

Chloride-binding Effect of Blast Furnace Slag in Cement Pastes Containing Added Chlorides

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ABSTRACT

Corrosion of rebar in concrete is commonly associated with, and to a large degree influenced by, the free chloride concentration in the pore water. It is standard industry practice to add various mineral admixtures such as pulverised fuel ash (PFA), or fly ash, ground granulated blast furnace slag (GGBS) and silica fume (SF), to concrete mixtures to increase the corrosion resistance of the reinforcement in the matrix and its subsequent design life span. Various investigations have reported on the effect of mineral admixtures and additions on chloride binding in cementitious matrices, and the current study contributes further to knowledge in this field. Unlike previous investigations, this study attempted to make a clear distinction between the contributions of the two components in a blended cement consisting of ordinary Portland cement (OPC) and ground blast furnace slag (BFS). These contributions of each component have been quantified. Relationships between the total amount of chloride bound, the level of BFS additions, and the levels of initial chloride content present in the matrix were determined. It was found that the OPC/BFS blended cement with partial BFS replacements of up to 50 % displayed a lower binding capacity than that of the OPC on its own. This observation was derived based on the assumption that the OPC and slag reactions were treated as competing and equivalent and did not take any potential time delays into account, nor the degree of cement hydration. The chloride-binding efficiency by the BFS is dependent on both the BFS partial replacement addition level as well as the initial amount of chloride present in the matrix. It is shown that both the OPC and BFS contribute to chloride binding in cement pastes, depending on the amount of BFS that replace the OPC component in the matrix.

KEYWORDS

Chloride binding, granulated blast furnace slag, pore solution, permeability, corrosion.

1. Introduction

Corrosion of rebar in concrete is a well known phenomenon, and one that is responsible for substantial financial losses as a result of maintenance and replacement in concrete structures, such as bridges, decks in parking garages, piers, etc. where it occurs. The most common cause of rebar corrosion is chloride ions that destroy the passive film on the rebar. This situation is further aggravated in cases where the concrete has been carbonated and the alkalinity that maintains the passive film on the rebar has been compromised. The chloride ions can originate from two sources, namely, an internal source of chloride present in the mixing water, aggregates, cement used in the process or chloride ingress into the concrete matrix from an external source such as de-icing salts.

Chloride induced corrosion is caused by chloride ions present in the pore water solution of concrete, or those referred to as free chloride ions. It is a well-established that the calcium aluminate phase in cement (C_3A) can react with chloride to form a compound known as Friedel's salt ($C_3A \cdot CaCl_2 \cdot 10H_2O$), and bind the chloride ions present in the concrete matrix. A number of authors have described the extent, way and mechanism in

which chloride can be bound as Friedel's salt. The work of Brown and Bothe¹ and Siegwart *et al.*² indicated that both the C_3A and the C_4AF phases contribute to chloride binding, although C_4AF to a lesser extent than the C_3A .³ Birnin-Yauri and Glasser⁴ also suggested the formation of oxychloride $Ca(OH)_2 \cdot CaCl_2 \cdot H_2O$ and $3Ca(OH)_2 \cdot CaCl_2 \cdot 12H_2O$ as a lesser known mechanism for chloride binding in cement matrixes.

Tuutti⁵ and Tritthart^{6,7} found that the bound chloride content in relation to the free chloride content is independent of the water/cement ratio, if the bound chloride was considered per unit weight of the cement. The amount of bound chloride could be as much as 40 to 60 % of the total chloride content present.⁸ Some bound chloride is irreversibly combined into the hydrated products by chemical reactions, while some could be released when the free chloride concentration in the pore water decreases.⁹ Several authors have used classical physical adsorption isotherms to describe the adsorption of chloride ions in selected concretes.⁹⁻¹² It has been found that chloride binding in OPC obeys the Freundlich isotherm at high concentrations of free chloride (0.1 mol L^{-1}) and the Langmuir equation at low concentrations (0.05 mol L^{-1}).⁹⁻¹¹ Both Tritthart⁷ and Byfors *et al.*¹³ established that the hydroxide ion concentration in pore water has an effect on the degree of chloride binding in OPC.

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When the chloride ions ingress into the concrete matrix from the environment, any way in which the permeability of the concrete can be reduced and the physical access of the chloride ions can be hindered, will obviously improve the resistance of the rebar in the concrete to corrosion attack. The use of various mineral admixtures such as fly ash (FA), blast furnace slag (BFS) and silica fume (SF) to decrease the permeability and reduce the diffusion of chloride ions in the concrete, is a well established industry practice. In cases where BFS was used, it was reported that the internal binding capacity of cement pastes and mortars increases greatly when up to 70 % of OPC is replaced by BFS,¹⁴ while the chloride ion diffusion coefficient decreases by a factor of 10 compared to the case of pure OPC concrete when the BFS content was 60 %.¹⁵ Hirao and Yokohama¹⁶ investigated the chloride binding in a blended OPC-BFS cement to which chloride was added. Their results confirmed increased chloride binding in the blended cement compared to that of OPC alone. Arya and Xu¹⁷ came to the same conclusion when measuring the chloride concentration in various OPC-mineral admixture matrices. They concluded that the chloride binding decreased in the order OPC/GGBS(65 %) > OPC/PFA(35 %) > OPC. However, they did not normalize the chloride-binding ability of the various matrices to compensate for the fact that the GGBS specimens only contained 35 % OPC and the fly ash blend specimens had only 65 % OPC. Yeau and Kim¹⁸ confirmed that the chloride diffusion decreased substantially in concrete matrices with GGBS additions and therefore decrease the corrosion of reinforcement steel. It was also demonstrated that the degree of chloride binding and subsequent ingress causing corrosion of rebar depended on the type of cation salt^{13,19,20} and the form in which it is present in the matrix, as well as the type of cement used.¹⁸ Work by Dhir *et al.*²¹ concluded that with increase in chloride concentration, there is a linearly increasing relationship between the amount of chloride bound and BFS content in blended OPC-BFS mortars. Furthermore, they concluded that for a particular chloride concentration, different levels of BFS present in the concrete show almost the same and a constant degree of chloride binding, until a critical concentration of free chloride is reached and then saturation occurs.

The majority of investigations reported in literature deal with chloride ingress from the environment, and how this is limited and hindered by mineral admixture additions, such as BFS, in the concrete matrix. Only a few more recent studies^{16–18} deal directly with binding behaviour of admixture chloride inside the matrix. Another aspect is that investigations often do not take the moisture content of the total matrix into consideration, but simply observe decreases in chloride concentrations and contents in pore water solutions or solid sections as indications of chloride binding occurring in the matrix. Furthermore, it is often not clear from the procedures employed whether comparisons with OPC should take into account the replacement content by the mineral admixture and subsequently much lower OPC content in the final mixture, or use relative comparisons between bulk matrices. When comparing the effect of the BFS to the OPC, one can follow one of two approaches: comparing a two-component system's performance with that of a single component, or alternatively, separate the effect of the BFS addition from the two-component system and then compare the effect it has on the performance/behaviour of the second component (OPC) when it is added to it. This paper follows the second approach to establish whether BFS additions to OPC increases the chloride-binding capacity of the two-component system when compared to the OPC on its own, as often claimed. In this way, it is possible to discriminate between physical (permeabil-

ity change) and or chemical (formation of Friedel's salt) binding of chloride in the presence of varied quantities of BFS additions. One can best establish this by eliminating the chloride diffusion influence into the matrix and this is why the chloride was added directly to each mixture.

This paper describes the effect of low to medium amounts of BFS additions to OPC on the chloride-binding capacity of the matrix, in contrast to much higher addition level investigations previously reported in the literature.^{15–17} The purpose is to contribute to the knowledge of chloride binding in the matrix itself once ingress has already occurred. An effort is made to determine whether there is a minimum BFS level addition required to successfully bind the chloride. The aim is to contribute to the current information on the role of BFS additions to cement and concrete to prevent rebar corrosion.

2. Experimental

Various sodium chloride additions were used as part of the mixing water in a number of cement mortar specimens with varying BFS additions. Pore water was extracted from the different materials at various curing time intervals according to the pressing procedure described by Diamond²² and Tritthart.^{6,7} After expressing the pore water and measuring the chloride concentration, the amount of chloride remaining bound in the matrix was calculated. This was corrected to the dry mass of chloride added at the beginning of the mixing process. The values obtained for the various two-component systems (total chloride-binding capacity – TCBC) were proportionally calculated to account for the OPC's contribution (cement chloride binding CCB). The effect of the BFS to the chloride-binding capacity of the blend was calculated by subtracting CCB from the value obtained for the pure OPC paste (OPC₁₀₀).

For the baseline experiment, OPC and four different chloride concentrations of 0.25, 0.5, 1 and 2 % of total mass of cement paste were used. For the blended cements, part of the OPC content was replaced with 5, 10, 15 and 30 % BFS, respectively. The procedure for a 1 % chloride in cement paste and 5 % BFS are as follows:

First a 65.92 g (± 0.01 accuracy) of sodium chloride, that is 40 g of chloride, was weighed and dissolved in 2400 g (± 0.01 accuracy) de-ionized H₂O. All samples were produced with a water to cement ratio of 0.6. The chloride water solution was placed in a Hobart mixer. Five percent BFS, calculated as 200 g ± 0.01 (of the initial 4000 g of OPC) and 3800 g ± 0.01 OPC was slowly added to the bowl during mixing. The mixer was run for another 20 min to make sure that a homogeneous mix was achieved. The mix was then placed in a cylindrical plastic bag of 375 ± 5 cm³ then sealed, placed in the sample cylinders and tumbled for homogeneous setting. Three replicates were made for each mixture to ensure reasonable repeatability.

The sample curing occurred in sealed plastic bags at 25 ± 5 °C for 1, 7, 14, 28, 56 and 84 days in which the samples were originally placed and tumbled. Traditional wet-curing was not considered since the water to binder ratio of 0.6 is 1.5 times higher than the theoretical required amount. It was therefore assumed that the sealed conditions and high water to binder ratio would ensure that the hydration process is not altered substantially. At each time interval, three samples were taken from the bulk specimens. A quarter of each sample was chiselled off and weighed, then placed in a Labotech oven at 50 °C and left for 12 hours to dry, after which each sample was weighed again. A further heating period of two hours did not result in a further mass change (loss). The percentage water mass loss was then determined.

Table 1 XRF chemical composition of materials used (mass per mass %).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	Mn ₂ O ₃	P ₂ O ₅	SO ₃	LOI/%	Total	Particle size/ μ m
OPC	21.9	4.3	2.1	0.3	62.6	4.2	0.7	0.1	0.9	<0.1	2.2	0.4	99.8	<150
BFS	35.1	17.6	–	–	37.8	5.6	1.0	–	–	–	0.3	9.4	101.8	<150

The rest of the sample was placed in the pore water expression device, which was fabricated according to Tritthart^{6,7} and Diamond's descriptions.²² The free chloride in the expressed pore water solutions was measured using a direct potentiometric measurement. Two Metrohm electrodes, namely the chloride ion-selective electrode (6.0502.120) and the Ag/AgCl reference electrode (6.0726.107) were used in the electrode assembly. The electrode assembly was calibrated by means of a series of standard solutions that were made up from analytical pure sodium chloride (Merck) in ultra-pure de-ionized water. The calibrated electrode set was also verified by means of a Merck 0.1 N sodium chloride Titrisol (9945) standard solution.

The millivolt (mV) signal of the free chloride in the pore water was converted to grams per millilitre (g mL⁻¹) by means of the calibration curve and the corrected mass (g mL⁻¹) was calculated by taking the percentage water mass loss of the sample in consideration. The bound chloride content was calculated as the difference between the initial chloride addition and the free chloride for the cement and the BFS mineral admixture.

The chemical composition of OPC and BFS used were determined by X-ray fluorescence spectroscopy (Philips PW 1840) according to standard procedures²⁴ and is given in Table 1.

3. Results and Discussion

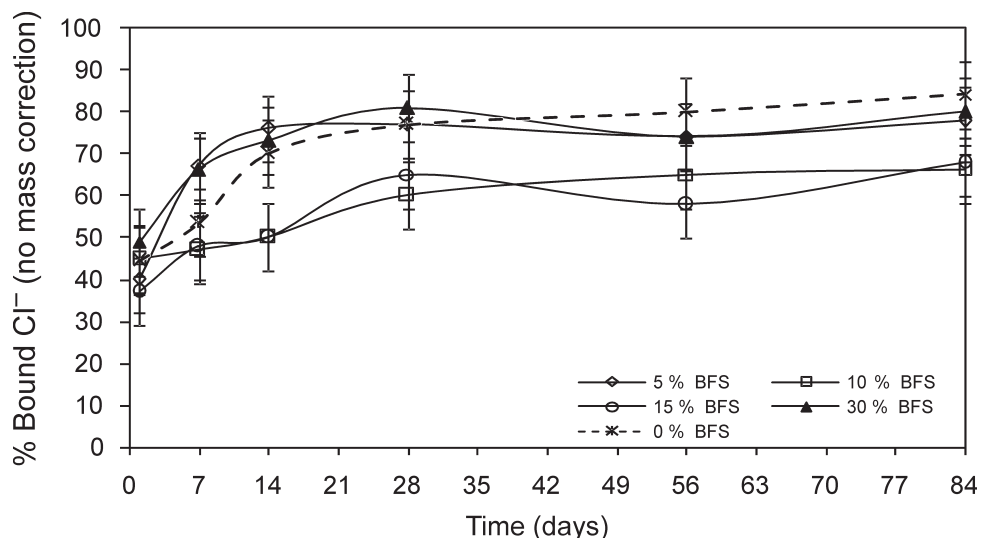
The bound chloride results are shown graphically in Fig. 1 as a function of curing time for the 0.25 % chloride addition to OPC and various OPC-BFS blended combinations. The values were not normalized to a 100 % OPC content, and took chloride binding by all possible mechanisms into account. It can be seen that there is a gradual increase in the percentage chloride bound towards constant or little changing values after 28 days by all the cementitious mixtures, after which the amount of chloride bound stayed more or less constant for each particular mixture. OPC had the highest binding capacity after 28 days. It is not clear why the 5 % and 30 % BFS additions, as well as the 10 % and 15 % additions, seem to be similar, but clearly all the mixtures reached a plateau in their chloride binding after 28 days as shown for the

0.25 % chloride addition. At the final curing age of 84 days all the bound chloride contents were between 68 and 80 %. A similar pattern was observed for the 0.5 % and 1.0 % chloride additions to these blends. At a 2.0 % chloride addition level, the order of chloride-binding efficiency changed to the following: OPC > 30 % BFS/OPC > 15 % BFS/OPC > 10 % BFS/OPC > 5 % BFS/OPC (Fig. 3).

The XRD patterns in Fig. 2 confirmed that Friedel's salt formation occurred in both the OPC and blended samples.

Figure 3 illustrates the performance of the OPC₁₀₀ and the various BFS blends in binding chloride already present in the matrix at 84 days. The single-component system of OPC outperforms all the blends containing BFS additions made in the range of 5 to 30 % BFS. When considering mass of chloride bound per gram of binder (OPC), the results obtained agree with those by Dhir *et al.*²¹ and confirmed that there is a near-linear increasing relationship between the amounts of chloride bound for a particular BFS content, when the concentration of the chloride increases up to 1 % (Fig. 4). However, it contradicts the results by Hirao and Yokohama¹⁶ who found that blended OPC-BFS cement had increased chloride binding compared to OPC alone, although it has to be borne in mind that their investigation involved a 60 % BFS addition to OPC.

In order to separate the effect of BFS addition from the two-component system the values of the total chloride bound were normalized as if it were a single-component OPC system only, therefore indicating the potential of the OPC to bind the chloride without interference from the BFS. For the normalized values, the 30 % BFS blend values were multiplied by 100/70, based on the assumption that the BFS does not contribute to the chloride binding, and that chloride binding only takes place in the OPC and/or its hydration products. The rationale for this was that if there is then a difference in bound chloride between OPC and the normalized values obtained for the blends, it would be because of the effect of the BFS. This approach allows one to not only separate the effect of the two components in the binary blend, but also allows direct comparisons because the

**Figure 1** Percentage bound chloride in cement pastes containing up to 30 % BFS additions and 0.25 % admixed chloride cement paste samples.

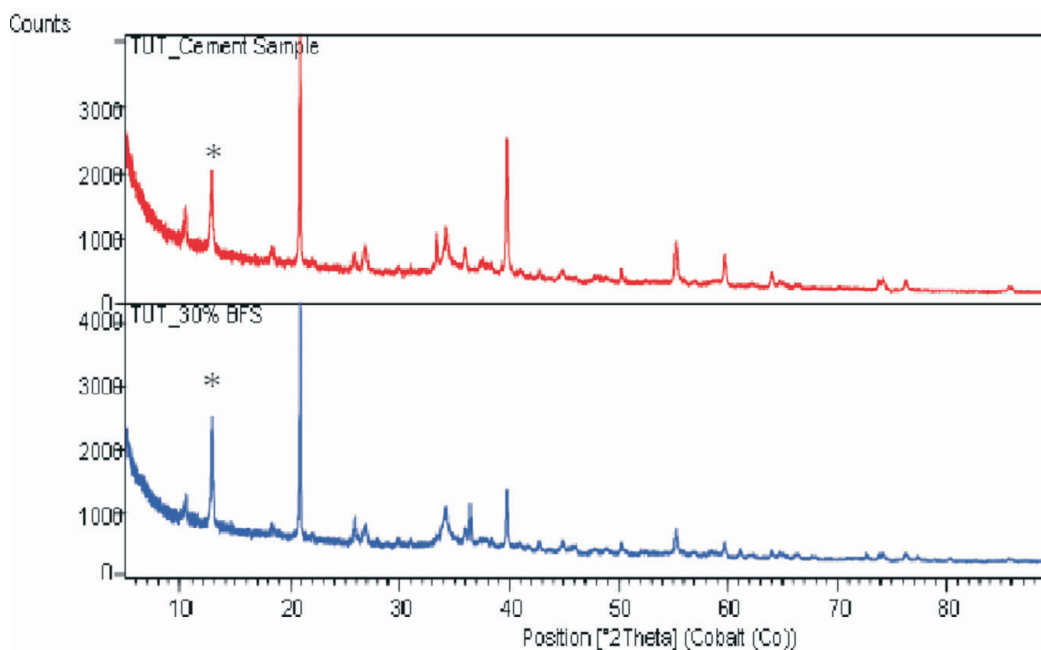


Figure 2 XRD patterns of 30 % BFS pastes and 0.25 % admixed analysed in cement and with the $13^{\circ} 2\theta$ Friedel's salt peaks in both diffractograms, as indicated by (*).

dilution effect of the BFS additions were taken into account.

Tables 2 and 3 summarize all the results of chloride binding obtained in this investigation, both in the format where a moisture correction was done only to determine the total chloride bound on a dry mass basis referred to as total chloride-binding capacity, as well as the normalized values as if there were 100 % OPC present in each case, referred to as matrix adsorption/cement chloride binding (CCB_N). Normalizations were done based on the assumption that the OPC and slag reactions were treated as competing and equivalent and no potential time delays caused by the partial replacement were taken into account. In addition, no compensation has been made to account for potential variations in the degree of cement hydration in the different blends. For example if the binding matrix contained 70 % cement it was normalized by multiplying the obtained chloride-binding value by a factor of 100/70 to allow comparison with a binding matrix consisting of 100 % OPC alone. The difference between the latter values and the non-normalized ones gives the contribution to chloride binding in each case because of the blast furnace slag presence. The results are given for 84 days to ensure that

stable conditions, not influenced by any slow hydration reactions of the slag existed, and that valid comparisons could be made.

One observes a few interesting trends from the data presented in Tables 2 and 3. Firstly, it is clear from the values that not all the chloride is bound and that some of it always remains as free chloride in the pore water solution. If one considers only 100 % OPC, it is clear that the chloride-binding capacity through the formation of Friedel's salt and or adsorption *via* the C-S-H phase is not sufficient to immobilize all the chloride added to the system. In addition, this capacity is compromised by the addition of BFS to the OPC, as is illustrated by the changes in the masses of chloride bound ($CCB_N - CCB_{100}$) by the blends as seen in Fig. 5. It is observed that only the 30 % BFS does not negatively influence the % chloride bound.

Both Hirao and Yokohama¹⁶ and the Dhir group²¹ pointed to the significance of the amount of calcium aluminate and calcium ferrite/aluminoferrite phases present in the mineral admixture as an important contributing factor to the total amount of chloride that can be bound in the final cementitious matrix, because

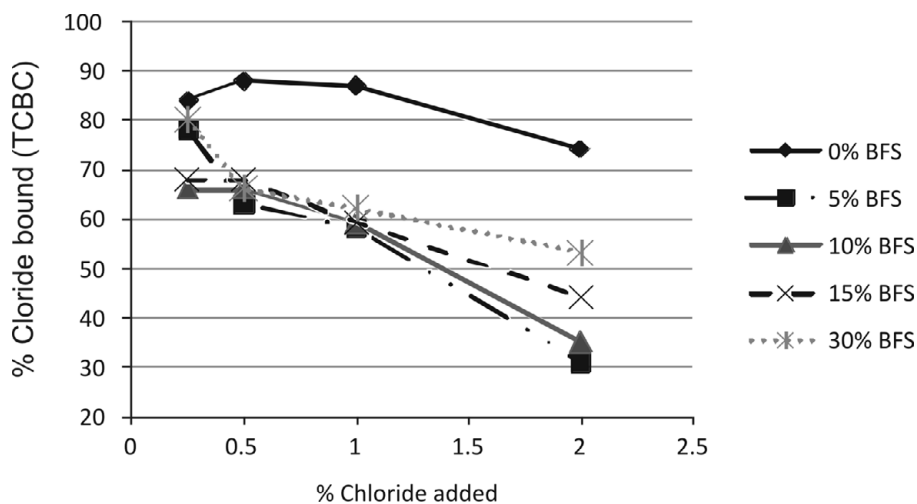


Figure 3 Percentage total chloride-binding capacity (TCBC) of the various samples as a function of varying amounts of chloride added to each paste.

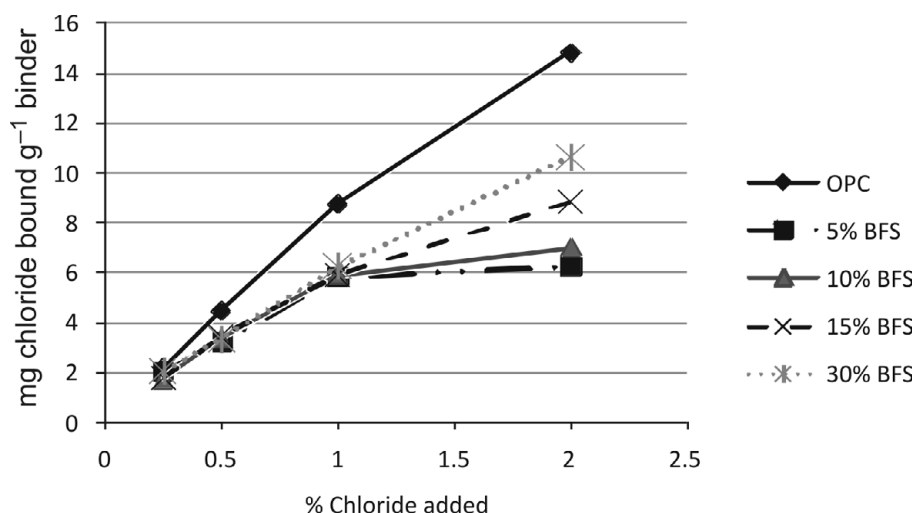


Figure 4 Bound chloride in mg per g of binder for the various blends as a function of percentage chloride added to each paste.

these phases can also form Friedel's salt in the presence of chlorides. In practical terms, it means that an ever increasing or constant chloride concentration in a BFS-OPC concrete will at some stage exhaust the capacity of the matrix to bind it, except if the slag hydration product create an additional sink (trap) for chloride ions. At an increasing BFS replacement level up to 30%, it seems that some free chloride ions may remain in the pore solutions, thus allowing the risk of the ions reaching rebar reinforcement to cause corrosion.

When considering the total chloride binding by the cement paste, or blended cement pastes, one notices that the OPC on its own displayed a greater amount and degree of chloride binding than any of the blended cement pastes. It is also evident that, for up to a 1% chloride level, there is very little difference in the amount of chloride bound by the different blended cement pastes, and that within experimental error their binding of the free chloride is similar. However, it seems that when the chloride addition is increased beyond 1 to 2%, the blended cement pastes of up to 15% BFS reached a point of saturation and could not bind the free chloride to the same extent any longer. At 2% chloride concentrations the amount of chloride bound becomes more dependent on the level of BFS present in the blend, and the

larger the BFS content, the more chloride is bound due to lesser OPC in the matrix.

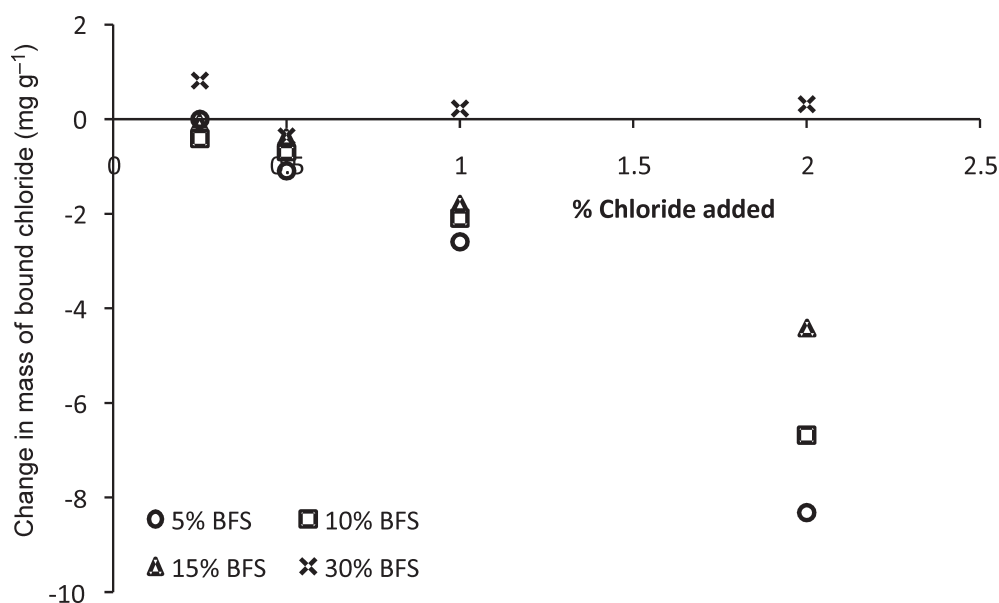
Most literature does not always distinguish between the different stages in the chloride ingress and binding process and the subsequent effect on rebar corrosion. The chloride binding by BFS additions or partial replacements are influenced by a number of factors, such as: the amount of BFS in the final matrix, the difference in hydrations rates between the cement and the BFS, the degree of hydration in the matrix as a whole, the type and composition of slag used, etc. Therefore, one has to be careful in predicting the mitigating ability and influence of BFS replacements to reduce rebar corrosion. This implies that one needs to distinguish between the influence of the BFS additions in blends to decrease the permeability of the matrix and decrease the ingress of chloride from the process of chloride binding taking place once the chloride ions have penetrated or are internally present in the matrix. In the first instance the BFS plays the dominant role in decreasing the permeability and in turn reducing the potential for corrosion attack on the rebar present, while in the latter instance the level of OPC present becomes the primary important factor, and especially so once a critical level of chloride content in the matrix is reached and exceeded.

Table 2 Comparison of the percentages of corrected and non-corrected masses of bound chloride data in paste mixtures containing up to 30% BFS and 0.25 to 2% chloride additions, hydrated for 84 days (CCB_{100} = cement chloride binding of 100% OPC, CCB_N = cement chloride binding of normalized value and TCBC = total chloride-binding capacity).

		Bound chloride/%			
		0.25% Cl ⁻ addition /% (±σ)	0.5% Cl ⁻ addition /% (±σ)	1% Cl ⁻ addition /% (±σ)	2% Cl ⁻ addition /% (±σ)
100% OPC	CCB_{100}	84 ± 1	88 ± 1	87 ± 1	74 ± 1
5% BFS	CCB_N	82 ± 1	66 ± 1	61 ± 8	33 ± 3
	$CCB_N - CCB_{100}$	-2	-22	-26	-41
	TCBC	78 ± 1	63 ± 1	58 ± 8	31 ± 3
10% BFS	CCB_N	73 ± 2	73 ± 2	66 ± 4	39 ± 5
	$CCB_N - CCB_{100}$	-11	-15	-21	-35
	TCBC	66 ± 2	66 ± 2	59 ± 4	35 ± 5
15% BFS	CCB_N	80 ± 3	80 ± 3	69 ± 7	52 ± 3
	$CCB_N - CCB_{100}$	-4	-8	-18	-22
	TCBC	68 ± 3	68 ± 3	59 ± 7	44 ± 3
30% BFS	CCB_N	114 ± 1	94 ± 2	89 ± 1	76 ± 4
	$CCB_N - CCB_{100}$	30	6	2	2
	TCBC	80 ± 1	66 ± 2	62 ± 1	53 ± 1

Table 3 Comparison of the mass of chloride bound per gram of binder containing zero to 30 % BFS and 0.25 to 2 % chloride additions, hydrated for 84 days.

		mg bound chloride per gram of binder			
		0.25 % Cl ⁻ addition /mg g ⁻¹ ($\pm\sigma$)	0.5 % Cl ⁻ addition /mg g ⁻¹ ($\pm\sigma$)	1 % Cl ⁻ addition /mg g ⁻¹ ($\pm\sigma$)	2 % Cl ⁻ addition /mg g ⁻¹ ($\pm\sigma$)
100 % OPC	CCB ₁₉₈₄ , ₁₀₀	2.1 \pm 0.03	4.4 \pm 0.02	8.7 \pm 0.02	14.8 \pm 0.02
5 % BFS	CCB _N	2.1 \pm 0.04	3.3 \pm 0.05	6.1 \pm 0.21	6.5 \pm 0.70
	CCB _N – CCB ₁₀₀	0	-1.1	-2.6	-8.3
	TCBC	2.0 \pm 0.04	3.2 \pm 0.05	5.8 \pm 0.21	6.2 \pm 0.70
10 % BFS	CCB _N	1.8 \pm 0.06	3.7 \pm 0.13	6.6 \pm 0.12	7.8 \pm 1.14
	CCB _N – CCB ₁₀₀	-0.4	-0.7	-2.1	-6.7
	TCBC	1.7 \pm 0.06	3.3 \pm 0.13	5.9 \pm 0.12	7.0 \pm 1.14
15 % BFS	CCB _N	2.0 \pm 0.07	4.0 \pm 0.18	6.9 \pm 0.18	10.4 \pm 0.75
	CCB _N – CCB ₁₀₀	-0.1	-0.4	-1.8	-4.4
	TCBC	1.7 \pm 0.07	3.4 \pm 0.18	5.9 \pm 0.18	8.8 \pm 0.75
30 % BFS	CCB _N	2.9 \pm 0.04	4.0 \pm 0.11	8.9 \pm 0.18	15.1 \pm 0.88
	CCB _N – CCB ₁₀₀	0.8	-0.4	0.2	0.3
	TCBC	2.0 \pm 0.04	3.3 \pm 0.11	6.2 \pm 0.18	10.6 \pm 0.88

**Figure 5** Change in chloride-binding capacity (mg of chloride per gram of binder) in cement pastes as a result of varying amounts of BFS additions at 84 days.

4. Conclusions

While taking into consideration the experimental limitations and methods employed, the following conclusions may be made from this investigation:

1. Chloride binding in OPC/BFS blends is a combination of Friedel's salt formation by the OPC component, and binding by the BFS component.
2. OPC performed better than the OPC-BFS blended pastes of up to a 30 % addition of BFS, in terms of chloride binding.
3. An increasing BFS content yielded increased admixture binding capacity to the different blends once a saturation point in the level of chloride present inside the matrix was reached.
4. OPC and BFS, as well as blends, have limited chloride binding-capacity and once this is exceeded, chloride ions will be freely available in pore water solutions and can pose corrosion threat to reinforcement bars.
5. It is evident that a distinction is required between the role of BFS in preventing chloride ingress into a cementitious

matrix, and its further contribution to chloride-binding process once the ions are present inside the matrix. An extended investigation including greater than 50 % BFS replacements, a wider range of chloride concentrations, and different curing conditions could assist to provide more light on this phenomenon.

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