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

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

This document is the Accepted Version [AM]

Citation:

MANGAT, Pal and OJEDOKUN, Olalekan O (2020). Free and bound chloride relationships affecting reinforcement cover in alkali activated concrete. Cement and Concrete Composites, p. 103692. [Article]

Free and bound chloride relationships affecting reinforcement cover 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

This paper investigates the free chloride profiles, diffusion parameters and chloride binding capacity of an alkali activated concrete (AACM) together with a control Portland cement (PC) concrete. Ggbs based AACM concrete specimens with different molarity of activator were exposed to a 5% NaCl solution for 540days to determine their free chloride diffusion properties. The relationships between the free and bound chloride concentration were determined by applying Freundlich and Langmuir isotherms. The required cover to steel reinforcement for corrosion prevention is derived to satisfy the limiting thresholds of free and bound chloride concentrations.

The results show that Fick's second law of diffusion applies to the free chloride profiles of AACM concrete and provides higher values of diffusion coefficients than a similar grade of PC concrete. The relationship between the free and bound chlorides is defined by the Langmuir isotherm. PC concrete has higher chloride binding capacity than AACM concrete for both water and acid soluble chlorides. Less concrete cover to steel reinforcement is required in AACM than PC concrete when calculated by using the bound chloride concentration threshold limit. The values of cover based on the corresponding free chloride limit in AACM concrete are higher than its bound chloride values.

Keywords: Alkali activated cementitious materials (AACM) concrete. Chloride binding isotherms. Free chloride concentration. Total bound chloride concentration. Chloride diffusion coefficient $(D_c)_f$. Surface chloride concentration $(C_0)_f$.

Notations:

AACM	alkali activated cementitious materials
PC	Portland cement
GGBS	ground granulated blast furnace slag
SRPC	sulphate-resisting Portland cement
C_{tb}	total bound chloride concentration *(mg/g. by binder)*
C_f	free chloride concentration (mol/L)
C_{as}	acid soluble chloride concentration *(mg/g. by binder)*
C_{ws}	water soluble chloride concentration *(mg/g. by binder)*
$(C_0)_f$	free surface chloride concentration (mol/L)
$C_{(x,t)\,f}$	free chloride concentration at distance x and time t
$(D_c)_f$	free chloride diffusion coefficient (x 10^{-12} m^2/s)
$(D_c)_{tb}$	total bound chloride coefficient
$(D_c)_{as}$	acid soluble chloride coefficient
$(D_c)_{ws}$	water soluble chloride coefficient
α and β	binding constants
SRA	shrinkage reducing admixture
R42	retarder
C_3A	tricalcium aluminate
C_4AF	tetracalcium aluminate
$Ca_6Al_2O_6.CaCl_2.10H_2O$	friedel's salt (FS)

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

1.0 Introduction

The use of Portland cement in construction is environmentally challenging due to huge amount of CO_2 emissions and the high energy demand during its production [1–3]. New innovations in low impact construction materials require a reduction in the use of Portland cement with alternative binders, preferably utilising industrial waste materials and aggregates made from recycled waste. Alkali activated cementitious materials (AACMs) show potential benefits when used in place of Portland cement in the construction industry. However, strong market forces go against the acceptance of AACMs which are partly supported by limited knowledge of the service life of AACM concrete structures due to inadequate durability investigations available in literature.

Chloride induced corrosion in concrete is a major cause of deterioration in reinforced concrete structures such as bridge decks exposed to deicing salts and concrete exposed to marine environment. Chlorides exist in the concrete matrix as acid soluble (chemically bound), water soluble (physically bound) and free chlorides [4,5]. The free chloride which is present in the pore solution of concrete is known to initiate corrosion by providing the electrolyte for the electrochemical reactions. The free chloride content in concrete pore solution together with oxygen and water are decisive factors in the initiation and propagation of chloride induced corrosion in reinforced concrete [4]. Free chloride is dependent on the water soluble chloride which is bound to the walls of the binder gel and the acid soluble chloride which forms a part of the hydration or geopolymerization products in concrete. The relationship between the free and bound chlorides (physically and chemically bound), which is termed as the chloride binding capacity, regulates the amount of free chloride available to initiate corrosion. Therefore, the chloride binding capacity of a concrete is an important parameter for service life predictions of reinforced concrete structures. The relationship between the bound and free chloride in AACM concrete remains to be fully understood. Quantifying the parameters of this relationship will improve AACM mix design.

The pore solution chemistry and chloride binding capacity of AACMs is likely to differ from PC concrete due to differences in their bound chlorides caused by low amounts of acid soluble chloride in AACM concrete [6]. The water soluble chloride in AACM concrete is in abundance which is influenced by the volume of pozzolanic constituents and their pore properties [7]. On the other hand, a large proportion of the bound chloride in PC concrete is found to be chemically bound to its hydration products while a smaller proportion is physically bound between the interface of its hydrated products, which is contrary to AACM concrete [6]. The presence of relatively low amount of chemically bound chloride and a high amount of physically bound chloride in AACM concrete will affect its chloride binding capacity relative to PC concrete.

The chloride binding capacity of PC concrete is attributed to many factors such as pH of concrete pore solution, temperature, Tricalcium Aluminate (C_3A) content and exposure period in a chloride solution. For example, the chloride binding capacity of sulphate-resisting Portland cement (SRPC) and PC with supplementary cement replacement binder was reported to be lower than PC concrete [4]. This was due to lower C_3A content of SRPC (PC ~ 15% and SRPC~ 2%) [5]. An increase in the Tricalcium Aluminate, C_3A, decreases the free chloride concentration in the pore solution by increasing the chemical binding capacity of chloride. Similarly, lower alkalinity (pH) of concrete containing supplementary cementitious materials decreases its chloride binding capacity relative to normal PC concrete and, therefore, increases its free chloride concentration [8]. Some of these factors are not present in AACM concrete, for example AACMs can be low on Tricalcium Aluminate, C_3A while their alkalinity, pH, can be higher. These differences will, therefore, influence the chloride binding capacities of AACM and PC concrete independently.

The chloride binding in concrete removes its free chloride from the pore fluid thereby reducing the mobile chloride ions that can attack steel reinforcement in concrete. Nevertheless, since the chloride diffusion process is based on attaining chemical equilibrium between the pore solution and the exposure environment (external chloride solution), the concentration of free chloride continues to increase with time [9] and ultimately reaches the threshold level to initiate reinforcement corrosion. Chloride ingress may have varying influence on the pore structure of AACM and PC concrete by the formation of Friedel's salt ($Ca_6Al_2O_6.CaCl_2.10H_2O$) and Kuzel's salt ($Ca_6Fe_2O_6.CaCl_2.10H_2O$) during chloride binding. This reduces the porosity and, therefore, limit further chloride ingress in concrete [7,10].

The relationships between free and total bound (chemical and physical) chlorides for PC concrete have been defined by the Freundlich and Langmuir isotherms [9,11]. These models are suitable for high and low free chloride concentrations and are applicable within a specific range of chloride concentration. The equation of Freundlich isotherm applies to free chloride levels exceeding 0.01 mol/L in the concrete pore fluid while the Langmuir equation applies to free chloride levels below 0.05mol/L [11]. Freundlich binding isotherm is adopted for the range of free chloride concentrations in seawater which are usually high. The Langmuir binding isotherm defines the free-bound chloride relationship of normal PC concrete with relatively low free chloride concentration of its pore fluid [10].

This paper is part of a comprehensive durability investigation of AACMs being undertaken by the authors. It investigates the chloride binding capacity of AACMs, free chloride diffusion parameters (C_0 and D_c) and determines the required concrete cover to steel reinforcement based on total bound and free chloride thresholds.

2.0 Experimental programme

2.1 Materials and mixes

Three AACM concrete mixes 1, 2 and 3 and a control PC concrete were produced as shown in Table 1. The mixes are similar to the compositions used to investigate the bound chloride ingress in alkali activated concrete [6]. AACM and PC mortars, as shown in Table 1, were also produced to determine and quantify the geopolymerization and hydration products. Ground granulated blast furnace slag (GGBS) and CEM 1 cement of grade 42.5R [12] were used as binders for AACM and PC concrete mixes respectively. The AACM binder was activated with a sodium silicate solution of molarity 6.5mol/L and modulus 2% together with NaOH of molarity 4.8mol/L. AACM 1, 2 and 3 mixes were produced by diluting the activator with water at 0%, 3.88% and 7.76% respectively as shown in Table 1, to optimize workability. Liquid/binder ratios of 0.47 and 0.5 were used for all concrete and mortar mixes respectively. 10mm uncrushed gravel, 6 mm limestone and a medium grade sand of 80% particle size passing 1mm sieve were used as coarse and fine aggregates. The properties and oxide compositions of these aggregates conform to BS 882:1992 [13]. AACM concrete and mortar mixes contain 0.5% by binder weight of shrinkage reducing admixture (SRA) made from Alkyl-ether and 0.2% by binder weight of retarder R42 made from a blend of high grade polyhydroxycarboxylic acid derivatives. The shrinkage reducing admixture also enhances workability while the retarder reduces the setting time of AACM concrete. 5% by weight of NaCl was added to the mortar composition only during mixing in order to investigate its chloride binding capacity.

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)	-	-	-

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

2.2 Mixing and casting

2.2.1 Mortar specimens

Four 75 x 75 x 75mm specimens of each AACM and PC mortar were produced to determine and quantify the geopolymerization and hydration products. The fresh mortar specimens were prepared in a 12litre, 3 speed Hobart mixer. The mix constituents together with 5% NaCl were mixed for 3mins at the lowest speed (option 1) to avoid dispersing the powder into the atmosphere. The specimens were cast in steel moulds in three layers and each layer was compacted on a vibration table. The cast specimens were placed on a flat surface in the laboratory air (20 ± 2^0C, 65% R.H.) and covered with polythene sheets for 24hrs. The mortar specimens were demoulded after 24hrs and cured in water (20 ± 2^0C) for 1day and 27days in laboratory air (20 ± 2^0C, 65% R.H.).

2.2.2 Concrete specimens

Concrete specimens were produced and exposed to a 5% NaCl solution for up to 540days similar to specimens used for bound chlorides investigation [6,14]. The fresh concrete was mixed in a 150kg capacity Cretangle mixer and then cast into 250 x 250 x 75mm polystyrene moulds in three layers, each layer being compacted by vibration. The cast specimens were placed on a flat surface in the laboratory (20 ± 2^0C, 65% R.H.) and covered with polythene sheets for 24hrs. A total of twenty-four specimens were produced and demoulded 24hrs after casting followed by curing in water (20 ± 2^0C) for 27days. The concrete specimens were then removed from water and surface dried. Two coats of bituminous paint were applied to five faces of each slab except the bottom cast face (250 x 250mm) and allowed to dry for 24hrs. The slabs were then immersed in a 5% by weight NaCl solution for 540days to expose the uncoated face to chloride diffusion. Concrete coring was carried out at 180, 270 and 540days of chloride exposure for pore fluid extraction.

2.3 Test Procedures

2.3.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on powder samples of AACM and PC mortar samples to determine and quantify the main geopolymerization and hydration products using a NETZSCH STA 409 PC/PG device. 19 and 17 grams of AACM and PC powder samples were subjected to heating up to 1000^0C at a rate of 20^0C/min using nitrogen gas. The geopolymerization and hydration products and their mass losses per unit temperature were determined for AACM and PC samples after heating up to 1000^0C.

2.3.2 X-ray diffraction (XRD)

The mineralogical compositions of AACM and PC concrete were analysed using a Philips X-Pert X-ray diffractometer operating with a Cu Kα radiation source (40 KV and 40 mA, wavelength λ=0.154056 nm [6.07 x10-9 in.]). XRD analyses of the samples were performed by scanning from 50 to 800 at an angle of 2Θ; the scan step size is 0.016711 and a counting time step of 0.1 s.

2.3.3 pH Analysis

The ex-situ leaching method of concrete [15] was adopted to obtain the solution for the pH analysis of the concrete and mortar samples. A double junction electrode connected to a 3-in-1 benchtop meter was dipped inside a filtered solution of powder sample to measure pH of AACM and PC dissolved in distilled water at a ratio of 1:1. This device measures pH ranging from 0.00 to 14.00 and can measure sample volumes as small as 0.2mL with an accuracy of ± 0.01.

2.3.4 Concrete coring and pore solution expression

Four cores of 50mm diameter x 60mm depth were obtained from each AACM and PC concrete specimen. The concrete coring was performed at 180, 270 and 540days chloride exposure in a solution of 5% NaCl by weight. Each core was sawn into three discs of 50mm diameter x 20mm depth representing depths of 0 - 20mm, 20 - 40mm and 40 - 60mm from the surface of the concrete.

The pore solution expression was performed on the 20mm thick concrete discs obtained from the AACM and control PC concrete. This was carried out by placing three discs from the same depth, for example 0 - 20mm depth obtained from three cores for each mix, into a pore fluid extraction device. The pore solution extraction device with the three discs inside it was placed in a compression testing machine under its loading platen and a compressive load was applied at a steady rate of 10KN/sec. The pore solution was extracted through a suction action without allowing contact with air and was immediately stored in plastic vials, labelled and sealed with parafilm. The same procedure was repeated on concrete core discs representing 20 - 40mm and 40 - 60mm depths.

2.3.5 Free chloride concentration

The free chloride concentration of pore solutions in AACM and PC concrete was determined by dipping a chloride ion selective electrode (ISE) into the pore solution. The ISE has a white reference contact near the tip of the electrode which was immersed in the pore solution without entrapping air bubbles below it. The ISE was held in the aqueous solution until the reading stabilized and the displayed reading was then recorded. The ISE was rinsed by spraying with a jet of deionised water and dabbed dry with a low-lint laboratory tissue between measurements. The ISE was calibrated before and after each measurement. The calibration was done by using a pre-prepared 1000mg/l and 10mg/l of standard NaCl solution. The coefficient of variance of repeatability was less than 5%.

3.0 Results and discussion

3.1 Geopolymer and Hydration products

Thermogravimetric analysis (TGA) was performed on AACM and PC mortar samples containing 5% NaCl to determine the geopolymerization and hydration products and the nature of chloride binding in the matrix. Figures 1 show the derivatives of thermogravimetry DTG showing peaks of hydration products on the primary axis while the secondary axis has the thermogravimetry (TG) showing incremental loss of hydration products during heating for AACM and PC concrete.

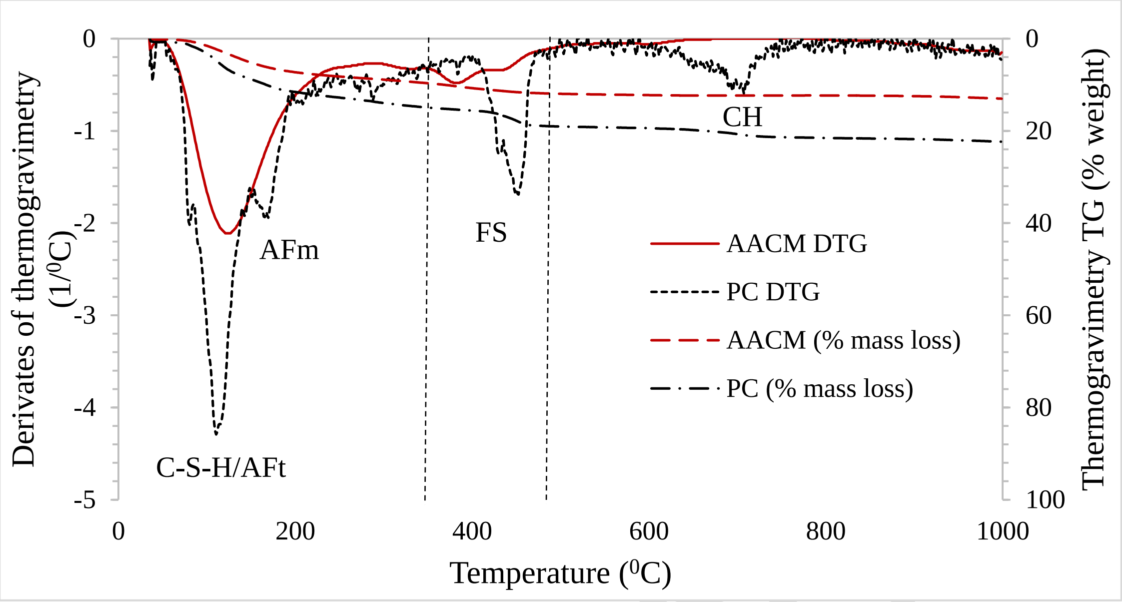

Fig. 1: Derivation of thermogravimetry (DTG) and thermogravimetry (TG) curves of AACM and PC mortar

*FS is the Friedel's salt

The main geopolymerization products observed after heating AACM powder to 1000^0C are Friedel's salt (FS), calcium silicate hydrate (C-S-H) and ettringite (AFt). The main hydration products observed after heating PC powder to 1000^0C are Friedel's salt (FS), portlandite (CH), calcium silicate hydrate (C-S-H), ettringite (AFt) and monosulfoaluminate (AFm), similar to other research [16–18] on hydraulic cement. Portlandite (CH) and monosulfoaluminate (AFm) were not observed in the derivatives of thermogravimetry (DTG) of AACM mortar. This explains the limited amount of Friedel's salt (FS) observed in AACM mortar since Portlandite (CH) is its main reaction constituent for binding chloride in the matrix. The amount of Friedel's salt ($Ca_6Al_2O_6.CaCl_2.10H_2O$) is largely dependent on the Ca/Al ratio (Table 2) as discussed in section 3.2. AACM concretes have low Ca/Al ratios relative to PC concrete thus forming less monocarboaluminate compound which reacts with chloride to form a lower amount of Friedel's salt as shown in Fig. 1. Monocarboaluminate compound which converts to Friedel's salt on reaction with chloride is formed at high Ca/Al ratio while stratlingite compound which does not covert to Friedel's salt is formed at low Ca/Al ratio [19]. The relative volumes of Friedel's salt (FS) present in AACM and PC mortars shown in Fig. 1 conform with the research findings on the chemically bound chlorides in AACM concrete [6]. The greater mass loss of 22% by weight of the hydration product in PC mortar compared with 12% weight of geopolymerization product in AACM concrete, as represented by the TG loss, also confirms that greater amount of Friedel's salt (FS) is present in PC mortar.

3.2 pH and ions concentrations

Chemical compositions showing oxides of various ions present in AACM and PC mortar samples at 180days chloride exposure are shown in Table 2. pH values of powder samples of AACM and PC mortar at 180days chloride exposure is also shown in Table 2.

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

Higher pH is seen in powder sample of AACM mortar (11.1) than PC mortar (10.8) at 180days chloride exposure as shown in Table 2. Their corresponding chloride concentrations are 1.1% and 1.9% respectively in Table 2. pH values of both concrete types affected the chloride binding capacity due to competition between OH^- and Cl^- at the adsorption sites of the hydration/geopolymerisation products. It has been observed [20] that as more chloride ions were chemically adsorbed, fewer adsorption sites were left for other ions such as OH^- which could not be adsorbed simultaneously. This hypothesis [20] was suggested for the higher binding capacity of PC concrete with a low pH since the low pH results in more adsorption sites for free chloride compared with AACM concrete which has high pH.

Chloride binding in AACM and PC mortars is significantly influenced by the Ca/Al ratio. PC concrete has higher Ca/Al ratio (7.6) compared with 2.2 for AACM concrete of similar strength [7]. High Ca/Al ratio of 7.6 in PC mortar resulted in the formation of greater amount of Friedel's salt ($Ca_6Al_2O_6.CaCl_2.10H_2O$) as shown in Fig. 1. AACM 3 mortars, however, have small amount of Friedel's salt as shown in Fig. 1 due to their lower Ca/Al ratio (2.2). High amount of Friedel's salt at high Ca/Al ratios was also observed by other research [19]. The formation of Friedel's salt at high Ca/Al ratio was attributed to the reaction between chloride concentration and monocarboaluminate compound, however, at low Ca/Al ratio, chloride concentration reacts with less monocarboaluminate thus resulting in less Friedel's salt [19].

Chloride binding in AACM and PC mortars is also influenced by the Ca/Si ratio. PC concrete has higher ratio of Ca/Si (3.5) compared with 0.8 for AACM concrete. The influence of Ca/Si ratio is less prominent than Ca/Al ratio for chloride binding in PC concrete but this is not valid for AACM concrete. The effect of Ca/Si ratio is more dominant than Ca/Al ratio in AACM concrete resulting in the formation of more gel binder sites for binding Kuzel's salt ($Ca_6Fe_2O_6.CaCl_2.10H_2O$). This is discussed in more details in section 3.5.

3.3 Free and total bound chloride concentrations

Table 3 shows the free and total bound chloride concentrations of AACM and PC concrete at mean depths of 10, 30 and 50mm from the concrete surface. AACM 1, 2, 3 and PC concrete were exposed to 5% NaCl solution for 180 and 270days; chloride exposure of AACM 1 was further extended to 540days. Details of the bound chloride study are given in the authors' previous publication [6]. Total bound chloride is the summation of both acid and water soluble chlorides.

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

		Free Cl^- (mol/L)			Total bound Cl^- (mg/g of binder)		
	Mean Depth	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	-

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

3.4 Chloride binding isotherms

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].

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

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

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.

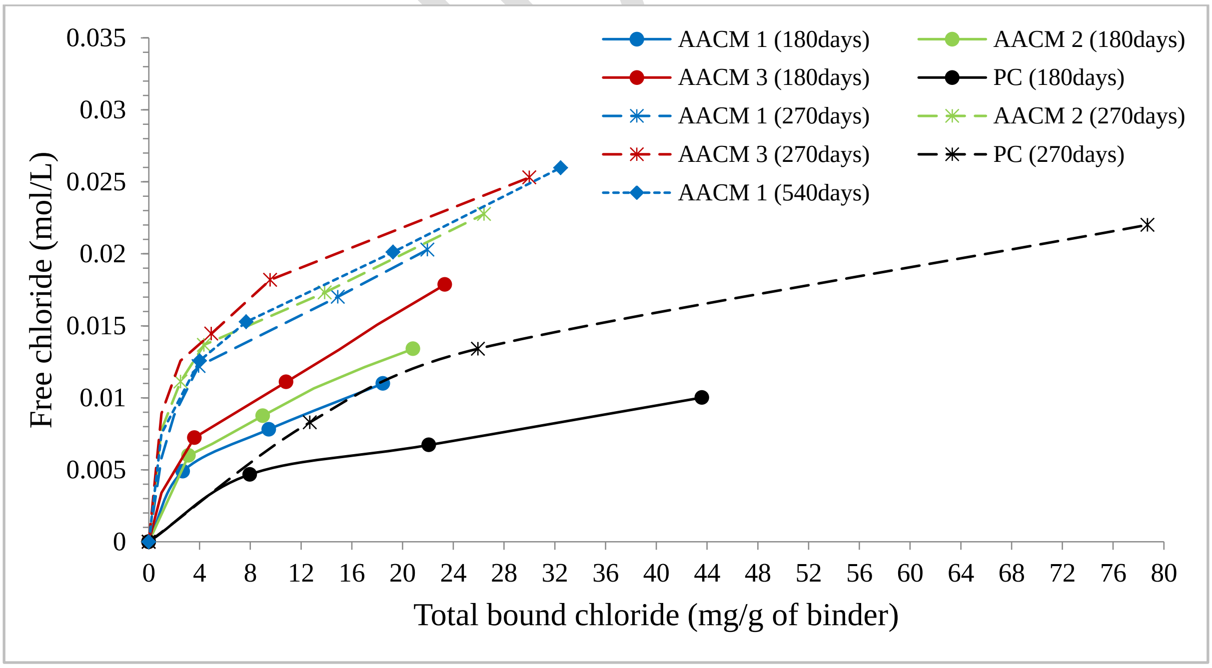

Fig. 2: Langmuir binding isotherms for AACM 1, 2, 3 and PC concrete at 180, 270 and 540 (for AACM 1) days of chloride exposure

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 chloride exposure (Table 3, Fig. 2). These concentrations are less than the 0.05mol/L limit suggested by Tang and Nilsson [11] for the Langmuir isotherm to describe the effective binding of free chloride concentrations. This isotherm model shows the best correlation with the experimental data of AACM and PC concrete given in Fig. 2. Yuan et al. [10] suggested that the Langmuir binding isotherm indicates that at longer chloride exposure, all adsorption sites are occupied by chloride ions thereby resulting in lower chloride concentrations in the pore solution.

Freundlich binding isotherms are usually applicable to concrete with high free chloride concentrations. For example, Thomas et al. [21] used Freundlich binding isotherm to relate their experimental free chloride data greater than 0.1M (0.1mol/L) for supplementary cementitious materials. The concrete mixes investigated by Thomas et al. [21] showed that 8% cement replacement with silica fume exhibited the lowest chloride binding capacity (therefore, maximum free chloride) while 25% cement replacement with fly-ash had the highest binding capacity among the supplementary materials.

3.5 Chloride binding capacity

3.5.1 Introduction

The chloride binding capacity of the AACM and PC concrete mixes relating to their acid and water soluble chloride concentrations is discussed in this section. The acid soluble chlorides are chemically bound in the matrix while the water soluble chlorides are physically bound in the capillaries of the matrix [6].

Some factors such as mix design, age of concrete, type of rebar and construction practices influence the critical chloride threshold for reinforcement corrosion in PC concrete structures [22,23]. Also the use of SCMs such as slag can have significant influence due to factors discussed in section 3.2. However, the permissible chloride concentration for corrosion initiation used in this paper is 4mg/g (0.4% by weight) of binder in accordance with British

Standards BS EN 206 [12] to start evaluating the relative performance of AACM and PC mixes until ongoing research by the authors and others provides further insights. However, with so many factors affecting this value [22,23], certain degree of approximation will be inevitable. This value relates to the acid soluble chloride determined by the tests given in international standards [24,25] for PC concrete. This limiting value of acid soluble chloride in PC concrete is similar to its total (chemically plus physically) bound chloride concentration [6]. However, for AACM concrete mixes, the water soluble chloride determined according to ASTM standard [26] is representative of its total bound chloride concentration [6] and, therefore, it is recommended for use as the permissible chloride concentration for design of AACMs against corrosion.

However, the free chloride concentration in the pore fluid which serves as the electrolyte for steel reinforcement corrosion is the actual initiator of reinforcement corrosion but it is impractical to determine for use in the design against chloride induced corrosion [4]. Therefore, the relationship between the free and bound chlorides (acid and water soluble) is investigated in this section. The reinforcement cover required in AACM concrete relative to PC concrete will be determined based on both the bound chloride concentration of 0.4% stipulated in international standards for PC concrete [12] and the corresponding free chloride reaching the steel reinforcement.

3.5.2 Acid soluble chloride

Figure 3 shows the relationship between free chloride and bound chlorides for AACM 3 and PC concrete at 270days chloride exposure. The bound chlorides represented in the graphs of Fig. 3 are the total bound chloride C_{tb}, the acid soluble chloride C_{as} and the water soluble chloride C_{ws}. The free chloride concentrations, C_f, corresponding to the permissible bound chloride of 4mg/g (0.4%) of binder for AACM 3 and PC concrete are indicated on Fig. 3. The graphs of AACM 3 are typical of AACM 1 and 2 which are not plotted to avoid congestion.

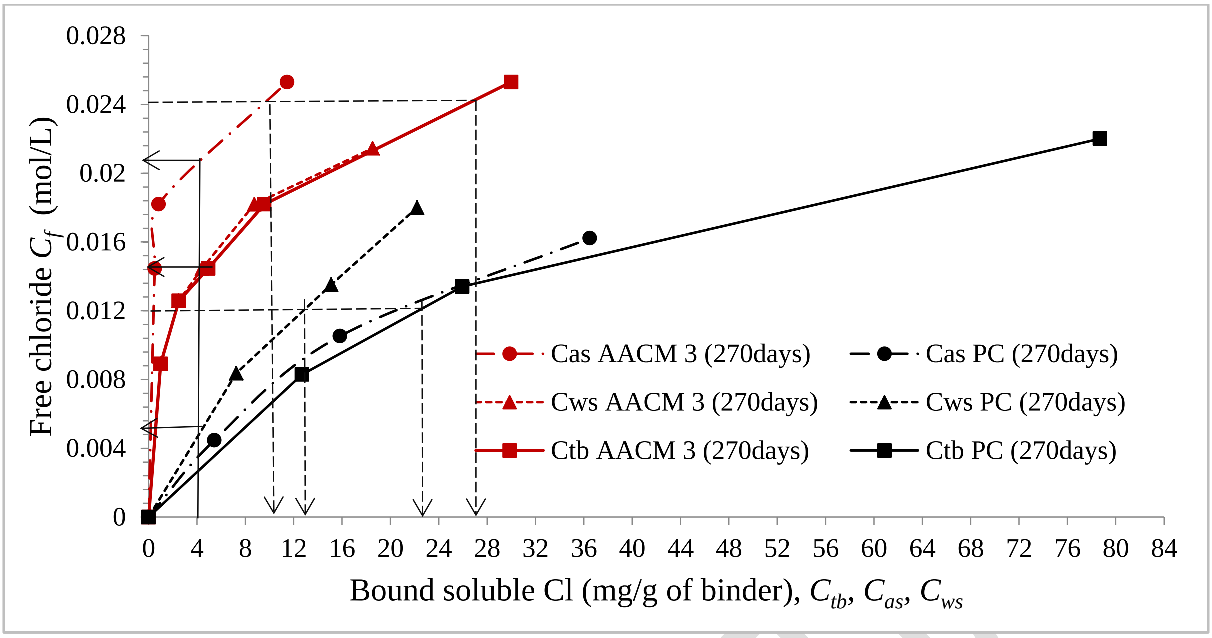

Fig. 3: Relationship between free and bound (total, acid and water soluble) chlorides for AACM 3 and PC concrete at 270days chloride exposure

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.

Chemical and mineral admixtures which are present in AACM concrete are known factors which reduce the chloride binding capacity in PC concrete. For example, mineral additives like silica fume, fly-ash, ground granulated blast furnace slag and gypsum reduce the binding capacity due to their lower unhydrated C_3A content that is required for chemically bound chlorides [10,20]. Zhang et al. [27] observed limited chemical binding of chloride in AACM concrete containing 100% slag similar to the results in Fig. 1. However no chemical binding of chloride was seen in AACM concrete containing both slag and fly ash in 60/40 ratio. Alkali activated fly ash mortar immersed in NaCl solution for 2 years does not produce any Friedel's salt [28]. The fly ash in AACM concrete dissolves Al forming more zeolite phases and N-A-S-H inhibiting the formation of Friedel's salt [27]. Conversely, high unhydrated C_3A content promotes the formation of Friedel's salt ($Ca_6Al_2O_6.CaCl_2.10H_2O$) in PC concrete which is seen in Fig. 1.

It has been reported that the presence of superplasticizers tends to lower the chloride binding capacity in PC concrete [29] when NaCl is admixed in the fresh concrete. Chemical admixtures such as superplasticizers and shrinkage reducing admixtures release bound water into its pore solution in fresh PC concrete [22,23] which affect the value of admixed bound chloride. Cement particles have surface charges which causes them to flocculate when in contact with water while the addition of chemical admixtures into the fresh concrete mix releases the trapped bound water within the gel matrix [22,23]. However, other research reports that the effect of these chemical admixtures is to increase the amount of bound chloride when chloride diffusion into hardened concrete occurs from external sources [30,31]. This is due to the greater surface area of the hydration products produced by the flocculation of cement particles and release of bound water caused by the admixtures [30,31]. However, this topic needs further research, particularly for AACM concrete, which will be the subject of future publications.

3.5.3 Water soluble chloride

The free chloride C_f corresponding to 4mg/g (0.4%) by binder weight of water soluble chloride C_{ws} at 270days exposure is 0.014 and 0.006mol/L for AACM 3 and PC concrete respectively (Fig. 3). The concentration of free chloride in the pores of AACM concrete at 4mg/g (0.4%) by weight of water soluble chloride C_{ws} is greater than PC concrete. Both the acid and water soluble chlorides bound in PC concrete are greater than AACM concrete (Figures 3) thus producing less free chloride in PC concrete at the 4mg/g (0.4%) acid and water soluble chlorides.

AACM concrete has a higher binding capacity of water soluble chloride than acid soluble chloride. For example, at a fixed free chloride concentration of C_f of 0.024mol/L, the acid and water soluble chlorides are 10mg/g and 27mg/g of binder respectively. PC concrete, on the other hand, shows a lower binding capacity of water soluble chloride than acid soluble chloride. For example, at a free chloride C_f concentration of 0.012mol/L, the acid and water soluble chlorides are 23mg/g and 13mg/g of binder respectively. The results in Figures 3 show that while the chemically bound chloride represented by acid soluble chloride is high in PC concrete, the physically bound chloride (water soluble) is also significant whereas in AACMs the physically bound chloride (water soluble) is dominant while chemically bound chloride (acid soluble) is insignificant. Zhang et al. [27] observed that AACM mix formulation containing slag/fly ash in the ratio 60/40 resulted in more physically bound chloride than in composition of lower fly ash content. The inclusion of fly ash increases the surface area of aluminosilicate gel which allows more physical absorption of chloride in AACM concrete [32]. Fly ash dissolves Al in AACM concrete matrix forming zeolite, halite and chabazite creating more physical bound chlorides [27].

In the case of PC concrete, the higher chemical chloride binding caused by factors discussed in section 3.5.2 results in lower amount of free chloride present in the pore fluid. However, physical chloride binding is higher in AACMs due to higher volume of the binder gel than PC concrete [7], it is still notable in PC concrete due to its significant binder gel. Consequently, the loss of free chloride due to both chemical and physical chloride binding is much higher in PC than AACM concrete that have a low chemical chloride binding capacity due to factors discussed in section 3.5.2.

3.6 Chloride diffusion parameters

3.6.1 Free chloride profiles

Equation 1 of the Langmuir isotherm is re-arranged to give equation 3 in order to calculate free chloride values from the considerable total bound chloride, C_{tb}, data reported elsewhere [6] for the AACM and PC concrete mixes.

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

where: C_{tb} is the total bound chloride concentration (% weight of binder); C_f is the corresponding free chloride concentration (mol/L); α and β are the chloride binding coefficients from table 3.

The free chloride concentrations, C_f, at 8, 15, 20, 25, 35, 50 and 65mm depth from the concrete surface were determined by applying equation 3 to their corresponding total bound chloride, C_{tb}, values at 55, 90, 120 and 180days chloride exposure. The coefficients α and β of the Langmuir binding isotherm which are given in Table 3 were used in the analysis.

For example for AACM 1 at 180days chloride exposure, the bound chloride at 20mm depth C_{tb} =1.44% by weight of binder [6] while α and β are 1.8 and 7 respectively (Table 3). Substituting these values in equation 3 gives a value of C_f = 0.0085mol/L.

The resulting free chloride concentration graphs against depth are plotted in Fig. 4. Non-linear regression analyses were performed on the free chloride concentration data by applying equation 4 which is based on Fick's 2^{nd} law of diffusion [33].

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

where: x is the distance from concrete surface (m); t is the time (seconds); $(D_c)_f$ is the free chloride diffusion coefficient (m^2/s); $(C_0)_f$ is the free chloride concentration on the concrete surface; $C_{(x,t)\,f}$ is the free chloride concentration at distance x and time t.

The best fit profiles (curves) with depth obtained by this analysis are shown in Fig. 4 together with the experimental data of free chloride (data points) from table 2. The coefficients of correlation range from 0.70 to 0.99.

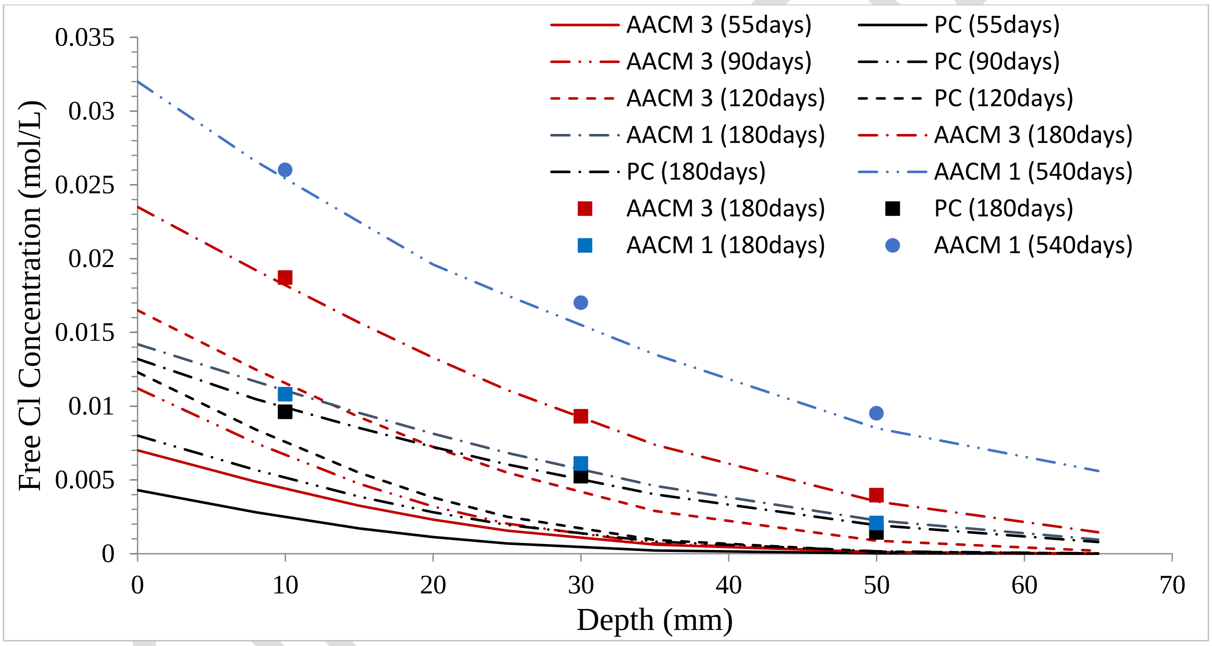

Fig. 4: Free chloride profiles with depth of AACM 1, 3 and PC concrete derived from Langmuir isotherm.

AACM 3 concrete has higher free chloride profiles than PC concrete at all exposure periods. The lower free chloride concentrations in PC concrete are due to its higher chloride binding than AACMs. On the other hand, the free chloride concentrations are similar in AACM 1 and PC concrete at 180days chloride exposure. Increasing molarity of the activator in AACM concrete reduces its free chloride concentration.

3.6.2 Free chloride diffusion coefficients Dc and C_0

The non-linear regression analysis by applying Fick's diffusion equation 4 to the free chloride data also provided the $(C_0)_f$ and $(D_c)_f$ values of the AACM and PC concretes at each period of exposure. These chloride diffusion coefficients change with time due to changes in the properties, such as porosity and chloride binding in concrete [34–37]. In order to account for these changes, age factors are introduced in the Fick's 2nd law of diffusion $\delta C/\delta t = D\ \delta^2 C/\delta x^2$ [34–37] which assumes D_c to be constant in equation 4. The relationships between exposure period and $(D_c)_f$, $(C_0)_f$, are presented in Figures 5 and 6 respectively.

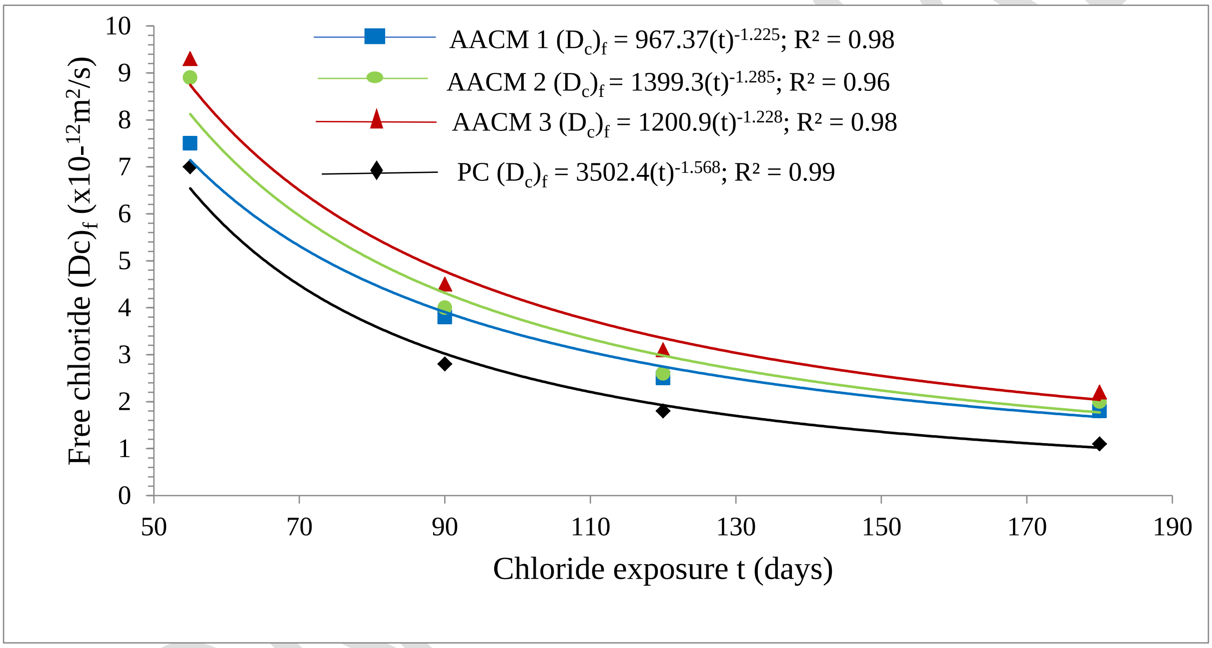

Fig. 5: Relationship of free chloride diffusion coefficient, $(D_c)_f$, with exposure period for AACM 1, 2, 3 and PC concrete

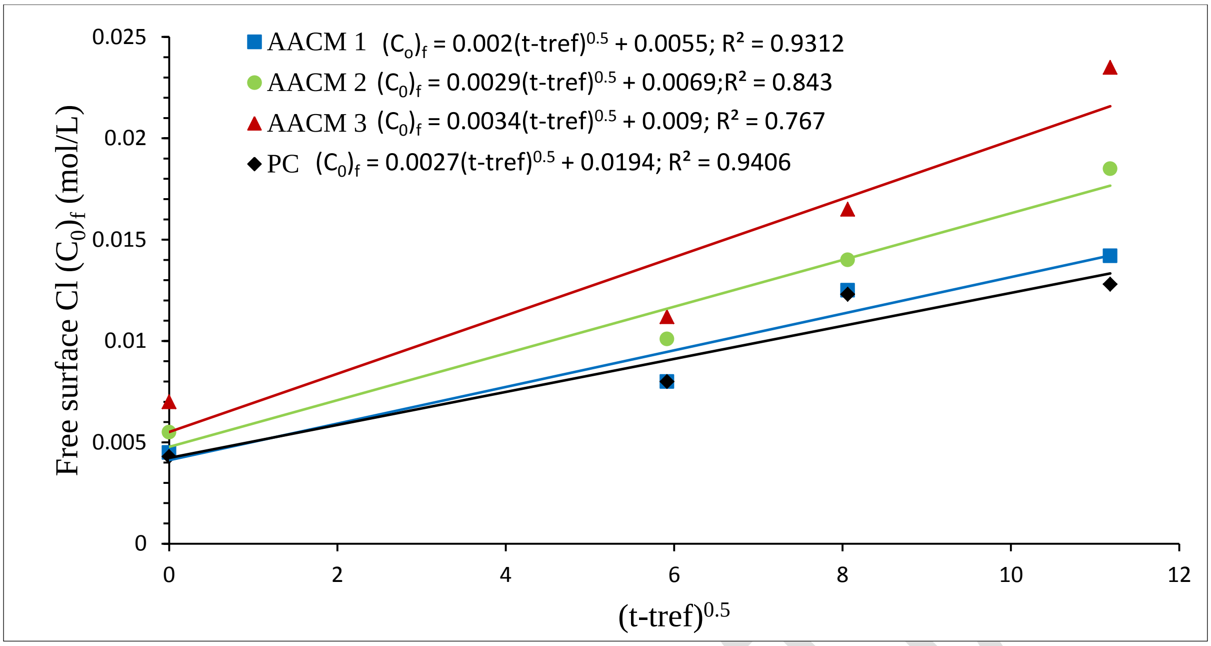

Fig. 6: Relationship between $(C_0)_f$ and square root of chloride exposure period $(t\text{-}t_{ref})^{0.5}$ for AACM 1, 2, 3 and control PC concrete.

Figure 5 shows a reduction in $(D_c)_f$ in both AACM and PC concrete while Fig. 6 shows an increase in $(C_0)_f$ with increasing chloride exposure period. The free chloride diffusion coefficient $(D_c)_f$ is lower in PC than AACM 1, 2 and 3 concrete mixes unlike the total bound chloride coefficient $(D_c)_{tb}$ which is higher in PC concrete [6]. The lower free chloride in PC concrete compared with AACM concrete is due to higher chloride binding caused in PC concrete by the formation of Friedel's salt during hydration while the AACM concrete produces less Friedel's salt as shown in Fig 1.

The resulting equations for $(D_c)_f$ and $(C_0)_f$ with exposure period are shown in Figures 5 and 6. Similar relationships have also been derived for the bound chloride diffusion parameters $(D_c)_{tb}$ and $(C_0)_{tb}$ [6].

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

The direct determination of $(D_c)_f$ is impractical in practice due to the need for concrete coring, pore fluid extraction and chemical analysis. Also, the accuracy of determining free chloride concentration is sensitive to the moisture state of concrete. An indirect approach for determining $(D_c)_f$ is to relate it to its total bound chloride coefficient $(D_c)_{tb}$ which is easier to determine with specifications given in standards [24,25]. The relationship between the free and total bound chloride diffusion coefficients, $(D_c)_f$ and $(D_c)_{tb}$, for AACM 1, 2, 3 and PC concrete is shown in Fig. 7. The data of total bound chloride diffusion coefficients $(D_c)_{tb}$ are from the previous paper by the authors [6].

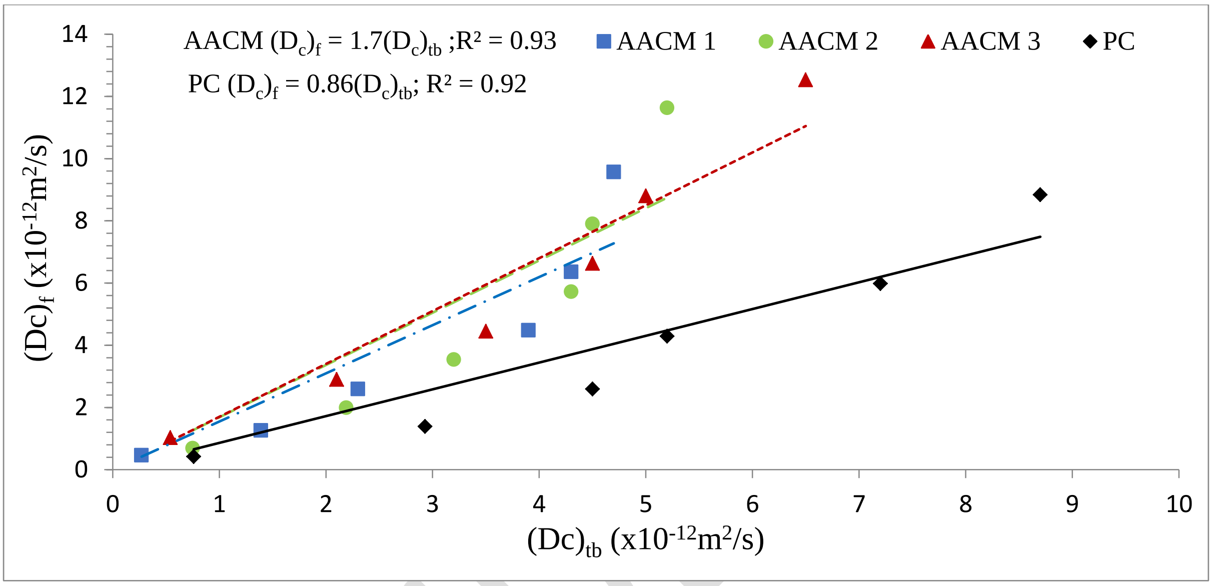

Fig. 7: Relationship between $(D_c)_f$ and $(D_c)_{tb}$ of AACM 1, 2, 3 and control PC concrete

The relationship between the free chloride diffusion coefficient $(Dc)_f$ and total bound chloride diffusion coefficient $(D_c)_{tb}$ is similar for AACM 1, 2 and 3 but different for PC concrete as shown in Fig. 7. Both concretes show a linear relationship between $(D_c)_f$ and $(D_c)_{tb}$ as follows:

For AACM concrete,

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

For PC concrete,

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

The relationship between $(D_c)_{tb}$ and $(D_c)_f$ is an important tool for service life prediction of reinforced AACM concrete because it can be used to evaluate the time taken for free chloride concentrations at the steel surface to reach critical levels and cause corrosion as discussed in the next section.

3.7 Concrete cover to reinforcement

3.7.1 Introduction

The concrete covers required to prevent reinforcement corrosion in AACM and PC concrete samples exposed to the 5% NaCl solution are calculated from the accelerated chloride diffusion data reported in this paper. The chloride concentration of the 5% NaCl solution is 0.88mol/L compared with 0.54mol/L for see water [24,25]. Therefore, the calculated covers from the experimental data represent conservative values but provide useful guidelines on the cover required in AACMs relative to PC concrete. The cover calculations are based on chloride considerations only while other factors such as pore properties and pH which could favour AACMs against reinforcement corrosion [2] are not included. These will be addressed in a future publication by the authors.

The minimum required concrete covers to steel reinforcement to prevent chloride induced corrosion were determined for AACM 1, 2, 3 and PC concrete. These values correspond to the depths at which the permissible total bound chloride value of 4mg/g (0.4%) by weight of binder has been reached. This value is stipulated in standards for conventional reinforced concrete based on the acid soluble chloride test [12]. The free chloride concentration in PC concrete corresponding to 0.4% (4mg/g) of total chloride is 0.003mol/L as shown in Fig. 3. This free chloride value of 0.003mol/L in PC concrete is, therefore, considered as the threshold for corrosion initiation since the pore fluid provides the electrolyte for the corrosion process [4]. Considering that this critical free chloride concentration (0.003mol/L) applies to both the AACM and PC concretes for corrosion initiation, the cover required to steel reinforcement is also calculated to satisfy this free chloride limit. The ratio of the cover required in AACM concrete relative to the control PC concrete at the same exposure periods for both the limits of total bound chloride (0.4%) and the corresponding free chloride limit (0.003mol/L) are plotted in Fig. 8, and discussed in section 3.6.2.

3.7.2 Cover ratios based on total bound and free chloride thresholds

The ratios of AACM to PC concrete covers at different chloride exposure periods are shown in 9. These ratios were determined based on the total bound and free chloride thresholds, as described below.

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

Concrete covers based on the total bound chloride threshold limit of 4mg/g (0.4%) by weight of binder were determined from equation 5 which is a re-arrangement of equation 4 representing Fick's 2^{nd} law of diffusion.

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

where: x is the minimum concrete cover depth (m); t is the time (seconds); $(D_c)_{tb}$ is the total bound chloride diffusion coefficient (m^2/s); $(C_0)_{tb}$ is the total bound chloride concentration on the concrete surface; C_{tb} is the total bound chloride concentration of 4mg/g (0.4%) by binder weight at the concrete cover x and time t.

For example, the cover x for AACM 1 at 180days chloride exposure is calculated by substituting the following values of parameters in equation 5:

C_{tb} = 4mg/g

t = 180 x 24 x 60 x 60 seconds

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

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

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

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

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

3.7.2.2 Cover ratios based on free chloride limit, C_f

The free chloride threshold value of 0.003mol/L which corresponds to the total bound chloride limit of 4mg/g (0.4%) in PC concrete was used as the limiting value of free chloride C_f in the calculation of cover from equation 6 which is a re-arranged form of equation 4.

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

where: x is the minimum concrete cover depth (m); t is the time (seconds); $(D_c)_f$ is the free chloride diffusion coefficient (m^2/s); $(C_0)_f$ is the free chloride concentration on the concrete surface; C_f is the free chloride threshold of 0.003mol/L at the concrete cover x at time t.

The $(D_c)_f$, $(C_0)_f$ and the limiting C_f values were then inserted into equation 6. For example, the cover x for AACM 1 at 180days chloride exposure is calculated by substituting the following values of parameters in equation 6:

C_f = 0.003mol/L

t = 180 x 24 x 60 x 60 seconds

$(D_c)_f = 2.3 \times 10^{-12} m^2/s$ and $(C_0)_f$ = 0.0142mol/L derived from nonlinear regression analysis of free chloride data in Fig.4.

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

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

The cover x values were determined for all the AACM and PC concrete mixes at exposure periods 55, 90, 120 and 180days. The cover ratios of AACM to PC concrete at different chloride exposure periods are shown in Fig. 8.

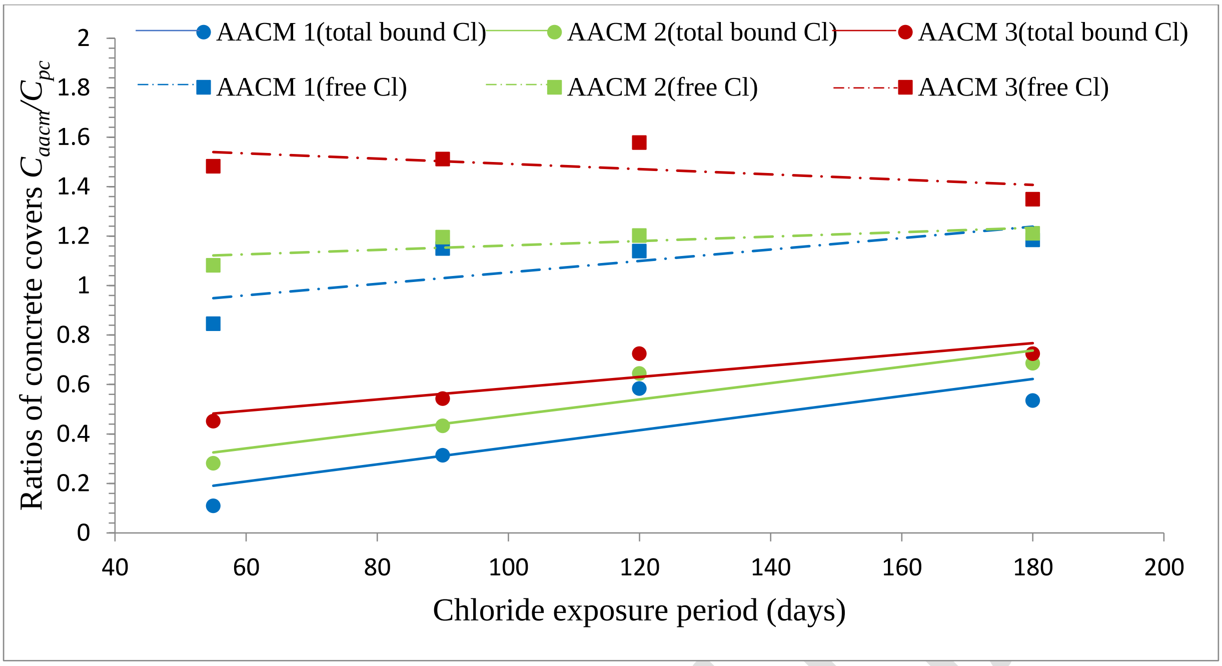

Fig. 8: Cover ratios of AACM and PC concrete with chloride exposure period based on the free and total bound chloride thresholds (the cover ratio of PC concrete is unity at all exposure periods).

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

AACM 3 concrete than an equivalent strength PC concrete if based on the free chloride limit of 0.0023mol/L which corresponds to 4mg/g of total bound chloride. The PC concrete mix is the control for the AACM 3 concrete since the two have similar strength and workability [6,7]. The cover ratios of higher strength AACMs 1 and 2 concrete decrease towards unity. This result assumes that the chloride threshold limits for corrosion initiation in AACM and PC concrete are the same and their porosity and pH are not considered.

3.8 Free Cl^- diffusion parameters and porosity relationship

Figure 9 shows the relationships between porosity and free chloride diffusion parameters $(D_c)_f$ and $(C_0)_f$ of AACM concrete. The porosity data represents mortar mixes with the same binder and activator content (liquid/binder ratio of 0.47) as the concrete mixes of this study. The pore properties which were determined by mercury intrusion porosimetry have been reported by the authors [7,38] and represent AACM mixes with different pore properties such as pore interconnectivity due to differences in the molarity of activator (activator dilution) used in each mix (Table 1) and wet, wet/dry and dry curing conditions.

The relationship between porosity and free chloride diffusion parameters in Fig 9 does not apply to PC concrete or AACMs with different C_3A content affecting binding properties, such as fly ash based AACMs. For example, 13.3% porosity in PC concrete gave free chloride diffusion parameters $(D_c)_f$ and $(C_0)_f$ of 1.1 x $10^{-12}m^2/s$ and 0.0128mol/L respectively, which fall outside the curves in Fig.9.

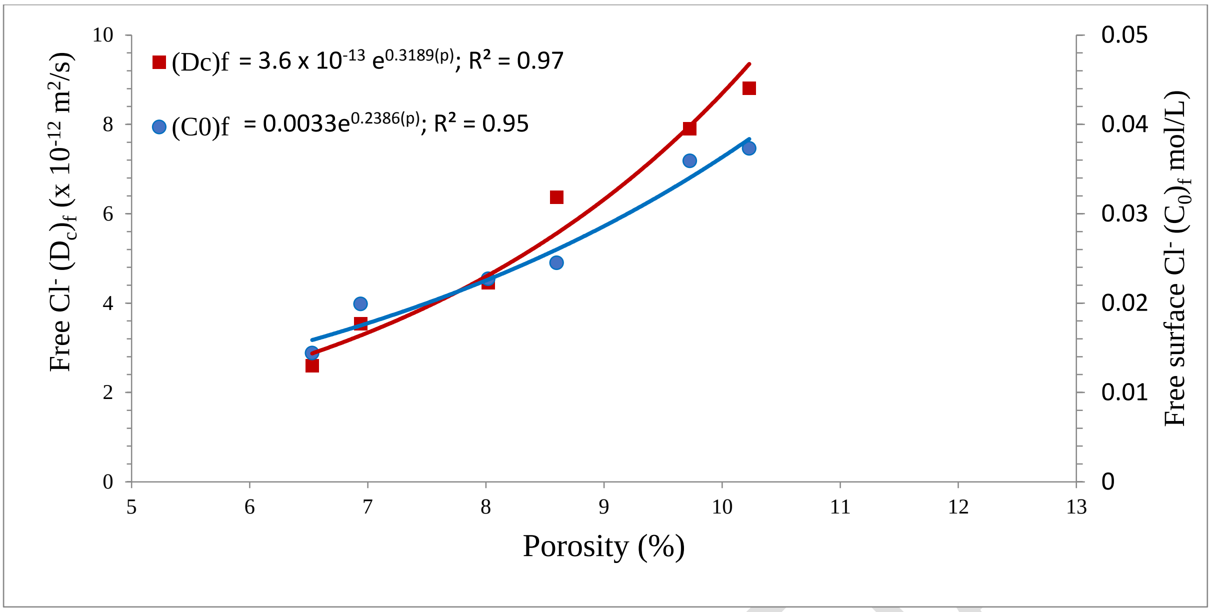

Fig. 9: Relationship between free chloride diffusion parameters and porosity of AACM 1, 2 and 3 concrete mixes.

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 $3.34 \times 10^{-12} m^2/s$ and $8.69 \times 10^{-12} m^2/s$ 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.

The chloride diffusion parameters are related to porosity [39] and also chloride binding capacity in concrete as shown in this study. Each data point in Figure 9 reflects different grades of ggbs based AACM concrete mixes having different formation and interconnectivity of pores, which are reported elsewhere by the authors [7]. The line curves between chloride diffusion parameters and porosity show high level of correlation thus validating that the relationship can be transferred to other types of ggbs based AACM concrete.

4.0 Conclusions

The free chloride diffusion parameters and chloride binding capacity of an alkali activated concrete (AACM) together with a control Portland cement (PC) concrete were determined in this paper. AACM and PC concretes were immersed in a 5% NaCl solution for 540days to determine their free chloride diffusion properties. Freundlich and Langmuir isotherms were used to define the relationship between the free and bound chlorides. The following conclusions can be drawn from the study,

- A greater amount of Friedel's salt (FS) is present in PC than AACM mortar when exposed to a chloride environment. The hydration and geopolymerization products have mass losses of 22% and 12% in PC and AACM concrete respectively after heating to 1000^0C.
- Langmuir binding isotherm is valid for the relationship between free and bound chloride in both AACM and PC concrete for the range at free chloride concentrations 0.01 to 0.036mol/L investigated. The following equation gives the relationship;

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

  where the values of α are 1.8, 1.3, 1.2 for AACM concrete of different activator molarity and 2.5 for PC concrete while the values of β are 7 for all AACMs and 2 for PC concrete

- 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 more conservative parameter to design against chloride induced corrosion in AACM concrete. Increasing molarity of the activator reduces the required cover in AACMs. However, this conclusion on cover requirement is based on chloride concentrations only and other factors such as pH affecting corrosion will be evaluated in future publications.

- 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 Cl^- (mol/L) and diffusion coefficient (m^2/s) respectively and p is the porosity (%).

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the Materials and Engineering Research Institute, Sheffield Hallam University and the funding provided to the second author for postgraduate study by the Tertiary Education Trust Fund, Ministry of Education, Federal Republic of Nigeria. The authors also acknowledge the recent award by the UK - India Newton - Bhabha programme through funding provided by Innovate UK, EPSRC (EP/P026206/1) and the Government of India for research on AACMs.

Funding: This study was funded by Innovate UK, EPSRC and the Government of India (Grant No.: EP/P026206/1) and Tertiary Education Trust Fund, Ministry of Education, Federal Republic of Nigeria

Conflict of Interest Statement: The authors declare that they have no conflict of interest.

REFERENCES

[1] P.C. Aïtcin, Cements of yesterday and today - concrete of tomorrow, Cem. Concr. Res. 30 (2000) 1349–1359. https://doi.org/10.1016/S0008-8846(00)00365-3.

[2] John L. Provis, J.S.J. van Deventer, Alkali-Activated Materials State-of-the-Art Report, RILEM TC 224-AAM, 2014.

[3] N.A. Madlool, R. Saidur, M.S. Hossain, N.A. Rahim, A critical review on energy use and savings in the cement industries, Renew. Sustain. Energy Rev. 15 (2011) 2042–2060. https://doi.org/10.1016/j.rser.2011.01.005.

[4] A.M. Neville, Properties of Concrete, Pearson Education Limited, 2011.

[5] P. Lambert, C.L. Page, P.R.W. Vassie, Investigations of reinforcement corrosion. 2. Electrochemical monitoring of steel in chloride-contaminated concrete, Mater. Struct. 24 (1991) 351–358. https://doi.org/10.1007/BF02472068.

[6] P.S. Mangat, O.O. Ojedokun, Bound chloride ingress in alkali activated concrete, Constr. Build. Mater. 212 (2019) 375–387. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2019.03.302.

[7] P.S. Mangat, O.O. Ojedokun, Influence of curing on pore properties and strength of alkali activated mortars, Constr. Build. Mater. 188 (2018) 337–348. https://doi.org/10.1016/J.CONBUILDMAT.2018.07.180.

[8] B.H. Oh, S.Y. Jang, Y.S. Shin, Experimental investigation of the threshold chloride concentration for corrosion initiation in reinforced concrete structures, in: Mag. Concr. Res., 2003: pp. 1–9. https://doi.org/10.1680/macr.55.2.117.37558.

[9] G.K. Glass, N.R. Buenfeld, The influence of chloride binding on the chloride induced corrosion risk in reinforced concrete, Corros. Sci. (2000). https://doi.org/10.1016/S0010-938X(99)00083-9.

[10] Q. Yuan, C. Shi, G. De Schutter, K. Audenaert, D. Deng, Chloride binding of cement-based materials subjected to external chloride environment - A review, Constr. Build. Mater. 23 (2009) 1–13. https://doi.org/10.1016/j.conbuildmat.2008.02.004.

[11] T. Luping, L.O. Nilsson, Chloride binding capacity and binding isotherms of OPC

pastes and mortars, Cem. Concr. Res. 23 (1993) 247–253. https://doi.org/10.1016/0008-8846(93)90089-R.

[12] BS EN 206, Concrete — Specification, performance, production and conformity, British Standards Institution, 2014.

[13] BS 882:1992, Specification for aggregates from natural sources for concrete, British Standards Institution, 1992.

[14] O.O. Ojedokun, P.S. Mangat, Chloride diffusion in alkali activated concrete, in: II Int. Conf. Concr. Sustain. ICCS16, Madrid, Spain, 2016: pp. 521–530.

[15] G. Plusquellec, M.R. Geiker, J. Lindgard, J. Duchesne, B. Fournier, K. De Weerdt, Determination of the pH and the free alkali metal content in the pore solution of concrete: Review and experimental comparison, Cem. Concr. Res. 96 (2017) 13–26. https://doi.org/10.1016/j.cemconres.2017.03.002.

[16] U.A. Birnin-Yauri, F.P. Glasser, Friedel’s salt, Ca2Al(OH)6(Cl,OH)·2H2O: Its solid solutions and their role in chloride binding, Cem. Concr. Res. 28 (1998) 1713–1723. https://doi.org/10.1016/S0008-8846(98)00162-8.

[17] J.O. Ukpata, P.A.M. Basheer, L. Black, Slag hydration and chloride binding in slag cements exposed to a combined chloride-sulphate solution, Constr. Build. Mater. 195 (2019) 238–248. https://doi.org/10.1016/j.conbuildmat.2018.11.055.

[18] C. Shi, X. Hu, X. Wang, Z. Wu, G. de Schutter, Effects of Chloride Ion Binding on Microstructure of Cement Pastes, J. Mater. Civ. Eng. 29 (2016) 04016183. https://doi.org/10.1061/(asce)mt.1943-5533.0001707.

[19] H. Zibara, R.D. Hooton, M.D.A. Thomas, K. Stanish, Influence of the C/S and C/A ratios of hydration products on the chloride ion binding capacity of lime-SF and lime-MK mixtures, Cem. Concr. Res. 38 (2008) 422–426. https://doi.org/10.1016/j.cemconres.2007.08.024.

[20] J. Tritthart, Pore solution of concrete: The equilibrium of bound and free chloride, in: Mater. Corros., 2009. https://doi.org/10.1002/maco.200905277.

[21] M.D.A. Thomas, R.D. Hooton, A. Scott, H. Zibara, The effect of supplementary cementitious materials on chloride binding in hardened cement paste, Cem. Concr. Res. 42 (2012) 1–7. https://doi.org/10.1016/j.cemconres.2011.01.001.

[22] I. Galan, F.P. Glasser, Chloride in cement, Adv. Cem. Res. 27 (2015) 63–97. https://doi.org/10.1680/adcr.13.00067.

[23] M.R. Rixom, N.P. Mailvaganam, Chemical Admixture for Concrete, 2nd Editio, E. & F.N. Spon Ltd, New York, 1986.

[24] NT BUILD 443, Concrete, Hardened: Accelerated Chloride Penetration, 1995.

[25] DD CEN/TS 12390-11, DD CEN/TS 12390-11: Testing hardened concrete, Part 11: Determination of the chloride resistance of concrete, unidirectional diffusion, 2010.

[26] ASTM C-1218-15, Standard Test Method for Water-Soluble Chloride in Mortar and Concrete, Practice. 15 (2012) 15–17. https://doi.org/10.1520/C1218.

[27] J. Zhang, C. Shi, Z. Zhang, Chloride binding of alkali-activated slag/fly ash cements, Constr. Build. Mater. 226 (2019) 21–31. https://doi.org/10.1016/j.conbuildmat.2019.07.281.

[28] J. Zhang, C. Shi, Z. Zhang, Z. Ou, Durability of alkali-activated materials in aggressive environments: A review on recent studies, Constr. Build. Mater. (2017). https://doi.org/10.1016/j.conbuildmat.2017.07.027.

[29] M.N. Haque, O.A. Kayyali, Free and water soluble chloride in concrete, Cem. Concr. Res. 25 (1995) 531–542. https://doi.org/10.1016/0008-8846(95)00042-B.

[30] B. Ma, T. Zhang, H. Tan, X. Liu, J. Mei, W. Jiang, H. Qi, B. Gu, Effect of TIPA on Chloride Immobilization in Cement-Fly Ash Paste, Adv. Mater. Sci. Eng. (2018). https://doi.org/10.1155/2018/4179421.

[31] N. Tsuyuki, Y. Umemura, Effects of Chemical admixture and Mineral admixture on the Penetration of Chloride Ion and Chloride Binding Capacity, Concr. J. (2001). https://doi.org/10.3151/coj1975.39.7_19.

[32] N.K. Lee, H.K. Lee, influence of the slag content on the chloride and sulfuric acid resistances of alkali-activated fly ash/slag paste, Cem. Concr. Compos. 72 (2016) 168–179. https://doi.org/10.1016/j.cemconcomp.2016.06.004.

[33] R. Collepardi, M., Marcialis, A, and Turrizuani, The Kinetics of Chloride ions Penetration in Concrete, II Cem. 67 (1970) 157–164.

[34] P.B. Bamforth, W.F. Price, M. Emerson, An international review of chloride ingress into structural concrete, Contract. Report. (1997) 162.

[35] M. Maage, S. Helland, E. Poulsen, Ø. Vennesland, J.E. Carlsen, Service life prediction of existing concrete structures exposed to marine environment, ACI Mater. J. 93 (1996) 602–608. https://doi.org/http://dx.doi.org/10.14359/9866.

[36] P.S. Mangat, K. Gurusamy, Long-term properties of steel fibre reinforced marine concrete, Mater. Struct. 20 (1987) 273–282. https://doi.org/10.1007/BF02485924.

[37] P.S. Mangat, B.T. Molloy, Prediction of long term chloride concentration in concrete, Mater. Struct. 27 (1994) 338–346. https://doi.org/10.1007/BF02473426.

[38] O.O. Ojedokun, P.S. Mangat, Characterization and pore structure of rice husk ash cementitious materials, in: Am. Concr. Institute, ACI Spec. Publ., 2018.

[39] K.D. Stanish, R.D. Hooton, M.D.A. Thomas, Testing the Chloride Penetration Resistance of Concrete: A Literature Review, 1997.