

1 **INFLUENCE OF CONCRETE CARBONATION ON ELECTROMAGNETIC PERMITTIVITY**
2 **MEASURED BY GPR AND CAPACITIVE TECHNIQUES**

3
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8
9 **ABSTRACT**

10 This paper addresses the effect of concrete carbonation on the propagation and dispersion of electromagnetic
11 (EM) waves and the capability of two electromagnetic non-destructive techniques to detect this pathology. A
12 capacitive technique operating at low frequency (around 33 MHz) and a ground penetrating radar (GPR -
13 called the 1.5-GHz antenna) are tested for the monitoring of reinforced concrete structures. To better
14 understand the phenomena involved in concrete carbonation, the results of two complementary experimental
15 campaigns are analyzed for saturated concretes. First, the dispersion curves of complex permittivity are
16 measured for both carbonated and non-carbonated samples by a cylindrical coaxial EM cell. Due to
17 carbonation, the permittivity decreases and the level of dispersion reduces slightly. Second, using GPR
18 (coupled at approx. 900 MHz) and capacitive measurements conducted on controlled slabs, it is confirmed
19 that the real part of the relative permittivity decreases within a range of 2 at 33 MHz and a range of 1 toward
20 900 MHz, while the radar signal amplitude increases.

21
22 **1. Introduction**

23 The diagnosis of concrete structures has become a major issue over time. Among the main durability
24 indicators, salt ingress and carbonation constitute the major causes in most deterioration processes, facilitated
25 by water content as a common agent, thus leading to rebar corrosion. Electromagnetic (EM) non-destructive
26 testing (NDT) techniques have, through numerous studies, revealed their sensitivity and efficiency in
27 evaluating such durability indicators. These studies have mainly been devoted to water content evaluation or
28 chloride ingress monitoring in concrete [Robert, 1998; Soustos *et al.*, 2001; Laurens *et al.*, 2002; Peer *et al.*,
29 2003; Hugenschmidt and Loser, 2008; Dérobert *et al.*, 2008; Kalogeropoulos *et al.*, 2013; Villain *et al.*, 2015;
30 Hong *et al.*, 2017; Dérobert and Villain, 2017a], but little emphasis has been paid to carbonation [Hong *et al.*,
31 2017; Balayssac *et al.*, 2012; Dérobert and Villain, 2017b].

32 Carbonation is a major contributor to concrete degradation. Due to climate change, carbon dioxide (CO₂)
33 content has been drastically increasing in the atmosphere, reaching above 400 ppm in the world and in 2016
34 extending to the less polluted parts of the Indian Ocean [Ballantyne *et al.*, 2012; Ramonet *et al.*, 2016]. In
35 urban areas, the mean value is even higher. Moreover, due to human activity, daily variations are

Preprint

Journal of Environmental and Engineering Geophysics (2018), 23 (4)

<http://dx.doi.org/10.2113/JEEG23.4.443>

36 considerably higher in suburban areas than in rural zones; for example, in suburban London and coastal
37 Ireland, variation factors of 72 can be found [Hernández-Paniagua *et al.*, 2015]. Concrete structures are
38 therefore slightly more affected by carbonation [De Larrard *et al.*, 2014]. The acidification in cover concrete
39 leads to severely corrosive pathologies of reinforced concrete structures [Tuutti, 1982; Parrott, 1987;
40 Dunster, 1989; Papadakis *et al.*, 1991a-b; Villain and Platret, 2006; Villain and Thiéry, 2005].

41 In light of this context and given that the wave propagation of EM NDT techniques is sensitive to both
42 porosity and chemical changes in concrete material, such techniques can become useful tools in estimating
43 the carbonation level of cover concrete. The aim of this paper is to study the effect of carbonation on the
44 propagation and dispersion of EM waves at low and higher radar frequencies in order to make use of the
45 capacitive technique and GPR during inspections of reinforced concrete structures. A previous study
46 [Dérobert and Villain, 2017b] found a negligible effect of carbonation on dry concrete mix, hence the present
47 paper is focused on saturated mixes.

48 After an overview of the concrete carbonation process and its consequences provided in the next section,
49 the experimental programs of two complementary research projects [Balayssac *et al.*, 2012; Dérobert and
50 Villain, 2017b] are presented, including their concrete mixes, conditioning and the EM NDT techniques
51 employed. The final section is devoted to reporting results and discussing their analysis.

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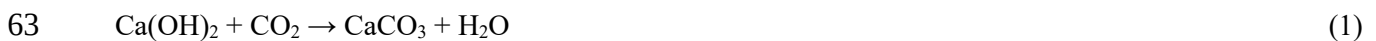
53

2. The concrete carbonation process

54 One of the main causes of corrosion in reinforced concrete structures is carbonation, a phenomenon due
55 to the penetration of carbon dioxide into cover concrete [Tuutti, 1982; Parrott, 1987]. The carbonation
56 process leads to physicochemical changes in the cover concrete, which can be detailed as follows.

57 2.1 Carbonation process

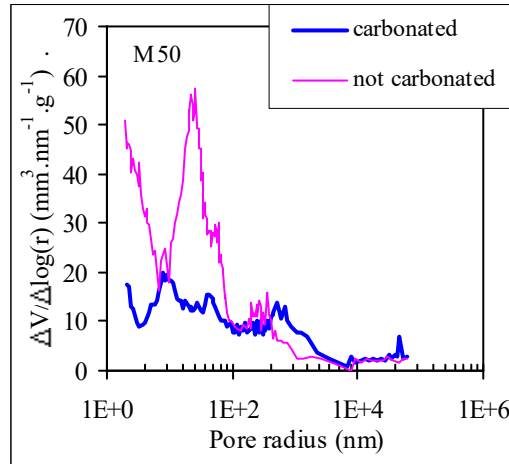
58 The reinforcing bars in reinforced concrete structures are physically and chemically protected from
59 corrosion by the concrete. From a chemical point of view, the very high pH-value of concrete (around 12.6)
60 leads to a passivation of the reinforcement. Over time, atmospheric carbon dioxide (CO₂) can penetrate into
61 concrete, dissolve in the pore solution and react with portlandite (Ca(OH)₂), as illustrated by Equation (1) or
62 with C-S-H according to Equation (2):



65 These effects result in water formation, the precipitation of calcium carbonates (CaCO₃) and amorphous
66 silica gels [Dunster, 1989]. The equilibrium between portlandite, C-S-H and the hydroxide ions of the pore
67 solution is thus changed, leading to the gradual consumption of all reserve basicity and then to a drop in pH-
68 value from about 13 to 9. The reinforcement is no longer chemically protected and more likely to corrode.

69 According to numerous studies [Tuutti, 1982; Parrott, 1987; Dunster, 1989; Papadakis *et al.*, 1991a-b;
70 Villain and Thiéry, 2005; Villain and Platret, 2006], carbonated depth increases with the square root of time

71 following a simplified Fick's diffusion law. The parameters of this law depend on many factors, including
72 concrete mix design, especially the water-cement ratio, and fabrication and environmental exposure
73 conditions. Among existing carbonation models, Papadakis *et al.* [1991a-b] were able to determine the depth
74 of carbonation and induced mass changes in the various mix components; their work encompassed the
75 cement chemical analysis and external conditions detailed in Section 3.



76

77

78 Fig. 1: Example of pore size distribution in both carbonated and non-carbonated concrete
79 [Villain and Platret, 2006].

80

80 2.2 Consequences on physical properties

81 The carbonation of concrete induces several consequences. The first is a reduction in porosity due to
82 CaCO_3 precipitation and the formation of amorphous silica gels filling the small pores [Parrott, 1987;
83 Dunster, 1989; Villain and Thiéry, 2005; Glass *et al.*, 1991], as shown in Figure 1. The order of magnitude of
84 this porosity reduction lies between 2% and 4% for two concretes mixed with Portland cement (namely M25
85 and M50), with a mean compressive strength of 25 MPa and 50 MPa at 28 days, according to Villain and
86 Thiéry [2005].

87 The other major consequences are: the release of liquid water that can locally change the water content
88 (hence the preference for conducting comparative measurements under saturated conditions); the pH-value
89 decrease from roughly 13 to 9; and carbonation-induced change in the ionic content of the pore solution.

90 Three indirect and secondary consequences can be cited. First, let's observe the increase in mechanical
91 strength [Parrott, 1987]. Second, carbonation induces a change in both permeability and the diffusion
92 coefficient. These transport coefficients often decrease following a drop in porosity; conversely, an increase
93 can be noted for very porous concretes, witnessed as a larger pore appearance and a tortuosity reduction
94 [Villain and Thiéry, 2005]. Third and last, the resistivity of concrete, which increases with carbonation, is
95 attributed to a loss of porosity and the disappearance of mobile ions (OH^-) from the pore solution [Alonso *et*
96 *al.*, 1988; Glass *et al.*, 1991]. The ratio of resistivities measured on saturated carbonated (C) and non-
97 carbonated (NC) specimens equals between 1.8 and 8 for M25 to M50 concretes mixed with Portland cement
98 [Villain and Thiéry, 2005].

99 Various experimental methods can be performed to evaluate concrete carbonation. The best known and

100 easiest to use is a pH-indicator, like phenolphthalein, sprayed onto a freshly broken surface sample. This
 101 method allows defining a depth of carbonation P_c correlated with the pore solution pH-value [AFPC-
 102 AFREM, 1997]. Another method, based on CO₂ fixation, entails tracking the mass increase by weighing. The
 103 weakness of this method lies in the fact that weight can be biased by moisture change, e.g. concomitant
 104 drying due to accelerated carbonation taking place in a chamber with relative humidity (RH) controlled at
 105 around 50%. For both non- and fully-carbonated specimens, the bulk porosity reduction can be measured by
 106 water saturation under vacuum [AFPC-AFREM, 1997].

107

108

3. Experimental campaigns

109 The results presented herein stem from two complementary research programs sponsored respectively by the
 110 French Ministry of Ecology (MTES) and EDF company (electric utility), and the French National Research
 111 Agency (ANR). The first program, called Epsilon, seeks to quantify, through several large experimental
 112 designs [Dérobert and Villain, 2017a-b], the influence of composition parameters and concrete conditions on
 113 permittivity within a frequency band of approx. [50 MHz - 1 GHz]. The second program, ANR-SENSO, was
 114 devoted to evaluating durability indicators (namely porosity and carbonation depth) by applying various
 115 types of NDT methods [Balayssac *et al.*, 2012] on several controlled homogeneous mixes in the laboratory.
 116 Since the aggregate and cement contents were identical, these common components offer the possibility of
 117 collating results for the two projects.

118

3.1 Concrete mix design from the Epsilon project

120 The mix design used for the Epsilon experimental program is presented in Table 1, which lists 12 concretes
 121 submitted to carbonation. The codes employed to design these concrete mixes are kept similar to the original
 122 ones (C1 to C31), as presented in [Dérobert and Villain, 2017b], in order to facilitate subsequent studies by
 123 readers. The effective water-cement ratio (W/C) ranges from 0.35 to 0.55, resulting in a porosity varying
 124 from 6.7% to 17.1%. Standard Portland cement CEM I 42.5 R (Heidelberg Group) has been used, and the
 125 aggregates originating in the Nantes (FR) region are either calcareous (Boulonnais) or siliceous (Palvadeau).

126

127

Table 1: Concrete mix design and average porosity (Epsilon project)

Code	Aggregate type	Gravel 4/20 (kg/m ³)	Sand 0/4 (kg/m ³)	CEM I (kg/m ³)	W/C (-)	AEA* Fosroc	Poro. (%)
C1	Calcareous	1008	1008	350	0.35	-	13.7
C3	Siliceous	932	932	410	0.35	-	8.9
C5	Siliceous	985	985	350	0.35	Yes	6.7
C7	Calcareous	953	953	410	0.35	Yes	10.8
C13	Siliceous	917	917	350	0.5	-	10.8

C15	Calcareous	872	872	40	0.5	-	14.6
C17	Calcareous	939	939	350	0.5	Yes	15.5
C19	Siliceous	853	853	410	0.5	Yes	16.9
C25	Calcareous	916	916	350	0.55	-	13.5
C27	Siliceous	826	826	410	0.55	-	13.6
C29	Siliceous	894	894	350	0.55	Yes	17.1
C31	Calcareous	845	845	410	0.55	Yes	14.9

128 *Air-entraining agent (AEA)

129

130 Three cylindrical samples (ϕ 75 x 70 mm) per test concrete were cored and 3 slabs (230 x 230 x 70 mm)
 131 sawn. Additional non-carbonated (NC) samples enabled determining the porosity. One core was preserved
 132 from carbonation (sample A) per concrete. Another core (sample B) was dried in an oven in order to reach a
 133 constant mass corresponding to an equilibrium at RH = 50%. Similarly, for each mix, 3 slabs (~22 x 22 x 6
 134 cm) were sawn for capacitive measurements.

135 All the B samples and slabs were then placed in a chamber at approx. T = 20°C, RH = 50% and [CO₂] = 50%
 136 for 3 months, with samples being weighed once a month. The mass increased substantially during the first 2
 137 months, while the last month tapered off or stabilized. The relative mass increase measured and calculated
 138 between times t₀ and t₀ + 3 months, as well as the predicted mean values and variation ranges using
 139 Papadakis' model, are summarized in Table 2: the values remain similar, with the measured values being
 140 slightly lower. For each concrete, porosity was measured by means of water saturation on one core per state.

141

142 **Table 2: Comparison of relative mass increases due to carbonation: estimated values by Papadakis' model**
 143 **with measured and calculated values after 3 months of accelerated carbonation (color legend: dark-**
 144 **medium-light gray and white as high, middle, low and very low levels of uncertainty, respectively).**

Code	Relative mass increase (%)			Color code	Increase/Estimated (-)
	Estimated	Slabs	Cylinders		
C1	4.±0.1	4.5	3.7		
C3	4.8±0.1	3.2	2.9		
C5	4.2±0.1	2.6	3.1		
C7	4.6±0.3	4.4	3.7		
C13	4.6±0.3	4.9	4.2		
C15	5.4±0.4	5.8	5.3		
C17	4.6±0.4	4.7	3.2		
C19	5.6±0.3	4.5	3.5		
C25	4.6±0.3	5.3	4.2		
C27	5.6±0.3	5.6	4.7		
C29	4.8±0.5	3.3	2.4		
C31	5.4±0.6	4.7	3.7		

	[-0.4, -0.55]
	[-0.2, -0.4]
	[+0.2, -0.2]

145

146 For low-porosity concretes (C3 and C5), the measured values are less than the estimated values of relative
147 mass increases. This result can be attributed to incomplete carbonation. For very porous concretes (C19 and
148 C29), the samples should be completely carbonated; meanwhile, these carbonated samples were stored in the
149 carbonated chamber at RH = 50% and thus could have been subjected to drying concomitant to carbonation.
150 Furthermore, for all concretes mixed with an air-entraining agent (C5 and C7, C17 and C19, C29 and C31),
151 porosity is high and may lead to overestimating the mass increase with Papadakis' model, which could
152 provide a second plausible explanation of the differences observed in Table 2 for porous concretes C19 and
153 C29.

154 Once the carbonation process had been performed, samples A and B were saturated under vacuum and tested
155 in the cylindrical coaxial EM cell.

156

157 3.1 Concrete mix design from the ANR-SENSO project

158 The mix design used for the ANR-SENSO experimental program, in which only 5 concretes were subjected
159 to carbonation, is presented in Table 3. Two additional slabs, cured just like the others, were cored in order to
160 characterize the concretes [Balayssac *et al.*, 2012]. For each design, porosity was measured by means of
161 water saturation on four cores from the first additional slab. The mean value and standard deviation are given
162 in Table 3. The effective water-cement ratio ranges from 0.57 to 0.9, thus inducing a porosity from 14.9% to
163 18.1%.

164 Similarly to the Epsilon project, Portland cement CEM I and aggregates, either calcareous or siliceous, were
165 used. Combining both projects extends the water-cement ratio from 0.35 to 0.9, corresponding to a range of
166 porosity from 6.7% to 18.1%.

167

168 **Table 3: Concrete mix design and average porosity (ANR-SENSO project)**

Code	Aggregate type	Gravel 4/14 (kg/m ³)	Sand 0/4 (kg/m ³)	CEM I (kg/m ³)	Water (kg/m ³)	W/C (-)	Poro. (%)
G3	Siliceous	1069	774	370	211.6	0.57	15.5±0.5
G3a	Siliceous	1069	774	370	211.6	0.57	16.0±0.7
G7	Siliceous	1047	839	320	216.32	0.68	15.9±0.8
G8	Siliceous	1016	938	240	217.2	0.9	18.1±1.0
G6	Calcareous	1138	758	370	214	0.58	14.9±0.4

169

170 A total of 9 slabs (50 x 25 x 12 cm) were cast per test concrete. After a campaign devoted to studying water
171 content [Dérobert and Villain, 2017b], 4 slabs per concrete were dried in an oven in order to reach a constant
172 mass, corresponding to an equilibrium at RH = 50%, and then wrapped to homogenize water content inside
173 the slabs. They were then subjected to accelerated carbonation under controlled conditions at about T =

174 20°C, RH = 50% and [CO₂] = 50% until the corresponding small sample had reached the required
 175 carbonation depth Pc at around 10, 20, 40 and 60 mm. The accelerated carbonation was verified by
 176 carbonation depth measurements conducted on additional samples (Table 4). For this step, several cores
 177 (from the 2nd additional slab) were subjected to the same curing, preconditioning and accelerated carbonation
 178 conditions. For each concrete, a core was split and sprayed with a phenolphthalein solution at different test
 179 times in order to determine carbonation depth according to the RILEM procedure "TC56-MHM
 180 Hydrocarbon materials, CPC-18 Measurement of hardened concrete carbonated depth". Once the targeted
 181 carbonation depth had been reached on this reference core, two carbonated slabs of the same concrete were
 182 removed from the carbonation chamber and carefully protected until the non-destructive test.
 183 Parameters P0, P40 and P60, appended to the codes in Table 4, correspond to the following carbonation
 184 depth target values: 0, 40, and 60 mm, respectively.

185
186

Table 4: Carbonation depths and porosity decreases

Code	Targeted Pc (mm)	Porosity (%)	Poro. difference (%)	Measured Pc (mm)
G3-Pc0	0	16.2	2.8	1
G3-Pc40	40	13.4		31
G3a-Pc0	0	15	2.6	1
G3a-Pc40	40	12.4		29
G7-Pc0	0	15.8	1.6	3
G7-Pc40	40	14.2		42
G8-Pc0	0	18.1	2.8	5
G8-Pc60	60	15.3		60
G6-Pc0	0	17.2	4.5	2
G6-Pc40	40	12.7		27

187

188 Note the extreme difficulty in reaching Pc = 40 mm, as the actual value in most cases was closer to 30 mm.
 189 Moreover, the decrease in porosity is slightly too small for G7, ~~perhaps because a too high porosity of the~~
 190 ~~non-carbonated (NC) sample that should be around 15% (Table 3).~~ In fact, except for G8, it proved to be
 191 very difficult, or even impossible, to reach complete carbonation corresponding to Pc = 60 mm (on both
 192 faces) after several months in the carbonation chamber. All slabs were then saturated and tested using
 193 different NDT methods, in particular capacitive and GPR techniques (as described in the following section).

194

195 3.2 NDT methods

196 Within the framework of this study, two EM NDT techniques were used (i.e. capacitive technique and GPR),
 197 complemented by measurements in an EM cell. All 3 techniques and methodologies will be described below.

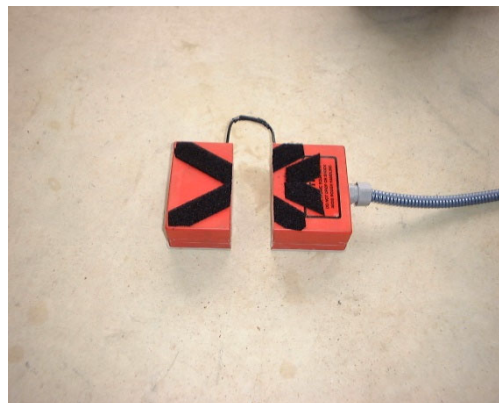
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199 **3.2.1 GPR technique**

200 The radar technique employed relied on a commercial GPR system, using SIR-3000 systems from
201 Geophysical Survey Systems, Inc. (GSSI®) and two separate ground-coupled 1.5-GHz antennas. GPR relies
202 on the principle that electromagnetic wave pulses are transmitted through the investigated medium. As the
203 EM signal passes through this medium, partial reflections occur at each interface, thus presenting EM
204 contrasts that can be acquired as time signals by the receiving antenna. The recent literature detailing this
205 technique includes Jol [2009], Pajewski and Benedetto [2011], Persico [2014] and Utsi [2017]. As regards
206 concrete, the signals received are mainly analyzed in terms of time delay and pulse echo amplitude [Laurens,
207 *et al.*, 2002; Dérobert *et al.*, 2008].

208 The GPR methodology proposed herein focuses on the direct wave in the medium recorded by the bistatic
209 antennas using four offsets (transmitter-receiver distance) ranging from 7 to 14 cm, which in most instances
210 are compatible with rebar mesh sizes. For our purposes, a commercial bistatic antenna was adapted to
211 variable offsets while separating the shielded antennas and retaining the electronics and their connection
212 (Fig. 2). An absorbent foam was placed between the transmitter and receiver during static measurements in
213 order to measure the wave without distortion due to the direct air wave [Villain *et al.*, 2012]. All
214 measurements were performed in air as the initial step, and subsequently on the concrete at three
215 measurement points for each offset (Fig. 3a). After peaking the maximum direct wave (DW) for every offset,
216 the velocity and relative permittivity can then be calculated (Fig. 3b). Since the antennas are coupled to the
217 surveyed medium, the central frequency decreases towards approx. 900 MHz on saturated concretes, which
218 is why results derived from GPR will be associated with the 900-MHz frequency in the following.
219 Few observables are studied with this configuration, i.e.: velocity, the corresponding relative permittivity,
220 and attenuation from the direct wave. For this attenuation, the studied observable corresponds to the slope
221 coefficient of the logarithm of normalized amplitudes of the four offsets (herein called amplitude-slope): the
222 greater the slope, the less electromagnetically attenuating the medium.

223



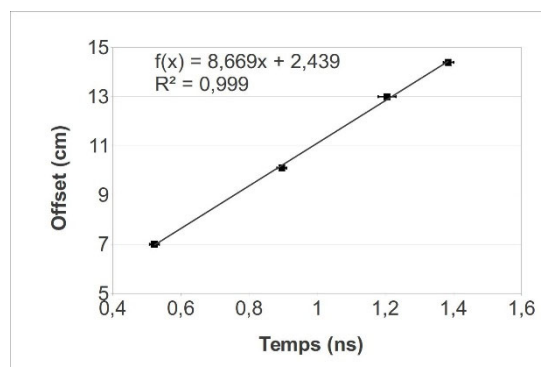
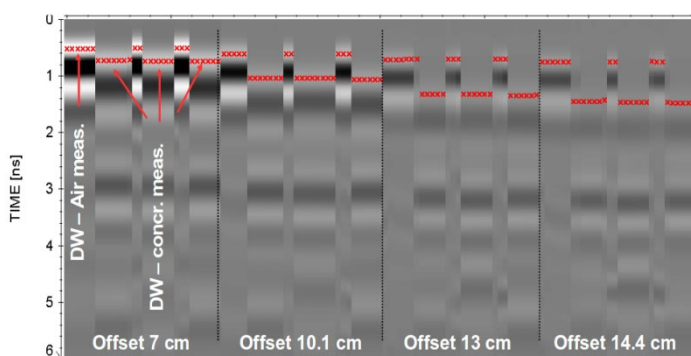
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Fig. 2: Adaptation of a variable-offset bistatic configuration from one commercial 1.5-GHz antenna

a)

b)

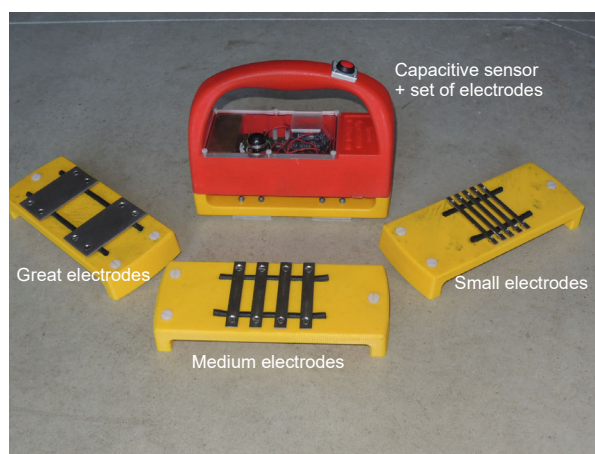


226 Fig. 3a) Example of GPR CMP performed on concrete G3 before carbonation - Presentation of the direct waves (DW)
 227 from air and concrete measurements at three positions; b) Calculation of GPR velocity from the peaking data

228 **3.2.2 Capacitive technique**

229 The principle of the capacitive technique relies on the resonance frequency measurement of an oscillating
 230 circuit (approx. 33 MHz) between electrodes lying on the upper face of the test plane medium [Dérobert *et*
 231 *al.*, 2008; Fares *et al.*, 2016]. This set-up forms a coplanar capacitor. The changes in capacitance, which
 232 induce a shift in resonance frequency, are indicative of concrete constituents and conditions. A preliminary
 233 calibration on known materials outputs the relative permittivity of the tested material, which is viewed as a
 234 homogeneous medium. A panel of three sets of electrodes (investigation depth equal to 2-3 mm for
 235 electrodes labeled SE, 1-2 cm for ME, 7-8 cm for GE) yields information on a possible gradient depth
 236 function (Fig. 4).

237 For the present study, only those results obtained with the GE electrodes are shown. The thickness coupled
 238 with a set of electrodes, most closely resembling that from the GPR direct wave, actually corresponds to GE
 239 electrodes. Moreover, since a thin superficial layer was carbonated on ANR-SENSO slabs during NDT
 240 measurements (1 to 2 mm), the GE electrodes were least sensitive to this layer, leading to the assumption that
 241 its effect was negligible.



242
 243 Fig. 4: Capacitive measurement system with 3 different sets of electrodes (SE, ME, GE)
 244

245 **3.2.3 Coaxial cylindrical EM cell**

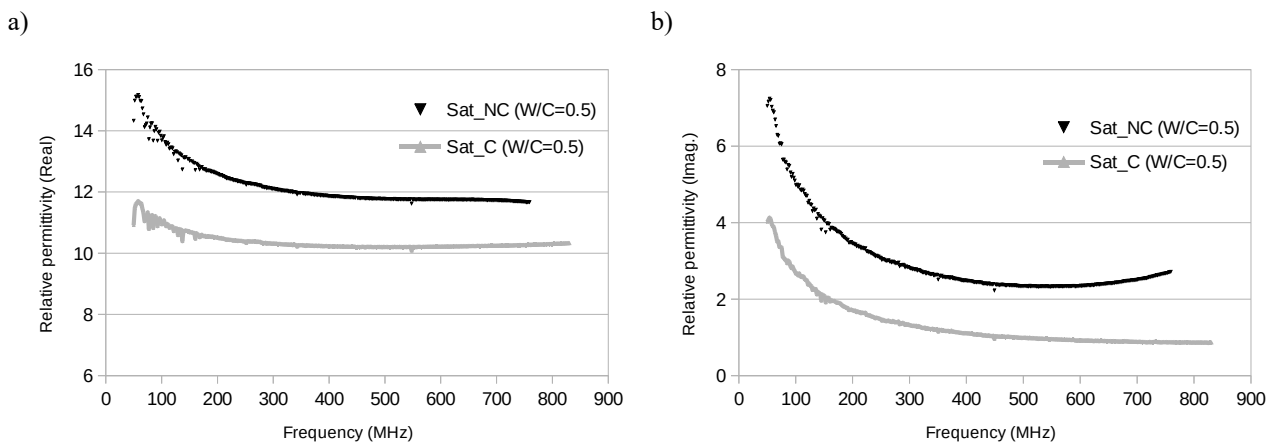
246 An EM cell measurement was designed to characterize bound civil engineering materials, i.e. cement as well
 247 as bituminous concrete, through complex relative permittivity at radar frequencies typically extending from
 248 50 MHz to about 1-1.4 GHz, with the upper limit depending on material permittivity. An iterative inversion

249 procedure enabled retrieving the complex relative permittivity of the material from the reflection coefficient
250 measurements [Adous *et al.*, 2006], thus deriving the dispersion curve (relative permittivity vs. frequency).
251 The benefit of such an EM cell is twofold: to characterize civil engineering mixes over a large radar
252 frequency band; and to correlate the measurements conducted by the two NDT techniques, namely capacitive
253 and GPR, operating at both ends of this frequency band. In order to extrapolate the relative permittivity at
254 33 MHz (or 1 GHz) from EM cell measurements and compare all results with those of the NDT technique, a
255 Jonscher's model was then introduced to fit the dispersion curve [Ihamouten *et al.*, 2011].
256

258 4.1 Effect of carbonation on the complex relative permittivity

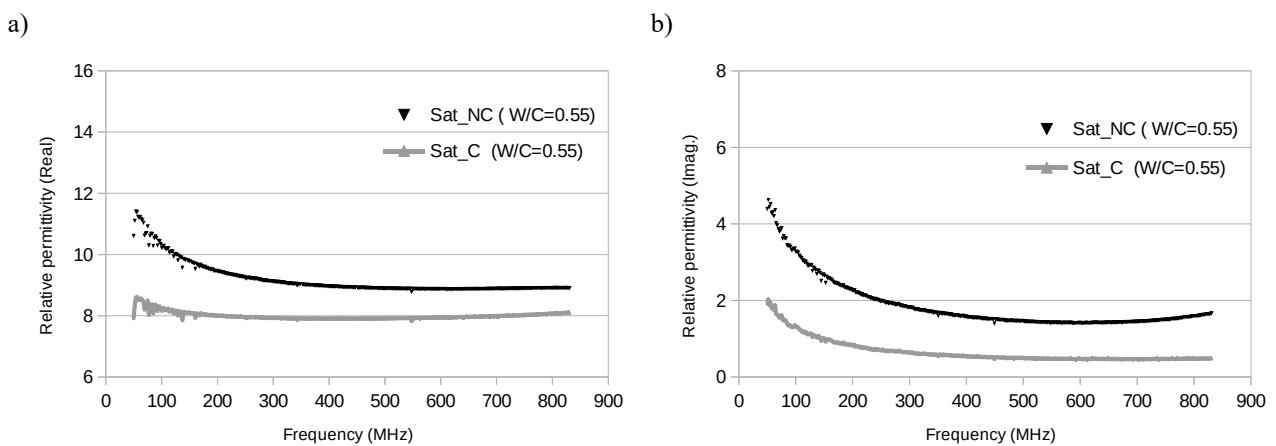
259 The NC cores (A) and carbonated cores (B) from Table 1 were tested in the EM coaxial cell under saturated
 260 conditions. The dispersion curve of the complex relative permittivity was obtained with an averaged higher
 261 frequency, depending on the value of the real part of permittivity (dielectric constant), limited at between
 262 approx. 750 MHz and 1 GHz. An example for concretes mixed with calcareous aggregates (C15) is given in
 263 Figure 5 and another with siliceous aggregates (C27) in Figure 6. As is the case for all concretes (except C3
 264 and C29, which were not sufficiently carbonated, see Table 2), the complex permittivity decreases
 265 significantly with carbonation, especially at low frequency for the real part. Moreover, the carbonated
 266 saturated samples are less dispersive than the other samples.

267



268 Fig. 5: Complex permittivity of carbonated (C) and non-carbonated (NC) saturated concrete C15 (calcareous
 269 aggregates, cement 410 kg.m^{-3} and $W/C = 0.5$): a) Real part; b) Imaginary part

270



271 Fig. 6: Complex permittivity of carbonated (C) and non-carbonated (NC) saturated concrete C27 (siliceous aggregates,
 272 cement 410 kg.m^{-3} and $W/C = 0.55$): a) Real part; b) Imaginary part

273

274 This decrease in permittivity may be due to the porosity reduction, estimated at approx. 4% (absolute value)
 275 for ordinary concretes by Villain *et al.* [2007], which induces an overall decrease in the pore solution of
 276 saturated samples. The diminished dispersive effects at low frequency (below 200 MHz) might also be due to

277 the decrease in small mobile hydroxyl ions (OH⁻). Another explanation could be the filling of smaller pores
278 (Fig. 1) combined with less tortuosity, which induces a reduction in the capacitive effects of the various ions
279 contained in these pores.

280 Note that these explanation are similar to those given for the increase in resistivity induced by carbonation
281 [Alonso *et al.*, 1988; Glass *et al.*, 1991].

282 The second observation focuses on the dispersive effects of permittivity at low frequency, which increase due
283 to the Maxwell-Wagner effect as the W/C ratio decreases, as explained by the lower pore diameters.

284 Let's also note the carbonation of high performance concretes, with such a low W/C ratio and hence low
285 porosity, is a very long and difficult process. Despite 3 months of exposure to a high carbon dioxide content,
286 the carbonation process might still be incomplete for less porous concretes. A model based on a Portland
287 cement quantity and W/C established by Papadakis *et al.* [1991a-b] found that the mass increase of a
288 complete carbonation process is bound to be slightly overestimated, with the less porous concretes not being
289 fully carbonated (dark and medium gray in Table 4).

290 Concerning concretes C3 and C29, ~~there must be an experimental problem, as C29 is a highly porous-~~
291 ~~concrete (ϕ 1/4 17.1%) that should carbonate easily. This lack of carbonation may be due to the air-entraining~~
292 ~~agent that induces a closed porosity, but this is merely a hypothesis although noted on the other mixes-~~
293 ~~containing AEA.~~ even though permittivity results show similar trends to those of C15 and C27, with slight
294 decreases in permittivity, they should not be taken into account and are thus not presented herein.

295 Lastly, the difference in permittivity observed between NC samples of concretes mixed with calcareous and
296 siliceous aggregates is solely due to the permittivity of the coarse aggregates.

297

298 4.2 Effect of carbonation on EM NDT techniques

299 The primary results from the ANR-SENSO project are listed in Table 5, with all mixes being considered
300 homogeneous. The mean value and standard deviation correspond to several measurements performed at 3
301 points on the surface of the same slab. First, it can be underscored that the real part of the relative
302 permittivity (or dielectric constant) is lower for carbonated slabs than for NC slabs, at low frequency for
303 capacitive measurements as well as at higher frequencies for GPR measurements (though to a much lesser
304 extent). This decrease is attributed to a drop in porosity, thus leading to less volumetric water content in the
305 mixes.

306 A special comment is warranted for concrete G6, since its aggregates are of a different type. Calcareous
307 coarse aggregates do involve mostly higher permittivity values, as G6 behaves like the other mixes under a
308 carbonation process from an EM standpoint. For GPR, the measurement conducted on the G6_NC slab
309 seems to be compromised and has thus been excluded.

310

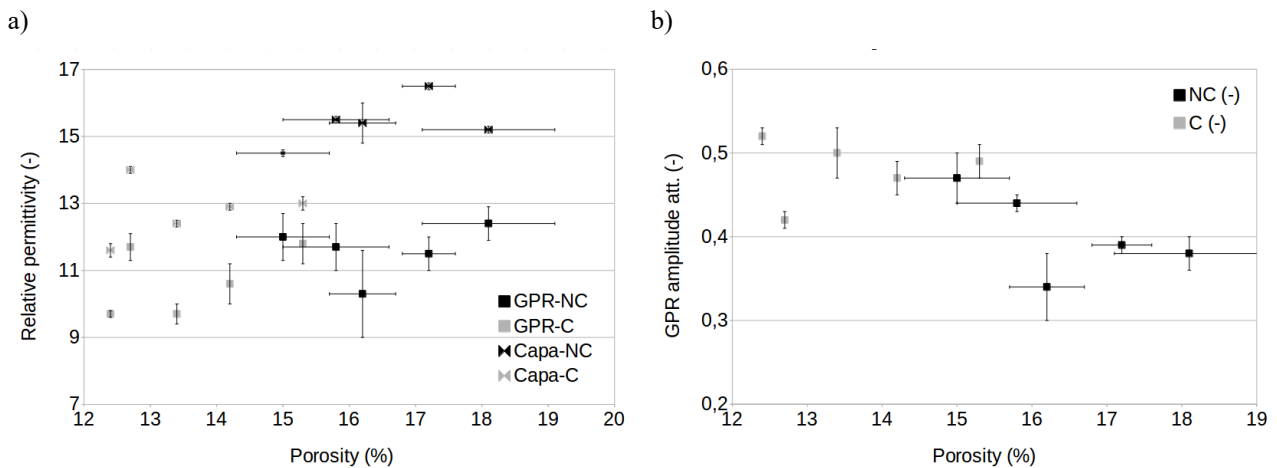
311
312

Table 5: Variation in permittivity (GPR and capacitive) and radar amplitude-slope due to carbonation (ANR-SENSO project)

Code	Porosity (%)	Capa_GE permittivity (-)	GPR permittivity (-)	GPR amplitude-slope (-)
G3-P0	16.2	15.4 ± 0.6	10.3 ± 1.3	0.34 ± 0.04
G3-P40	13.4	12.4 ± 0.1	9.7 ± 0.3	0.50 ± 0.03
G3a-P0	15	14.5 ± 0.1	12.0 ± 0.7	0.47 ± 0.03
G3a-P40	12.4	11.6 ± 0.2	9.7 ± 0.1	0.52 ± 0.01
G7-P0	15.8	15.5 ± 0.1	11.7 ± 0.7	0.44 ± 0.01
G7-P40	14.2	12.9 ± 0.1	10.6 ± 0.6	0.47 ± 0.02
G8-P0	18.1	15.2 ± 0.1	12.4 ± 0.5	0.38 ± 0.02
G8-P60	15.3	13.0 ± 0.2	11.8 ± 0.6	0.49 ± 0.02
G6-P0	17.2	16.5 ± 0.1	11.5 ± 0.5	0.39 ± 0.01
G6-P40	12.7	14.0 ± 0.1	11.7 ± 0.4	0.42 ± 0.01

313

314 The increase in the radar amplitude-slope of the direct wave (Fig. 7b), in the carbonated material, deserves to
 315 be highlighted; it is correlated with the decrease in wave attenuation, hence with the decrease in the
 316 imaginary part of the relative permittivity, due to less volumetric water quantity in the saturated concretes. In
 317 assuming two outliers, the GPR amplitude-slope and relative permittivity show linear sensitivities to porosity
 318 (Fig. 7b). However, the lower level of uncertainty of the amplitude-slope leads to considering this observable
 319 as more efficient for carbonation detection.

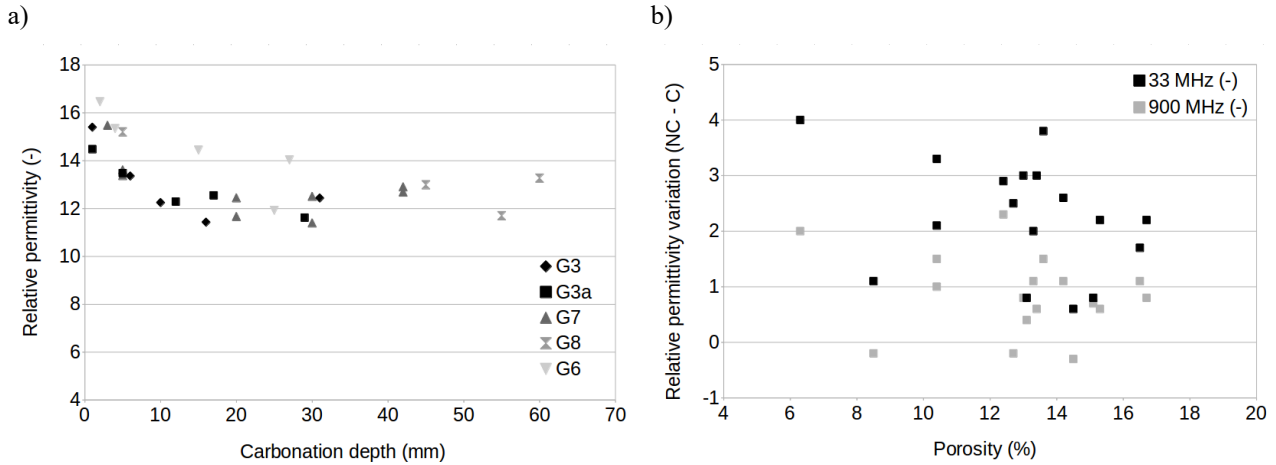


320
321
322

Fig. 7: a) GPR relative permittivity and (b) GPR amplitude-slope vs. porosity for carbonated and non-carbonated concrete mixes (ANR-SENSO project)

323 NDT techniques could be performed during the carbonation process as the carbonation depth could be
 324 measured. Figure 8 presents the evolution in relative permittivity vs. carbonation depth measured by both
 325 capacitive and GPR techniques on all mixes. We can detect a decreasing slope over the first 20 millimeters
 326 until reaching a plateau, which is clearly visible in Figure 8a for capacitive measurements. This finding can
 327 be interpreted as an increase in the share of carbonation thickness within the volume coupled to the GE

328 electrodes (assimilated to a depth penetration). Once the carbonation thickness has exceeded the coupled
 329 volume limit, the capacitive technique designates the concrete as homogeneous and shows stable values.
 330 These results indicate that, in practice, GE electrodes remain sensitive until roughly 20 mm for carbonation
 331 detection, i.e. much less than reported in previous studies for water content detection [Fares *et al.*, 2016].
 332



333 Fig. 8: Relative permittivity vs. carbonation depth during the carbonation process obtained by: a) capacitive technique,
 334 b) GPR
 335

336 For the GPR results, the measurements display a slight decrease in evolution vs. carbonation depth (Fig. 7b),
 337 which is more visible over the first 20 millimeters. The underlying interpretation remains quite complex as
 338 several phenomena are interacting. The direct wave, whose maximum amplitude has peaked, corresponds to
 339 the sum of the direct wave in the medium, the faint direct air wave (as the antennas are shielded) and a
 340 possible guided wave propagating in the carbonated layer.

341 Concerning the Epsilon project, the deduced relative permittivity values, as obtained from EM cell
 342 measurements using Jonscher's model fitting at 33 and 900 MHz, are presented in Table 6. These results are
 343 rather similar to those from the ANR-SENSO project (Table 5), by showing decreases in relative permittivity
 344 with carbonation that are more pronounced at low frequencies than at the GPR frequency.

345 Moreover, capacitive measurements could be performed, following the project, on carbonated slabs (B
 346 samples) after saturation. The limitation with this method lies in the fact that the capacitive system was not
 347 available during the Epsilon project, in which concrete slabs (A samples) were not subjected to natural
 348 carbonation. Once available, the natural carbonation had progressed and was therefore no longer negligible
 349 in the capacitive measurements, which then could no longer be carried out on non-carbonated mixes.

350 The capacitive results, as featured in Table 6, show good agreement with the results obtained from the EM
 351 cell at the same frequency.

352

Table 6: Variation in relative permittivity values at 33 and 900 MHz due to carbonation (Epsilon project)

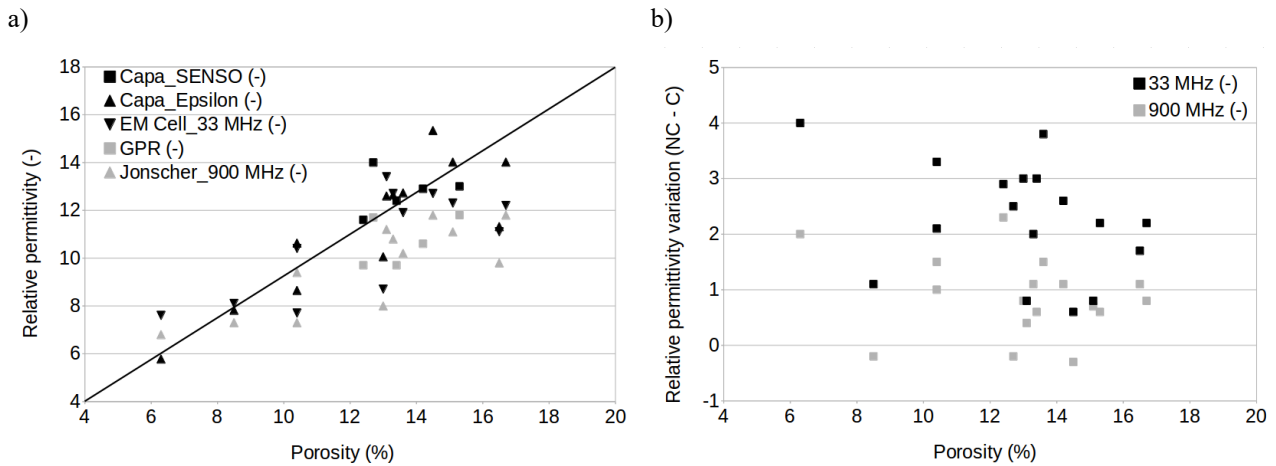
Code	Capa_GE (-)	Jonscher's fitting 33 MHz (-)	Decrease 33 MHz	Jonscher's fitting at 900 MHz (-)	Decrease 900 MHz
C1_NC		14.7		11.9	
C1_C	12.64	12.7	2.0	10.8	1.1
C3_NC		9.2		7.1	
C3_C	7.82	8.1	1.1	7.3	-0.2
B5A_NC		11.6		8.8	
B5B_C	5.78	7.6	4.0	6.8	2.0
B7A_NC		12.5		10.4	
B7B_C	10.63	10.4	2.0	9.4	1.0
B13A_NC		11.0		8.8	
B13B_C	8.65	7.7	3.3	7.3	1.5
B15A_NC		15.7		11.7	
B15B_C	12.73	11.9	3.8	10.2	1.4
B17A_NC		13.1		11.8	
B17B_C	14.02	12.3	0.8	11.1	0.8
B19A_NC		12.8		10.9	
B19B_C	11.32	11.1	1.7	9.8	1.0
B25A_NC		14.2		11.6	
B25B_C	12.60	13.4	0.8	11.2	0.4
B27A_NC		11.7		8.8	
B27B_C	10.06	8.7	3.1	8.0	0.8
B29A_NC		14.4		12.6	
B29B_C	14.02	12.2	2.2	11.8	0.8
B31A_NC		13.3		11.5	
B31B_C	15.34	12.7	0.5	11.8	-0.2

354

355 4.3 Comparison with the EM results

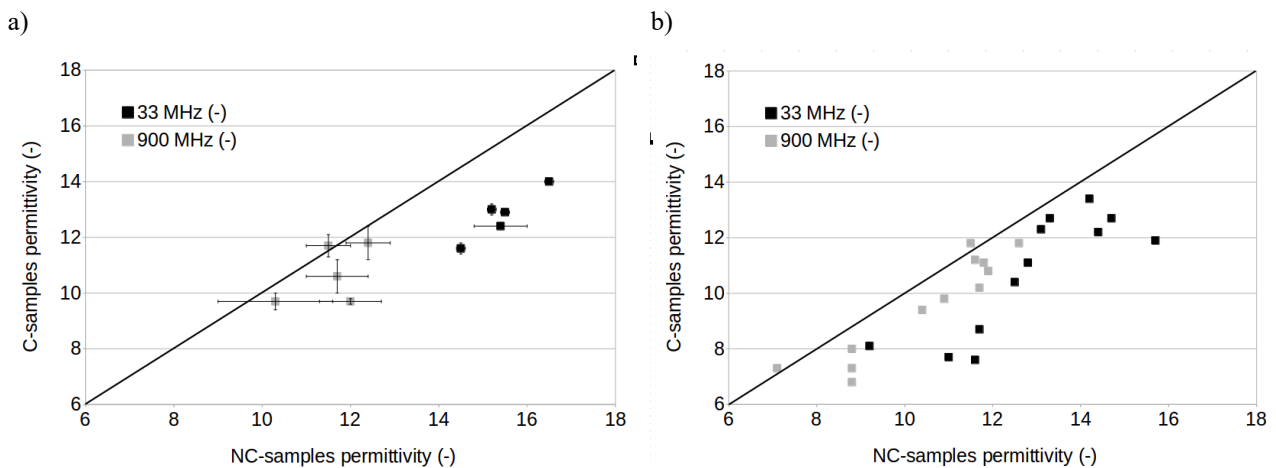
356 Figure 9a compiles all EM results, in focusing on the relative permittivity of saturated carbonated mixes vs.
357 porosity. The measurements performed at 33 MHz are depicted in black dots and those at 900 MHz in gray.
358 Let's note an apparent linear increase with porosity, mainly due to an increase in the volumetric water content
359 filling the pores. The variation in relative permittivity between non-carbonated and carbonated mixes is
360 highlighted in Figure 9b. These variation values are roughly in the range of 2 at 33 MHz and 1 towards 900
361 MHz.

362



364 Fig. 9a) Relative permittivity vs. porosity obtained by capacitive and GPR techniques, and by EM cell measurements, as
 365 fitted by Jonscher's model on carbonated mixes; b) Variation of permittivity vs. carbonated porosity, derived by
 366 capacitive and GPR techniques, and by EM cell measurements fitted by Jonscher's model, compiled by frequency band.
 367

368 While comparing non-carbonated and carbonated mixes, from the standpoint of EM NDT techniques, Figure
 369 10 shows the level of permittivity shift at both ranges of frequency: a high one at 33 MHz and a low one at
 370 900 MHz. The different presentations in Figures 9 and 10 are due to the fact that for the latest information,
 371 the separation step is based on aggregate type.



372 Fig. 10: Sensitivity to carbonation on capacitive techniques at 33 MHz and on GPR at 900 MHz
 373 using saturated concretes: a) ANR-SENSO project; b) Epsilon project
 374

375 The decrease in the real part of permittivity, as determined by the GE capacitive technique, ranges from 2.2
 376 to 3.0 (Table 5 and Fig. 5a) or from 0.8 to 4.0 (Table 6 and Fig. 5b). On the other hand, the decrease
 377 determined by GPR ranges between 0.6 and 2.2 or between 0.4 and 2.0.

378 These findings confirm that the results of both projects are in good agreement and moreover that the
 379 capacitive technique at 33 MHz is more sensitive than a GPR equipped with 1,500-MHz antennas to
 380 carbonation. This observation is in agreement with the higher sensitivity at low frequency revealed by the
 381 dispersion curves (Fig. 5). In addition, the uncertainty of capacitive measurements is much lower than that of
 382 GPR, as evidenced in Figures 7a and 10a.

384

5. Conclusion

385 The effect of carbonation on EM wave propagation and dispersion has been presented on (12+5) different
386 saturated concretes, along with the capability of two electromagnetic non-destructive techniques, namely
387 capacitive and GPR, to detect this pathology. Carbonation leads to a decrease in both the real and imaginary
388 parts of permittivity. Wave attenuation is smaller and EM wave dispersion is reduced. This outcome can be
389 attributed both to the porosity reduction that lowers the overall water content and to ionic changes in the pore
390 solution. The pore distribution with fewer nano-pores and more micro-pores, which modifies tortuosity,
391 could also exert an impact, mainly at low frequencies. The reason for choosing saturated mixes was twofold:
392 maximize the variation in permittivity of non-carbonated and carbonated mixes, and remove any bias due to
393 water content uncertainty in the mixes.

394 The results obtained from two national research projects are in agreement, indicating that carbonation
395 induces a decrease in the range of 2 at 33 MHz and 1 towards 900 MHz for the permittivity of concretes.
396 Moreover, saturated carbonated mixes display a general linear trend of permittivity vs. porosity due to the
397 volumetric water content filling the pores.

398 Capacitive and GPR techniques could constitute useful tools for monitoring carbonation in concrete.
399 Nevertheless, great care must be taken regarding the degree of saturation in the concrete samples since this
400 parameter also heavily influences the EM results. For on-site ND structural evaluations, all durability
401 indicators (porosity and degree of saturation) and degradation monitoring parameters (carbonation depth)
402 must be assessed. Since all these indicators are capable of influencing EM NDT techniques, combining
403 several complementary ND techniques might be required to perform independent evaluations.

404

Acknowledgments

406 The authors are grateful to O. Coffec, J.L. Geffard and G. Gugole for their technical support. The Electricité
407 de France (EDF) company and the French Ministry of Ecology (MTES) are also acknowledged for their
408 financial support of the EPSILON research project. Also, the French National Research Agency (ANR) has
409 generously sponsored the ANR-RGCU SENSO project.

410

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