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1 **Chloride binding and diffusion in slag blends: influence of slag composition**

2 **and temperature**

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11 **Abstract**

12 This study has investigated the impact of a change in GGBS chemical composition

13 on the chloride ingress resistance of slag blended cements under different

14 temperature regimes. Two slags, having alumina contents of 12.23 and 7.77%

15 respectively, were combined with a CEM I 52.5 R at 30 wt% replacement. Chloride

16 binding and diffusion tests were conducted on paste and mortar samples

17 respectively. All tests were carried out at temperatures of 20℃ and 38℃. The higher

18 temperature resulted in an increase in chloride binding; attributed to greater degrees

19 of slag hydration. Despite this, chloride ingress was greater at 38℃; attributed to

20 changes in the pore structure and the chloride binding capacities of the slag blends.

21 The more reactive, aluminium-rich slag performed better in terms of chloride binding

22 and resistance to chloride penetration, especially at the high temperature and this

23 was attributed to its higher alumina content and greater degree of reaction at 38℃.

24 Keywords: Chloride binding, Granulated Blast-Furnace Slag, Temperature, Diffusion,

25 Microstructure

1. Introduction

Chloride-induced corrosion of steel reinforcement is one of the major causes of premature deterioration and degradation of concrete structures built in marine environments. Chlorides may be introduced into concrete through a variety of routes, for example as de-icing salts, through the penetration of seawater, through the use of aggregates contaminated with chlorides or through the mix water [1]. The presence of chlorides in concrete may cause disruption to the passive film on the surface of steel reinforcement, thereby accelerating corrosion.

Chlorides in concrete exist either as free ions dissolved in the pore water, or bound. The bound chlorides are either chemically bound with the tricalcium aluminate (C_3A) phase in the form of Friedel's salt ($3CaO.Al_2O_3.CaCl_2.10H_2O$) and Kuzel's salt ($3CaO \cdot Al_2O_3 \cdot 1/2CaCl_2 \cdot 1/2CaSO_4 \cdot \sim 11H_2O$) or physically bound to the surface of the hydration products (C-S-H gel). It is the free chlorides present in the pore water that are responsible for steel depassivation, so when more chlorides are bound, less free chlorides will be available for depassivation. Several factors have been reported to affect the formation of bound chlorides, such as the quantity of C_3A in the cement, the incorporation of supplementary cementitious materials (SCMs) in the mix, the alkalinity of the pore solution, the cation type of the salt, and the presence of other anions, like sulphates and carbonates [2–9].

The use of ground granulated blast furnace slag (GGBS), a common SCM, to partially replace Portland cement in the making of concrete has been shown to be beneficial in terms of chloride binding and resistance to the penetration of chloride ions [3,10–13]. This has been reflected in standards, e.g. EN197-1, where CEM IIA/B-S and CEM III A/B/C cements are commonly used for marine construction. The improved chloride resistance of slag composite cements has been attributed to

51   their high alumina content [3,10–12], which increases the tendency for Friedel's salt

52   formation. Furthermore, slag composite cements also contain more C-S-H phase,

53   which is responsible for the binding of about two-thirds of the chloride [14].

54   Generally, the higher the level of slag replacement, the higher the chloride binding

55   capacity [3]. A recent study by Otieno et al. [13] showed that particle fineness, as

56   well as difference in chemical composition of slags, had an impact on their chloride

57   ingress resistance. However, amongst the three types of slags they studied, only one

58   of them was GGBS. The other two were by-products of the Corex process and FeMn

59   arc-furnace slag.

60   In practice, while the chemical composition of GGBS from a single plant may be

61   constant, due to the varying sources from which GGBS is obtained the chemical

62   composition from plant to plant may vary. The chemical composition has often been

63   used as an indicator of the slag's reactivity. Oxide/basicity ratios have been

64   prescribed by several authors [15–17] for assessing the reactivity of slags. These are

65   usually based on the CaO, Al_2O_3, MgO and SiO_2 contents. While it is known that the

66   chemical composition of a slag is important as it may affect its performance, the

67   relationship between composition and performance is not clear-cut. Several

68   researchers have investigated the impact of variation of chemical composition of

69   GGBS on its performance, but most of these studies have been focused on the

70   strength performance [16–19].

71   Apart from the chemical composition, other factors such as the glass content,

72   particle fineness, alkalinity of the reacting system and temperature, have also been

73   reported to affect the reactivity of slags [20]. For example, in a recent work by the

74   authors [21] it was shown that temperature had more influence on the reactivity of

75   slags than the difference in chemical composition. Due to the variability in the use of

76   GGBS as an SCM in different temperature environments, like the tropical and

77   temperate regions, it is important to look at how temperature affects the performance

78   of slag blended cements in chloride environments. This paper focuses on the impact

79   of a difference in slag composition on the chloride binding and diffusion in slag

80   blended cements, relating it to the microstructure, and how the whole process is

81   affected by changes in both curing and testing temperature.

82   **2. Materials and methods**

83   2.1 Materials

84   Two slags (S1 and S2) were selected for this study, alongside a CEM I 52.5 R,

85   designated as C52.5R. Both slags met the requirement as specified in EN 197-

86   1:2011 [22]. They had similar physical properties and particle morphologies, but

87   different chemical compositions. The $CaO+MgO/SiO_2$ of slag 1 (1.28) was higher

88   than that of slag 2 (1.18). The oxide and phase composition of the as-received

89   cementitious materials are shown in Table 1. The particle size distribution of the

90   slags and the X-ray diffraction patterns are shown in Fig. 1 and Fig. 2 respectively.

91   Other physical properties of the cementitious materials are shown in Table 2. The

92   fine aggregate used complied with the specification for fine aggregates as given in

93   EN 12620:2002+A1.

94 **Table 1:** Oxide and phase composition of the cementitious materials

Oxide composition (%)				Phase composition (%)		
	C52.5 R	S1	S2		C52.5R	S1	S2
LOI 950℃	2.54	(+1.66)	(+0.40)*	Alite, C_3S	62.1		
SiO_2	19.10	36.58	40.14	Belite, C_2S	8.9		
Al_2O_3	5.35	12.23	7.77	C_3A	9.1		
TiO_2	0.25	0.83	0.30	Ferrite, C_4AF	8.5		
MnO	0.03	0.64	0.64	Calcite	1.8	0.3	0.5
Fe_2O_3	2.95	0.48	0.78	Anhydrite	0.6		
CaO	62.38	38.24	37.90	Hemihydrate	2.4		
MgO	2.37	8.55	9.51	Gypsum	1.7		
K_2O	1.05	0.65	0.55	Others	5.0		
Na_2O	0.05	0.27	0.36	Merwinite		<0.1	2.3
SO_3	3.34	1.00	1.47	Akermanite		0.2	<0.1
P_2O_5	0.10	0.06	0.02	Illite		0.2	<0.1
Total	99.50	99.88	99.43	Total crystalline phases	100.1	0.7	2.9
Na_2O equiv.	0.74			Glass content		99.3	97.1

95 *The sample was oxidized with HNO_3 before the determination of LOI

96 **Table 2:** Physical properties of cementitious materials

Property	Unit	C52.5R	S1	S2
Density	g/cm^3	3.18	2.94	2.95
Blaine	cm^2/g	5710	4490	4090
Particle size, d50	μm	-	11.0	11.9
Workability from flow table test	mm	-	13.13	13.55

97

98

99 **Fig. 1.** Particle size distribution of slag 1 and slag 2

C   Mw
Ml
S1
S2

10   20   30   40   50   60   70
2θ (⁰)

C - Calcite, Ml - Melilite, Mw - Merwinite

100

Fig. 2. XRD of the anhydrous slags

2.2 Details of mixes, curing and exposure conditions

Two series of mixes were used for this study, with each slag being combined with a CEM I 52.5 R at 30% replacement level to produce blends designated as CS1 and CS2 respectively. The blends were prepared by mixing the various portions of the slag and cement in a laboratory ball mill for a period of about 4 hours, using polythene balls as charges.

Mortar samples were prepared and cured in accordance with EN 196-1:2005 [23]. The details of the mixes are shown in Table 3. Mixing was done in batches using a Hobart mixer. Each batch contained approximately 450 grams of cementitious materials, 1350 grams of fine aggregates and 225 grams of water. After mixing, the mortar samples were poured into moulds of 40 x 40 x 160 mm prisms or 50 mm cubes, covered with thin polythene sheets and left to cure under ambient laboratory conditions for a period of 20 – 24 hours. After the initial curing, the samples were de-moulded and cured under water at two different temperatures (20℃ and 38℃) for a period up to 28 days. 20℃ was chosen as a reference temperature, w hich is typical

117   of laboratory conditions, while 38℃ was chosen as a representative temperature for

118   tropical, arid or semi-arid zones.

119   **Table 3:** Mix ratios for the mortar specimens

Mix	w/b	C52.5R	S1	S2	Water	Fines
1	0.5	0.7	0.3	0	0.5	3
2	0.5	0.7	0	0.3	0.5	3

120

121   Cement paste samples were prepared by manual mixing of the cementitious

122   materials and water by hand for 2 mins. After mixing, the resulting paste was poured

123   into 14 or 25 mm ϕ cylindrical plastic vials. The top of the plastic vials were sealed

124   with polythene and allowed to rotate vertically at 20 rpm for 24 hours so as to

125   prevent bleeding. After 24 hours, the samples were demoulded and cured in

126   saturated lime water at temperatures of 20℃ or 38℃.

127   After curing, the mortar samples used for the chloride ingress studies were

128   submerged in 3% NaCl solutions kept at temperatures of 20℃ or 38℃, for up to 90

129   days. For the samples exposed at 20℃, the solutions were renewed every 4 weeks

130   to maintain the salinity of the solution, and the liquid to solid ratio was kept above

131   12.5 millilitres per square centimetre of exposed surface as specified in EN

132   12390:2015 [24]. For the samples exposed to the sodium chloride solution at 38℃,

133   the solutions were renewed every fortnight so as to minimise the effect of

134   evaporation on the salinity of the solutions.

135   2.3 Test methods

136   2.3.1 Chloride binding

137   Paste samples that had been cured for 8 weeks were wet-crushed and water-sieved

138   to obtain particles ranging in size from 250 to 630 microns. The samples were dried

139 under a moderate vacuum (0.75 bar) in a desiccator at room temperature for a

140 period of 3 days to remove most of the water, then stored in a desiccator with

141 decarbonized air at 11%RH kept by saturated LiCl solution for 14 days.

142 Bound chloride content was measured using the equilibrium method, as developed

143 by Luping and Nilsson [25]. 20g of the sample dried at 11%RH was put in a plastic

144 cup and filled with approximately 50 ml of a given concentration of NaCl solution

145 saturated with $Ca(OH)_2$. The cup was sealed and stored at temperatures of either 20

146 or 38°C for a period of 6 weeks, to attain equilibrium. After equilibri um was reached,

147 the chloride concentration of the resulting solution was determined by ion

148 chromatography. Knowing the initial concentration of the NaCl solution, the content

149 of bound chlorides was determined using the expression:

150

$$C_b = \frac{35.45V(C_i - C_f)}{W} \tag{1}$$

151   where:

152   C_b bound chloride content in mg/g-sample

153   V   volume of solution in ml

154   C_i initial concentration of the chloride solution in mol/l

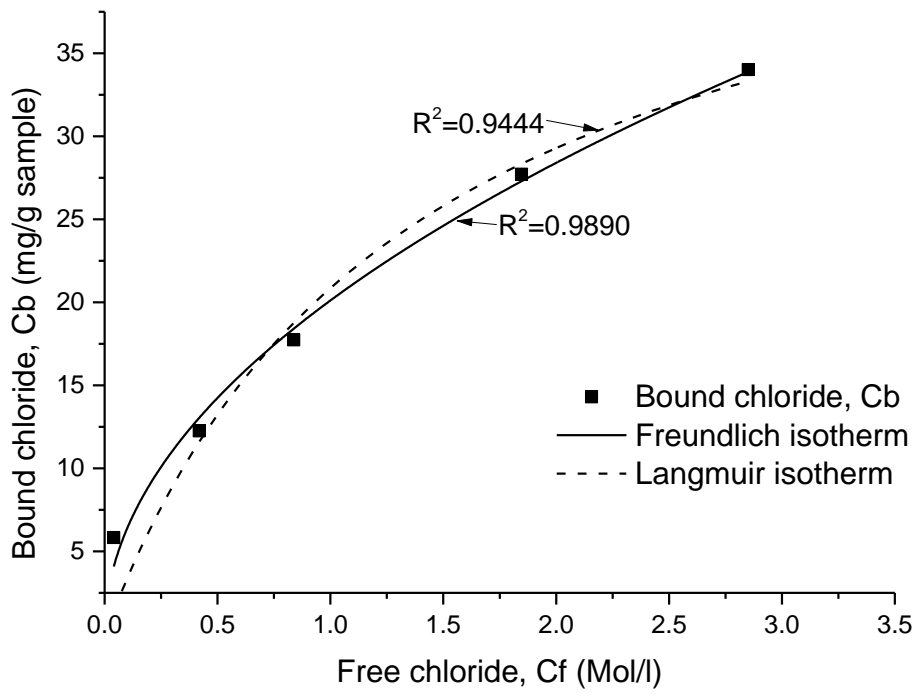155 C_f equilibrium concentration of the chloride solution in mol/l

156   W   weight of the dry sample in g, which is calculated from the difference in

157   weight of the sample dried in a desiccator at 11%RH and in an oven at

158   105°C.

159 In order to obtain chloride binding isotherms, various concentrations of NaCl solution

160 were used (0.1, 0.5, 1.0, 2.0 and 3.0M). The bound chloride content (C_b) obtained

161 was then plotted against the equilibrium concentration (C_f), after which the chloride

162 binding coefficients (α and β) of the mixes were determined using Freundlich and

163 Langmuir binding isotherms [12] shown respectively in the equations below:

$$C_b = \alpha C_f^{\beta} \tag{2}$$

$$C_b = \frac{\alpha C_f}{\left(1 + \beta C_f\right)} \tag{3}$$

164   Fig. 3 shows the chloride binding coefficients α and β obtained for one of the mixes

165   using Freundlich and Langmuir binding isotherms. The Freundlich binding isotherm

166   has been widely used by several researchers [12,26–28], and from the figure, it is

167   seen that it gives the best fit to the data; hence it was used in determining the

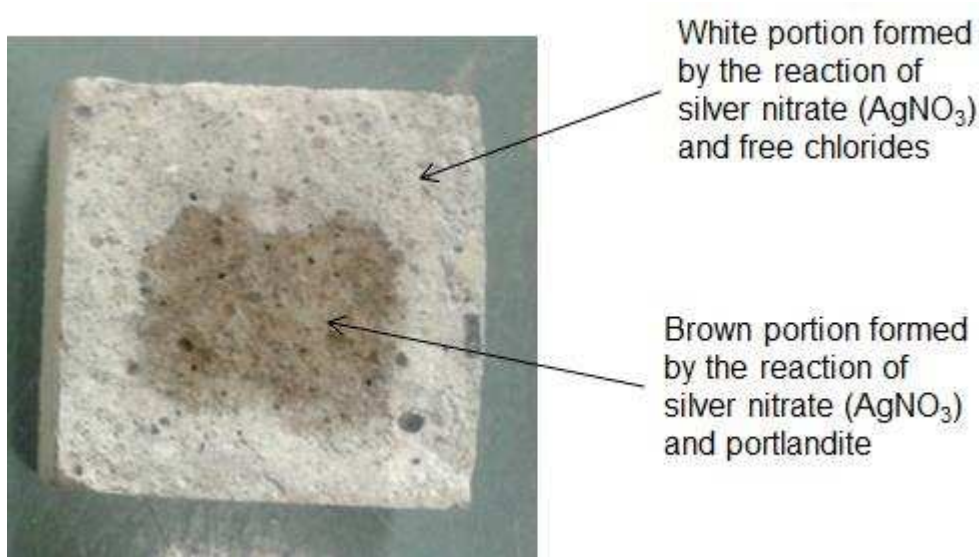168   chloride binding coefficients of all the mixes.

169
170   **Fig. 3.** Best fit binding isotherm for determining chloride binding coefficients

171   2.3.2 Penetration of free chlorides

172   The depth of free chloride ion penetration was determined using the silver nitrate

173   (AgNO$_3$) spray technique. 50 mm mortar cubes were initially cured for 28 days, at

174   temperatures of 20℃ and 38℃. They were then immers ed in a 3% NaCl solution

175   and withdrawn at 14, 28, 56 and 90 days to determine the depths of chloride ion

176   penetration. The withdrawn samples were split in half and the surfaces of the freshly

177   split samples were sprayed with a 0.1M AgNO$_3$ solution. The presence of free

178 chlorides was indicated by the formation of a white precipitate of silver chloride

179 (AgCl), while in the absence of free chlorides the reaction between silver nitrate and

180 portlandite resulted in a brown coloration, due to the formation of silver hydroxide

181 (Fig. 4). By taking linear measurements from the edge of the specimen up to the

182 colour change boundary, the depth of free chloride penetration could be determined.

183 Six to eight measurements were taken per sample. It should be noted that this

184 technique can only indicate the presence of free chloride ion if the concentration is

185 greater than 0.15% by weight of cement [29].

White portion formed
by the reaction of
silver nitrate ($AgNO_3$)
and free chlorides

Brown portion formed
by the reaction of
silver nitrate ($AgNO_3$)
and portlandite

186

187 **Fig. 4.** Colour changes for chloride ingress sample sprayed with 0.1M $AgNO_3$
188 solution
189

190 2.3.3 Acid soluble or total chloride content

191 40 x 40 x 160 mm mortar samples were cast and cured for 28 days at temperatures

192 of 20°C and 38°C. After curing, about 20 mm thick slice was sawn off from one end

193 of the samples so as to obtain a fresh surface. An epoxy – based paint was used to

194 coat all the sides of the sample except the fresh surface so as to allow for

195 unidirectional chloride ingress. The coated samples were left in the laboratory for 2

196 days to allow for proper curing of the paint, after which they were saturated in

deionised water for 24 hours. The saturated samples were then immersed in a tub containing 3% NaCl solution for an exposure/ soaking period of 90 days. The liquid to solid ratio was kept above 12.5 millilitres per square centimetre of exposed surface as recommended in EN 12390:2015 [24], all through the exposure period.

At the end of the exposure period, the samples were removed from the tub and wiped dry with a clean cloth. Layers were extracted from the sample by dry cutting. The thickness of the cutting blade was approximately 3 mm. A total of 7 layers (each approximately 5 mm thick) were cut from each sample (See Fig. 5). After cutting, each of the layers was placed in separate polythene bags for grinding. Grinding was done for most of the samples using a mortar and a pestle. The samples were ground such that the particles would pass through a 300 microns sieve. The ground samples were further dried in an oven at 105°C for 24 hours before they were analysed for total chloride content.

Total chloride content was determined for each layer using the procedure recommended by RILEM [30]. About 1 gram of the dried samples was weighed and placed in a beaker. 50 ml of concentrated nitric acid (HNO_3) diluted to 1 in 2 parts was added to the sample. After the effervescence had stopped, the solution was heated and allowed to boil for about 1 min. 5 ml of 0.1N silver nitrate solution ($AgNO_3$) was added to the beaker and the resulting solution was allowed to boil for another 1 min. After this, the solution was allowed to cool down to room temperature and filtered over a filter paper under vacuum. The filter paper and beaker were washed with diluted HNO_3 (diluted to 1 in 100 parts), and collected alongside the filtrate. The final volume of the filtered solution was made up to 200 ml by adding diluted HNO_3. This was titrated against a 0.05M ammonium thiocyanate solution (NH_4SCN). A blank test was also run using the same procedure outlined above, but

222 without any sample. The total chloride content per mass of the dried sample was

223 determined using the expression below:

$$\%Cl = \frac{3.5453 V_{Ag} M_{Ag} (V_2 - V_1)}{m V_2} \tag{4}$$

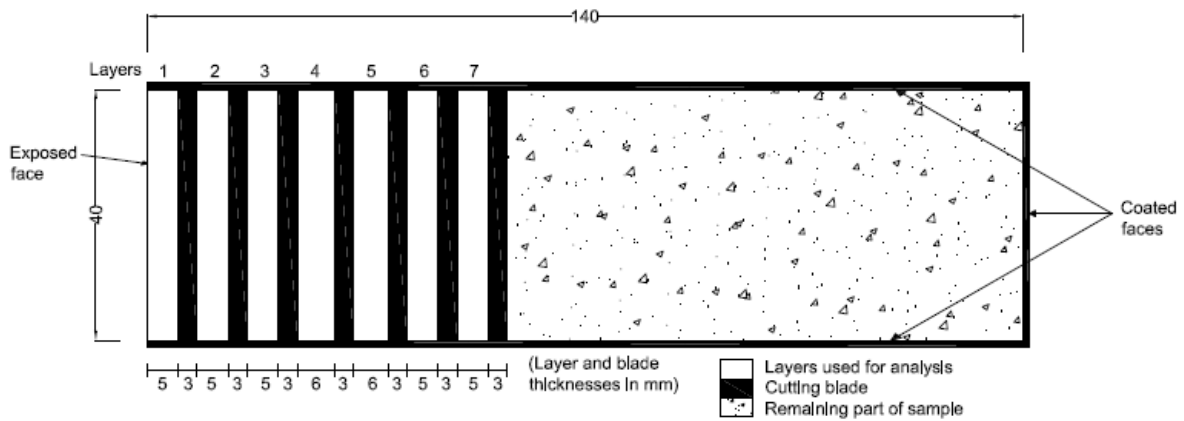224   where:

225   V_{Ag} volume of $AgNO_3$ added in cm^3

226   M_{Ag} molarity of the $AgNO_3$ solution

227   V_1 volume of NH_4SCN used in the sample in cm^3

228   V_2 volume of NH_4SCN used in the blank test in cm^3

229   m   mass of the dried sample used for the test in grams

230 At least three measurements were taken per layer, depending on the amount of

231 ground sample obtained from the cutting and grinding process. The average total

232 chloride content obtained per layer was plotted against the distance of the centre of

233 each layer from the exposed face (fresh surface), to obtain total chloride profiles.

234

235 **Fig. 5.** Schematic showing how layers were extracted from samples after ponding in
236 3% NaCl solution for 90 days at 20 and 38℃

237 2.3.4 Water soluble chloride content

238 Water soluble chloride content is defined here, as the amount of chloride ion in a

239 concrete specimen which can be leached out by water at room temperature [31]. It

240 should be noted that this is not the same as the free chloride content, which is taken

241 as the amount of chloride ion dissolved in the pore solution that can be obtained by

242 squeezing concrete samples at high pressures [31].

243 In determining the water soluble chloride content, 5 grams of ground sample was

244 taken from each layer of the samples used for the total chloride content

245 determination test. The ground sample was placed in a plastic bottle. A solid to liquid

246 ratio of 1:20 was used [32], hence 100 ml of distilled water was added to the sample

247 and the plastic bottle was sealed and left to stand for 72 hours at 20℃. A t the end of

248 the standing period, the solution was filtered off and the chloride concentration of the

249 filtrate was determined by ion chromatography.

250 The water soluble chloride content, which was taken as the chloride concentration of

251 the filtrate, was expressed in parts per million (ppm) and plotted against the distance

252 of the centre of each layer from the exposed face, to obtain the water soluble

253 chloride profile.

254 2.3.5 SEM-BSE image analysis

255 SEM-BSE image analysis does not provide a detailed 3-dimensional representation

256 of the pore structure, but it can be used to assess the coarse porosity of paste

257 samples [43]. 2 mm thick discs were cut from 28 days old paste samples, which had

258 been cured under saturated lime water at 20℃ and 38℃ . The samples were

259 hydration stopped using isopropanol, then resin impregnated before polishing. BSE-

260 SEM images were collected for the polished samples using a Carl Zeiss EVO SEM.

261 An accelerating voltage of 15keV was used, combined with a spot size of 500 nm.

262 Electron images were collected at a magnification of x800 and a working distance of
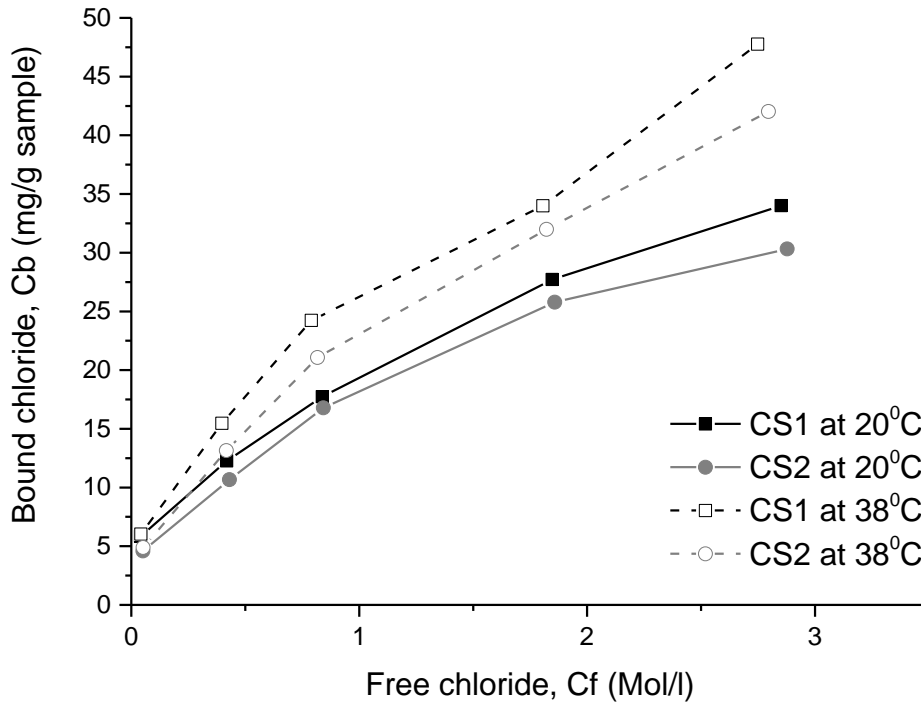
263 8 – 8.5 mm.

264 This approach enabled differentiation between anhydrous material, hydrated paste

265 and pores. The latter features usually appear as dark spots in the electron images

266 and can be easily distinguished from the hydrated phases by image analysis [33,34].

267 A total of 50 electron images were collected per sample at random and analysed,

268 and the average was taken as the degree of coarse porosity.

269 **3. Results and discussion**

270 3.1 Chloride binding

271 3.1.1 Influence of slag composition

272 Fig. 6 shows the bound chloride content, C_b, obtained from the samples exposed to

273 the different concentrations (C_i) of NaCl solution at 20°C and 38°C. The bound

274 chloride levels were greater for sample CS1 than CS2, and at higher temperatures.

275 There are two explanations for the differences in chloride binding between the two

276 slag blends. Bound chloride in blend CS1, with an overall bulk alumina content of

277 about 7.41%, was consistently higher than that of CS2 (alumina content of 6.08%).

278 Several studies have shown that chloride binding increases with the alumina content

279 [3,10–12] and decreases with the sulphate content [6,11,35] of the cementitious

280 materials. Secondly, it is known that chlorides are also bound on to C-S-H. Previous

281 work has shown that the more basic slag 1 ((C+M)/S = 1.28) hydrated to a greater

282 degree than slag 2 ((C+M)/S = 1.18). As shown in Table 4, after 28 days, about 55%

283 and 62% of slag 1 had hydrated at 20°C and 38°C respectively; while for the slag 2

284 blend, only about 44% and 49% of the slag portion had hydrated [21]. This is

285 supported by the DTG data shown in Fig. 7, where a larger signal attributed to C-S-H

286 was seen in the CS1 blends.

287

Fig. 6. Chloride binding relationship for the slag blends at 20°C and 38°C

Table 4: Degree of slag hydration at 28 days as determined by SEM image analysis (taken from [21])

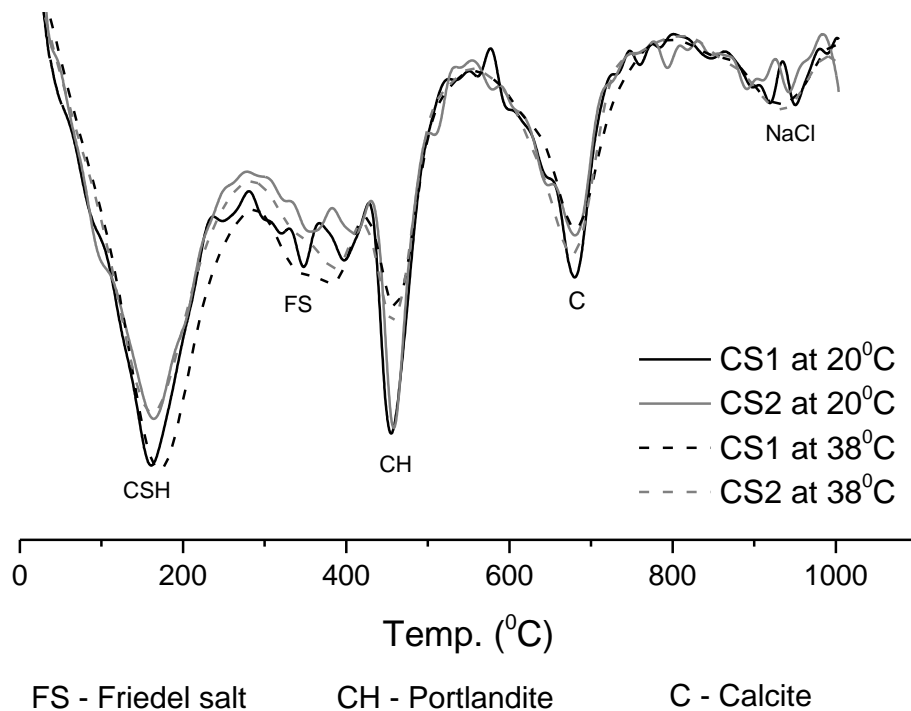| Mix	Temperature	Degree of Hydration (%)	Error
CS1	20°C	54.85	1.00
	38°C	62.40	1.01
CS2	20°C	43.76	1.55
	38°C	48.92	1.50

3.1.2 Influence of temperature

From Fig. 6, at C_i = 0.1M, there was no significant difference in the bound chloride contents obtained at 20°C and 38°C but at C_i of 0.5M and beyond, bound chloride contents were higher for samples cured and exposed at 38°C. This agrees with earlier results obtained by Arya et al. [36] in their study of factors influencing chloride binding in concrete, where they cured OPC paste samples for 4 weeks at temperatures of 8, 20 and 38°C, and introduced the chlorides into the samples at the
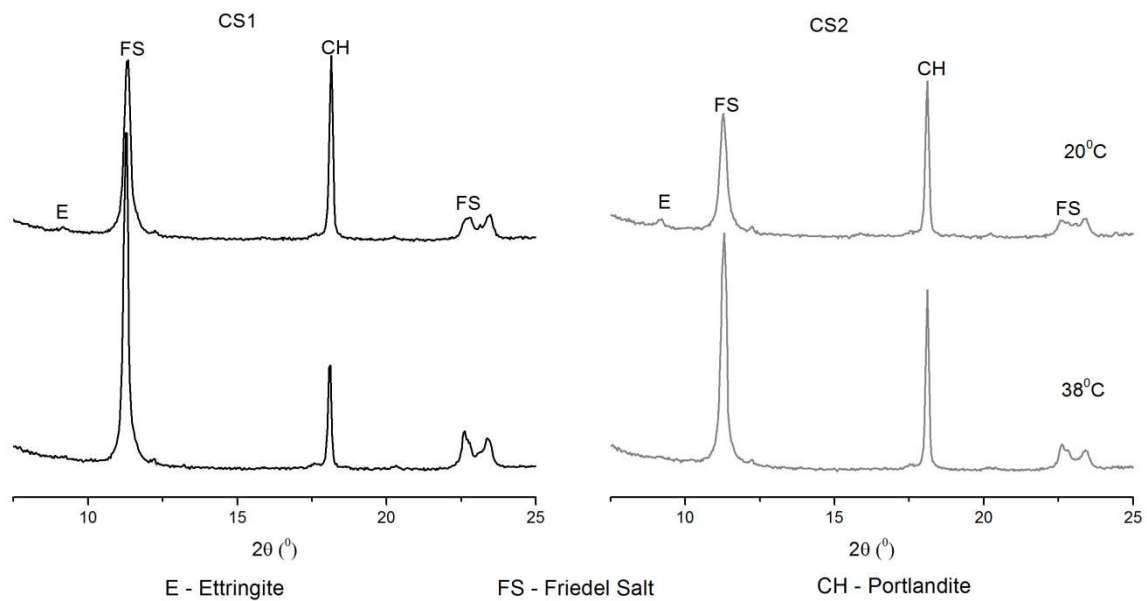
299   point of mixing. They observed that the bound chloride content increased with

300   temperature, and attributed it to faster reaction rates occurring at higher

301   temperatures. Although, the results reported here are for slag blended systems

302   which have been cured for 8 weeks, before testing for binding of external chlorides,

303   the trend is similar. In another study by Zibara [37], an increase in temperature from

304   23℃ to 38℃ resulted in a decrease in the amount of bound chlorides fo r host

305   solutions having chloride concentrations between 0.1M and 1.0M, and an increase in

306   the amount of bound chlorides at a concentration of 3.0M. However, the difference at

307   1.0M was minor compared to the increase at 3.0M. Also, it is important to point out

308   that all their test samples were cured at the same temperature of 23 ± 2℃ an d

309   tested for chloride binding at temperatures ranging from 7℃ to 38℃. In this study ,

310   the samples were cured and tested for chloride binding at temperatures of 20℃ and

311   38℃.

312   The increased chloride binding at higher temperatures can be attributed to the higher

313   degree of slag hydration [21]. C-S-H and aluminate phases are principally

314   responsible for chloride binding. These phases are more prevalent at 38℃ du e to

315   the accelerating effect of temperature on the hydration reaction [38,39]. More so,

316   there is increase in the amount of sulphate ions bound reversibly within the C-S-H

317   phase at higher temperatures, and less calcium sulphate remains available for a

318   reaction with C_3A [40]. Slag hydration is more gradual than that of clinker[41–43],

319   and more greatly affected by temperature [39,44]. Therefore, while clinker hydration

320   would be almost complete after 8 weeks, i.e. the age at which the samples were

321   tested, the degree of slag hydration differed between the samples. Thermal analysis

322   of the samples (Fig. 7) revealed lower portlandite contents in the blends hydrated at

323   38℃. This is due to the consumption of the portlandite by the slags [1 9,45], thus

324   indicating that the slags had reacted more at 38°C, confirming earlier findings [21].

325   This can be related to the study by Loser et al. [46], where they showed that chloride

326   binding was strongly related to the hydration degree of the cement and of the mineral

327   admixtures. Thermal analysis (Fig. 7) and XRD data (Fig. 8) performed on the

328   samples at the end of the test show increased signals due to Friedel's salt (FS) for

329   the samples cured at 38°C, thus confirming the increased chloride binding.

FS - Friedel salt   CH - Portlandite   C - Calcite

330
331   **Fig. 7.** DTG plots showing peaks of Friedel's salt (FS) for slag 1 and 2 blend at 20°C
332   and 38°C for paste samples after immersion in NaCl solution (C_i = 2.0M)

Fig. 8. XRD patterns showing peaks of Friedel's salt (FS) for slag 1 and 2 blend at 20°C and 38°C for paste samples after immersion in NaCl solution ($C_i = 2.0M$)
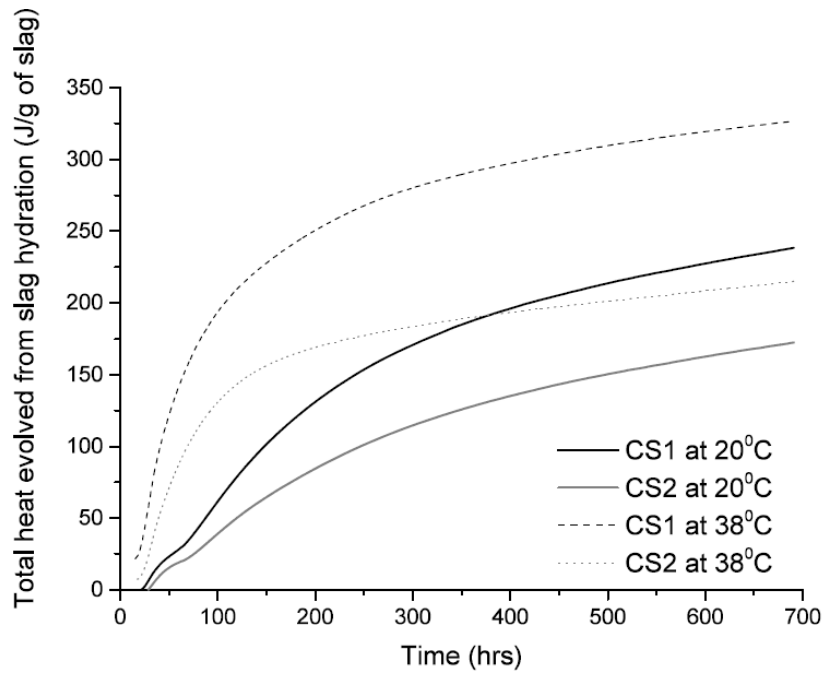
3.1.3 Chloride binding isotherms

The chloride binding coefficients (α and β) obtained by fitting Freundlich's binding isotherm to the data are shown in Table 5. These coefficients don't have any physical meaning as they are not material properties, but can be used to give an indication of the chloride binding capacities of the cementitious materials. The chloride binding coefficient (α) was greater for the more basic, alumina-rich slag 1 and at higher temperatures. When the temperature was increased from 20°C to 38°C, α increased by about 32% and 27% for CS1 and CS2 respectively. Meanwhile, α for CS1 was about 11% and 15% higher than that for CS2 at 20°C and 38°C respectively. The values of α and β shown here are somewhat higher than those reported by Thomas et al. [12] for similar samples at 23°C. This can be attributed to the type of samples used. While Thomas et al. [12] used 3 mm thick disc paste samples, ground samples were used here. Zibara [37] showed that the amount of chlorides bound by ground samples were higher than that of disc samples.

350 **Table 5:** Chloride binding coefficients obtained using Freundlich's binding isotherm

Mix	Temperature (°C)	α	β	Adj. R^2
CS1	20	20.11	0.50	0.9890
	38	26.46	0.55	0.9839
CS2	20	18.07	0.51	0.9908
	38	23.00	0.58	0.9972

351

352 An interesting observation was that the difference between the chloride binding

353 coefficient *(α)* of CS1 and CS2 increased as the temperature was raised from 20°C

354 to 38°C (Table 5). This reflects the increase in the degree of hydration (see Table 4),

355 where temperature has a greater effect on the more basic slag 1. Isothermal

356 calorimetry tests conducted on paste samples from the slag blends at 38°C (see Fig.

357 9), indeed confirmed this. Furthermore, referring back to the portlandite contents

358 from Fig. 7, while the levels were similar for both samples at 20°C, the portlandite

359 content of CS1 was lower than that of CS2 at 38°C, indicating that slag 1 had
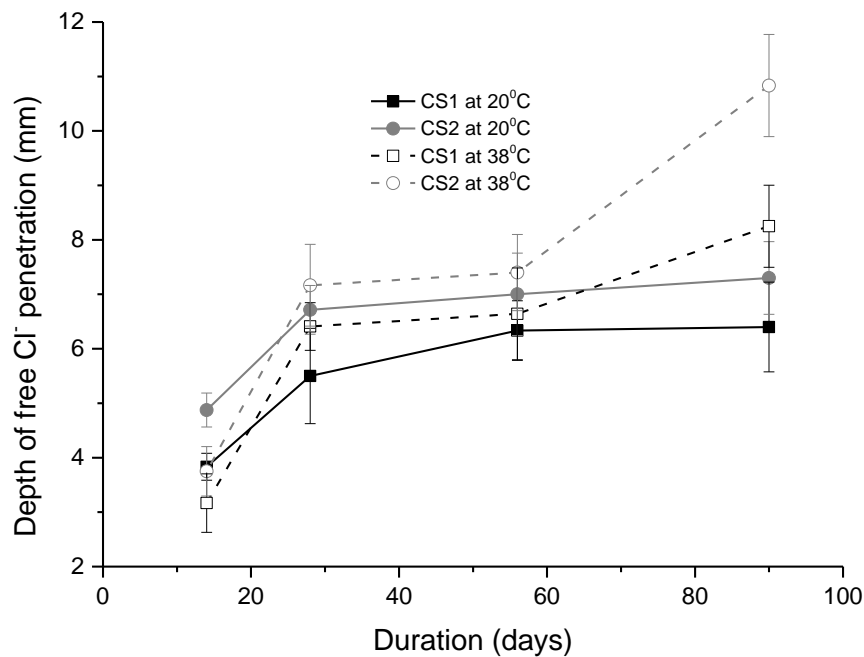
360 reacted more.

361

Fig. 9: Slag contribution to total heat evolved as measured by isothermal calorimetry

363 3.2 Chloride diffusion

364 3.2.1 Free chloride penetration

365 The depth of free chloride penetration measured on samples which had been cured

366 for 28 days before exposure to a 3% NaCl solution is shown in Fig. 10. The

367 penetration depths were lower for sample CS1 than CS2 at all durations and both

368 temperatures. After 90 days of exposure at 38℃ the depth of pe netration of free

369 chloride ions into CS2 was about 31% higher than that of CS1, compared to a

370 difference of about 14% at 20℃. This again reflects the degree of slag h ydration,

371 where chlorides are bound (and therefore by definition not free) by hydration

372 products. This correlates with the results of the chloride binding, where it was seen

373 that CS1 had a higher chloride binding capacity, and is in agreement with previous

374 findings by Otieno et al. [13].

375

Fig. 10. Depth of penetration of free Cl⁻ into mortar samples cured for 28 days before exposure to a 3% NaCl solution for a period of 90 days.
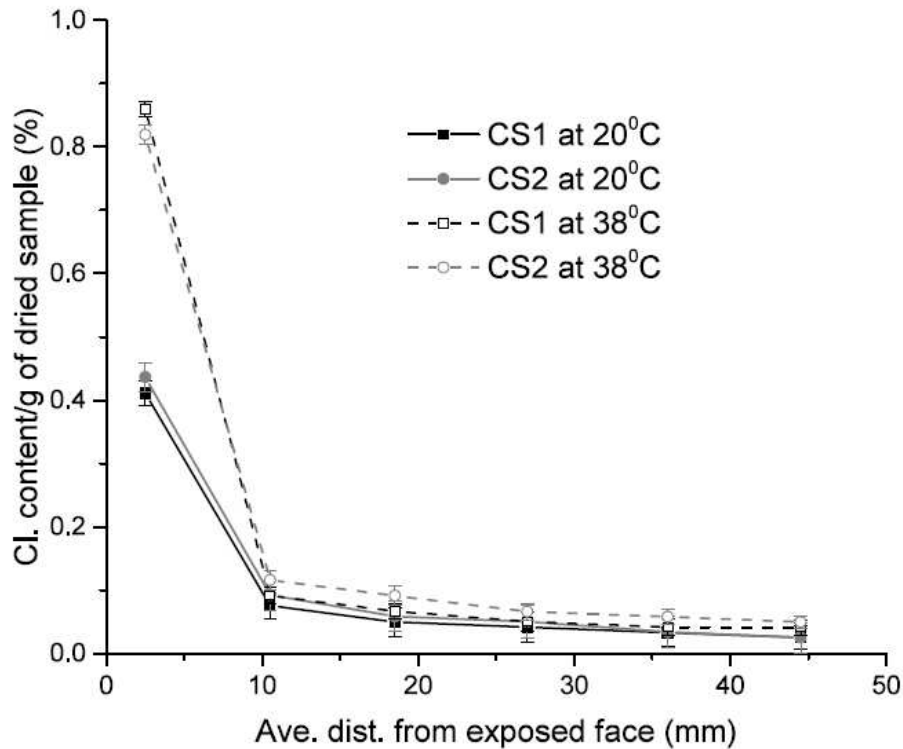
As chloride binding was increased at 38℃, this was expected to reflect in the resu lts of the penetration of free chloride ions (Fig. 10) in that there should be less free chlorides in the pore solution. This was true for the first 14 days of exposure, as samples cured and exposed at 38℃ had lower chloride penetration d epths than those cured and exposed at 20℃. However, as the samples were exposed for longer periods, those cured and exposed at the higher temperature showed greater chloride penetration. Thus, despite the higher chloride binding occurring at 38℃ due to a greater degree of hydration, there was still an increase in the amount of free chlorides. This is because the porosity at 38℃ was much coarser (as seen later in Section 3.3), allowing greater penetration into the samples. This explains the huge difference between the chloride penetration depths measured at 20℃ and 38℃ for ages beyond 28 days (as seen in Fig. 10), and also agrees with previous studies

391 [47–51] showing that an increase in exposure temperature leads to an increase in

392 the rate of chloride ingress.

393 For the samples cured at 20℃, the depth of chloride penetration did no t increase

394 much after 14 days of exposure whereas there was continuous increase at 38℃. A

395 previous study by Goñi et al. [52], where paste samples were cured in demineralised

396 water for 28 days at 20℃ before exposing them to NaCl solutions, showed t hat the

397 ingress of sodium and chloride ions into the paste caused the formation of Friedel's

398 salt in the pores, resulting in a denser microstructure. Other studies [53,54] have

399 shown that curing in chloride environments can influence hydration of the

400 cementitious materials. High temperature curing results in a high initial rate of

401 hydration, retarding subsequent hydration. This produces a non-uniform distribution

402 of hydration products compared with the case of a lower curing temperature [38,55].

403 In this study, the samples exposed at the higher temperature had hydrated to a

404 greater degree, but had a much more open microstructure as evidenced by their

405 coarse porosity (shown later in Section 3.3). However, the samples cured at the

406 lower temperature continued to hydrate in the chloride solution, resulting in the

407 formation of a dense microstructure, thus reducing the rate of chloride ingress into

408 the samples. This might be the reason why the depth of chloride penetration

409 measured for the samples cured at 20ºC did not increase much after 14 days of

410 exposure, as compared to at 38ºC (Fig. 10).

411 3.2.2 Total and water soluble chloride content

412 Total chloride profiles obtained for samples at the end of the soaking period (90

413 days) are shown in Fig. 11.

414

Fig. 11. Total chloride profile obtained for mortar samples cured for 28 days before exposure to a 3% NaCl solution for a period of 90 days.
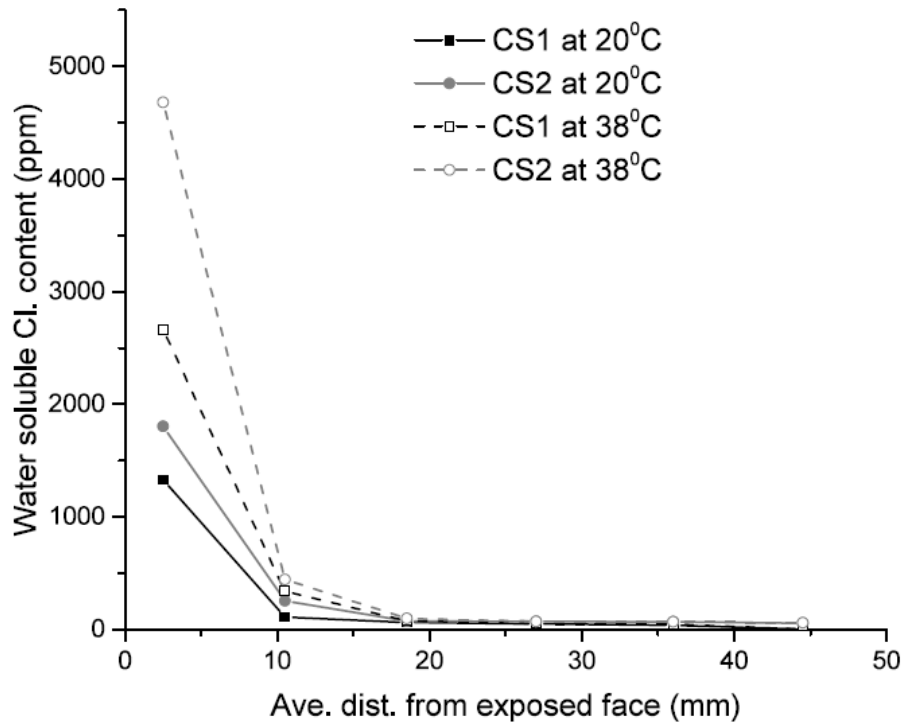
The total chloride profiles at 38℃, when compared to those at 20℃ are characterised by very high chloride concentrations at the surface, which decrease to much lower values within a short distance, and are characteristic of mixes having high chloride binding capacities [56]. Indeed, the chloride binding results shown in Fig. 6 showed that there was higher chloride binding at 38℃. This agrees with results from previous studies [47,49,51,57], and supports the chloride penetration results (Fig. 10), which showed that there was greater chloride penetration at 38℃. As seen in Fig. 11, the difference in temperature only had a significant effect on the total chloride content at the region close to the exposed face. At further depths within the samples, there was no significant difference between the total chloride contents for the samples cured and exposed at 20℃ and 38℃. The reason for this can also be linked to chloride binding. Since chloride binding was greater at 38℃, this implies

430 that more Friedel's salt was formed. This phase can have a pore blocking effect,

431 slowing down the rate of subsequent chloride ingress [52,58,59].

432 In Fig. 10, CS1 was seen to have lower depths of free chloride penetration than CS2,

433 regardless of temperature. However, Fig. 11 shows only a slight difference between

434 the total chloride contents of CS1 and CS2, with that of CS1 being lower than that of

435 CS2 at both temperatures. The reason for this can be explained from Fig. 12, which

436 shows the water soluble chloride content obtained from the same samples that were

437 used for the total chloride content test.

438 Fig. 12 shows that there was a clear difference in the water soluble chloride contents

439 of CS1 and CS2, especially in the near subsurface region. This supports the results

440 shown in Fig. 10 and can also be linked to chloride binding. While similar amounts of

441 chloride diffused into both slag samples (as seen in Fig. 11), CS1 having a higher

442 chloride binding capacity (see Fig. 6 and Table 5) bound more of the chlorides, thus

443 leading to lower water soluble chloride contents. Fig. 12 also shows that the

444 difference between the water soluble chloride content of CS1 and CS2 is greater at

445 38℃ than at 20℃. This also correlates with the chloride binding results shown in

446 Fig. 6 and Table 5, where it was seen that the chloride binding capacity of CS1 was

447 far greater than that of CS2 at 38℃ as compared to 20℃, due to the increase in the
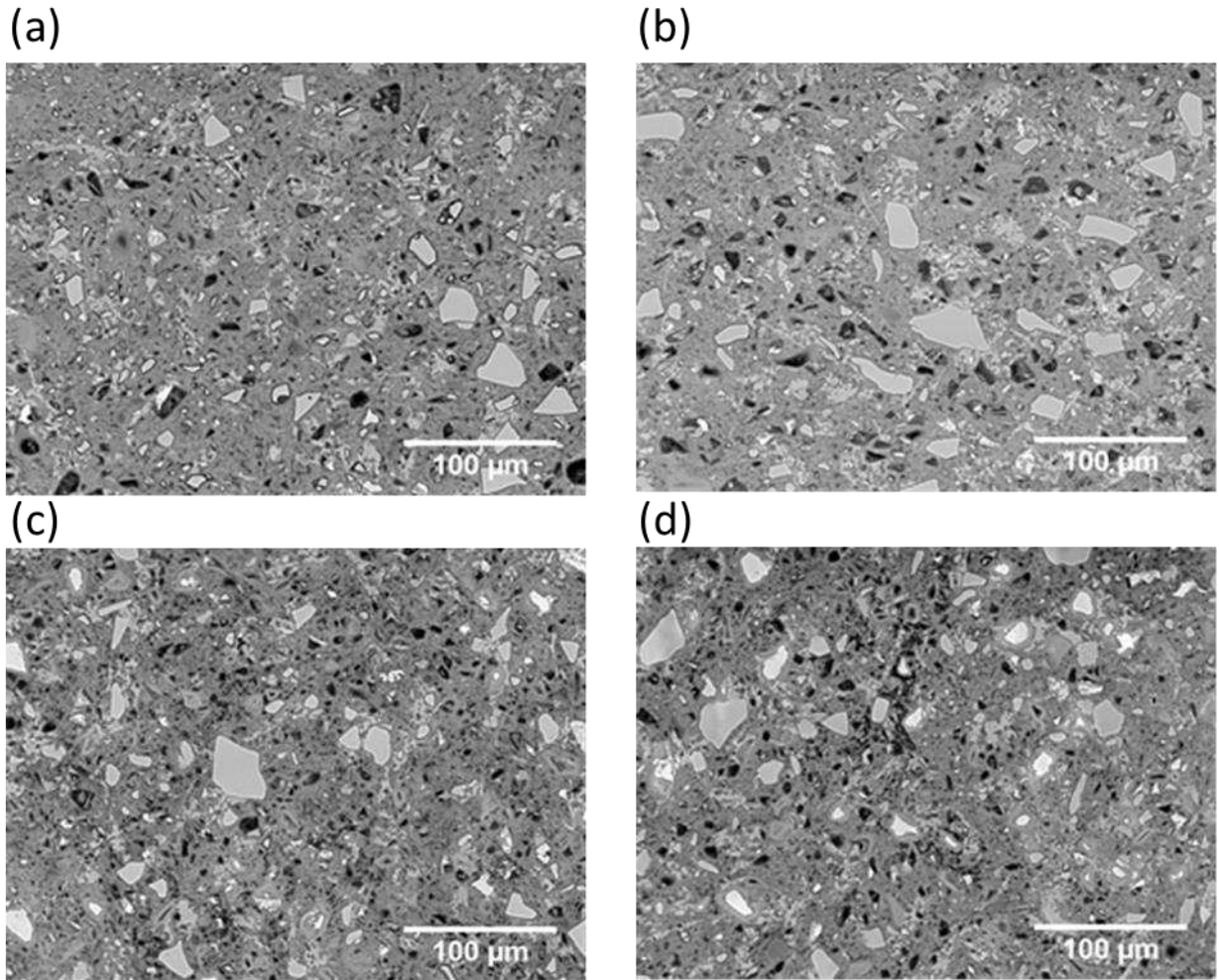
448 degree of slag hydration [21].

449

Fig. 12: Water soluble chloride profile obtained for mortar samples cured for 28 days before exposure to a 3% NaCl solution for a period of 90 days.

3.3 Degree of coarse porosity

Representative SEM-BSE images of the samples are shown in Fig. 13. The pore structures of the samples cured at 38℃ appeared coarser, consisting of a large number of clustered pores distributed randomly throughout the sample. Table 6 shows the average coarse porosity measured by grey level imaging from 50 SEM-BSE images selected at random from paste samples of the two slag blends, cured for 28 days at temperatures of 20℃ and 38℃. Increasing the temperature from 20° C to 38℃ resulted in an increase in the capillary porosity of about 36%. In a nother study [21], water sorptivity tests conducted on mortar samples prepared from these same blends showed that the sorptivity coefficient of 28 day old samples increased by about 90% when curing samples at higher temperature. This explains the increase in the ingress of chloride ions seen at the high temperature of 38°C, and is consistent with previous findings [38,60].

Fig. 13. SEM-BSE images of 28 day old samples (a) CS1 at 20℃ (b) CS2 at 20℃ (c) CS1 at 38℃ (d) CS2 at 38℃. The white coloured features are the anhydrous cement grains, while the light grey coloured, angular features are the anhydrous slag grains. The CH and C-S-H phases appear as light and dark grey respectively, while the dark spots are the capillary pore clusters.

Comparing the two blends, the coarse porosity of CS1 was only about 7% lower than that of CS2 at each temperature. This explains the only slight difference in total chloride contents as seen in Fig. 11. This implies that the diffusion of chlorides into the slag blends was principally governed by two factors – the chloride binding capacity of the slag blends and the pore structure, both of which are influenced by the slags' chemical composition and the curing temperature. Temperature has a bigger impact than the difference in the chemical composition of the slags.

Table 6: Degree of capillary porosity of paste samples cured for 28 days under saturated lime water at 20℃ and 38℃

Mix	Temperature	Coarse porosity (%)	Std. dev.
CS1	20℃	6.5	0.79
	38℃	8.9	0.56
CS2	20℃	7.0	0.47
	38℃	9.5	0.65

4. Summary and Conclusions

This study has shown that chloride binding capacity and the pore structure are two key factors affecting the ingress of chloride ions into slag blended cements. Both of these factors are further influenced by the chemical composition of the slag and the curing temperature. In summary, the following points have been highlighted:

- The higher chloride binding capacity of the slag 1 blend was a result of its chemical composition. The higher alumina content led to the formation of more Friedel's salt. The greater basicity led to a higher degree of hydration (formation of more C-S-H phases), which resulted in the formation of a finer pore structure and increased chloride binding. These factors, in turn, resulted in lower chloride penetration depths.

- Curing samples at elevated temperatures (38℃ rather than 20℃) resulted in an increase in the degree of slag hydration, which in turn led to an increase in chloride binding. However, the pore structure became coarser, resulting in an increase in chloride ingress.

These results should be considered in high temperature environments like tropical marine regions, where concrete structures may be exposed to high temperature conditions and higher concentrations of chloride. Since it is the free

chlorides in the concrete that induce corrosion of the embedded steel reinforcement, if SCMs such as slags are to be used in these areas, it is not just sufficient to look at how they influence the rate of chloride diffusion by virtue of their lower porosity, but also on their chloride binding capacities. For such environments, it might be more suitable to use slags of higher basicity and higher alumina content.

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