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1 **Macro/Micro-pore structure characteristics and the chloride penetration of self-**
2**compacting concrete incorporating different types of filler and mineral admixture**

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31 **14Abstract**

32
33 The relationship between the internal pore structure features at different scales and the local
34
35 micro-characteristics of the interfacial transition zone (ITZ) to the non-steady state chloride
36
37 migration coefficient (D_{nssm}) is investigated for one normal and three types of sustainable high
38
39 performance self-compacting concrete mixes. The pore structure classification at different
40
41
42
43 scales and the percolation degrees of the ITZ's pores were determined using both vacuum-
44
45 saturated and mercury intrusion porosimetry (MIP) techniques. Further, the local micro-
46
47 permeation features of the ITZ, such as thickness, porosity and the chemistry of its hydration
48
49 products is examined using the SEM coupled with the EDX analysis on polished, carbon-
50
51 coated, flat specimens. Chloride movement was achieved using a modified rapid migration
52
53
54
55 test.

56
57 It was deduced that the degree of percolation of the pores of the ITZ had a significant role in
58
59
60 controlling the chloride penetration process. Further, it is proposed that the ITZ thickness

27 might be, primarily, responsible in determining the chloride ions' migration velocity
28 especially when coarse and unreactive filler is used. At nano scale, it is also suggested that the
29 critical pore diameter in the cement matrix is more significant than is the average pore
30 diameter in controlling the chloride resistance in SCC.

31 **Keywords:** Chloride penetration, rapid migration test, self-compacting concrete;
32 microstructure; interfacial transition zone; cement replacement, pores percolation

34 **1. Introduction**

35 As reported by many investigations, the chloride ion penetration from an external source (sea,
36 underground and de-icing water) is considered as one of the main causes of the initiation of
37 steel reinforcement corrosion which then leads to reduction in the serviceability life of the
38 affected concrete structure. This topic has become an increasingly important area in the study
39 of concrete durability since the middle of the last century[1]. With the widespread use of SCC,
40 which is relatively a new type of concrete, in different concrete structures exposed to severe
41 chloride environments such as bridges, culverts, tunnels, tanks, dams, and precast concrete
42 products, much information is needed to assess the chloride ingress and its relationship to the
43 concrete's internal microstructure at macro, micro and even at Nano-scales.

44 Since concrete/mortar is considered as a porous composite material with three different
45 phases (cement matrix, aggregate and ITZ between them), the chloride ions can penetrate the
46 concrete through the continuous pores of each phase. The aggregate phase (fine/coarse) has
47 less effect on the chloride penetration due to the lower diffusion coefficient in comparison
48 with cement matrix [2]. However, from a mix design point of view, the existence of high
49 amounts of aggregate (high volume fraction) could have two, conflicting, effects on the
50 transport properties of the concrete including the chloride movement. On the one hand, it
51 leads to more numerous ITZs, and more volume of this region, which may assist the chloride

ion movement due to the high porosity in compression with the background matrix porosity.

On the other hand, it increases the tortuosity of penetration paths through the matrix [3]. It is known that the SCC has a dense microstructure due to the use of low water to cementitious material ratios, and a dense cement matrix containing reactive and non-reactive fillers as compared with normal vibrated concrete (NVC) [4, 5]. Although SCC sometimes had the same or higher water to cementitious material ratio as a NVC, the use of fillers and mineral admixtures and high dosages of SP might also make the difference. Thus, the SCC could have a less easily penetrated microstructure. However, as reported by Assié et al. [6], referencing Zhu et al.[7], the modification of the microstructure might not be enough to assure sufficient resistance to the chloride penetration as this property might be governed by the tortuosity, the percolation and the connectivity of the internal pore network.

Although research work has been done to estimate the chloride penetration resistivity as part of the durability assessment of SCC, the available experimental data about the SCC showed that no definite conclusion could be drawn about whether SCC has similar, larger or smaller resistance to chloride penetration than NVC at the same strength level. Assié et al.[6] claimed that a SCC having a similar or, even better, compressive strength than a NVC, although at a higher w/c ratio, had equivalent chloride diffusion and water absorption. In their study, the SCC investigated employed limestone filler for all mixes. On the other hand, the results of Audenaert et al.[8] revealed that no definite conclusion was possible about whether SCC has a larger or smaller chloride migration coefficient in comparison with NVC. Recently, Dinakar et al.[9] noticed that, in spite of higher permeable voids and higher water absorption, high fly ash SCC showed lower chloride penetrability in comparison with NVC at any strength grade. The authors suggested that it could be as a result of a higher chloride binding capacity of the cement matrix caused by the presence of high available C_3A in the cementitious materials system with increased fly ash content. .

77 Understanding the relationship between the microstructure of the concrete as it relates to
78 degradation, especially chloride penetration and carbonation, still presents a great challenge
79 for the concrete technologist. This is due to both the complexity of the chemistry and the
80 microstructure of SCC, in particular the different macro/micro/nano scale characteristics and
81 the complexities of these two physico-chemical phenomenon as well. For SCC, questions
82 have been raised as to which has the dominant role: the micro permeation characteristics of
83 the ITZ or the pore characteristics of the bulk cement matrix?

84 To attempt an answer to this question, Leemann et al. [10] studied the effect of using different
85 types of cement on the porosity of the ITZ and its relationship to chloride resistance, using
86 the rapid chloride migration test according to the Swiss standard SIA 262/1. In this study, the
87 authors concluded that the change of the internal pore structure of the cement matrix, as
88 caused by the use of different types of cement in SCC mixes, had a stronger effect on the
89 non-steady state chloride migration coefficients obtained than did the pore volume in the ITZ.
90 However, the long curing time (62 days) used in this investigation might reduce any
91 controlling effect of the local microstructure characteristics of the ITZs. Moreover, Leemann
92 et al. made no attempt to address how the change of the internal pore structure, including the
93 tortuosity effect of the aggregate and the percolation of pores in the ITZ, nor the nature of the
94 pore system in the matrices, could affect the chloride resistance of SCC as only one technique
95 was used (Image analysis) for characterising the ITZ pores microstructure. This cannot give
96 enough information about the effect of the internal capillary pores and their percolation to
97 fully defend their conclusion. While the Leemann et al. results were based on the use of
98 different cement types to examine the chloride resistivity of SCC, the current research work is
99 designed to examine the effects of the internal microstructure and its role in determining the
100 chloride ingress process in normal and sustainable high performance SCC.

101 In previous research work [11, 12] the authors have attempted to develop a further
102 understanding of the relationship between carbonation and the microstructural properties of

103 sustainable SCC via accelerated tests. In the present paper they aim to quantitatively analyse
104 the correlation between these characteristics, in terms of the internal pore structure and the
105 local micro-permeation of the ITZ properties as consequence of a change of filler and mineral
106 admixture type at high cement replacement percentages, to the chloride penetration velocity.
107 To achieve this, a non-steady state accelerated test was modified from the recommendations
108 of NT Build 492 - Nordtest method [13] and used in the present study. The modification, as
109 described in Section 3.3, was mainly performed in order to reduce the time of the test to, as
110 much as possible, avoid the change of the ionic composition of the pore water solution (pH
111 value) due to the migration of the OH^- ions and hence, limiting the local chloride binding
112 ability due to the difference in reactivity levels of the fillers and the mineral admixtures used
113 through the relatively long time of the standard test. The main issues addressed in this paper
114 are:

115 i) Effect of using different types of filler and mineral admixtures, at relatively high rates
116 of cement replacement, on the internal pore structure and the local micro-permeation
117 characteristics of ITZ of different types of SCC.

118 ii) Determination of the non-steady state chloride migration coefficient (D_{nssm}) for SCCs
119 with different binder types using a modified rapid migration test.

120 iii) Macro/micro and nano internal pore structure property relationships with the D_{nssm} .

121 These issues have been studied in order to provide further understanding of the
122 microstructure of the sustainable SCC and the part it plays in determining the resistance to
123 chloride penetration.

124 **2. Experimental**

125 **program 2.1 Materials**

126 Ordinary Portland cement CEM I, 52.5 R conforming to EN 197-1 was used to produce all the
127 SCC and mortars. Natural limestone filler (LP) from Longcliffe quarry (Derbyshire, UK), fly ash
128 (FA) class F confirming to BS EN 450-1 produced by the Cemex Company and Densified

129 silica fume (SF) produced by the Elkem Microsilica Company were used as a fillers and
130 mineral admixtures. Table 1 shows the chemical and physical properties of these
131 materials. The mineralogical and microstructural properties of the cement, fillers and
132 mineral admixtures were characterized using the XRD and SEM techniques respectively.
133 Fig.1 a, b and c show selected SEM micrographs of both the cement and the SF at high
134 magnification whilst Fig 2a and b show the XRD patterns obtained from these powders. For
135 LP and FA, such SEM micrographs and XRD spectra are presented in an earlier paper [11].
136 The SEM micrographs revealed that the surface texture of both the cement and LP particles
137 are extremely rugous, the particles also being angular in shape. In contrast, the FA particles
138 are spherically shaped with a very smooth surface texture. The SF showed two particle shapes,
139 first: spheroid agglomerates with diameter in the range between (5-25) μm , second: very fine
140 particle agglomerations with diameters in the range between approximately (0.05-10) μm .
141 These measurements were based on different micrographs at various magnifications. Both
142 types of SF particles demonstrated a very rugous surface texture.
143 Using the XRD technique, the major compounds of the cement powder were identified from
144 the XRD pattern: C_3S , C_2S in the form of calcium silicate, C_3A in the form of calcium
145 aluminum oxide, C_4AF in the form of the Brownmillerite phase as well as Anhydrate
146 (CaSO_4) from the gypsum which is usually added to the cement to control the setting process.
147 The XRD traces clearly indicated that the LP consisted of purely (100 %) calcite phase
148 without a presence of any amorphous material. On the other hand, the FA comprised a
149 vitreous medium with two main crystalline phases: Quartz (SiO_2) and Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$)
150 with a presence of amorphous material. The distinct hump in the XRD pattern revealed the
151 presence of amorphous silica [11]. The SF XRD pattern was completely different from those
152 of LP and FA with very small peaks of Potassium Magnesium Silicate ($\text{K}_2\text{MgSi}_3\text{O}_8$) being
153 detected. The absence of the peaks in the XRD-spectra of the SF signifies a very high
154 proportion of amorphous silicon dioxide (SiO_2).

155 Local river quartz sand with a maximum particle size of 5 mm was used as a fine aggregate for
156 both SCC and mortars. The specific gravity and the water absorption of this type of sand were
157 2.65 and 1.5 % respectively. Natural quartz uncrushed gravel with a nominal maximum size of
158 10 mm was used as coarse aggregate. The specific gravity and the water absorption of the gravel
159 were 2.65 and 0.8 % respectively. Superplasticizer (SP) based on polycarboxylic ether (PCE)
160 polymer, was used to maintain the required fresh properties of SCC.

2.2 Mix design and production of SCC

163 The mix design of SCC mixes and their fresh requirements are shown in Table 2. All the
164 mixtures were designed to have a compressive strength grade of 50–60 MPa. The main
165 difference between the mixes was the type of the binder (cement for the reference-SCC and
166 cement plus fillers or mineral admixtures at relatively high cement replacement for the other
167 three mixes). Approximately 33% of cement was replaced for these mixes, the exact
168 proportion of admixture and of the coarse aggregate content depending on the differences
169 between the specific weights of binder materials. The SCC mortars contained the same
170 constituent but without coarse aggregate. The water quantity for the mortar was reduced by
171 about 0.8% (coarse aggregate absorption) in order to ensure the same available water content
172 for the full concrete. The adopted SP dosages to maintain the required fresh properties were
173 based on several trial mixes. After mixing and optimizing the fresh requirements in terms of
174 slump flow, T_{50} , B_j and $SI\%$ for the concrete (See Table 2) and the mini slump flow for the
175 mortars (240-300 mm), the fresh SCC and mortars were filled into the moulds in one go
176 without any applied compaction, demoulded after 48 hours, and finally cured at 20 ± 2 °C in a
177 water tank until the date of the test (28 days). For the compressive strength test, 100 mm
178 cubes were used. The test was conducting according to BS EN 12390-3 [14] and the listed
179 values represent an average of three readings.

181 **3. Methodology and tests performed**

182 **3.1 Pore structure investigation**

183 **3.1.1 MIP test**

184 Small pieces of mortar weighing (1- 3) g obtained from the middle part of 70 mm mortar
185 specimens (near the core block that was used for preparing the flat polished sections as
186 described in section 3-2) were used for Mercury Intrusion Porosimetry (MIP) testing. In order
187 to stop the hydration, the specimens were dried at 100 °C for approximately 24 hours (until a
188 constant weight was achieved as determined by a high sensitive balance) and then they were
189 kept in sealed containers until the day of the test. A Micrometrics Autopore IV mercury
190 porosimeter, which can detect the pores as small as 7 nanometers with a maximum pressure
191 of 414 MPa, was used. The pressure step was applied for 10 seconds and the test was
192 conducted on an average of 3 samples for each mix.

193 **3.1.2 Vacuumed Saturated Porosity (Macro Porosity)**

194 Mortar discs with dimensions of 60mm in diameter and 10-13 mm in depth, cut from original
195 cylinders 120 mm tall was used to assess the Macro porosity. The mortar disks were
196 vacuumed using 100 mb for 3 hours followed by 2 hours vacuumed with saturated Ca(OH)₂
197 solution and left until the second day. This was done to ensure a full saturation of all the
198 pores in the tested specimens. The porosity % is calculated using Eq.1 [15].

199
$$P = (B - A) / (B - C) \times 100 \dots \dots \dots \text{Eq. 1}$$

200 P: Porosity, B: Saturated surface dry weight, A= Oven-dry weight, C= Saturated submerged
201 weight

202 Completing the MIP results, the vacuum saturation results were used to deduce a complete
203 picture about all the pore size ranges, as the larger pores that cannot be detected by the MIP
204 test is considered as additional macro-pores. Thus, the percentage of macro/micro pores of
205 the mixes was re-calculated (see Table 3).
206

207 3. 2 Microstructure of the ITZ

208 The ITZ microstructural examinations were conducted on a core block (20x20x15mm)
209 obtained from the middle part of 70 mm mortar cubes. Full details can be found in an earlier
210 paper [11]. The preparation steps of flat-polished epoxy-impregnated specimens as described
211 by Kjellsen et al. [16] was followed carefully. The specimens were coated with carbon and
212 then stored in a vacuum chamber until capturing the BSE images. A Philips XL 30 SEM fitted
213 with an Oxford Instruments INCA model spectrometer for energy-dispersive X-ray (EDX)
214 analysis was used with an accelerating voltage of 15–25 kV. Eight images were selected
215 randomly at different aggregates' locations (at a magnification of 500X) and analysed for
216 each mix in order to detect the ITZ porosity and thickness. The same image analysis
217 procedure for duplicated BSE micrograph images as described more fully in an earlier paper
218 was adopted[11]. However, the average upper porosity threshold values for all the analysed
219 images were 80, 70, 50 and 60 for cement LP, FA and FA + SF matrix systems respectively.
220 The defined upper threshold value was based on the recommendation of the overflow method
221 as shown in Fig3. In a very recent work [17], this method is considered as an accurate method
222 for the pore segmentation of the cement matrix with different types of blended cement. A T-
223 distribution statistical analysis with a confidence interval of 95% was used to examine the
224 results' accuracy as the images were randomly selected and the error bars in Fig.8 tends to
225 confirm the regularity of the deduced porosity in the analyzed bands (each 10 μm from the
226 aggregate interface).

227 For the chemical analysis of the ITZ, X-ray line spectrum analysis using EDX (energy
228 dispersive X ray analysis system) linked with SEM as described by Erdem et al. [18] was
229 performed to identify the main hydrous compounds in both the ITZ and cement matrix(CM).
230 However, due to the inhomogeneous nature of the ITZ, 3 to 4 lines per different aggregate
231 interface for each mix were analysed. The average detected Ca/Si values come from 30 to 40
232 values in different spots in the ITZ and the cement matrix regions. The upper and lower limits

233 obtained from the standard deviation about the mean values were adopted to determine the
234 accuracy of the results (See Table 4).
235 The analyses were conducted each 5 μm along a line that crossed the aggregate, ITZ and the
236 bulk matrix. Four EDX spectra were collected in the aggregate and 10 in the ITZ and cement
237 matrix (See Fig. 4). Firstly, the BSE image was rotated using the control software of the
238 Scanning Electron Microscope so the X-ray line spectrum was selected to be perpendicular to
239 the ITZ. Secondly, an image was captured for the area of interest using the ENCA-EDX
240 software. Then, the spectrum line was drawn and the acquisition time for the detection of all
241 elements of each spectrum was set to 60 seconds. This allowed detection at each spectrum
242 point on the three or four lines in approximately 60 to 75 minutes. Finally, ENCA- EDX
243 software was used to assess the proportion of each of the following elements: Ca, Si, Al, S, Fe,
244 Na, Mg, K and O. However, the oxygen was normalized by the software stoichiometry. These
245 elements were used for the purpose of identifying the main cementitious compounds in the
246 ITZs and the cement matrix (Fig 4 gives an example of one X-ray line analysed for the regular
247 SCC). As reported by several investigators e.g. [18, 19], the C-S-H, CH and AFm products
248 could be identified from knowing the Ca/Si ratio. The ranges of this ratio for the different
249 products are: $0.8 \leq \text{Ca/Si} \leq 2.5$, $\text{Ca/Si} \geq 10$ and $\text{Ca/Si} \geq 4.0$ respectively.

3.3 Rapid chloride migration test

252 The same type of specimen that was used for the Marco porosity test in section 3.1.2 was used
253 to determine the none-steady state chloride migration coefficient (D_{nssm}). Before the test, the
254 mortar discs were vacuumed and saturated with a Ca(OH)_2 solution. The same arrangement
255 as suggested by the Nordtest standard [13] as shown in Fig.5, was adopted in performing the
256 experiment. However, the main difference is the dimension of the specimens, especially the
257 thickness, which can affect the chloride penetration depth considerably. According to the

258 standard, the time of the test should be determined dependent on the initial reading of the
259 current under an applied voltage of 30V.

260 First, a preliminary work was conducted on one sample of each mix with an external voltage of
261 30V to find the initial current (I_{30V}) and, hence, a suitable time for the modified test so that
262 chloride does not breakthrough nor achieve only a shallow penetration depth through the
263 sample. None of these samples produced an initial current in the range suggested by the
264 standard due to the difference in thickness of the used specimens leading to different electrical
265 resistance. The initial currents were all in the range 80-320 mA. Thus, the challenge was to
266 find an appropriate time that would keep the chloride penetration within the thickness of the
267 specimen (10-13) mm under the initial current. As stated by McGrath and Hooton[20], the
268 calculated non-steady chloride penetration coefficient was reasonably constant over the voltage
269 range tested up to 30 V. For the modified arrangement just described, 30 V would cause a
270 considerably greater voltage gradient and this gave cause for concern regarding possible heat
271 generation and consequential specimen damage which would affect chloride ingress. For this
272 reason during the preliminary work, the temperature of the anolyte (0.3M NaOH) and the
273 catholyte (10% NaCl) solutions was measured continuously using a thermocouple. The range
274 of the recorded temperatures was 18.6 - 25.4 °C showing that there was no substantial change
275 in the temperature of the specimen during the test. The standard [13] stipulates an operating
276 temperature range of 20 to 25 °C, thus the modified arrangements appear acceptable in this
277 respect.

278 Several trials were performed on each specimen for 6, 5, 4, 3, 2 or 1 hours. Finally, the test
279 duration then was specified to be 1 h as the chloride penetration was within the thickness of
280 specimen for all types of SCC mortars whereas complete breakthrough of the chloride
281 occurred under larger test durations.

282 Fig.6 shows examples of some samples broken in half to expose an internal cross section and the
283 use of 0.1 M silver nitrate solution indicator ($AgNO_3$). White silver chloride precipitation

284 (AgCl) on the split surface appeared clearly after 5-10 minutes where the chloride ions have
 285 penetrated. Then, the D_{nssm} was calculated as an average value of duplicated successful
 286 samples for each mix using the modified Nernst-Planck equation [13]:

$$D_{nssm} = \frac{0.0239(273+T)L}{(U-2)t} \left(x_d - 0.0238 \sqrt{\frac{(273+T)L x_d}{U-2}} \right) \dots\dots\dots \text{Eq.2}$$

291 D_{nssm} : non-steady-state migration coefficient, $\times 10^{-12} \text{ m}^2/\text{s}$

292 U: absolute value of the applied voltage, V

293 T: average value of the initial and final temperatures in the analyte solution, °C

294 L: thickness of the specimen, mm

295 x_d : average depth of penetration over central zone as revealed by AgCl coloring (see
 296 Fig 2) , mm

297 t: test duration, h

36 4. Results and discussions

38 4-1 Macro, Micro and Nano characteristics of the pore structure

39 The Mercury cumulative intrusion curves and their derivatives as shown in Fig 7 a, b and
 40 the normal vacuum porosities results were used to quantify the pore structure characteristics
 41 at different scales and are summarized Table3.
 42

43 The MIP porosity natures of the SCC mixes were determined in which the micro pores is
 44 bigger than 65 %. At this percentage the refinement of the pore structure is expected as stated
 45 by Erdem et al. [21]. Further, all the detected critical pore diameters (CPDs) and the average
 46 pore diameters (APDs) were in the Nano scale.
 47

48 The macro and micro pores percentages were firstly calculated from these cumulative
 49 intrusion versus pore diameter curves considering $0.1 \mu\text{m}$ to be the boundary between these
 50

310 pore classes and then they were corrected using the macro porosity results (normal vacuum
311 method as described earlier). The results demonstrate that the sustainable high
312 performance SCC exhibited a micro-porous nature except in the case of the LP-SCC. This
313 may be compared with the R-SCC which, marginally, is classified as macro-porous nature.
314 On the other hand, all the detected CPDs which might demonstrate the nature of the pores'
315 interconnectivity were determined to be of nano scale and they can be considered to be in the
316 cement matrix far away from the ITZ regions. For the MIP test, it is already reported [22] that
317 the mercury is expected to intrude into the large pores in the ITZ region if they are percolated.
318 Consequently, the smaller pores (including the smallest ones (CPD)) will be allocated in the
319 nearby cement matrix. Conversely, this is not the case for non-percolated ITZ [22]. The
320 results of the present study showed that in spite of the macro porosity nature, the R-SCC
321 exhibited similar or lower CPD as compared to the FA-SCC and LP-SCC respectively.
322 However, the FA-SF-SCC demonstrated the lowest critical pore diameter signifying the
323 lowest cement matrix' pore percolation.
324 For the SCC mortars, the volume fraction of the fine aggregate should be between 40-50%
325 in order to reduce the segregation and obtain the stability for the mix as reported by
326 published guidance and research findings [23-25]. Therefore, the probability of the ITZ
327 having percolating pores is likely to be high even when ITZ thickness is small. For the
328 adopted aggregate : mortar volume fraction (49.7-51.2%), the experimental results obtained
329 for the minimum detected ITZ-thickness (15 micron for FA-SF-SCC) was analysed in
330 conjunction with a numerical model adopted by Winslow et al. [26] for concrete mortars
331 with different aggregate volume fractions. The analysis revealed that the degree of ITZ pores
332 interconnectivity is more than 78%. These degrees were approximately greater than 90%,
333 88% and 95% for the R, FA, and LP-SCC respectively. Thus, the chloride penetration might
334 largely be governed by ITZ pores percolations in such a way that the tortuosity effect of the

335 aggregate could be neglected due to the use of same volume fractions of all the mixes. The
336 change in tortuosity effect of the aggregate is not entirely eliminated, but should be too small.

337

338 **4.2 ITZ micro characteristics (Thickness, Porosity)**

339 Fig. 8 shows the detected porosity profiles of the ITZs regions for the different SCCs as a
340 function of the distance from the aggregate-cement paste interface up to 50 μm . These
341 curves were used to determine both the approximate thickness and porosity of the ITZs.

342 The exact determination of the ITZ thickness is difficult and not straightforward, with various
343 proposed methods [10, 27, 28]. In the present study, the ITZs thicknesses were determined
344 using the image analysis procedure described by Mohammed et al.[11]. In general, the
345 analysis showed that all the deduced ITZs-thicknesses were less than 30 μm for the SCC
346 mixes including that made with normal Portland cement (R-SCC). They were approximately
347 19.9 μm , 27.5 μm , 18.5 μm and μm 15 μm for R, LP, FA and FA-SF self-compacting
348 concretes respectively. Olivier et al. [27] stated that the typical thickness of the ITZ region is
349 about 50 μm for OPC paste in NVC so these SCC values are much smaller. At a microscopic
350 scale, the absence of vibration, which is the case of SCC, could play an essential role in
351 reducing the volume of the localized water around the aggregate surface[29]. This might
352 explain the small thicknesses of the ITZ in all the investigated types of SCC.

353 Nevertheless, relative to the R-SCC without cement replacement, the FA and FA-SF-SCC
354 exhibited similar or slightly smaller ITZ thicknesses respectively. A higher amount of
355 anhydrous cement was observed beyond the ITZ thickness of the R-SCC (Fig.6) indicating a
356 higher local (ITZ) water to cement ratio which reduced the effective water content outside the
357 ITZ leading to incomplete cement grain hydration. Thus, a higher ITZ thickness might be
358 expected. It was already supposed by Laugesen (1993), quoted by Scrivener and Nematy [30],
359 that the difference in the amount of anhydrous cement in the bulk cement matrix and the ITZ
360 could be produced by the differences in the amount of water adhering to the aggregate surface.

361 However, the increase in ITZ thickness in the case of using LP as a partial replacement of
362 cement, relative to the other three mixes, could suggest a “dilution” effect provided by the
363 large LP unreactive grains in the ITZ. Also the presence of high amounts of CH or unreactive
364 LP and the lack of CSH gels in this region was deduced for LP-SCC with the selected
365 percentage of cement replacement, as explained in the previous paper [10].
366 ITZs porosities between 14.5-25 % were deduced for the investigated normal and sustainable
367 high performance SCC within the detected ITZ thicknesses (Fig.8). Although the same water
368 to binder ratio is adopted for all the mixes, the use of different types of fillers and mineral
369 admixtures at high cement replacement has generated different ITZ porosities. This may
370 attributed to both a physical filling effect and the chemical activity of the fillers and mineral
371 admixtures used. R-SCC presented the highest ITZ porosity as compared with the other mixes
372 and this might be related to the high ITZ local water as mentioned above.
373 Generally, the higher porosity of the ITZ might be related to the inability of the anhydrous
374 cement grains to pack very well with the smooth surface of the aggregate due to the wall
375 effect [27]. This concept might be different when reactive and non-reactive fillers are used
376 leading to reduce the ITZ localised water. However, the inability of the hydration products
377 to achieve a complete packing with the aggregate boundary might also be the cause of a
378 porous interface. Therefore, the deduced ITZ-porosities using the image analysis were
379 supported by the examination of the chemistry of the ITZ. The slight reduction in the ITZ
380 porosity for the FA-SCC relative to R-SCC might indicate the inability of the FA to improve
381 the ITZ chemistry. In contrast, FA-SF-SCC showed lower ITZ porosity relative to the FA-
382 SCC and this suggests that the reduction of the ITZ porosity may be as a result of the filling
383 effect of the very fine grains of SF improving the packing ability of the cement particles near
384 the aggregate surface. The chemical analysis of the ITZs in the next section also showed a
385 substantial modification in the chemistry of the ITZ especially in the FA-SF-SCC.
386

387 4.3 ITZ Chemistry

1 388 The chemical compositions of the ITZ and the cement matrix (CM) were investigated using
2
3 389 the EDX-technique as described earlier. Table 4 summarizes the average Ca/Si ratios across
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6 390 the thickness of the ITZ and in the background cement matrix.

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8 391 The analysis showed that the average Ca/Si ratio in the ITZ of the FA-SCC was greater than
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11 392 that which identifies the presence of CSH gel demonstrating a presence of considerable
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13 393 amount of CH. However, the ITZ of the FA-SCC showed a lower ITZ porosity than that of R-
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16 394 SCC and this may be due to the microstructural packing effect of the small spherical particles
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18 395 of FA. As reported by Zhang et al. [31], the packing state might be affected by the addition of
19
20 396 pozzolans and decrease the amount of water that is needed for void filling and this might
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23 397 depend on the grain size of the pozzolanic material. This proposes that the improvement of
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25 398 the ITZ chemistry due to the high replacement of cement by FA may be attributed to the
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28 399 filling effect of the small particles of the FA only. However, it is known that the amorphous
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30 400 silica in the pozzolanic materials can consume the CH in the presence of water and produce
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32 401 another form of CSH gel or, at the least it can change the orientation of the large CH crystals.
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34 402 Consequently, further chemical development may occur. The chemical activity of the FA due
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36 403 to the amorphous silica detected by the XRD spectra recommends that full modification of the
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39 404 matrix in this region will take longer than 28 days, hindering a full comparison with the
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41 405 normal SCC in which hydration will be largely complete by that time.
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45 The chemical analysis also indicated that incorporation of the combined partial replacement of
46
47 407 cement by SF+FA led to the formation of an extraordinary quantity of CSH gel in the ITZ where
48
49 408 the detected Ca/Si ratio was less than 2.08%. This may explain the lower detected ITZ thickness
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51 409 and lower porosity in this type relative to the other mixes. The EDX analysis also indicated a
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53 410 presence of high amount of CH or unreacted LP in the ITZ of the LP-SCC. The deduced average
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56 411 Ca/Si ration was greater than 14.43 indicating a dilution effect to this region which might cause
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58 412 an increase in ITZ thickness as explained in details in a previous work [11]
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4.4 Relationships between the chloride penetration and the microstructure

In order to establish microstructure property relationships with the obtained chloride

migration coefficients (D_{nssm}), an overview of the results obtained in the previous sections are summarised all together in Table 5.

Fig. 9 plots the relationships between ITZ porosity and thickness of the different SCC and the chloride migration coefficient. It can be seen clearly that the migration coefficient is simply related to ITZ thickness and, with the exception of the anomalous LP result discussed earlier, to the ITZ porosity. The latter relationship is in line with Jiang et al. [32] who stated that the increase of the porosity of the ITZ could facilitate the penetration of destructive agents including chloride and carbon dioxide. Taking the two relationships together, and assuming the distribution of the pores through the ITZ thickness around the aggregate, this might suggest that the chloride penetration in all types of SCC is likely to be controlled by the pore percolation in the ITZs, as a high degree of interconnected pores were deduced (78-95 %) in this region (Section 4.1). For LP-SCC, the higher ITZ thickness allows more capillary pores to be interconnected to adjacent ITZs in this mix type. Thus, a more porous path is anticipated and, thus, a decreased chloride resistance for this mix.

Fig.10 plots the relationships between the CPDs, the APDs and the chloride migration coefficients of the SCC. A broadly linear relationship was observed in both cases. Although the figure shows that the chloride migration coefficient had a higher correlation with the critical pore diameters than the average pore diameters, there are insufficient data to assess the relative reliability of these correlations. Moon et al. [33] observed a very high correlation (0.91) between the average pore diameter and the chloride diffusion coefficient for some high performance concrete specimens. On the basis of the present investigation alone, it would seem that the CPD in the cement matrix is a more important factor than the average pore diameter in controlling the chloride penetration velocity of SCC. Therefore, it is proposed that the chloride resistance of a SCC with high replacement of cement could be increased

439 /decreased according to the ability of its filler or mineral admixture to alter the
440 interconnectivity nature of the pores in the cement matrix (CPD at the nano scale). This is
441 independent on the resulting average capillary pores diameter in the ITZ and the cement
442 matrix at this scale or the porosity value/nature and of the pore diameters at the micro or
443 macro scales.

444

445 **5. Conclusion**

446

Based on the results obtained in this investigation, the following concluding remarks are derived:

447

- The use of LP at relatively high replacement of cement increased the chloride penetration velocity of LP-SCC as compared with both the use of cement only (without any replacement) and the incorporating of mineral admixture such as FA and FA+SF at the same replacement percentage.

451

- The ITZ micro characteristics for the investigated SCCs suggest that the use of a low water to binder ratio might be primarily responsible for determining the ITZ thickness while the agglomerations of the coarser unreacted LP near the aggregate-paste interface might also contribute to increasing the ITZ thickness. Further, the internal pore structure analysis at different scales and micro-permeation properties of the ITZ also indicated a diluting effect of this filler type in both the ITZ and the cement matrix as well.

457

- The average Ca/Si ratios in the ITZ regions (3.4, 3.6 and 14.43) for the R, FA and LP SCCs respectively revealed substantial amounts of CH. However, the reduced presence of this compound in the FA-SF-SCC suggests that the ITZ of this mix contains a high amount of CSH gel with an average Ca/Si of 2.08 only.

461

- The modification in the chemistry of the ITZ due to the use of different fillers and mineral admixture as a high partial replacement leads to different ITZ porosities. This was more noticeable in the case of using the FA+SF replacement rather than when using the simple FA or LP replacement.

464

465 • The chloride migration coefficient was proportional to both the thickness and the porosity
1 466 of the ITZ. However, the ITZ porosity of the LP-SCC did not fit with this relation. This
2 3 467 suggests that high deduced ITZ thickness increased the capillary pore's percolation in the
4 5 468 ITZ and thus ITZ thickness was more responsible than ITZ porosity alone in determining
6 7 469 the chloride ingress.
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10 470
11 • The internal pore structure analysis at different scale revealed that the macro or micro
12 471 porosity natures of the SCC did not relate to the chloride penetration resistivity as it is the
13 472 interconnectivity of the pores in the cement matrix (represented by the change in the CPD)
14 473 and the percolation degree of the pores in the ITZ that play a more important controlling
15 474 role.
16 475
17 • At the nano-scale, the comparison of the results of the chloride migration assessment and
18 476 of the characteristics of the internal pore structure demonstrated that the chloride
19 477 penetration velocities were more closely related to the change in the CPDs in the cement
20 478 matrix than to the APDs, including the capillary pores, in both the ITZ and the cement
21 479 matrix as detected by the MIP.
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33 502 **Captured figures and tables**

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Captured figures

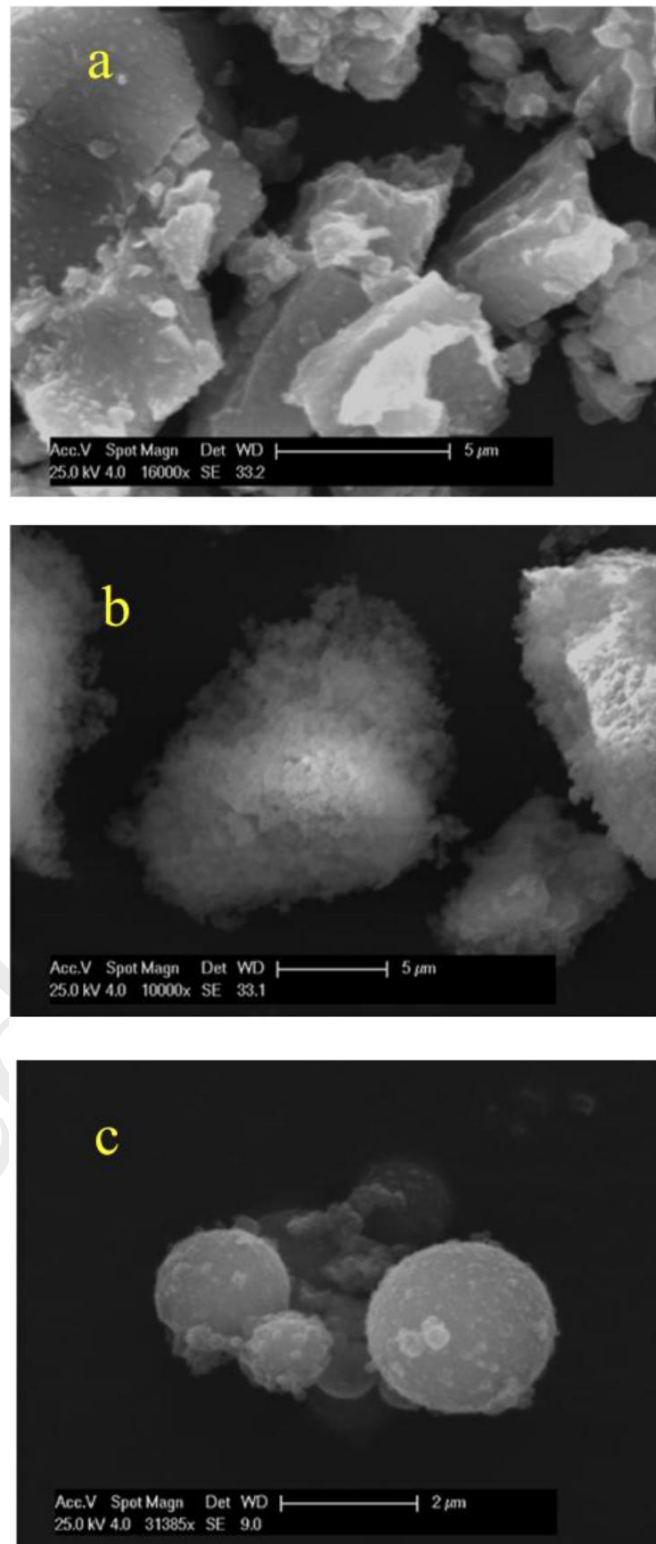


Figure 1 Selected SEM micrographs of: a) Cement b) Silica fume C) silica fume at high magnification

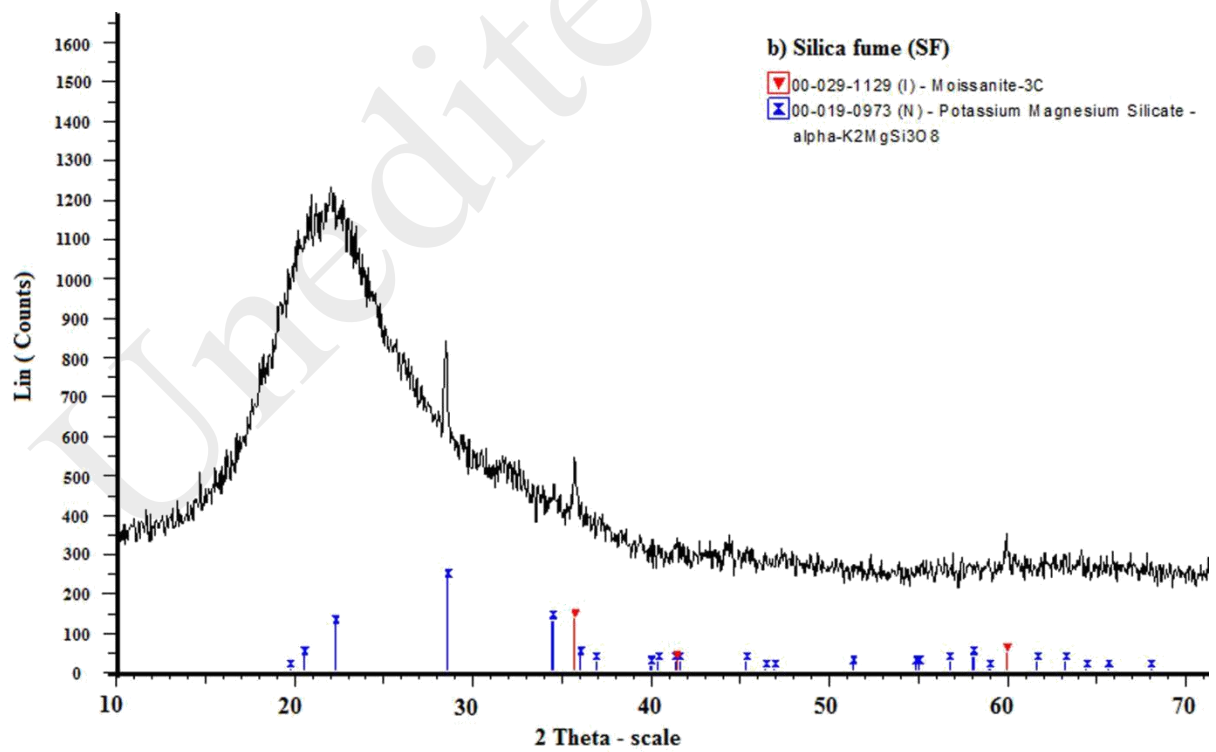
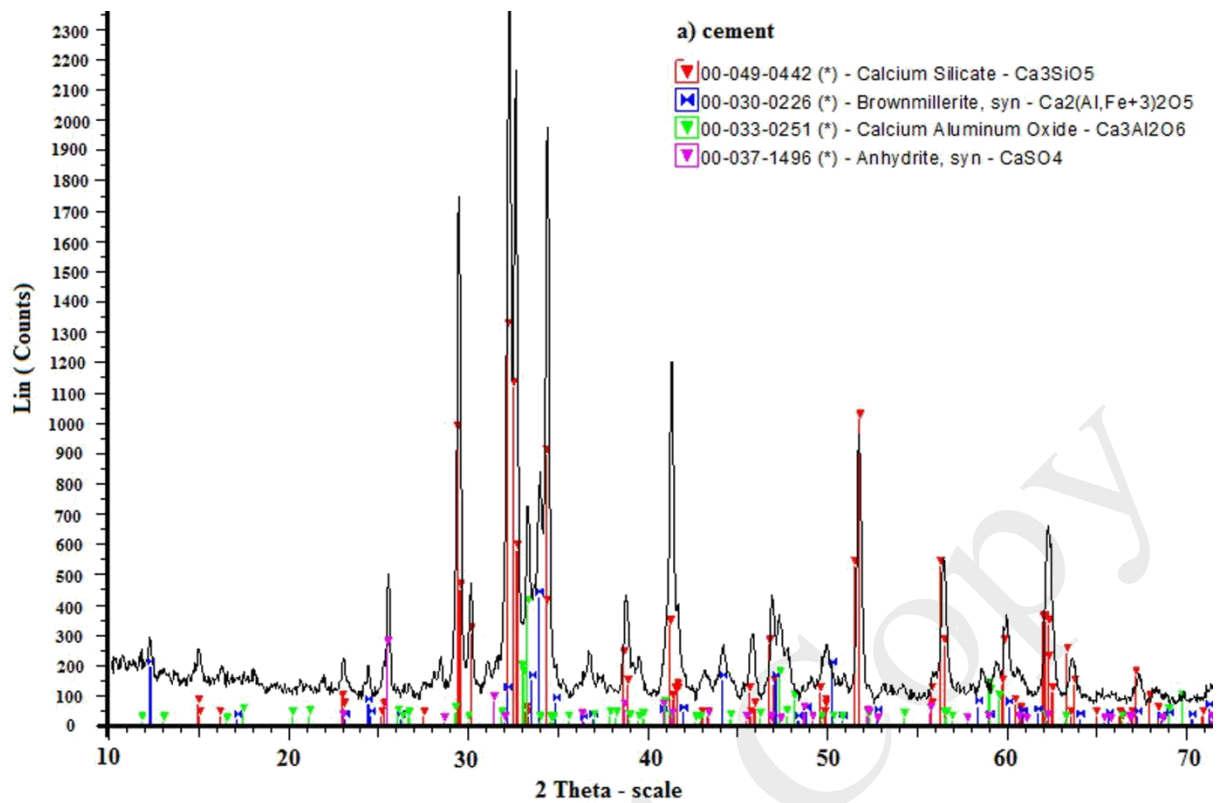


Figure 2 XRD spectra for: a) Cement b) Silica fume

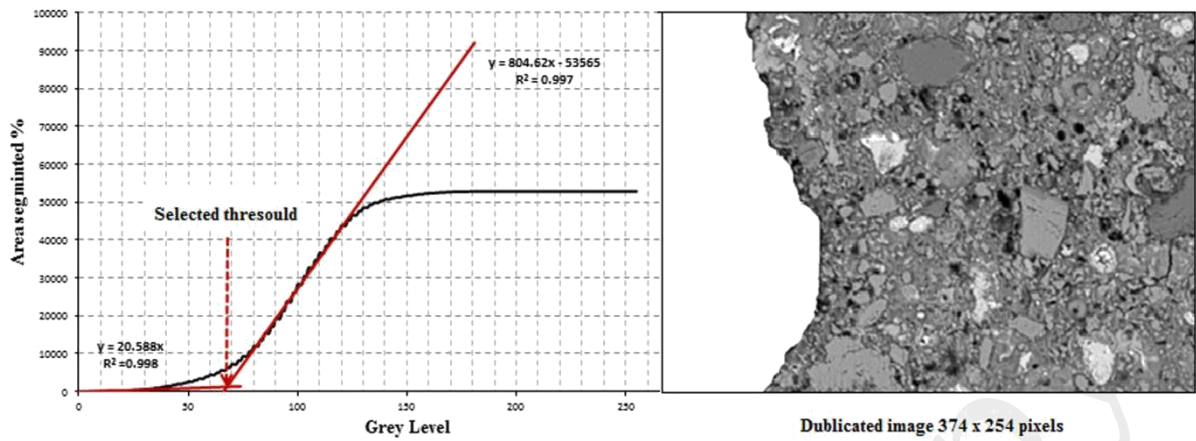


Figure 3 Example of the selection of upper porosity threshold using overflow method

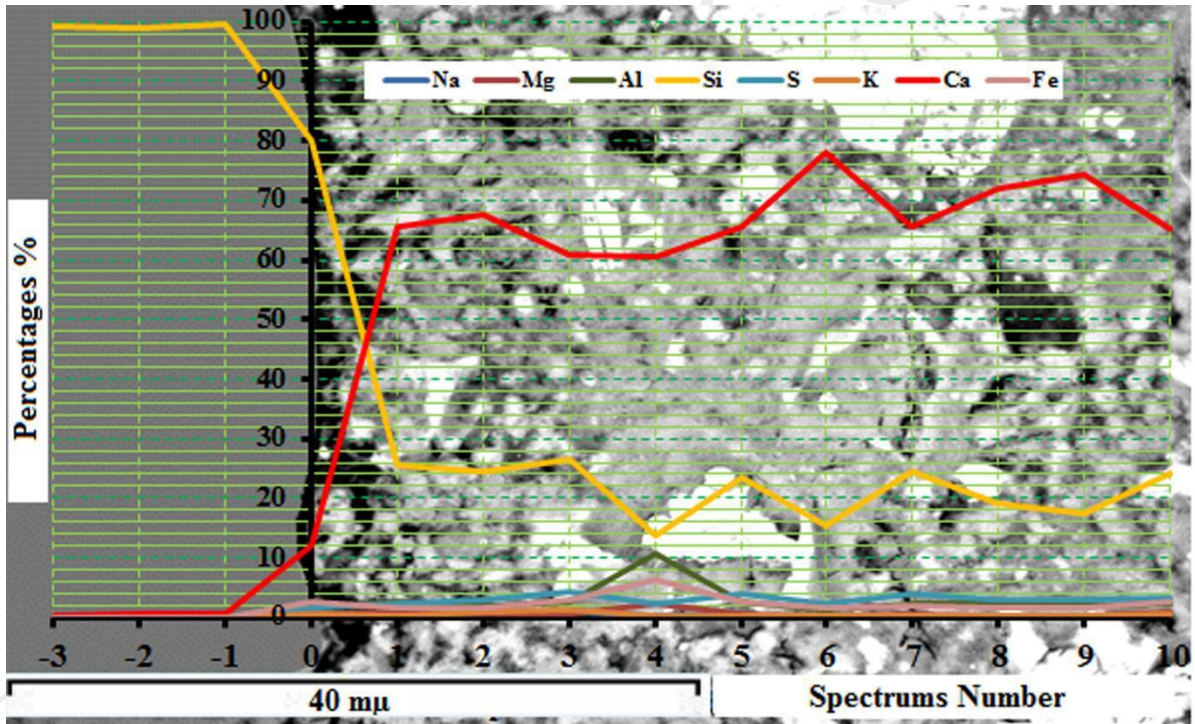


Figure 4 Example of X-ray line spectrum analyses (one line analysis for R-SCC)

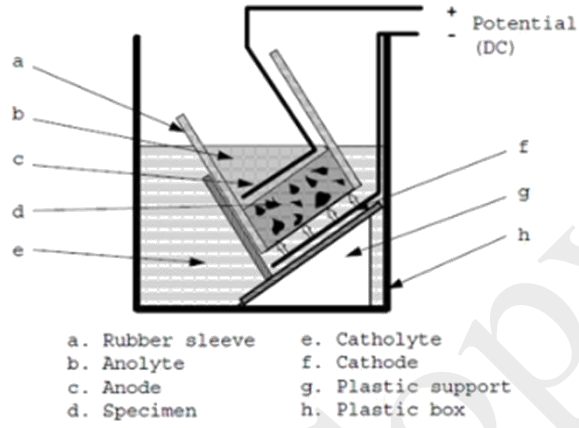
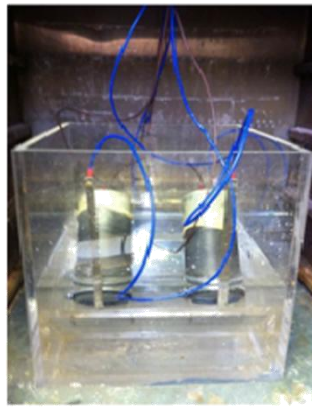


Figure 5 Photographs and schematic diagram for the rapid chloride migration test

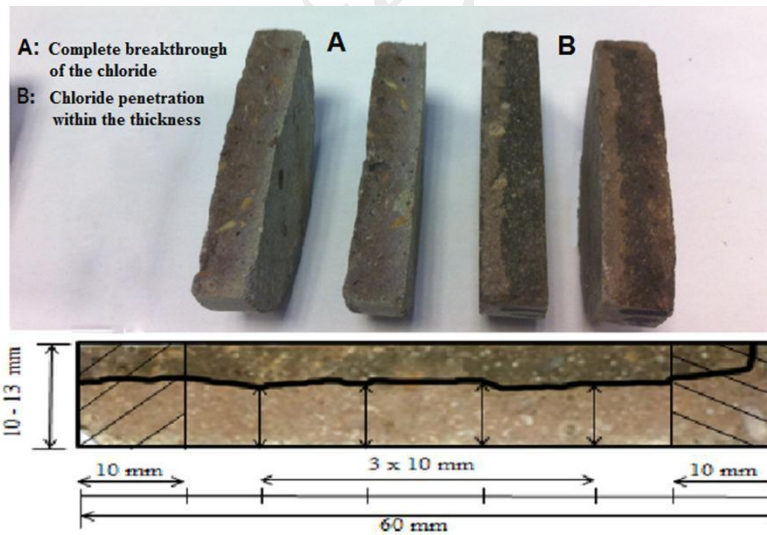


Figure 6 Examples of some tested specimens and the chloride penetration distance (x_d) revealed by AgCl

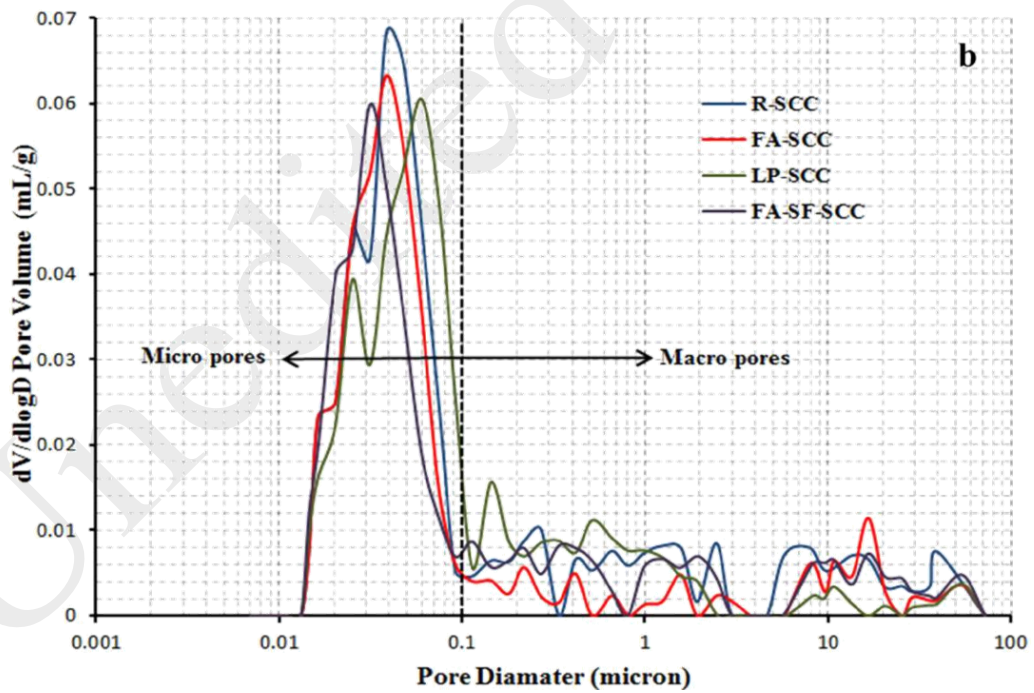
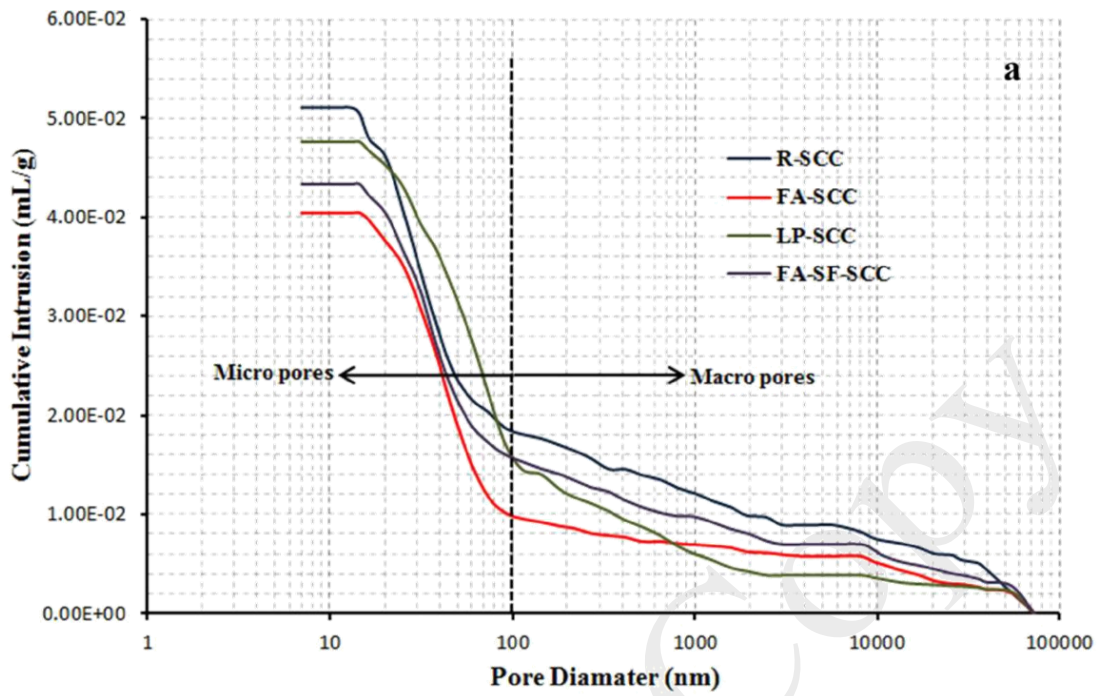


Figure 7 a) Mercury intrusion curves b) Derivatives of Mercury intrusion curves

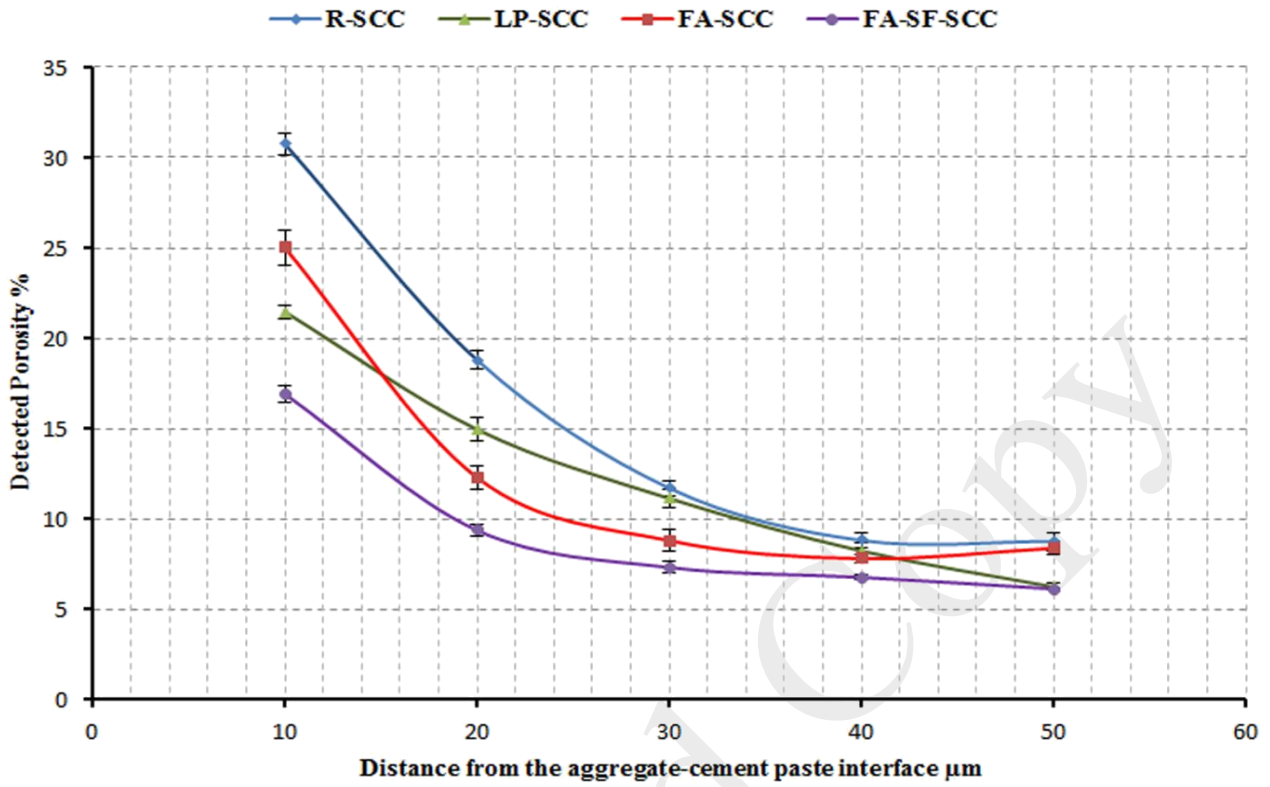


Figure 8 ITZ porosity profiles for the mixes

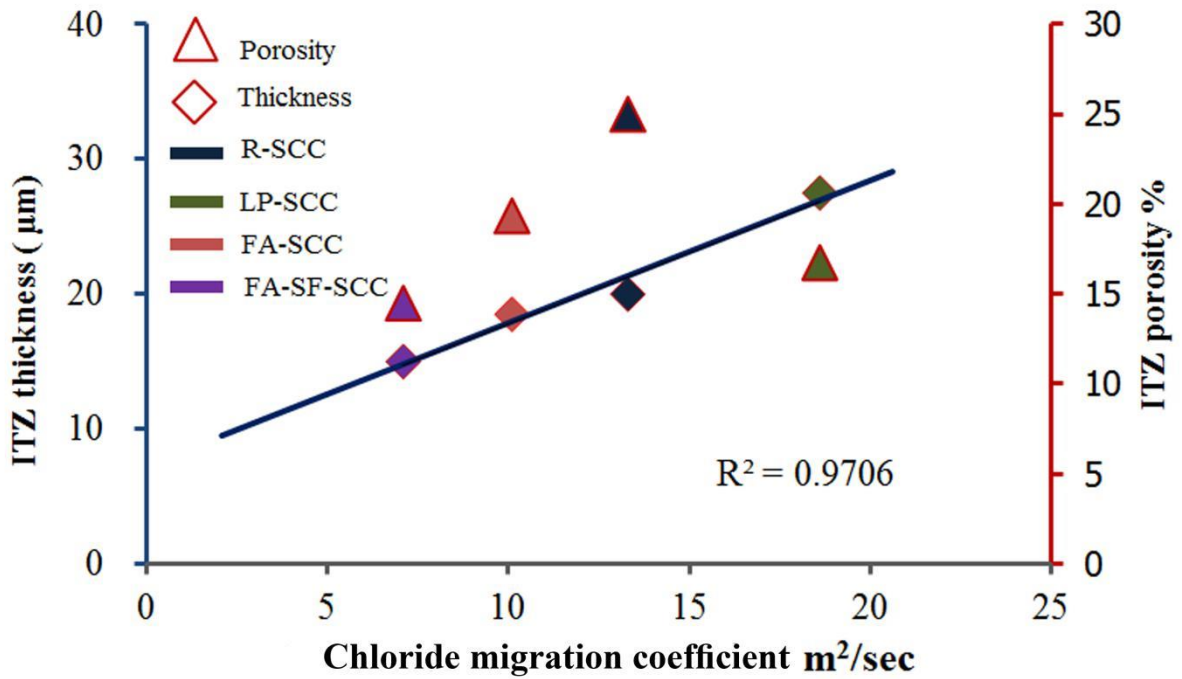


Figure 9 Relationship between the chloride migration coefficients, ITZs thicknesses and ITZs porosities

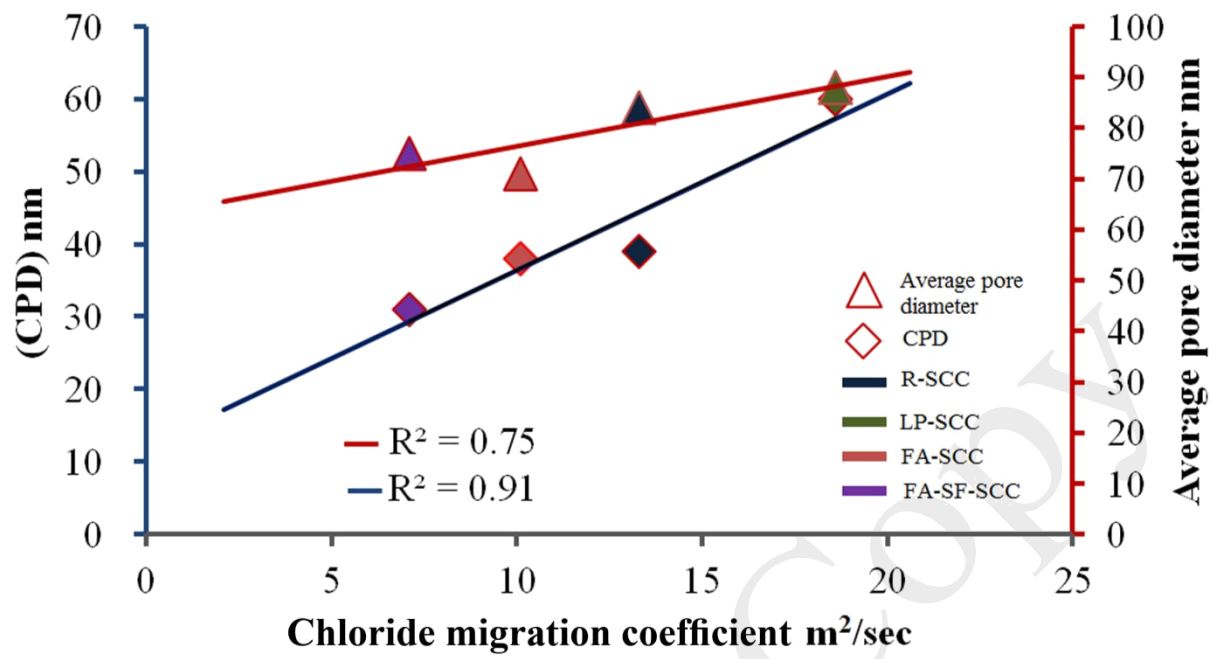


Figure 10 Relationship between the chloride migration coefficients and pore structure characteristics

Table 1 Chemical and physical properties of the used cement, fillers and mineral admixtures

Chemical compounds	Cement	Limestone (LP)	Fly ash (FA)	Silica fume (SF)
SiO ₂	20.09	0.3	50%	> 90
Al ₂ O ₃	4.84	---	26%	---
CaCO ₃	---	99	---	---
Loss On Ignition	2.36	42.9	< 3	< 3
Specific gravity	3.15	2.7	2.21	2.2
Blain finesse m ² /kg	395	1550	388.5	22400

Table 2 Mix design and fresh requirements of SCC mixes

Mix type	R-SCC	LP-SCC	FA -SCC	FA-SF-SCC
Cement (kg/m ³)	450	300	300	300
Coarse agg. (kg/m ³)	875	860	825	825
Fine aggregate (kg/m ³)	900	900	900	900
Water (kg/m ³)	180	180	180	180
Fly ash (kg/m ³)	---	---	150	120
Limestone (kg/m ³)	---	150	---	---
Silica fume (kg/m ³)	---	---	---	30
V _{coarse agg./V_{total}}	33.6	33.1	31.7	31.7
V _{fine agg./V_{mortar}}	51.2	50.7	49.7	49.7
V _{cement paste/V_{total}}	32.3	33.0	34.3	34.3
Slump flow (mm)	610	700	720	680
T ₅₀ (sec)	3.7	4.5	3.2	3.6
B _j (±2mm)	10	7.0	6.25	5
SI (%)	3	11.2	9.25	8.2
SP % by weight	3.9	2.6	1.83	3.1
Compressive Strength	56.1	50	56.5	57.9

T₅₀: time to obtain slump flow of 50 cm **B_j**: blocking step (J-ring test) **SI**: Segregation Index

Table 3 Internal pore characterizations at different scales (macro/micro and nano)

Mix ID	Micro pores % (MIP)	Macro pores % (MIP)	CPDs (nm) (MIP)	APDs (nm) (MIP)	Porosity% (MIP)	Porosity% (vacuum)	Micro pores % (Total)	Macro pores % (Total)
R-SCC	64.7	35.3	39	84	19.4	21.1	63	37
FA-SCC	75	25	38	71	8.7	14.7	69	31
LP-SCC	66.6	33.4	60	88	10.5	14.1	63	37
FA-SF-SCC	71	29	31	75	9.3	12.2	68.1	31.9

Table 4 Average Ca/Si ratio in the ITZ and cement matrix for SCC

Mix ID	R-SCC	LP-SCC	FA-SCC	FA-SF-SCC
Upper limit	3.68	19.1	4.6	3.1
Average Ca/Si ratio- ITZ	3.40	14.43	3.63	2.08
Lower limit	3.12	9.74	2.63	1.1
Upper limit	3.38	9.8	2.2	2.46
Average Ca/Si ratio- CM	3.16	8.285	1.99	2.17
Lower limit	2.93	6.77	1.7	1.88

Table 5 Overview of the pore structure, the ITZ features and the chloride migration coefficient results

Internal pore structure features						
Mix ID Property	R-SCC	LP-SCC	FA-SCC	FA-SF-SCC	Evidence	Comment
Porosity % Macro/Micro	21.1 (Macro)	14.7 (Macro)	14.1 (Micro)	12.2 (Micro)	Vacuum saturated + MIP	Section 4.1
Pores features Nano scale (nm)	CPD/APD 39/84	CPD/APD 60/88	CPD/APD 38/71	CPD/APD 31/75	MIP	Section 4.1 and Fig.10
ITZ micro-permeation features						
ITZ porosity %	Rather high 25	Low 16.8	Low 19.4	Very low 14.5	Image analysis	Section 4.2 and Fig.10
ITZ thickness (µm)	Thin 19.9	Rather thick 27.5	Thin 18.5	Very thin 15	Image analysis	Section 4.2 and Fig.10
ITZ chemistry	Ca/Si=3.40 Intermixed (CH+CSH)	Ca/Si=14.43 Intermixed (CH+CSH)	Ca/Si=3.63 Intermixed (CH+CSH)	Ca/Si=2.08 high CSH content	EDX analysis	Section 4.3
ITZ percolation degree %	Very high 90%	High 88%	Very high 95%	High 78%	Winslow et al. [26]	Depends on ITZ thickness and the fine aggregate volume fraction
Chloride penetration velocity						
Chloride migration coefficient (Dnssm) m2/sec	13.3	18.6	10.1	7.1	Modified rapid migration test	Figs.9 and 10 correlates with pore structure and ITZ