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Free and bound chloride relationships affecting reinforcement cover in alkali activated concrete

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1 **Free and bound chloride relationships affecting reinforcement cover in**

2 **alkali activated concrete**

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6 **ABSTRACT**

7 This paper investigates the free chloride profiles, diffusion parameters and chloride binding

8 capacity of an alkali activated concrete (AACM) together with a control Portland cement

9 (PC) concrete. Ggbs based AACM concrete specimens with different molarity of activator

10 were exposed to a 5% NaCl solution for 540days to determine their free chloride diffusion

11 properties. The relationships between the free and bound chloride concentration were

12 determined by applying Freundlich and Langmuir isotherms. The required cover to steel

13 reinforcement for corrosion prevention is derived to satisfy the limiting thresholds of free and

14 bound chloride concentrations.

15 The results show that Fick's second law of diffusion applies to the free chloride profiles of

16 AACM concrete and provides higher values of diffusion coefficients than a similar grade of

17 PC concrete. The relationship between the free and bound chlorides is defined by the

18 Langmuir isotherm. PC concrete has higher chloride binding capacity than AACM concrete

19 for both water and acid soluble chlorides. Less concrete cover to steel reinforcement is

20 required in AACM than PC concrete when calculated by using the bound chloride

21 concentration threshold limit. The values of cover based on the corresponding free chloride

22 limit in AACM concrete are higher than its bound chloride values.

23 **Keywords:** Alkali activated cementitious materials (AACM) concrete. Chloride binding

24 isotherms. Free chloride concentration. Total bound chloride concentration. Chloride

25 diffusion coefficient $(D_c)_f$. Surface chloride concentration $(C_0)_f$.

26

27 **Notations:**

28 AACM   alkali activated cementitious materials

29 PC   Portland cement

30 GGBS   ground granulated blast furnace slag

31 SRPC   sulphate-resisting Portland cement

32 C_{tb} total bound chloride concentration *(mg/g. by binder)*

33 C_f free chloride concentration (mol/L)

34 C_{as} acid soluble chloride concentration *(mg/g. by binder)*

35 C_{ws} water soluble chloride concentration *(mg/g. by binder)*

36 $(C_0)_f$ free surface chloride concentration (mol/L)

37 $C_{(x,t)f}$ free chloride concentration at distance x and time t

38 $(D_c)_f$ free chloride diffusion coefficient (x $10^{-12}\,m^2$/s)

39 $(D_c)_{tb}$ total bound chloride coefficient

40 $(D_c)_{as}$ acid soluble chloride coefficient

41 $(D_c)_{ws}$ water soluble chloride coefficient

42 α and β binding constants

43 SRA   shrinkage reducing admixture

44 R42   retarder

45 C_3A tricalcium aluminate

46 C_4AF tetracalcium aluminate

47 $Ca_6Al_2O_6.CaCl_2.10H_2O$ friedel's salt (FS)

2

48	$Ca_6Fe_2O_6.CaCl_2.10H_2O$	kuzel's salt (KS)
49	ISE	ion selective electrode
50	D_{ref}	diffusion coefficient at reference time t
51	t_{ref}	reference age (days)
52	m	age factor
53	C_{ref}	surface chloride concentration corresponding to the time
54	k	constant for surface chloride concentration
55	C-S-H	calcium silicate hydrate
56	CH	portlandite
57	AFm	monosulfoaluminate
58	AFt	ettringite
59	C-S-H	calcium silicate hydrate
60	N-A-S-H	sodium aluminosilicate hydrate
61	SCMs	supplementary cementitious materials

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68   **1.0   Introduction**

69 The use of Portland cement in construction is environmentally challenging due to huge

70 amount of CO_2 emissions and the high energy demand during its production [1−3]. New

3

71   innovations in low impact construction materials require a reduction in the use of Portland

72   cement with alternative binders, preferably utilising industrial waste materials and aggregates

73   made from recycled waste. Alkali activated cementitious materials (AACMs) show potential

74   benefits when used in place of Portland cement in the construction industry. However, strong

75   market forces go against the acceptance of AACMs which are partly supported by limited

76   knowledge of the service life of AACM concrete structures due to inadequate durability

77   investigations available in literature.

78   Chloride induced corrosion in concrete is a major cause of deterioration in reinforced

79   concrete structures such as bridge decks exposed to deicing salts and concrete exposed to

80   marine environment. Chlorides exist in the concrete matrix as acid soluble (chemically

81   bound), water soluble (physically bound) and free chlorides [4,5]. The free chloride which is

82   present in the pore solution of concrete is known to initiate corrosion by providing the

83   electrolyte for the electrochemical reactions. The free chloride content in concrete pore

84   solution together with oxygen and water are decisive factors in the initiation and propagation

85   of chloride induced corrosion in reinforced concrete [4]. Free chloride is dependent on the

86   water soluble chloride which is bound to the walls of the binder gel and the acid soluble

87   chloride which forms a part of the hydration or geopolymerization products in concrete. The

88   relationship between the free and bound chlorides (physically and chemically bound), which

89   is termed as the chloride binding capacity, regulates the amount of free chloride available to

90   initiate corrosion. Therefore, the chloride binding capacity of a concrete is an important

91   parameter for service life predictions of reinforced concrete structures. The relationship

92   between the bound and free chloride in AACM concrete remains to be fully understood.

93   Quantifying the parameters of this relationship will improve AACM mix design.

94   The pore solution chemistry and chloride binding capacity of AACMs is likely to differ from

95   PC concrete due to differences in their bound chlorides caused by low amounts of acid

96 soluble chloride in AACM concrete [6]. The water soluble chloride in AACM concrete is in

97 abundance which is influenced by the volume of pozzolanic constituents and their pore

98 properties [7]. On the other hand, a large proportion of the bound chloride in PC concrete is

99 found to be chemically bound to its hydration products while a smaller proportion is

100 physically bound between the interface of its hydrated products, which is contrary to AACM

101 concrete [6]. The presence of relatively low amount of chemically bound chloride and a high

102 amount of physically bound chloride in AACM concrete will affect its chloride binding

103 capacity relative to PC concrete.

104 The chloride binding capacity of PC concrete is attributed to many factors such as pH of

105 concrete pore solution, temperature, Tricalcium Aluminate (C_3A) content and exposure

106 period in a chloride solution. For example, the chloride binding capacity of sulphate-resisting

107 Portland cement (SRPC) and PC with supplementary cement replacement binder was

108 reported to be lower than PC concrete [4]. This was due to lower C_3A content of SRPC (PC ~

109 15% and SRPC~ 2%) [5]. An increase in the Tricalcium Aluminate, C_3A, decreases the free

110 chloride concentration in the pore solution by increasing the chemical binding capacity of

111 chloride. Similarly, lower alkalinity (pH) of concrete containing supplementary cementitious

112 materials decreases its chloride binding capacity relative to normal PC concrete and,

113 therefore, increases its free chloride concentration [8]. Some of these factors are not present

114 in AACM concrete, for example AACMs can be low on Tricalcium Aluminate, C_3A while

115 their alkalinity, pH, can be higher. These differences will, therefore, influence the chloride

116 binding capacities of AACM and PC concrete independently.

117 The chloride binding in concrete removes its free chloride from the pore fluid thereby

118 reducing the mobile chloride ions that can attack steel reinforcement in concrete.

119 Nevertheless, since the chloride diffusion process is based on attaining chemical equilibrium

120 between the pore solution and the exposure environment (external chloride solution), the

121 concentration of free chloride continues to increase with time [9] and ultimately reaches the

122 threshold level to initiate reinforcement corrosion. Chloride ingress may have varying

123 influence on the pore structure of AACM and PC concrete by the formation of Friedel's salt

124 ($Ca_6Al_2O_6.CaCl_2.10H_2O$) and Kuzel's salt ($Ca_6Fe_2O_6.CaCl_2.10H_2O$) during chloride binding.

125 This reduces the porosity and, therefore, limit further chloride ingress in concrete [7,10].

126 The relationships between free and total bound (chemical and physical) chlorides for PC

127 concrete have been defined by the Freundlich and Langmuir isotherms [9,11]. These models

128 are suitable for high and low free chloride concentrations and are applicable within a specific

129 range of chloride concentration. The equation of Freundlich isotherm applies to free chloride

130 levels exceeding 0.01 mol/L in the concrete pore fluid while the Langmuir equation applies to

131 free chloride levels below 0.05mol/L [11]. Freundlich binding isotherm is adopted for the

132 range of free chloride concentrations in seawater which are usually high. The Langmuir

133 binding isotherm defines the free-bound chloride relationship of normal PC concrete with

134 relatively low free chloride concentration of its pore fluid [10].

135 This paper is part of a comprehensive durability investigation of AACMs being undertaken

136 by the authors. It investigates the chloride binding capacity of AACMs, free chloride

137 diffusion parameters (C_0 and D_c) and determines the required concrete cover to steel

138 reinforcement based on total bound and free chloride thresholds.

139 **2.0   Experimental programme**

140 *2.1   Materials and mixes*

141 Three AACM concrete mixes 1, 2 and 3 and a control PC concrete were produced as shown

142 in Table 1. The mixes are similar to the compositions used to investigate the bound chloride

143 ingress in alkali activated concrete [6]. AACM and PC mortars, as shown in Table 1, were

144 also produced to determine and quantify the geopolymerization and hydration products.

145 Ground granulated blast furnace slag (GGBS) and CEM 1 cement of grade 42.5R [12] were

146 used as binders for AACM and PC concrete mixes respectively. The AACM binder was

147 activated with a sodium silicate solution of molarity 6.5mol/L and modulus 2% together with

148 NaOH of molarity 4.8mol/L. AACM 1, 2 and 3 mixes were produced by diluting the activator

149 with water at 0%, 3.88% and 7.76% respectively as shown in Table 1, to optimize

150 workability. Liquid/binder ratios of 0.47 and 0.5 were used for all concrete and mortar mixes

151 respectively. 10mm uncrushed gravel, 6 mm limestone and a medium grade sand of 80%

152 particle size passing 1mm sieve were used as coarse and fine aggregates. The properties and

153 oxide compositions of these aggregates conform to BS 882:1992 [13]. AACM concrete and

154 mortar mixes contain 0.5% by binder weight of shrinkage reducing admixture (SRA) made

155 from Alkyl-ether and 0.2% by binder weight of retarder R42 made from a blend of high grade

156 polyhydroxycarboxylic acid derivatives. The shrinkage reducing admixture also enhances

157 workability while the retarder reduces the setting time of AACM concrete. 5% by weight of

158 NaCl was added to the mortar composition only during mixing in order to investigate its

159 chloride binding capacity.

160 Table 1: Concrete and mortar mixes of AACM 1, 2, 3 and the control PC

	Mix	Binder Content (%)	Fine Agg. (%)	Coarse Agg. (%)		Liquid/ Binder Ratio	Activator Dilution (%)	R42	SRA
				10mm Gravel	6mm Limestone			(% by weight of binder)	
Concrete	AACM 1	25	18	29.3	15.7	0.47	0	0.2	0.5
	AACM 2	25	18	29.3	15.7	0.47	3.88	0.2	0.5
	AACM 3	25	18	29.3	15.7	0.47	7.76	0.2	0.5
	Control PC	20	26	28.9	15.5	0.47(w/c)	-	-	-
Mortar	AACM	30.5	64.5	-	-	0.5	0	0.2	0.5
	Control PC	30.5	64.5	-	-	0.5(w/c)	-	-	-

161 *R42 is the retarder; SRA is the shrinkage reducing admixture

162 *2.2   Mixing and casting*

163 *2.2.1   Mortar specimens*

7

164 Four 75 x 75 x 75mm specimens of each AACM and PC mortar were produced to determine

165 and quantify the geopolymerization and hydration products. The fresh mortar specimens were

166 prepared in a 12litre, 3 speed Hobart mixer. The mix constituents together with 5% NaCl

167 were mixed for 3mins at the lowest speed (option 1) to avoid dispersing the powder into the

168 atmosphere. The specimens were cast in steel moulds in three layers and each layer was

169 compacted on a vibration table. The cast specimens were placed on a flat surface in the

170 laboratory air (20 ± 2^0C, 65% R.H.) and covered with polythene sheets for 24hrs. The mortar

171 specimens were demoulded after 24hrs and cured in water (20 ± 2^0C) for 1day and 27days in

172 laboratory air (20 ± 2^0C, 65% R.H.).

173 *2.2.2   Concrete specimens*

174 Concrete specimens were produced and exposed to a 5% NaCl solution for up to 540days

175 similar to specimens used for bound chlorides investigation [6,14]. The fresh concrete was

176 mixed in a 150kg capacity Cretangle mixer and then cast into 250 x 250 x 75mm polystyrene

177 moulds in three layers, each layer being compacted by vibration. The cast specimens were

178 placed on a flat surface in the laboratory (20 ± 2^0C, 65% R.H.) and covered with polythene

179 sheets for 24hrs. A total of twenty-four specimens were produced and demoulded 24hrs after

180 casting followed by curing in water (20 ± 2^0C) for 27days. The concrete specimens were then

181 removed from water and surface dried. Two coats of bituminous paint were applied to five

182 faces of each slab except the bottom cast face (250 x 250mm) and allowed to dry for 24hrs.

183 The slabs were then immersed in a 5% by weight NaCl solution for 540days to expose the

184 uncoated face to chloride diffusion. Concrete coring was carried out at 180, 270 and 540days

185 of chloride exposure for pore fluid extraction.

186 *2.3   Test Procedures*

187 *2.3.1   Thermogravimetric analysis*

188 Thermogravimetric analysis (TGA) was performed on powder samples of AACM and PC

189 mortar samples to determine and quantify the main geopolymerization and hydration

190 products using a NETZSCH STA 409 PC/PG device. 19 and 17 grams of AACM and PC

191 powder samples were subjected to heating up to 1000^0C at a rate of 20^0C/min using nitrogen

192 gas. The geopolymerization and hydration products and their mass losses per unit

193 temperature were determined for AACM and PC samples after heating up to 1000^0C.

194 *2.3.2   X-ray diffraction (XRD)*

195 The mineralogical compositions of AACM and PC concrete were analysed using a Philips X-

196 Pert X-ray diffractometer operating with a Cu Kα radiation source (40 KV and 40 mA,

197 wavelength λ=0.154056 nm [6.07 x10-9 in.]). XRD analyses of the samples were performed

198 by scanning from 50 to 800 at an angle of 2Ө; the scan step size is 0.016711 and a counting

199 time step of 0.1 s.

200 2.3.3   pH Analysis

201 The ex-situ leaching method of concrete [15] was adopted to obtain the solution for the pH

202 analysis of the concrete and mortar samples. A double junction electrode connected to a 3-in-

203 1 benchtop meter was dipped inside a filtered solution of powder sample to measure pH of

204 AACM and PC dissolved in distilled water at a ratio of 1:1. This device measures pH ranging

205 from 0.00 to 14.00 and can measure sample volumes as small as 0.2mL with an accuracy of ±

206 0.01.

207 *2.3.4   Concrete coring and pore solution expression*

208 Four cores of 50mm diameter x 60mm depth were obtained from each AACM and PC

209 concrete specimen. The concrete coring was performed at 180, 270 and 540days chloride

210 exposure in a solution of 5% NaCl by weight. Each core was sawn into three discs of 50mm

211 diameter x 20mm depth representing depths of 0 - 20mm, 20 - 40mm and 40 - 60mm from

212 the surface of the concrete.

213 The pore solution expression was performed on the 20mm thick concrete discs obtained from

214 the AACM and control PC concrete. This was carried out by placing three discs from the

215 same depth, for example 0 - 20mm depth obtained from three cores for each mix, into a pore

216 fluid extraction device. The pore solution extraction device with the three discs inside it was

217 placed in a compression testing machine under its loading platen and a compressive load was

218 applied at a steady rate of 10KN/sec. The pore solution was extracted through a suction

219 action without allowing contact with air and was immediately stored in plastic vials, labelled

220 and sealed with parafilm. The same procedure was repeated on concrete core discs

221 representing 20 - 40mm and 40 - 60mm depths.

222 *2.3.5 Free chloride concentration*

223 The free chloride concentration of pore solutions in AACM and PC concrete was determined

224 by dipping a chloride ion selective electrode (ISE) into the pore solution. The ISE has a white

225 reference contact near the tip of the electrode which was immersed in the pore solution

226 without entrapping air bubbles below it. The ISE was held in the aqueous solution until the

227 reading stabilized and the displayed reading was then recorded. The ISE was rinsed by

228 spraying with a jet of deionised water and dabbed dry with a low-lint laboratory tissue

229 between measurements. The ISE was calibrated before and after each measurement. The

230 calibration was done by using a pre-prepared 1000mg/l and 10mg/l of standard NaCl

231 solution. The coefficient of variance of repeatability was less than 5%.

232 **3.0   Results and discussion**

233 *3.1   Geopolymer and Hydration products*

234 Thermogravimetric analysis (TGA) was performed on AACM and PC mortar samples

235 containing 5% NaCl to determine the geopolymerization and hydration products and the

236 nature of chloride binding in the matrix. Figures 1 show the derivatives of thermogravimetry

237 DTG showing peaks of hydration products on the primary axis while the secondary axis has

238   the thermogravimetry (TG) showing incremental loss of hydration products during heating

239   for AACM and PC concrete.
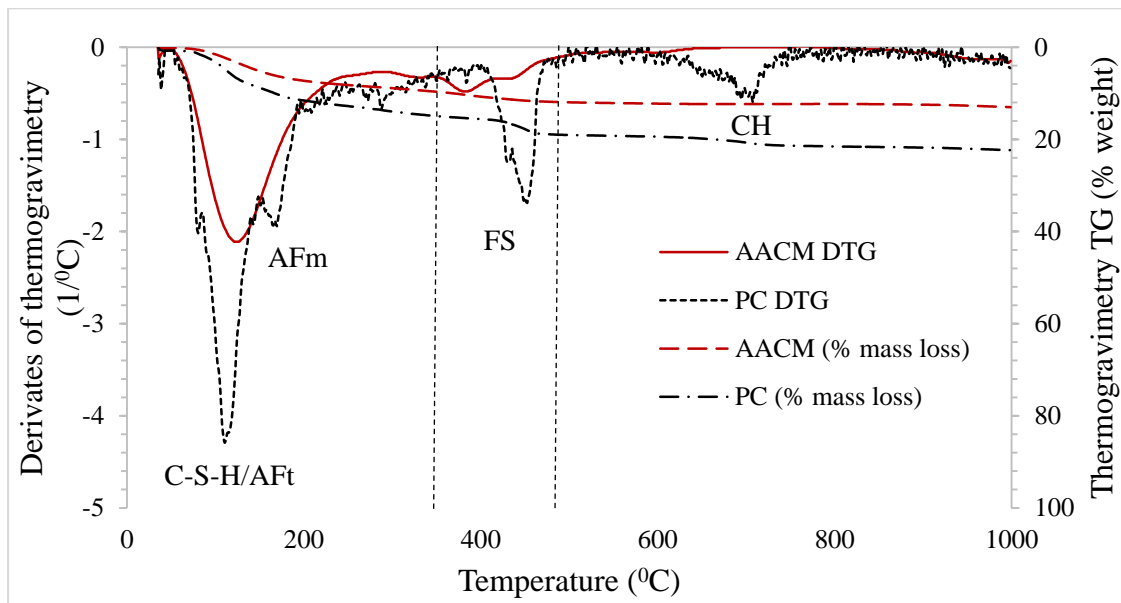
240

241   Fig. 1: Derivation of thermogravimetry (DTG) and thermogravimetry (TG) curves of AACM

242   and PC mortar

243   *FS is the Friedel's salt

244   The main geopolymerization products observed after heating AACM powder to 1000^0C are

245   Friedel's salt (FS), calcium silicate hydrate (C-S-H) and ettringite (AFt). The main hydration

246   products observed after heating PC powder to 1000^0C are Friedel's salt (FS), portlandite

247   (CH), calcium silicate hydrate (C-S-H), ettringite (AFt) and monosulfoaluminate (AFm),

248   similar to other research [16–18] on hydraulic cement. Portlandite (CH) and

249   monosulfoaluminate (AFm) were not observed in the derivatives of thermogravimetry (DTG)

250   of AACM mortar. This explains the limited amount of Friedel's salt (FS) observed in AACM

251   mortar since Portlandite (CH) is its main reaction constituent for binding chloride in the

252   matrix. The amount of Friedel's salt ($Ca_6Al_2O_6.CaCl_2.10H_2O$) is largely dependent on the

253   Ca/Al ratio (Table 2) as discussed in section 3.2. AACM concretes have low Ca/Al ratios

254   relative to PC concrete thus forming less monocarboaluminate compound which reacts with

11

255 chloride to form a lower amount of Friedel's salt as shown in Fig. 1. Monocarboaluminate

256 compound which converts to Friedel's salt on reaction with chloride is formed at high Ca/Al

257 ratio while stratlingite compound which does not covert to Friedel's salt is formed at low

258 Ca/Al ratio [19]. The relative volumes of Friedel's salt (FS) present in AACM and PC

259 mortars shown in Fig. 1 conform with the research findings on the chemically bound

260 chlorides in AACM concrete [6]. The greater mass loss of 22% by weight of the hydration

261 product in PC mortar compared with 12% weight of geopolymerization product in AACM

262 concrete, as represented by the TG loss, also confirms that greater amount of Friedel's salt

263 (FS) is present in PC mortar.

264 *3.2   pH and ions concentrations*

265 Chemical compositions showing oxides of various ions present in AACM and PC mortar

266 samples at 180days chloride exposure are shown in Table 2. pH values of powder samples of

267 AACM and PC mortar at 180days chloride exposure is also shown in Table 2.

268 Table 2: Chemical composition (%) and pH of AACM and PC mortar samples at 180days
269 chloride exposure

	CaO	SiO_2	Al_2O_3	Na_2O	MgO	SO_3	Cl	Fe_2O_3	K_2O	TiO_2	SrO	pH	OH^-
AACM 3	28.6	37.4	12.8	11.0	4.4	2.1	1.1	1.4	0.7	0.3	0.1	11.1	1.3e-3
PC	62.2	18.0	8.2	2.2	0.6	2.6	1.9	2.5	1.1	0.1	0.1	10.8	0.6e-3

270 Higher pH is seen in powder sample of AACM mortar (11.1) than PC mortar (10.8) at

271 180days chloride exposure as shown in Table 2. Their corresponding chloride concentrations

272 are 1.1% and 1.9% respectively in Table 2. pH values of both concrete types affected the

273 chloride binding capacity due to competition between OH^- and Cl^- at the adsorption sites of

274 the hydration/geopolymerisation products. It has been observed [20] that as more chloride

275 ions were chemically adsorbed, fewer adsorption sites were left for other ions such as OH^-

276 which could not be adsorbed simultaneously. This hypothesis [20] was suggested for the

12

277 higher binding capacity of PC concrete with a low pH since the low pH results in more

278 adsorption sites for free chloride compared with AACM concrete which has high pH.

279 Chloride binding in AACM and PC mortars is significantly influenced by the Ca/Al ratio. PC

280 concrete has higher Ca/Al ratio (7.6) compared with 2.2 for AACM concrete of similar

281 strength [7]. High Ca/Al ratio of 7.6 in PC mortar resulted in the formation of greater amount

282 of Friedel's salt ($Ca_6Al_2O_6.CaCl_2.10H_2O$) as shown in Fig. 1. AACM 3 mortars, however,

283 have small amount of Friedel's salt as shown in Fig. 1 due to their lower Ca/Al ratio (2.2).

284 High amount of Friedel's salt at high Ca/Al ratios was also observed by other research [19].

285 The formation of Friedel's salt at high Ca/Al ratio was attributed to the reaction between

286 chloride concentration and monocarboaluminate compound, however, at low Ca/Al ratio,

287 chloride concentration reacts with less monocarboaluminate thus resulting in less Friedel's

288 salt [19].

289 Chloride binding in AACM and PC mortars is also influenced by the Ca/Si ratio. PC concrete

290 has higher ratio of Ca/Si (3.5) compared with 0.8 for AACM concrete. The influence of Ca/Si

291 ratio is less prominent than Ca/Al ratio for chloride binding in PC concrete but this is not

292 valid for AACM concrete. The effect of Ca/Si ratio is more dominant than Ca/Al ratio in

293 AACM concrete resulting in the formation of more gel binder sites for binding Kuzel's salt

294 ($Ca_6Fe_2O_6.CaCl_2.10H_2O$). This is discussed in more details in section 3.5.

295 *3.3   Free and total bound chloride concentrations*

296 Table 3 shows the free and total bound chloride concentrations of AACM and PC concrete at

297 mean depths of 10, 30 and 50mm from the concrete surface. AACM 1, 2, 3 and PC concrete

298 were exposed to 5% NaCl solution for 180 and 270days; chloride exposure of AACM 1 was

299 further extended to 540days. Details of the bound chloride study are given in the authors'

300 previous publication [6]. Total bound chloride is the summation of both acid and water

301 soluble chlorides.

13

302 Table 3: Free and total bound chloride concentration of AACM and PC concrete at 180, 270
303 and 540days chloride exposure.

	Mean Depth	Free Cl$^-$ (mol/L)			Total bound Cl$^-$ (mg/g of binder)		
		180days	270days	540days	180days	270days	540days
AACM 1	10	0.011	0.020	0.026	18.46	21.96	32.46
	30	0.006	0.017	0.0201	9.46	14.90	19.25
	50	0.002	0.012	0.0153	2.68	3.93	7.68
AACM 2	10	0.015	0.023	-	20.83	26.42	-
	30	0.008	0.017	-	8.99	13.86	-
	50	0.003	0.014	-	3.14	4.93	-
AACM 3	10	0.018	0.025	-	23.34	29.99	-
	30	0.010	0.018	-	10.83	9.57	-
	50	0.004	0.014	-	3.6	4.93	-
PC	10	0.010	0.022	-	43.6	78.71	-
	30	0.005	0.013	-	22.08	25.94	-
	50	0.002	0.008	-	7.96	12.69	-

304 The control PC concrete shows the lowest free chloride concentrations at 180 and 270days
305 exposure compared with AACM 1, 2 and 3 concrete. For example, the free chloride
306 concentrations at 10mm mean depth for 180days chloride exposure is 0.01mol/L for the
307 control PC concrete compared with 0.011, 0.015 and 0.018mol/L for AACM 1, 2 and 3
308 concrete respectively. Similar trend is observed at 30 and 50mm mean depths (Table 3). The
309 free chloride concentrations increase with exposure period in both AACM and PC concretes
310 suggesting that some chlorides are accumulating in the pore fluid while the rest are
311 combining physically or chemically with the binder gel. For example, AACM 1 at 10mm
312 mean depth has free chloride concentrations of 0.011, 0.020, 0.026mol/L at 180, 270 and
313 540days chloride exposure respectively. The corresponding free chloride concentrations for
314 PC concrete at 10mm mean depth are 0.01 and 0.022mol/L at 180 and 270days chloride
315 exposure respectively.
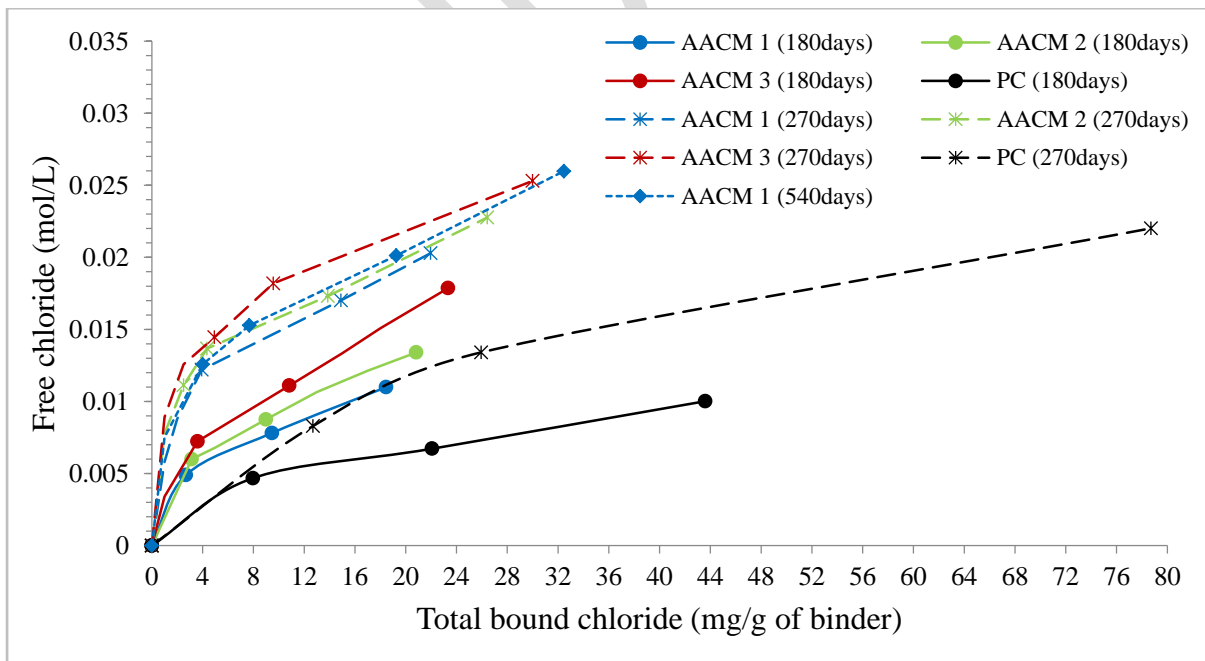
316 *3.4   Chloride binding isotherms*

14

The relationships between free and total bound (physically and chemically) chloride concentrations for AACM and control PC concretes at 180, 270 and 540days (for AACM 1) were determined by non-linear regression analysis using Langmuir and Freundlich chloride binding isotherms in equations 1 and 2 respectively [10,11,21].

$$C_{tb} = (\propto C_f)/(1 + \beta\, C_f) \qquad\qquad 1$$

$$C_{tb} = \propto C_f^{\beta} \qquad\qquad 2$$

where: C_{tb} is the total bound chloride concentration (mg/g of binder) at any depth; C_f is the corresponding free chloride concentration (mol/L); α and β are the binding constants.

The graph of Langmuir chloride binding isotherms for AACM 1, 2, 3 and control PC at 180, 270 and 540days of chloride exposure are shown in Figure 2. The chloride concentrations at depths 10, 30, and 50mm are plotted by the different symbols representing each mix and exposure period. The chloride concentration decreases with increasing depth into the specimen.

Fig. 2: Langmuir binding isotherms for AACM 1, 2, 3 and PC concrete at 180, 270 and 540 (for AACM 1) days of chloride exposure

Similarly, Freundlich binding isotherms were applied to the chloride concentration data to calculate coefficients α and β by non-linear regression analysis. Coefficients α and β together with the level of correlation with the experimental data, R^2, are presented in Table 4.

Table 4: Binding coefficients for Langmuir and Freundlich isotherms at 180, 270 and 540days of chloride exposure

Mix	Langmuir binding coefficients								
	180day			270day			540day		
	α	β	R^2	α	β	R^2	α	β	R^2
AACM 1	1.8	7.0	0.99	1.8	7.0	0.99	1.8	7.0	0.99
AACM 2	1.3	7.0	0.99	1.3	7.0	0.99	-	-	-
AACM 3	1.2	7.0	0.99	1.2	7.0	0.98	-	-	-
PC	2.5	2.0	0.98	2.5	2.0	0.99	-	-	-
Mix	Freundlich binding coefficients								
	180day			270day			540day		
	α	β	R^2	α	β	R^2	α	β	R^2
AACM 1	0.009	0.05	0.68	0.02	0.035	0.84	0.031	0.055	0.75
AACM 2	0.011	0.045	0.62	0.023	0.51	0.84	-	-	-
AACM 3	0.013	0.01	0.58	0.027	0.55	0.80	-	-	-
PC	0.021	0.023	0.82	0.04	0.023	0.76	-	-	-

The values of coefficients α and β under Langmuir binding isotherm are the same for each mix at 180, 270 and 540days (for AACM 1) of chloride exposure while they are different for each mix under Freundlich binding isotherm. For example, the constants α and β for AACM 1 concrete under Langmuir isotherm are 1.8 and 7.0 respectively at 180, 270 and 540days chloride exposure while they are 2.5 and 2 respectively for PC concrete. The same values are obtained for AACM 1, 2, 3 at 180 and 270days exposure. The Langmuir binding isotherm best fits the experimental data for both AACM and PC concrete with the highest coefficient of correlation of 0.99 while the Freundlich binding isotherm has a lower correlation coefficient of 0.58 to 0.84 as shown in Table 4.

The maximum free chloride concentrations (at 10mm depth) in AACM 1, 2, 3 and PC concrete are 0.020mol/L, 0.023mol/L, 0.025mol/L and 0.022mol/L respectively at 270days

347 chloride exposure (Table 3, Fig. 2). These concentrations are less than the 0.05mol/L limit

348 suggested by Tang and Nilsson [11] for the Langmuir isotherm to describe the effective

349 binding of free chloride concentrations. This isotherm model shows the best correlation with

350 the experimental data of AACM and PC concrete given in Fig. 2. Yuan et al. [10] suggested

351 that the Langmuir binding isotherm indicates that at longer chloride exposure, all adsorption

352 sites are occupied by chloride ions thereby resulting in lower chloride concentrations in the

353 pore solution.

354 Freundlich binding isotherms are usually applicable to concrete with high free chloride

355 concentrations. For example, Thomas et al. [21] used Freundlich binding isotherm to relate

356 their experimental free chloride data greater than 0.1M (0.1mol/L) for supplementary

357 cementitious materials. The concrete mixes investigated by Thomas et al. [21] showed that

358 8% cement replacement with silica fume exhibited the lowest chloride binding capacity

359 (therefore, maximum free chloride) while 25% cement replacement with fly-ash had the

360 highest binding capacity among the supplementary materials.

361 *3.5   Chloride binding capacity*

362 *3.5.1   Introduction*

363 The chloride binding capacity of the AACM and PC concrete mixes relating to their acid and

364 water soluble chloride concentrations is discussed in this section. The acid soluble chlorides

365 are chemically bound in the matrix while the water soluble chlorides are physically bound in

366 the capillaries of the matrix [6].

367 Some factors such as mix design, age of concrete, type of rebar and construction practices

368 influence the critical chloride threshold for reinforcement corrosion in PC concrete structures

369 [22,23]. Also the use of SCMs such as slag can have significant influence due to factors

370 discussed in section 3.2. However, the permissible chloride concentration for corrosion

371 initiation used in this paper is 4mg/g (0.4% by weight) of binder in accordance with British

17

372   Standards BS EN 206 [12] to start evaluating the relative performance of AACM and PC

373   mixes until ongoing research by the authors and others provides further insights. However,

374   with so many factors affecting this value [22,23], certain degree of approximation will be

375   inevitable. This value relates to the acid soluble chloride determined by the tests given in

376   international standards [24,25] for PC concrete. This limiting value of acid soluble chloride in

377   PC concrete is similar to its total (chemically plus physically) bound chloride concentration

378   [6]. However, for AACM concrete mixes, the water soluble chloride determined according to

379   ASTM standard [26] is representative of its total bound chloride concentration [6] and,

380   therefore, it is recommended for use as the permissible chloride concentration for design of

381   AACMs against corrosion.

382   However, the free chloride concentration in the pore fluid which serves as the electrolyte for

383   steel reinforcement corrosion is the actual initiator of reinforcement corrosion but it is

384   impractical to determine for use in the design against chloride induced corrosion [4].

385   Therefore, the relationship between the free and bound chlorides (acid and water soluble) is

386   investigated in this section. The reinforcement cover required in AACM concrete relative to

387   PC concrete will be determined based on both the bound chloride concentration of 0.4%

388   stipulated in international standards for PC concrete [12] and the corresponding free chloride

389   reaching the steel reinforcement.

390   *3.5.2   Acid soluble chloride*

391   Figure 3 shows the relationship between free chloride and bound chlorides for AACM 3 and

392   PC concrete at 270days chloride exposure. The bound chlorides represented in the graphs of

393   Fig. 3 are the total bound chloride C_{tb}, the acid soluble chloride C_{as} and the water soluble

394   chloride C_{ws}. The free chloride concentrations, C_f, corresponding to the permissible bound

395   chloride of 4mg/g (0.4%) of binder for AACM 3 and PC concrete are indicated on Fig. 3. The

396   graphs of AACM 3 are typical of AACM 1 and 2 which are not plotted to avoid congestion.

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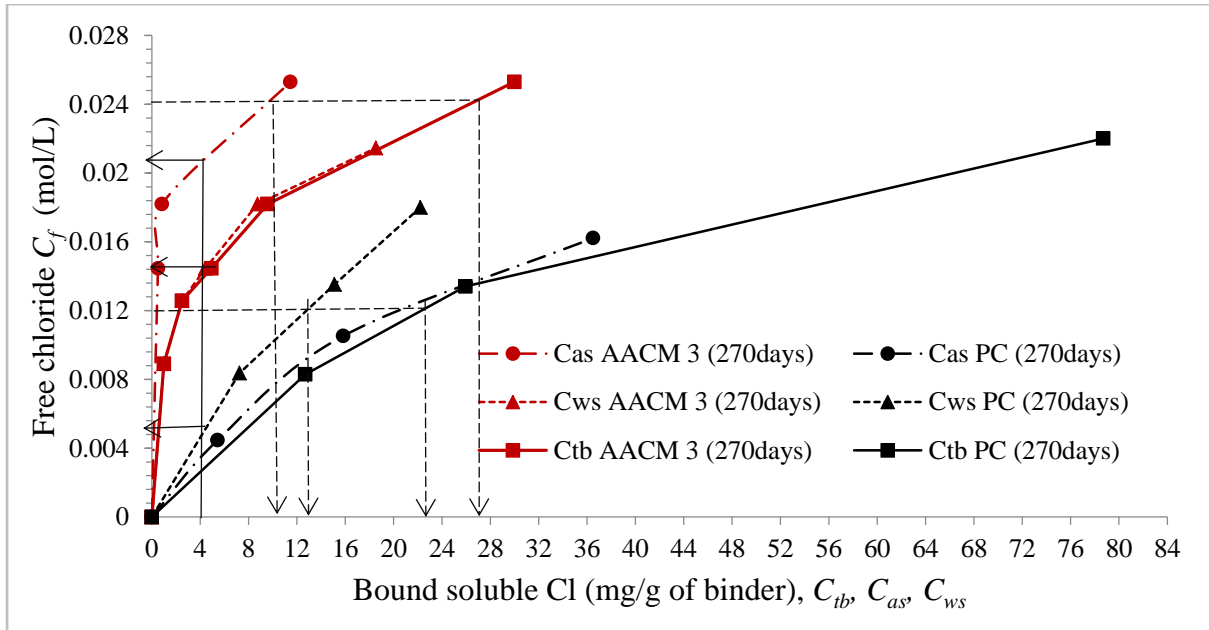
Fig. 3: Relationship between free and bound (total, acid and water soluble) chlorides for

AACM 3 and PC concrete at 270days chloride exposure

The free chlorides corresponding to the permissible 4mg/g (0.4%) by binder weight of acid

soluble chloride C_{as} in Fig. 3, are 0.02mol/L and 0.003mol/L for AACM 3 and PC concrete

respectively at 270days chloride exposure. At any fixed value of acid soluble chloride

concentration (e.g. 4mg/g) the free chloride concentration is much greater in AACM

concrete. The graphs for PC concrete in Figure 3 also show that the C_{tb} versus C_f graph

coincides with the C_{as} versus C_f graph and the C_f value at C_{as} of 4mg/g is common to both

curves. The graph representing the relationship between C_{ws} and C_f does not relate to the total

bound chloride C_{tb} versus C_f graph. This confirms the previous statement that the total bound

and acid soluble chloride values are similar in PC concrete. The C_f value is 0.003mol/L at

4mg/g C_{as} and C_{tb}. In the case of AACM 3, it is the C_{ws} versus C_f graph which coincides with

its C_{tb} versus C_f graph and both give the same value of C_f (0.015mol/L) corresponding to

4mg/g C_{ws} and C_{tb}. This confirms that the total bound and water soluble chloride values are

similar in AACM concrete. The C_f value at 4mg/g C_{ws} and C_{tb} for AACM 1 and 2 are

0.012mol/L and 0.013mol/L respectively.

19

414   Chemical and mineral admixtures which are present in AACM concrete are known factors

415   which reduce the chloride binding capacity in PC concrete. For example, mineral additives

416   like silica fume, fly-ash, ground granulated blast furnace slag and gypsum reduce the binding

417   capacity due to their lower unhydrated C_3A content that is required for chemically bound

418   chlorides [10,20]. Zhang et al. [27] observed limited chemical binding of chloride in AACM

419   concrete containing 100% slag similar to the results in Fig. 1. However no chemical binding

420   of chloride was seen in AACM concrete containing both slag and fly ash in 60/40 ratio.

421   Alkali activated fly ash mortar immersed in NaCl solution for 2 years does not produce any

422   Friedel's salt [28]. The fly ash in AACM concrete dissolves Al forming more zeolite phases

423   and N-A-S-H inhibiting the formation of Friedel's salt [27]. Conversely, high unhydrated

424   C_3A content promotes the formation of Friedel's salt $(Ca_6Al_2O_6.CaCl_2.10H_2O)$ in PC

425   concrete which is seen in Fig. 1.

426   It has been reported that the presence of superplasticizers tends to lower the chloride binding

427   capacity in PC concrete [29] when NaCl is admixed in the fresh concrete. Chemical

428   admixtures such as superplasticizers and shrinkage reducing admixtures release bound water

429   into its pore solution in fresh PC concrete [22,23] which affect the value of admixed bound

430   chloride. Cement particles have surface charges which causes them to flocculate when in

431   contact with water while the addition of chemical admixtures into the fresh concrete mix

432   releases the trapped bound water within the gel matrix [22,23]. However, other research

433   reports that the effect of these chemical admixtures is to increase the amount of bound

434   chloride when chloride diffusion into hardened concrete occurs from external sources

435   [30,31]. This is due to the greater surface area of the hydration products produced by the

436   flocculation of cement particles and release of bound water caused by the admixtures [30,31].

437   However, this topic needs further research, particularly for AACM concrete, which will be

438   the subject of future publications.

439 *3.5.3   Water soluble chloride*

440 The free chloride C_f corresponding to 4mg/g (0.4%) by binder weight of water soluble

441 chloride C_{ws} at 270days exposure is 0.014 and 0.006mol/L for AACM 3 and PC concrete

442 respectively (Fig. 3). The concentration of free chloride in the pores of AACM concrete at

443 4mg/g (0.4%) by weight of water soluble chloride C_{ws} is greater than PC concrete. Both the

444 acid and water soluble chlorides bound in PC concrete are greater than AACM concrete

445 (Figures 3) thus producing less free chloride in PC concrete at the 4mg/g (0.4%) acid and

446 water soluble chlorides.

447 AACM concrete has a higher binding capacity of water soluble chloride than acid soluble

448 chloride. For example, at a fixed free chloride concentration of C_f of 0.024mol/L, the acid

449 and water soluble chlorides are 10mg/g and 27mg/g of binder respectively. PC concrete, on

450 the other hand, shows a lower binding capacity of water soluble chloride than acid soluble

451 chloride. For example, at a free chloride C_f concentration of 0.012mol/L, the acid and water

452 soluble chlorides are 23mg/g and 13mg/g of binder respectively. The results in Figures 3

453 show that while the chemically bound chloride represented by acid soluble chloride is high in

454 PC concrete, the physically bound chloride (water soluble) is also significant whereas in

455 AACMs the physically bound chloride (water soluble) is dominant while chemically bound

456 chloride (acid soluble) is insignificant. Zhang et al. [27] observed that AACM mix

457 formulation containing slag/fly ash in the ratio 60/40 resulted in more physically bound

458 chloride than in composition of lower fly ash content. The inclusion of fly ash increases the

459 surface area of aluminosilicate gel which allows more physical absorption of chloride in

460 AACM concrete [32]. Fly ash dissolves Al in AACM concrete matrix forming zeolite, halite

461 and chabazite creating more physical bound chlorides [27].

462 In the case of PC concrete, the higher chemical chloride binding caused by factors discussed

463 in section 3.5.2 results in lower amount of free chloride present in the pore fluid. However,

464 physical chloride binding is higher in AACMs due to higher volume of the binder gel than PC

465 concrete [7], it is still notable in PC concrete due to its significant binder gel. Consequently,

466 the loss of free chloride due to both chemical and physical chloride binding is much higher in

467 PC than AACM concrete that have a low chemical chloride binding capacity due to factors

468 discussed in section 3.5.2.

469 *3.6   Chloride diffusion parameters*

470 *3.6.1   Free chloride profiles*

471 Equation 1 of the Langmuir isotherm is re-arranged to give equation 3 in order to calculate

472 free chloride values from the considerable total bound chloride, C_{tb}, data reported elsewhere

473 [6] for the AACM and PC concrete mixes.

$$C_f = \frac{C_{tb}}{[(\alpha * 100) - (\beta * C_{tb})]} \qquad\qquad 3$$

474 where: C_{tb} is the total bound chloride concentration (% weight of binder); C_f is the

475 corresponding free chloride concentration (mol/L); α and β are the chloride binding

476 coefficients from table 3.

477 The free chloride concentrations, C_f, at 8, 15, 20, 25, 35, 50 and 65mm depth from the

478 concrete surface were determined by applying equation 3 to their corresponding total bound

479 chloride, C_{tb}, values at 55, 90, 120 and 180days chloride exposure. The coefficients α and β

480 of the Langmuir binding isotherm which are given in Table 3 were used in the analysis.

481 For example for AACM 1 at 180days chloride exposure, the bound chloride at 20mm depth

482 C_{tb} =1.44% by weight of binder [6] while α and β are 1.8 and 7 respectively (Table 3).

483 Substituting these values in equation 3 gives a value of C_f = 0.0085mol/L.

484 The resulting free chloride concentration graphs against depth are plotted in Fig. 4. Non-

485 linear regression analyses were performed on the free chloride concentration data by applying

486 equation 4 which is based on Fick's 2nd law of diffusion [33].

$$C_{f(x,t)} = (C_0)_f \left(1 - erf\left[\frac{x}{2\sqrt{(D_c)_f}\, t} \right] \right) \qquad 4$$

487   where: x is the distance from concrete surface (m); t is the time (seconds); $(D_c)_f$ is the free

488   chloride diffusion coefficient (m^2/s); $(C_0)_f$ is the free chloride concentration on the concrete

489   surface; $C_{(x,t)f}$ is the free chloride concentration at distance x and time t.

490   The best fit profiles (curves) with depth obtained by this analysis are shown in Fig. 4 together

491   with the experimental data of free chloride (data points) from table 2. The coefficients of

492   correlation range from 0.70 to 0.99.
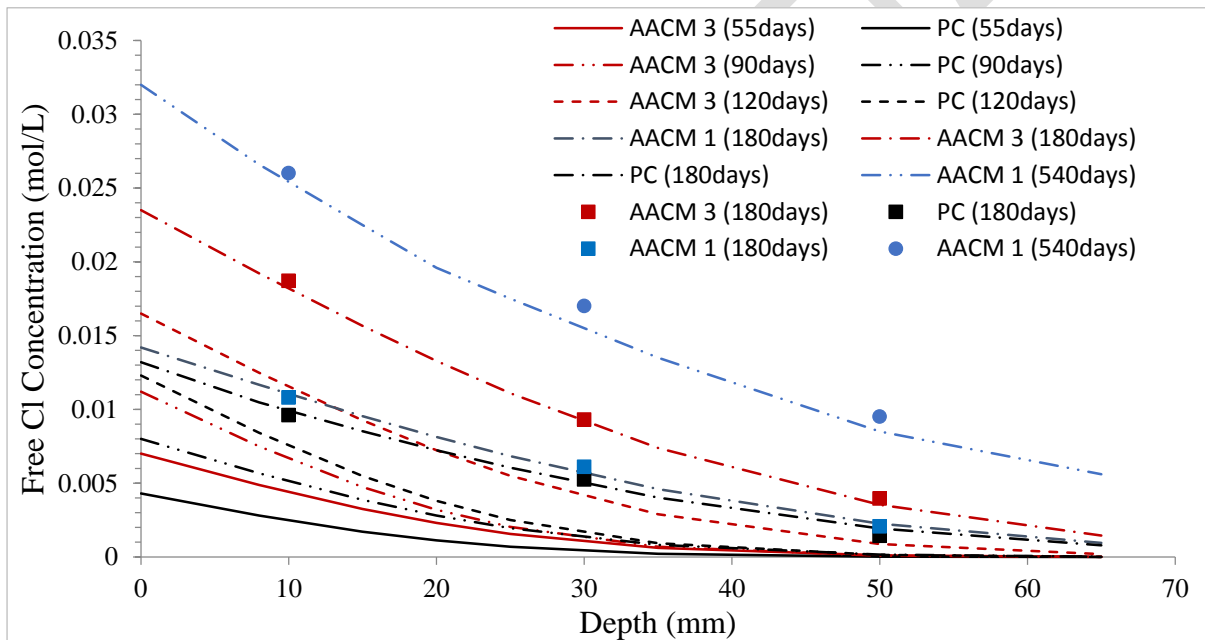
493

494   Fig. 4: Free chloride profiles with depth of AACM 1, 3 and PC concrete derived from
495   Langmuir isotherm.

496   AACM 3 concrete has higher free chloride profiles than PC concrete at all exposure periods.

497   The lower free chloride concentrations in PC concrete are due to its higher chloride binding

498   than AACMs. On the other hand, the free chloride concentrations are similar in AACM 1 and

499   PC concrete at 180days chloride exposure. Increasing molarity of the activator in AACM

500   concrete reduces its free chloride concentration.

501   *3.6.2   Free chloride diffusion coefficients Dc and C$_0$*

502 The non-linear regression analysis by applying Fick's diffusion equation 4 to the free

503 chloride data also provided the $(C_0)_f$ and $(D_c)_f$ values of the AACM and PC concretes at each

504 period of exposure. These chloride diffusion coefficients change with time due to changes in

505 the properties, such as porosity and chloride binding in concrete [34–37]. In order to account

506 for these changes, age factors are introduced in the Fick's 2nd law of diffusion $\delta C/\delta t = D$

507 $\delta^2 C/\delta x^2$ [34–37] which assumes D_c to be constant in equation 4. The relationships between

508 exposure period and $(D_c)_f$, $(C_0)_f$, are presented in Figures 5 and 6 respectively.
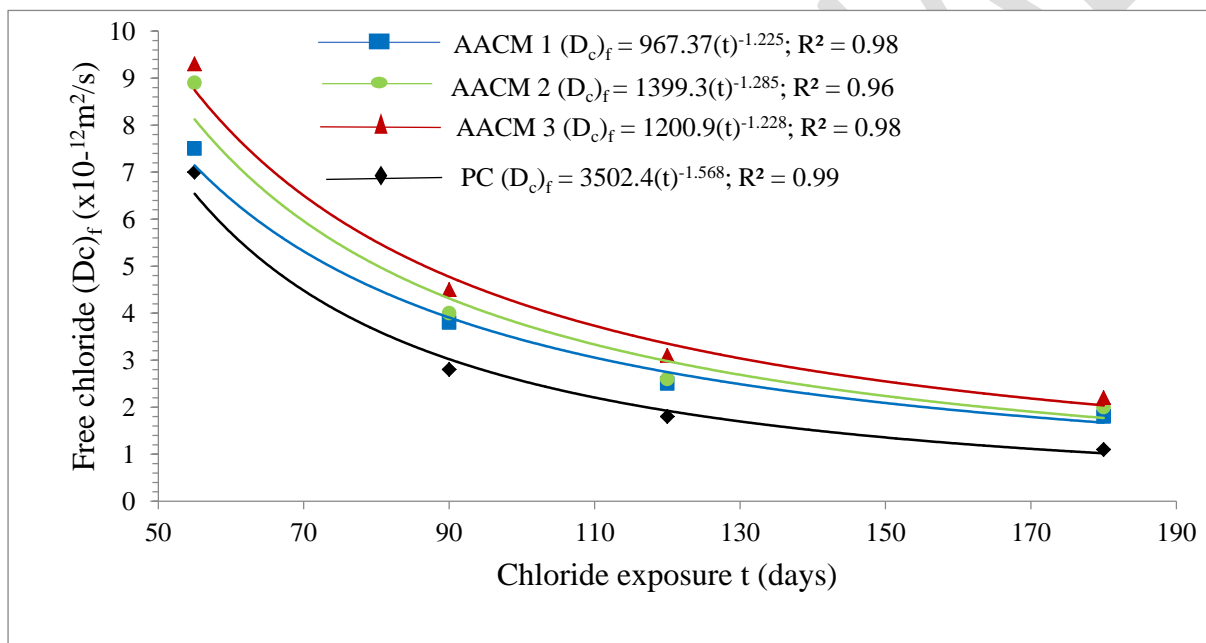
509

510 Fig. 5: Relationship of free chloride diffusion coefficient, $(D_c)_f$, with exposure period for
511 AACM 1, 2, 3 and PC concrete

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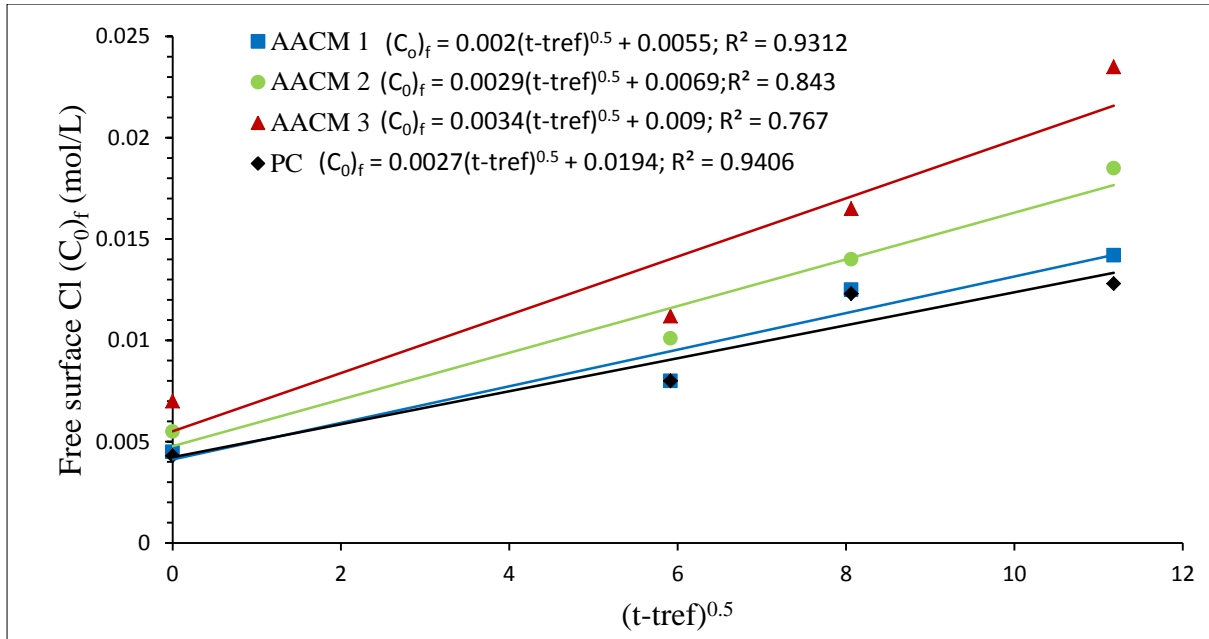
512

513   Fig. 6: Relationship between $(C_0)_f$ and square root of chloride exposure period $(t-t_{ref})^{0.5}$ for
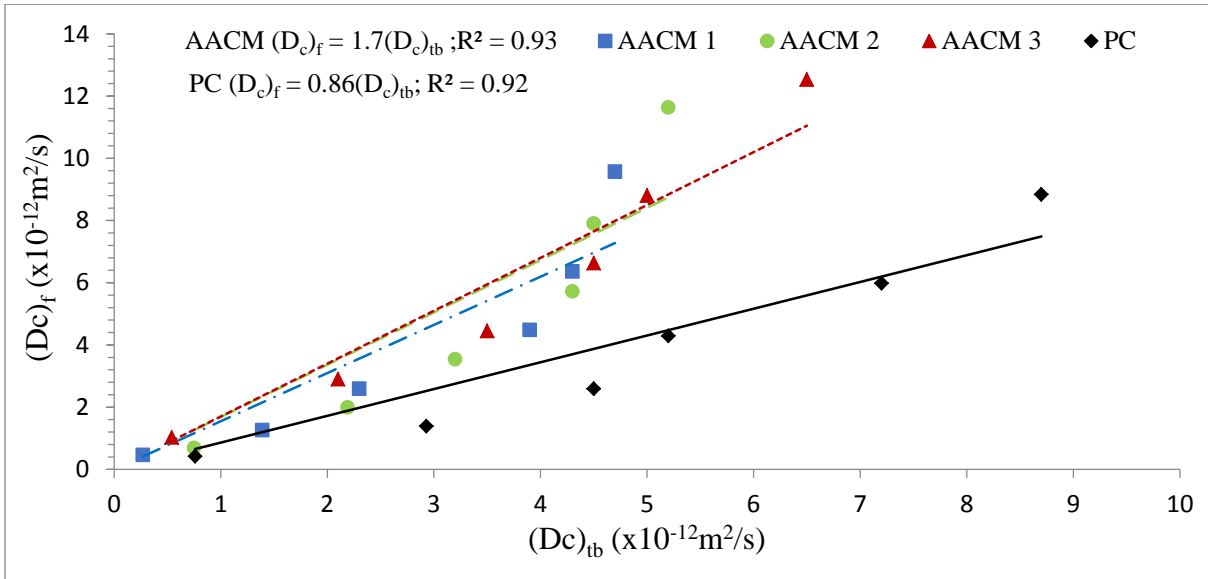
514   AACM 1, 2, 3 and control PC concrete.

515   Figure 5 shows a reduction in $(D_c)_f$ in both AACM and PC concrete while Fig. 6 shows an

516   increase in $(C_0)_f$ with increasing chloride exposure period. The free chloride diffusion

517   coefficient $(D_c)_f$ is lower in PC than AACM 1, 2 and 3 concrete mixes unlike the total bound

518   chloride coefficient $(D_c)_{tb}$ which is higher in PC concrete [6]. The lower free chloride in PC

519   concrete compared with AACM concrete is due to higher chloride binding caused in PC

520   concrete by the formation of Friedel's salt during hydration while the AACM concrete

521   produces less Friedel's salt as shown in Fig 1.

522   The resulting equations for $(D_c)_f$ and $(C_0)_f$ with exposure period are shown in Figures 5 and

523   6. Similar relationships have also been derived for the bound chloride diffusion parameters

524   $(D_c)_{tb}$ and $(C_0)_{tb}$ [6].

525   *3.6.3   Chloride diffusion coefficients $(D_c)_f$ and $(D_c)_{tb}$*

526   The direct determination of $(D_c)_f$ is impractical in practice due to the need for concrete

527   coring, pore fluid extraction and chemical analysis. Also, the accuracy of determining free

528   chloride concentration is sensitive to the moisture state of concrete. An indirect approach for

25

529   determining $(D_c)_f$ is to relate it to its total bound chloride coefficient $(D_c)_{tb}$ which is easier to

530   determine with specifications given in standards [24,25]. The relationship between the free

531   and total bound chloride diffusion coefficients, $(D_c)_f$ and $(D_c)_{tb}$, for AACM 1, 2, 3 and PC

532   concrete is shown in Fig. 7. The data of total bound chloride diffusion coefficients $(D_c)_{tb}$ are

533   from the previous paper by the authors [6].

534

Fig. 7: Relationship between $(D_c)_f$ and $(D_c)_{tb}$ of AACM 1, 2, 3 and control PC concrete

536   The relationship between the free chloride diffusion coefficient $(Dc)_f$ and total bound chloride

537   diffusion coefficient $(D_c)_{tb}$ is similar for AACM 1, 2 and 3 but different for PC concrete as

538   shown in Fig. 7. Both concretes show a linear relationship between $(D_c)_f$ and $(D_c)_{tb}$ as

539   follows:

540   For AACM concrete,

541                    $(D_c)_f = 1.7\ (D_c)_{tb}$ with $R^2 = 0.93$ 5

542   For PC concrete,

543                    $(D_c)_f = 0.861\ (D_c)_{tb}$ with $R^2 = 0.92$ 6

544   The relationship between $(D_c)_{tb}$ and $(D_c)_f$ is an important tool for service life prediction of

545   reinforced AACM concrete because it can be used to evaluate the time taken for free chloride

26

546 concentrations at the steel surface to reach critical levels and cause corrosion as discussed in

547 the next section.

3.7   Concrete cover to reinforcement

3.7.1   Introduction

550 The concrete covers required to prevent reinforcement corrosion in AACM and PC concrete

551 samples exposed to the 5% NaCl solution are calculated from the accelerated chloride

552 diffusion data reported in this paper. The chloride concentration of the 5% NaCl solution is

553 0.88mol/L compared with 0.54mol/L for see water [24,25]. Therefore, the calculated covers

554 from the experimental data represent conservative values but provide useful guidelines on the

555 cover required in AACMs relative to PC concrete. The cover calculations are based on

556 chloride considerations only while other factors such as pore properties and pH which could

557 favour AACMs against reinforcement corrosion [2] are not included. These will be addressed

558 in a future publication by the authors.

559 The minimum required concrete covers to steel reinforcement to prevent chloride induced

560 corrosion were determined for AACM 1, 2, 3 and PC concrete. These values correspond to

561 the depths at which the permissible total bound chloride value of 4mg/g (0.4%) by weight of

562 binder has been reached. This value is stipulated in standards for conventional reinforced

563 concrete based on the acid soluble chloride test [12]. The free chloride concentration in PC

564 concrete corresponding to 0.4% (4mg/g) of total chloride is 0.003mol/L as shown in Fig. 3.

565 This free chloride value of 0.003mol/L in PC concrete is, therefore, considered as the

566 threshold for corrosion initiation since the pore fluid provides the electrolyte for the corrosion

567 process [4]. Considering that this critical free chloride concentration (0.003mol/L) applies to

568 both the AACM and PC concretes for corrosion initiation, the cover required to steel

569 reinforcement is also calculated to satisfy this free chloride limit. The ratio of the cover

570 required in AACM concrete relative to the control PC concrete at the same exposure periods

27

571   for both the limits of total bound chloride (0.4%) and the corresponding free chloride limit

572   (0.003mol/L) are plotted in Fig. 8, and discussed in section 3.6.2.

573   *3.7.2   Cover ratios based on total bound and free chloride thresholds*

574   The ratios of AACM to PC concrete covers at different chloride exposure periods are shown

575   in 9. These ratios were determined based on the total bound and free chloride thresholds, as

576   described below.

577   *3.7.2.1 Cover ratios based on total bound chloride limit, C_{tb}*

578   Concrete covers based on the total bound chloride threshold limit of 4mg/g (0.4%) by weight

579   of binder were determined from equation 5 which is a re-arrangement of equation 4

580   representing Fick's 2nd law of diffusion.

$$x = \left[erf^{-1} \left[1 - \frac{C_{tb}}{(C_0)_{tb}} \right] \right] * 2\sqrt{(D_c)_{tb} * t} \qquad\qquad 5$$

581   where: x is the minimum concrete cover depth (m); t is the time (seconds); $(D_c)_{tb}$ is the total

582   bound chloride diffusion coefficient (m^2/s); $(C_0)_{tb}$ is the total bound chloride concentration on

583   the concrete surface; C_{tb} is the total bound chloride concentration of 4mg/g (0.4%) by binder

584   weight at the concrete cover x and time t.

585   For example, the cover x for AACM 1 at 180days chloride exposure is calculated by

586   substituting the following values of parameters in equation 5:

587     $C_{tb} = 4$mg/g

588   t = 180 x 24 x 60 x 60 seconds

589   The values of $(C_0)_{tb}$ and $(D_c)_{tb}$ are as follows [6]

590     $(C_0)_{tb} = 2.09\%$ wt. of binder

591     $(D_c)_{tb} = 2.3 \times 10^{-12} m^2$/s

592   Substituting these values in equation 5 gives x =11.04mm.

593   Similarly, the cover x for PC concrete is calculated to give a cover ratio $C_{aacm}/C_{pc} = 0.53$

594   *3.7.2.2 Cover ratios based on free chloride limit, C_f*

595   The free chloride threshold value of 0.003mol/L which corresponds to the total bound

596   chloride limit of 4mg/g (0.4%) in PC concrete was used as the limiting value of free chloride

597   C_f in the calculation of cover from equation 6 which is a re-arranged form of equation 4.

$$x = \left[erf^{-1} \left[1 - \frac{C_f}{(C_0)_f} \right] \right] * 2\sqrt{(D_c)_f * t} \qquad 6$$

598   where: x is the minimum concrete cover depth (m); t is the time (seconds); $(D_c)_f$ is the free

599   chloride diffusion coefficient (m^2/s); $(C_0)_f$ is the free chloride concentration on the concrete

600   surface; C_f is the free chloride threshold of 0.003mol/L at the concrete cover x at time t.

601   The $(D_c)_f$, $(C_0)_f$ and the limiting C_f values were then inserted into equation 6. For example,

602   the cover x for AACM 1 at 180days chloride exposure is calculated by substituting the

603   following values of parameters in equation 6:

604   C_f = 0.003mol/L

605   t = 180 x 24 x 60 x 60 seconds

606    $(D_c)_f$ = 2.3 x 10^{-12}m^2/s and $(C_0)_f$ = 0.0142mol/L derived from nonlinear regression analysis of

607   free chloride data in Fig.4.

608   Substituting these values in equation 6 gives x =10.6mm.

609   Similarly, the cover x for PC concrete is calculated to give a cover ratio C_{aacm}/C_{pc} = 1.2

610   The cover x values were determined for all the AACM and PC concrete mixes at exposure

611   periods 55, 90, 120 and 180days. The cover ratios of AACM to PC concrete at different

612   chloride exposure periods are shown in Fig. 8.

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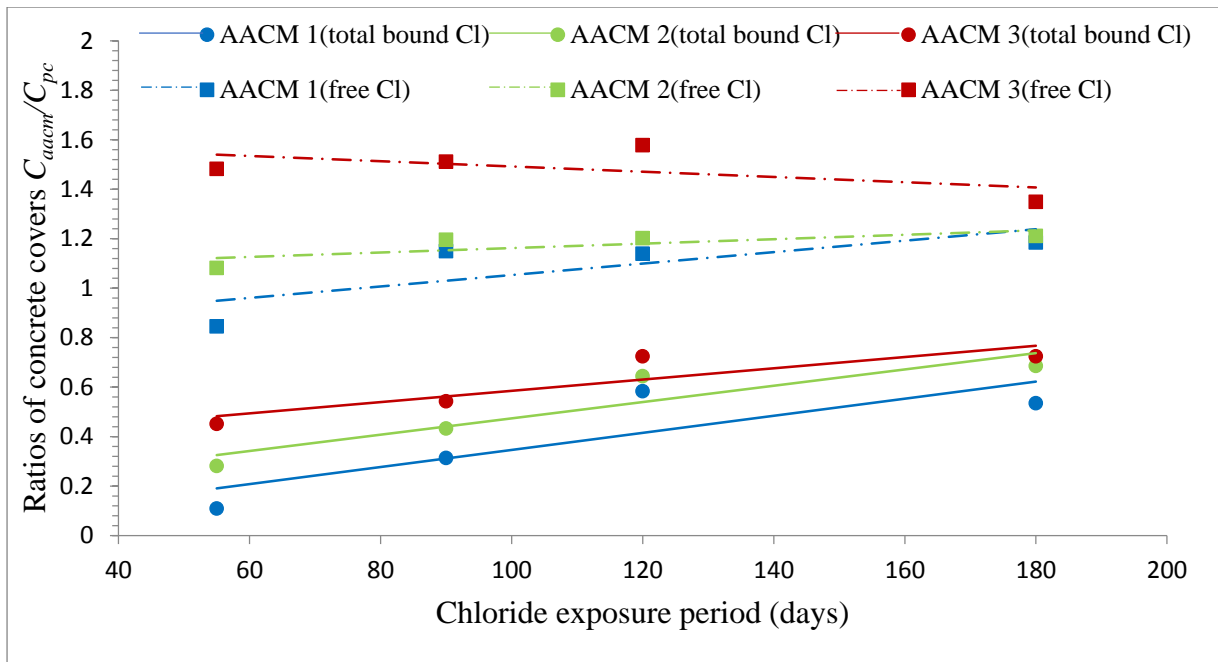
Fig. 8: Cover ratios of AACM and PC concrete with chloride exposure period based on the free and total bound chloride thresholds (the cover ratio of PC concrete is unity at all exposure periods).

Figure 8 shows the cover ratios C_{aacm}/C_{pc} versus chloride exposure period graphs. The control PC concrete in Figure 8 has a unitary value of cover ratio at all chloride exposures while the values for AACM 1, 2 and 3 are less or greater than unity, depicting lesser or greater concrete cover requirements than PC concrete. The concrete cover ratio of AACM concrete is less than unity, at all exposure periods based on the total bound chloride threshold. For example, concrete cover ratios at 180days exposure are 0.72 and 1 for AACM 3 and PC concrete respectively based on the total bound chloride threshold. However, the cover ratio for AACM concrete exceeds unity when the calculation is based on the free chloride threshold. For example, at 180days exposure, the concrete covers ratios for AACM 3 and PC concrete are 1.35 and 1 respectively.

Therefore, the plots in Figure 8 show that the cover to reinforcement required for AACM concrete to satisfy the total bound chloride of 4mg/g stipulated in standards [24,25] is lower than an equivalent PC concrete. However, the cover required is up to about 40% greater in

630   AACM 3 concrete than an equivalent strength PC concrete if based on the free chloride limit

631   of 0.0023mol/L which corresponds to 4mg/g of total bound chloride. The PC concrete mix is

632   the control for the AACM 3 concrete since the two have similar strength and workability

633   [6,7]. The cover ratios of higher strength AACMs 1 and 2 concrete decrease towards unity.

634   This result assumes that the chloride threshold limits for corrosion initiation in AACM and

635   PC concrete are the same and their porosity and pH are not considered.

636   *3.8   Free Cl⁻ diffusion parameters and porosity relationship*

637   Figure 9 shows the relationships between porosity and free chloride diffusion parameters

638    $(D_c)_f$ and $(C_0)_f$ of AACM concrete. The porosity data represents mortar mixes with the same

639   binder and activator content (liquid/binder ratio of 0.47) as the concrete mixes of this study.

640   The pore properties which were determined by mercury intrusion porosimetry have been

641   reported by the authors [7,38] and represent AACM mixes with different pore properties

642   such as pore interconnectivity due to differences in the molarity of activator (activator

643   dilution) used in each mix (Table 1) and wet, wet/dry and dry curing conditions.

644   The relationship between porosity and free chloride diffusion parameters in Fig 9 does not

645   apply to PC concrete or AACMs with different C_3A content affecting binding properties,

646   such as fly ash based AACMs. For example, 13.3% porosity in PC concrete gave free

647   chloride diffusion parameters $(D_c)_f$ and $(C_0)_f$ of $1.1 \times 10^{-12} \text{m}^2/\text{s}$ and 0.0128mol/L respectively,

648   which fall outside the curves in Fig.9.

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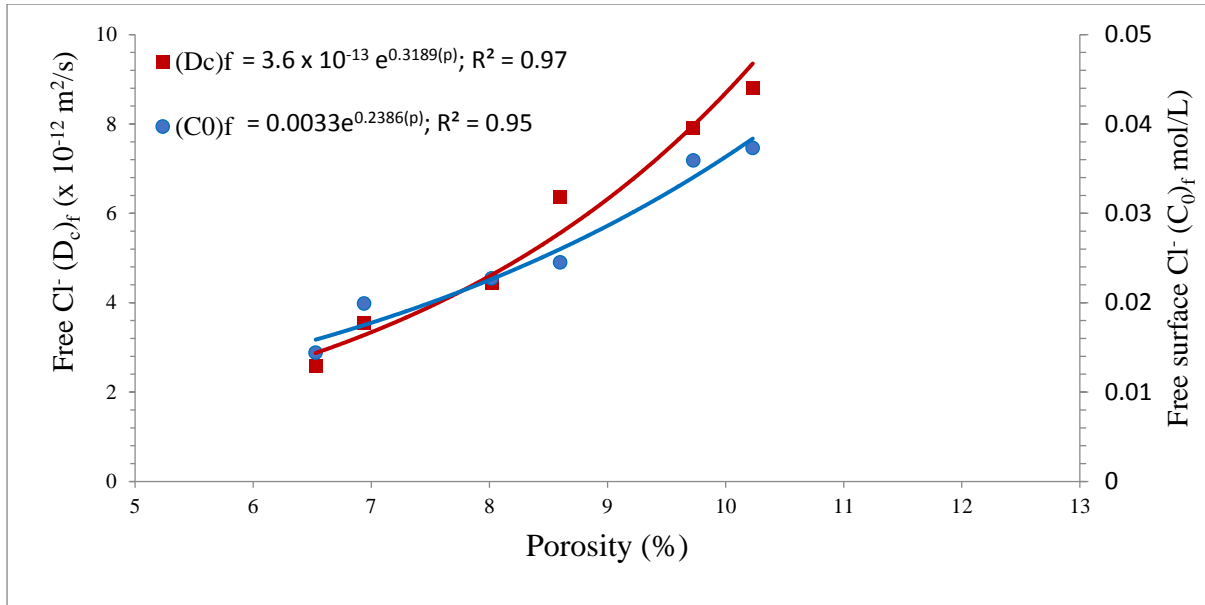
Fig. 9: Relationship between free chloride diffusion parameters and porosity of AACM 1, 2 and 3 concrete mixes.

The relationships between porosity and free chloride diffusion parameters of AACM concrete are as follows:

$(C_0)_f = 0.0033e^{0.24(p)}$ with $R^2 = 0.95$

$(D_c)_f = 3.6 \times 10^{-13} e^{0.32(p)}$ with $R^2 = 0.97$

where; $(C_0)_f$ and $(D_c)_f$ are the free surface chloride (mol/L) and diffusion coefficient (m^2/s) respectively, $(C_0)_{tb}$ and $(D_c)_{tb}$ are the total surface chloride (% wt. of binder) and diffusion coefficient (m^2/s) respectively and p is the porosity (%).

The refined pore properties in AACMs decrease their $(D_c)_f$ and $(C_0)_f$. For example, 7% and 10% porosity of AACM concrete gave $(D_c)_f$ of 3.34×10^{-12}m^2/s and 8.69×10^{-12}m^2/s respectively. The corresponding $(C_0)_f$ values are 0.018mol/L and 0.036mol/L. Lower dilution of sodium silicate activator used in the AACM mixes resulted in lower porosity [7]. Activator dilution of 0% to 7.76% produced porosity of 6.53% to 10.23% respectively. Higher concentration of the activator reacts with excess silica to produce a greater volume of N-A-S-H gel in AACM concrete [30] as explained in section 3.5.3, thus restricting the movement of chloride ions from the curing solution into the concrete matrix.

667 The chloride diffusion parameters are related to porosity [39] and also chloride binding

668 capacity in concrete as shown in this study. Each data point in Figure 9 reflects different

669 grades of ggbs based AACM concrete mixes having different formation and interconnectivity

670 of pores, which are reported elsewhere by the authors [7]. The line curves between chloride

671 diffusion parameters and porosity show high level of correlation thus validating that the

672 relationship can be transferred to other types of ggbs based AACM concrete.

673 **4.0   Conclusions**

674 The free chloride diffusion parameters and chloride binding capacity of an alkali activated

675 concrete (AACM) together with a control Portland cement (PC) concrete were determined in

676 this paper. AACM and PC concretes were immersed in a 5% NaCl solution for 540days to

677 determine their free chloride diffusion properties. Freundlich and Langmuir isotherms were

678 used to define the relationship between the free and bound chlorides. The following

679 conclusions can be drawn from the study,

680 • A greater amount of Friedel's salt (FS) is present in PC than AACM mortar when

681   exposed to a chloride environment. The hydration and geopolymerization products

682   have mass losses of 22% and 12% in PC and AACM concrete respectively after

683   heating to 1000^0C.

684 • Langmuir binding isotherm is valid for the relationship between free and bound

685   chloride in both AACM and PC concrete for the range at free chloride concentrations

686   0.01 to 0.036mol/L investigated. The following equation gives the relationship;

$$C_{tb} = (\propto C_f)/(1 + \beta C_f)$$

687   where the values of α are 1.8, 1.3, 1.2 for AACM concrete of different activator

688   molarity and 2.5 for PC concrete while the values of β are 7 for all AACMs and 2 for

689   PC concrete

33

- PC concrete has higher chloride binding capacity than AACM concrete for both water and acid soluble chlorides which results in lower free chloride. AACM concrete is effective only in binding water soluble chlorides while the acid soluble chloride binding capacity is low.

- AACM concretes have a lower chloride (acid and water) binding capacity than PC concrete. At a given concentration of free chloride, the bound chloride concentration is lower in AACMs. For example, at 0.012mol/L free chloride (C_f) concentration, the total bound chloride C_{tb} concentrations at 180days exposure are 2mg/g and 23mg/g for AACM 3 and PC concrete respectively.

- The free chloride diffusion coefficients of AACM concrete are greater than PC concrete. For example, the $(C_0)_f$ and $(D_c)_f$ of AACM 3 at 180days chloride exposure are 0.0235mol/L and 2.2 x 10^{-12}m^2/s respectively compared with 0.0128mol/L and 1.1 x 10^{-12}m^2/s for the control PC concrete.

- A linear relationship exists between free chloride diffusion coefficient $(Dc)_f$ and total bound chloride diffusion coefficient $(D_c)_{tb}$ for AACM concrete with different molarity of activator and for PC concrete, as follows:

  $(D_c)_f = 1.7 \, (D_c)_{tb}$ for AACM concrete

  $(D_c)_f = 0.861 \, (D_c)_{tb}$ for PC concrete

- Fick's law equation for chloride diffusion determines the cover required to steel reinforcement in AACM concrete based on the threshold for free and bound chloride concentrations for corrosion initiation. The total bound chloride threshold yields lower AACM concrete cover for reinforcement than the free chloride limit. The predicted cover in AACM concrete by the free chloride threshold approach is up to 40% greater than PC concrete while it is up to 20% lower than PC concrete when based on the bound chloride threshold. The free chloride threshold is, therefore, a

34

715   more conservative parameter to design against chloride induced corrosion in AACM

716   concrete. Increasing molarity of the activator reduces the required cover in AACMs.

717   However, this conclusion on cover requirement is based on chloride concentrations

718   only and other factors such as pH affecting corrosion will be evaluated in future

719   publications.

720   • The relationships between porosity and free chloride diffusion parameters of AACM

721   concrete are as follows:

722     $(C_0)_f = 0.0033e^{0.24(p)}$ with $R^2 = 0.95$.

723     $(D_c)_f = 3.6 \times 10^{-13}e^{0.32(p)}$ with $R^2 = 0.97$.

724   Where; $(C_0)_f$ and $(D_c)_f$ are the free surface Cl^- (mol/L) and diffusion coefficient (m^2/s)

725   respectively and p is the porosity (%).

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