



Mohammed, Mahmoud khashaa and Dawson, Andrew and Thom, Nicholas (2014) Carbonation of filler typed self-compacting concrete and its impact on the microstructure by utilization of 100% CO2 accelerating techniques. *Construction and Building Materials*, 50 . pp. 508-516. ISSN 1879-0526

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1 **Carbonation of filler typed self-compacting concrete and its impact on the**
2 **microstructure by utilization of 100% CO₂ accelerating techniques**

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9 **Abstract**

10 Via the use of accelerated carbonation techniques with 100% CO₂ concentration, an
11 experimental programme was performed to investigate the carbonation and associated
12 microstructural changes of three different Self-Compacting Concrete (SCC) in which some of
13 the cement had been replaced by limestone powder, fly ash and/or silica fume . Accelerated
14 carbonation tests were conducted on these “filler-typed” SCCs after 28 days water
15 curing .Approximately 33% of the total binder (450 kg/m³) was replaced by limestone powder,
16 fly ash or a fly ash-silica fume blend.

17 The results revealed that the replacement of limestone powder (LP) increased the depth of
18 carbonation during the accelerated test relative to the effect of the fly ash (FA) or the
19 combination of the fly ash and the silica fume (FA+SF) replacements. However, the
20 modelling of the normal pressure accelerated carbonation tests with 100% CO₂ showed all the
21 SCCs studied have no risk of carbonation induced corrosion in the natural environment.

22 Overall, the research suggests that carbonation of filler typed SCC may not be chemically
23 controlled, rather, the internal pore structure may play an important role. Furthermore, the
24 effect of carbonation on the internal pore structure and the chemistry of the concrete matrices
25 were more noticeable in SCC containing FA+SF than in those with LP and FA replacements.

26 **Keywords:** accelerated carbonation, 100% CO₂, self-compacting concrete; microstructure;
27 pore size distribution; cement replacement

28

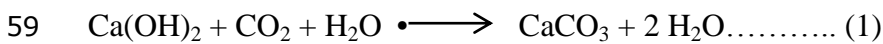
29 **1. Introduction**

30 The durability of self-compacting concrete SCC structures exposed to aggressive
31 environmental conditions is still a major concern of many concrete investigators [1-3].
32 Carbonation, beside chloride attack has been considered as one of the most disruptive
33 phenomena that can affect the concrete durability, potentially causing a significant reduction
34 in service life [4, 5]. Until now, the carbonation of SCC is a somewhat controversial topic.
35 SCC has sometimes a larger and sometimes a smaller carbonation penetration as compared
36 with the Normal Vibrated Concrete (NVC) at the same strength level. Based on previous
37 experimental works, the high amount of CH and CSH found in SCC might reduce the
38 carbonation hazard[6]. However, this might mainly depend on the type of filler and its impact
39 on the composition of the cement paste. Substantial research work [7, 8] has reported that a
40 beneficial outcome of carbonation is in reducing the porosity and improving the
41 microstructure of the cementitious materials.

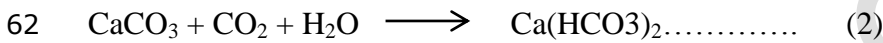
42 The macro and micro diffusivity properties of the concrete may alter due to the change of the
43 porosity and the pore distribution caused by the carbonation process. Furthermore,
44 carbonation might cause a significant alteration in the concrete properties that are strictly
45 related to the microstructure, such as the capillarity of the pores in addition to the change of
46 the pH of the pore solution. The change in the pore solution has a strong effect on the
47 concentration of the destructive ions such as sulphate and chlorine. However, in aggressive
48 environments, the permeability and diffusivity of the concrete is mainly governed by the
49 capillary pores and their interconnectivity[9, 10]. Another form of carbonation attack
50 comprises the neutralization of the alkalinity (pH value) of the hydrated cement paste. The
51 process consists of the diffusion of the gas through the pores system and then the reaction

52 with the hydration products especially CH in the presence of water. Carbonation can cause the
53 pH value of pore water inside the concrete to decrease to about 8.3. This will terminate the
54 passive layer of the embedded steel and permit the corrosion of steel rebar to commence [11,
55 12].

56 According to Stehlik et. al [13] and Matouek and Drochytka (1998), there are four stages in
57 the carbonation process of concrete. The first stage is the reaction between carbon dioxide and
58 the calcium hydroxide in the presence of humidity as shown in Equation 1:



60 The second stage (Equation 2) is the transformation of the insoluble resulting CaCO_3 into a
61 soluble phase:



63 The third stage consists of recrystallizing the resulted insoluble carbonates to large calcite and
64 aragonite crystals and the fourth stage is referred to as full carbonation (100% carbonation).

65 It is important to highlight that the first stage has a significant impact on the porosity and
66 permeation properties of the concrete because of the crystallization of CaCO_3 in the pores.

67 Yet the overall process may significantly disturb the pH level and might even alter tortuosity,
68 porosity and pores size distribution of the matrix. The metastable calcium carbonate

69 $\text{Ca(HCO}_3)_2$ is considered as one of the main causes of the changes in the pore size

70 distribution [9]. However, Borges et. al [14] claimed that not only may the CH be attacked by

71 CO_2 , but even more the CSH gel, with the overall porosity and permeability potentially being

72 increased if the main phase (CSH) is also attacked. The pore structure and diffusion properties

73 of hydrated cement pastes after complete carbonation were studied by Ngala et. al. [15]. They

74 found that there was a decline in the total porosity of three cement paste systems (Ordinary

75 Portland cement (OPC), fly ash and slag pastes) after carbonation, but the most interesting

76 find of their research was the redistribution of the pore sizes; the percentage of large capillary

77 pores (diameter >30 nm) was increased somewhat for the OPC pastes while it was increased
78 considerably more for the fly ash and slag pastes.

79 **2. Research significance**

80 The carbonation of the concrete is considered one of the major concrete durability problems
81 especially with the continuous increase of CO₂ concentration in the atmosphere. Traditionally,
82 carbonation is of concern due to its ability to reduce the service life via the initiation of the
83 corrosion of embedded steel due to the neutralization of the pH value of the cement paste,
84 without causing any harm to the concrete itself. However, in modern types of concrete such as
85 High Performance Concrete (HPC), Self-Compacting Concrete (SCC) and Reactive Powder
86 Concrete (RPC), this concern may prove to be unfounded due to the use of different reactive
87 and non-reactive filler materials in which the impact of the carbonation on the microstructure
88 and chemistry of the concrete may have different features.

89 For the SCC, and from a practical point of view, there is a lack of information about actual
90 carbonation due to the relatively young age of SCC structures. Recently, several laboratory
91 studies have been performed to investigate the durability characteristics of SCC including the
92 carbonation. The most common approach has been to compare the carbonation penetration
93 rate between SCC and NVC.

94 In mature SCC with a high filler-replacement rate, the question that may be raised: which has
95 the dominant effect in determining the carbonation propensity: the chemical composition,
96 represented by the CH content of the matrix or its pore system? In addition, how does the
97 carbonation change the pore distribution, the microstructure and the chemistry of the
98 carbonated SCC? Thus, the main aim of the present study is to investigate the carbonation
99 progression of filler-typed SCC and its impact on the microstructure of the matrices. This is
100 achieved using two types of carbonation accelerating test considering 100% CO₂
101 concentration along with microscopic studies.

102

103 **3. Accelerated carbonation techniques**

104 It is well known that the carbonation is a very slow process in concrete, especially in HPC and
105 it may take a very long time to occur. Therefore, the use of accelerated carbonation becomes
106 necessary for most concrete researchers[11, 16]. Accelerated carbonation testing is crucial to
107 accelerate the slow reaction between CO₂ and the hydration products in cement paste.

108 Although various standards such as the BS EN standard [17] recommend use of (4 ± 0.5) % by
109 volume of carbon dioxide concentration, temperature at (20 ± 2) °C and relative humidity at
110 (55 ± 5) % for the evaluation of the carbonation depth, the accelerated carbonation test has
111 been utilized by many researchers in order to investigate the carbonation process both to
112 compare carbonation rates of different types of cementations materials and to predict the
113 actual carbonation rate[18-23].

114 It is argued by the researchers that the higher concentration of CO₂ might increase the
115 carbonation velocity. On the other hand, others demonstrated that the high concentration may
116 lead to rapid carbonation of the concrete surface and, consequently, this could reduce the
117 penetration of CO₂. A 98% CO₂ concentration was successfully used by Stehlik and Novak
118 [13] when making a correlation between the carbonation in the natural environment and in an
119 accelerated test using Fick's first law of diffusion . Sanjuan et. al [16] pointed out that the rate
120 of carbonation under 100 % CO₂ and a relative humidity of 60 % was 40 times than in natural
121 condition. This was when testing the carbonation of normal vibrated concrete with cement
122 contents of 250 kg/m³ and 350 kg/m³ with w/c ratios 0.69 and 0.49, respectively. For studying
123 the carbonation induced corrosion and electrochemical re-alkalization technique after
124 carbonation, Al-Kadhimi et al [11] proposed a pressurised accelerated carbonation procedure
125 with a pure atmosphere of CO₂ and a pressure up to 15 bars. They revealed that the
126 microstructural characteristics of carbonated concrete at high pressure strictly agreed with
127 those obtaining from naturally carbonated concrete. Thus, the proposed accelerated technique

128 could be useful for examining the vulnerability of materials to carbonation. Accordingly, two
129 types of accelerated testing were utilised in the present investigation:

- 130 • Normal pressurised accelerated carbonation test with 100% CO₂ for the purpose of
131 carbonation depth monitoring and predicting the service life of the mature filler typed
132 SCC.
- 133 • Pressurised accelerated carbonation test to study the change of pore structure, the
134 microstructure and chemistry of the matrices after carbonation.

135 **3.1 Normal pressure accelerated carbonation test with 100% CO₂**

136 A plastic box with dimensions 605x370x355mm was used to design a simple carbonation
137 chamber. It had one inlet for providing the gas from a CO₂ tank and one outlet for releasing
138 any pressure inside the box. A saturated NaCl solution was used to maintain a humidity of
139 75± 5 % [24]. However, the recorded humidity was between 50 to 80 % through the period of
140 the accelerated test with a temperature between 19 -24 °C. The specimens were stored over a
141 steel mesh, to avoid contact with the saturated NaCl solution and the chamber was filled by
142 CO₂ each two weeks (by allowing the exhaust valve to vent while CO₂ is injected from the
143 inlet valve) and sealed very well to ensure 100% concentration of CO₂. A schematic diagram
144 and photograph of the chamber are shown in Fig.1.

145

146 **3.2 Pressurized accelerated carbonation test**

147 The Pressure Aging Vessel (PAV) which is mainly used to simulate the long term aging of
148 asphalt binder was modified as a pressurized accelerated carbonation test vessel (Fig.2). The
149 original oxygen cylinder was replaced by a CO₂ tank to provide the vessel with 100%
150 concentration of CO₂ at a pressure of 2.8 bars. Three SCC mortar samples discs 60 mm in
151 diameter by 10±3 mm high with between 50-70 % partial saturation, cut from cylinders (60 x
152 120 mm), were used for each filler typed SCC mortars as shown in Fig. 2. One was used for
153 monitoring the progress of the carbonation using the phenolphthalein indicator through the

154 cross section of the specimen and the others were kept inside the vessel until complete
155 carbonation. After approximately 15 days, a full carbonation was achieved when the
156 phenolphthalein pink colour of a specimen disappeared completely indicating the drop of the
157 pH value below 9.5 as recommended by RILEM[25].

158

159 **4. Materials, mix design and production of the mixes**

160 **4.1 Materials**

161 Ordinary Portland cement CEM I, 52.5 R was used to produce the SCC. Local river quartz
162 sand with a maximum particle size of 5 mm was used as a fine aggregate for both SCC and
163 mortars. The specific gravity and the water absorption of this type of sand were 2.65 and 1.5
164 %. Natural quartz uncrushed gravel with a nominal maximum size of 10 mm was used as
165 coarse aggregate. The specific gravity and the water absorption of the gravel were 2.65 and
166 0.8 %. Natural limestone filler come from Longcliffe quarry (Derbyshire, UK) with a particle
167 size less than 65 μm . A fly ash produced by the Cemex Company had a density of 800-1000
168 kg/m^3 . Densified silica fume produced by the Elkem Microsilica Company was used with a
169 bulk density 500-700 kg/m^3 and more than 90% SiO_2 content was used at a dosage of 10% of
170 the cement in case (partially replacing the fly ash) . Polycarboxylate-based superplasticizer
171 was used in all mixes. Several trial mixes were conducted to obtain these selected dosages of
172 SP.

173

174 **4.2 Mix design and production of SCC mixtures**

175 Table 1 shows the mix proportions, the fresh properties tested and the 28 day compressive
176 strength of the SCC studied. The same amount of water was used in all SCC batches. For the
177 mortar specimens, the amount of water was reduced by 0.8 % (coarse aggregate absorption) to
178 ensure the same water to binder ratio as for the full SCC.

179

180 Slump flow diameter and the time taken to reach a slump diameter of 50cm, T_{50} , were used to
181 assess the flowability of the mixes. The fresh SCC and mortars were filled into the moulds
182 without any compaction. Thereafter, the specimens were left in their moulds for 48 hours, and
183 finally cured at 20 ± 2 °C in a water tank for 28 days.

184

185 **5. Experimental work**

186 **5.1 TGA, MIP and SEM tests at 28 days**

187 Powder samples (that passed through a $75\mu\text{m}$ sieve) and small mortar pieces weighing 1- 3g
188 were taken from the middle part of healthy 70 mm mortar cubes before the accelerated
189 carbonation test and used for the Thermo Gravimetric Analysis (TGA) and mercury intrusion
190 porosimetry (MIP) tests respectively. Similar MIP specimens were taken after carbonation.
191 Further, SEM images were acquired to check the capillary pore structure of the matrices using
192 plutonium-coated fractured surfaces, before carbonation. The same technique was used to
193 identify the microstructural change of the pores after full carbonation (See 5.3).

194 **5.2 Carbonation depth measurement**

195 Cylindrical concrete and mortar specimens were prepared for carbonation depth measurement.
196 The specimens had a diameter of 60 cm and a height of 120 cm. After water curing for 28
197 days, the top and bottom ends of the cylinders were sealed using plastic caps to ensure the
198 radial movement of the carbonation. They were stored inside the unpressurized chamber for
199 240 days. At ages of 30, 60, 90, 120 and 240 days, the specimens were removed from the
200 chamber and the following steps were conducted to observe the progression of the
201 carbonation depth:

- 202 • After removing the plastic caps, a 15 mm long (60 mm diameter) disks were cut from
203 the bottom side of each cylinder using a machine saw.
- 204 • The sectioned surface was cleaned from any dust and the depth of carbonation through
205 the circumference of the disks was detected by a phenolphthalein indicator.

- 206 • The depth of carbonation was recorded as an average value of four readings taken 90°
207 from other on the disk. In some cases especially for the concrete samples, another two
208 readings were added to evaluate the minimum depth of carbonation. The procedure of
209 detecting and measuring the carbonation depth is shown in Fig 3.
- 210 • The shortened cylinders were then sealed again and loaded into the chamber for
211 further carbonation.

212

213 **5.3 Tests after carbonation in the pressurised chamber**

214 In contrast to the partially carbonated specimens obtained in the normal pressure container
215 (Fig.1), 100% carbonated specimens were obtained from the pressurised accelerated
216 carbonation (Fig.2). Two types of tests were conducted on these carbonated samples:

- 217 • Small pieces weighing 1-3 g from the middle part of fully carbonated mortar samples
218 were used for the MIP test in order to detect the change of the internal pore structure
219 compared to that already evaluated before carbonation at 28 days.
- 220 • SEM images were acquired to check the change of the morphology of the carbonated
221 sample and to detect the change of the chemistry inside the pores using plutonium-
222 coated fractured surfaces compared to those before carbonation.

223

224 **6. Results and discussion:**

225 **6.1 Thermo gravimetric test TGA and the carbonation progress**

226 The detected amount of CH% due to the dehydration at 420 and 550°C of the powder samples
227 heating to about 950°C before the exposure to accelerated carbonation is summarised in Table
228 2 .The results show that the amount of CH% was significantly lower in the SCCs containing
229 FA and FA+SF as compared with that of LP-SCC. It is well known that the reaction of such
230 pozzolanic materials can generate additional different form of CSH due to the reaction with
231 the CH in the presence of water [26]. Thus, this behaviour might be as a result of the higher

232 pozzolanic activity of the FA and SF in consuming the CH compound as compared to the
233 unreactive LP filler.

234 Fig. 4 represents the change of the carbonation depth of the self-compacting concretes and
235 mortars with time as a result of testing under normal accelerating test with 100% CO₂
236 conditions up to 240 days. The results indicated that both LP self-compacting concretes and
237 mortars showed the highest carbonation depth at all ages. This was followed by FA-SCC
238 which exhibited approximately the same 28 day compressive strength as the FA-SF-SCC.
239 However, the latter revealed the lowest carbonation depth at all test ages. Before the exposure
240 to the accelerated carbonation, the TGA analysis demonstrated that LP-SCC exhibited the
241 highest amount of CH due to the dehydration relative to the other two filler typed SCCs,
242 followed by FA-SCC and FA-SF-SCC.

243 Chemically, this suggests that the LP-SCC should have the highest resistance to carbonation
244 due to the high amount of CH in the cement paste which can capture the CO₂ and prevent it
245 from further diffusion. However, physically, the analysis of the pore structure before
246 carbonation clearly showed that this type exhibited a more porous microstructure than the
247 other SCC mixes see Table 4. The results appear to demonstrate that modification of the pore
248 structure in both FA and FA-SF-SCC increase the resistance to carbonation and offset the
249 effect of reducing the CH.

250

251 **6.2 predicting of actual carbonation depth**

252 The monitoring for eight months of the carbonation depth of the filler typed SCC was used to
253 predict the carbonation depth in a natural environment and the results are summarized in
254 Table 3. The accelerated coefficient of diffusion for SCC mixes was calculated as the slope of
255 the carbonation depth- square root relationship as shown in Fig. 5 according to the first Fick's
256 law (Equation 3) which was mainly used for carbonation modelling [27]. The experimental
257 results showed an excellent correlation factors with the regression lines (at least 96.37 %).

258 $X = K_{acc} \cdot \sqrt{t} \dots\dots\dots (3)$

259

260 X: Depth of carbonation (mm)

261 K_{acc} : Carbonation coefficient (mm/ $\sqrt{\text{year}}$)

262 t: time (year)

263

264 The actual carbonation diffusion coefficient (K_{act}) was calculated using the formula
265 developed by Sisomphon and Franke [21] for the accelerated test under 3% CO₂
266 concentration but here altered for 100% CO₂ concentration. The ratio of the accelerated and
267 the actual diffusion coefficients could be stated in terms of CO₂ concentrations at the
268 accelerated and natural conditions considering that 0.04% is the actual CO₂ concentration in
269 the atmosphere. Fig. 6 shows the CO₂ concentration increase in the atmosphere from 1955 to
270 June 2013 measured at Mauna Loa observatory by U.S. Department of Commerce-National
271 Oceanic and Atmospheric Administration [28]. According to this measurement, this is the
272 first time that the CO₂ concentration has reached to about 400 ppm in May 2013 since 1955.

273 K_{acc} is 50 times than K_{act} considering 100 % CO₂ (Equation 4):

274
$$\frac{K_{acc}}{K_{act}} = \sqrt{\frac{[CO_2] 100 \%}{[CO_2] 0.04\%}} = 50 \dots\dots\dots (4)$$

275 The analysis, Table 3, demonstrates that the predicted carbonation depths were only 5.44 mm,
276 4.60mm and 3.61mm for LP-, FA- and FA-SF-SCC after 50 years of exposure to natural
277 environment. Therefore, there is no risk of carbonation-induced corrosion during the service
278 life. If atmospheric carbon should rise to 0.06% in 50 years' time [refer to the
279 Intergovernmental Panel on Climate Change (IPCC) worse case estimate] then these
280 predictions rise to 6.7, 5.66 and 4.42 for LP-, FA- and FA-SF-SCC respectively (a
281 conservative assumption as concentration is taken as 0.06% thought those 50 years).
282 Therefore, even increased greenhouse gas isn't likely to lead the initiation of steel corrosion
283 over the same time scale.

284 **6.3 Quantitative analysis of the pore structure (MIP) before and after carbonation**

285 In general, the carbonation can promote blocking of the pore structure of the matrix for the
286 concrete. However, the incorporating of fine reactive and non- reactive filler and higher
287 amounts of SP, such as in the case of SCC, can modify the pore structure to a large extent and
288 the impact of the carbonation on the internal structure of the SCC might be different. Thus, it
289 would be interesting to identify the change in pore characterization after carbonation of each
290 SCC. Changes in the pore connectivity and pore concentration after carbonation could have a
291 major impact on the diffusivity of water and of aggressive agents through the concrete.

292 Fig. 7 (a) shows the cumulative MIP intrusion volume against the pore diameter of the LP-
293 SCC matrix while Fig. 7 (b) shows the frequency distribution of these pores. Fig. 8 (a) and (b)
294 display the change in the pore frequency distribution for the FA and FA-SF SCC before and
295 after carbonation.

296 In general, the results of MIP after carbonation demonstrated a noticeable redistribution of the
297 pore structure of the all filler typed SCC matrices. The calculated percentages of the total
298 pores (micro and macro pores considering 0.1μ to be the boundary between these pore classes)
299 before and after carbonation and the CPD are presented in Table 4.

300 From Table 4, the results of LP-SCC indicated that the carbonation promoted the micro pores
301 to about 18 % from the original micro pores before carbonation. In addition, the critical pore
302 diameter (CPD) reduced from 0.06 micron to 0.027 micron .The corresponding development
303 of the micro pores was about 3.1 % for the FA-SCC while it showed a small decrease in the
304 CPD from 0.038 micron to 0.027 micron as compared with the LP-SCC.

305 On the other hand, the percentage of the micro pores in FA-SF-SCC shifted from 71 % to
306 79.5%. However, the most surprising result was the slight increase of the CPD for this type
307 after carbonation from 0.031 micron to 0.038 micron. This may be as a result of the
308 carbonation of the CSH gel which is expected to have been present at a higher percentage in
309 this type of SCC due to the high activity of SF in consuming the CH and producing further

310 CSH. Perhaps the carbonation of CSH in the cement paste of this type explains the changes
311 observed especially at the micro pores level (See Fig.9). Recently, the work conducted by
312 Borges et.al [14] to investigate the carbonation of CH and CSH in composite cement pastes
313 containing high amounts of blast furnace slag (BFS) indicated that overall porosity and
314 permeability may increase if the main phase (CSH) is attacked by CO₂. If the resistance of the
315 cement paste is sufficiently high to prevent a constant CO₂ penetration, the probability of the
316 reaction between CO₂ and CSH might increase. On the other hand, for blended pastes with
317 low resistance to the CO₂ access, they pointed out that carbonation of CSH having a low Ca/Si
318 ratio might not cause a considerable change in the capillary pores structure.

319

320 **6.4 Pore structure change linked with the SEM observation after carbonation**

321 The quantitative results obtained from the cumulative MIP test intrusion volume against the
322 pore diameter before and after carbonation are summarized in Fig. 9. The results show
323 noticeable changes in the cumulative pore percentages especially in the range of (0-100) μ for
324 the FA-SF-SCC matrix as compared with the other two mixes.

325 The SEM observations of the matrix of the FA-SF-SCC after carbonation indicated the
326 presence of coarse pores in several areas in comparison with the matrices of the LP- and FA-
327 SCC. The detailed SEM examination of the pores before and after carbonation of the LP- ,
328 FA- and FA-SF-SCC matrices are shown in Figs. 10, 11 and 12. The results revealed that the
329 Ettringite occurred in the capillary pore structure in two forms after carbonation as shown in
330 Figs. 11 and 12. Monosulfate needles, which are not an expansive form, were found in both
331 LP- and FA- SCC cement pastes after carbonation. However, this compound was much more
332 prominent in the pores of the LP -SCC rather than in those of the FA-SCC.

333 The transformation of the monosulfate into the hexagonal Ettringite shape is associated with
334 approximately 2.3 times increase in the volume [29]. This form of Ettringite (hexagonal shape)
335 was found in the pores of the FA-SF-SCC (Fig.12). The presence of the first form could lead

336 to an increase in the proportion of micro pores in the LP-SCC and FA-SCC matrices and a
337 decrease in the CPD as well.

338 The occurrence of the second form of the Ettringite in the FA-SF-SCC might have caused a
339 kind of microscopic damage to the pore structure due to the expansion pressure caused by the
340 volume increase as this form of Ettringite developed. This might, thus, be responsible for a
341 substantial change of the pores in the range of 0.1-100 μ (See Fig. 9) and the slight increase in
342 the CPD as detected by the MIP test.

343 This delayed Ettringite formation (DEF) (i.e. Ettringite not found during initial curing) could
344 be associated with pore changes after heat-treatment, freeze-thaw attack with and without de-
345 icing salt, sulphate attack and in the presence of the combined action of the CO_2 and water
346 (carbonation) in the cement paste due to the low pH value. Ettringite results from the
347 decomposition of the monosulfate in the cement paste to produce CaCO_3 , $\text{Al}(\text{OH})_3$, gypsum,
348 and water. A part of original monosulfate then combines with the liberated gypsum to form
349 the Ettringite. However, whether the formation of the this compound during the carbonation
350 has a practical impact or not is a subject of controversy [29].

351

352 **7. Conclusion and recommendations**

353 Based on the experimental work in the present study, the following concluding remarks can
354 be drawn:

- 355 • Under normal pressure 100 % CO_2 accelerated testing, the carbonation depth of LP-
356 SCC or mortars was higher than FA- and FA-SF-SCC or mortars at all ages of the test.
357 In contrast, the FA-SF-SCC revealed the lowest carbonation depth. Before the
358 exposure to the accelerated test, the first type showed a higher amount of CH than the
359 latter. This result might indicate that the carbonation progression in SCC is not
360 chemically controlled but, instead, that the pore structure could play a substantial role
361 in determining the progression of the carbonation.

- 362 • Whatever the type of the filler, whether non-reactive (LP) or reactive (FA and SF)
363 with 33% replacement of binder, the actual predicted carbonation diffusion coefficient
364 did not change much after 28 days water curing. Stating the finding in another way,
365 the change of the chemistry of the matrix due to the addition of different fillers had
366 little impact on the actual carbonation rate. Therefore, none of the filler-typed SCC
367 mixes is at risk of carbonation induced corrosion in natural exposure. The predicted
368 carbonation depths were only 5.44 mm, 4.6 mm and 3.61 mm for LP-, FA- and FA-
369 SF-SCC respectively after 50 years in the natural environment.
- 370 • The extrapolated carbonation depth due to unpressurised 100% CO₂ testing could be
371 used for estimating the actual carbonation depth of concrete that has a high resistance
372 to carbonation, such as SCC with a strength grade of 50-60 MPa, in a fairly short time.
373 However, carbonation depth results from actual SCC structures should be maintained
374 to check the validity of the predicted results as current SCC installations progressively
375 age.
- 376 • The modification of the internal pore structure in LP and FA-SCC matrices after
377 carbonation was more pronounced in comparison with the FA-SF-SCC matrix and this
378 was likely related to the presence of more macro pores before carbonation and the
379 nature of the carbonation products.
- 380 • The combined results of the MIP test and SEM observations after carbonation
381 suggesting that the addition of SF could have a positive effect on modifying the
382 internal pore structure while it had a negative effect on the connectivity of the
383 capillary pores after carbonation especially at the micro scale level. Therefore, the
384 permeation characteristics of a concrete cover might be affected in the case of the
385 interaction of carbonation with water or other aggressive substances.
- 386 • The two forms of the Ettringite observed in the SEM examinations in the pore
387 structure of the filler-typed SCC after carbonation could play a significant role in

388 determining the nature of the internal pores and its connectivity after carbonation,
389 especially at the micro level scale.

390

391 **Acknowledgements**

392 The principle author would like to express his gratitude for his PhD scholarship sponsored by
393 Higher Committee for Education Development in Iraq (HCED). The authors would like to
394 gratefully acknowledge Mr Mick Winfield (Operations Support Manager NTEC, Faculty of
395 Engineering), Mr Richard Blakemore (senior technician for mixtures area of NTEC, Faculty
396 of Engineering) and Miss Nancy Milne (Technician, Faculty of Engineering) for their help in
397 in manufacturing the normal pressure carbonation chamber, utilizing the pressurized
398 carbonation chamber and cutting the concrete samples. The authors wish also thanks Mr Keith
399 Dinsdale (Chief Experimental Officer, University of Nottingham - Faculty of Engineering),
400 Miss Vikki Archibald (Analytical Technician, University of Nottingham- Faculty of
401 Engineering) and Dr Nigel Neate (University of Nottingham - Faculty of Engineering) for
402 their help in conducting the MIP, TGA and SEM tests.

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410 **Captured figures**

411 Fig.1 Schematic diagram and photograph of the normal pressurized accelerated carbonation
412 test with 100% CO₂

413 Fig.2 Schematic diagram of the pressurized accelerated carbonation test with 100% CO₂ and
414 the samples used

415 Fig.3 Phenolphthalein carbonation depth measurements

416 Fig.4 carbonation depth of SCC and mortars versus the exposure time

417 Fig.5 Carbonation depths versus the square root of time (year) relationships

418 Fig.6 CO₂ concentration increase in atmosphere from 1955 to June 2013

419 Fig.7 LP-SCC matrix: (a) MIP intrusion volume against the pore diameter (b) frequency
420 distribution of the pores

421 Fig.8 Frequency distribution of the pore before and after carbonation (a) FA-SCC matrix (b)
422 FA-SF-SCC matrix

423 Fig.9 Quantitative analysis of pores percentages change % versus the pores ranges before and
424 after carbonation MIP test

425 Fig.10 Morphology of capillary pore-structure at 28 days before carbonation (No presence of
426 Ettringite (a) LP-SCC (b) FA-SF-SCC

427 Fig.11 Monosulfate form after carbonation in the pores of (a) LP-SCC (b) FA-SCC

428 Fig.12 DEF (Ettringite) after carbonation in the pores of FA-SF-SCC (a) low magnification
429 (b) high magnification

430

431 **Tables**

432 Table 1 Concrete mix designs

Concrete ID	LP-SCC	FA-SCC	FA-SF-SCC
Cement (kg/m ³)	300	300	300
Coarse aggregate (kg/m ³)	860	825	825
Fine aggregate (kg/m ³)	900		
Water (kg/m ³)	180		
Fly ash (kg/m ³)	---	150	120
Limestone (kg/m ³)	150	---	---
Silica fume (kg/m ³)	---	---	30
SP % by weight	2.6	1.83	3.1
Slump flow	700	720	680
T ₅₀ (sec)	4.5	3.2	3.6
Compressive strength 28 day MPa	57.9	56.5	50

433

434 Table 2 CH % content of the mixes at 28 days

Mix ID	LP-SCC	FA-SCC	FA-SF-SCC
CH % dehydration	6.3	4.7	4.2

435

436

437 Table 3 Predicted carbonation depths for SCC in natural environment

Mix ID	K _{acc.} mm/(year) ^{1/2}	K _{act.} mm/(year) ^{1/2}	Carbonation depth (mm) after number of years				
			10	20	30	40	50
LP-SCC	38.6	0.77	2.43	3.44	4.22	4.87	5.44
FA-SCC	32.6	0.65	2.05	2.91	3.56	4.11	4.60
FA-SF-SCC	25.5	0.51	1.61	2.28	2.79	3.22	3.61

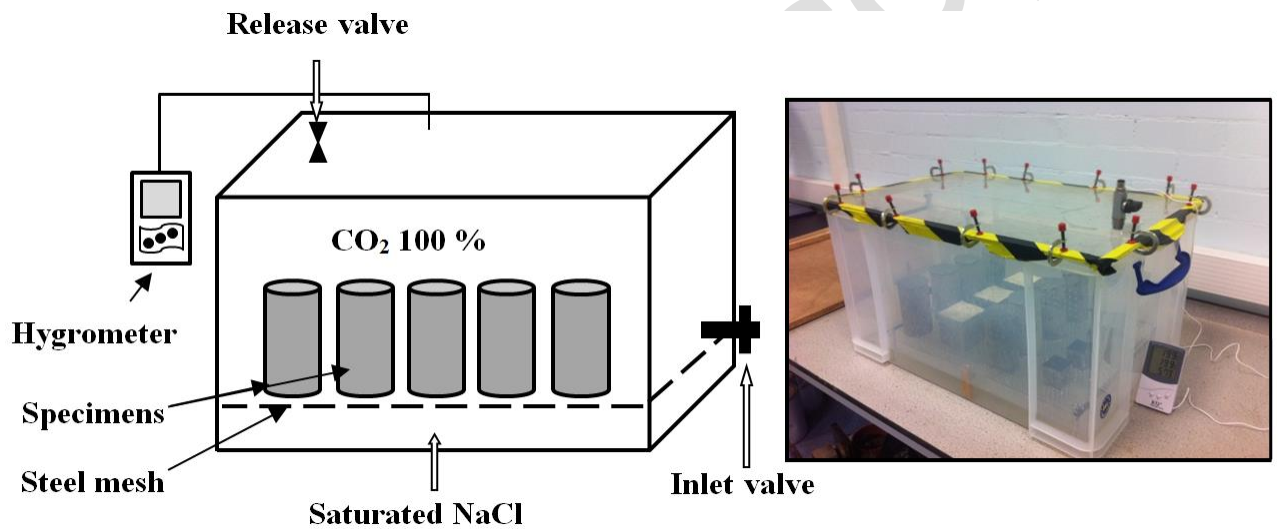
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439 Table 4 Micro, macro pores and CPD before and after carbonation of the mixes

Mix ID	Before carbonation			After carbonation		
	Macro pores %	Macro pores %	CPD (μm)	Macro pores %	Macro pores %	CPD (μm)
LP-SCC	66.7	33.3	0.06	78.7	21.3	0.027
FA-SCC	75	25	0.038	77.3	22.7	0.027
FA-SF-SCC	71	29	0.031	79.5	20.5	0.038

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441 Captured figures

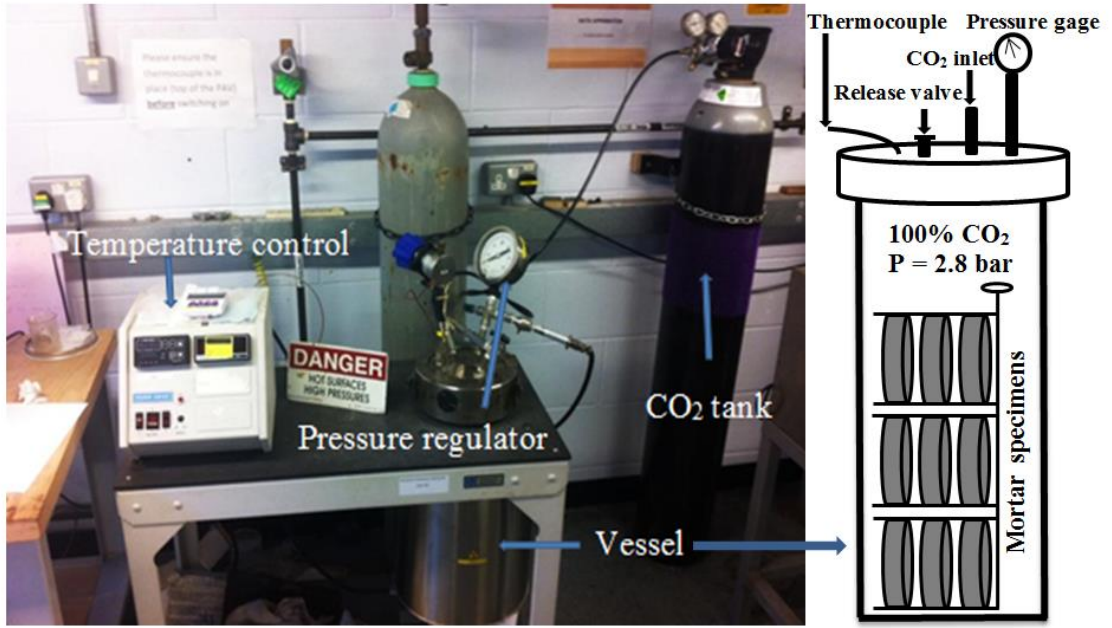


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443 Fig.1 Schematic diagram and photograph of the normal pressurized accelerated carbonation

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test with 100% CO₂

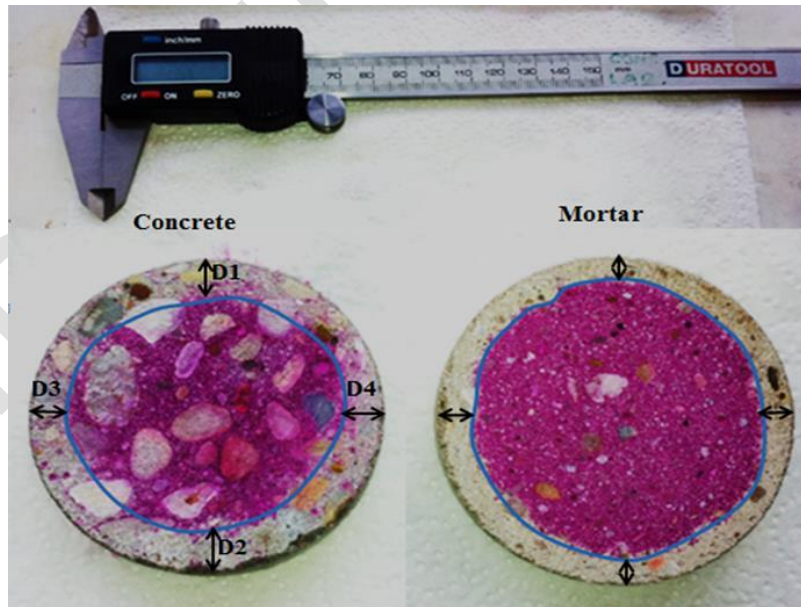


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446 Fig.2 Schematic diagram of the pressurized accelerated carbonation test with 100% CO₂ and
 447 the samples used

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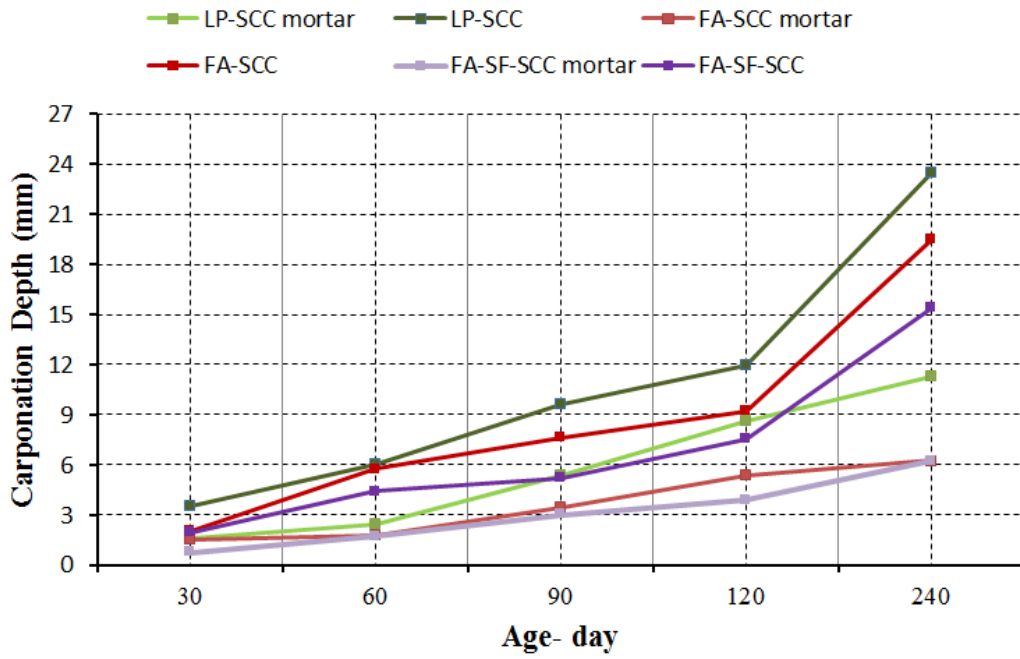
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451 Fig.3 Phenolphthalein carbonation depth measurements

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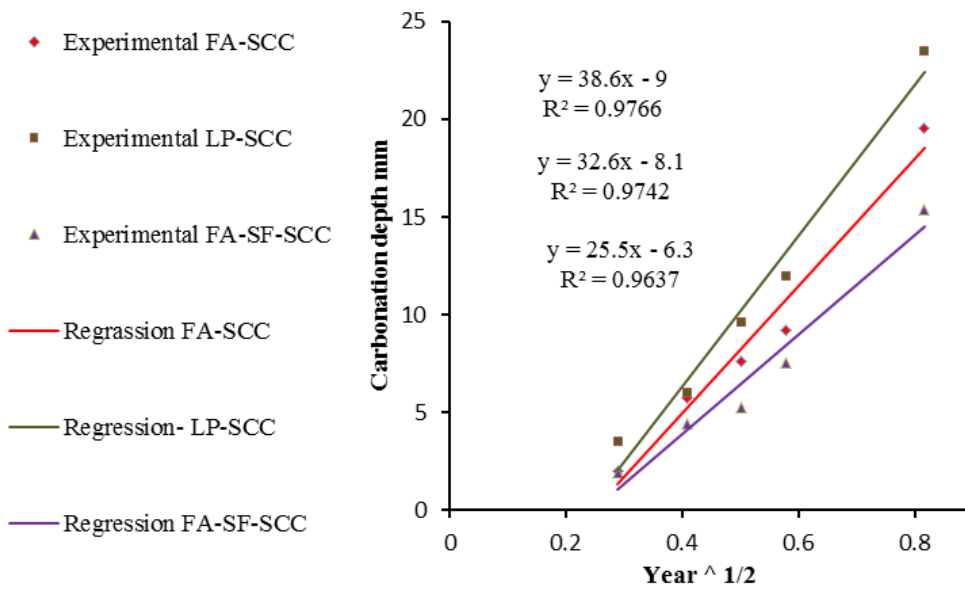
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Fig.4 carbonation depth of SCC and mortars versus the exposure time

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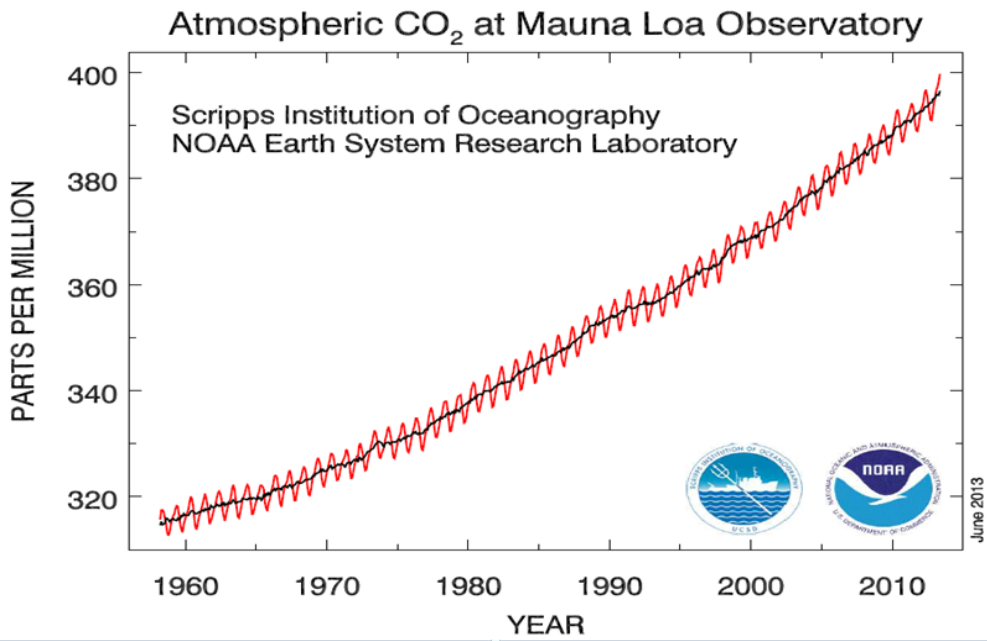


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Fig.5 Carbonation depths versus the square root of time (year) relationships

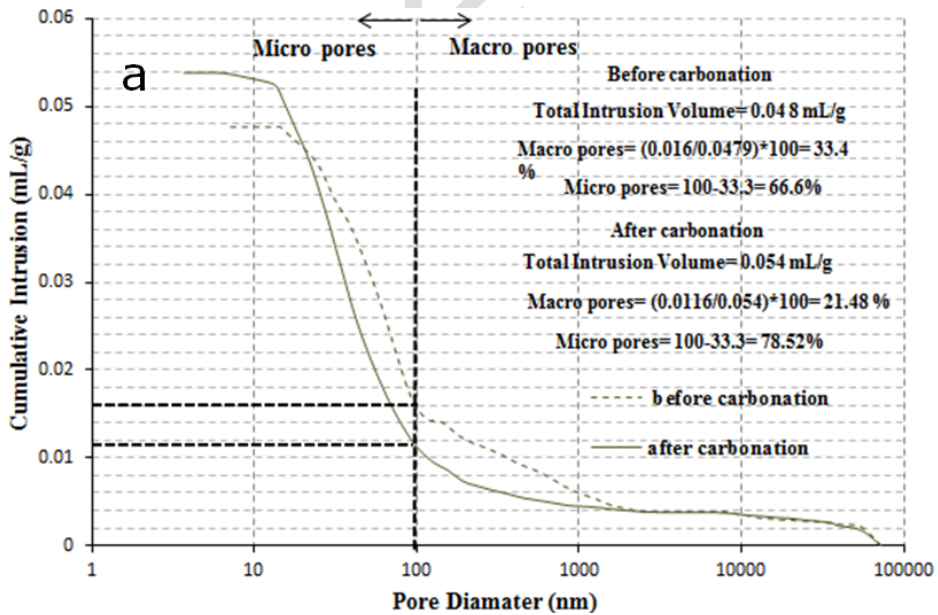
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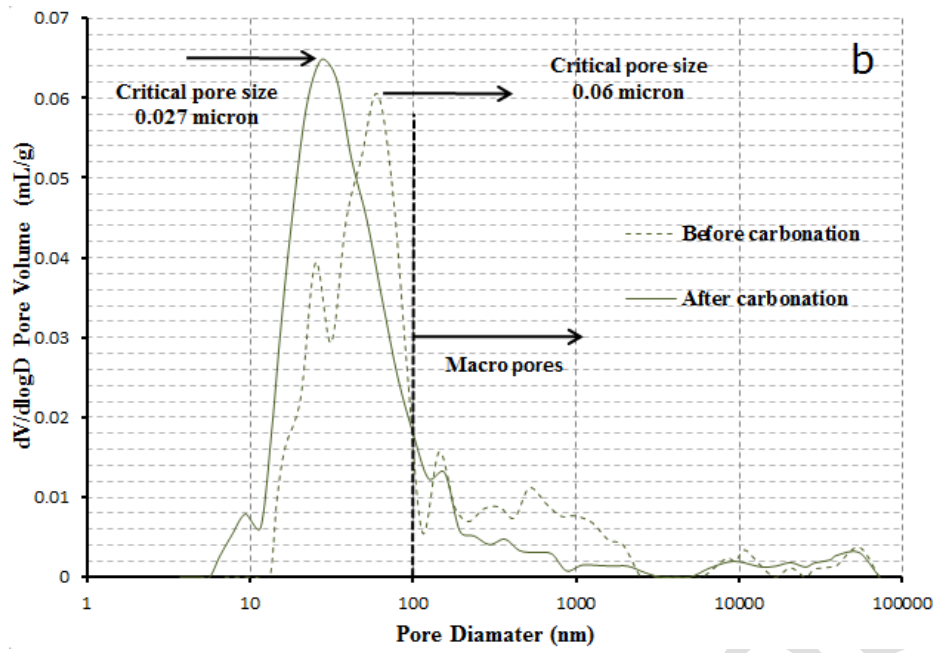
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461 Fig.6 CO₂ concentration increase in atmosphere measured at Mauna Loa observatory from
 462 1955 to June 2013 [28]

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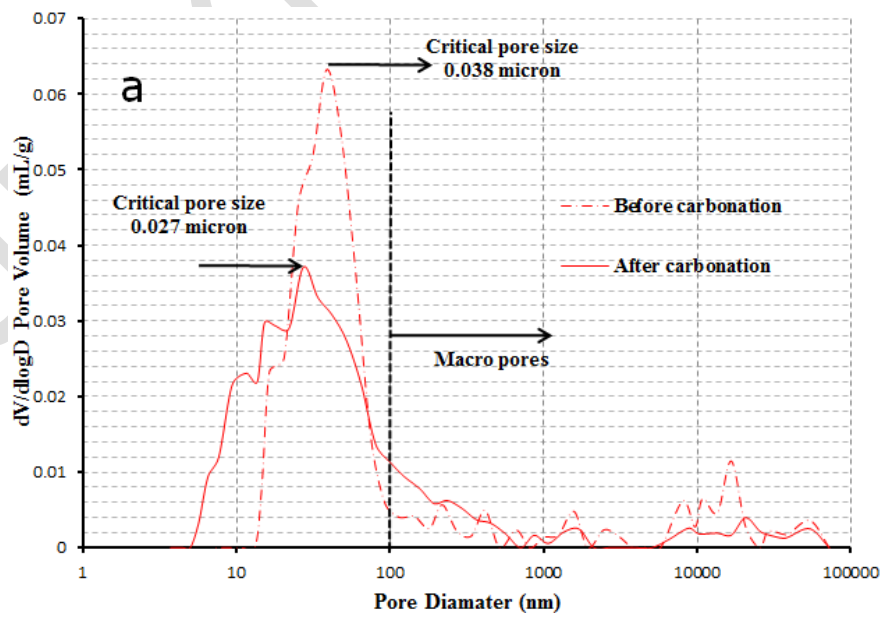
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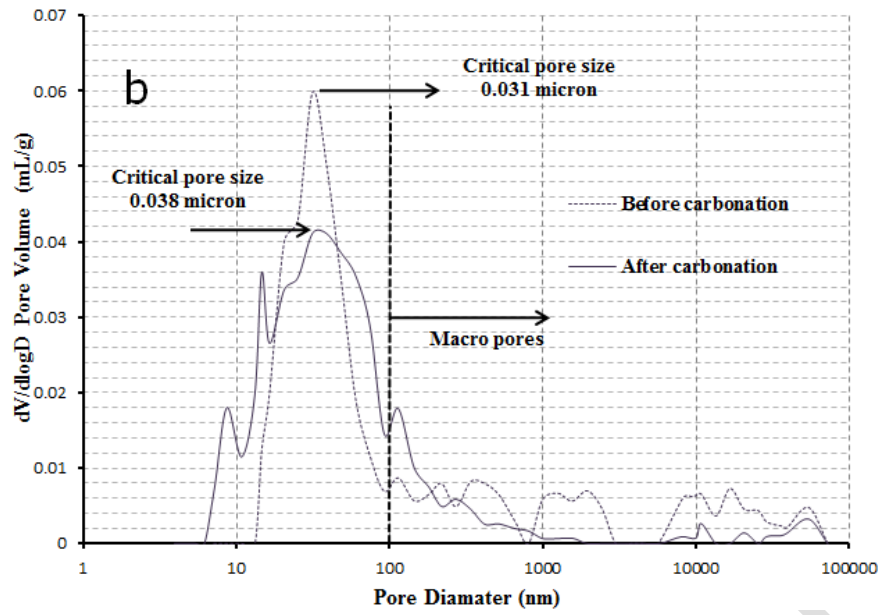
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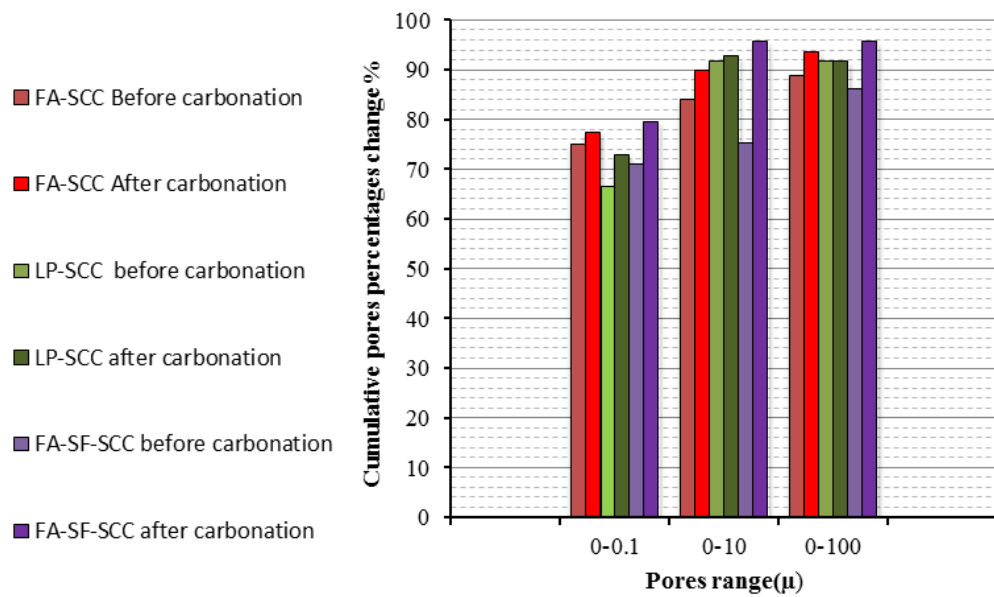
475 Fig.8 Frequency distribution of the pore before and after carbonation (a) FA-SCC matrix (b)

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FA-SF-SCC matrix

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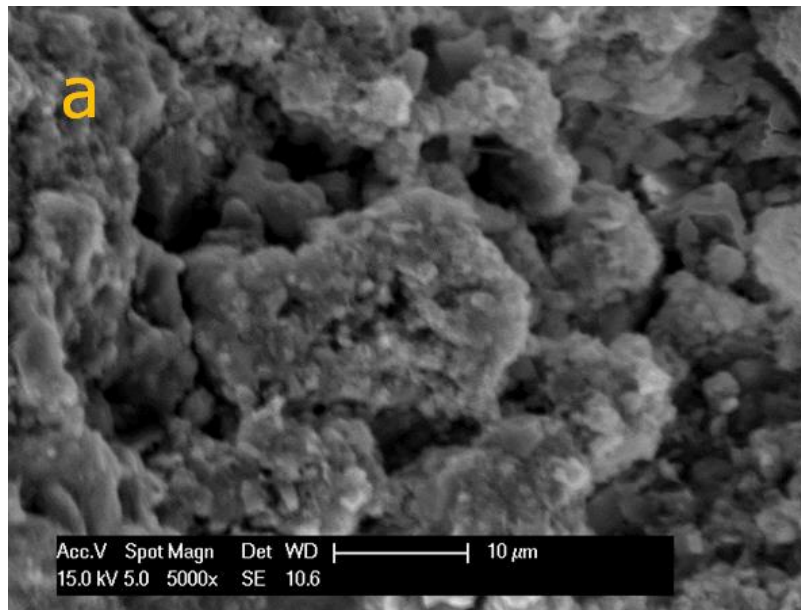


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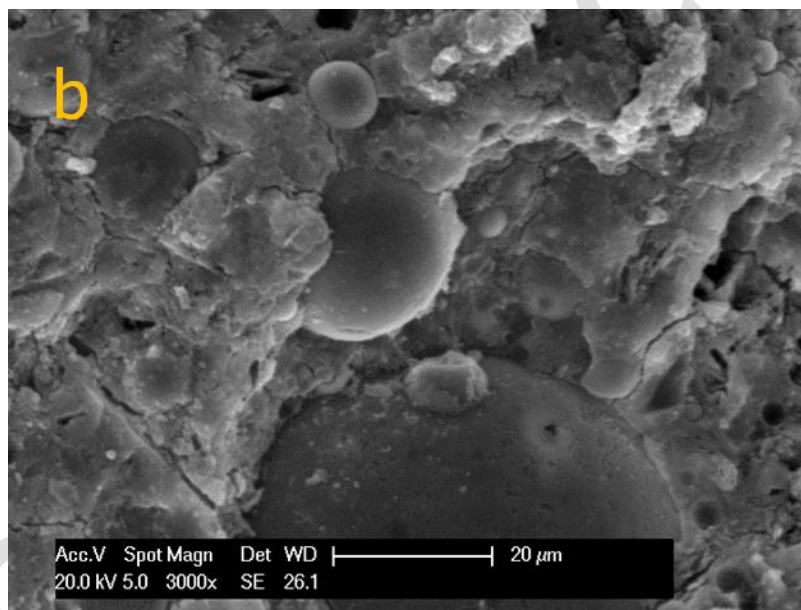
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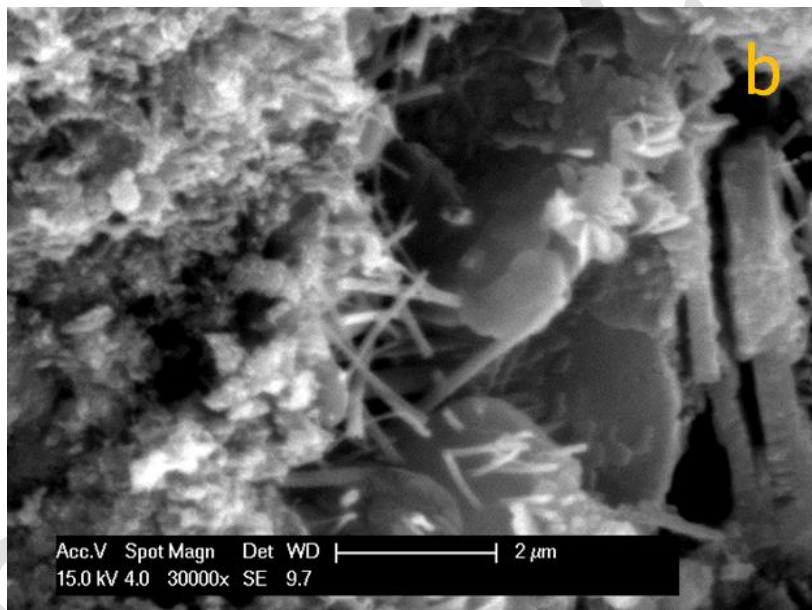
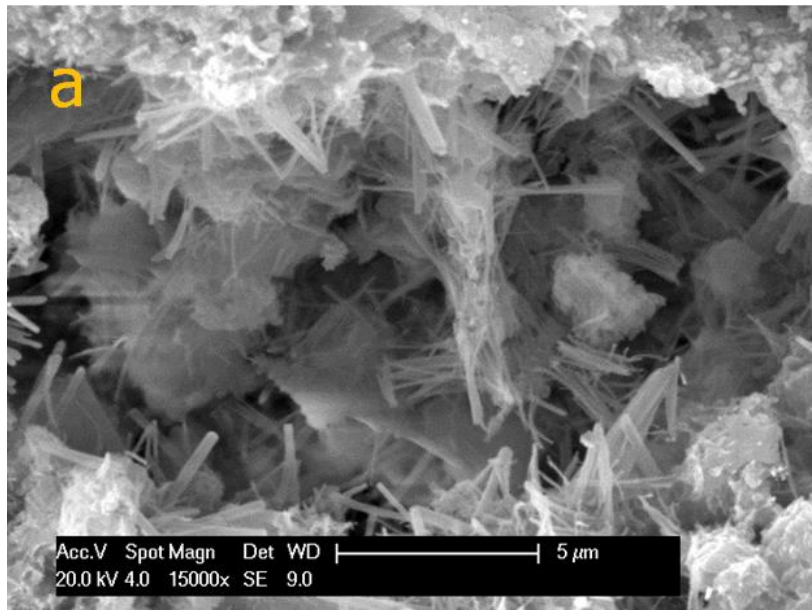
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Ettringite (a) LP-SCC (b) FA-SF-SCC

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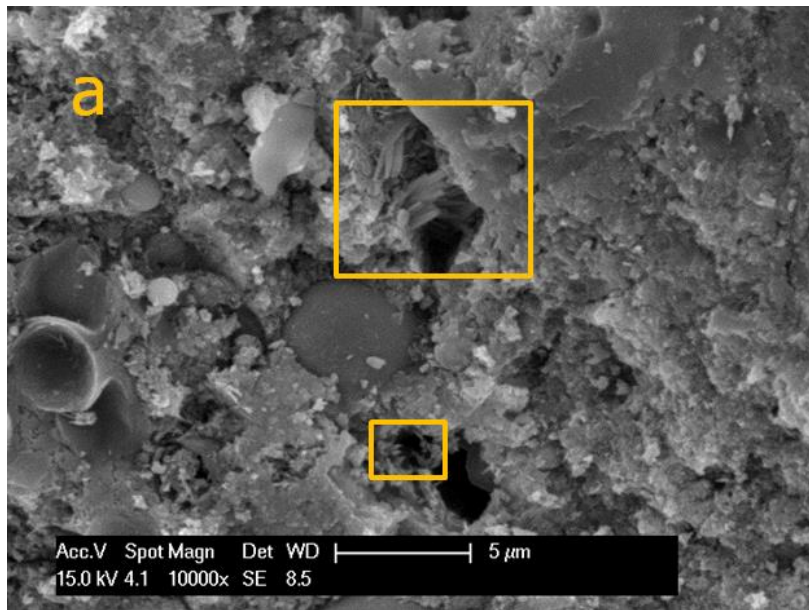
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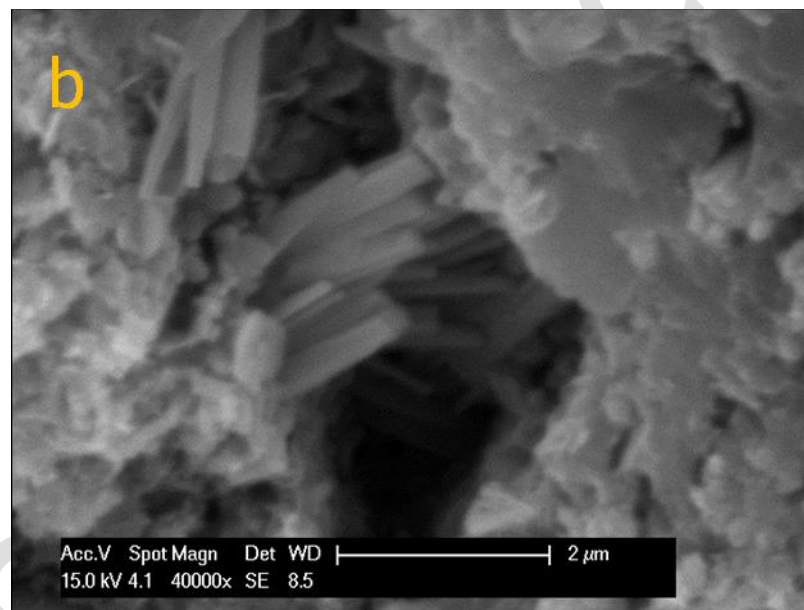
493 Fig.11 Monosulfate form after carbonation in the pores of (a) LP-SCC (b) FA-SCC

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Fig.12 DEF (Ettringite) after carbonation in the pores of FA-SF-SCC (a) low magnification

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(b) high magnification

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