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Friedel's Salt and Hydrotalcite – Layered Double Hydroxides and the Protection against Chloride Induced Corrosion

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Abstract. This paper discusses some aspects of corrosion protection that fly ash and GGBFS offer to steel reinforcement in concrete. It focuses on the formation of two types of Layered Double Hydroxides (LDH's). These are Friedel's salt and Hydrotalcite. While Friedel's salt is known to form in fly ash blends, the authors support the evidence of hydrotalcite formation in GGBFS blends as a result of the magnesium content in the slag. The paper discusses the corrosion protection performance of GGBFS concrete and compares it to that of fly ash concrete. The paper shows the superior advantage of including GGBFS for corrosion protection. The authors explored the probable reasons for this significant advantage and relate it to the formation of hydrotalcite in GGBFS concretes.

1 Introduction

Extensive research has been done on the ability of Friedel's salt to bind chlorides and thus protect steel reinforcement from corrosion. However, another compound that has been only scarcely mentioned in the context of cementitious hydration products is hydrotalcite. Hydrotalcite is a naturally occurring carbonate mineral. It was found in magnesite deposits in Norway, and was first reported in 1842 by Carl Christian Hochstetter who gave it its name because of its high water content and its resemblance to talc [1]. It is a layered double hydroxide and is often expressed as $Mg_6 Al_2CO_3(OH)_{16}\cdot 4(H_2O)$ and has been described as anionic clay [2]. This compound was first synthesized in 1942 [3]. It has attracted special attention because of its anionic exchange capability and applications in the industry [4] and medicine [5].

The structure of hydrotalcite constitutes layers of magnesium and aluminium hydroxides that carry net positive charge, and interlayers that are occupied by water and anions with negative charge. The typical cation is Mg^{2+} but is replaceable by other cations, especially by Al^{3+} and Fe^{3+} [6]. The anions can be OH^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}, Cl^-, etc. [7] and they also, are interchangeable [6].

However, hydrotalcite assumes a prominent presence in slag cements [8]. The formation of this hydration product is influenced mainly by the presence of magnesium oxide. The quantity of this oxide in Portland cement should be kept below a maximum of 2% [9]. This is because the magnesium oxide in portland cement is in the form of periclase which is 'dead burnt' crystalline MgO [9] that causes severe unsoundness [8]. On the other hand, blast furnace slag cement can contain as much as 20% MgO without causing unsoundness. This is due to the fact that MgO in GGBFS is vitreous, which upon hydration forms a solid solution series [10] with its end members C_4Aaq and M_4Aaq that provides stability to the hydrated GGBFS cement [8].

The formation of hydrotalcite in GGBFS cement paste was first reported in 1972 by Kuhle and Ludwig [11]. This finding was confirmed by Taylor in 1973 [12]. Quite recently, Taylor et al. identified its presence in 20 year old, as well as 14 month old GGBFS cement blends, but did not report any presence of it in plain Portland cement pastes of the same age [13]. In their paper, it is interesting that they noted the absence of carbonation in the GGBFS pastes while carbonation was observed in normal cement pastes.

This paper is mainly concerned with the chloride-induced corrosion of steel reinforcement in concrete. The discussion focuses on, and compares the protection that the two pozzolanic materials; fly ash and GGBFS offer. It further relates this protection to the two Layered Double Hydroxides types, namely Friedel's salt and hydrotalcite.

2 The role of Friedel's salt

Typical C_3A content in Portland cements ranges from 2 - 11 % and for C_4AF, the typical content ranges from 7 -

17%. In the presence of chlorides, calcium chloro aluminate hydrate forms. This salt is expressed as $3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$ or, if iron is present; $3CaO\cdot Al_2O_3\cdot Fe_2O_3.CaCl_2\cdot 10H_2O$ and is called Friedel's salt (after G. Friedel who discovered it) [14].

This compound also belongs to the Layered Double Hydroxides (LDHs) [15] because it consists of positively charged hydroxide layers such as $[Ca_2Al(OH)_6]^+$ or $[Ca_2(Al,Fe)(OH)_6]^+$ with the water molecules and negatively charged ions occupying the interlayer spaces.

Talero et al [16] found that Friedel's salt that derives its origin from the aluminium oxides of a pozzolana, such as fly ash, is fast forming. In contrast, Friedel's salt that derives its origin from the C_3A of the Portland cement is slow forming.

This type of LDH, accommodates Cl^- ions within its interlayers and has been thought to be insoluble [17]. Friedel's salt being of the LDH category, possesses the capability of exchanging the anions. It is claimed that it has the capability of binding chlorides through two mechanisms; the first is by adsorption and the second is by exchanging the OH^- with Cl^- ions [18]. Many researchers, e.g. [19-21] have postulated that Friedel's salt is a main, if not the most important factor responsible for the improved performance of fly ash blended concrete in chloride rich environments.

3 Effect of fly ash on chloride initiated corrosion

In a prolonged chloride ponding test, Ahmed [22] and recently, Kayali and Ahmed [23] showed that a 25% class F fly ash replacement has reduced corrosion current of steel bar reinforcement in concrete slabs from 0.1 $\mu A/cm^2$ in plain Portland cement concrete, to 0.055 $\mu A/cm^2$. They also showed that the improvement in corrosion resistance of the 50% blend is only marginal compared to that of the 25% blend (Figures 1 and 2).

This led to the postulation that there must be another level of replacement between 25% and 50% where an optimum improvement may be achieved. Hence, increasing the fly ash content above an apparently optimum level positioned somewhere between 25% and 50%, must have steadily increased (in the negative direction) the corrosion potential as well as the rate of corrosion. It would have been thought that increasing fly ash beyond that range would significantly increase the binding of chloride ions and thus decrease the corrosion current rate. Yet, the opposite was observed. It may therefore, be reasonably argued that the increased fly ash content beyond an optimum level, may have increased the permeability to chloride and this may have counter affected the binding of chloride by the increased fly ash. However, the evidence in [24] showed that with the exception of the 70% fly ash replacement level, the 25% and the 50% replacement levels did not significantly increase the total chloride permeability. This leads to conclude that what must have started the increase in the rate of corrosion is an increase in the free chloride available in the pore solution. That is; there must be a certain limit by which the capacity of fly ash to bind chloride would be exhausted.

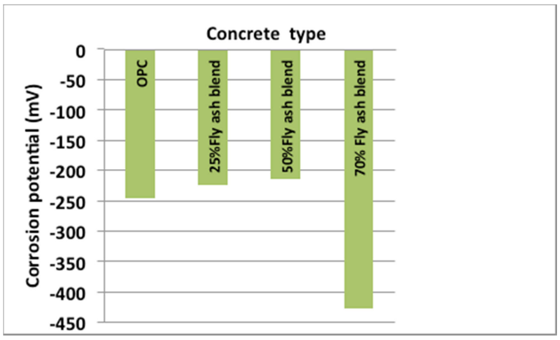


Fig. 1. Corrosion potentials for plain and fly ash blend reinforced concrete slabs ponded with 3% sodium chloride solution for over two years

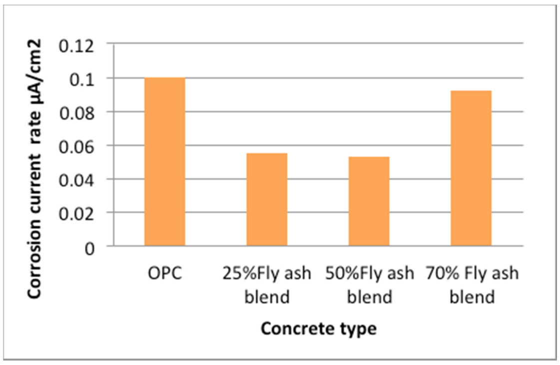


Fig. 2. Corrosion current rate for plain and fly ash blend reinforced concrete slabs ponded with 3% sodium chloride solution for over 2 years

Kouloumbi and Batis [25] have shown that the ratio of free chloride to total chloride after 5 months immersion in 3.5% NaCl solution reduced from 0.077 for concrete without fly ash to 0.052 and 0.032 for concrete with 15% and 30% fly ash replacement respectively. The rate of reinforcement corrosion in the two fly ash concretes was also reduced by 25% and 30% compared to the reinforcement corrosion in the plain OPC concrete [25]. Their work supports the above postulation that an optimum level, probably in the 30% fly ash replacement vicinity must exist.

Since it is well established that fly ash pozzolanic reactions consume the calcium hydroxide formed as a product of Portland cement hydration [26], it may be inferred that Friedel's salt formation is closely linked to the pozzolanic reactions. Thus, the exhaustion of calcium hydroxide results in a limitation to the pozzolanic reactions and hence a limitation to the production of Friedel's salt. Subsequently, an increase in the fly ash replacement level beyond a certain optimum value may only increase porosity and permeability of the concrete and any little increase in the porosity and permeability would adversely affect the corrosion rate.

4 Effect of carbonation on chloride binding in fly ash blended concretes

Kayyali and Haque [27, 28] have reported that in the presence of accelerated carbonation of mortars, whose cementitious material comprised 30% fly ash and 70% Portland cement, free chloride ions were released into the pore solution after they had been initially bound. They reported furthermore, that with prolonged curing of fly ash mortars, the situation related to the released chloride in the presence of carbonation became far worse. Prolonged initial curing helped to retain bound chlorides in the case of Portland cement mortar subjected to carbonation. However in the case of the prolonged initial curing of mortars with fly ash, carbonation resulted in significant release of the chloride that was initially bound. Kayyali and Haque attributed this effect to the fact that prolonging the initial curing in fly ash blends, results, through the pozzolanic reactions, in the consumption of free calcium hydroxide to form more complex products of hydration. The consequence of the depletion of $Ca(OH)_2$ is that any further CO_2 will only have the opportunity to react with the complex hydration products to produce carbonates and water, thus making it more possible for the chloride ions to be released in the pore solution [27]. The present authors suggest that in the case of carbonation, the penetrating carbon dioxide quickly forms carbonic acid [29] and thus creates a conducive environment for the dissolution of Friedel's salt.

Goni and Guerrero have produced evidence of the disappearance of Friedel's salt in the case of accelerated carbonation and the resulting reduction of the pH value from about 12 before carbonation to just 6.3 after carbonation [30].

Thus, Friedel's salt, although generally known as being insoluble, has been acknowledged to decompose in the presence of carbonation [19]. The decomposition of Friedel's salt has been clearly attributed to the reduced pH [31]. This further confirmed the observation by Page and Vennesland that Friedel's salt solubility increases as a result of reduced alkalinity as they demonstrated when silica fume [32] was incorporated.

The authors suggest that since Friedel's salt would form in the presence of chlorides in fly ash blends [19, 33], it follows that if the concrete is then subjected to carbonation, the production of calcium bicarbonate is readily ionised in the solution. The negatively charged bicarbonate ion replaces the chloride ion as the carbonates are preferably selected by LDH-like compounds [7].

5 Comparison of fly ash with GGBFS blended concretes

5.1 Effect on carbonation

More recently, Ahmed [22] conducted extensive testing on high volume fly ash subjected to carbonation at the average rate of 0.3% which is expected in a large city environment [9]. He tested carbonation depth up to 2 years of exposure on two grades of concrete; one whose w/binder ratio was 0.38 while the other had w/binder ratio of 0.48. The results are shown in Figures 3 and 4. It can be seen from these two Figures that in both cases of w/binder ratio, the concrete made with GGBFS has performed far better in carbonation resistance than its counterpart in which fly ash was used. At this point of the discussion, the authors point out to the following relevant observations:

1. If the replacement level is taken as the criterion of comparison, then it can be concluded that for fly ash, a replacement of 50% or larger would cause deep carbonation in a relatively very short time. The depth of carbonation after 2 years would approach steel reinforcement location and thus make corrosion highly probable, even if caused only by carbonation. On the other hand, replacing Portland cement by GGBFS as high as 70% did not cause alarming carbonation penetration depth. Thus, according to this criterion, it may seem obvious that GGBFS performs far better than fly ash as a safe replacement for cement.
2. One must consider the fact that fly ash replacement has to be limited to approximately 25-30% of the binder quantity in order to match higher replacement proportions of GGBFS without compromising the strength.

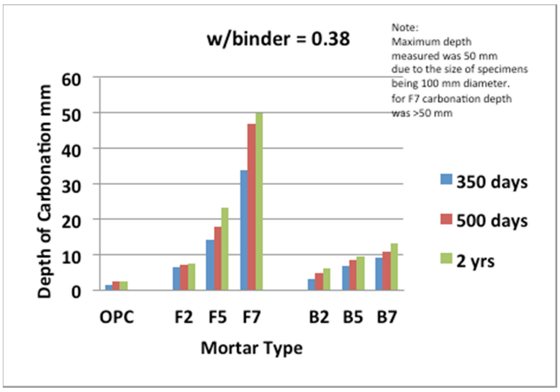


Fig. 3. Depth of carbonation in OPC, fly ash-OPC and GGBFS-OPC concretes, all at 0.38 w/binder. F2 means 25% fly ash replacement of OPC, F5 means 50% replacement and F7 means 70% replacement. B2 means 25% GGBFS replacement of OPC, B5 means 50% replacement and B7 means 70% replacement. 1 year strength; OPC: 77 MPa, F2: 59 MPa, F5: 35 MPa, F7: 16 MPa, B2: 69 MPa, B5: 56 MPa and B7: 59 MPa

5.2 Effect on corrosion performance

From the durability aspects, and in particular that related to reinforcement corrosion, it has been established that fly ash is beneficial in causing significant protection to steel reinforcement [34]. In the case where corrosion initiation was related to chlorides, this protection capability has been related to the decrease in the permeability of concrete to chloride ion penetration [35] and to the formation of chloroaluminates [36].

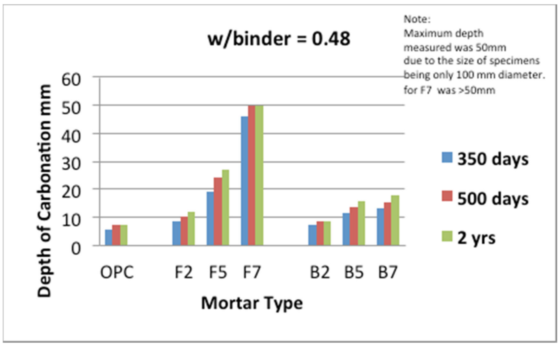
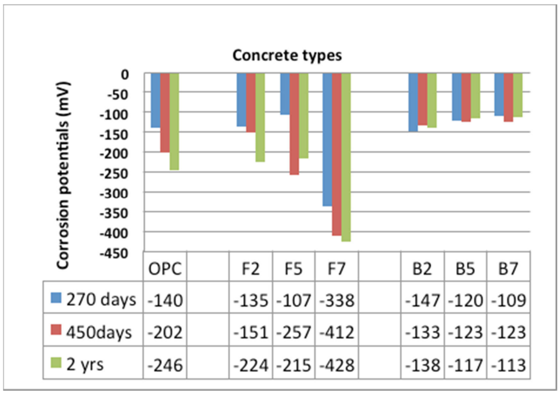


Fig. 4. Depth of carbonation in OPC, fly ash-OPC and GGBFS-OPC concretes, all at 0.48 w/binder.
1 year strength values; OPC: 56 MPa, F2: 46 MPa, F5: 28 MPa, F7: 11 MPa, B2: 56 MPa, B5: 43 MPa and B7: 37MPa

Comparison of the performance based on the pozzolanic material replacement level, it can be seen in Figure 5 that comparing the corrosion potentials of OPC concrete slabs with fly ash blends slabs (F2, F5 and F7) it may be concluded that fly ash reduced corrosion potentials only slightly when the replacement levels were 25% and 50%. However, at 70% replacement level, corrosion potentials were significantly higher than in OPC concrete slab and indeed much more negative than the -300 mV considered by ASTM as the indicator for 95% probability of corrosion occurrence [37]. In contrast, effectively, all the reinforced slabs in which the concrete was a blend of OPC and GGBFS, gave results that are less negative than OPC concrete and fly ash-OPC concretes. In fact, all the corrosion potentials of GGBFS blends did not approach the most conservative threshold of -200 mV for corrosion probability occurrence [38].

More importantly it is observed that the GGBFS blends showed less potential to reinforcement corrosion when the slag replacement level increased from 25% to 50% and 70%.

The results of corrosion current measurement shown in Figure 6 indicate a generally better performance in all blended concretes compared with the Portland cement concrete.



	OPC	F2	F5	F7	B2	B5	B7
🟦 270 days	-140	-135	-107	-338	-147	-120	-109
🟥 450days	-202	-151	-257	-412	-133	-123	-123
🟩 2 yrs	-246	-224	-215	-428	-138	-117	-113

Fig. 5. Corrosion potential values for reinforced concrete slabs with plain, fly ash blends, and slag blends, ponded with 3% sodium chloride solution (Note: nomenclature is the same as for Fig. 3)

The corrosion current measurements for the fly ash and the slag concretes did not follow their trend shown in the potentials measurements. Therefore the reinforcement meshes of selected slabs were exposed and inspected for corrosion. Their corrosion rate was measured by Ahmed [22] in terms of mass loss per unit area of reinforcement per year, after 2 years of exposure. Ahmed found that the mass losses in the reinforcement due to corrosion were 3.9% and 15.9% for fly ash blend concrete at 50% and 70% replacement levels respectively. The mass loss for the 70% GGBFS blend was only 0.63%. Although these results are not conclusive and did not cover all the slabs involved, yet they were, together with the visual inspection, indicative enough of the negligible corrosion occurring in GGBFS slabs and the significant corrosion occurring in the fly ash of 70% replacement slab.

Furthermore it was observed that:

1. The corrosion potentials for GGBFS concretes, at 70% replacement level were lower than those of fly ash concretes at 50% and 70% replacement, without

reducing the compressive strength level below that obtained with the 25% fly ash concrete blend.

2. Measurements carried out on the active corrosion current gave slightly different results from those given by potential values. This is expected because potential values are only indicative of the probability of corrosion occurrence rather than of active corrosion. Figure 6 shows that the reinforcement in the slabs with OPC concrete had a current density value associated with the start of low corrosion activity [39]. The results showed that the 25% fly ash blend and the 25% GGBFS blend both produced very low corrosion activity while the slab of 70% GGBFS blend resulted in negligible corrosion current in its reinforcement mesh.

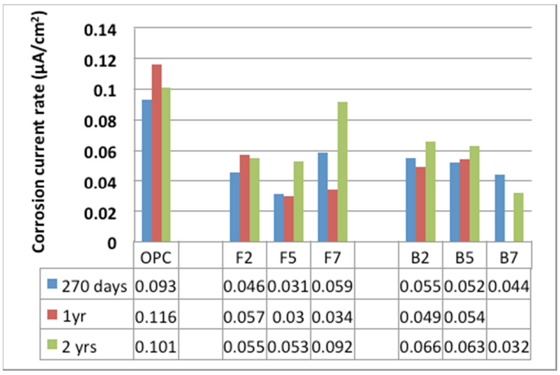


Fig. 6. Corrosion current rate values for reinforced concrete slabs with plain, fly ash blends, and slag blends, ponded with 3% sodium chloride solution (Note: nomenclature is the same as for Fig. 3)

5.3 The ability of hydrotalcite to bind chlorides in concrete

Hydrotalcite's ability to bind anions has been known and very much utilised in the past in numerous uses, like removing contaminants in water [40], neutralising acids in the stomach [5] and as a corrosion protective film applied on metals [41]. Moreover, the ability of GGBFS to bind chlorides and reduce steel corrosion has been reported. For example Arya and Xu [42] have found that GGBFS performed better than fly ash blends and OPC concrete in binding chloride. They also found that fly ash concrete blends performed poorly as far as resisting corrosion is concerned. They attributed that poor performance to fly ash's lower chloride binding capacity [42]. Dhir et al [43] reported a high chloride binding capacity in GGBFS concrete. They attributed this behaviour to the high aluminate content of GGBFS which they believed that it leads to an increase in the production of Friedel's salt [43].

In a very interesting paper, Page et al reported drastic reduction in free chloride ions as a result of using GGBFS in cement paste [19]. In their paper, they reported comparison of the capacity to bind chloride, between several cement paste blends including fly ash as well as GGBFS blends. They found that the proportion of the free chloride ions remaining in the pore solution of fly ash-OPC paste blend was 0.47 of the corresponding value for plain OPC paste. However, the proportion of remaining free chloride in the corresponding GGBFS paste was 0.34 that in the OPC paste. They also found that the proportion of the OH^- concentration in the pore solution of fly ash-OPC paste was reduced to 0.62 of its value in OPC paste, and that the OH^- concentration in GGBFS paste was reduced to the same value as in the fly ash case. This is quite interesting as it resulted in the ratio of Cl^-/OH^- to be 0.085 in fly ash blend while it was 0.061 in the GGBFS blend. This ratio has been claimed to be a significant criterion defining the onset of chloride initiated corrosion in reinforced concrete [19, 20]. This result ties well with the observation that GGBFS-OPC concrete offers better corrosion resistance than fly ash-OPC concrete. It is also significant to note, that the binding of OH^- ions has occurred, and to the same extent, as a result of fly ash or GGBFS inclusion. However, it may be inferred from their results that on the presumption of Friedel's salt being the LDH type formed in the case of fly ash, while hydrotalcite being the type formed in the GGBFS case, there does not appear that there is an indication of preference of binding OH^- over that of Cl^- in the interlayers of either type of the LDH's**.** This observation is of particular importance and needs further confirmation in cases of high alkalinity internal environment, such as when using high molarity activators, in concretes that may be subjected to chloride ingress.

However, until quite recently, and to the best of the authors' knowledge, there has been no attempt to link the phenomena of good corrosion performance and high chloride binding, to mainly hydrotalcite formation. It was not until 2012 when such linkage appeared in a study by Kayali et al. [44] on the role of hydrotalcite in chloride binding in concrete and its beneficial effect on corrosion protection. This has been followed by two other papers by Yang et al [45, 46] in which they supported the findings in [44] and presented synthesized modified hydrotalcites as additives for anti corrosion application in reinforced concrete.

Kayali et al [44] Found out that synthetic calcined hydrotalcite could remove more than 70% of chloride ions from 3% NaCl solution. Using XRD they were able to identify the formation of hydrotalcite in pastes of GGBFS contaminated with chlorides. Using Rietveld method [47] together with Rietica software [48] for quantification of the crystalline material, they found that hydrotalcite comprised more than 50% of the crystalline phases in hydrated GGBFS paste. Thus hydrotalcite constitutes the highest proportion of the crystalline phases in hardened GGBFS. In a very recent study, Khan et al [49] were able to quantify both Friedel's salt and hydrotalcite formations in GGBFS pastes. They found that in those pastes, hydrotalcite constitutes more than five times the amount of Friedel's salt. They further found that the presence of Portland cement together with GGBFS helped maintaining the supply of hydrotalcite.

6 Conclusions

In this paper, two types of layered double hydroxides (LDH's) were presented from the point of view of their effect in protecting reinforcement from chloride-initiated corrosion. The first LDH is Friedel's salt and the second is hydrotalcite.

It has been known that Friedel's salt was formed in concretes in which fly ash is used to replace a portion of Portland cement (OPC). Several advantages could be reaped as a result of such replacement. However there are also certain drawbacks and precautions that must be known and taken, especially when using fly ash in excess of 50% replacement and in polluted or chloride-laden environments. In this context, the following points may be drawn:

1. There is a limit to which chloride may be bound to fly ash as a result of the Friedel's salt effect. It is very likely that an optimum replacement exists between 30% and 50%. Exceeding such optimum may result in accumulation of chloride ions in the pore solution.
2. There has been reasonable evidence to conclude that Friedel's salt formation is associated with the pozzolanic reactions between fly ash and calcium hydroxide. Thus, the depletion of calcium hydroxide is expected to severely limit the formation of Friedel's salt and subsequently limit the binding of chlorides.
3. There is now compelling evidence that carbonation in the presence of chloride in fly ash blended cements can lead to accelerated corrosion. This is caused mainly by the drastic reduction of alkalinity in the pore solution surrounding the steel bars, the release of chloride ions from Friedel's salt in favour of carbonate and bicarbonate ions and the dissolution of Friedel's salt in low pH media.
4. There is sufficient evidence that hydrotalcite forms as a result of magnesia's presence in ground granulated blast furnace slag (GGBFS) in the cement. This type of the LDH's family possesses a high capability of binding chloride ions in solutions. Thus the use of GGBFS to replace large proportions of OPC may result in the following effects:

a) It has been observed that there is a much wider tolerance for a high GGBFS replacement than there is for fly ash replacement. It has been clear that concretes of comparable workability and mixture proportions were more resistant to carbonation if they contained high volume GGBFS rather than high volume fly ash.

b) There is growing evidence that the tolerance to carbonation is larger in GGBFS concrete than it is in fly ash concrete. This tolerance is believed to be caused by the greater capacity of hydrotalcite to bind large amounts of chlorides within its interlayers. This observation however, is in need for further conclusive confirmation.

c) There has been strong evidence that corrosion potentials, corrosion current density and mass loss are far less in GGBFS concrete than in OPC or high volume fly ash-OPC concrete in chloride-laden environment. The observed remarkable improvement in this performance has been linked to the formation of hydrotalcite, which is believed to be unique to GGBFS concrete. More importantly it has been found that the more GGBFS replacement to OPC, the less corrosion occurred. This observation has been linked to evidence that hydrotalcite formation has increased with the increase in the proportion of added GGBFS. Thus it is believed that the capacity of hydrotalcite to bind chloride ions is not impeded by very high GGBFS replacement to OPC. This may be considered a point of superior performance compared to that of fly ash concretes in as far as chloride induced corrosion is concerned.

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