Effect of Chloride Exposure Condition on the Performance of Concretes Containing PFA

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ABSTRACT
Over the past number of decades the use of different supplementary cementing materials have been investigated, with a view to increasing the resilience of reinforced concrete to chloride-induced corrosion. The slow nature of chloride-ion ingress has meant much of the information available on the relative performance of different concretes has been derived from accelerated testing, with the majority of these tests conducted under fully saturated conditions. While there is merit to such practices, there is also a need to examine the relative performance of different concretes under unsaturated conditions. This need is highlighted by the fact that reinforced concrete elements in the splash, spray and tidal zones of marine structures, which are subject to wetting and drying cycles, are most susceptible to reinforcement corrosion. This paper examines the effect of different wetting and drying cycles on the relative performance of OPC self-compacting concrete, and self-compacting concrete containing PFA. This was achieved through three sets of salt fog chamber tests, each with different wetting and drying cycles. It was found that, when compared to the OPC option, the relative chloride ingress resistance of the OPC + PFA concrete reduced when the degree of drying in the test increased. This indicates that fully saturated tests may somewhat overestimate the practical benefits of incorporating PFA into concrete in chloride rich environments.

Keywords: Chloride Ingress, Pulverised Fuel Ash, Supplementary Cementing Materials, Exposure Conditions, Concrete Durability, Self-compacting concrete

1.0 INTRODUCTION
The natural progression of chlorides into concrete is a slow process. Consequently, much of the information currently available on the relative performance of newer concretes such as Self Compacting Concrete (SCC), is obtained from highly accelerated testing (Li, 2001, Castro et al., 1997). While some of these studies compare concretes in unsaturated conditions, the majority of this laboratory testing has been carried out with concrete specimens in a fully submerged state (Yildirim et al., 2011, Audenaert et al., 2010, Hooton and Titherington, 2004, Guneysiz et al., 2005, Ampadu et al., 1999, Stanish and Thomas, 2003, Zhu and Bartos, 2003, Loser et al., 2010, Guneysiz et al., 2011, Sahmaran et al., 2009, Pathak and Siddique, 2012). There are valid reasons behind the popularity of fully saturated tests when examining the chloride resistance of concrete. Firstly, and perhaps most importantly, testing in fully submerged conditions means that a current can be applied to accelerate the process of chloride movement, allowing results to be obtained in a matter of days. This represents a considerable time saving when considering that natural chloride migration tests, which examine chloride transport in concrete without the application of an electric current, have durations of the order of months to years. Fully submerged testing allows testing to be standardised in a way that is difficult for tests incorporating wetting and drying. There is also merit to fully saturated test condition in terms of the moisture condition of the interior of the concrete during real marine exposure. It is recognised that the interior of concrete remains constantly saturated in most marine environments (Neville, 1995). This is due to the fact that wetting of concrete occurs very rapidly, while the drying of concrete is much slower (Neville, 1995). However, it is also recognised that wetting and drying cycles, and the relative length of the wetting and drying times, experienced by concrete in the marine environment can have a significant influence on chloride movement (Hong and Hooton, 1999, Neville, 2011). Testing of concrete in a fully saturated state, without any drying component incorporated, ignores this fact, focusing solely on the transport of chlorides by diffusion.

An important consideration, pointed out by Neville (1995), and proven experimentally by Hussain (2011), is that corrosion does not, in general, occur in fully saturated concrete due to a lack of oxygen at the depth of the reinforcement. Thus due to the
availability of oxygen at the reinforcement, and the role of absorption, leading to rapid chloride movement to a shallow depth, reinforced concrete elements in the splash, spray and tidal zones of marine structures, which are subject to wetting and drying cycles, are most at risk of reinforcement corrosion (Neville, 1995, Dhir et al., 1994, Ye et al., 2012). While testing concrete in a submerged condition allows a standard and uniform test to be developed, the discussion above highlights the fact that there is a need to also examine the marine durability characteristics of concrete in conditions which facilitate some level of concrete drying. This is especially true when comparing different concrete types, as relative performance may be affected by the wetting and drying conditions, which will be experienced in the critical zones of a reinforced concrete structure in service. For example, an OPC + PFA concrete could perform far better than an OPC concrete in the fully saturated condition, but could be only marginally better than the OPC concrete under exposure conditions with wetting and drying, i.e. the critical tidal and splash zone conditions experienced in service.

The authors are not aware of any papers in the published literature which examine the performance of different SCCs across varying exposure conditions. This may be due to the fact that such testing, with wetting and drying cycles, would have to be conducted under natural chloride migration conditions i.e. no application of electric current. As pointed out by Spiesz and Brouwers (2010) this slower form of concrete testing is far less common in the literature due to the time consuming, costly and labour intensive nature of these tests. This paper uses a series of three natural chloride migration tests, each having a different exposure condition. These tests were carried out in salt fog spray chambers. The experimental results presented herein thus allow examination of the effect of exposure condition on the relative performance of an OPC + PFA SCC, when compared to an OPC SCC.

2.0 EXPERIMENTAL TESTING

The mix designs for the OPC SCC and the OPC + PFA SCC are presented below in Table 1. The water/binder ratio for the mixes was 0.44 in accordance with the XS3 exposure class in EN206-1:2000 (European Standard Institution CEN, 2000). The mix designs and materials mimicked those used in the repair of Ferrycarrig bridge, an Irish marine bridge, which was repaired in 2007 using a number of different SCC options (Ryan and O’Connor, 2014).

Table 1. Mix design details per m³ of concrete

<table>
<thead>
<tr>
<th>SCC</th>
<th>OPC (kg)</th>
<th>PFA (kg)</th>
<th>Total Binder (kg)</th>
<th>Water (Ltrs)</th>
<th>w/b ratio</th>
<th>10mm Agg. (kg)</th>
<th>Sand (kg)</th>
<th>Plast. 1 (kg)</th>
<th>Plast. 2 (kg)</th>
<th>Plast. 3 (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>500</td>
<td>-</td>
<td>500</td>
<td>220</td>
<td>0.44</td>
<td>500</td>
<td>1140</td>
<td>2.7</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>OPC + PFA</td>
<td>350</td>
<td>150</td>
<td>500</td>
<td>220</td>
<td>0.44</td>
<td>500</td>
<td>1140</td>
<td>2.7</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

| 1 Aggregate; 2 Plastisiser; 3 Superplasticiser

Eurocode Standards (Centre European de Normalisation CEN, 2010a, Centre European de Normalisation CEN, 2010c, European Standard Institution CEN, 2010, Centre European de Normalisation CEN, 2010d, Centre European de Normalisation CEN, 2010e, Centre European de Normalisation CEN, 2010b). Compressive strength testing was carried out at 7, 28 and 56 days on 100mm concrete cube samples for both of the SCC mixes. Three cubes were tested at each of the three maturity points in accordance with EN 12390-3:2000 (Centre European de Normalisation CEN, 2009). Concrete absorption tests were carried out in accordance with BS 1881-122:1983 and ASTM C 642-06 (ASTM, 2006) to investigate the capacity of the two concretes to absorb chloride laden water after periods of drying.

A simple drying test was also conducted to investigate any differences in the drying potential of the two concretes. Concretes which dry out faster between chloride solution wetting cycles will be more prone to the absorption of chlorides in the outer millimetres of concrete cover upon commencement of a wetting cycle. The drying characteristics of various concrete options are, however, rarely considered in the context of the marine durability of different concretes. The simple procedure used for the drying tests for this paper was as follows: three duplicate 100mm concrete samples for each concrete type were soaked in a curing tank for 3 days, then dried with a paper towel and weighed. The samples were placed on gridded timber sheeting, which facilitated uniform drying for all samples. The order of the samples on the grid was arranged so that each row and column contained one of each sample type tested. The timber sheeting was then placed in an environmental chamber which was run on a dry cycle. The samples were removed at intervals and weighed. The percentage change in weight of the test specimens was calculated in the same manner as for the absorption test in accordance with (ASTM, 2006)

2.1 Chloride Transport Properties

As stated in the Introduction chloride transport properties for the SCCs were obtained from natural chloride migration testing i.e. testing which did not incorporate the use of an electric current to accelerate chloride movement. The form of testing utilised involved a two-step experimental process whereby: 1) samples were exposed to a chloride rich environment for 36 weeks, and 2) specimens were analysed after the exposure period to determine
chloride transport properties. For step one a salt fog chamber (Fig.1) was used to subject the SCC test specimens to the aggressive chloride environment. This specialised environmental chamber subjected concrete test samples to periodic wetting and drying cycles. During the wetting cycles a 5% (or 0.86M) NaCl solution fog fills the chamber (see Fig.2). Further details of the salt fog chamber used can be found in (Ryan and O’Connor, 2013). Three sets of 36 week tests were carried out, each with a different wetting and drying cycle. The relative humidity plot shows how the three weekly cycles vary, with the wettest cycle labelled exposure condition one, and the driest cycle labelled exposure condition three.

Three duplicate specimens were prepared and exposed in the salt fog chamber for both the OPC+PFA SCC and the OPC SCC for each test series. Step 2 of the experimental process commenced after the 36 week exposure period, and involved obtaining chloride transport properties for each concrete specimen. This test procedure, which is described in detail in (Ryan and O’Connor, 2016), involved profile grinding at 2mm depth increments in accordance with NT Build 442 (Nordtest Method, 1999), and subsequent analysis of concrete dust samples using acid soluble potentiometric titration in accordance with BS EN 14629:2007 (Centre Europeen de Normalisation CEN, 2007). Fick’s second law of diffusion with Crank’s error solution (Eq. 1) was then fitted to the resulting chloride profiles using regression analysis, allowing values for the chloride transport properties Cₛ and Dₜ to be obtained.

\[
C(x,t) = C_s \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{D_{app} t}} \right) \right]
\]  

Fig. 1. Salt spray chamber with samples in position and door open during wet cycle.

Fig. 2. Relative humidity plot showing weekly cycle for three exposure conditions

where \( C(x,t) \) is the percentage chloride content at depth x and time t, \( C_s \) is the surface chloride content, \( \text{erf} \) is the error function, x is the depth below the concrete surface being considered, \( D_{app} \) is the apparent diffusion coefficient and t is time.

It is noted that, by definition, the \( D_{app} \) values obtained from the testing in this manner, as with \( D_{app} \) values obtained from real structures in the tidal, splash and spray zones, incorporate chloride transport due to both diffusion and an element of absorption (Saassouh and Lounis, 2012). Obtaining apparent or effective diffusion coefficients from Fick’s second law, which incorporate an element of absorption, is accepted practice in the literature for real structures (Pack et al., 2010, Kwon et al., 2009), marine exposure sites (Thomas and Bamforth, 1999), and for laboratory based experiments (McPolin et al., 2005).

For the chloride exposure tests 300 x 300 x 150 mm slab samples, which were formed using timber formwork, were tested in exposure condition three, while 100 mm cube samples, formed in plastic moulds, were tested in exposure condition two. Both specimen types were tested in exposure condition one. Thus, to avoid the influence of unknown effects relating to differing mould types, or size effects, exposure condition one will be compared to both exposure condition two and three, but exposure condition two will not be compared to exposure condition three i.e. results from cube specimens will be compared to cubes, and results for slab specimens will be compared to slabs.

3.0 EXPERIMENTAL RESULTS

3.1 Workability and Strength Tests

Both the OPC and PFA SCC were within the SCC acceptable ranges for slump flow, V-Funnel, J-ring
and segregation tests in accordance with (Centre Européen de Normalisation CEN, 2010a). The OPC SCC had an SF2 slump and a T\textsubscript{500} time of 2.1 seconds, while the PFA SCC had an SF3 slump, with a T\textsubscript{500} of 3.0 seconds. Both concretes fell into the VF1 V-funnel classification, the PJ2 J-ring classification, and the SR1 segregation test classification. A picture of the OPC slump flow test is shown below, which illustrates the good cohesion in the mix.

The 7 day, 28 day and 56 day concrete compressive strength for the OPC SCC were 61 N/mm\textsuperscript{2}, 68 N/mm\textsuperscript{2}, and 74 N/mm\textsuperscript{2}, respectively. The corresponding values for the PFA SCC were 36 N/mm\textsuperscript{2}, 55 N/mm\textsuperscript{2}, and 64 N/mm\textsuperscript{2}.

### 3.2 Absorption and Drying Test Results

The purpose of the absorption testing, and indeed the drying test, was to give insight into the effect of changing exposure conditions on chloride transport properties across the two concretes. In this context the absolute values of test results for absorption and drying are of little interest. It is instead the comparative absorption and drying performance between the two SCCs which is of interest. In light of this, the PFA SCC absorption results are presented in Table 2 as a percentage of the OPC absorption. The OPC values are shown in the table as a reference. The drying test results are also presented in this manner. As can be seen from Table 2, the OPC+PFA SCC absorbed approximately 90% of the water the OPC SCC absorbed at the two time intervals. The OPC+PFA SCC was however found to dry notably faster than the OPC SCC, especially at earlier time intervals. In real exposure the drying time and wetting time will vary depending on the height of a reinforced concrete element above the low-tide line, or the susceptibility to sea-water splash or spray. Drying times will be longer in the splash and spray zones.

### 3.3 Chloride Transport Results

A chloride transport profile for the OPC SCC under exposure condition one is shown below in Fig. 4. The plot also shows Fick’s second law with Crank’s error solution fitted to the data. As can be seen from the Fig. 4, good fit was obtained with an r\textsuperscript{2} value of 0.99. Across the three duplicate OPC SCC samples and the three duplicate OPC+PFA SCC samples, the minimum $r^2$ value obtained from fitting Fick’s law with Crank’s error solution was 0.94.

### Table 2. Absorption and drying test results

<table>
<thead>
<tr>
<th>Mix</th>
<th>30 min Absorption (% of OPC)</th>
<th>24 hour Absorption (% of OPC)</th>
<th>30 min Drying (% of OPC)</th>
<th>10 hour Drying (% of OPC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>OPC+PFA</td>
<td>87</td>
<td>93</td>
<td>146</td>
<td>115</td>
</tr>
</tbody>
</table>

### Table 3. Mean chloride transport properties

<table>
<thead>
<tr>
<th>Exposure 1</th>
<th>Exposure 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$</td>
<td>$D_{app}$</td>
</tr>
<tr>
<td>OPC</td>
<td>1.16</td>
</tr>
<tr>
<td>PFA</td>
<td>1.17</td>
</tr>
</tbody>
</table>

In terms of the OPC+PFA vs OPC comparison, it is difficult to identify from Table 3, which concrete performs better over the testing period. It is more difficult still to answer the research question posed in the introduction: how is the relative performance of the two concretes affected by changes in exposure condition. To help answer this question two steps
were taken. Firstly, predicted $T_i$ values were calculated for each of the concrete specimens. It is noted that the aim of this calculation is not to predict when corrosion might occur under such high levels of chloride exposure. The calculation is rather to facilitate the comparison of the OPC and OPC+PFA concretes’ overall performance over the experiment, considering the combined influences of the $C_s$ parameter and the $D_{app}$ parameter. For the purpose of the calculation of $T_i$, a cover depth of 50mm was used in accordance with the guidelines of EN 1992-1-1-2004 for exposure class XS3 (Centre Europeen de Normalisation CEN, 2004). A critical chloride content, $C_{cr}$, of 0.07% by weight of concrete is utilised for the normalisation CEN, 2004 for exposure class XS3 (Centre Europeen de Normalisation CEN, 2004). A critical chloride content, $x$ is chloride content in the concrete, all obtained experimentally. $C_{cr}$ is the critical chloride content, all obtained experimentally. $C_{cr}$ is the critical chloride content, $x$ is the assumed cover depth, $C_{cr}$ is the critical chloride content, and $T_i$ is the time to initiation of corrosion.

Having calculated the $T_i$ values, the next step was to quantify the performance of the OPC+PFA SCC, relative to the OPC SCC. This was done by normalizing the OPC+PFA $T_i$ value with respect to OPC $T_i$ value i.e. dividing the OPC+PFA SCC $T_i$ value by the OPC SCC $T_i$ value. This value, termed the relative merit of the OPC+PFA, allows quantification of the experimental performance of the OPC+PFA SCC relative to the OPC SCC for each exposure condition.

The change in the OPC+PFA SCC relative performance values from exposure condition one to two, and from exposure condition one to three are shown below in Fig. 5. As can be seen from the plot, the performance of the PFA SCC, relative to the OPC SCC, reduces with increased drying in the exposure condition. This will be discussed further in the next section.

4.0 DISCUSSION

A number of researchers to date, including (Bentz et al., 1996, Thomas and Matthews, 2004, Loser et al., 2010, Elahi et al., 2010, McPolin et al., 2005, Yang and Cho, 2003), have shown that the incorporation of PFA as a partial cement replacement improves concrete chloride resistance. As discussed in the introduction however, the majority of such published comparative studies examine the relative performance under fully saturated conditions, be it via the bulk diffusion test (ASTM, 2011), the RCMT (Nordtest Method, 1999), or the RCPT (ASTM, 2012), or real marine exposure (Bentz et al., 1996).

Importantly however, the results presented in this paper allow examination of the relative performance of OPC+PFA SCC, when compared to equivalent OPC SCC across different exposure conditions, with different cycles of controlled and measured wetting and drying.

The results indicated that the relative performance of OPC+PFA SCC reduced when greater levels of drying were introduced into the test regime. The wettest exposure condition examined (12 wetting, 12 hours drying) showed the PFA SCC to perform approximately 75% better than the equivalent OPC SCC. However, the results from the driest exposure condition (1 day wet, 3 days dry), showed a reversal, with the OPC SCC performing slightly better than the PFA SCC. This is an important finding, as it questions the thinking that the addition of PFA as a partial cement replacement will notably improve the chloride ingress resistance of concrete. The results herein indicate that, in circumstances where there is more drying, for instance in the critical tidal splash zone, the addition of PFA as a cement replacement could actually lead to slightly reduced performance.

The observed reduction in performance with increased drying is likely due to the consequential increased role of absorption in the chloride transport process. It was recognised by Neville (2011) and by Richardson (2002), that the transport of chlorides by absorption may be significant in concrete which is subject to cyclic wetting and drying. In light of this the absorption characteristics of both the OPC and OPC+PFA SCCs were measured as part of the experimental programme. The results indicated that the OPC SCC has approximately 10% more absorption capacity than the OPC+PFA SCC. This is a small gap in the context of fully submerged test results published in the literature, which indicate that OPC+PFA concretes perform orders of magnitude better than equivalent OPC concretes (Bentz et al., 1996, Elahi et al., 2010, Yang and Cho, 2003).

Fig. 5. Relative performance of OPC+PFA SCC across three exposure conditions
While the absorption results could explain a reduced performance with increased drying time, they cannot account for the OPC+PFA SCC performance reducing to a level on par, or slightly below the OPC SCC. However, the results of the simple concrete drying test presented in the previous section provide further insight in this regard. The transport of chlorides by absorption takes place when water borne chlorides ingress into void spaces in the concrete due to capillary suction. Logically then, a concrete which dries out more quickly during dry periods will have a greater volume of pore space available for absorption upon wetting with chloride solution. The influence of drying characteristics of concretes are less developed than absorption characteristics in the literature, and the authors are not aware of researchers who have studied the area of concrete drying in the context of chloride-ion ingress into different concretes. The simple experiment conducted herein indicated that the PFA SCC dried out more quickly, and to a greater extent, than the equivalent OPC concrete. Thus, the combination of drying test results, and the absorption test results, provide some insight into the findings of the extensive chloride ingress test programme presented.

5.0 CONCLUSIONS

The majority of information published in the literature relating to the relative performance of different concretes in chloride rich environments is obtained from tests conducted in fully submerged conditions. However, reinforcement corrosion rarely occurs in fully submerged concrete, with concrete in the tidal and plash zones must susceptible to reinforcement corrosion. There is thus a practical need for more information on how the relative performance of difference concretes might varying when different levels of drying are introduced. This is particularly true for new concrete technologies, which are not service proven.

The comprehensive experimental programme herein examined the relative performance of OPC SCC and OPC+PFA SCC across different exposure conditions using a salt fog chamber test, and subsequent profile grading and titration analysis. The results showed that the relative performance of the OPC+PFA concrete reduced when the level of drying in the exposure condition increased. The OPC+PFA concrete performed 75% better than the OPC concrete for the wettest exposure condition, and slightly poorer than the OPC concrete for the driest exposure condition. Absorption test results and concrete drying test results gave insight into the chloride ingress findings in the context of chloride absorption mechanisms. Overall, the results indicate that fully saturated tests may somewhat overestimate the practical benefits of incorporating PFA in concrete in chloride rich environments. The authors are conducting further work in this area, with other supplementary cementing materials being examined, and detailed modelling planned.

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