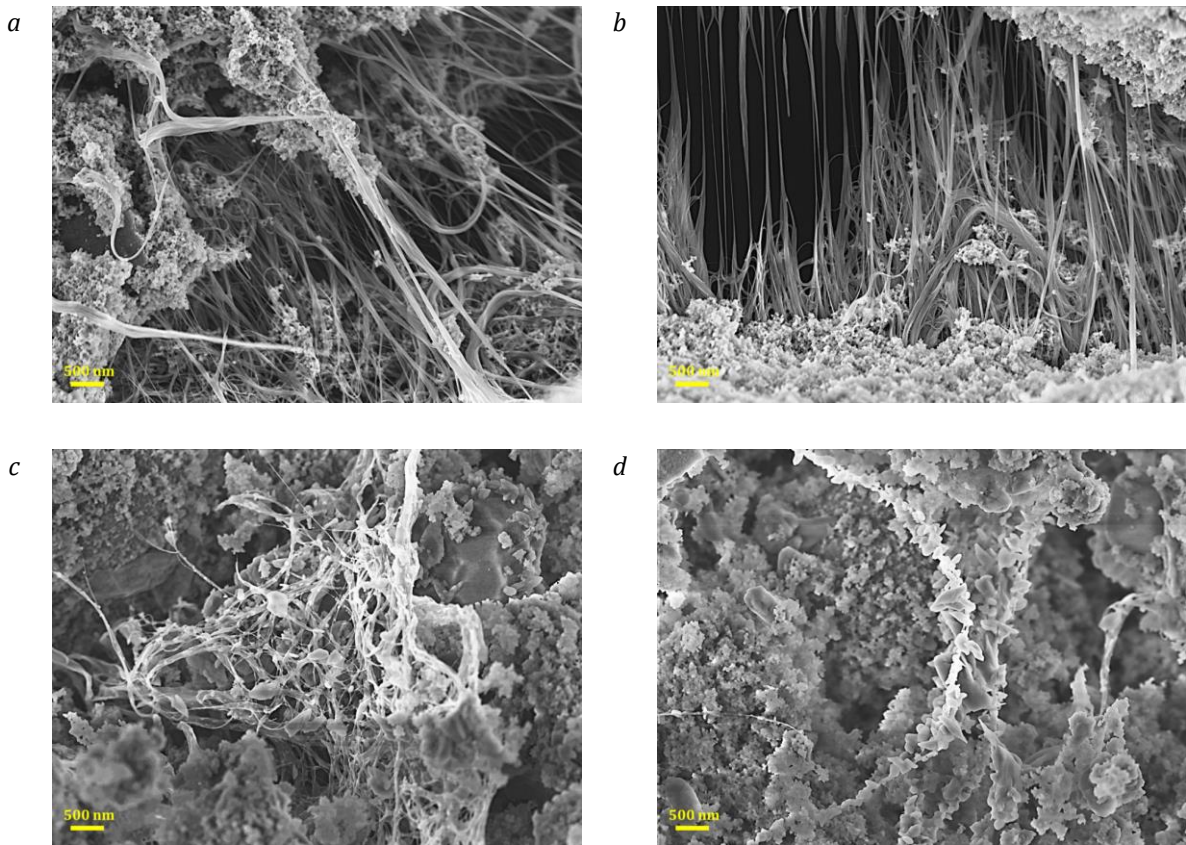
563 The existence of micron-scale holes and cavities in the matrix can interrupt the SWCNTs'
564 networking efficiency if not covered by or connected to the surrounding network members. The
565 utilized SWCNTs herein have a length of $\approx 5 \mu\text{m}$, however, this length can be extended to $\geq 10+$ μm ,
566 considering the agglomeration geometry and configuration of SWCNTs (Figure 11 a). According
567 to Figure 11 a, a giant hole is covered by the SWCNTs' network members at a length of 10 μm and
568 15 μm . The hole's interior surface is additionally lined with fabric-like SWCNTs, marked by a
569 yellow arrow in the image, evidencing the SWCNTs' conductive network consistency. In addition
570 to the mentioned mechanism, long span cavities are bridged by SWCNTs as illustrated in Figure
571 11 b. The conductive network consistency is retained here by $\approx 5 \mu\text{m}$ long aligned SWCNTs which
572 densely bridge a 20-micron-span cavity.





573 *Figure 11. Conductive network integrity maintenance of SWCNTs (SWCNT conc. 0.100 wt.%); a- hole surface*
 574 *lining and coverage by SWCNTs; b- dense bridging of a cavity by aligned SWCNTs.*
 575

576 Embedment of SWCNTs into the matrix material determines the accessibility degree of
 577 SWCNTs by analytes and consequently the intensity of transmitted signals. Since the inert
 578 SWCNTs have reactive SDBS in the vicinity, it is highly probable that they are extemporaneously
 579 involved in the core formation and become a constituent part of the framework. Depending on the
 580 evolution of the matrix, SWCNTs will be incorporated more intensively into the microstructure;
 581 therefore, SWCNTs in 28-day nanocomposites look more entangled (Figure 12 c) or deeply buried
 582 (Figure 12 d) in comparison to the 7-day counterparts (Figure 12 a & b). Even in several parts of
 583 28-day nanocomposites, SWCNTs contributed to the skeleton of the core framework, where they
 584 are not highly agglomerated (Figure 12 d vs c). Such ageing behaviours are highly advantageous
 585 for the electrical (Table 1) and mechanical improvements [45] but they have a negative impact on
 586 the sensing capacity of SWCNTs (Figure 7 & Figure 10). As explained before, 28-days sensors had
 587 better conductivity but worse sensing capability. Because the huge surface area of SWCNTs is
 588 partially or completely covered by the core alkali activated material and is not accessible by the
 589 analytes. As shown in Figure 12 a & b, several spontaneously aligned SWCNTs are found in the 7-
 590 day nanocomposites that expose enormous free surfaces to the analyte.



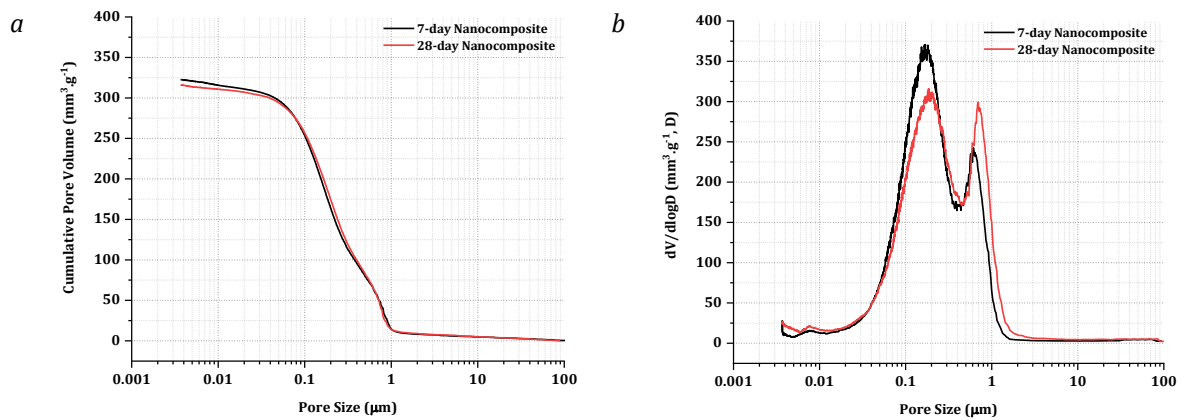
591 *Figure 12. SWCNTs interactions with the alkali activated matrix (SWCNT conc. 0.100 wt.%); a & b- aligned*
 592 *SWCNTs in 7-day nanocomposites; c- entangled and partially covered SWCNTs in 28-day nanocomposites; d-*
 593 *completely covered SWCNTs in 28-day nanocomposites.*
 594

595 3.4.2. Matrix porosity

596 The porosity of 7-day and 28-day nanocomposites exhibit approximately very similar
 597 distributions (Figure 13), therefore, it cannot be used to explain sensing behaviours. The applied
 598 ambient curing can be the main impetus of this occurrence, similar to what observed in FTIR
 599 spectrometry of the nanocomposites (Figure 9). The total porosity of sensors is almost 45%, and
 600 their cumulative pore volume reaches around $320 \text{ mm}^3 \cdot \text{g}^{-1}$. The most frequent pore dimensions of
 601 nanocomposites are located in a broad pore span of 40 nm to $2 \mu\text{m}$ with two distinct peaks for 7
 602 days at 165 nm and 600 nm, and for 28 days at 180 nm and 700 nm. This substantiates a compact
 603 nanostructure but a porous microstructure of the material because of the abundance of capillary
 604 and air-entrained pores as demonstrated by SEM images in the previous sections.

605 The porosity level is an essential prerequisite of the herein proposed class of sensors and
 606 it should even be increased to a greater degree. A higher number of pathways and channels
 607 throughout the sensor will allow the analyte to reach the embedded SWCNTs with much faster
 608 kinetics. The alkali activated nanocomposites in previously published work [45], demonstrated a
 609 cumulative pore volume of approximately a third less ($\approx 100 \text{ mm}^3 \cdot \text{g}^{-1}$) with the most frequent pore
 610 size located in $<10 \text{ nm}$ region i.e., a porous nanostructure but a compact microstructure. This huge
 611 favourable increase of this-research porosity is attributable to the destructive impacts of SBDS on
 612 the material microstructure, both chemically (constitution of less binding material) and physically

613 (air bubbles entrapment) in comparison to the previously utilized surfactant, naphthalene
614 sulfonate. The fabrication methodology has furthermore significant influence herein, i.e., using
615 one-part technology and ambient curing methodology.



616 *Figure 13. Porosity analysis (MIP) of SWCNT alkali activated nanocomposites (SWCNT conc. 0.100 wt.%); a-*
617 *cumulative distribution; b- differential distribution.*

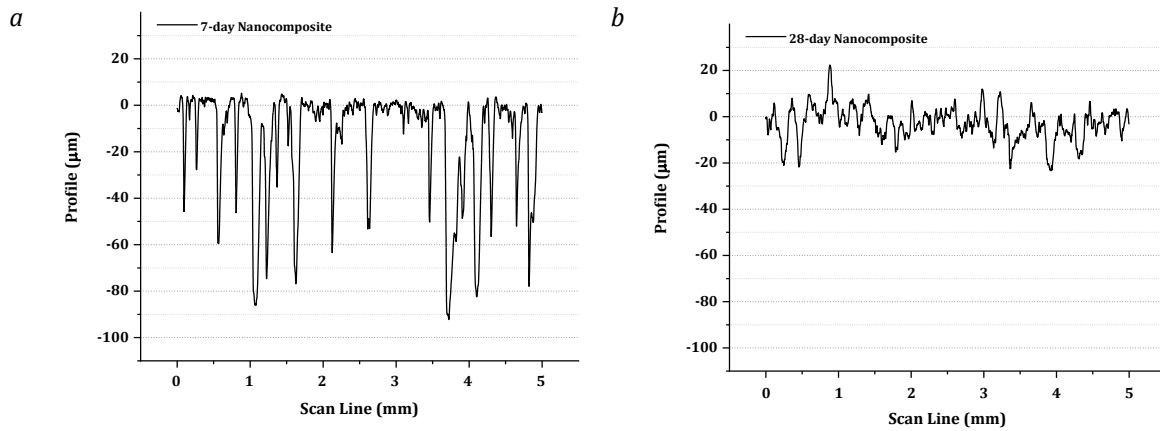
618

619 3.4.3. Matrix roughness

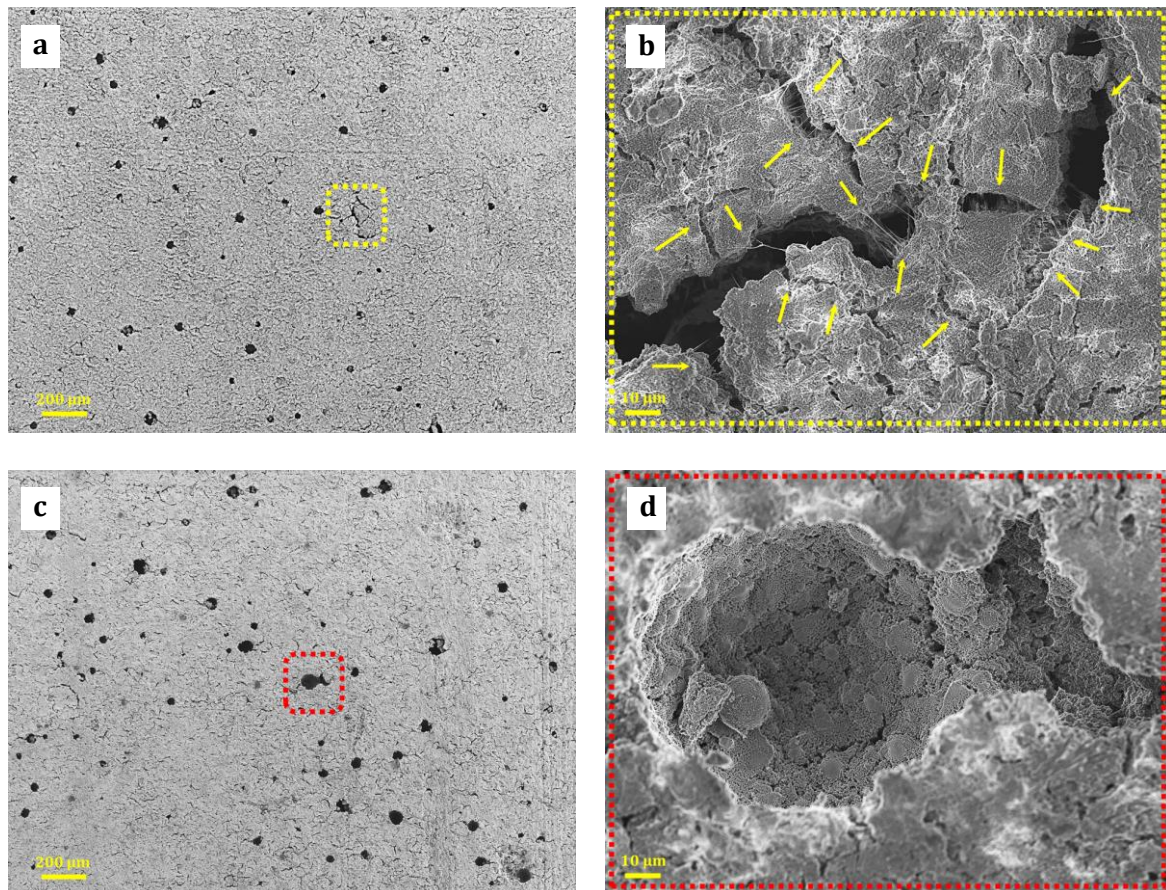
620 Notwithstanding the pore distributions (Figure 13), the topography and profile
621 characteristics of 7-day and 28-day nanocomposites show a considerable contrast (Figure 14 a vs
622 b). The 7-day nanocomposites have a much higher roughness compared to the 28-day
623 nanocomposites, which exhibit a relatively smoother surface. According to the profile mapping of
624 the 7-day nanocomposites, there are many facial micro-cavities penetrating as deep as 80 μm into
625 the body of specimens (Figure 14 a). Those cavities are composed of many air holes and fractures
626 on the surface texture of the nanocomposites, which could be detected effortlessly by SEM (Figure
627 15). The cavities could provide required pathways for inflow and diffusion of sulphuric acid
628 species and water into the alkali activated sensor bulk mass and increase the probability of
629 interactions with the SWCNTs exterior tubes. This phenomenon is observed to a very lesser extent
630 in the 28-day nanocomposites. Mainly, the topography of 28-day nanocomposites consists of
631 many height fluctuations and deviations, i.e., relief, within a range of ±20 μm according to Figure
632 14 b, resulting in a great operational difficulty in the topography observations by the SEM.

633 As explained, the topography of 7-day nanocomposites composed of fractures and air
634 holes. In particular, most of the facial fractures are covered or bridged by the SWCNTs, which put
635 forward additional assistance to the sensing features of the 7-day nanocomposites (Figure 15 a &
636 b). On the contrary, observed air holes were principally CNT-free and merely participated in the
637 penetration of sulphuric acid and water into the bulk mass of the sensor (Figure 15 c & d).
638 Altogether, the highly fractured and rough profile of 7-day sensors results in accelerated analyte
639 diffusion into the alkali activated microstructure. Furthermore, in the bulk mass of the 7-day
640 nanocomposites, less covered and buried SWCNTs are more accessible (Figure 12) and able to

641 release the signals with higher intensity (Figure 6, Figure 7 & Figure 10) in comparison to the 28-
642 day nanocomposites.



643 *Figure 14. Profile mapping and roughness of SWCNT alkali activated nanocomposites (SWCNT conc. 0.100*
644 *wt.%); a- 7-day nanocomposites; b- 28-day nanocomposites.*
645



646 *Figure 15. Topography of two different areas of the SWCNT alkali activated 7-day nanocomposites (a & c)*
647 *(SWCNT conc. 0.100 wt.%); c- magnified image of the surface cavities and fractures: filled with SWCNTs; d-*
648 *magnified image of the air holes: not covered by SWCNTs.*
649

650 **4. Conclusion and outlook**

651 An innovative and unconventional H_2SO_4 sensing concept for the SWCNT alkali activated
652 chemiresistors has been created in this research. An electronic conductive network was

653 established by incorporating SWCNTs into the sodium-based fly-ash-GGBS alkali activated matrix.
654 The developed chemiresistors could generate discriminative signals upon sulphuric acid and
655 water exposures. Based on the conducted measurements and characterizations, it can be
656 concluded that:

- 657 • The chemiresistors' conductivity with incorporation of 0.100 wt.% SWCNT are 4.80 S.m⁻¹ for
658 7-day nanocomposites and 6.02 S.m⁻¹ for 28-day nanocomposites.
- 659 • The chemiresistors sense the existence and differentiate the concentration of H_2SO_4 species
660 by transmitting distinguishable signals. The H_2SO_4 low detection threshold is 1.00E-03 M in
661 concentration and 2.73 in pH.
- 662 • The 7-day sensors convey more intensified signals than 28 days, because SWCNTs are more
663 accessible through pathways and less buried under the core material.
- 664 • The alkali activated material and sulphuric acid have mutual interactions. The pH of H_2SO_4 is
665 neutralized after exposure to the matrix alkaline environment, resulting in HSO_4^-
666 consumption and SO_4^{2-} production. In parallel, the core material of the alkali activated matrix
667 appears to be susceptible to a slight deterioration due to H_2SO_4 exposure.

668 The described mechanisms and accomplished results can be considered as a conceptual
669 study for the development of a quantified and discriminative SWCNT alkali activated sensor for
670 aggressive ion detection. Considering the concrete infrastructures' operational lifespan, sensor
671 long-term behaviour and recovery, and matrix durability regarding corrosive ion penetration to
672 the material microstructure would be attractive issues.

673

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686

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