

## **Bound chloride ingress in alkali activated concrete**

MANGAT, Pal <<http://orcid.org/0000-0003-1736-8891>> and OJEDOKUN, Olalekan <<http://orcid.org/0000-0002-9573-4976>>

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# Bound chloride ingress in alkali activated concrete

P.S. Mangat and Olalekan O. Ojedokun

Centre for Infrastructure Management, Materials and Engineering Research Institute, Sheffield Hallam  
University, Sheffield S1 1WB, UK

## Abstract

Alkali activated cementitious material (AACM) concrete and conventional concrete specimens of similar strength, developed for structural applications, were exposed to a 5% NaCl solution. Bound chloride concentrations (water and acid soluble) were determined up to 270 days of chloride exposure. Chloride diffusion profiles with depth and diffusion parameters  $C_0$  and  $D_c$  were derived from the data for water soluble, acid soluble and total bound chloride concentrations in order to develop long term chloride prediction relationships. The results show that the practice of using acid soluble chloride data for long term chloride predictions in conventional concrete is not valid for AACMs due to their low chemical binding capacity. Instead the physically bound chloride (water soluble) is more predominant in AACMs and is suitable for the chloride prediction models. Therefore, relationships of chloride diffusion parameters  $C_0$  and  $D_c$  with time have been derived for water soluble chloride. These correlate with total bound chlorides and are suitable for long term predictions of chloride concentrations for the design and maintenance of AACM concrete structures against corrosion.

**Keywords:** Alkali activated cementitious material AACM; water soluble chloride; acid soluble chloride; bound chloride; surface chloride concentration; chloride diffusion coefficients; chloride prediction models.

25 **Notations:**

26	AACM	alkali activated cementitious material
27	PC	Portland cement
28	GGBS	ground granulated blast-furnace slag
29	SRA	shrinkage reducing admixture
30	R42	retarder
31	$V_1$	ammonium thiocyanate solution used in the first titration [ml]
32	$V_2$	ammonium thiocyanate solution used in the second titration [ml]
33	$m$	mass of the binder [g]
34	$f$	molarity of silver nitrate solution
35	$x$	distance from concrete surface (m)
36	$t$	time (seconds)
37	$D_C$	diffusion coefficient ( $m^2/s$ )
38	$(D_C)_{as}$	acid soluble diffusion coefficient ( $m^2/s$ )
39	$(D_C)_{ws}$	water soluble diffusion coefficient ( $m^2/s$ )
40	$(D_C)_{tb}$	total bound diffusion coefficient ( $m^2/s$ )
41	$C_0$	surface chloride concentration (% wt. of binder)
42	$C_{as}$	acid soluble chlorides (% wt. of binder)
43	$(C_0)_{as}$	acid soluble surface chlorides (% wt. of binder)
44	$(C_0)_{ws}$	water soluble surface chlorides (% wt. of binder)
45	$(C_0)_{tb}$	total bound surface chlorides (% wt. of binder)
46	$(C_0)_{as, 180}$	acid soluble surface chlorides at 180days exposure (% wt. of binder)
47	$(C_0)_{ws, 180}$	water soluble surface chlorides at 180days exposure (% wt. of binder)
48	$(C_0)_{tb, 180}$	total bound surface chlorides at 180days exposure (% wt. of binder)
49	$C_{(x,t)}$	chloride concentration at distance $x$ and time $t$ .

50	$(C_{20})_{as}$	acid soluble chloride at 20mm depth (% wt. of binder)
51	$(C_{20})_{ws}$	water soluble chloride at 20mm depth (% wt. of binder)
52	$(C_{25})_{as}$	acid soluble chloride at 25mm depth (% wt. of binder)
53	$(C_{25})_{ws}$	water soluble chloride at 25mm depth (% wt. of binder)
54	NaOH	sodium hydroxide
55	NaCl	sodium chloride
56	NaNO <sub>3</sub>	sodium nitrate
57	ISE	ion selective electrode
58	C <sub>3</sub> A	tricalcium aluminate
59	C <sub>4</sub> AF	tetracalcium aluminate
60	Ca <sub>6</sub> Al <sub>2</sub> O <sub>6</sub> .CaCl <sub>2</sub> .10H <sub>2</sub> O	Friedel's salt
61	D <sub>ref</sub>	diffusion coefficient at reference time t
62	t <sub>ref</sub>	reference age (days)
63	m	age factor
64	C <sub>ref</sub>	surface chloride concentration corresponding to the time t <sub>ref</sub>
65	k	constant for surface chloride concentration
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75 **1.0 Introduction**

76 Alkali activated cementitious materials (AACMs) which do not use the traditional Portland  
77 cement (PC) are the basis of alkali activated (AACM) concrete. There is growing interest in  
78 the use of alkali activated concrete as a viable alternative to conventional Portland cement  
79 (PC) concrete due to its superior sustainability credentials and high performance such as fire  
80 resistance [1] and durability properties such as chemical resistance [2]. Considerable  
81 information on the sustainability of AACM concrete is available in literature which shows a  
82 lower CO<sub>2</sub> emission [3] and energy consumption [4] than PC concrete. However, there is  
83 strong resistance to the use of steel reinforced AACM concrete in significant structural  
84 applications until its resistance to chloride and carbonation induced corrosion is proven and  
85 its design procedures for corrosion resistance are established. The lack of standards has also  
86 been a critical limiting factor in the use of AACMs in practice, however, the publication of  
87 PAS 8820:2016 [5] starts to overcome this problem.

88 Serious chloride-induced corrosion damage is common in conventional (PC) reinforced  
89 concrete structures exposed to the marine environment and to de-icing salts, such as bridge  
90 decks. For example, the annual cost of the maintenance and repair of existing bridges in the  
91 US is estimated to be about \$12billion [6]. Chloride ingress in AACM concrete is also a  
92 major durability concern because it will cause corrosion of steel reinforcement embedded in  
93 it [1,7]. The presence of chloride ions in conventional Portland cement (PC) concrete above  
94 the established threshold limits [8] cause corrosion of steel reinforcement, however, these  
95 threshold limits have not yet been determined for AACM concrete to enable its design for  
96 corrosion resistant structures.

97 The three forms of chloride present in Portland cement (PC) concrete are water soluble, acid  
98 soluble and free chlorides [9,10]. A recent study on AACM concrete suggests a considerable  
99 reduction in the acid soluble (chemically bound) chloride present within its matrix especially

100 in low calcium systems [7]. However, these chloride concentration properties need to be  
101 quantified for different precursors such as high calcium systems and for engineering mixes of  
102 AACM concretes to establish threshold levels which initiate reinforcement corrosion. The  
103 balance between the three forms of chlorides present in AACMs and the factors involved  
104 requires further research. The reaction products and hardening process of AACMs are  
105 different from the hydration products of conventional PC concrete [11]. These products play  
106 a decisive role in chloride ingress. The differences in the water and acid soluble chlorides  
107 between AACM and PC concrete need to be quantified to determine their relative chloride  
108 binding properties. **Determining the relationship between the bound, free and total chloride in**  
109 **AACM concrete will provide a clearer understanding of chloride induced corrosion of**  
110 **reinforcement in AACM concrete.** The possibility of a reduction in the bound chlorides in  
111 AACM concrete raises potential concerns about its corrosion resistance.

112 The ingress of chloride in concrete is a complex interaction of both physical and chemical  
113 processes which are predominantly affected by the physical and chemical composition of the  
114 cement gel structure [12]. The chloride concentration profiles with depth of concrete exposed  
115 to a chloride environment, chloride diffusion coefficients  $D_c$ , surface chloride concentrations  
116  $C_0$ , are the properties and parameters used to assess the resistance of concrete to long term  
117 chloride ingress. These parameters are derived from Fick's second law of diffusion [13] in  
118 conventional PC concrete. However, the chloride diffusion parameters such as  $D_c$ ,  $C_0$  and  
119 chloride concentration profiles for practical AACM concrete mixes need to be established to  
120 realise their field applications. Research has shown that the apparent chloride diffusion  
121 coefficient  $D_c$  of PC concrete decreases with time  $t$ , indicating a progressive reduction in the  
122 rate of chloride diffusion [14,15]. The chloride diffusion in PC concrete is influenced by its  
123 physical properties and chloride binding capacity and their effect is represented by the age

124 factor [14,15]. AACM concrete has the potential to provide greater chloride resistance and a  
125 more durable construction material due to its distinctive refined pore structure [16].  
126 This paper presents an investigation on the water and acid soluble chlorides which represent  
127 the physically and chemically bound chlorides to the binder gel of high calcium (ggbs based)  
128 AACM concretes. It quantitatively differentiates the water and acid soluble chlorides under  
129 long term chloride exposure of AACM concrete mixes developed for structural applications.  
130 Direct chloride diffusion (bulk diffusion) tests under exposure to a chloride solution have  
131 been carried out to obtain long term data. Rapid chloride diffusion-cell tests developed for  
132 PC concrete [17] are not directly suitable for continuous long term monitoring plus their  
133 validity has not been proven for AACMs. The differences in the chloride binding properties  
134 and their effect on the chemical concentrations of the pore fluid of PC and AACM concrete  
135 are likely to affect the result of such tests. The analysis of the long term chloride diffusion  
136 test data of this research show that the practice of using acid soluble (chemically bound)  
137 chloride data to determine the diffusion parameters of PC concrete [18,19] for its corrosion  
138 prediction calculations is not valid for AACM concrete. Instead, water soluble (physically  
139 bound) chloride data are shown to be suitable for AACM concrete mixes. These data have  
140 been used to determine their chloride diffusion parameters ( $C_0$  and  $D_c$ ), including the  
141 relationships of these parameters with the period of chloride exposure. Expressions have been  
142 derived for long term predictions of chloride concentrations for use in the design and  
143 maintenance of AACM concrete structures.

## 144 **2.0 Experimental programme**

### 145 *2.1 Materials*

146 Ground granulated blast furnace slag (GGBS) and CEM 1 cement of grade 42.5R [8] were  
147 used as binders for AACM and PC concrete mixes respectively. The chemical composition of  
148 GGBS and PC is given in table 1. The AACM binder was activated with a sodium silicate

149 solution of molarity 6.5mol/L and modulus 2% together with NaOH of molarity 4.8mol/L.  
 150 AACM 1, 2 and 3 mixes were produced by diluting the activator with water at 0%, 3.88%  
 151 and 7.76% respectively as shown in Table 2, to optimize workability and determine the effect  
 152 of dilution on chloride diffusion. The liquid/binder ratio of 0.47 was used in the AACM and  
 153 PC concrete mixes.  
 154 10mm uncrushed gravel, 6mm limestone and a medium grade sand of 80% particle size  
 155 passing 1mm sieve were used as coarse and fine aggregates in this study. The properties and  
 156 oxide compositions of these aggregates conform to BS 882:1992 [20].  
 157 Retarder and shrinkage reducing admixtures were introduced in the AACM concrete mixes in  
 158 order to improve their workability and setting time (Table 2). The retarder R42 is a blend of  
 159 high grade polyhydroxycarboxylic acid derivatives while the shrinkage reducing admixture  
 160 (SRA) is made from Alkyl-ether. Each admixture contained less than 0.1% chloride ion and  
 161 3.5% sodium oxide.

162 Table 1: Chemical composition of Portland cement and GGBS binders

Chemical component	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	SO <sub>3</sub>
PC (mass %)	11.1	8.35	3.16	64.2	2.09	1.19	0.227	1.88	2.01	2.14	3.64
GGBS (mass %)	28.6	12.4	5.7	42.3	6.1	0.8	0.4	1.78	<0.1	0.3	0.08

163 Table 2: Composition of AACM 1, 2, 3 and control PC concrete mixes

Mix	Binder Content (%)	Fine Agg. (%)	Coarse Agg. (%)		Liquid/Binder Ratio	Activator Dilution (%)	R42	SRA
			10mm Gravel	6mm Limestone				
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)	-	-	-

164 \*R42 is the retarder; SRA is the shrinkage reducing admixture



165 2.2 *Specimen preparation*

166 The fresh AACM and PC concrete were mixed in a 150 kg capacity Cretangle mixer in  
167 accordance with BS EN 206:2013+A1:2016 standard [21]. A total of forty concrete slabs  
168 with dimensions of 250 x 250 x 75mm were produced for chloride ingress testing, ten slabs  
169 for each AACM 1, 2, 3 and PC concrete. The chloride ingress specimens were cured in the  
170 laboratory air at  $20 \pm 2^{\circ}\text{C}$  and 65% R.H, for 24hrs with their top surface covered with  
171 polythene sheets before demoulding. The hardened concrete was then cured in water ( $20 \pm$   
172  $2^{\circ}\text{C}$ ) for 27days after demoulding. The chloride ingress specimens were taken out of water  
173 and surface dried after the 28days' curing period. Two coats of bituminous paint were applied  
174 to five faces of the slabs except the bottom cast faces (250mm x 250mm) and allowed to dry  
175 for 24hrs. The slabs were then immersed in a 5% by weight NaCl solution to expose the  
176 uncoated face to chloride diffusion. The higher limit of 5% chloride concentration specified  
177 by the standards [22,23] was used to promote accelerated chloride ingress through the  
178 exposed uncoated surfaces. The NaCl solution was stirred frequently and replaced every 90  
179 days to maintain uniform concentration. Two slab specimens for each concrete mix were  
180 removed from the chloride solution at exposure periods of 55, 90, 120, 180 and 270 days to  
181 determine the water and acid soluble chloride concentrations at increments of depth from the  
182 face exposed to chloride diffusion.

183 Twenty four concrete cubes of dimensions 75mm X 75mm X 75mm were produced for  
184 compressive strength testing, 12 cubes were cured in water ( $20 \pm 2^{\circ}\text{C}$ ) and 12 cubes cured in  
185 laboratory air ( $20 \pm 2^{\circ}\text{C}$ , 65% R.H).

186 2.3 *Test Procedures*

187 2.3.1 *Workability and compressive strength*

188 Slump test was performed in accordance with BS EN 12350-2:2009 [24] to determine the  
189 workability of fresh AACM and PC concrete. The compressive strength was determined on

190 75mm concrete cubes at 28days under wet and dry curing regimes. The compressive strength  
191 test was performed in accordance with BS EN 12390-3:2009 [25]. The compressive test  
192 results reported in Figure 2 are an average value from three cubes.

### 193 2.3.2 Chloride diffusion testing

194 The collection of dry powder samples from the concrete specimens was carried out in  
195 accordance with NordTest 443 [22] and DD CEN/TS 12390-11 [23]. At each test age, two  
196 250 x 250 x 75mm concrete specimens were sawn into two equal halves along the  
197 longitudinal plane perpendicular to the chloride exposed uncoated face (Fig. 1). Dry powder  
198 samples were collected from seven parallel layers at 8, 15, 25, 35, 50 and 65mm depths from  
199 the uncoated surface. A minimum of six holes were drilled per each profile depth by means  
200 of a hammer drill using 4mm diameter SDS drill bits. The powder samples from each hole  
201 were combined to provide approximately 15grams of powder samples per each profile depth  
202 for the two specimens of each concrete mix. The powder samples for each depth were sieved  
203 and the fine powder passing through the 150 $\mu$ m sieve as shown in Fig. 1 was carefully stored  
204 in a self-sealing plastic bag and labelled accordingly. The retained coarse material was  
205 discarded while the fine powder samples were subjected to chloride analysis.



a



b

206 Fig. 1: (a) Location of drilled holes perpendicular to the chloride exposed uncoated face. (b)  
207 Concrete powder passing and retained on 150µm sieve.

### 208 2.3.3 Chloride analysis

209 A chloride ion selective electrode (ISE) was used to measure the water-soluble chloride  
210 concentrations. Five grams of the concrete powder passing through the 150µm sieve was  
211 dissolved in 50ml of distilled water. The effective ionic concentration, otherwise known as  
212 the chloride ion activity within the concrete powder solution, was buffered with NaNO<sub>3</sub> to  
213 avoid possible interference by other ions like iodine, bromide, cyanide and sulphide [26]. The  
214 procedure was done three times for each powder sample and the coefficient of variance of  
215 repeatability was less than 5%. Calibration of the chloride ISE was done by using a pre-  
216 prepared 1000 mg/l and 10 mg/l standard NaCl solution before each test.

217 The acid soluble chloride concentrations in hardened AACM and PC concrete were  
218 determined in accordance with BS EN 14629 [18]. Volhard's titration method was used to  
219 determine the chloride concentration on the second part of the concrete powder sample  
220 obtained at each profile depth from the exposed surface. The acid soluble chloride content,  
221  $C_{as}$  was calculated as a percentage of chloride ions by weight of the binder using equation 1.

$$C_{as} = 3.545 * f * \frac{(V_2 - V_1)}{m} \quad (1)$$

222 Where  $V_1$  is the volume of the ammonium thiocyanate solution used in the first titration [ml];  
223  $V_2$  is the volume of the ammonium thiocyanate solution used in the second titration [ml];  $m$   
224 is the mass of binder fraction in the concrete powder sample [g]; and  $f$  is the molarity of  
225 silver nitrate solution [18].

### 226 2.3.4 Chloride diffusion parameters

227 Fick's second law of diffusion was suggested as a suitable model for chloride diffusion in  
228 concrete by Collepardi et al. [13], which gives the following equation;

$$C_{(x,t)} = C_0 \left( 1 - \operatorname{erf} \left[ \frac{x}{2\sqrt{D_c t}} \right] \right) \quad (2)$$

229 Where:  $x$  is the distance from concrete surface (m);  $t$  is the time (seconds);  $D_c$  is the diffusion  
230 coefficient ( $\text{m}^2/\text{s}$ );  $C_0$  is the chloride concentration on the concrete surface;  $C_{(x,t)}$  is the  
231 chloride concentration at distance  $x$  and time  $t$ .

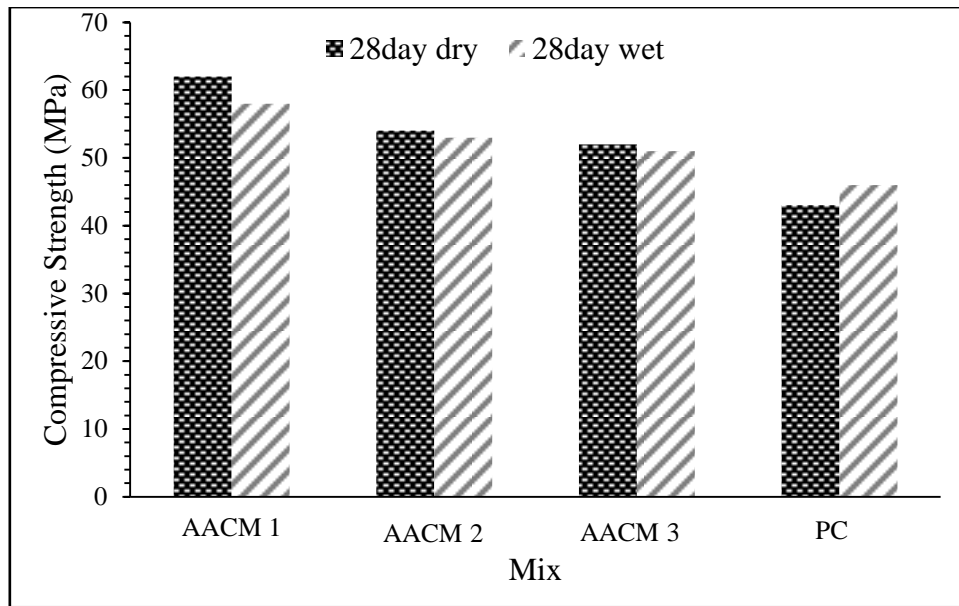
232 The experimental data of acid and water-soluble chloride concentrations with depth were  
233 plotted at every test age. An error function analysis using Fick's second law of diffusion  
234 equation 2 was performed on the chloride profiles to determine the constant values of the  
235 diffusion parameters  $C_0$  and  $D_c$  at each test age. These values were used to determine the age  
236 factor which accounts for the change in diffusion coefficients with time [27,28] and can  
237 ultimately enable long-term predictions of chloride diffusion in AACM concrete.

### 238 **3.0 Results and Discussion**

#### 239 *3.1 Workability and Compressive strength*

240 The slump of fresh AACM 1, 2, 3 and PC concrete was 30, 45, 70 and 75mm respectively.  
241 The workability (slump) of AACMs is lower than the PC concrete due to the sticky  
242 characteristics of silicate present in AACMs. However, AACM 3 and PC concrete gave fairly  
243 similar workability due to the lower silicate content in the activator used for AACM 3  
244 concrete (7.76% activator dilution).

245 The 28day compressive strengths of AACM 1, 2, 3 and PC concrete cured in water ( $20 \pm$   
246  $2^\circ\text{C}$ ) and under dry curing in the laboratory air ( $20 \pm 2^\circ\text{C}$ , 65% R.H) are shown in Fig. 2.



247

248 Fig. 2: 28day compressive strength of AACM and PC concrete cured in water ( $20 \pm 2^{\circ}\text{C}$ ) and

249 laboratory air ( $20 \pm 2^{\circ}\text{C}$ , 65% R.H).

250 AACM concrete mixes had greater strength than PC concrete under wet and especially dry  
 251 curing. AACM 3 has a similar workability as the PC concrete and their strength difference  
 252 under wet curing is within 10%. The two mixes have the same liquid/binder and  
 253 water/cement ratios of 0.47 respectively. The PC concrete provides the control specimen for  
 254 AACM 3 since wet curing is the standard quality control criteria for concrete. The 28day  
 255 strength of AACM 3 concrete under dry curing is 18% higher than PC concrete.

256 AACM 1 concrete with the highest activator concentration resulted in the highest strength  
 257 due to higher reaction rate and the formation of a less porous matrix [16]. For example, the  
 258 28-day compressive strength of AACM 1 (0% activator dilution) and AACM 3 (7.76%  
 259 activator dilution) was 62MPa and 52MPa respectively, under dry curing (Fig. 2).

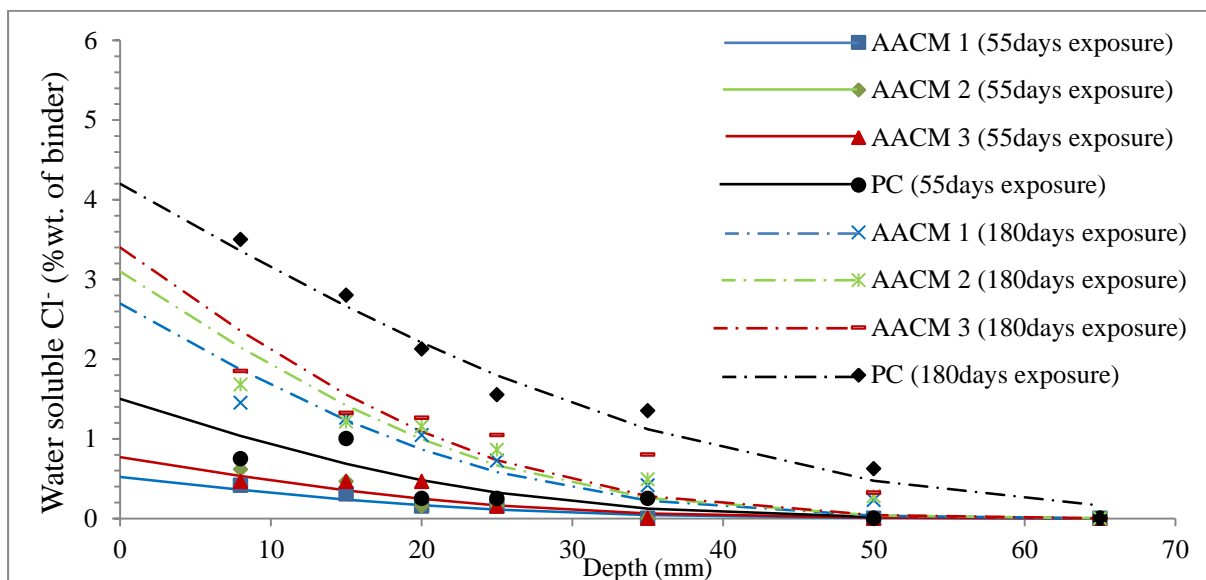
### 260 3.2 Chloride diffusion profiles

#### 261 3.2.1 Water soluble chloride

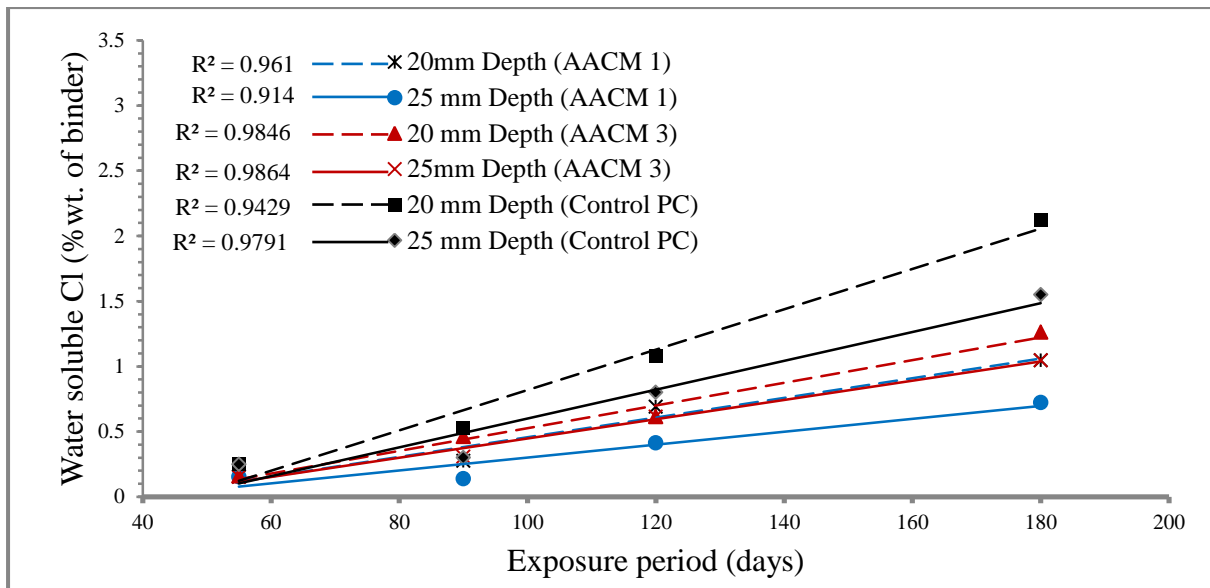
262 The profiles in Fig. 3 represent the water soluble chloride concentrations (% weight of  
 263 binder) along the depth (0-75mm) of the specimens. A non-linear regression analysis was

264 performed on the experimental data plotted in Figures 3 and 4 using Fick's second law of  
 265 diffusion equation 2 and the best-fit lines are plotted using excel software. The regression  
 266 analysis also provided the values of the diffusion coefficient  $D_c$  and surface chloride  
 267 concentration  $C_0$  at each exposure age. Discussion on the diffusion coefficient  $D_c$  and surface  
 268 chloride concentration  $C_0$  will follow in section 3.4.

269 The chloride profiles of AACM 1, 2, 3 and the control PC concrete at 55 and 180days  
 270 exposure periods are shown in Fig. 3 while Fig. 4 shows chloride concentrations in the  
 271 concrete cover zones (20 and 25mm depths) for exposure periods of 55, 90, 120 and 180days.  
 272 The 20 and 25mm depths represent the concrete cover zone which could be higher (up to  
 273 50mm) in marine structures. However, the exposure period represented in Figures 3 and 4 is  
 274 not sufficiently long-term to provide detectable differences at higher depths. Figure 4 shows a  
 275 linear increase in water-soluble chloride concentrations with longer chloride exposure. The  
 276 coefficient of correlation for the best-fit lines in Figures 3 and 4 ranged between 0.81 and  
 277 0.99.



278  
 279 Fig. 3: Water soluble chloride profiles of AACM 1, 2, 3 and control PC concrete at 55 and  
 280 180 days of chloride exposure.



281

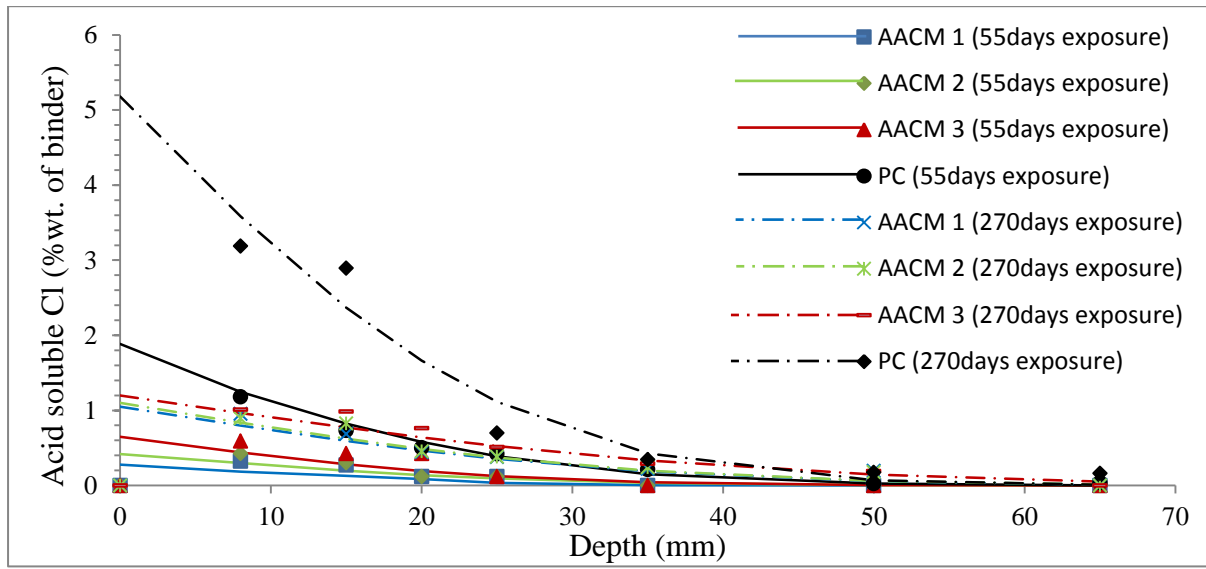
282 Fig. 4: Relationship between water soluble chlorides (20 and 25mm depth) and exposure  
 283 period of AACM 1, 3 and control PC concrete

284 A lower water-soluble chloride profile is exhibited by AACM 1, 2 and 3 concrete than the  
 285 control PC concrete at 55 and 180 days of chloride exposure (Fig. 3). For example, at 25mm  
 286 depth, the chloride concentration of AACM 3 concrete at 180days exposure is 1.05% by  
 287 weight of binder compared with 1.55% by weight of binder in PC concrete. Both of these  
 288 values are significantly greater than the corrosion threshold chloride concentrations given in  
 289 standards [8], which are 0.4% and 1.0% by weight of binder for concrete with and without  
 290 steel reinforcement respectively. This is due to the accelerated chloride diffusion test  
 291 providing continuous immersion in a 5% NaCl solution [23]. The high concentration of NaCl  
 292 is recommended in international standards [22,23] for comparative evaluation of mixes and  
 293 for determining diffusion coefficients  $C_0$  and  $D_c$ .

294 The water soluble chloride concentration is lower in AACM 3 compared with its control PC  
 295 concrete, which becomes more significant with longer exposure (Fig 4) due to greater  
 296 physical binding of chloride occurring in PC concrete with time.

297 3.2.2 Acid soluble chloride

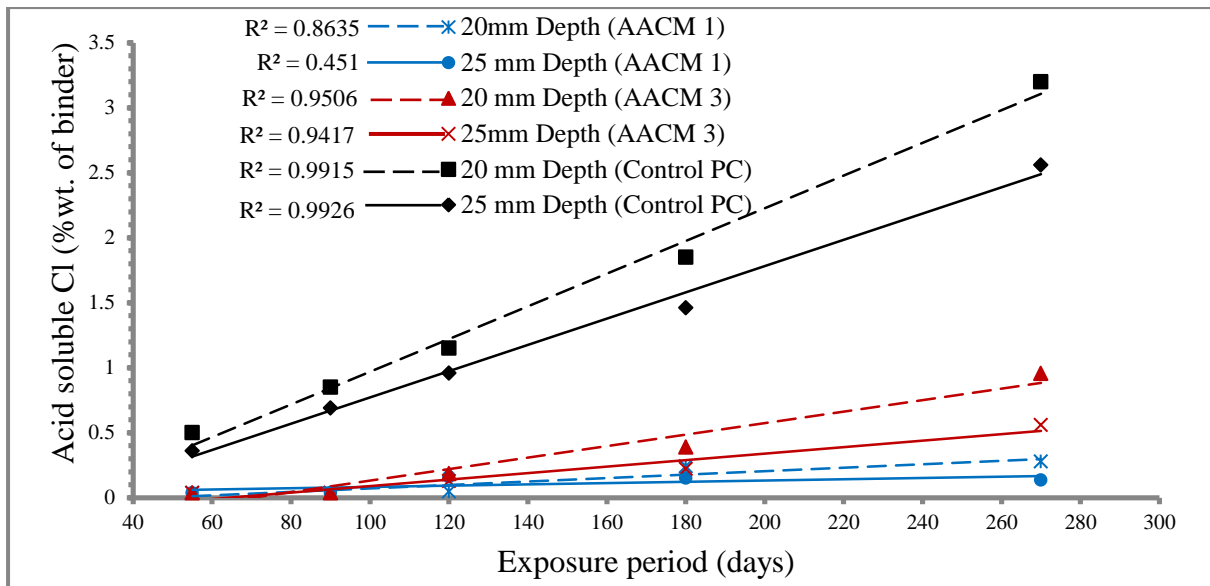
298 Figure 5 shows the experimental data points and the acid soluble chloride profiles of AACM  
 299 1, 2, 3 and the control PC concrete at 55 and 270days exposure. Non-linear regression  
 300 analysis of the experimental data against Fick's 2<sup>nd</sup> law of diffusion equation 2 gave the  
 301 chloride profiles plotted in Fig. 5. The coefficients of correlation range between 0.80 and  
 302 0.94.



303  
 304 Fig. 5: Acid soluble chloride profiles of AACM 1, 2, 3 and control PC concrete at 55 and 270  
 305 days of chloride exposure.

306 Acid soluble chloride profiles of AACM 1, 2, 3 and the control PC concrete show an increase  
 307 of chloride concentrations with exposure time, both on the concrete surface and at all depths  
 308 within the concrete matrix. The profiles of the control PC concrete show much higher  
 309 chloride concentrations than the AACM 1, 2 and 3 concrete at 55 and 270days exposures  
 310 (Fig. 5).





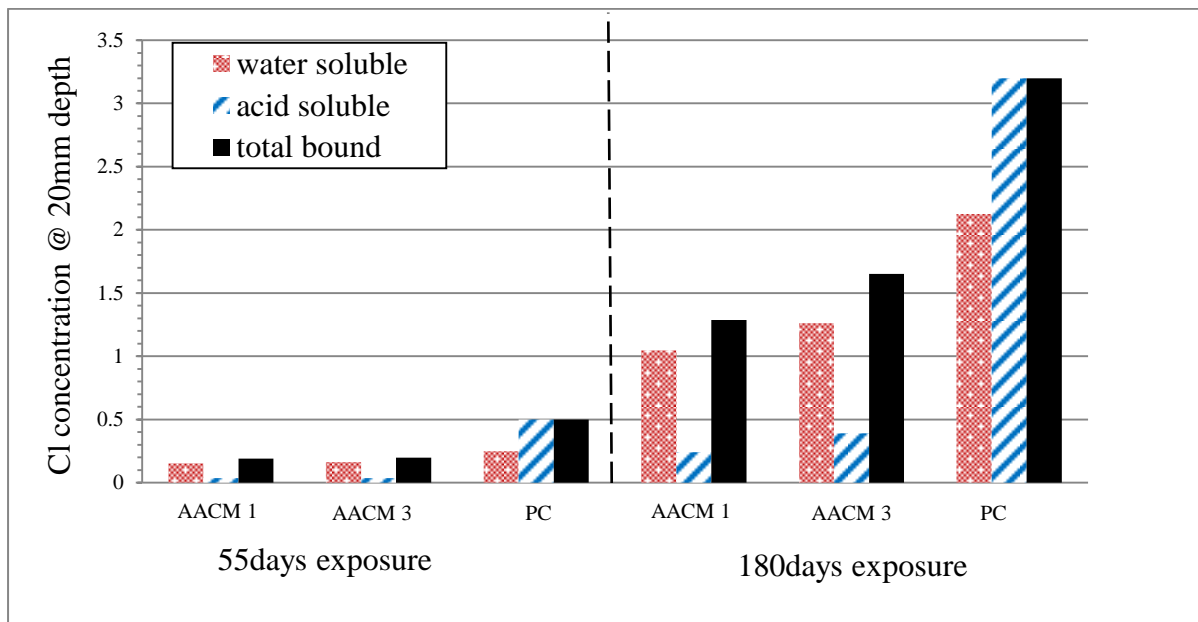
311

312 Fig. 6: Relationship between acid soluble chlorides (20 and 25mm depth) and exposure  
 313 period of AACM 1, 3 and control PC concrete

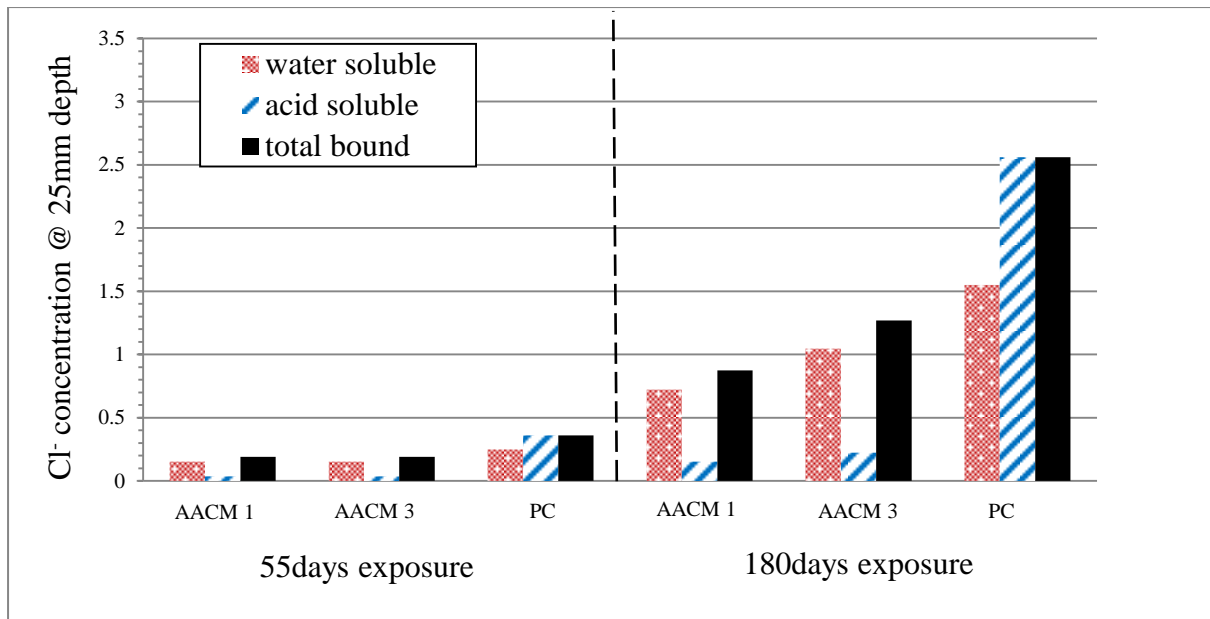
314 Figure 6 shows the acid soluble chloride concentrations at 20 and 25mm depths in AACM 1,  
 315 3 and control PC concrete at exposure periods of 55, 90, 120, 180 and 270days. The acid  
 316 soluble chloride concentrations of AACM 1 and 3 concrete are much lower than the control  
 317 PC concrete at different chloride exposure periods with the difference getting bigger with  
 318 increasing exposure period thereby indicating much higher chemical binding of chloride  
 319 occurring with time in PC concrete. For example, at 25mm depth, the chloride concentration  
 320 of AACM 3 concrete at 270days exposure is 0.56% by weight of binder compared with  
 321 2.56% in the control PC concrete (Fig. 6). The PC concrete has significantly greater value  
 322 than the corrosion threshold chloride concentrations given in standards [8] which are 0.4%  
 323 and 1.0% by weight of binder for concrete with and without steel reinforcement. The chloride  
 324 threshold values for initiating corrosion given in the standard [8] relate to the total bound and  
 325 acid soluble chloride in PC concrete. However, neither of these bound chlorides (acid and  
 326 water soluble) are the direct initiators of corrosion, the free chloride (pore fluid) being the  
 327 electrolyte which supports corrosion.

328 *3.3 Bound chlorides in AACM and PC concrete*

329 The water soluble, acid soluble and total bound chlorides in AACM 1, 3 and PC concrete at  
 330 20mm depth for 55 and 180days exposure are shown in Fig. 7. The corresponding results for  
 331 25mm depth are shown in Fig. 8. The total bound chlorides are represented as the sum of  
 332 water soluble and acid soluble chlorides for the AACM concretes. For PC concrete, the total  
 333 bound and acid soluble chlorides are taken to be equal as it is generally assumed in literature  
 334 and testing standards [18,19].



335  
 336 Fig. 7: Water, acid soluble and total bound chlorides at 20mm depth in AACM 1, 3 and  
 337 control PC concrete at 55 and 180days exposure.



338

339 Fig. 8: Water, acid soluble and total bound chlorides at 25mm depth in AACM 1, 3 and  
 340 control PC concrete at 55 and 180 days exposure.

341 The acid-soluble chlorides in AACM 1 and 3 concrete are considerably lower than the water-  
 342 soluble chlorides at both 55 and 180days exposure whereas the reverse is true for the control  
 343 PC concrete (Figures 7 and 8). For example, the water soluble chlorides of AACM 1 and 3  
 344 concrete at 180days exposure are 1.05% and 1.26% compared with 0.24% and 0.39% for acid  
 345 soluble chlorides at 20mm depth (Fig. 7). The corresponding values for PC concrete are  
 346 2.13% for water soluble chloride compared with 3.2% for acid soluble chloride at 20mm  
 347 depth. A similar trend is shown at 25mm depth which is presented in Fig. 8. The significant  
 348 observations from Figures 7 and 8 show that both water soluble and acid soluble chloride  
 349 contents in AACM concrete are less than the PC concrete. However, the reduction is much  
 350 greater in acid soluble chloride. The acid soluble chloride content in AACM concrete is much  
 351 lower than its water soluble chloride content, whereas it is the opposite in PC concrete.

352 The above observations indicate that the balance between chemical and physical binding of  
 353 chlorides in the matrix is different in PC and AACM concretes. The total bound chloride  
 354 content in Figures 7 and 8 comprises of the physically bound (water soluble) and chemically

355 bound (acid soluble) chlorides. Conventional PC concrete shows higher chemical binding  
356 than physical binding due to the  $C_3A$  and  $C_4AF$  in its PC binder. The unhydrated portion of  
357 aluminate ( $C_3A$ ) and aluminoferrite ( $C_4AF$ ) of PC binders reacts with the chloride ions in the  
358 pore solution during the exposure period, transforming it to Friedel's salt  
359 ( $Ca_6Al_2O_6.CaCl_2.10H_2O$ ) and calcium chloroferrite [29]. This is responsible for the increase  
360 in acid soluble chloride concentration in PC concrete with longer exposure period. The  
361 hydration reaction of aluminate ( $C_3A$ ) and aluminoferrite ( $C_4AF$ ) that takes place before the  
362 exposure of PC concrete to NaCl solution does not contribute to its acid soluble chlorides  
363 [29]. The lack of aluminate ( $C_3A$ ) and aluminoferrite ( $C_4AF$ ) in the AACM compositions of  
364 Table 1 results in low chemically bound chlorides (acid soluble) in the AACM matrix.  
365 Therefore, unlike PC concrete, AACM concrete has higher physical binding capacity than its  
366 chemical binding capacity. The chloride binding capacity of concrete is an important property  
367 that regulates the amount of free chlorides in the concrete matrix, which initiate corrosion  
368 when their permissible limits are exceeded.

### 369 3.4 Chloride diffusion parameters ( $C_0$ and $D_c$ )

#### 370 3.4.1 Long term $C_0$ and $D_c$ models

371 The solution of Fick's 2<sup>nd</sup> law of diffusion,  $\delta C/\delta t = D \delta^2 C/\delta x^2$ , which is given in equation 2  
372 assumes a constant value for the chloride diffusion parameters ( $C_0$  and  $D_c$ ). However,  
373 research has shown that these coefficients vary with time [14,15,27,28] due to changes in the  
374 properties of concrete with time, such as porosity and chloride binding in concrete. These  
375 effects are represented by the age factor,  $m$ , of concrete [30]. Research on the long-term  
376 diffusion coefficient of concrete,  $D_c$ , has derived an empirical relationship in the form of a  
377 power function given in equation 3 [15,28].

$$D_c = D_{ref} t^{-m} \quad 3$$

378 where:  $D_c$  is the apparent diffusion coefficient at time  $t$ ,  $D_{ref}$  is diffusion coefficient at  
 379 reference time  $t$  and  $m$  is the age factor.

380 A theoretical solution based on Fick's second law of diffusion which takes account of the  
 381 time variation of the diffusion coefficient by introducing the age factor,  $m$ , from equation 3  
 382 has been derived elsewhere [15,28] and given in equation 4.

$$C_{(x,t)} = C_{(0)} \left( 1 - erf \left[ \frac{x}{2 \sqrt{\frac{D_{ref} t^{(1-m)}}{\sqrt{1-m}}}} \right] \right) \quad 4$$

383 Similarly, the time dependent  $C_0$  has been shown to be proportional to the square root of  
 384 chloride exposure period [31,32], and the relationship is given in (Eqn. 5)

$$C_0 = C_{ref} + k \sqrt{t - t_{ref}} \quad 5$$

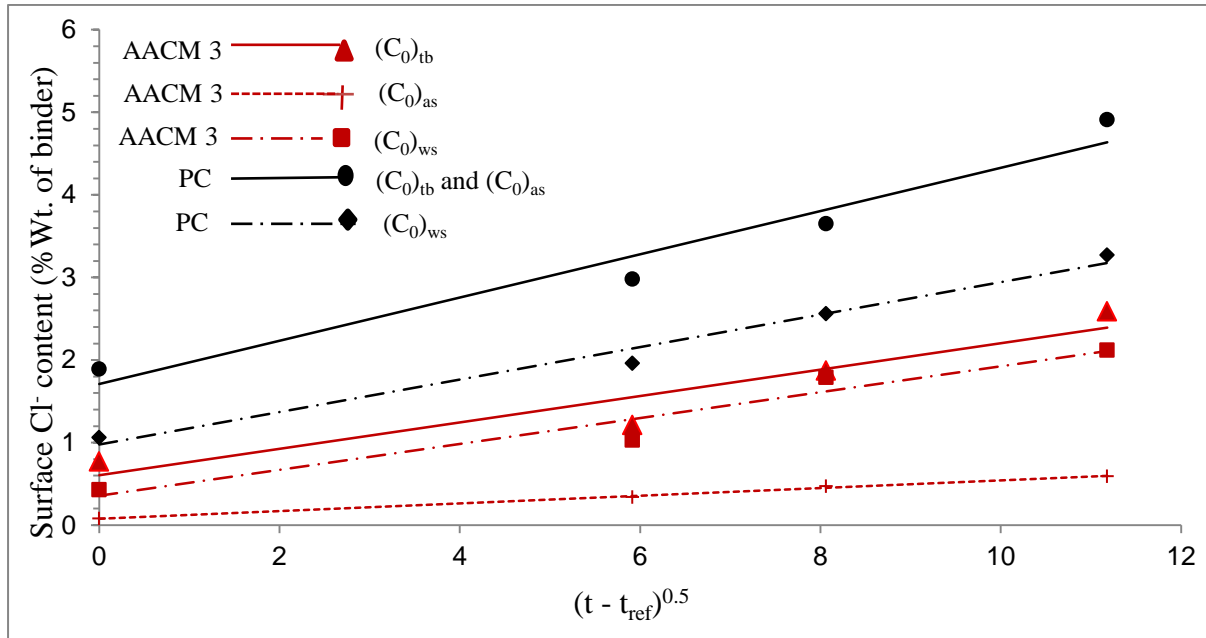
385 Where  $C_{ref}$  and  $t_{ref}$  are reference surface chloride and the reference time (=55days)  
 386 respectively,  $k$  and  $m$  are the age factors influencing the long-term surface chloride  
 387 concentrations and diffusion coefficients respectively,  $C_0$  is the chloride concentration on the  
 388 concrete surface,  $C_{(x,t)}$  is the chloride concentration at distance  $x$  and time  $t$ .

389 The following analysis given in the paper uses the chloride diffusion data at each test age (55,  
 390 90, 120, 180 and 270days) to determine  $C_0$  and  $D_c$  values using equation 2. The values of  
 391 coefficient  $m$  and  $k$  have been determined by regression analysis of the plots of  $C_0$  and  $D_c$   
 392 against exposure time.

### 393 3.4.2 Surface chloride concentration $C_0$

394 The surface chloride concentrations,  $C_0$ , were calculated at each age by applying the Fick's  
 395 2<sup>nd</sup> law of diffusion (equation 2) to all the chloride diffusion data obtained at 55, 90, 120 and  
 396 180days exposure to the chloride solution. The  $C_0$  values are plotted in Figure 9 and a  
 397 regression analysis by applying equation 5 have been carried out to determine relationships

398 for long term predictions of  $C_0$  for each concrete mix. Fig. 9 shows the relationship between  
 399 the chloride exposure period term  $(t-t_{ref})^{0.5}$  and water soluble  $(C_0)_{ws}$ , acid soluble  $(C_0)_{as}$ , total  
 400 bound  $(C_0)_{tb}$  surface chlorides. Similar relationships exist for the data of AACM 1 and 2.



401  
 402 Fig. 9: Relationship between  $(C_0)_{ws}$ ,  $(C_0)_{as}$ ,  $(C_0)_{tb}$  and chloride exposure period for AACM 3  
 403 and PC concrete.

404 The linear equations between  $C_0$  and  $(t - t_{ref})^{0.5}$  for AACM 1, 2, 3 and PC concrete and their  
 405 level of correlation are presented in Table 3. The surface chloride concentration at 180days  
 406 exposure,  $(C_0)_{180}$ , obtained from each equation is also listed in Table 3.

407 Table 3: Relationships of  $(C_0)_{ws}$ ,  $(C_0)_{as}$ ,  $(C_0)_{tb}$  with chloride exposure period  $(t - t_{ref})^{0.5}$

Mix	Surface Cl ( $C_0$ )	Linear equation	$R^2$	$(C_0)_{180}$ (%wt. of binder)
AACM 1	tb	$(C_0)_{tb} = 0.134(t-t_{ref})^{0.5} + 0.24$	0.97	1.74
	as	$(C_0)_{as} = 0.034(t-t_{ref})^{0.5} + 0.028$	0.98	0.41
	ws	$(C_0)_{ws} = 0.13(t-t_{ref})^{0.5} + 0.12$	0.95	1.57
AACM 2	tb	$(C_0)_{tb} = 0.139(t-t_{ref})^{0.5} + 0.52$	0.97	2.07
	as	$(C_0)_{as} = 0.039(t-t_{ref})^{0.5} + 0.06$	0.99	0.50
	ws	$(C_0)_{ws} = 0.134(t-t_{ref})^{0.5} + 0.25$	0.96	1.75

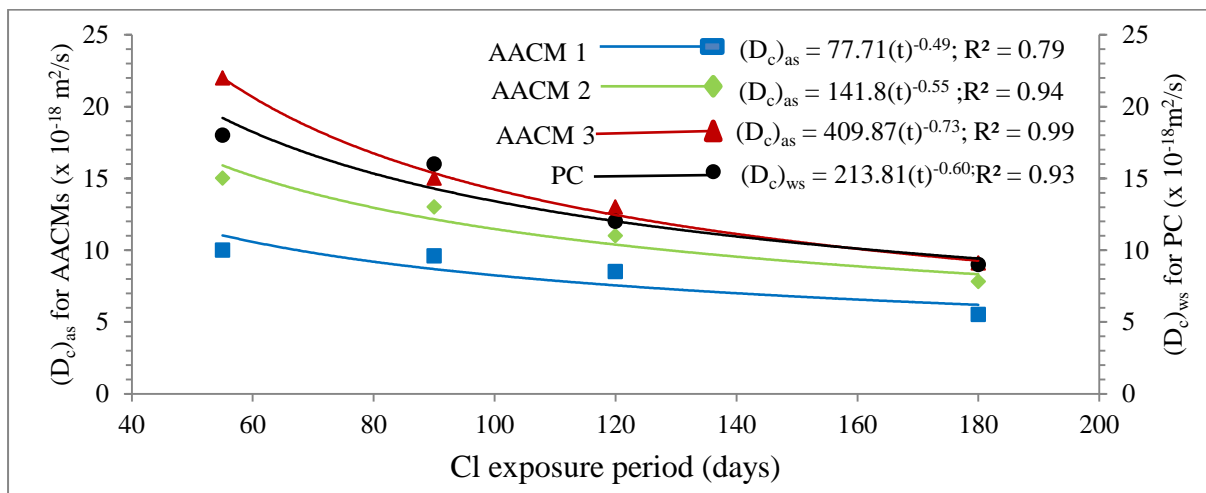
AACM 3	tb	$(C_0)_{tb} = 0.16(t-t_{ref})^{0.5} + 0.60$	0.90	2.39
	as	$(C_0)_{as} = 0.046(t-t_{ref})^{0.5} + 0.08$	0.99	0.60
	ws	$(C_0)_{ws} = 0.157(t-t_{ref})^{0.5} + 0.36$	0.94	2.11
PC	tb and as	$(C_0)_{tb}$ and $(C_0)_{as} = 0.262(t-t_{ref})^{0.5} + 1.71$	0.96	4.64
	ws	$(C_0)_{ws} = 0.197(t-t_{ref})^{0.5} + 0.98$	0.98	3.18

408 Where:  $(C_0)_{tb}$ ,  $(C_0)_{as}$  and  $(C_0)_{ws}$  are total bound, acid soluble and water soluble chlorides  
409 respectively,  $t$  is the exposure time (days) and  $t_{ref}$  is the reference exposure time (55days).  
410 The values of  $(C_0)_{180}$  in Table 3 show that for PC concrete, the  $(C_0)_{tb,180}$  and  $(C_0)_{as,180}$  are both  
411 equal to 4.64% wt. of binder. The corresponding  $(C_0)_{ws,180}$  is much lower at 3.18% wt. of  
412 binder. Therefore, both total bound and acid soluble chloride data are suitable for long term  
413 chloride prediction for PC concrete. This conforms with current practice where test  
414 procedures used for chloride ingress in PC concrete determine acid soluble chlorides only  
415 [18,19] and these values are used in long term prediction models [14,15,27,28].  
416 However, the data in Table 3 show that the  $(C_0)_{tb,180}$  and  $(C_0)_{as,180}$  for AACM 3 concrete are  
417 very different at 2.39% and 0.60% wt. of binder respectively. The acid soluble chloride  
418 values are too low to be suitable for long term chloride predictions and, therefore, the acid  
419 soluble chloride test procedure is not valid for AACMs.  
420 The water soluble surface chloride  $(C_0)_{ws,180}$  of the AACM 3 mix in Table 3 is 2.11% wt. of  
421 binder compared to 2.39% wt. of binder for  $(C_0)_{tb,180}$ . Their difference is within 15% and  
422 potentially the  $(C_0)_{ws,180}$  values could be used for long term predictions of chlorides in  
423 AACM concrete. The accuracy of this approach will be determined in section 3.4.4.  
424 The  $(C_0)_{as,180}$  and  $(C_0)_{ws,180}$  values are 0.60% and 2.11% wt. of binder respectively for AACM  
425 3 (Table 3). The very low acid soluble chloride shows that a higher proportion of the chloride  
426 is being physically bound to the walls of the binder gel in AACMs than forming chemically  
427 bound chloride compounds during geopolymerisation.

428 Higher  $(C_0)_{ws}$ ,  $(C_0)_{as}$  and  $(C_0)_{tb}$  are observed in PC concrete than AACM 3 concrete. For  
 429 example, the  $(C_0)_{ws}$ ,  $(C_0)_{as}$  and  $(C_0)_{tb}$  at 180days exposure are 3.18%, 4.64% and 4.64% by  
 430 weight of binder respectively for PC concrete while it is 2.11%, 0.60% and 2.39% for  
 431 AACM 3 concrete. Both the  $(C_0)_{ws}$  and  $(C_0)_{as}$  of the control PC concrete are significantly  
 432 higher than AACM 3 concrete, which represents higher physical and chemically bound  
 433 chlorides in PC concrete. These  $(C_0)_{as}$  values of PC concrete are in a similar range of 1.1% to  
 434 7.2% by binder weight given in literature from other research [33–36]. However, existing  
 435 literature lacks comparative data for AACM concrete.

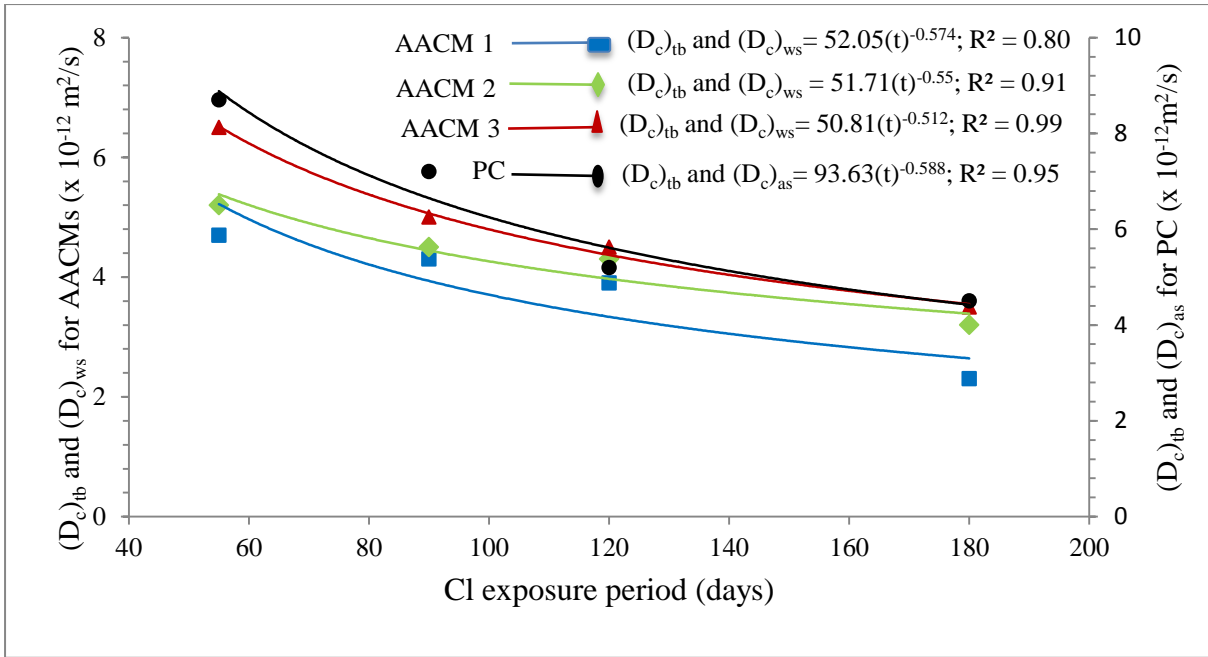
### 436 3.4.3 Chloride diffusion coefficient $D_c$

437 Equation 2 has been applied to all the chloride diffusion data to determine the chloride  
 438 diffusion coefficients at each test age by a non-linear regression analysis. The regression  
 439 equations and their coefficients of correlation are given in Figures 10 and 11. Figure 10  
 440 shows the relationship between acid soluble chloride  $(D_c)_{as}$  and chloride exposure period for  
 441 AACM 1, 2, 3 concrete, whereas the graph for PC concrete in Fig 10 represents  $(D_c)_{ws}$   
 442 instead of  $(D_c)_{as}$ . Fig. 11 shows the the relationship of both total bound chloride  $(D_c)_{tb}$  and  
 443 water soluble chloride  $(D_c)_{ws}$  against chloride exposure period for AACMs. However, the  
 444 graph for PC concrete in Fig. 11 represents the  $(D_c)_{as}$  instead of  $(D_c)_{ws}$ .



445  
 446 Fig. 10: Relationship of  $(D_c)_{as}$  for AACMs and  $(D_c)_{ws}$  for PC versus  $\text{Cl}^-$  exposure period





447

448 Fig. 11: Relationship of  $(D_c)_{tb}$ ,  $(D_c)_{ws}$  for AACMs and  $(D_c)_{tb}$ ,  $(D_c)_{as}$  for PC concrete versus Cl  
 449 exposure period

450 Chloride diffusion coefficient,  $D_c$ , values for AACMs given in literature are mainly based on  
 451 rapid chloride penetration test RCPT. Since the pore fluid and bound chloride properties of  
 452 AACMs and PC are different, this affects the migration of chlorides. The validity of these  
 453 tests to AACMs needs to be verified. The  $D_c$  values given in literature for AACMs usually  
 454 relate to the acid soluble  $(D_c)_{as}$  which are assumed to represent total bound  $(D_c)_{tb}$  [18,19].  
 455 This results in an under estimation of the total bound  $(D_c)_{tb}$  in AACMs. The graphs in Figures  
 456 10 and 11 show that the acid soluble chloride  $(D_c)_{as}$  values of AACM concretes (Fig. 10) are  
 457 orders of magnitude lower ( $10^{-18}$  against  $10^{-12}$ ) than their total bound chloride  $(D_c)_{tb}$  values  
 458 (Fig. 11) unlike PC concrete which has the same  $(D_c)_{as}$  and  $(D_c)_{tb}$  values of  $4.5 \times 10^{-12} \text{ m}^2/\text{s}$  at  
 459 180days exposure (Fig. 11). Therefore, the procedures and test standards adopted for PC  
 460 concrete using acid soluble chlorides [18,19] are not valid for AACMs.

461 On the other hand, the water soluble chloride  $(D_c)_{ws}$  values of AACMs are the same as their  
 462 total bound chloride  $(D_c)_{tb}$  as shown in Fig. 11. For example, both the water soluble  $(D_c)_{ws}$   
 463 and total bound  $(D_c)_{tb}$  for AACM 1, 2 and 3 are  $2.3 \times 10^{-12} \text{ m}^2/\text{s}$ ,  $3.2 \times 10^{-12} \text{ m}^2/\text{s}$  and  $3.5 \times 10^{-12}$

464  $12\text{m}^2/\text{s}$  respectively at 180days chloride exposure. Therefore, the water soluble  $(D_c)_{\text{ws}}$  in  
465 AACMs instead of  $(D_c)_{\text{as}}$  are representative of the diffusion coefficient of AACMs as they  
466 equal the total bound  $(D_c)_{\text{tb}}$ .

467 The chloride induced corrosion prediction of AACM concrete structures requires reliable  
468 chloride diffusion parameters ( $D_c$  and  $C_0$ ). The values based on total bound chlorides or  
469 equivalents should be used to determine the diffusion coefficients. Diffusion coefficients in  
470 literature (and in practice) are usually determined from acid soluble chloride data without  
471 considering the water soluble chlorides. This approach gives an incorrect assessment for  
472 AACM concrete because, as shown in Figures 9-11, the greater amount of chloride  
473 concentration is neglected when using  $(D_c)_{\text{as}}$ . Therefore, the test standards [18,19] for  
474 conventional PC concrete, which are based on acid soluble chloride measurements, are not  
475 suitable for AACMs. They need to be revised, focusing on water soluble chlorides.

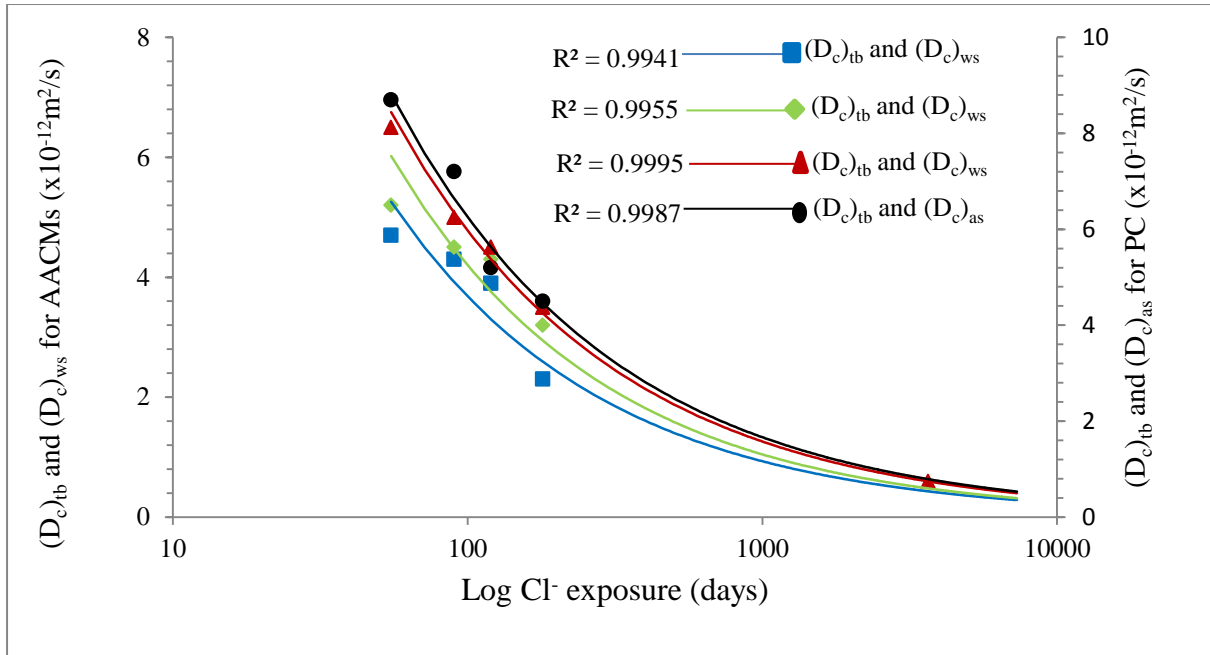
#### 476 3.4.4 Long term prediction of $D_c$ , $C_0$ and $Cl$ content

##### 477 3.4.4.1 Chloride diffusion coefficients $D_c$

478 Time dependent models for  $D_c$  and  $C_0$ , based on equations 3 and 5 [31,32], were used to  
479 predict long-term (20years) chloride diffusion parameters and chloride concentrations to  
480 determine the relative accuracy of predictions for AACM concrete using water soluble and  
481 total bound chloride data. Figure 12 shows the experimental data of  $(D_c)$  up to 270days  
482 exposure and predicted values beyond this age. The age factor  $m$  in equation 3 was derived  
483 by a regression analysis of the experimental data in Figure 10 and 11 for each AACM  
484 concrete. These values are used to predict the long-term total bound  $(D_c)_{\text{tb}}$ , acid soluble  $(D_c)_{\text{as}}$   
485 and water soluble  $(D_c)_{\text{ws}}$  for 20years chloride exposure period as shown in Figure 12 and  
486 Table 4. The chloride concentrations at 20mm depth after 20years chloride exposure are  
487 calculated from equation 2 using the diffusion parameters  $D_c$  and  $C_0$  which are calculated  
488 from equations 3 and 5.

$$D_c = D_{ref} t^{-m} \quad 3$$

$$C_0 = C_{ref} + k \sqrt{t - t_{ref}} \quad 5$$



489  
490 Fig. 12: Chloride diffusion coefficient prediction of AACM and PC concrete up to 20years of  
491 Cl<sup>-</sup> exposure

492 All the calculated values at 20years exposure are given in Table 4.

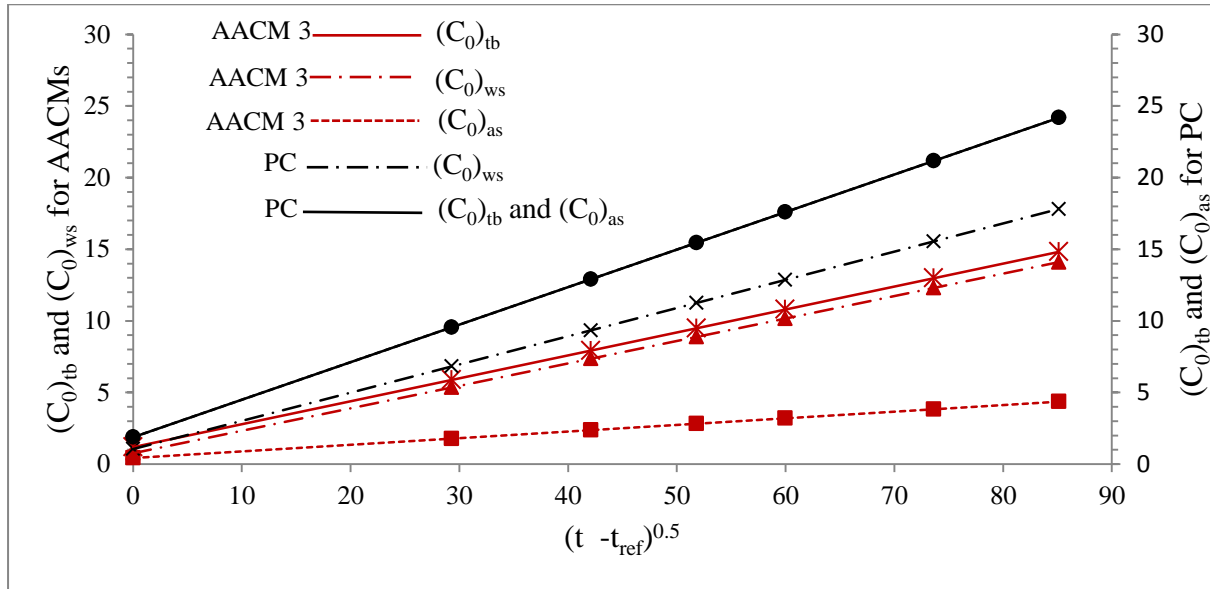
493 Table 4: Predicted chloride diffusion parameters at 20years exposure

Mix	(D <sub>c</sub> ) <sub>ws</sub>	(D <sub>c</sub> ) <sub>as</sub>	(D <sub>c</sub> ) <sub>tb</sub>	(C <sub>0</sub> ) <sub>ws</sub>	(C <sub>0</sub> ) <sub>as</sub>	(C <sub>0</sub> ) <sub>tb</sub>	(Cl <sub>20</sub> ) <sub>ws</sub>	(Cl <sub>20</sub> ) <sub>as</sub>	(Cl <sub>20</sub> ) <sub>tb</sub>
	(m <sup>2</sup> /s)			(% wt. of binder)			(% wt. of binder)		
AACM 1	2.89 x 10 <sup>-13</sup>	3.67 x 10 <sup>-19</sup>	2.89 x 10 <sup>-13</sup>	11.19	2.92	11.65	4.08	0	4.20
AACM 2	3.2 x 10 <sup>-13</sup>	7.48 x 10 <sup>-19</sup>	3.2 x 10 <sup>-13</sup>	11.66	3.38	12.35	4.46	0	4.66
AACM 3	4.0 x 10 <sup>-13</sup>	9.11 x 10 <sup>-19</sup>	4.0 x 10 <sup>-13</sup>	13.72	3.99	14.22	5.26	0	5.54
PC	8.2 x 10 <sup>-19</sup>	5.36 x 10 <sup>-13</sup>	5.36 x 10 <sup>-13</sup>	17.75	24.01	24.01	0	10.68	10.85

#### 494 3.4.4.2 Surface chloride C<sub>0</sub> and Cl<sup>-</sup> content

495 The equations for C<sub>0</sub> given in Table 3 together with C<sub>0</sub> values based on the experimental data  
496 up to 270days exposure are used to plot Fig. 13 to enable long-term predictions of chloride  
497 concentrations. The C<sub>0</sub> values at 20years exposure are given in Table 4.

498 The chloride concentrations at 20mm depth after 20years chloride exposure which are given  
 499 in Table 4 have been calculated from equation 2 using the diffusion parameters  $C_0$  and  $D_c$   
 500 given in Table 4.

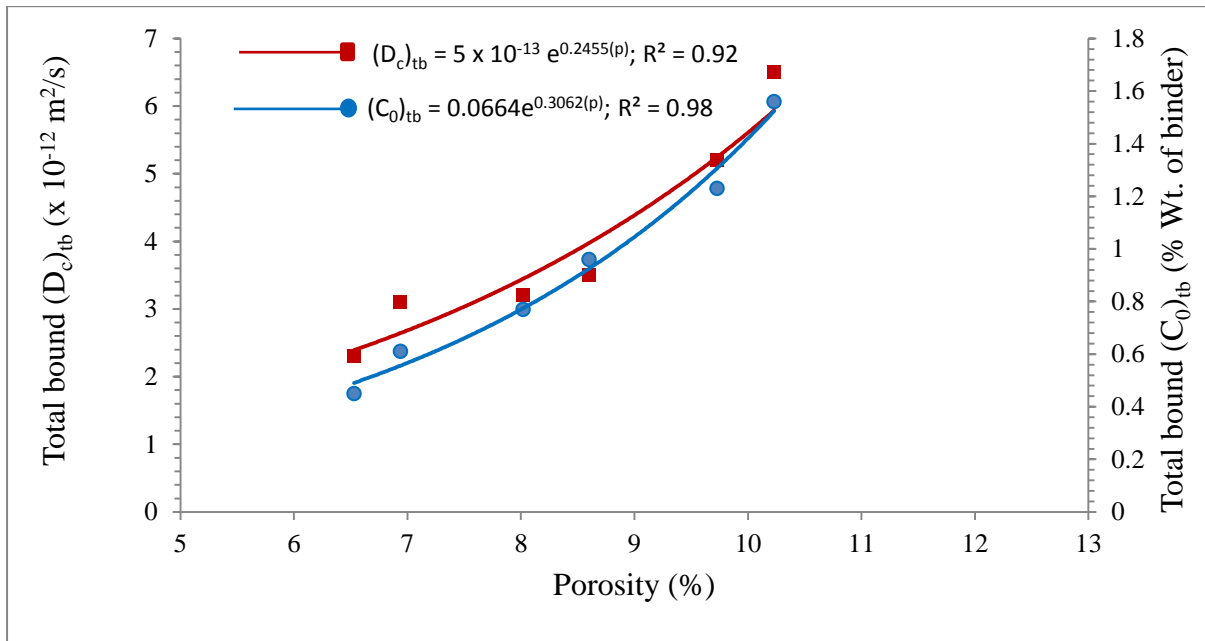


501  
 502 Fig. 13:  $(C_0)_{as}$ ,  $(C_0)_{ws}$  and  $(C_0)_{tb}$  prediction for AACM 3 and PC concrete up to 20yrs of  $Cl^-$   
 503 exposure

504 The results in Table 4 show that the chloride predictions of AACM 1 concrete after 20years  
 505 chloride exposure gave similar values of 4.08% and 4.20% wt. of binder when  $C_0$  and  $D_c$   
 506 based on water soluble and total bound chlorides respectively are used in the calculation. The  
 507  $Cl_{20}$  for AACM 2 and 3 are also similar when water soluble and total bound chloride based  $C_0$   
 508 and  $D_c$  are used for their calculations. However, the  $(Cl_{20})_{as}$  values for the AACM concretes  
 509 are 0% wt. of binder. Therefore, in practice the data of water soluble chlorides in AACMs  
 510 can be used to determine their diffusion coefficients for long term chloride predictions. The  
 511 use of acid soluble chloride data is unsuitable for AACM concretes. These results are  
 512 contrary to PC concrete for which chloride predictions based on acid soluble chloride data  
 513 (Table 4) are valid.

514 3.5 Chloride diffusion parameters and Porosity relationship

515 The relationships between chloride diffusion parameters ( $D_c$  and  $C_0$ ) and porosity of AACM  
 516 concrete are shown in Fig. 14. The porosity data at the core of 75mm cube specimens of  
 517 AACM mortar mixes corresponding to the concrete mixes of this study, with the same binder  
 518 and activator content (liquid/binder ratio of 0.47) have been reported by the authors  
 519 previously [16]. The pore properties were determined by mercury intrusion porosimetry.



520  
 521 Fig. 14: Relationship between  $(D_c)_{tb}$ ,  $(C_0)_{tb}$  and porosity of AACM concrete at 28days.

522 The relationships between porosity and diffusion parameters of AACM concrete are as  
 523 follows:

524  $(C_0)_{tb} = 0.0664e^{0.31(p)}$  with  $R^2 = 0.98$ .

525  $(D_c)_{tb} = 5 \times 10^{-13} e^{0.25(p)}$  with  $R^2 = 0.92$ .

526 Where;  $(C_0)_{tb}$  and  $(D_c)_{tb}$  are the total surface chloride (% wt. of binder) and diffusion  
 527 coefficient ( $\text{m}^2/\text{s}$ ) respectively and  $p$  is the porosity (%).

528 The chloride diffusion parameters  $C_0$  and  $D_c$  depend on a number of factors such as the  
 529 chloride concentration of the exposure solution, porosity and pore size distribution. These  
 530 factors differ between AACM and PC concrete which affects the adsorption and absorption  
 531 of chlorides to the binder gel. The porosity of AACMs is lower than the control PC concrete

532 [16] and the pore structure is more restricted to chloride diffusion. The relationships of  $C_0$   
533 and  $D_c$  with porosity are different for AACMs and PC concrete. The porosity of the control  
534 PC mortar mix was 10% with  $(D_c)_{tb}$  and  $(C_0)_{tb}$  of  $4.5 \times 10^{-11} \text{m}^2/\text{s}$  and 5.2% weight of binder  
535 respectively, which fall outside the graphs for AACMs in Figure 14.

## 536 CONCLUSIONS

537 This paper investigates chloride ingress in structural grade AACM concretes and a control PC  
538 concrete. The concrete mixes were exposed to 5% NaCl solution up to 270 days. The water  
539 and acid soluble chlorides in AACM and PC concrete were determined at 55, 90, 120, 180  
540 and 270days exposure. Chloride concentration profiles with depth were determined and  
541 chloride diffusion parameters such as surface chloride concentration and chloride diffusion  
542 coefficient were calculated to enable long term chloride predictions. The following  
543 conclusions can be drawn from the study.

544 1. The water and acid soluble chloride concentrations in AACM concrete increase with  
545 exposure period. Both chloride concentration profiles with depth show good correlation with  
546 Fick's second law of diffusion.

547 2. AACM concrete shows a greater increase with time in water-soluble chloride  
548 (physically bound chloride) than the acid soluble chloride (chemically bound chloride) while  
549 the control PC concrete shows more acid soluble chloride than water-soluble chloride.  
550 However, the total bound chloride is greater in PC concrete. For example, the water and acid  
551 soluble chlorides at 20mm depth for AACM 3 concrete are 1.26% and 0.39% respectively  
552 while they are 2.13% and 3.20% for the control PC concrete at 180days chloride exposure.  
553 The total bound chlorides for AACM 3 and PC concretes of similar strength are 1.65% and  
554 3.2% by weight of binder respectively.

555 3. The chloride diffusion parameters  $C_0$  and  $D_c$  of AACM concrete based on the water  
556 soluble (ws) and total bound (tb) chlorides give similar values. For example, the  $(C_0)_{ws}$  and

557  $(C_0)_{tb}$  values of AACM 3 are 2.11% and 2.39% wt. of binder respectively at 180days chloride  
558 exposure. The corresponding  $(D_c)_{ws}$  and  $(D_c)_{tb}$  values are equal at all exposure periods. Hence  
559 water soluble (physically bound) chloride data is suitable for characterizing chloride diffusion  
560 of AACM concrete. This is contrary to the practice (and test standards) for conventional PC  
561 concrete where acid soluble (chemically bound) chloride data are used for characterizing  $C_0$   
562 and  $D_c$ . The test data on PC concrete in the paper also validate this practice.

563 4. The  $C_0$  values of AACM concrete relating to both physically and chemically bound  
564 chlorides increase with chloride exposure period in a relationship of the form:

$$C_0 = C_{ref} + k \sqrt{t - t_{ref}}$$

565 Where  $C_0$  is the surface chloride concentration at time  $t$ .  $C_{ref}$  is the surface chloride  
566 concentration corresponding to the reference time  $t_{ref}$  and  $k$  is constant.

567 The corresponding  $D_c$  values of AACM concrete decrease with longer chloride exposure  
568 period following the relationship:

$$D_c = D_{ref} t^{-m}$$

569 where:  $D_c$  is the apparent diffusion coefficient at time  $t$ ,  $D_{ref}$  is diffusion coefficient at  
570 reference time  $t_{ref}$ , and  $m$  is the age factor ranging between 0.512 and 0.574 for the AACM  
571 concrete. The value of  $m$  decreases with decreasing molarity of the alkaline activator which  
572 reflects greater chloride diffusion with decreasing molarity of activator.

573 5. The long-term prediction model for  $D_c$  and  $C_0$  (conclusion 4) can be used to predict long  
574 term chloride concentration in AACM concrete using either water soluble or total bound  
575 chloride data obtained at an early age. For example, the predicted water soluble and total  
576 bound chloride concentrations at 20years are 11.19% and 11.65% by weight of binder  
577 respectively in AACM 1 concrete.

578 6. The difference in chloride diffusion coefficient  $D_c$  of AACM and PC concrete of  
579 similar strength is greater at early age and reduces with age. This is reflected in the long term

580 predicted values of chloride concentrations. For example, the  $(D_c)_{tb}$  at 55days chloride  
581 exposure are  $6.5 \times 10^{-12} \text{m}^2/\text{s}$  and  $8.7 \times 10^{-12} \text{m}^2/\text{s}$  for AACM 3 and PC concrete respectively  
582 and their corresponding values after 20years exposure period are  $4.0 \times 10^{-13} \text{m}^2/\text{s}$  and  $5.36 \times$   
583  $10^{-13} \text{m}^2/\text{s}$ .

584 7. The chloride diffusion in AACM concrete is controlled by its porosity. The pore  
585 refinement in AACM concrete aids lower diffusion of chloride. The chloride diffusion  
586 parameters  $C_0$  and  $D_c$  are related to porosity as follows:

587  $(C_0)_{tb} = 0.0664e^{0.31(p)}$  with  $R^2 = 0.98$

588  $(D_c)_{tb} = 5 \times 10^{-13} e^{0.25(p)}$  with  $R^2 = 0.92$ .

589 Where;  $(C_0)_{tb}$  and  $(D_c)_{tb}$  are the total surface chloride (% wt. of binder) and diffusion  
590 coefficient ( $\text{m}^2/\text{s}$ ) respectively and p is the porosity (%).

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