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CHLORIDE BINDING IN GGBS CONCRETE

R.K. Dhir, M.A.K. El-Mohr and T.D. Dyer
Concrete Technology Unit
Department of Civil Engineering, University of Dundee
Dundee, DD1 4HN, Scotland, UK

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ABSTRACT

This paper reports the results of chloride binding measurements of GGBS pastes, as well as chloride diffusion and permeability measurements of GGBS concrete mixes. Chloride binding capacity was found to increase with increasing GGBS replacement levels and the chloride exposure concentration. Thermal analysis measurements suggest that much of the improvement in chloride binding is a result of high aluminate levels in GGBS leading to the production of higher quantities of Friedel's salt. When concrete mixes with relatively similar permeabilities are used the chloride binding capacity of the cement matrix becomes a major determining factor in how resistant the concrete is to chloride permeation.

Introduction

Recently work has been carried out at the University of Dundee into developing concrete mixes that are highly resistant to the ingress of chloride ions. The approach has been to design mixes with both low permeability (by using a design method that minimizes voids in the concrete matrix), and using binders that are known to be effective in providing resistance to chloride ingress. One binder material that has been used for this purpose is ground granulated blastfurnace slag (GGBS).

A great deal of research has been conducted on the binding of chlorides in cement matrices. The C_3A phase in Portland cement is known to react with chloride ions to produce the AFm phase $C_3A \cdot CaCl_2 \cdot 10H_2O$, or Friedel's salt [1]. There is generally a good correlation between C_3A content and chloride binding capacity [2]. An AFm phase containing what are thought to be alternating interlayers of Cl^- and SO_4^{2-} ions, $C_6A_2 \cdot CS \cdot CaCl_2 \cdot 24H_2O$ also exists. An iron (III) analogue of Friedel's salt is produced by the reaction of the C_4AF cement phase [1], and in sulphate resistant cements the role of this compound in immobilising chloride ions is believed to be important [3].

There is also evidence for the binding of chloride ions in CSH gel, possibly in the interlayer spaces [4]. However, work conducted using pore solution expression techniques contradicts this [5]. Analysis of pore solutions expressed from cement pastes containing admixed chlorides have demonstrated the dependence of chloride binding capacity on pH. As pH increases the binding capacity at first increases and then declines [6,7].

The use of GGBS as a part binder with Portland cement has been observed to cause a reduction in the coefficient of diffusion of chloride ions through concrete and a reduction in reinforcement corrosion [2,8]. Whilst both microstructural and chemical effects are likely to be contributory factors, a large portion of the work undertaken with GGBS has shown that the chloride binding capacity of pastes containing this material is improved in comparison to those containing only Portland cement [2,9]. The high aluminate levels present in GGBS are most likely to be responsible for its good binding characteristics.

Determination of chloride binding capacities of the cement matrices was conducted using the technique developed by Tang and Nilsson [10]. The technique involves exposing a granulated sample of the paste to a chloride solution of known concentration and measuring the depletion after allowing sufficient time to achieve equilibrium. These measurements were backed up with TG and XRD analysis of the exposed paste samples in an attempt to determine the fate of the bound chlorides. The findings of these measurements were compared with the results obtained with the concrete mixes developed during the course of this study.

Chloride Binding Capacity

Measurement of Chloride Binding. Chloride binding capacity was measured on paste samples containing PC alone and blends of PC and GGBS. To study the effect of the GGBS replacement level, it was added as a percentage of 0, 33.3, 50 and 66.7 percent of the total binder. The water/binder ratio was kept constant at 0.55.

Standard 70 mm cubes were cast from each mix. After water curing the cubes at room temperature for 6 weeks, the outer layer of the samples was removed using a hammer and chisel and the central portions were crushed and wet sieved to provide samples with a particle size distribution of between 0.2 mm and 2 mm. The sieved samples were vacuum dried in a desiccator with silica gel for 3 days to remove most of the water. They were then stored for 7 days in a desiccator with silica gel and soda lime at 11% RH. About 25 g of the sample was put in a glass beaker, vacuum dried for 2 hours, and then filled with 30 ml of sodium chloride solution saturated with $Ca(OH)_2$. Sodium chloride concentrations used were 0.1, 0.5, 1.0 and 5.0 mole/litre. The beakers were covered tightly and stored in the room temperature for two weeks to reach adsorption equilibrium [10]. The inside solution was pipetted and chloride ion concentration was measured using the thin film XRF technique described in a previous publication [11]. Chloride binding capacity was calculated using the equation used by Tang and Nilsson [10].

Effect of GGBS Replacement Level. Figure 1(a) shows the relationship between GGBS replacement level and the chloride binding capacity for the range of concentrations. As the replacement level increases, the chloride binding capacity also increases for all chloride concentrations. For a GGBS replacement level of 66.7%, the chloride binding capacity is around 5 times that of the PC control for the case of 5 mole/litre exposure concentration.

Effect of Chloride Solution Concentration. Figure 1(b) shows the relationship between chloride exposure concentration and chloride binding capacity for different levels of GGBS replacement. As the chloride concentration increases, the binding capacity increases for all GGBS levels. The chloride binding capacity appears to be directly proportional to the exposure concentration. It can be attributed to the sensitivity of the chloride binding capacity to

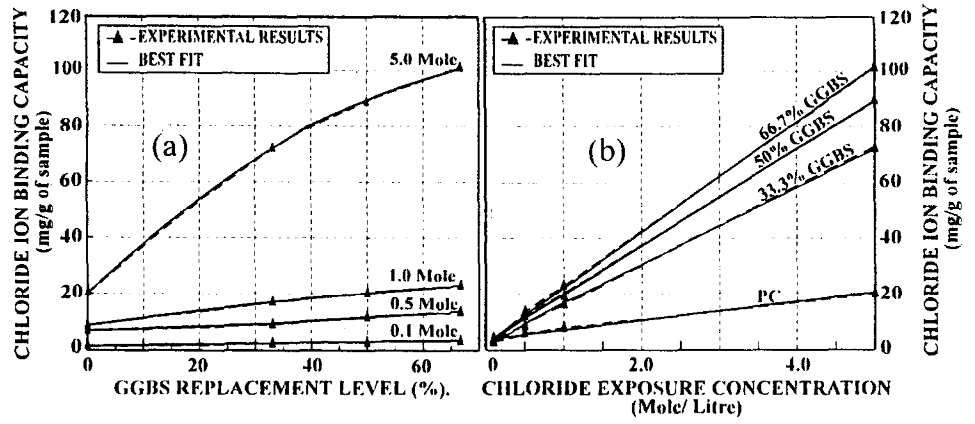

FIG. 1.

Dependence of chloride binding capacity on (a) GGBS replacement level with different chloride exposure concentration and (b) chloride exposure concentration with different replacement levels.

the ratio of Cl^-/OH^- ions in the cement pore solutions, (in this case, the chloride solutions to which the pastes were exposed). As the Cl^-/OH^- ratio increases chloride binding capacity increases.

Also shown in Figure 1 are the best fit curves for the experimental data. These relationships can be combined to provide an equation (with a correlation coefficient of 0.983) that relates the influence of GGBS replacement level and chloride exposure concentration to the chloride ion binding capacity of a cement paste, as stated below :

$$C_b = (-22.21G^{2+}39.45G + 3.36)X + (6.84G^2-6.40G + 3.64)$$

Where,

C_b = Chloride ion binding capacity in mg/g of sample,
G = GGBS/total binder ratio, and
X = Chloride exposure concentration in mole/litre.

There are, of course, other factors that influence chloride binding, one of the main ones being the temperature. However, as a means of describing the trends observed in GGBS pastes this is still a fairly useful relationship. All experimental work has, so far, been carried out using just one type of GGBS. Whilst the chemical composition of iron blastfurnace slags is generally limited to a relatively small region of the CaO-SiO_2-Al_2O_3 system, it remains to be seen how well the above relationship follows the behaviours of other GGBS/Portland cement pastes.

Chemistry of Chloride Binding

The PC and 50% GGBS paste samples exposed to chloride solutions were analysed using TG/DTA and XRD techniques. Differential Thermogravimetry (DTG) traces from ambient temperatures to 1000°C for the exposed samples are shown in Figure 2 along with traces

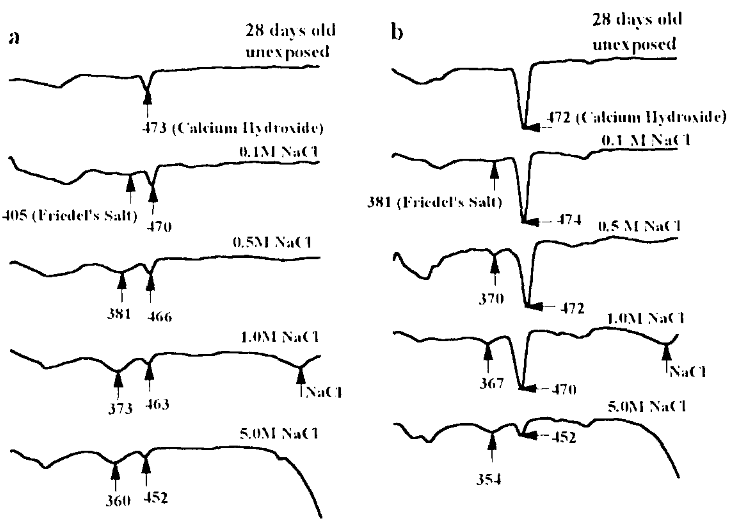

FIG. 2.
DTG traces for cement pastes exposed to different concentrations of chloride solutions, (a) GGBS and (b) PC (Temperatures indicated are in °C).

obtained for unexposed pastes. The presence of Friedel's salt is indicated at around 370°C due to a loss of water [12]. This can be seen to become more prominent as the exposure concentration increases.

The results of the TG measurements are shown in Figure 3. They are expressed as a fraction of the residual specimen weight at 800°C minus the sodium chloride content measured using XRD. The weight loss observed from the specimens due to the dehydration of Friedel's salt does not follow the trends observed when measuring chloride binding. Whilst the quantity of water lost at around 370°C increases with exposure concentration, it is not the linear relationship observed before. As discussed previously, Friedel's salt can exist as both an AFm phase with all its interlayer spaces occupied by chloride ions, or as a compound in which the interlayers are alternately occupied by chloride ions and sulphate ions. The relationship observed can therefore be attributed to an increase in the quantities of the chloride-rich phase in comparison to the phase containing both chloride and sulphate ions as the chloride exposure concentration increases.

Concrete Study

The four concrete mixes tested in this study were designed using a method developed by Dewar [13] which allows the minimization of voids in the concrete matrix. All the mixes had the same total binder content of 300 kg/m^3 with GGBS replacement levels of 0, 33.3, 50 and 66.7%. The mixes are detailed in Table 1. Standard 100 mm cubes, were cast for strength and the intrinsic permeability tests and 100 mm diameter × 300 mm high cylinders, for chloride diffusion measurements. Air permeability testing was conducted at ages of 28 days and 90 days, whilst chloride diffusion testing was carried out at 28 days only. The details of the test apparatus, test procedures and techniques are given in previous publica-

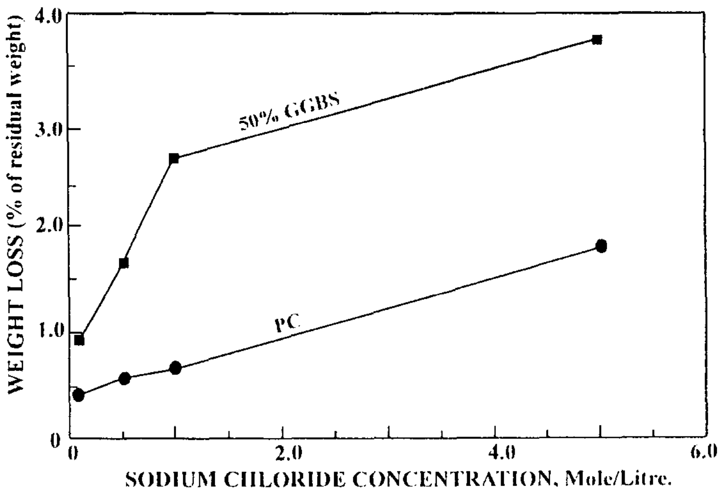

FIG. 3.
Weight loss for Friedel's Salt measured using TG.

tions [14,15]. The chloride diffusion tests were carried out at a temperature of 20°C with a chloride solution containing 5 mole/litre of sodium chloride and saturated with $Ca(OH)_2$.

Strength and Intrinsic Permeability. The results in Table 1, show that the 28 day cube strength decreases as the GGBS replacement level increases. However, at 90 days, the strengths of GGBS and PC concrete mixes are much closer. At 28 days, despite the lower compressive strengths of the GGBS concrete, compared to the control, the intrinsic permeabilities were similar. At 90 days, the intrinsic permeability of the GGBS became much better.

Chloride Diffusion. Figure 4 shows the influence of GGBS replacement levels on Cl^- binding capacity, the coefficient of chloride diffusion and intrinsic permeability for concrete at an age of 28 days. As the GGBS replacement level increases the coefficient of chloride diffusion steeply decreases. Obviously, the coefficient of chloride diffusion will be deter-

TABLE 1

PC and GGBS Concrete Details

GGBS REPLACEMENT LEVEL %	MIX DETAILS			CUBE STRENGTH, N/mm^2		INTRINSIC PERMEABILITY, m^{2}x10^{-17}	
	PC (C) kg/m^3	GGBS (G) kg/m^3	W/(C+G) Ratio	28 Day	90 Day	28 Day	90 Day
0	300	00	0.55	45.0	51.0	2.08	1.85
33.3	200	100	0.55	41.0	51.5	1.87	1.61
50.0	150	150	0.55	34.0	47.0	2.06	1.72
66.7	100	200	0.55	32.0	45.0	2.31	1.93

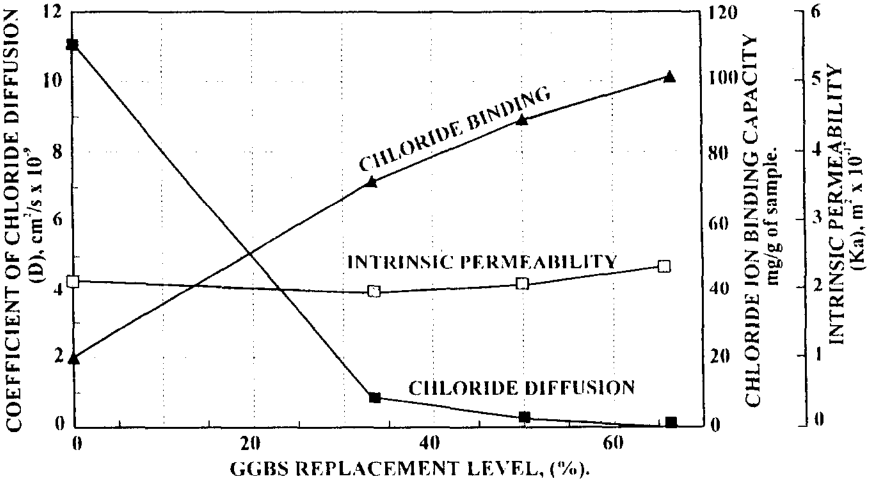

FIG. 4.

Effect of GGBS replacement level on intrinsic permeability, chloride ion binding capacity and chloride diffusion coefficient.

mined by both the permeability of the concrete and the ability of its cement matrix to bind chlorides. However, since at 28 days all the concretes show relatively similar intrinsic permeabilities due to the design method and the materials used, the better chloride binding characteristics of GGBS can therefore be assumed to be mainly responsible for the improved protection against chloride ingress.

Conclusions

1. GGBS pastes have a higher chloride binding capacity compared with the PC control, and the difference increases with increasing GGBS replacement level.
2. Thermal analysis measurements suggest that the improvement in chloride binding capacity is a result of the increase of the aluminate content of the pastes, which leads to an increase in the quantities of Friedel's salt produced.
3. In concrete designed to have a minimum volume of voids, the chloride binding capacity of the cement matrix becomes the dominant factor in how resistant the concrete is to chloride permeation.

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