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Quantification and prediction of water uptake by soot deposited on ventilation filters during fire events

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Abstract

Soot samples from different fuels were produced in small and pilot combustion test benches at various O₂ concentrations, then characterized in terms of primary particle diameter, BET specific surface area and oxygen content. Water sorption measurements were then carried out for soot compacted into pellet and let in powder form, using both a gravimetric microbalance and a manometric analyzer. Water adsorption isotherms are all found of type V, and reveal the central role of the specific surface area and the oxygen content of soot. A single parametrization of the second Dubinin-Serpinsky model allows for a proper fitting of all isotherms. To our best knowledge, this is the first study to provide physicochemical parameters and water sorption results for fire soot. This enables a better description of the soot cake formed on filters during a fire, in particular in industrial confined facilities that were simulated in this study. The humidity can be then explicitly considered like other parameters influencing the aerologic resistance of cakes. These results can contribute to better predict the consequences of fires on the containment of toxic materials within such industrial facilities.

Keywords: fire soot, physical and chemical characterization, water adsorption, Dubinin-Serpinsky model

Introduction

Need for efficient filtration devices relevant for containment of hazardous materials as nuclear materials, nanoparticles or pathogens respectively in basic nuclear installations, nanomaterials

28 manufacturing industry and, with regard to the SARS-CoV-2 pandemic of 2020, of
29 biological/virological research institutes is of main importance. Beyond their initial efficiency,
30 which is generally fixed to high level and characterized as High Efficiency Particulate Air for
31 filters, their performance must be maintained despite hazardous situations which could
32 eventually occur within an industrial or research confined and ventilated facilities. Furthermore,
33 dramatic fires of the Notre-Dame Cathedral (15-16 April, 2019 in Paris, France), Lubrizol (26
34 September, 2019 in Rouen, France) and in contaminated surroundings of the Chernobyl site
35 (04-05 April 2020, Chernobyl exclusion site, Ukraine) highlight the need for developing tools
36 able to predict consequences of such fires in terms of dispersion of hazardous materials in the
37 atmosphere [1–3]. Exposition of firefighters but also of population to such hazardous airborne
38 transported during wildland or industrial fires is also of societal importance and open the
39 question of performance of protective personal equipment in such accidental situation and most
40 particularly on filtration efficiency and clogging of filtering face piece.

41 Soot particles, defined by Petzold et al. [4] as agglomerates of monomers consisting solely of
42 carbon with few amounts of hydrogen and oxygen, are inevitably produced during combustion
43 processes encountered during wildland or industrial fires. For facilities manufacturing or
44 handling hazardous materials, soot emitted during a fire can be confined in those installations
45 using high efficiency particulate air (HEPA) filters, but massive emission can clog those filters
46 by formation of “cakes” [5], increasing the aeraulic resistance of the air flow passing through
47 the filters. This enhances the mechanical strains applied on the structure of the filters, leading
48 in extreme case to their rupture. Similar phenomena could also occur for personal protective
49 equipment worn by firefighters or population, which could leads to an increase of the pressure
50 drop of the filtering part, enhancing leaks and, as a consequence, decreasing the protective
51 factor of those devices. For each of those applications and especially for safety analysis of
52 nuclear facilities, it is crucial to be able to describe this clogging phenomenon in order to predict
53 consequences of fires on the containment of radioactive materials. A main parameter
54 influencing the filters clogging is the cake porosity, formed by interstitial spaces between soot
55 aggregates. Typical porosity of soot cake has been reported above 95% [6]. Aeraulic resistance
56 of cakes depends also on humidity [7,8], which can reach high values when water aspersion
57 devices are used to extinguish the fire. The presence of organic vapors also influence the
58 aeraulic resistance [5]. Thus, refined clogging models should take into account the dynamic
59 regime of the clogging process, including high humidity variations and structural changes to
60 which the filter and the cake are subjected to [9,10]. Furthermore, cake can be restructured in

61 presence of liquid water due to capillary condensation [11,12], also changing the aeraulic
62 resistance [13]. Yet, all these phenomena have not been specifically modelled for soot emitted
63 during a realistic fire. Indeed, due to their morphology and their potential hydrophilic character,
64 fire soot particles can strongly adsorb water molecules leading to such capillary condensation.
65 To develop a relevant clogging model, it is necessary to determine the water uptake of fire soot
66 as a function of humidity and, in this context, it is particularly interesting to determine the
67 transition between adsorption and capillary condensation. It is also relevant to understand the
68 effect of the fire conditions (O_2 concentration, air flux) on the water uptake, as these conditions
69 can influence the physicochemical properties of soot [14]. Water uptake measurements have
70 been performed for chemically or thermally treated synthetic carbons, such as activated carbon
71 [15,16], mesoporous carbon [17] and commercial carbon blacks [18,19], but have never been
72 reported for fire soot. Carbon blacks could be considered, from a size and morphological point
73 of view, as relevant surrogates of soot [20], but not from a chemical point of view since they
74 are mostly composed of elemental (graphitic) carbon, while combustion soot usually denotes
75 significant oxygen [20] and organic content [14]. Water uptake has been also measured on
76 reference soot, emitted by laboratory burners or engines with various fuels, like diesel and
77 kerosene [21,22]. In all cases, the main parameters influencing the water uptake are the sample
78 porosity and the particles' chemical composition, and the main adsorption mechanism is the
79 formation of water clusters at hydrophilic adsorption sites [23]. Numerous models for water
80 adsorption on carbon have been proposed, especially for very porous activated carbon [24].
81 Among them, the Dubinin-Serpinsky (DS) adsorption model [25] is valid either for porous and
82 non-porous carbonaceous materials. In the case of cakes of fire soot, the DS model seems
83 relevant, as water adsorption can take place at the surface of the non-porous soot aggregates
84 forming the cake.

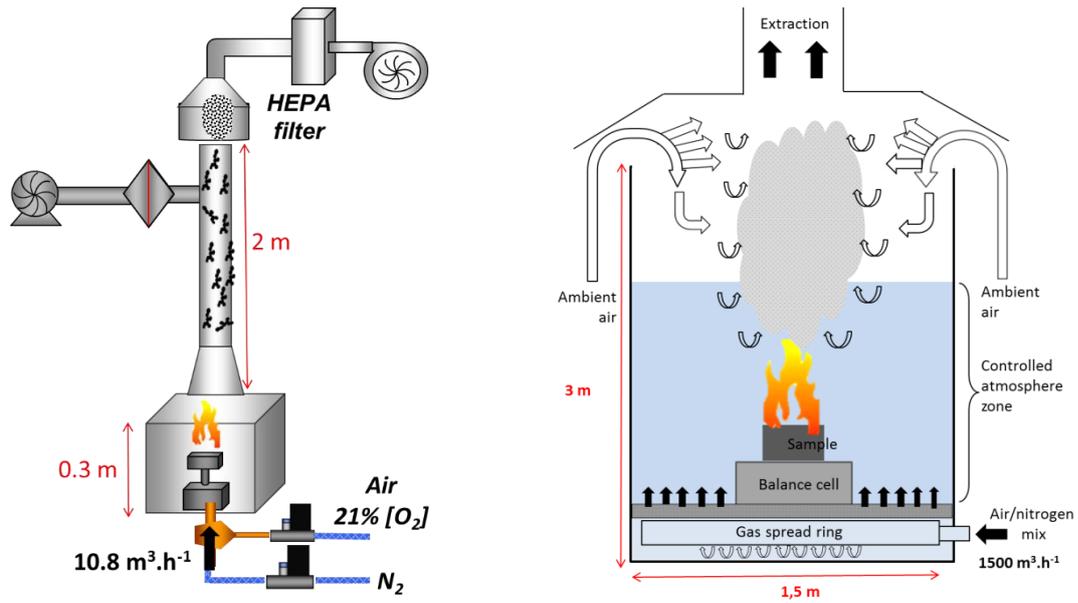
85 Using small and pilot combustion test benches, we have produced fire soot under
86 conditions representative of fire events [14,26]. Different O_2 concentrations of the oxidizing
87 gas have been used to mimic the real case of a poorly ventilated and confined fire, representative
88 of industrial facility handling hazardous materials (biological and radioactive nanoparticles).
89 For nuclear safety application, we have considered fuels commonly found in nuclear facilities
90 or extensively studied in the past [14]. Significant amounts of soot have been collected in order
91 to perform physicochemical analysis and sorption measurements. TEM image analysis [27],
92 nitrogen sorption measurements [28], elementary and XPS analysis [29] have been used to
93 determine respectively the soot primary particles diameters, the BET specific surface area and

94 the global and surface oxygen contents. Water sorption measurements were carried out for soot
95 compacted into pellet and let in powder form, using respectively a gravimetric microbalance
96 and a manometric analyzer.

97 **1. Experimental procedure**

98 *a. Soot production*

99 Soot samples were produced in two cones calorimeters, one at laboratory or “lab” scale
100 and one at “pilot” scale, differing in their dimensions, their oxidizing gas flowrates and the
101 residence times of the emitted particles inside their combustion chamber (Figure. 1). The
102 calorimeter at laboratory scale consists of a combustion chamber of 0.03 m³ topped with a
103 column in which the combustion aerosol is transported to the sampling point. We used as fuel
104 40 mL of heptane (Sigma-Aldrich) or DTE Medium (Exxon Mobil), a hydraulic oil used in the
105 French nuclear industry, placed in a cylindrical container of 5.7 cm of internal diameter. We
106 have also tested polymethyl methacrylate (PMMA), the major compound of gloveboxes walls
107 usually used for the containment of hazardous materials (along with polycarbonate). The total
108 flowrate of the oxidizing air was fixed at 10.8 Nm³.h⁻¹, and the O₂ concentration was varied by
109 changing the air to nitrogen ratio with two mass flow controllers (model 5853S, Brooks). We
110 chose three O₂ concentrations of 15% (highly depleted air), 18% (depleted air) and 21%
111 (ambient air) in the oxidizing gas for fires with heptane, DTE and PMMA. For each fuel, the
112 soot samples are named accordingly to these oxidation conditions (*e.g.* heptane 15%, heptane
113 18% and heptane 21%). Soot was collected on a cellulose acetate membrane (type 11106,
114 Sartorius Stedium Biotech) placed in a high-volume air sampler (TE-2000PX, TISCH
115 Environmental Inc, Ohio) at a flowrate of 8 Nm³.h⁻¹. In order to carry out different *ex situ*
116 analysis, soot has been kept in a dry hermetic desiccated container, and away from light. The
117 calorimeter at pilot scale has a significantly larger size and residence times compared to the
118 laboratory scale ones [26]. PMMA sheets and heptane pools were used as fuels, and their
119 respective dimensions are reported in Table 1.



120 Figure 1: Experimental setup of the controlled atmosphere cones calorimeters at lab scale (left) and at pilot scale
 121 (right)

122

123 Table 1: Summary of operational conditions for fire tests in the laboratory and pilot scale cone calorimeters

		Laboratory scale	Pilot scale
Combustion chamber volume (m ³)		0.03	22
Oxidizing gas flowrate (Nm ³ .h ⁻¹)		10.8	1500
Residence time (seconds)		10	53
Flowrate of high-volume air collector (Nm ³ .h ⁻¹)		8	60
Fuels and dimension (cm)	PMMA plate	5x5x1	40x40x3
	Liquid fuel in a cylindrical container	Heptane	Ø: 21
		Hydraulic oil	Ø: 5.7

124

125

127 The true density of the primary particles of carbonaceous aggregates was determined
128 using a measurement technique based on the displacement of a liquid induced by the immersion
129 of a known mass of sample. This method, described in the ISO 787-23 standard and based on
130 the Archimedes buoyancy principle (using ethanol as displacement liquid), has been recently
131 demonstrated to be relevant despite type of soot samples [30]. The diameters of the soot primary
132 particles were determined by transmission electron microscopy (TEM). For TEM sampling,
133 soot particles have been first diluted in ethanol and mixed in an ultrasonic bath during several
134 minutes resulting to a homogeneous suspension. A microliter of this solution has been deposited
135 on TEM grids (holey carbon film 300 mesh Cu (X25), S-147-3H from Agar Scientific®) and
136 let drying. Soot micrographs were recorded with a Jeol 100CXII microscope equipped with a
137 CCD camera (Gatan® Erlangshien Dualvision 300W, 780 model). A hundred of TEM images
138 were analyzed for each sample, both manually and automatically using respectively the ImageJ
139 software and a semi-automatic software [27]. Measurements of nitrogen sorption at 77 K using
140 a manometric analyzer (ASAP 2020, Micromeritics) provided the specific surface area of each
141 sample from the conventional BET analysis [31]. Prior to the measurements, the powdered
142 samples were pumped into a primary vacuum during at least 12 hours at a temperature of 25°C.
143 The elemental compositions of soot were determined with an organic elemental analyzer
144 (FlashEA 1112, Thermo Scientific). Carbon, hydrogen, nitrogen and sulfur (CHNS) contents
145 are inferred from the gas analysis emitted during a flash combustion at 920°C under oxygen.
146 According to previous studies on carbon black samples [15,20,32], the soot oxygen content
147 $[O]_{\text{diff}}$ (in weight %) can be determined from this analysis. In the present study, soot particles
148 were produced from fuels mostly composed of carbon and hydrogen, and we thus expect to
149 detect no other elements than C and H, except nitrogen and oxygen resulting from the reactions
150 with the oxidizing gas [20,33]. The surface oxygen concentration $[O]_{\text{XPS}}$ of several soot
151 produced at laboratory scale were determined by X-ray photoelectron spectroscopy (XPS).
152 Prior to the XPS analysis, the samples were compacted into 7 mm diameter pellets with a hand
153 press (Pike Technologies®). The experiments were then performed under ultra-high vacuum
154 using a Resolve 120 hemispherical electron analyzer (PSP Vacuum) and a TX400 (PSP
155 vacuum) unmonochromatized X-ray source (Mg K α at 1253.6 eV) operated at 100 W. The XPS
156 lines were deconvoluted with the CasaXPS program, using Gaussian/Lorentzian profiles and
157 after Shirley-type background subtraction. Elemental composition is obtained from the analysis
158 of the survey spectra and after correction by the relative sensitivity factors provided in the

159 program [29]. Those analytical methods have been preferred to thermo-desorption analysis of
160 organic to elemental carbon ratio (OC/EC) since this method is not specific to surface
161 composition and not only includes oxygen containing species but also alkyl or aliphatic groups
162 [34] as examples.

163 *c. Water uptake measurement*

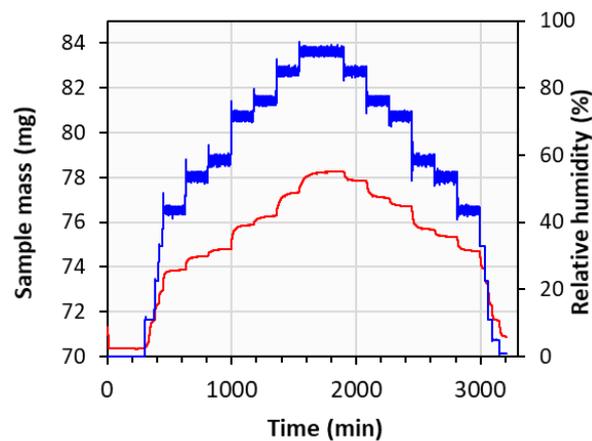
164 For water uptake measurements, soot samples were either in their natural powdered
165 form, or compacted into a cylindrical pellet using a laboratory-made press functioning with a
166 torque wrench (torque set at 0.5 N.m). Knowing the true density of soot, the global porosity
167 (Table 2) of uncompact ϵ_{powder} or compacted samples ϵ_{pellet} can be respectively deduced either
168 from the volume of the powder in the cylindrical glass container, or from the diameter and the
169 height of the pellet. Water sorption measurements were performed using gravimetric and
170 manometric methods [35,36]. They are in good agreement whether conducted under static or
171 dynamic sorption conditions [37,38]. Gravimetric measurements were performed only on
172 pellets using a “dynamic vapor sorption” (DVS) Vacuum microbalance (Surface Measurements
173 Systems, SMS). Pellets are first pumped into high vacuum during several hours at 25°C to
174 remove water and adsorbed impurities at the sample surface. For water sorption measurements,
175 this degassing is more recommended [39] than the conventional thermal pre-treatment that
176 could alter surface properties, for instance by removing of hydrophilic adsorption sites. Then,
177 the initial mass of the dried sample is determined. Subsequently, humidity steps are gradually
178 applied at a constant water vapor flowrate. Water sweeps the sample with a limited residence
179 time in the cell of the microbalance system, enabling to continuously renew the vapor phase in
180 contact with the soot surface. The relative humidity RH (in %) in the microbalance is defined
181 as the ratio between partial pressure of water $P_{\text{H}_2\text{O},\text{vap}}$ within the cell divided by the saturation
182 pressure $P_{\text{H}_2\text{O},\text{sat}}$ (Eq. 1) at the measurements’ temperature T:

$$183 \quad RH = \frac{P_{\text{H}_2\text{O},\text{vap}}}{P_{\text{H}_2\text{O},\text{sat}}(T)} \times 100 \quad (\text{Eq. 1})$$

184 The water uptake $a(RH)$ (eq. 2) is then defined as the ratio of the mass of water adsorbed
185 ($m_{\text{H}_2\text{O}, \text{adsorbed}}$), determined according to sample mass at each relativity humidity $m_{\text{sample}}(RH)$,
186 and the reference mass $m_{\text{reference}}$, which is measured at RH= 0%.

$$187 \quad a(RH) = \frac{m_{\text{sample}}(RH) - m_{\text{reference}}}{m_{\text{reference}}} = \frac{m_{\text{H}_2\text{O},\text{adsorbed}}(RH)}{m_{\text{reference}}} \quad (\text{Eq. 2})$$

188 The transition between two humidity steps depends on the time needed to reach the
189 thermodynamic equilibrium and the stabilization of the sample mass with an accuracy of 0.1
190 μg , according to SMS. Following this value and the uncertainty propagation principle, the water
191 uptake uncertainty is lower than 10^{-4} %. One obtains the time evolution of the mass and the
192 maximal water uptake for a defined humidity (Figure 2) which, *in fine*, provides the sorption
193 data needed to plot the sorption isotherms with a high accuracy. Manometric measurements
194 were performed on uncompact powdered soot only, using a 3FLEX analyzer
195 (MICROMERITICS). Soot samples were first degassed in a cell at 0.1 mbar and 25°C using
196 the low vacuum pump VacPrep 061. The cell is then introduced in the 3FLEX analyzer, and
197 water is flowed in the cell. Pressure measurements are then performed only when a stabilization
198 criterium of $0.01 \text{ mbar}\cdot\text{min}^{-1}$ is reached.



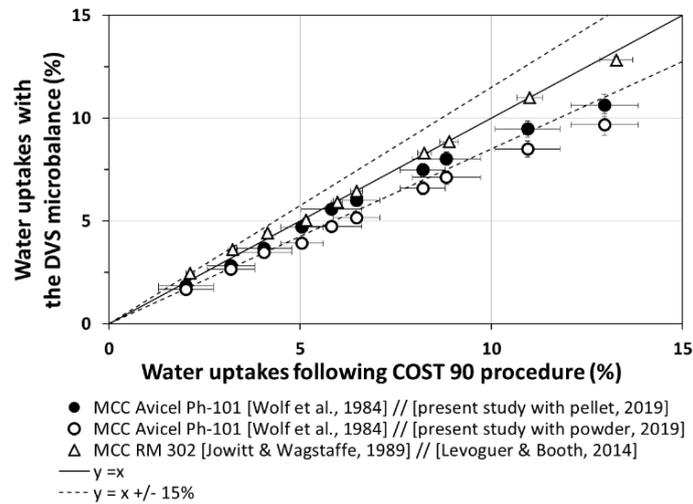
199

200 Figure 2: Example of a gravimetric measurement with the DVS microbalance (in red the evolution of sample
201 mass and in blue the evolution of relative humidity)

202 *d. Qualification of water uptake measurement protocol*

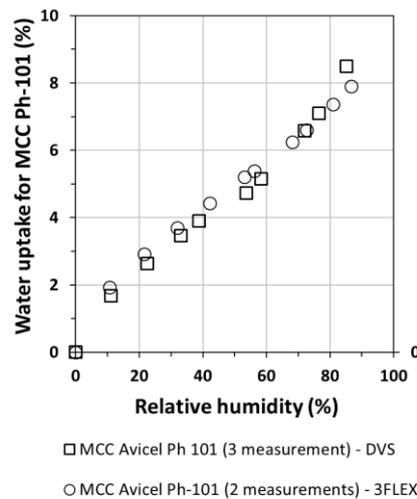
203 Prior to the measurements on soot, the experimental protocols and apparatus were
204 validated using microcrystalline cellulose (MCC) as a reference. For MCC, gravimetric, static
205 and discontinuous sorption data are available for two kinds of samples, MCC Avicel Ph-101
206 provided by FMC [36] and MCC RM 302 [40], which are used as references for the COST90
207 standard European procedure. Figure 3 shows the water uptakes of these two MCCs following
208 the COST90 procedure at different RH ensured by salt solutions [36], and those obtained with
209 the DVS microbalance at the same RH steps [41]. Our results are in good agreement with the
210 COST90 data, except slight discrepancies at high water uptakes for the MCC Avicel Ph-101.
211 This can be explained by differences in the samples, such as size distribution or specific surface
212 area [42]. Figure 4 compares water uptakes obtained on the MCC Avicel Ph101 at powdered

213 form with the 3FLEX analyzer (circles symbols) and those obtained with the gravimetric (DVS)
 214 methods (squares symbols). One can see a good agreement between the methods, as reported
 215 by previous authors [35].



216

217 Figure 3: Comparison of water sorption data on different microcrystalline celluloses (MCC Avicel Ph-101 and
 218 RM302) obtained with the COST90 procedure and DVS microbalance



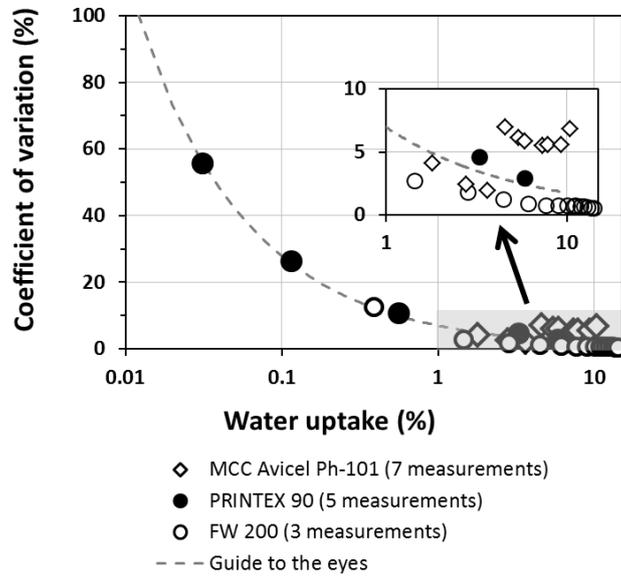
219

220 Figure 4: Water adsorption isotherms of MCC Avicel Ph-101 obtained with the DVS microbalance (squares) and
 221 with the 3FLEX analyzer (circles)

222 The quantities of soot being limited, experimental isotherms were generally determined
 223 once. Prior to this determination the experimental repeatability of the DVS microbalance has
 224 been checked with the MCC and two commercially available carbon black samples as
 225 size/morphological and size/morphological/chemical surrogates for this preliminary tests,
 226 respectively Printex 90 and FW200 (which denotes oxygen content close to soot particles) from
 227 Orion®. Figure 5 shows the coefficient of variation (eq. 3) for MCC Avicel Ph-101, Printex 90
 228 and FW200 for respectively seven, five and three repeated measurements. The coefficient of

229 variation is lower than 10 % at water uptakes higher than 1%, indicating an excellent
 230 repeatability of the measure.

231
$$\text{coefficient of variation} = 100 \times \frac{\text{standard deviation}}{\text{mean value}} \quad (\text{Eq. 3})$$



233 Figure 5: Repeated water sorption measurements for different samples (MCC Avicel Ph-101, PRINTEX 90 and
 234 FW200)

235 **2. Results**

236 *a. Samples properties*

237 The measured soot densities ρ_{true} range from 1492 kg.m⁻³ up to 1780 kg.m⁻³ (Table 2).
 238 Upper values are in good agreement with the literature for soot having a low oxygen content
 239 [43,44]. Lower density values measured for some of our samples can be explained by the
 240 presence of an organic carbon phase, which is less dense than the elemental carbon phase,
 241 reducing the overall density [30]. The diameter of the primary particles d_{pp} ranges from 22.3
 242 nm to 43.3 nm (Table 2), in agreement with values reported for soot emitted by gaseous flames
 243 [45,46], and for more complex liquid and solid fuels [14]. For all samples, particles denote
 244 fractal morphology typical of soot particles and examples of TEM images are available in
 245 supplementary information in tables SI-1 and SI-2. Close agreement, in terms of size and
 246 morphology could then be reported between carbon black and soot samples. The specific
 247 surface area S_{BET} ranges between 52 m².g⁻¹ and 100 m².g⁻¹ (Table 2). This is also typical of non-
 248 porous adsorbents and agrees with values determined for soot emitted in various combustion

249 processes [20–22,47]. This surface area is mostly due to the surface developed by the primary
 250 particles composing soot aggregates [27]. The smaller the primary particle diameter, the higher
 251 the specific area. This explains the high surface area of PRINTEX 90 (341 m².g⁻¹), whose
 252 particles are small (25 nm) compared to FLAMMRUSS 101, whose surface area is 24.4 m².g⁻¹
 253 because of large particles of 136 nm. We note that the S_{BET} of soot coming from hydraulic oil
 254 fire is slightly lower (53.3 to 54.2 m².g⁻¹) than the other soot produced with PMMA and heptane
 255 (75.5 to 97.9 m².g⁻¹), due to larger diameters of their primary particles. The elemental oxygen
 256 content [O]_{diff} ranges between 6.4 wt. % and 11.8 wt. %, in agreement with values commonly
 257 reported in the literature [20,48]. The oxygen content is higher (up to 10 wt. %) in soot than in
 258 carbon blacks, which are known to be mostly composed of elemental carbon with oxygen
 259 concentrations lower than 2 wt. %. The oxygen concentration at the surface of the particles
 260 [O]_{XPS} (Table 2) is in good agreement with the oxygen content found in the bulk [O]_{diff},
 261 indicating a homogeneous repartition of oxygen within the particles.

262 Global porosity ε (eq. 4) has been estimated using true density ρ_{true} composing the
 263 material of soot particles, the sample mass m_{sample} , the radius r and height H of the cylindrical
 264 soot pellet or of the glass container for the uncompacted samples. For soot pellets, the global
 265 porosity ε_{pellet} ranges between 29% and 66%. This wide range of values probably results from
 266 different adhesion properties of each sample during the compaction process. The global
 267 porosity of the powdered soot samples ε_{powder} is around 96% for all samples, close to typical
 268 soot cake porosities reported on HEPA filter [6].

$$269 \quad \varepsilon = 1 - \frac{m_{sample}}{\pi r^2 H \rho_{true}} \quad (\text{Eq.4})$$

270 *b. Water isotherms of soot particles produced under different fire conditions*

271 Fig. 6 presents the gravimetric water adsorption isotherms for soot compacted into
 272 pellets. The water uptakes are obtained considering a reference mass $m_{reference}$ as the mass of
 273 sample at RH=0%. Overall, all the samples present the same slopes and the water uptakes range
 274 from 2.4% and 3.6% (at RH=90%). This results from similar physicochemical properties of all
 275 soot in terms of structure and composition. From RH= 0% to 80%, the isotherms are of Vth type
 276 according to the IUPAC classification [49]. They present a rather slight convex curvature at RH
 277 < 30%. On the isotherms, this convexity combined with a positive slope is characteristic of low

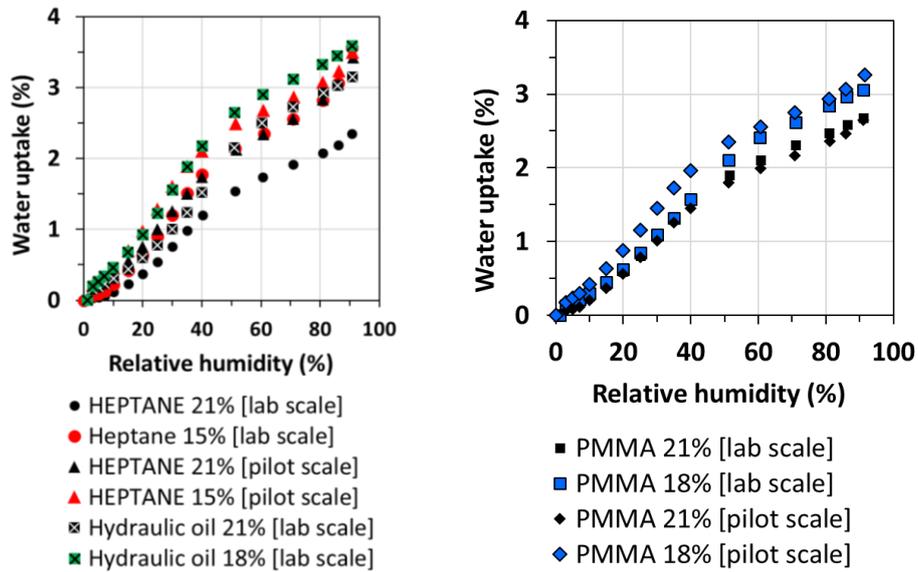
Table 2: Summary of the physicochemical properties of soot and carbon black samples studied

Samples	ρ_{true} ($\text{kg}\cdot\text{m}^{-3}$)	d_{pp} (nm)	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	$[\text{O}]_{\text{diff}}$ (wt.%)	$[\text{O}]_{\text{XPS}}$ (wt.%)	ϵ_{pellet} (%)	ϵ_{powder} (%)
Soot							
Heptane 21% (lab scale)	1780±20 ¹	35.1±1.3	75.5±0.7	7.6±0.8	7.4	62±3	96±1
Heptane 15% (lab scale)		22.8±0.5	97.9±2.3	11.8±1.2	8.8	54±4	
PMMA 21% (lab scale)	1492±12 ¹	39.9±0.8	79.3±1.1	6.7±4.8	9.9	54±4	
PMMA 18% (lab scale)		32.2±0.8	84.4±1.2	9.2±0.6	8.1	29±7	
DTE Medium oil 21% (lab scale)	1593±336	42.1±1.2	53.3±1.1	9.2	8.8	58±10	
DTE Medium oil 18% (lab scale)		38.6±1.1	54.2±1.2	9.9±0.4	9	56±10	
Heptane 21% (pilot scale)	1780±20 ¹	34.1±1.3	69.5±0.7	6.8±0.8	n.d.	66±3	
Heptane 15% (pilot scale)		29.9±0.9	86.9±1.2	9.1±0.6		58±4	
PMMA 21% (pilot scale)	1492±12 ¹	35.9±1.1	69.2±1.4	6.4±0.8		59±4	
PMMA 18% (pilot scale)		37.2±1.2	63.7±1.4	7.1±1.8		52±4	
Carbon blacks							
PRINTEX 90	1783±45	25±1	340.0±1.6	1.1	n.d.	62±5	88±2
FLAMMRUS 101	1712±85	136±8	24.4±0.1	2.1		71±4	78±3
COLOUR BLACK FW200	1800 ²	21±2	506±2.0	18.6±0.2		54±1	-

¹ From [30]

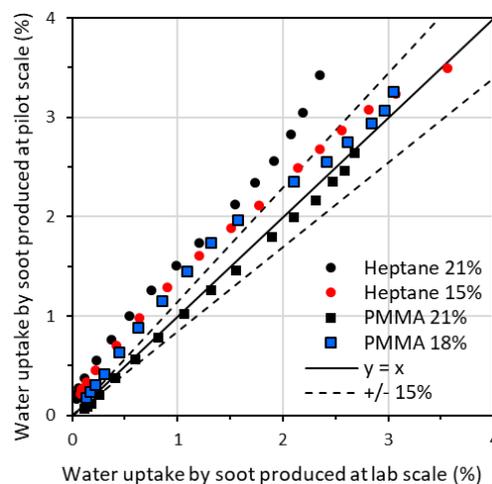
² From manufacturer

277 interactions of water at the surface, with locally high interaction with some hydrophilic
 278 adsorption sites of the soot surface [50]. A slight inflexion point is observed at RH=80% for
 279 the heptane 15% soot obtained at pilot scale (Figure 6 left, red triangles), revealing the
 280 beginning of capillary condensation.



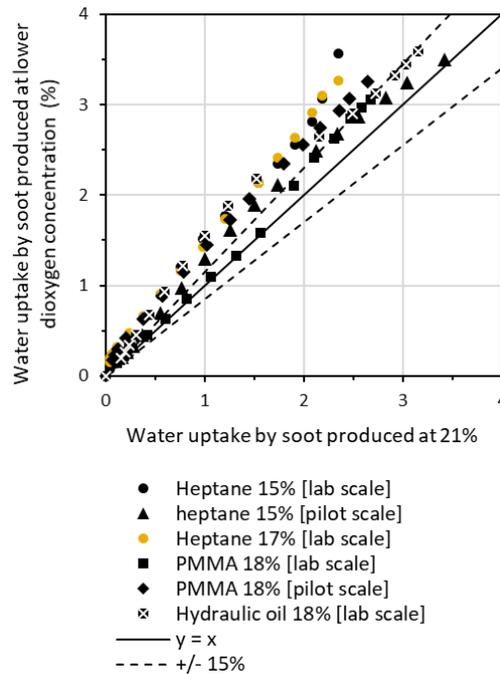
281
 282 Figure 6: Water adsorption isotherms for soot produced with liquid fuels (left) and PMMA (right)

283 The water uptakes measured on the DTE hydraulic oil soot samples are slightly higher
 284 than for the heptane and PMMA soot samples. Figure 7 compares the water uptakes obtained
 285 on fire soot samples produced at laboratory scale and at pilot scale. Except for the heptane soot
 286 produced at 21% of O₂ concentration, water uptakes are globally similar whatever the scale,
 287 with a maximal difference of ±15%. For the considered fuels, fire scale has no major influence
 288 on the water adsorbing properties.



289
 290 Figure 7: Comparison between water uptakes of soot samples produced at pilot and laboratory scale

291 Figure 8 compares the water uptakes on soot produced at 21% of O₂ concentration
 292 (ambient air value) with those produced at depleted O₂ concentrations (15%, 17% and 18 %),
 293 which adsorb up to 50% more water than soot produced at ambient concentration (see Figure
 294 SI-1 in supplementary information). This highlights the significant modification of size
 295 (decrease of primary particle size and increase of specific surface area) and composition
 296 (increase of oxygen content) of soot particles with decreasing oxygen concentration reported in
 297 Table 2 and in agreement with previous findings [14,51]



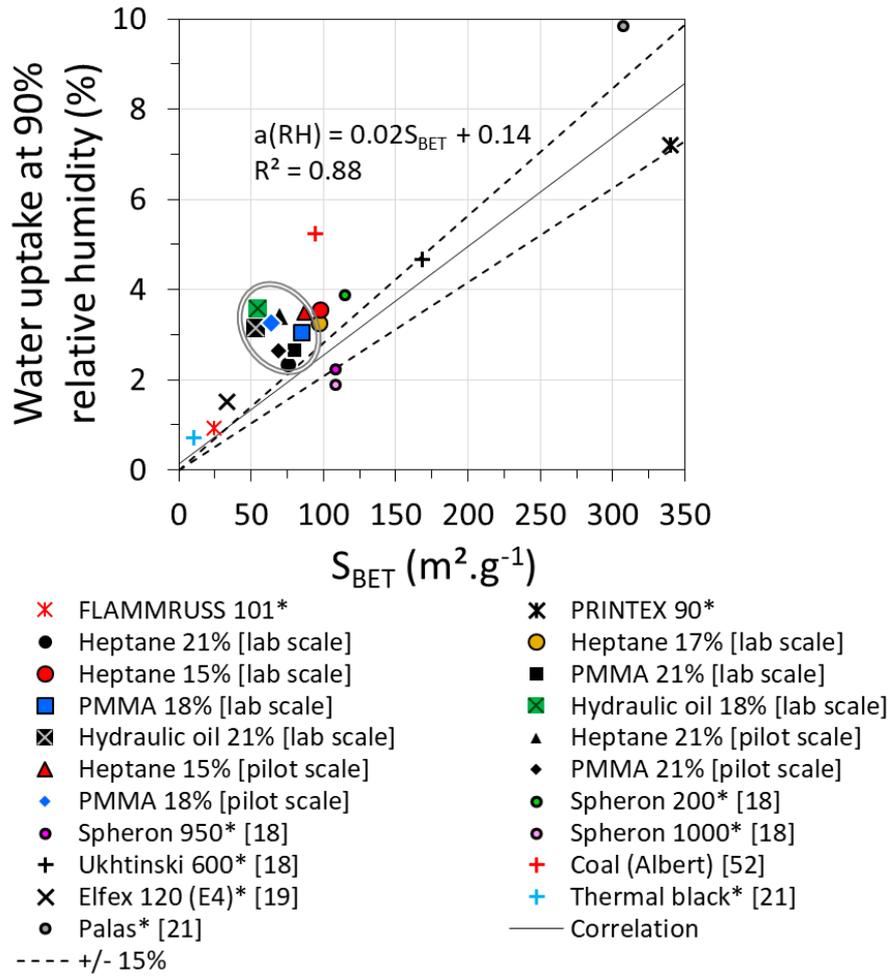
298

299 Figure 8: Comparison between water uptakes obtained for soot samples produced at depleted oxygen
 300 concentrations (15-18%) and ambient oxygen concentration (21%)

301 *c. Influence of specific surface area and oxygen surface content of water*
 302 *uptake*

303 Figure 9 presents the water uptakes obtained at the maximal RH of 90% as a function
 304 of the specific surface area, for all fire soot samples and for PRINTEX 90 and FLAMMRUSS
 305 101. These carbon black samples are mostly composed of elemental carbon. Their water
 306 adsorption isotherms are of type III (see supplementary information, Figure SI-2), which
 307 indicates low carbon black-water interactions and a water uptake related to the specific surface
 308 area only. Additional data on carbon black samples available in the literature - whose
 309 compositions are globally similar to our samples - are also plotted in Fig. 10 (identified with an
 310 asterisk “*” [18,19,21,52]). Over the whole specific surface area range, soot particles present
 311 higher water uptakes than carbon blacks and do not follow the linear correlation proposed on

312 Fig.10. Those discrepancies between soot and carbon blacks can be explained, beyond the
 313 geometric surface associated to the cake structure, by their specific chemical composition.



314

315 Figure 9: Effect of specific surface area on water uptake at 90% of relative humidity

316 To assess the influence of the sample composition on the water sorption capacity, water
 317 uptake can be expressed as the number of water statistical monolayers (ML) needed to cover
 318 entirely the sample surface (Eq. 5). This unravels the effect of the surface area from the
 319 chemical composition:

320

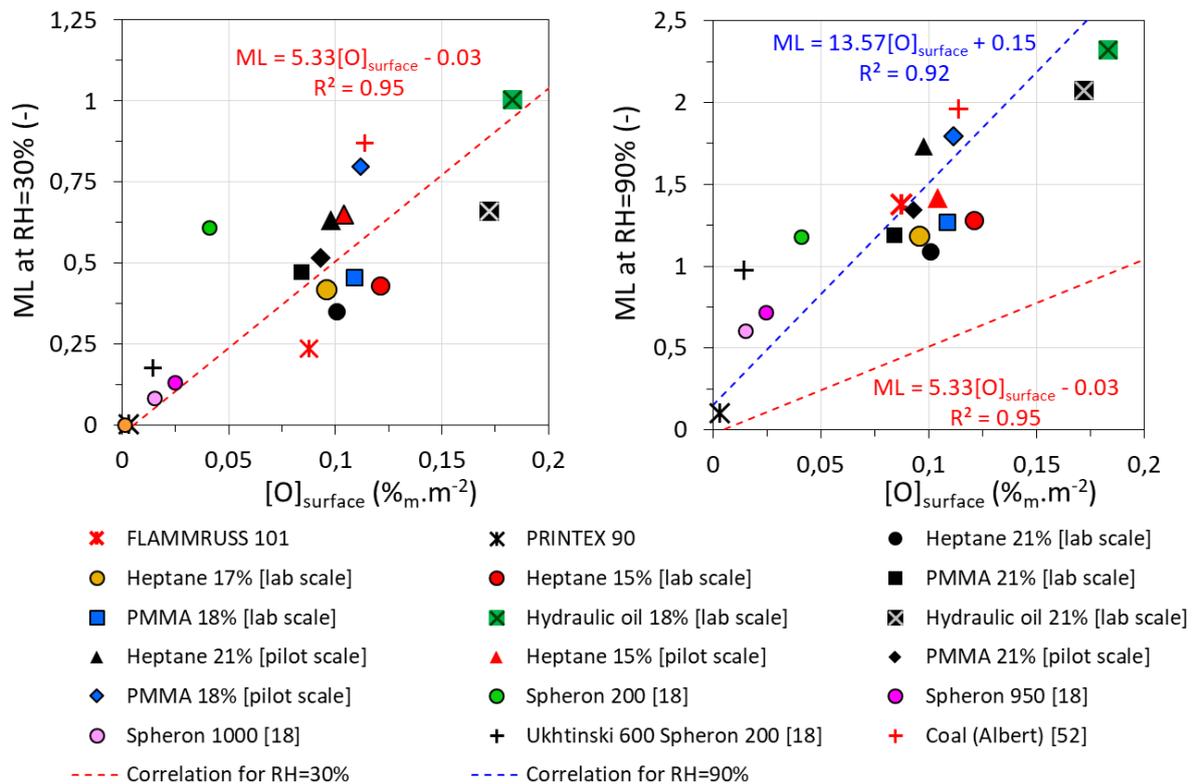
$$ML = \frac{(a(mmol \cdot g^{-1}) \times 10^{-3}) \times N_A(mol^{-1})}{\frac{S_{BET}(m^2 \cdot g^{-1})}{\sigma_{H_2O}(m^2)}} \quad (Eq. 5)$$

321 Where σ_{H_2O} is the surface occupied by a water molecule ($1.05 \cdot 10^{-19} m^2$), a the amount of
 322 adsorbed water per mass of sample, N_A the Avogadro number ($6.022 \cdot 10^{23} mol^{-1}$) and S_{BET} the
 323 specific surface area ($m^2 \cdot g^{-1}$).

324 Figure 10 shows the evolution of ML with the surface concentration of oxygen $[O]_{\text{surface}}$,
 325 calculated as the mass of oxygen per surface area (Eq. 6).

$$326 \quad [O]_{\text{surface}} (g \cdot m^{-2}) = \frac{[O]_{\text{diff}}(\text{wt.}\%)}{100 \cdot S_{\text{BET}}(m^2 \cdot g^{-1})} \quad (\text{Eq. 6})$$

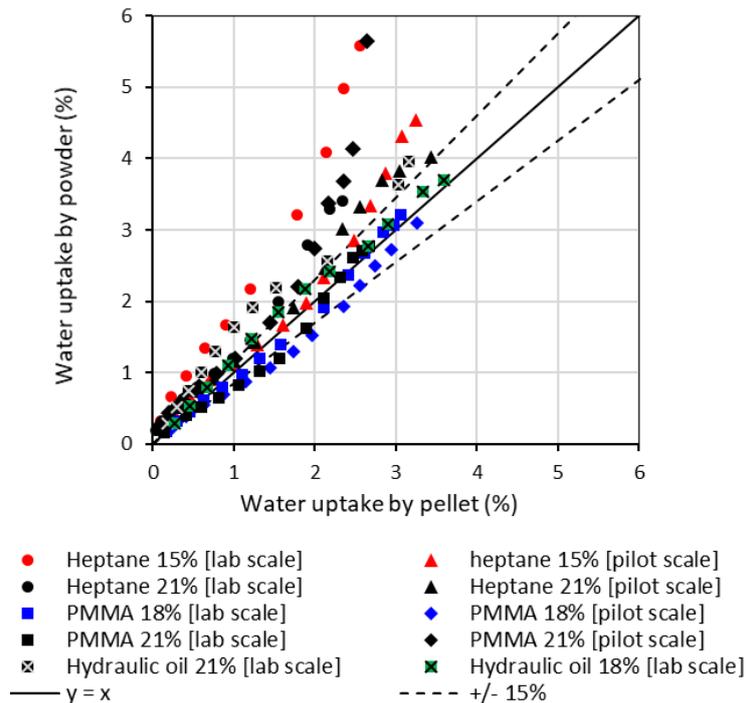
327 The oxygen content is known to significantly influence the water sorption [23]. The
 328 oxygenated chemical functions located at the surface strongly interact with water molecules,
 329 especially in the range of low humidity where they represent the energetically most favorable
 330 adsorption sites [50]. To highlight this effect, we have plotted ML at RH= 30% and RH= 90 %
 331 (left and right sides on Fig. 10 respectively) as a function of $[O]_{\text{surface}}$ for all our samples and
 332 those available in the literature. ML linearly increases with $[O]_{\text{surface}}$ with a slope of 5.33
 333 (RH=30%) and 13.57 (RH=90 %). This clearly shows that the oxygen concentration at the
 334 surface significantly enhances the adsorption process, with a similar physico-chemical
 335 mechanism within relative humidity range 30-90 % (as a same linear dependence is observed
 336 at RH= 30 % and 90 %).



337
 338 Figure 10: Evolution of the number of ML with the surface concentration of oxygen, at RH = 30% (left) and RH
 339 = 90% (right)

340 Figure 11 compares, for each relative humidity step (+/- 1%), the water uptakes obtained
 341 for the pellets with the DVS microbalance and for the powders with the 3FLEX analyzer (the

342 corresponding water adsorption isotherms are available for 3FLEX as supplementary
 343 information, Fig. SI-3). This figure shows that water uptakes for powder and compacted
 344 samples are globally equivalent in a +/- 15% interval. However, exceptions can be observed for
 345 heptane 15%, heptane 21% and PMMA 21% [pilot scale], where adsorption is higher for
 346 powder than for pellet, especially at high water uptake (related to higher relative humidity).
 347 This could be explained by different mesostructures of these soot samples when they are
 348 characterized in pellet or in powder forms, changing the surface and volume available for water
 349 adsorption.



350

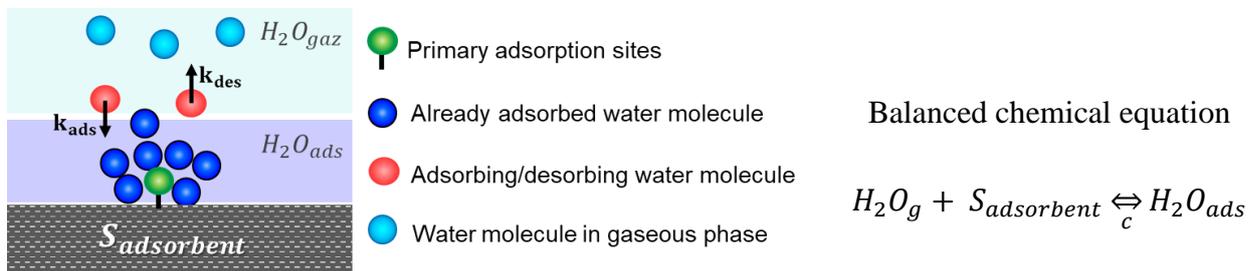
351 Figure 11: Parity diagram comparing the water uptakes between pellets and powders at different humidity steps

352 4. Discussion

353 Until now, the water sorption on carbon systems have been mostly modelled for
 354 activated carbon or carbon/zeolite [53] whose isotherms are systematically of V^{th} type. Several
 355 common water sorption models have been established for such isotherms, considering a primary
 356 adsorption on specific hydrophilic surface sites followed by adsorption on already adsorbed
 357 water molecules. This second adsorption process is driven by water-water interactions, which
 358 are, overall, more favorable than those between water and a globally hydrophobic carbonaceous
 359 surface. Being an associating fluid, water can finally fill in the micro-and-mesoporous pore
 360 volume. Unlike activated carbon, soot particles are made of non-porous hydrophobic carbon,

361 porosity being only due to interstitial spaces between the primary particles in the soot cakes,
 362 which also varies with the sample conformation (powder or pellet). The surface of soot is mostly
 363 hydrophobic, with some hydrophilic adsorption sites related to the presence of surface oxygen.
 364 As previously mentioned, one of the most suitable sorption model for such porous solid is the
 365 Dubinin-Serpinsky (DS) one [54,55]. This model describes a mechanism of water clusters
 366 formation on the adsorbent surface sites, which can be followed by a pore volume filling
 367 [56,57]. In the DS model, the adsorption process is considered as an equilibrium state of a
 368 chemical reaction between water molecules in the gaseous phase H_2O_{gas} and the adsorption sites
 369 located on the adsorbent surface $S_{adsorbent}$ (Figure 12). Those sites can be primary or secondary,
 370 corresponding respectively to the initial number of hydrophilic sites a_0 ($\%g.g^{-1}_{adsorbent}$) and the
 371 already adsorbed water molecules a per gram of sample (expressed here in terms of $\%g.g^{-1}$
 372 $_{adsorbent}$). This equilibrium is formalized by the equilibrium constant c (defined as the ratio
 373 between kinetic constants associated to adsorption k_{ads} and desorption k_{des}), enabling to express
 374 a , the total amount of adsorbed water (Eq. 7), including the water vapor relative pressure h .

375
$$c = \frac{k_{ads}}{k_{des}} = \frac{a}{ha_0} \quad (\text{Eq. 7})$$



376 Figure 12: Scheme of the proposed mechanism of water adsorption and formula used to express the Dubinin-
 377 Serpinsky model

378 Among all the DS model versions [24], the second version, commonly called DS2, has
 379 the simplest analytical form and takes into account the limitation of adsorption with the water
 380 uptake due to the steric hindrance. To this aim, a dimensionless and strictly positive factor ($1-$
 381 ka), decreasing with the adsorbed water amount, has been added to the original DS equation
 382 (Eq. 8). The constant k has therefore a value that ranges from 0 to strictly inferior to $1/a$. This
 383 constant corresponds to the proportion of water molecules which does not act anymore as a
 384 secondary adsorption site (steric hindrance). It leads to the analytical form of 2nd version of DS
 385 model (eq. 8).

386

$$a = c(a_0 + a)h(1 - ka) \quad (\text{Eq. 8})$$

387 Where k is the coefficient related to the steric hindrance due to the formation of water clusters
 388 ($\%g_{\text{adsorbent}} \cdot g^{-1}$). The adsorption isotherms obtained in the present study have all been
 389 successfully fitted with the DS2 model in the relative humidity range of 0%-90% (Fig. SI-4).
 390 Fitted parameters k , a_0 and c for all samples are also available in Table SI-3, with regression
 391 coefficients R^2 all above 0.99. This indicates a unique adsorption process consisting in the
 392 formation of water clusters on few hydrophilic sites, which we assume to occur on the oxidized
 393 surface sites.

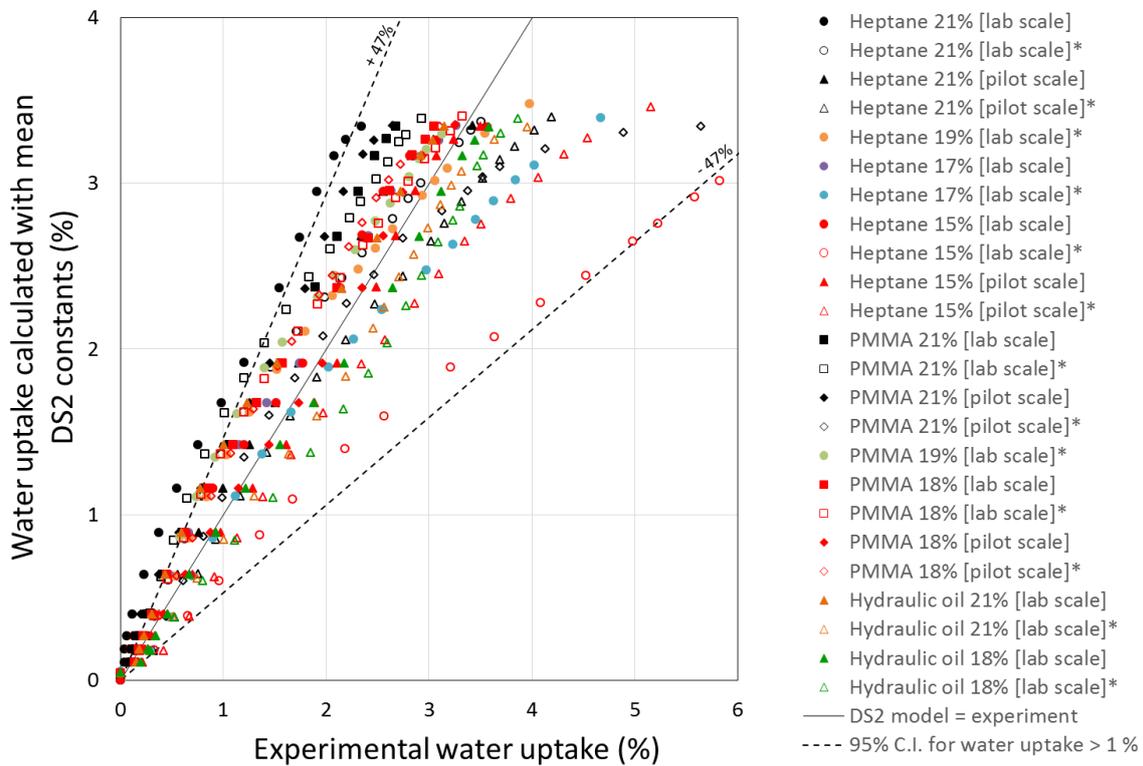
394 The fitted values of k are 0.24 ± 0.02 and 0.14 ± 0.03 for pellets and powders, respectively. The
 395 higher k value for pellets is a consequence of a limited secondary adsorption process, indicating
 396 a higher steric hindrance to clusters formation compared to powders. This is likely due to the
 397 higher compaction of the pellets, which facilitates the blocking of interstitial spaces between
 398 the soot particles. Decrease of k values is consistent with the increase of mean concentrations
 399 of primary adsorption sites a_0 (in $\%g \cdot g^{-1}_{\text{adsorbent}}$), from $1.0\% \pm 0.4\%$ for pellets to $2.6\% \pm 0.4\%$
 400 for powders. The lower value of a_0 for pellets indicates a lower accessibility to the adsorption
 401 sites by the filling of the pores where the primary adsorption sites are located, while more sites
 402 are available in powders. The mean values of equilibrium constant c , corresponding to the ratio
 403 of the kinetic constants between adsorption and desorption processes, are 2.6 ± 0.4 and $1.6 \pm$
 404 0.4 for the pellets and powders respectively. Taking into account their uncertainties, these
 405 values remain quite close and, at this stage, we cannot explain such a slight difference in the
 406 kinetic constant without any further investigations.

407 As previously reported in the literature [6], porosity of soot cake formed at HEPA filters surface
 408 are generally between those considered in the present study for pellets (mostly 50-60%) and
 409 powder (95%). To provide useable values of k , a_0 and c that could be implemented in clogging
 410 models for similar kinds of hydrophobic soot [5,58], we have averaged the fitting parameters
 411 k , a_0 and c of the 22 studied samples, whether compacted into pellet or not. These values are
 412 reported in Table 3, along with their standard deviation. Figure 13 presents the computed water
 413 uptakes using these averaged values and deviations plotted against the experimental water
 414 uptakes for all soot samples. We observe that 95% of the water uptakes (limited in the present
 415 case to water uptake values higher than 1%) can be satisfactorily represented by the DS2 model
 416 using these averaged parameters, within a confidence interval of $\pm 47\%$.

Table 3: Calculated values from 22 water adsorption isotherms

	k (%)	a_0 (%g · g _{adsorbent} ⁻¹)	c (-)
Mean value	0.20	1.54	2.23
Standard deviation	0.056	0.85	0.69
Expanded uncertainty for a 95% confidence interval	0.012	0.18	0.15

418



419

420 Figure 13: Comparison between DS2 model, computed according to mean constants, and experimental water
 421 uptakes

422

5. Conclusion

423 This study aimed at measuring the water uptake in soot cakes representative of those formed
 424 on HEPA filters during fire occurring in a nuclear plant. For this purpose, soot was produced at
 425 laboratory and pilot scales with different fuels - heptane, PMMA and hydraulic oil-
 426 representative of fuels encountered in a real nuclear plant. The physicochemical properties of
 427 these samples have been determined *ex situ* with analytical techniques providing the specific

428 surface area, the primary particle diameters and the oxygen contents, found respectively in the
429 ranges of $52 \text{ m}^2\cdot\text{g}^{-1} - 100 \text{ m}^2\cdot\text{g}^{-1}$, $22.3 \text{ nm} - 43.3 \text{ nm}$ and $6.7\text{wt. \%} - 9.9 \text{ wt. \%}$. We have shown
430 that these physicochemical properties are only slightly influenced by the fire scale, the fuel
431 type, or the O_2 concentration of the oxidizing gas. Using gravimetric and manometric
432 techniques, we have measured the water uptake of these samples as well as two additional
433 carbon black samples, let in powder form or compacted into pellets. Gravimetric and
434 manometric approaches have been proven equivalent, with a variation coefficient lower than
435 10% for the whole relative humidity range (0%-100%). The adsorption isotherms of soot are of
436 V^{th} type and present maximal water uptakes between 2% and 4% at $\text{RH}=90\%$. Under the
437 investigated conditions, fire scale does not significantly impact the isotherms classification.
438 Two physicochemical properties of soot directly impact the sorption process: the specific
439 surface area and the oxygen concentration per surface area. The very good fit of the
440 experimental isotherms with the second Dubinin-Serpinsky model (DS2) indicates that
441 adsorption occurs by nucleation of water clusters on few oxidized and hydrophilic surface sites.
442 The DS2 parameters have been obtained for the 22 studied samples, either compacted or as
443 powders, and their average allows for a proper simulation of 95% of the experimental data. This
444 model will contribute to the improvement of simulation codes and consequently to better predict
445 the HEPA filter clogging phenomenon during a fire in nuclear facility. In addition, the use of
446 the second Dubinin-Serpinsky model appears relevant to represent the water sorption isotherms
447 of fire soot.

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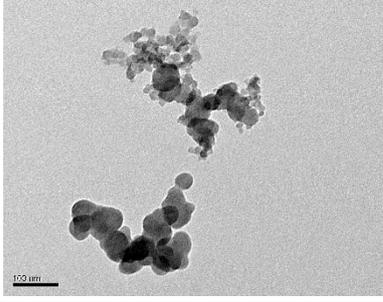
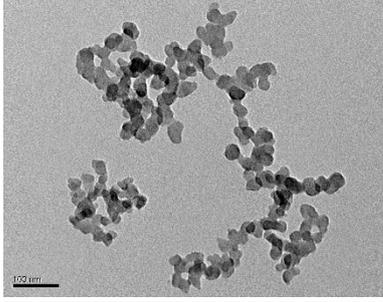
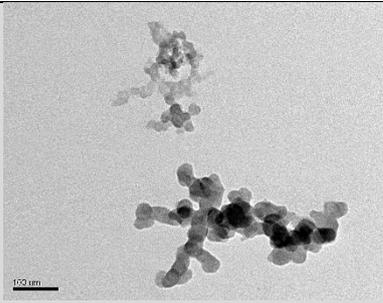
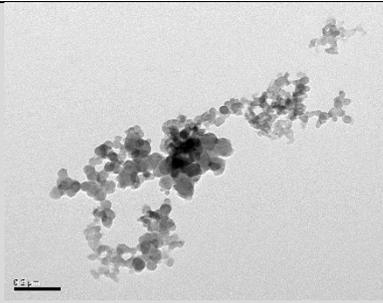
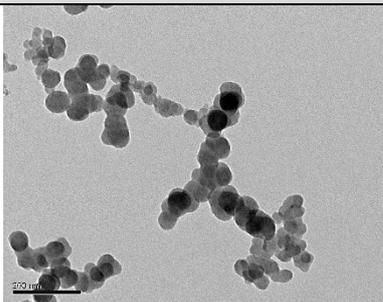
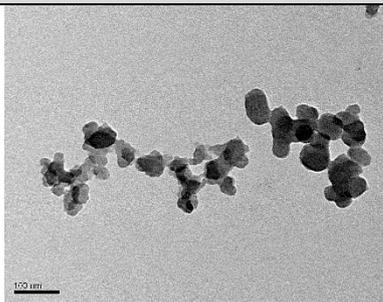
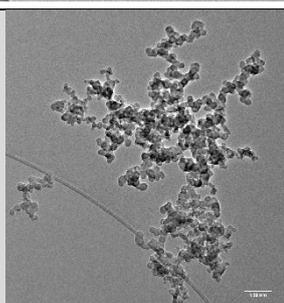
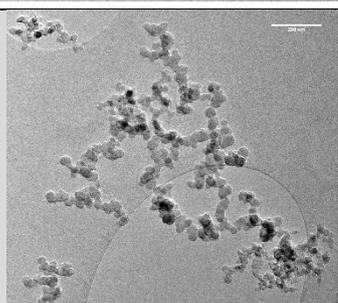
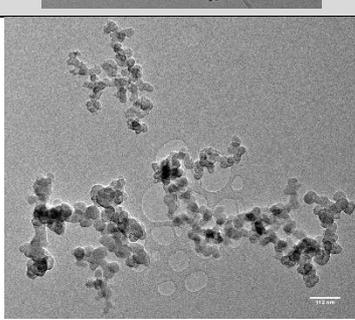
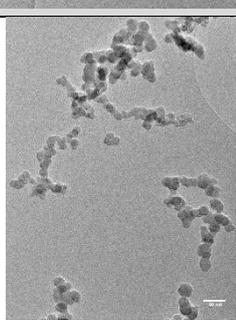
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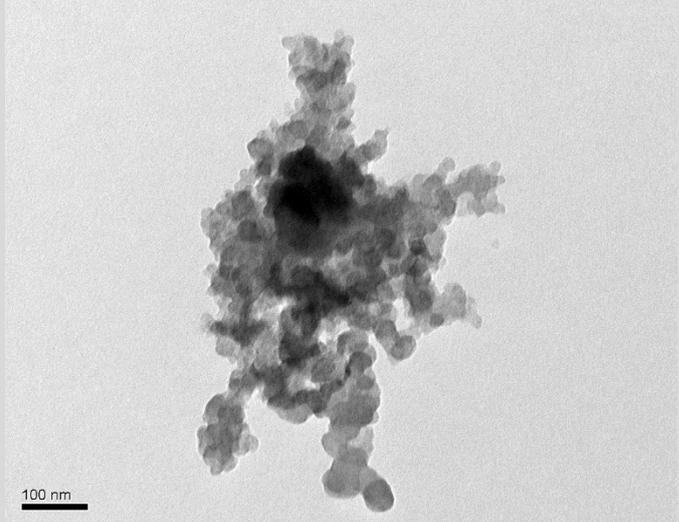
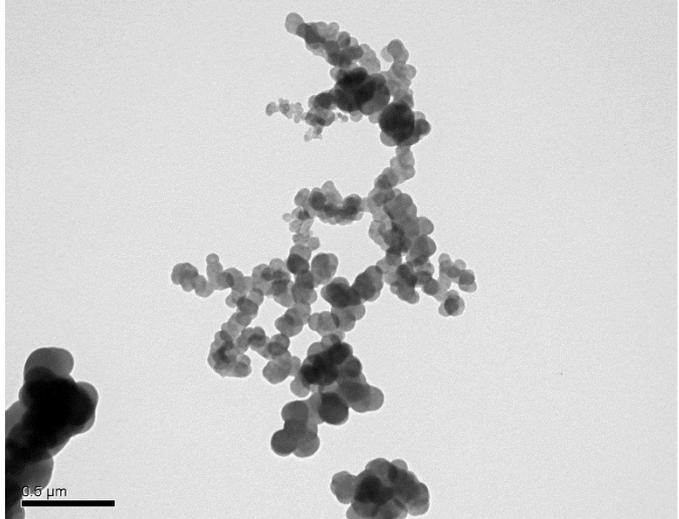
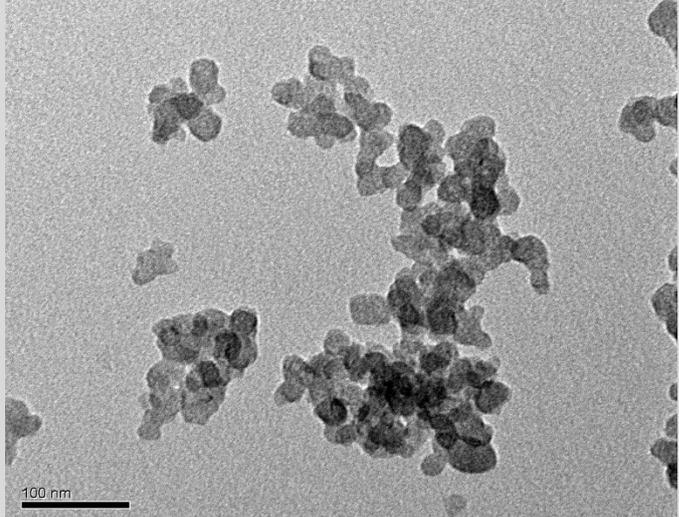
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641 **Supplementary information I: Table SI-1: TEM illustrations of particles composing soot**
 642 **samples**

Samples	TEM illustration	TEM illustration
Soot		
Heptane (lab scale) <ul style="list-style-type: none"> • Left : 21 % [O2] • Right : 15 % [O2] 		
PMMA (lab scale) <ul style="list-style-type: none"> • Left : 21 % [O2] • Right : 18 % [O2] 		
DTE Medium oil (lab scale) <ul style="list-style-type: none"> • Left : 21 % [O2] • Right : 18 % [O2] 		
Heptane (pilot scale) <ul style="list-style-type: none"> • Left : 21 % [O2] • Right : 15 % [O2] 		
PMMA (pilot scale) <ul style="list-style-type: none"> • Left : 21 % [O2] • Right : 18 % [O2] 		

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Supplementary information I: Table SI-2: TEM illustrations of particles composing carbon blacks samples

Samples	TEM illustration
Carbon blacks PRINTEX 90	
FLAMMRUS 101	
COLOUR BLACK FW200	

646

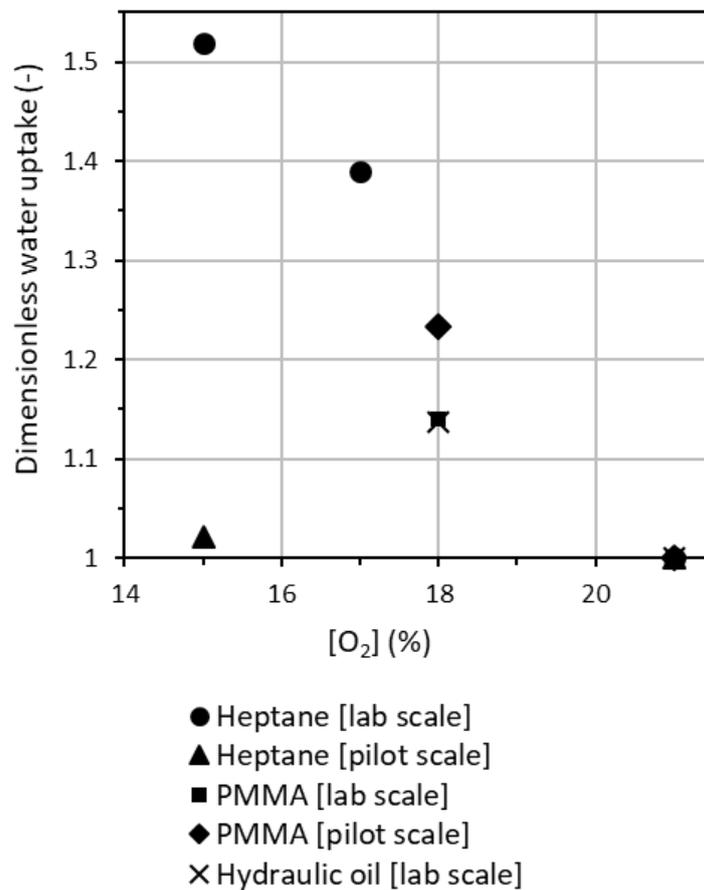
Supplementary information II: oxygen depletion effect on water uptake

647

648 Fig. SII-1 presents the evolution, as a function of dioxygen concentration, of the dimensionless
649 water uptake, defined as ratio between water uptake at considered oxygen concentration and
650 water uptake at dioxygen concentration of 21%. One must notice that this ratio has been
651 computed for the maximum water uptake, i.e. for a relative humidity of 90%.

$$652 \quad \text{Dimensionless water uptake (RH)} = \frac{a_{[O_2]}(RH)}{a_{[O_2]=21\%}(RH)} \quad (\text{Eq. S-1})$$

653

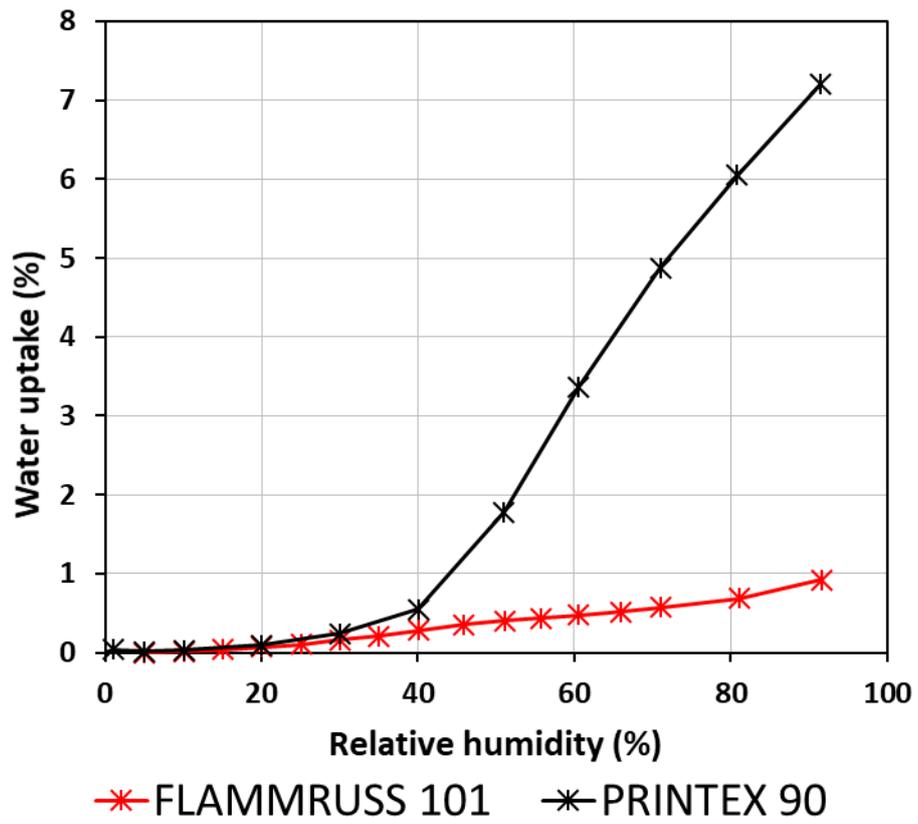


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655 Figure SI-1: Evolution of dimensionless water uptake as a function of dioxygen concentration

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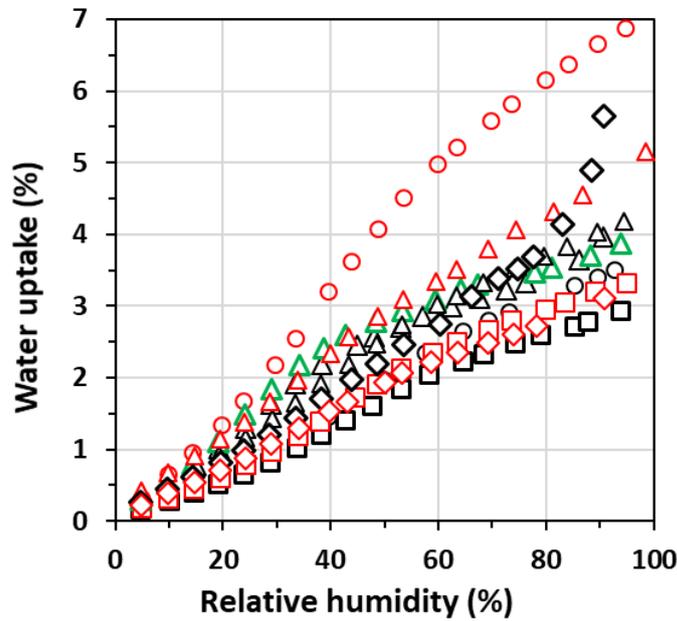
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Figure SI-2: water adsorption isotherms for Flammruss 101 and Printex 90

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- HEPTANE 21% [lab scale]*
- PMMA 21% [lab scale]*
- △ Hydraulic oil 21% [lab scale]*
- △ HEPTANE 21% [pilot scale]*
- ◇ PMMA 21% [pilot scale]*
- HEPTANE 15% [lab scale]*
- PMMA 18% [lab scale]*
- △ Hydraulic oil 18% [lab scale]*
- △ HEPTANE 15% [pilot scale]*
- ◇ PMMA 18% [pilot scale]*

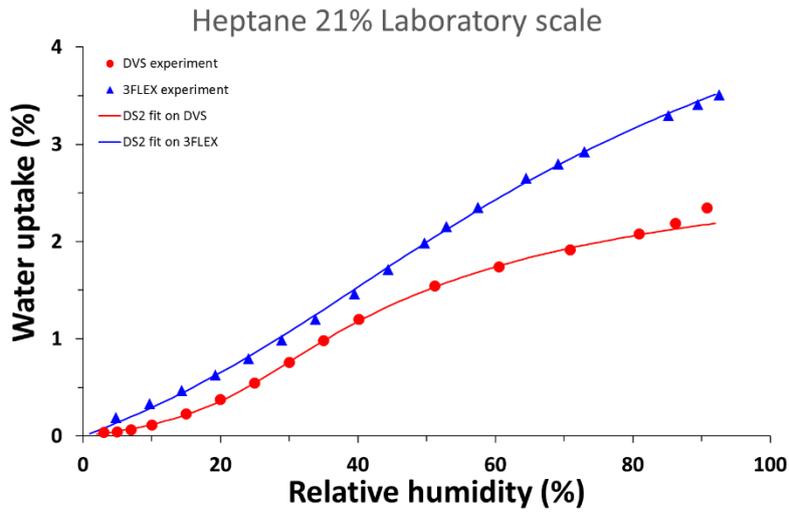
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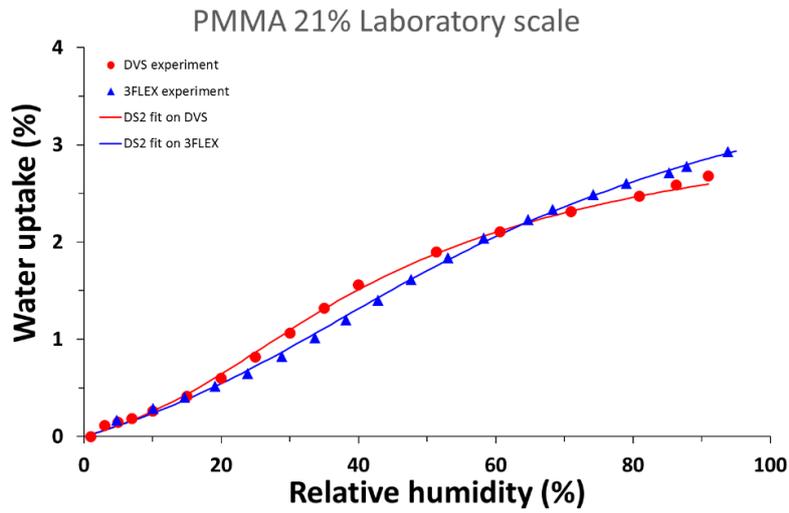
Figure SI-3: Water adsorption isotherms obtained for samples in powder forms

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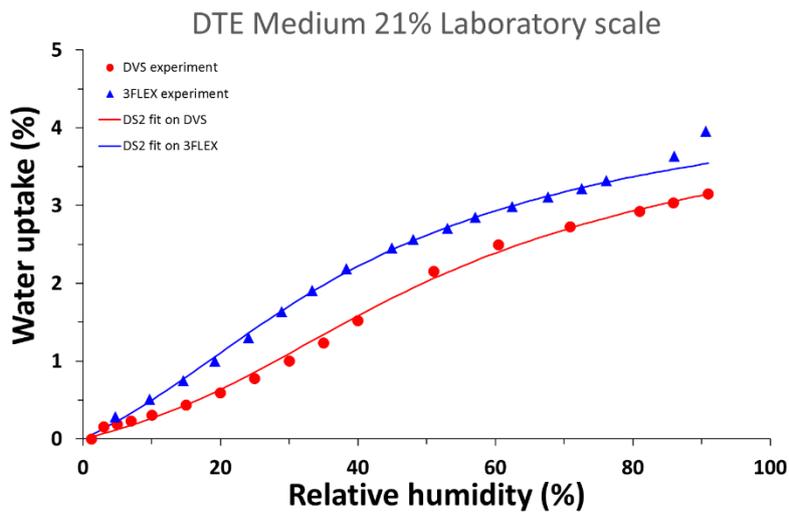
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Figure SI-4: DS2 fitting of experimental water adsorption isotherms

Supplementary information VI: Table SI-3: Summary of DS2 model's constants of studied soot samples

Samples	Pellet form					Powder form				
	ε_{pellet} (%)	k (%)	a_0 (%g·g _{ads.} ⁻¹)	c (-)	R ²	ε_{powder} (%)	k (%)	a_0 (%g·g _{ads.} ⁻¹)	c (-)	R ²
Heptane 21% (lab scale)	62±3	0.323	0.254	3.317	0.999	96 ± 1	0.149	1.688	1.542	0.999
Heptane 15% (lab scale)	54±4	0.242	0.554	3.185	0.997		0.088	2.807	1.884	1.000
PMMA 21% (lab scale)	54±4	0.269	0.711	2.864	0.999		0.197	1.153	1.797	0.999
PMMA 18% (lab scale)	29±7	0.209	1.069	2.242	0.999		0.177	1.354	1.823	0.999
DTE Medium oil 21% (lab scale)	58±10	0.200	0.962	2.276	0.996		0.200	1.632	2.593	0.999
DTE Medium oil 18% (lab scale)	56±10	0.191	1.709	2.297	0.998		0.206	1.246	3.339	0.999
Heptane 21% (pilot scale)	66±3	0.213	1.805	1.876	0.998		0.127	3.822	1.174	0.999
Heptane 15% (pilot scale)	58±4	0.229	1.395	2.825	0.998		0.059	28.323	0.221	0.999
PMMA 21% (pilot scale)	59±4	0.290	0.510	3.143	0.999		0.021	12.910	0.313	0.999
PMMA 18% (pilot scale)	52±4	0.235	1.211	2.801	0.999		0.191	2.170	1.481	0.999
average values	55±10	0.24 ± 0.02	1.0 ± 0.4	2.6 ± 0.4	-	96±1	0.14 ± 0.03	2.6 ± 0.4	1.6 ± 0.4	-