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1 Multi-scale investigation of the effect of γ irradiations on the 2 mechanical properties of cementitious materials

3
4 **M. Robira^{1,2,3}, B. Hilloulin², A. Loukili², G. Potin¹, X. Bourbon⁴, A. Abdelouas³**

5
6 ¹ *Tractebel Engineering – Le Delage, 5 rue du 19 Mars 1962 92622 Gennevilliers CEDEX France*

7 ² *Laboratoire GeM – Ecole Centrale de Nantes, 1 rue de la Noë 44321 Nantes*

8 ³ *Laboratoire SUBATECH – Ecole des Mines de Nantes, CNRS/IN2P3, Université de Nantes 4 rue Alfred*
9 *Kastler 44307 Nantes cedex 3 France*

10 ⁴ *Agence nationale pour la gestion des déchets radioactifs – 1-7, Rue Jean-Monnet – 92298 Chatenay-*
11 *Malabry Cedex*

16 **Highlights**

- 17 - Mechanical properties of gamma irradiated mortar and cement paste were studied.
- 18 - Gamma irradiation induced Physico-chemical and mechanical modification of the
19 uncarbonated cement materials.
- 20 - Water content influence the effect of gamma radiation on mechanical properties.
- 21 - Micro-indentation agrees with macroscopic observations.
- 22

23 **ABSTRACT.**

24

25 We studied the effects of low doses of gamma radiations on physical and hydro-thermo-
26 mechanical behavior of concrete in the context of radioactive wastes storage. Mortar samples
27 were irradiated with a Cs-137 gamma source to perform three-points bending, compression
28 and physical analysis. Dry, humid and carbonated mortars and dry and carbonated cement
29 pastes were used. The structural and mineralogical modifications at microscopic scale due to
30 irradiations are determined. The results show an important drop of mechanical strengths
31 except in the case of carbonated samples. Thus, the hydrated phases of the mortar/cement are
32 likely involved in the degradation of the mechanical properties.

33

34

35 **KEY WORDS:** Radioactive wastes, Microstructure, Mechanical properties, Creep, Image
36 analysis, Gamma irradiation

37

38 1. Introduction

39

40 Concrete is a multi-phases material often used as structural material for the storage and
41 disposal of radioactive wastes [1][2]. As the structures are exposed to different types of
42 radiation (mainly neutrons and gamma), it is essential to understand their effects of on
43 concrete and determine the evolution of its mechanical properties after irradiation over long-
44 term period.

45

46 Concrete behavior under radiations has long been studied mainly under neutron radiations in
47 the case of nuclear power plants. For this radiation type, Hilsdorf [3] showed that the
48 mechanical properties of concrete and particularly the strength characteristics may deteriorate
49 because of nuclear radiations if the cumulated dose exceeds limiting values (1.10^{19} n/cm²).
50 Some authors agreed that RIVE phenomenon (radiation induced volumetric expansion) is the
51 predominant phenomenon which occurs in concrete after irradiation [4]. Kontani [5] suggests
52 neutron or high dose rate gamma radiation effects are mainly concentrated at the level of
53 hydrated and crystalline phases even though gamma radiations have a lesser impact on
54 crystalline phases. Indeed, their effects mainly concern aggregates, suggesting that the
55 variation of the concrete strength would be mainly created by cement paste intrinsic damages
56 due to the volume variations of aggregates. The variation of the mechanical properties of
57 concrete depends therefore on aggregates composition under neutronic radiation. Reviewing
58 literature, Field [6] shows that whatever is the chemical composition of the aggregate type, a
59 variation of the material strength appears only beyond specific threshold. This variation is
60 also observed by Maruyama [7] under gamma radiations but for high doses (2.10^8 Gy). Giorla
61 [8] describes this strength variation as a result of three steps, an initial damage located in the
62 aggregates/paste interface (ITZ), an increase of these damages as a result of the various
63 applied constraints and a propagation of the damages through the paste. However, it is

64 important to note that the variation of mechanical strength is highly dependent on the type of
65 aggregates, studies having mainly been made on siliceous ones. Rosseel [9] describes these
66 variations as a result of the thermal expansion of the aggregates and of the radiolysis drying of
67 the paste. With their numerical model, Le Pape [10] and Maruyama go farther by explaining
68 that the radiation effect occurs in Si-O bonds situated in the CSH phases generating a
69 modification of the porosity of the material. Hence, pre-existing damage before irradiations in
70 the cement phases are aggravated by CSH degradation (modification of the organization of
71 the CSH chains) and volumetric expansion of aggregates after irradiations.

72 However, it is important to note that these conclusions were drawn in the case of high-dose
73 irradiation of cementitious materials, mainly in the case of neutronic radiation. Although
74 some effects of gamma irradiations on cementitious materials have been described in the
75 literature [7][11][12], the degradation mechanisms and their mechanical impact are not well
76 understood yet especially under low gamma irradiations where it is difficult to separate
77 radiation effects and environmental effects. Most of the studies focused on physico-chemical
78 evolutions, mainly because of radiolysis effects. Indeed, concrete is a material including an
79 important part of water that could be affected by the radiations. Water radiolysis is a
80 phenomenon that occurs under ionizing radiation (gamma radiation) and produces many
81 species which can react with each other or with the environment to produce gases especially
82 H_2 [13]. Hydrogen production occurs mainly with the radiolysis of the free water present in
83 macro porosity which can be composed by connected or unconnected pores [14]. Hence, H_2
84 gas produced by water radiolysis can be evacuated in the case of connected pores but is
85 trapped in the material in the case of unconnected pores. Bouniol [15][16] indicates that in a
86 closed system saturated in gas, a gas/solution equilibrium occurs. Therefore, the H_2 gas stays
87 in solution and reacts with other radicals according to the Allen cycle, in particular in the
88 smaller pores [17]. Indeed, if pore diameters are smaller than the radicals distribution area,

89 then the radicals reactions with each other are increased. Hydrogen gas production in closed
90 porosity can create constraints inside the material and generates cracks weakening the
91 concrete. However, porosity can be directly impacted by atmospheric carbonation. Indeed,
92 Groves and Kobayashi [18][19] showed carbonation deteriorate C-S-H and portlandite phases
93 which are the main phases constituting cement paste. Pihlajavaara and Houst [20][21]
94 described this deterioration as an important decrease of the material porosity impacting the
95 mechanical strengths and the gases production.

96

97 The main objective of the present work is to accurately understand the effects of low dose
98 gamma irradiation on the mechanical properties of cementitious materials. Such study, at the
99 crossroads of mechanical and chemical engineering, appears to be important in the context of
100 long-term nuclear waste storage. For this purpose, cementitious samples were irradiated under
101 gamma irradiations with a dose rate of approximately 8 Gy/min. Mechanical properties, in
102 particular compressive and bending strengths, were measured and compared to those
103 measured on pristine samples in regards with physico-chemical evolutions at a smaller scale.

104

105 **2. Materials and methods**

106

107 **2.1 Sample conditioning and irradiation conditions**

108

109 Samples were prepared with CEM I 52.5 (ULTRACEM 52.5 N SR3PM) and 0/4 mm
110 calcareous sand (INST. CRIB. LAV. BARVILLE) (table 1).

111

112 **Table 1.** Mortar compositions

Cement (kg/m ³)	Calcareous Sand 0/4 (kg/m ³)	Water (kg/m ³)	W/C	Paste volume (%)	Air (L/m ³)
566	1344	270	0.43	45	20

113

114 No silica sand was used to avoid the high reactivity of silica under irradiations and possible
 115 RIVE (Radiation Induced Volumetric Expansion). Organic additives like superplasticizer
 116 were not used to prevent a premature degradation by irradiations. Indeed, organic species are
 117 significantly affected by irradiations [22]. This formulation was determined to be as
 118 representative as possible of a high-performance concrete used in nuclear waste storage
 119 facility with a compressive strength close to 70 MPa at 28 days. Three mortar series (dried,
 120 carbonated and humid samples) and two cement paste series (dried and carbonated samples)
 121 were prepared for irradiation experiments (tables 2 and 3).

122

123 **Table 2.** Mortar samples description

Series	Name	Storage in			Irradiation	Storage in air-conditioned room
		sealed conditions	Drying	Carbonation		
Series 1	HM-257kGy-P1	X				X
	HM-257kGy-P2	X				X
	HM-257kGy-P3	X				X
	HM-257kGy-I1	X			X	
	HM-257kGy-I2	X			X	
	HM-257kGy-I3	X			X	
Series 2	DM-257kGy-P1		X			X
	DM-257kGy-P2		X			X
	DM-257kGy-P3		X			X
	DM-257kGy-I1		X		X	
	DM-257kGy-I2		X		X	
	DM-257kGy-I3		X		X	
Series 3	CM-257kGy-P1		X	X		X
	CM-257kGy-P2		X	X		X
	CM-257kGy-P3		X	X		X
	CM-257kGy-I1		X	X	X	
	CM-257kGy-I2		X	X	X	
	CM-257kGy-I3		X	X	X	

124

125

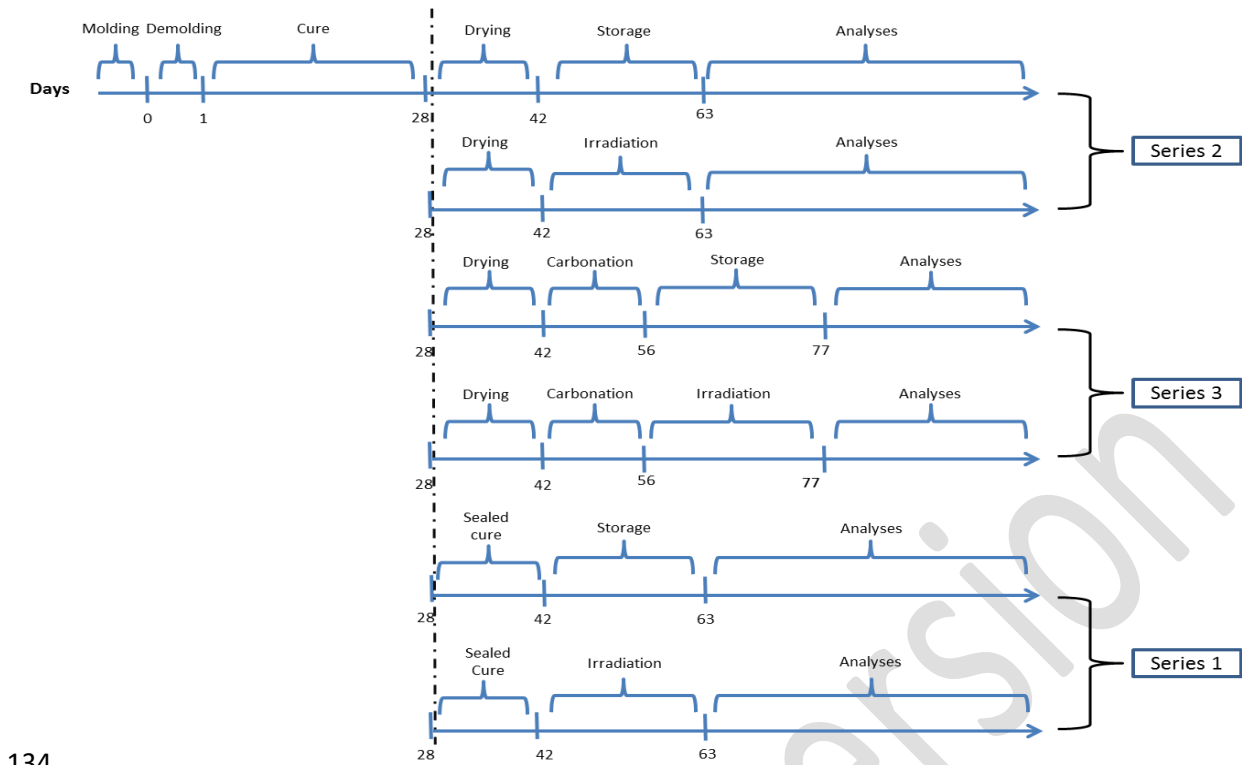
126 **Table 3.** Cement paste samples description

Series	Name	Storage in			Irradiation	Storage in air-conditioned room
		sealed conditions	Drying	Carbonation		
Series 1	DCP-85.7kGy-P1		X			X
	DCP-85.7kGy-P2		X			X
	DCP-85.7kGy-P3		X			X
	DCP-85.7kGy-P4		X			X
	DCP-85.7kGy-P5		X			X
	DCP-85.7kGy-I1		X		X	
	DCP-85.7kGy-I2		X		X	
	DCP-85.7kGy-I3		X		X	
Series 2	CCP-85.7kGy-P1		X	X		X
	CCP-85.7kGy-P2		X	X		X
	CCP-85.7kGy-P3		X	X		X
	CCP-85.7kGy-I1		X	X	X	
	CCP-85.7kGy-I2		X	X	X	
	CCP-85.7kGy-I3		X	X	X	

127

128 Samples names are composed by the sample type (HM : humid mortar, DM : dried mortar,
 129 CM : carbonated mortar, DCP : dried cement paste, CCP: carbonated cement paste), the value
 130 of the cumulated radiation dose (257 kGy for mortar and 85.7 kGy for cement paste) and the
 131 treatment type (P : pristine for unirradiated samples and I : for irradiated samples). The
 132 different cycles of preparation are detailed in figure 1.

133



134

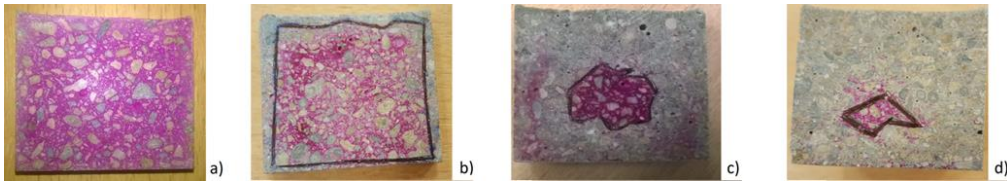
135 **Fig.1.** Preparation cycles of the different series studied.

136

137 Mortar and cement paste prisms, with dimensions of $4 \times 4 \times 16 \text{ cm}^3$, were casted in peek
 138 molds to avoid any metallic contamination due to the mold. After one day of curing under
 139 sealed and ambient conditions ($20 \text{ }^\circ\text{C}$ and 90 % relative humidity - RH), samples were
 140 demolded. They were then cured in lime-saturated water for 28 days. Then, the first series
 141 (series 1) was stored in sealed conditions for 14 days. The prisms were covered by aluminum
 142 foil, placed in airtight plastic bags and stored in ambient conditions. The other two series
 143 (series 2 and 3) were dried during 14 days in a ventilated oven at $45 \text{ }^\circ\text{C}$ to not degrade the
 144 ettringite phase ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26 \text{ H}_2\text{O}$) (a constant mass was measured after 10 days).
 145 After drying, one of the two (series 3) was carbonated in a CO_2 -rich atmosphere at 50 % of
 146 CO_2 and 63 % RH [23]. Samples were almost completely carbonated after 13 days (figure 2).

147

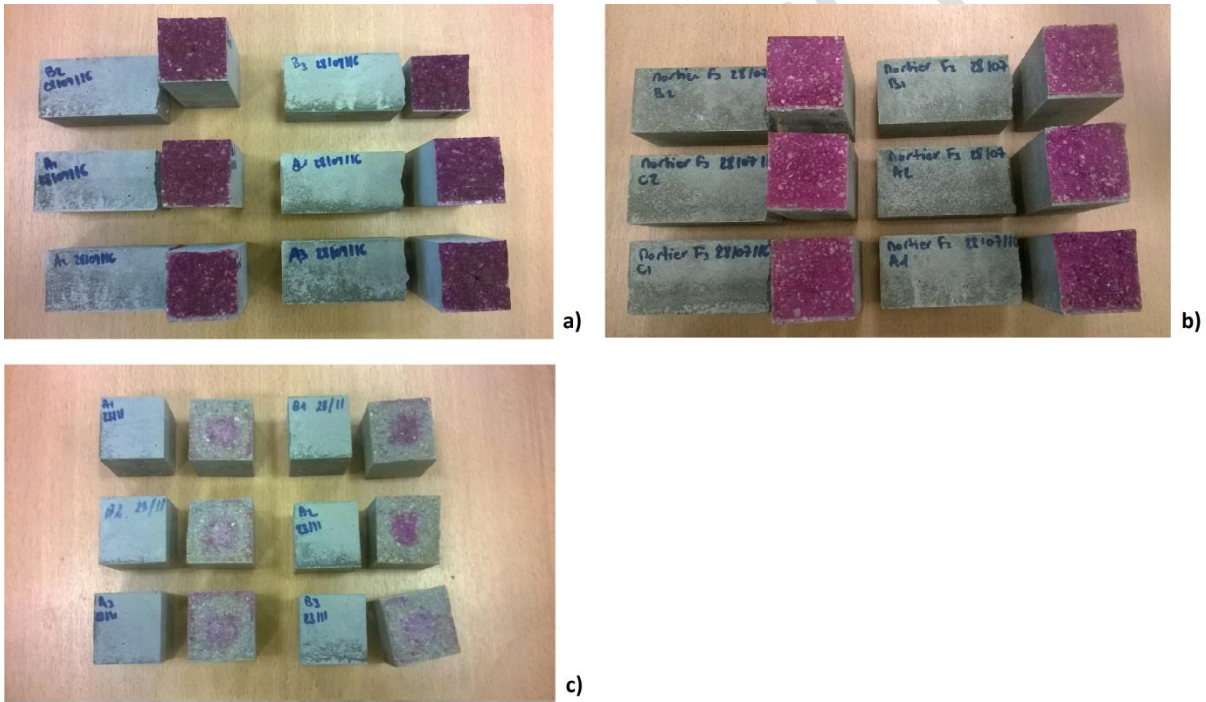
148



149 **Fig.2.** Evolution of the carbonation after 0 a), 1d b), 5d c) and 13 d) days. Carbonated zone in grey and
 150 pristine zone in purple discriminated using a phenolphthalein solution.

151

152 A phenolphthalein test was performed on all samples to confirm the non-carbonation and the
 153 carbonation of the different mortar series (figure 3 and 4). Except for the carbonated series no
 154 carbonation was noticed.

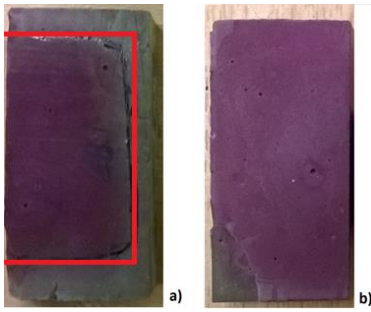


155

156 **Fig.3.** Phenolphthalein test on humid mortar a), dried mortar b) and carbonated mortar c).

157

158



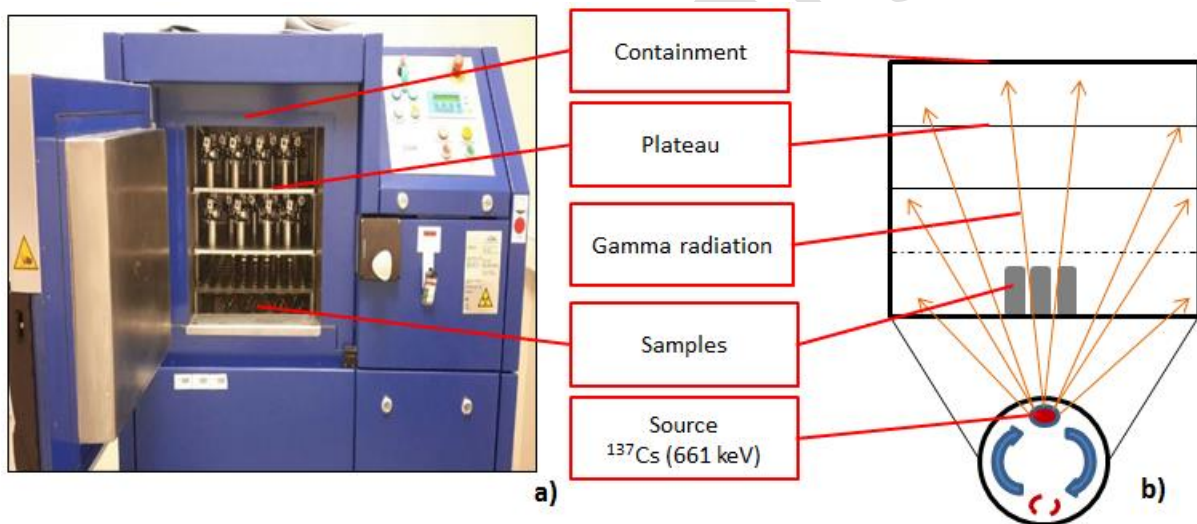
159

160 **Fig.4.** Phenolphthalein test on an half part of a carbonated cement paste slice a) and dried cement paste
 161 slice b) with carbonation front in red line.

162

163 For each series, half of the samples were exposed to γ irradiations in an irradiator with a ^{137}Cs
 164 source, 661 keV, 123.4 TBq (figure 5) during 21 days.

165



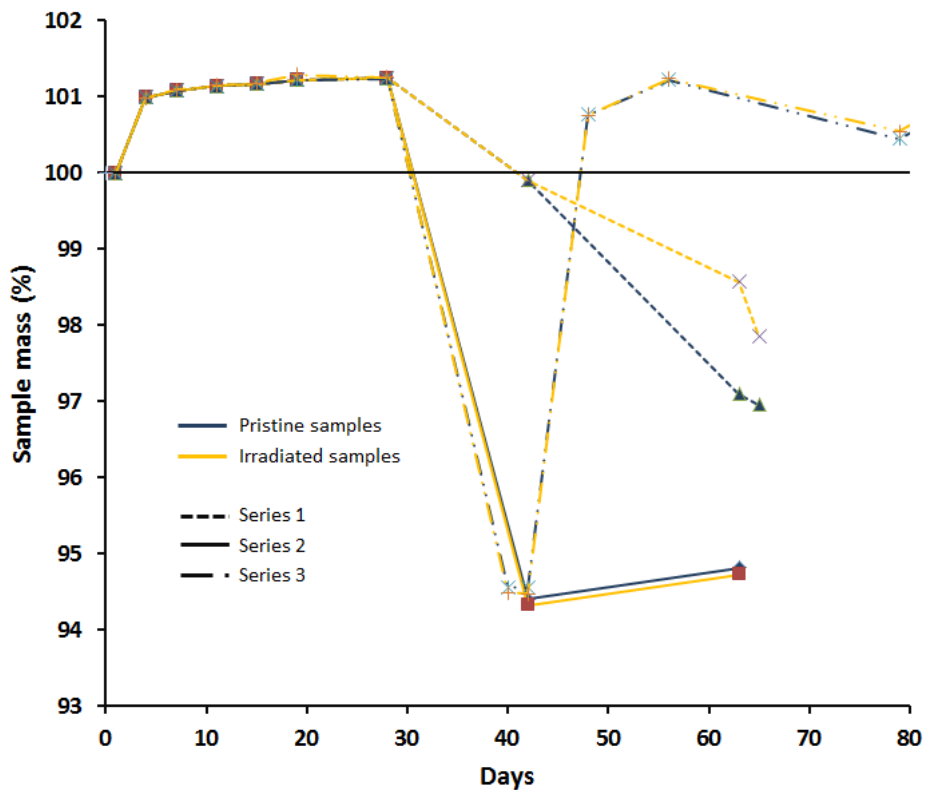
166

167 **Fig.5.** Picture of gamma irradiator a) and schematic representation b).

168

169 The total γ dose received by the specimens was estimated to be around 257 kGy (85.7 kGy in
 170 the case of cement pastes). It was based on a map of the different dose rate realized by Fricke
 171 dosimetry measurement [24]. The other half of the samples was stored in ambient conditions
 172 near the gamma irradiator during the irradiation duration. They were used as references and
 173 compared with the irradiated samples (used to standardized measures). After each step, the
 174 weight samples were monitored to dissociate the direct influence of the irradiation (radiolysis

175 phenomenon) from an eventual drying phenomenon due to irradiations. Mass variations of the
176 mortar prisms are shown in figure 6.



177

178 **Fig.6.** Monitoring of the mass evolution of mortar samples with 100 % corresponding to the mass of
179 mortar pouring. Black straight line corresponding to the initial mass measured after the demolding
180 phase at 24h.

181

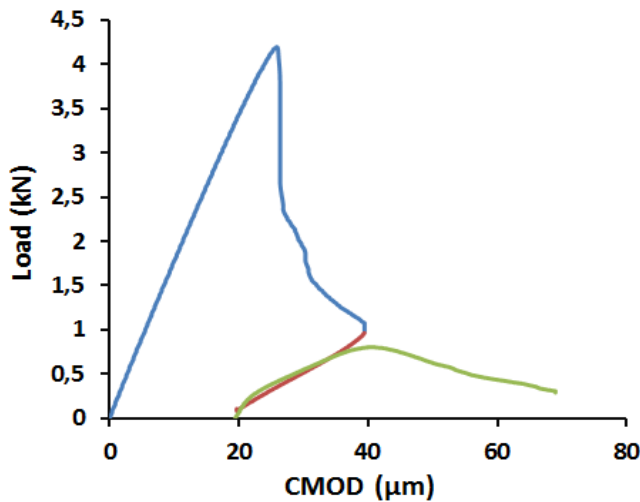
182 2.2 Multiscale analysis

183

184 Three-points bending tests

185 After the irradiation step, a crack-mouth opening displacement (CMOD) control three-point
186 bending test was performed. The sample was centered on top of two 10 cm-distant holders
187 and a force was applied in its center. Small 1 mm wide and 2 mm depth notches were sawn on
188 the face closer to the radiation source of the specimens to initiate cracking from the notch tip.

189 The force was regulated to ensure a CMOD opening rate of 0.1 $\mu\text{m/s}$ up to 40 μm before
190 unloading. An unloading stage was performed on the softening part of the curve and then, the
191 specimens were reloaded until a CMOD corresponding to a residual load of around 0.2 kN.
192 An example of a typical standard curve is shown in figure 7.



193

194 **Fig. 7.** Typical three-points bending curve obtained on mortar sample (MD-257kGy-P2).

195

196 Compression tests

197 After the three-points bending analysis, two $4 \times 4 \times 4 \text{ cm}^3$ cubes were sawn from the residual
198 parts of each prism aside from the central crack. Compression analyses were performed on a
199 press MTS 500 kN. Each cube was placed on a $4 \times 4 \text{ cm}^2$ base. A force with a load rate of
200 2.4 kN/sec was applied until the specimen break to measure the compressive strength.

201

202 Porosity analysis

203 Water and Mercury Intrusion Porosimetry (MIP) tests were performed on slices of the
204 specimens [25]. For water porosimetry, a slice of $2 \times 4 \times 4 \text{ cm}^3$ was used. Three masses were
205 measured:

- 206 - m_1 = mass of the dried sample,
- 207 - m_2 = mass of the sample immersed in water,
- 208 - m_3 = mass of the water-saturated sample.

209 Open porosity was calculated with the following equation:

$$\pi = 100 \times \frac{m_3 - m_1}{m_3 - m_2}$$

210 This method is used to measure the total open pores volume. To know the repartition of the
211 porosity, specimens were analyzed with mercury intrusion. Mercury porosimetry analysis is a
212 progressive intrusion of mercury into a porous structure under stringently controlled pressures
213 using a Micromeritics AutoPore IV-9500 device. Small cubic specimens, with $1 \times 1 \times 1 \text{ cm}^3$
214 dimensions were cut and placed in a penetrometer where a partial vacuum ($70 \text{ }\mu\text{mHg}$) is
215 established. Analysis consist in two step, one on applying a pressure of 30 psi by injecting
216 mercury through the capillary tube with nitrogen and the second on applying a high-pressure
217 (60 kpsi).

218 From the pressure versus intrusion data, the instrument generates volume and size
219 distributions in the material for sizes going of 5 nm to several hundred micrometer by using
220 the Washburn equation [26]:

$$221 \quad d.P = -4\gamma \cos\theta$$

222 with d : pore diameter, P : mercury intrusion pressure, γ : surface tension, θ : liquid solid
223 angle.

224

225 Indentation analysis

226 Micro-indentation testing is a method for measuring elastic and creep parameters of a material
227 at a microscopic scale. A precision diamond indenter is impressed into the material at a
228 specific load. The imprint depth and the test load are used to calculate a hardness value while
229 the unloading curve leads to the indentation modulus determination. Micro-indentation tests
230 were performed on a volume of $2 \times 2 \times 1.5 \text{ cm}^3$ from the middle part of a half of the
231 $4 \times 4 \times 16 \text{ cm}^3$ after the three-point bending test. The aim was to select a location to avoid
232 damage induced by the three-point bending test. Micro-indentation was performed using a
233 Vickers indenter probe over a grid of 20×20 indents spaced by $500 \mu\text{m}$ with a 2000 mN
234 force to investigate a representative surface of $1 \times 1 \text{ cm}^2$ of the mortar sample. Indentation
235 runs were performed under similar relative humidity conditions to avoid the influence of the
236 relative humidity on creep parameters. After measurement, cement paste properties were
237 extracted using hierarchical clustering and then further refined using a method combining the
238 deconvolution of the indentation tests and a 3D microscope image analysis. This method is
239 described in a dedicated paper [27].

240

241 ATR analysis

242 Attenuated total reflection (ATR) is a qualitative technique used in conjunction with infrared
243 spectrometry to measure the changes occurring in a totally internally reflected infrared beam
244 when the beam comes into contact with a sample. Samples can be examined in the solid or
245 liquid without preparation. ATR is a surface analysis which can determine the different
246 phases which constitute a sample. A $1 \times 1 \times 1 \text{ cm}^3$ cube was cut in the center of the prism and
247 analyzed with ATR to estimate the evolution of the different phases after irradiations. Tests
248 were performed on Bruker Tensor 27 analyzer. 16 scans per sample were realized between

249 600 cm⁻¹ and 4000 cm⁻¹ with a 4 cm⁻¹ resolution under ambient atmosphere. Sequences of 16
250 scans were repeated three times on three random areas and averaged.

251

252 **3. Results and discussion**

253 **3.1 Mechanical results on cement paste**

254

255 Compressive and bending strength were determined on cement paste samples. Raw results are
256 shown in table 4. Standardized strengths are then calculated. The mean of irradiated-
257 uncarbonated (DCP-85.7kGy-I1 to DCP-85.7kGy-I3) and irradiated-carbonated (CCP-
258 85.7kGy-I1 to CCP-85.7kGy-I3) samples are normalized in regards with respectively the
259 mean of unirradiated-uncarbonated (DCP-85.7kGy-P1 to DCP-85.7kGy-P5) and unirradiated-
260 carbonated (CCP-85.7kGy-P1 to CCP-85.7kGy-P3) samples (figure 8).

261

262 A trend can be extracted showing a decrease of mechanical strengths for all samples. Indeed,
263 a decrease of the compressive strength by 3.6 % between unirradiated and irradiated pristine
264 samples, and a 13 % decrease between unirradiated and irradiated carbonated sample can be
265 observed after a total dose of 85.7 kGy. Similarly, a decrease by 18 % and 3.6 % can be
266 observed concerning the bending strength. However, the dispersion of the data (around 10 %
267 of standard deviation) does not lead to any statistical difference (t-test < 1 %). ATG analyses
268 were performed on irradiated and pristine uncarbonated samples and no carbonation was
269 observed [28]. To confirm this trend, experiments were reiterated on mortars as described in
270 part 2.1.

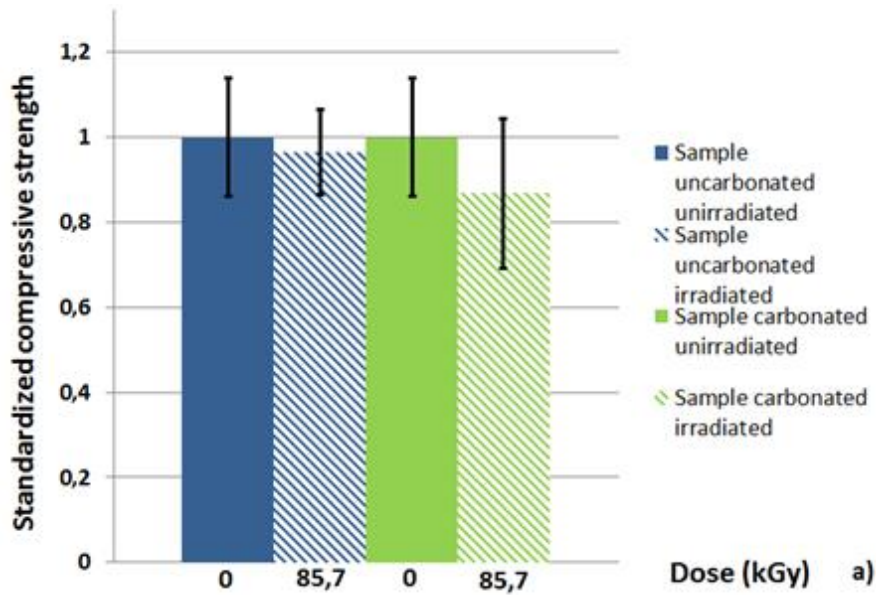
271

272 **Table 4.** Cement paste mechanical strength results with the standard deviation

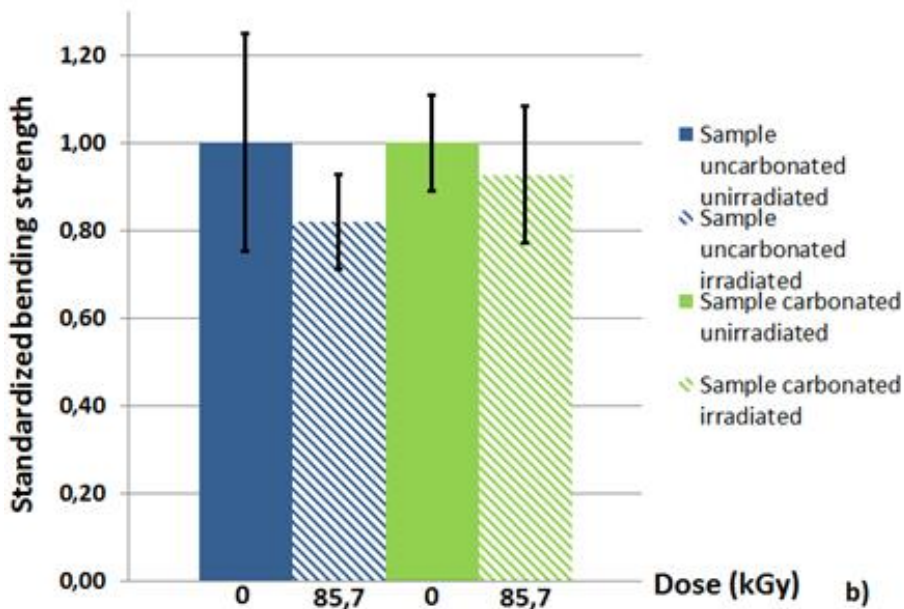
Series	Name	Compressive strength (MPa)	Bending strength (MPa)	Average compressive strength (MPa)	Average bending strength (MPa)		
Series 1	DCP-85.7kGy-P1	87.7 (± 5.4)	7.66	75.4 (± 10.5)	6.73 (± 1.67)		
	DCP-85.7kGy-P2	62.9 (± 7.4)	6.45				
	DCP-85.7kGy-P3	83.5 (± 5.7)	6.87				
	DCP-85.7kGy-P4	67.0 (± 7.9)	4.10				
	DCP-85.7kGy-P5	79.4 (± 7.3)	8.56				
	DCP-85.7kGy-I1	75.6 (± 6.3)	6.23				
	DCP-85.7kGy-I2	74.1 (± 4.3)	5.51			74.8 (± 7.6)	5.51 (± 0.73)
	DCP-85.7kGy-I3	59.1 (± 12.8)	4.78				
	Series 2	CCP-85.7kGy-P1	79.3 (± 9.5)			3.00	82.3 (± 10.1)
CCP-85.7kGy-P2		78.4 (± 12.4)	3.70				
CCP-85.7kGy-P3		80.0 (± 12.9)	3.21				
CCP-85.7kGy-I1		77.6 (± 12.1)	2.51				
CCP-85.7kGy-I2		75.6 (± 4.2)	3.54	71.4 (± 13.3)	3.06 (± 0.52)		
CCP-85.7kGy-I3		75.1 (± 19.8)	3.14				

273

274



275



276

277

278 **Fig. 8.** Standardized compressive strengths a) and bending strengths b) and standard deviations for
 279 cement paste, uncarbonated (blue) and carbonated (green), unirradiated and irradiated in regards with
 280 the mean of unirradiated samples.

281

282 **3.2 Mechanical results on mortars**

283

284 Compressive and bending strength were measured for all mortar samples. Raw results are
285 summarized in table 5 and standardized values are plotted in figure 9.

286 A significant (t-test < 1 %) 4% (resp. 9%) decrease of the compressive strength and a 15 %
287 (resp. 20 %) drop of the bending strength were measured on the humid samples (resp. dried
288 samples) after a total dose of 257 kGy (figure 9). For the carbonated samples, no significant
289 decrease of the compressive or bending strength was noticed (t-test > 80 %). Carbonation is a
290 phenomenon which induces portlandite transformation into calcite. Thus, after carbonation
291 calcite is a dominant phase in our sample. Irradiations don't seem to have mechanical
292 influence on calcite phase. Calcite is a phase studied under irradiations for a long time. This
293 observation is in accordance with the literature where authors agree to say gamma irradiation
294 doesn't have any effect on calcite [29][30]. Consequently, the decrease of the compressive
295 and bending strength observed for humid and dried samples cannot be related to macroscopic
296 degradation of the sand phase (99.9 % calcareous sand used for the mortar formulation) and
297 calcite phase obtained by natural carbonation during irradiation time.

298

299 **Table 5.** Mortar mechanical strength results with the standard deviation

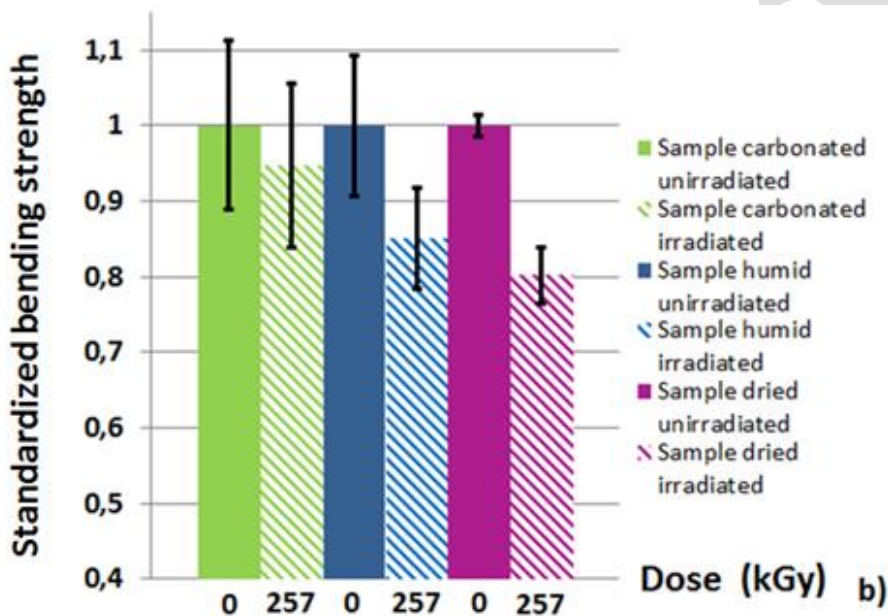
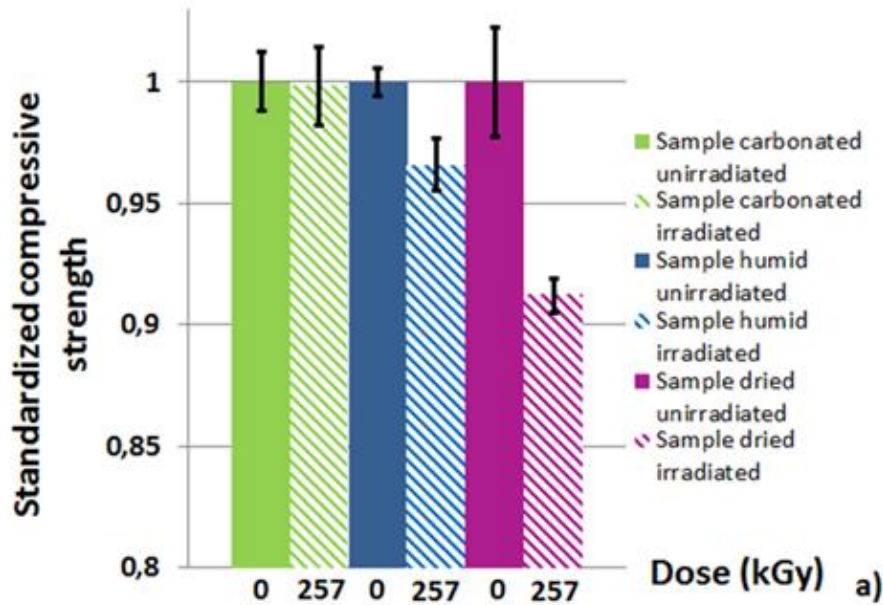
Series	Name	Compressive strength (MPa)	Bending strength (MPa)	Average compressive strength (MPa)	Average bending strength (MPa)
Series 1	HM-257kGy-P1	82.9 (± 0.7)	7.13		
	HM-257kGy-P2	83.3 (± 0.4)	7.27	83.0 (± 0.5)	7.60 (± 0.70)
	HM-257kGy-P3	82.8 (± 0.2)	8.41		
	HM-257kGy-I1	80.6 (± 0.8)	6.54		
	HM-257kGy-I2	79.3 (± 0.3)	6.94	80.2 (± 0.9)	6.47 (± 0.51)
	HM-257kGy-I3	80.9 (± 0.1)	5.93		
Series 2	DM-257kGy-P1	67.7 (± 0.1)	10.15		
	DM-257kGy-P2	69.6 (± 2.5)	10.22	69.1 (± 1.6)	10.10 (± 0.15)
	DM-257kGy-P3	69.2 (± 0.1)	9.94		
	DM-257kGy-I1	63.3 (± 0.1)	8.48		
	DM-257kGy-I2	62.8 (± 0.8)	8.09	63.0 (± 0.5)	8.10 (± 0.37)
	DM-257kGy-I3	62.8 (± 0.1)	7.73		
Series 3	CM-257kGy-P1	115.7 (± 0.9)	5.23		
	CM-257kGy-P2	113.7 (± 0.5)	5.95	114.9 (± 1.4)	5.91 (± 0.66)
	CM-257kGy-P3	115.4 (± 1.9)	6.54		
	CM-257kGy-I1	112.8 (± 1.1)	6.26		
	CM-257kGy-I2	115.4 (± 0.1)	5.56	114.7 (± 1.8)	5.59 (± 0.64)
	CM-257kGy-I3	116.2 (± 0.3)	4.97		

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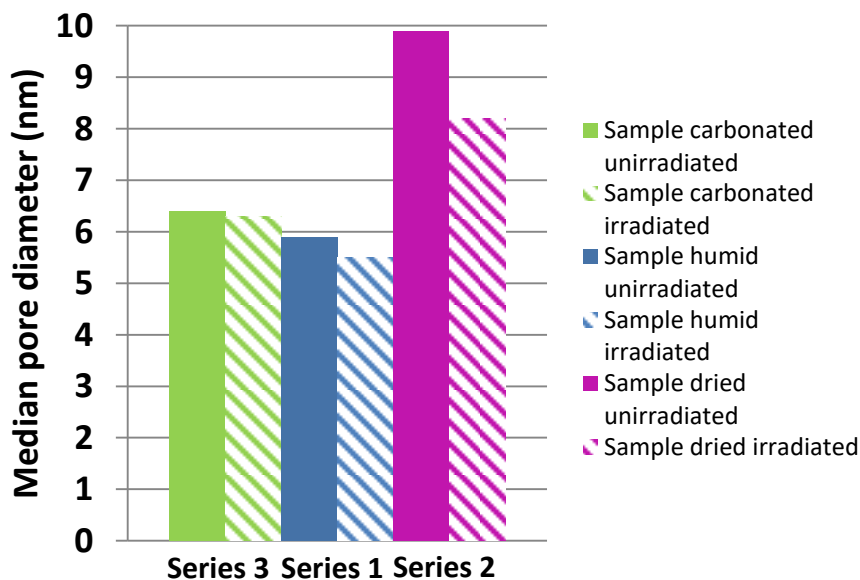
307 **Fig. 9.** Standardized compressive strengths a) and bending strengths b) and standard deviation for
 308 mortar dried (violet), humid (blue) and carbonated (green), unirradiated and irradiated in regards with
 309 the mean of unirradiated samples.

310

311 Furthermore, the quantity of free water, present in the sample, seems to influence the
 312 degradation by gamma radiations as mechanical losses are smaller for the humid samples
 313 than for the dried samples. It seems that free water attenuates the degradations by gamma

314 radiations. Quantity of free water and mechanical properties are directly affected by the
 315 porosity [31][32][33]. Water immersion porosimetry analysis shows that the total open
 316 porosity is similar before and after irradiations for all of the three series (20 % for series 1 and
 317 2 and 13 % for series 3). However, even if total pore volume stays unchanged, its distribution
 318 evolves after irradiation (figure 10). Mercury porosimetry analyses reveal a decrease of the
 319 median pore diameter except for carbonated prisms. Indeed, in the case of dried samples, the
 320 reduction of median pore diameter (9.9 nm to 8.2 nm) is greater than the decrease observed
 321 for humid prisms (5.9 nm to 5.5 nm). Likewise, calcite phase seems to protect the samples
 322 against gamma radiations (no variation of median pore diameter). A correlation appears
 323 between porosity evolution and compressive strength decrease as illustrated in figure 11. This
 324 relation may indicate an influence of the nanoporosity evolution on the macroscopic strength
 325 evolution of the mortars while their relation is not clear to the authors.

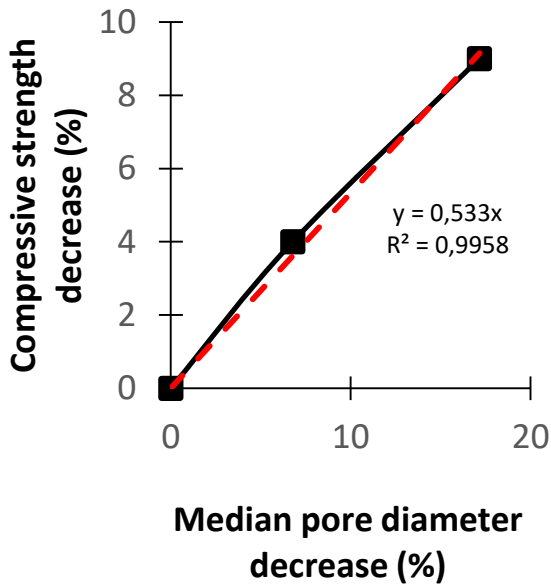
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328 **Fig. 10.** Comparison of median pore diameters of carbonated (green), humid (blue) and dried (violet)
 329 unirradiated and irradiated mortar.

330



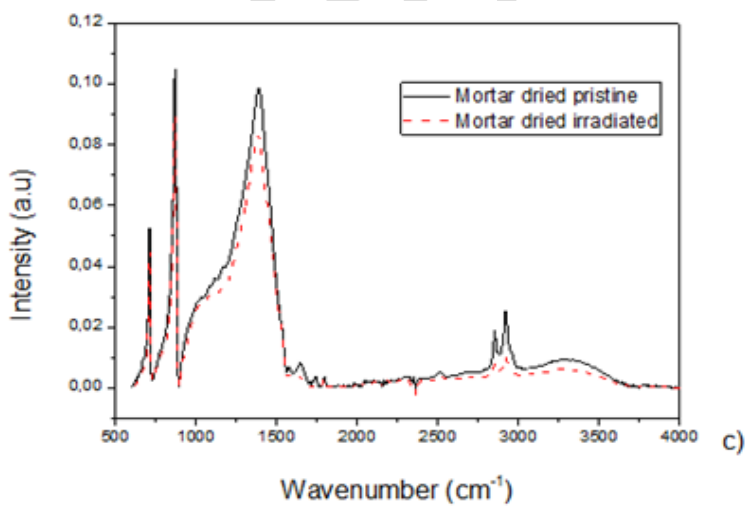
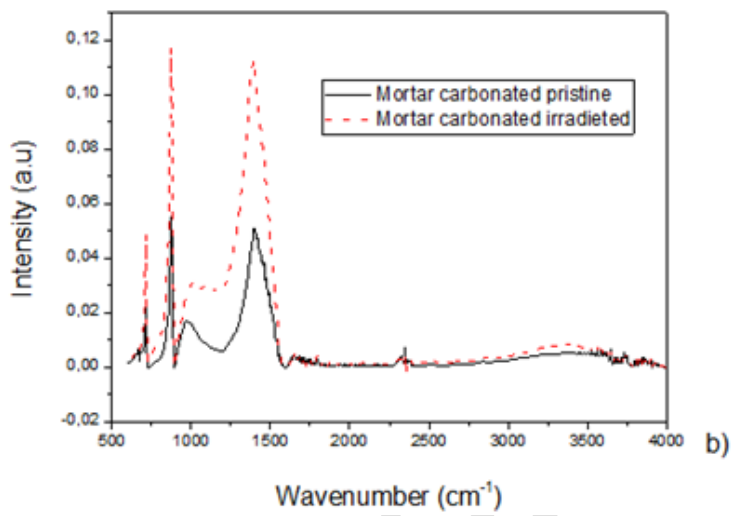
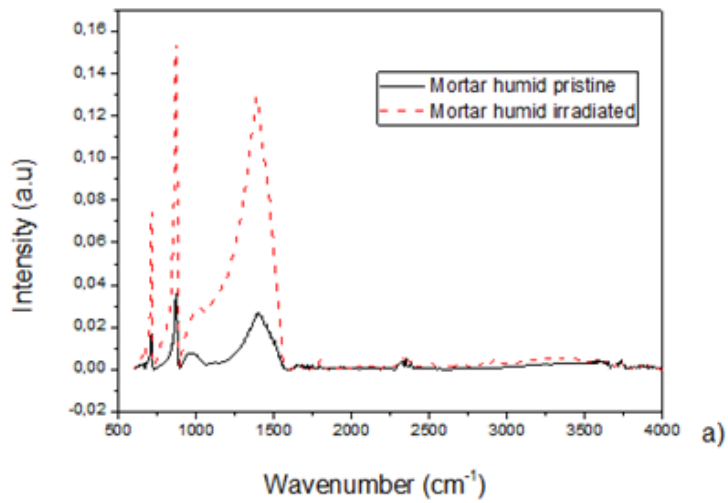
331

332 **Fig. 11.** Relation between porosity decrease and compressive strength decrease due to irradiations on
 333 the three different mortar series.

334

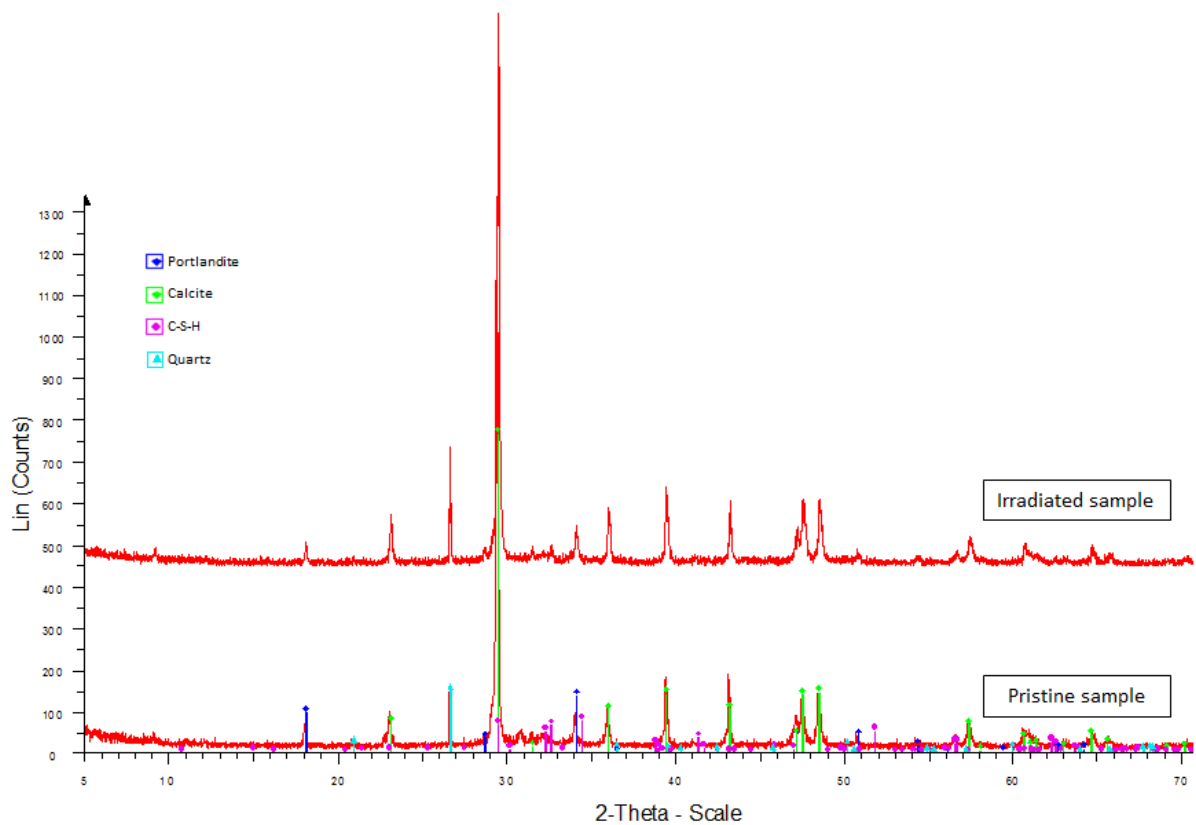
335 Porosity modification is usually assigned to chemical changes. It does not seem to be the case
 336 in our samples as ATR analysis shows no phase change before and after irradiations (figure
 337 12). Indeed, the wavenumber associated with every peak does not change for all samples.
 338 Furthermore, ATR is not a quantitative method; the intensity of peaks may not be
 339 representative of the quantity of a phase present in sample. Moreover, X-ray analyses were
 340 performed on mortar samples and none crystallographic changes were observed for all series
 341 (an example of X-ray diffractogram of dried mortar is given in figure 13).

342



346 **Fig. 12.** ATR spectrum of a) humid, b) carbonated and c) dried mortars both unirradiated (solid line)
347 and irradiated (broken line).

348



349

350 **Fig. 13.** X-ray diffractogram of irradiated and pristine dried mortar.

351

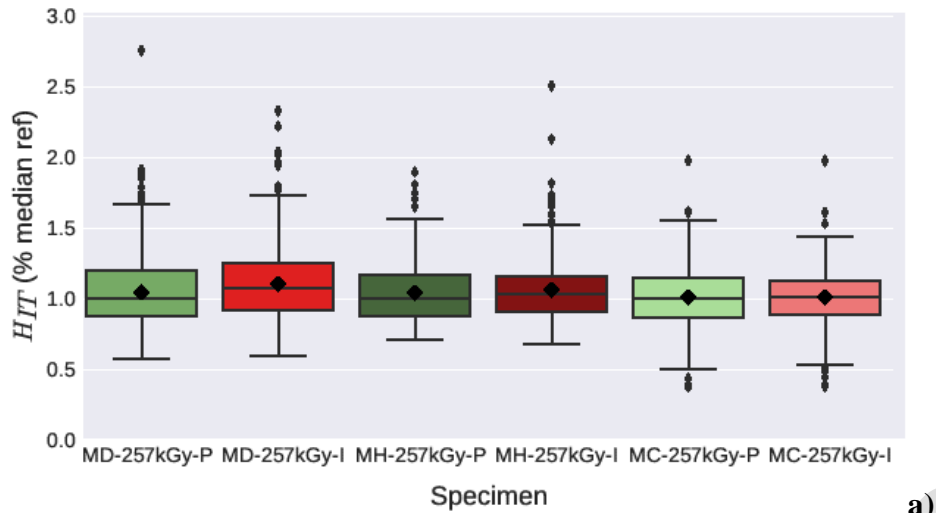
352 Micro-indentation results give some first insights on the evolutions of the multi-scale
 353 behavior of the irradiated mortars. Cement paste properties were successfully extracted from
 354 the statistical indentation performed on the mortars using the complementarity between
 355 numerical clustering and 3D imaging as exposed in an article from the authors [27]. The
 356 obtained distributions associated with the various variables characterizing the cement paste
 357 are mostly well-defined and normal-like which allows for a fast and accurate comparison. As
 358 illustrated in figure 14 a), a significant increase of the dried and humid mortars hardness can
 359 be observed. Indeed, unirradiated dried mortars have a median hardness of 388 MPa while the
 360 median hardness of irradiated corresponding series is increased by around 7.2 % (416 Mpa).
 361 Humid specimens exhibit the same evolution as the median hardness of irradiated specimens
 362 is around 3.5 % higher (346 MPa vs 334 MPa) than the one of unirradiated specimens. This
 363 increase of the specimens' hardness due to γ -radiations may be correlated with their strength.

364 On the other hand, similarly to the macroscopic observations, no significant micromechanical
365 evolution of the carbonated mortars was noticed (+ 1 %).

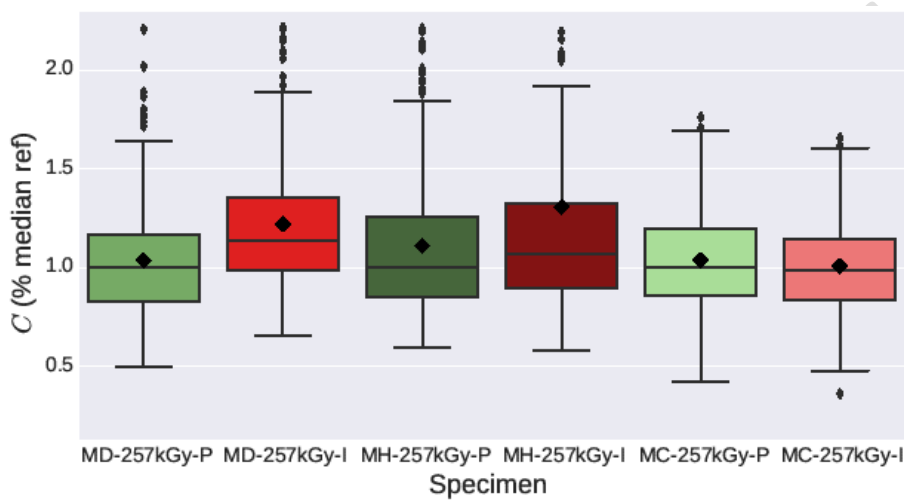
366 Creep parameters are affected similarly: indentation creep modulus of dried and humid
367 mortars regarding the median reference values are respectively increased by 13.7 % and 7.1 %
368 meaning that these two mortars creep less than the pristine reference samples. Their creep
369 characteristic time decreases, - 9.8 % for the dried specimens and - 6.1 % for the humid
370 specimens, which means that their long-term logarithmic behavior is attained after a short
371 period of time.

372 Creep parameters of the carbonated specimens are not affected much: indentation creep
373 modulus does not significantly evolve (- 1.4 %) and creep characteristic time increases
374 slightly by 5.5 %.

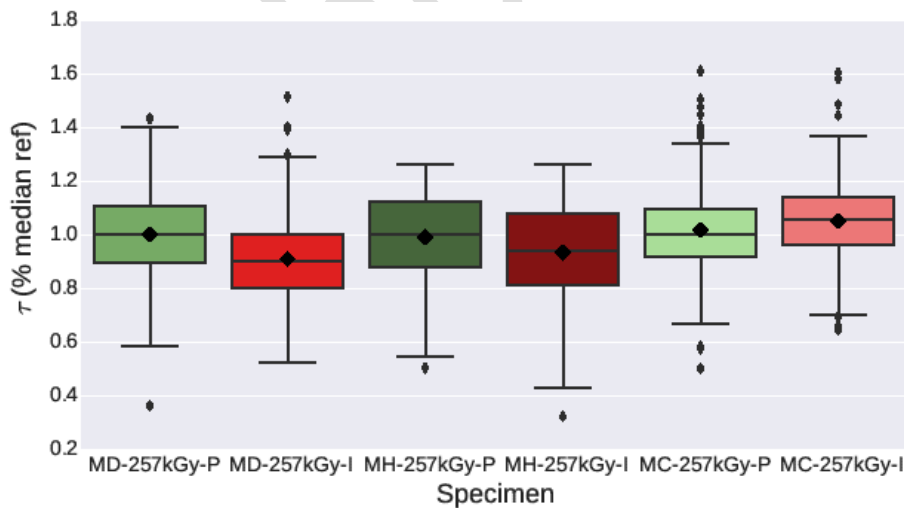
375



a)



b)



c)

376 **Fig. 14.** Standardized creep parameters of the mortar specimens : (a) indentation hardness, (b)
 377 indentation creep modulus, (c) indentation characteristic time. For each series, results were
 378 standardized relatively to the median value of the unirradiated specimen (upper and lower

379 lines of the box representing 1st and 3rd quartiles, the line inside the median value). Diamonds
380 represent mean values and external bars 1st and 9th decile.

381

382 **4. Summary and Conclusions**

383

384 The main objective of the present work was to accurately understand the alterations of
385 mechanical properties of cementitious materials under low doses of gamma irradiations. This
386 work is motivated by the increasing concern about the durability of nuclear wastes storage
387 facilities which will withstand similar exposure conditions. Thus, three different mortar (dry,
388 humid and carbonated) and two different cement pastes (dried and carbonated) were used.
389 Mechanicals properties were measured for each sample after an irradiation of 287 kGy for
390 mortars and 85,7 kGy for cement pastes. The results can be summarized as follows :

- 391 - Significant differences between pristine and irradiated cementitious materials have
392 been observed at doses which are largely lower than up-to-date reported thresholds
393 around $2 \cdot 10^5$ kGy [3][5],
- 394 - For the first time, a significant decrease of the compressive and bending strength for
395 humid and dried mortar can be accurately measured, and mechanical properties of
396 corresponding the cement paste should decrease too although dispersion of data does
397 not lead to any statistical difference,
- 398 - Mechanical decreases are greater for dried mortar than humid mortar. Water seems to
399 have an effect against mechanical deteriorations under gamma radiation. Thus water
400 radiolysis may not play a leading role in the degradation phenomenon at small doses,
- 401 - Carbonated mortars were not affected after 275 kGy gamma exposure. Gamma
402 radiations have no effects on calcite phase. Given that the sand used to prepare the
403 mortar is a 99.9 % calcareous sand, we can then assume that the gamma radiation has

404 mainly an effect on the cement paste phase. Nevertheless, a gamma irradiation study
405 on pure calcite phase is required to confirm these observations,
406 - No modification of the total porosity was observed. However, the repartition of the
407 porosity changes for humid and dried mortar indicating an evolution of the
408 macroporosity toward the nanoporosity and there is a correlation between the decrease
409 of the median pore diameter and the decrease of the compressive strength,
410 - Micro-indentation results, which are influenced by the local porosity, correlate well
411 with these macroscopic observations concerning the porosity evolution,
412 - No modification of the chemical composition was noticed. Presently, only the
413 variation of porosity can explain the decrease of the bending and compressive
414 strength.

415 There is an untapped opportunity to understand the phenomenon at the origin of these
416 mechanical modifications. Because gamma radiation seems to have a major effect on cement
417 paste, mainly composed by calcium silicate hydrates (C-S-H), future investigations will be
418 carried out to study mechanical modifications under gamma radiation at a smaller scale.

419

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424 irradiation experiments.

425

426 References

427 [1] J. Kořátková, J. Zatloukal, P. Reiterman, K. Kolář, Concrete and cement composites
428 used for radioactive waste deposition, J. Environ. Radioact. 178–179 (2017) 147–155.
429 doi:10.1016/j.jenvrad.2017.08.012.

- 430 [2] F. Bart, C. Cau-di-Coumes, F. Frizon, S. Lorente, Cement-Based Materials for Nuclear
431 Waste Storage, 1st ed., Springer-Verlag New York, New-York, 2013.
- 432 [3] H. Hilsdorf, J. Kropp, H. Koch, The Effects of Nuclear Radiation on Materials
433 Properties of Concrete, ACI SP 55. (1978) 223–251.
- 434 [4] Y. Le Pape, Structural effects of radiation-induced volumetric expansion on
435 unreinforced concrete biological shields, Nucl. Eng. Des. 295 (2015) 534–548.
436 doi:10.1016/j.nucengdes.2015.09.018.
- 437 [5] O. Kontani, S. Sawada, M. Takizawa, O. Sato, Evaluation of irradiation effects on
438 concrete structure - Gamma-ray irradiation tests on cement paste, Proc. ASME 2013
439 Power Conf. (2013) 1–8. doi:10.1115/POWER2013-98099.
- 440 [6] K.G. Field, I. Remec, Y. Le Pape, Radiation effects in concrete for nuclear power
441 plants - Part I: Quantification of radiation exposure and radiation effects, Nucl. Eng.
442 Des. 282 (2015) 126–143. doi:10.1016/j.nucengdes.2014.10.003.
- 443 [7] I. Maruyama, O. Kontani, A. Ishizawa, M. Takizawa, O. Sato, Development of System
444 for Evaluating Concrete Strength Deterioration Due to Radiation and Resultant Heat,
445 Non-Metallic Mater. Ageing Manag. (2016) 3–6.
- 446 [8] A. Giorla, M. Vaitova, Y. Le Pape, P. Stemberk, Meso-scale modeling of irradiated
447 concrete in test reactor, Nucl. Eng. Des. 295 (2015) 59–73.
448 doi:10.1016/j.nucengdes.2015.08.027.
- 449 [9] T.M. Rosseel, K.G. Field, Y. Le Pape, D.J. Nauss, I. Remec, J.T. Busby, Dommages
450 d’irradiation dans les cavités en béton des réacteurs aux Etats-Unis, Rev. Générale
451 Nucléaire. 1 (2015) 21–27.
- 452 [10] Y. Le Pape, K.G. Field, I. Remec, Radiation effects in concrete for nuclear power
453 plants, Part II: Perspective from micromechanical modeling, Nucl. Eng. Des. 282
454 (2015) 144–157. doi:10.1016/j.nucengdes.2014.10.014.

- 455 [11] P. Soo, L.M. Milian, The effect of gamma radiation on the strength of Portland cement
456 mortars, *J. Mater. Sci. Lett.* 20 (2001) 1345–1348.
- 457 [12] F. Vodák, K. Trtík, V. Sopko, O. Kapičková, P. Demo, Effect of γ -irradiation on
458 strength of concrete for nuclear-safety structures, *Cem. Concr. Res.* 35 (2005) 1447–
459 1451. doi:10.1016/j.cemconres.2004.10.016.
- 460 [13] B.G. Ershov, A. V. Gordeev, A model for radiolysis of water and aqueous solutions of
461 H₂, H₂O₂ and O₂, *Radiat. Phys. Chem.* 77 (2008) 928–935.
462 doi:10.1016/j.radphyschem.2007.12.005.
- 463 [14] E.M. Gartner, J.F. Young, D.A. Damidot, I. Jawed, Hydration of portland cement, in:
464 *Struct. Perform. Cem. Second Ed.*, Spon press, London, 2002: pp. 57–112.
- 465 [15] P. Bouniol, E. Bjergbakke, A comprehensive model to describe radiolytic processes in
466 cement medium, *J. Nucl. Mater.* 372 (2008) 1–15. doi:10.1016/j.jnucmat.2006.10.004.
- 467 [16] P. Bouniol, Water radiolysis in cement-based materials, in: *Radiat. Chem. from Basics*
468 *to Appl. Mater. Life Sci.*, 2008: pp. 117–129.
469 <https://books.google.co.uk/books?id=hcfbMzy3kAcC>.
- 470 [17] B. Tilquin, *Actions Biologique et Chimique des Rayonnements Ionisants*, Frison-Roc,
471 Paris, 2002.
- 472 [18] G.W. Groves, D.I. Rodway, I.G. Richardson, The carbonation of hardened cement
473 pastes, *Adv. Cem. Res.* 11 (1990) 117–125.
- 474 [19] K. Kobayashi, K. Suzuki, Y. Uno, Carbonation of concrete structures and
475 decomposition of CSH, *Cem. Concr. Res.* 24 (1994) 55–61. doi:10.1016/0008-
476 8846(94)90082-5.
- 477 [20] S.E. Pihlajavaara, Some results of the effect of carbonation on the porosity and pore
478 size distribution of cement paste, *Matériaux Constr.* (1968). doi:10.1007/BF02473640.
- 479 [21] Yves F. Houst, Folker H. Wittmann, Depth profiles of carbonates formed during

- 480 natural carbonation, *Cem. Concr. Res.* 32 (2002) 1923–1930. doi:10.1016/S0008-
481 8846(02)00908-0.
- 482 [22] A.N.M. Bagyo, W.A. Lindu, S. Sadjirun, E.K. Winarno, E. Widayat, Aryanti, H.
483 Winarno, Radiation Induced Degradation of Organic Pollutants in Waters and
484 Wastewaters, 1995. doi:10.1017/CBO9781107415324.004.
- 485 [23] AFNOR, Essai pour béton durci - Essai de carbonatation accélérée - Mesure de
486 l'épaisseur de béton carbonaté, XP P18-458 (2008).
- 487 [24] H. Fricke, E.J. Hart, *Chemical Dosimetry, Radiation Dosimetry*, New York, 1966.
- 488 [25] AFNOR, Béton - Essai pour béton durci - Essai de porosité et de masse Volumique, NF
489 P18-459 (2010).
- 490 [26] R.A. Cook, K.C. Hover, Mercury porosimetry of hardened cement pastes, *Cem. Concr.*
491 *Res.* 29 (1999) 933–943. doi:10.1016/S0008-8846(99)00083-6.
- 492 [27] B. Hilloulin, M. Robira, A. Loukili, Coupling statistical indentation and microscopy to
493 reduce uncertainties identifying phases mechanical properties: application on γ -
494 irradiated mortars, Submitted. (n.d.).
- 495 [28] N. Mobasher, S.A. Bernal, H. Kinoshita, C.A. Sharrad, J.L. Provis, Gamma irradiation
496 resistance of an early age slag-blended cement matrix for nuclear waste encapsulation,
497 *J. Mater. Res.* 30 (2015) 1563–1571. doi:10.1557/jmr.2014.404.
- 498 [29] J. Handin, D. V. Higgs, D.R. Lewis, P.K. Weyl, Effects of gamma radiation on the
499 experimental deformation of calcite and certain rocks, *Bull. Geol. Soc. Am.* 68 (1957)
500 1203–1224. doi:10.1130/0016-7606(1957)68[1203:EOGROT]2.0.CO;2.
- 501 [30] Z. Kabacińska, L. Yate, M. Wencka, R. Krzymiński, K. Tadyszak, E. Coy,
502 Nanoscale Effects of Radiation (UV, X-ray, and γ) on Calcite Surfaces: Implications
503 for its Mechanical and Physico-Chemical Properties, *J. Phys. Chem. C.* 121 (2017)
504 13357–13369. doi:10.1021/acs.jpcc.7b03581.

- 505 [31] E.P. Kearsley, P.J. Wainwright, The effect of porosity on the strength of foamed
506 concrete, *Cem. Concr. Res.* 32 (2002) 233–239.
- 507 [32] X. Chen, S. Wu, J. Zhou, Influence of porosity on compressive and tensile strength of
508 cement mortar, *Constr. Build. Mater.* 40 (2013) 869–874.
509 doi:10.1016/j.conbuildmat.2012.11.072.
- 510 [33] D.P.H. Hasselman, Relation Between Effects of Porosity on Strength and on Young's
511 Modulus of Elasticity of Polycrystalline Materials, *J. Am. Ceram. Soc.* 46 (1963) 564–
512 565. doi:10.1111/j.1151-2916.1963.tb14615.x.
- 513
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