Performance of Elotex® Copra900 as a Corrosion Inhibitor

Niall Holmes
Technological University Dublin, niall.holmes@dit.ie

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PERFORMANCE OF ELOTEX® COPRA900 AS A CORROSION INHIBITOR

N. Holmes ¹, P. A. M. Basheer ², M. Schottler³

¹ Dublin Institute of Technology,
Department of Civil & Structural Engineering,
Bolton Street,
Dublin 1,
Ireland.

² Queen's University Belfast,
School of Planning, Architecture and Civil Engineering,
Belfast,
Northern Ireland,
U.K.

³ Akzo Nobel Functional Chemicals GmbH & Co. KG,
Industriepark Höchst,
Building G 830,
D-65926 Frankfurt /Main
ABSTRACT

Corrosion inhibitors as cement additions consist of powders or solutions that are added to concrete when mixed to prevent or delay corrosion. This paper presents an early-age evaluation of a new corrosion inhibitor, namely ELOTEX® COPRA900 following a corrosion and durability study on concrete samples with different cementitious materials.

A comparison of the corrosion inhibition properties of ELOTEX® COPRA900 against a well known and established corrosion inhibitor on the market, namely Calcium Nitrite and a control with no corrosion inhibitor product. Calcium Nitrite works by increasing the threshold of chlorides required for corrosion to begin. ELOTEX® COPRA900 on the other hand surrounds the embedded reinforcement with a secondary protective layer that is activated when the passive oxide layer also surrounding the reinforcement breaks down due to the initiation of the chloride corrosion mechanism. The aim of this project is to evaluate ELOTEX® COPRA900 in concrete mixes exposed to accelerated corrosion conditions including CEM I, PFA and GGBS cements.

The results from this experimental programme have demonstrated that ELOTEX® COPRA900 is an effective corrosion inhibitor. The results have shown, in every case, that concrete containing ELOTEX® COPRA900 are less penetrable to chlorides than those without. The addition of ELOTEX® COPRA900 has been found to alter the pore structure so it becomes discontinuous and a capillary blocking effect occurs. In the case of those concretes containing PFA and GGBS, it was found that ELOTEX® COPRA900 made no significant improvement to the corrosion and durability performance.

However, one noticeable effect of the inclusion of ELOTEX® COPRA900 in the concrete mix is the consistent reduction in the compression strength. This has found to be due to the hydrophobic layer that forms on the cement particles which affects the hydration and strength development. However, it is expected that this will only affect low strength concretes which are uncommon in challenging exposures. Also, the quantity of
ELOTEX®COPRA900 used here (4% by mass of cement) would be seen as on the higher side of what would typically be recommended. Reducing the volume of ELOTEX®COPRA900 would therefore reduce these effects of loss in compressive strength.

**KEYWORDS:** ELOTEX®COPRA900, calcium nitrite, corrosion inhibitor, corrosion, durability, Encapsulated siloxane

### 1. INTRODUCTION

Corrosion of embedded steel reinforcement is the most common and destructive forms of deterioration found in concrete. To reduce or limit the effects of corrosion, inhibitors are commonly used as a concrete additive. One of these products, and perhaps the most well known, is Calcium Nitrite (CN). This product, in liquid form, increases the critical threshold of chlorides required before corrosion can begin. Modern additives are required to be non toxic and have no impact on the concretes fresh (workability and setting) and hardened properties (strength development). Another important aspect to consider is their ease of use and how they are added to the concrete.

However, there appears to be no corrosion protection agent or inhibitor on the market which combines long term protection to the reinforcement against chloride-ion attack with easy handling properties. For this, ELOTEX®COPRA900 has been developed to overcome the problems associated with existing corrosion inhibitor products. ELOTEX®COPRA900 is siloxane based in powder form which surrounds the reinforcement thus providing a secondary protective layer [1]. Water re-dispersible encapsulated siloxanes, in powder form, combines the positive properties of siloxanes which can efficiently distribute the powder homogeneously. This additional protective layer becomes active when the pH of the concrete drops in the presence of hydroxide ions produced during corrosion and subsequently re-passivates the reinforcement.
2. BACKGROUND AND RESEARCH SIGNIFICANCE

ELOTEX® COPRA900 is an encapsulated sloane in polyvinyl alcohol with inorganic anti-caking agents in powder form and can be added directly into the concrete mix or pre mixed with other cementitious materials. When water comes into contact with ELOTEX® COPRA900 in the concrete, the polyvinyl alcohol coating surrounding the powder is dissolved and is evenly distributed throughout the concrete. Siloxane is a chemical compound consisting of elements of hydrogen (R), silicone (Si) and oxygen (O) and is represented in the form R₂SiO. An illustration of this process is given in Figure 1 [1].

![COPRA900 Powder + water → Free Siloxane homogeneously distributed in fresh mixed concrete](image)

**Figure 1** Illustration of ELOTEX® COPRA900 ability to homogeneously distribute within a concrete mix [1].

At high pH values such as these found in concrete (>12), Si-oligomer hydrolyses and forms a protective layer at the surface of the reinforcement and at the aggregate interface, as demonstrated in Figure 2. Similarly at low pH values (<10), Si-oligomer also hydrolyses which results in the re-passivatation of the reinforcement which is illustrated in Figure 3.

The processes of corrosion due to chloride and carbonation mechanisms are well known. In concrete terms, the most obvious method to reduce it is to alter the transport properties (permeability, diffusion, porosity) of the cover-zone which affects the penetrability of chloride ions into the reinforcement. Pore liners such as silanes and siloxanes act as an effective barrier to prevent the ingress of water and water born ions such as chlorides. As
Figure 2 Illustration of hydrolysing Si-oligomer [1].

Figure 3 Illustration of re-passivatation characteristic of ELOTEX®COPRA900 [1].

Silane molecules are of similar size to water molecules, they can penetrate into the capillaries of the cover concrete and adhere to the pore walls. The silane then reacts with adsorbed water along the pore walls to form a hydrophobic layer which acts as a repellent to diffusing corrosive ions [2]. Silanes and siloxanes have been traditionally applied to exposed faces of concrete structures by brushing or spraying.

Results from Basheer and Cleland [3,4] using silanes and siloxanes applied to the surface of concrete samples conclude that they are an effective method of blocking the capillary pores in the concrete and minimising the absorption of water and water borne ions. These applications worked particularly well in improving the freeze-thaw properties of their concrete [4].

This paper presents the findings from an experimental study carried out at Queen’s University Belfast into the
performance of various concrete mixes containing CEM I cement and other supplementary materials, namely PFA and GGBS with and without ELOTEX® COPRA900 and CN. The results demonstrate the effectiveness of ELOTEX® COPRA900 as a corrosion inhibitor.

3. EXPERIMENTAL PROGRAMME

3.1 Mix Proportions

The concrete was manufactured with a fixed w/c ratio of 0.55 and a fixed cement content of 400kg/m³. Following a number of trial mixes, the final proportions were determined so a S3 class slump [5] between 100-150mm would be achieved. The slump was adjusted by adding different dosages of superplasticiser (SP). The mix proportions are summarised in Table 1. One control mix incorporating only CEM I cement and two other mixes containing CEM I + PFA and CEM I + GGBS at a replacement level of 35% were prepared.

3.2. Materials

CEM I cement complying with BS EN 197-1, 2000 [5a], PFA equivalent to BS 3892: Part 1 [6], and GGBS manufactured according to BS 6699 [7] were used as binders. Both the fine and coarse aggregates were obtained from local sources in Northern Ireland. The fine aggregate used was medium graded sand [8] and the coarse aggregate was crushed basalt with a maximum size of 20 mm. Before mixing, the water absorption of the aggregates was measured and the free-water added to the concrete was adjusted accordingly. Also, to ensure the w/b ratio of 0.55 was achieved, trial mixes were prepared with different amounts of SP so the required slump could be achieved. The water content in the SP was calculated and the free-water added to the concrete was further corrected.

The recommended dosage of CN according to the suppliers was 20 l/m³ [9]. This is deemed suitable for anticipated chloride levels in a marine environment (approximately 7.7 Kg/m²). In was also recommended that a retarder [10] be also added to those mixes containing CN at a dosage of 0.4% by weight of cement. The recommended quantity of ELOTEX® COPRA900 used was 4% by weight of cement [1].
3.3. Preparation of samples

The concrete was manufactured following the procedure set-out in [5] using a pan mixer. For each mix in Table 1, 3 ponding slabs (250x250x100mm with a 10mm dyke), 3 regular slabs (250x250x100) and 9 100x100x100mm cubes were manufactured. Each mix had a volume of 0.05m$^3$ including 10% for wastage.

The 250x250x100mm thick slabs, with the 10mm dyke (Figure 4) were used to weekly pond the concrete with a 0.55M of salt solution so the corrosion resistance of the concretes could be assessed. To create the dyke, a timber insert was centrally placed at the base of the mould. The 100x100x100mm cubes were manufactured to determine the compressive strength at different ages for each mix. In parallel, the 250x250x100mm slabs were manufactured to determine the permeation properties of the concretes and to provide cores for the freeze-thaw tests.

After mixing, the concrete was poured, in 50mm thick layers, into the timber moulds which had a release agent applied to ease de-moulding the following day. The concrete was vibrated on a vibrating table until no more air bubbles were visible on the surface. Curing to the concrete was provided by placing a polythene sheet over the specimens for 24 hours to trap evaporating moisture from the surface. Following demoulding, the slabs were wrapped in damp hessian and placed inside polythene bags for 7 days. The slabs were transferred to a constant temperature room with ambient temperature and humidities of 20 ± 1°C and 65% respectively. After the cubes were demoulded, they were placed in a water curing tank at 20 ± 1°C until testing.

After 7 days, the slabs were unwrapped and allowed to surface dry in the constant temperature room for 1 day so a water-proof sealer could be applied to four the sides of the slabs, each receiving 3 coats per side. After the paint has dried, each slab was placed in a water bath for 3 days to saturate so baseline values could be recorded for resistivity measurements. This also reduced the possibility of rapid absorption of the chlorides.
Table 1  Mix proportions

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>a/b</th>
<th>FA/CA</th>
<th>Mass of Ingredients (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Water</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10mm</td>
</tr>
<tr>
<td>1A</td>
<td>4.24</td>
<td>0.54</td>
<td>245.86</td>
</tr>
<tr>
<td>1B</td>
<td>4.12</td>
<td>0.55</td>
<td>245.28</td>
</tr>
<tr>
<td>1C</td>
<td>4.23</td>
<td>0.54</td>
<td>231.56</td>
</tr>
<tr>
<td>2A</td>
<td>4.22</td>
<td>0.54</td>
<td>245.73</td>
</tr>
<tr>
<td>2B</td>
<td>4.12</td>
<td>0.54</td>
<td>245.14</td>
</tr>
<tr>
<td>2C</td>
<td>4.21</td>
<td>0.54</td>
<td>231.43</td>
</tr>
<tr>
<td>3A</td>
<td>4.23</td>
<td>0.54</td>
<td>245.73</td>
</tr>
<tr>
<td>3B</td>
<td>4.12</td>
<td>0.54</td>
<td>245.14</td>
</tr>
<tr>
<td>3C</td>
<td>4.21</td>
<td>0.54</td>
<td>231.43</td>
</tr>
</tbody>
</table>

FA – Fine aggregate

CA – Course Aggregate

PFA – Pulverised fuel ash

BS – Ground granulated blast-furnace slag

a/b – aggregate-binder ratio

* In all cases where CN was used (mixes 1C, 2C and 3C), a retarder content of 1.60kg/m³ was added to the concrete
3.4. Tests carried out

3.4.1. Workability

The workability of concrete was measured in terms of slump, noted immediately after manufacturing the concrete. The slump test was carried out in accordance with BS EN 12350-2 [11]. These results are reported in Table 2 and shown in Figure 5. It can be seen from this table that the majority of the measured slump was within the target range of 100–150 mm. However, for those mixes with CN (1C, 2C and 3C), the measured slumps are far in excess of what was required.

The workability is slightly increased due to the addition of this corrosion inhibitor. This is confirmed by literature as well as by the experimental results given before. [12] reports that the addition of CN does have a minor influence on increasing the slump in higher w/c ratio concrete. However, in most cases, [12] reports that CN does not increase slump values and so it would appear that the retarder used to control slump loss is not taking effect.

3.4.2. Compressive strength

The compressive strength of the concrete was determined by crushing three cubes of 100 mm size at 7, 28 and 56 days for each mix. The test was carried out according to BS EN 12390-3 [13].
Table 2  
Workability (slump)

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>1A</th>
<th>1B</th>
<th>1C</th>
<th>2A</th>
<th>2B</th>
<th>2C</th>
<th>3A</th>
<th>3B</th>
<th>3C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slump (mm)</td>
<td>80</td>
<td>110</td>
<td>225</td>
<td>100</td>
<td>150</td>
<td>240</td>
<td>150</td>
<td>200</td>
<td>265</td>
</tr>
</tbody>
</table>

Figure 5  
Slump values

3.4.3. Air permeability and sorptivity

To measure the air permeability and the water absorption (sorptivity) of concrete, the Autoclam permeability system [14] was used (Figure 6). Tests were conducted on the 250x 250x100mm concrete blocks at xx and xx days. Prior to carrying the tests, the test blocks were dried in an oven for 14 days at a temperature of 40°C as [15] after which they were removed and allowed to cool for 24 hours before testing.

3.4.4 Corrosion Monitoring

Once every week half-cell and macro-cell testing was carried on all 36 ponding slabs. The half-cell apparatus [16], Figure 7, was connected to the top reinforcement bar acting as the anode and the values of potential were
recorded on three different positions along the length of the anodic bar. For macro-cell testing, a voltage across a
10Ω resistor connecting the anodic reinforcement bar with the 3 cathodic bars was measure in millivolts (mV).
The apparatus used for this is shown in Figure 8. Using Ohm’s Law, the corrosion current was calculated.

3.4.5 Freeze-thaw Testing

The freeze-thaw analysis was carried out using the RILEM TC-117 procedure [17]. A 70mm length of core was
prepared by painting with three coats of water proof coating. After saturation in a 3% sodium chloride solution, the cores were placed in containers with 15mm of the core in the solution test face down in specially designed containers for 7 days to prior to testing. Prior to inserting the specimens into the freeze-thaw chamber the level of the solution was reduced from 15mm to 5mm. The freeze-thaw chamber was programmed with the 12 hour cycle shown in Figure 9. After 14 cycles (or 7 days) the cores were removed and the test surface was brushed into the container removing any loose material and weighted. The sample was replaced back in the chamber and continued for a further 14 cycles after which the cores were removed and the weight of the material to fall off the core (residuals) was weighted.
3.4.6 Chloride ion migration test

The chloride diffusion was assessed using the Permit ion migration test (Figure 10) on the CEM I concrete slabs. The Permit apparatus is a unique non-destructive test which is capable of determining the chloride migration coefficient of cover concrete [17a, 17b] which correlates well with the conventional laboratory-based steady state diffusion and migration tests. The main advantage of this test is that it can provide a migration coefficient without having to remove cores from the structure. The apparatus is bolted onto the test surface and de-ionised water is poured into an outer chamber and a 0.55M chloride solution is poured into the inner chamber (see Figure 10). The test takes place between 8-10 hours until a steady state of diffusion is achieved as indicated by a graph of the conductivity time relationship which yields the $ds/dt$ value. This value is then adjusted to suit the calibration value of the PERMIT which gives the $dc/dt$ value to be used in the calculation of the migration coefficient. The $D_{mig}$ or migration coefficient is calculated using the formula;

$$D_{mig} = -\left(\frac{dc}{dt} T\right)\left(\frac{R}{z F C E}\right)\left(V \frac{L}{A}\right)$$  

Equation 1 [17c]

where, $dc/dt$ is the rate of change of the concentration in the anolte (mmol/l), $T$ is the absolute temperature averaged during the steady state (°K), $R$ is the universal gas constant (8.31 J/K.mol), $z$ is the valency of the ions (-1), $F$ is Faradays constant (9.65x10⁴ c/mol), $C$ is the concentration of the chloride solution (550 mol/m³ for the 0.55M solution), $E$ is the electrical potential applied between the anode and the cathode (30 V), $V$ is the volume of anolyte (6.5x10⁻⁴ m³) and $L/A$ is the flow length of the exposed area ration (taken as 3.76 m⁻¹).

Figure 9a The Permit Ion Permeability Tester (controller and the main body)
4. RESULTS AND DISCUSSION

4.1. Compressive strength

The compressive strength results are presented in Table 3 and Figures 10 to 12. As shown, when ELOTEX® COPRA900 has been added to the mixes, there is a reduction in strength. This reduction is most evident when ELOTEX® COPRA900 was added to the PFA (2B) and GGBS (3B) mixes for all ages in Figures 11 and 12. This reduction is due to the Poly Vinyl Alcohol (PVA) and oligomeric polysiloxane (OP) within ELOTEX® COPRA900 which disperses the powder in the mix. However, PVA also retards the hydration process of the cement as it forms a barrier to water completely hydrating the particle surface. Indeed, the OP can also form a hydrophobic layer on cement particles and again limits the hydration process. Therefore, all through the hydration process, the strength development is less, leading to lower compressive strength over time.

Despite this, it is important to highlight that the inclusion of ELOTEX® COPRA900 does not affect the hydration process when water does react the cement particle. When the cement gets sufficient water before the condensation reaction of siloxane takes place, it is able to hydrate and develop strength in the normal was, albeit slightly retarded.

Table 3 Average Compressive strength results (N/mm²)

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>1A</th>
<th>1B</th>
<th>1C</th>
<th>2A</th>
<th>2B</th>
<th>2C</th>
<th>3A</th>
<th>3B</th>
<th>3C</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 Days</td>
<td>26</td>
<td>14.7</td>
<td>27</td>
<td>14.4</td>
<td>6.5</td>
<td>13.6</td>
<td>23.6</td>
<td>9.3</td>
<td>25.2</td>
</tr>
<tr>
<td>28 Days</td>
<td>37.2</td>
<td>23.4</td>
<td>39.6</td>
<td>18.8</td>
<td>9.5</td>
<td>25.2</td>
<td>34.2</td>
<td>20.3</td>
<td>38.2</td>
</tr>
<tr>
<td>56 Days</td>
<td>40.8</td>
<td>27.8</td>
<td>46.6</td>
<td>27.8</td>
<td>13.4</td>
<td>30.1</td>
<td>38.3</td>
<td>25.1</td>
<td>42.9</td>
</tr>
</tbody>
</table>
Figure 10  Compressive strength results for the OPC concrete including ELOTEX®COPRA900 and CN

Figure 11  Compressive strength results for the PFA concrete including ELOTEX®COPRA900 and CN

Figure 12  Compressive strength results for the GGBS concrete including ELOTEX®COPRA900 and CN

These effects on compressive strength are greater on low strength concretes, which, for aggressive
environments like those in contact with chlorides (XD and XS in [5], would not be practicable. Therefore, provided high-strength concretes are being specified, these effects might be considered a ‘minor’ consequence or disadvantage. Also, a quantity of 4 % of ELOTEX®COPRA900 may be considered high and would yield very high corrosion protection. In most cases, a lower quantity of 2 to 3 % would be sufficient which would reduce the impact on strength development. However, determining the most efficient quantity of ELOTEX®COPRA900 for a particular environment is ongoing.

However, in terms of the addition of CN to the mixes, there appears to be a slight increase in the strength of the concrete at all ages. This increase in strength can be attributed to the water reducing effect of the CN. Previous research has also shown an increase in compressive strength by adding CN with a 12–13% higher compressive strength than similar mixes without CN [12]. Also, [12] reports that the compressive strength of concretes with CN at 28 days 8-9% higher than control mixes. Here, the CEM I and GGBS mixes showed an increase in compressive strengths between 7 and 28-day of 6-12%.

4.2. Air Permeability and Sorptivity

The air permeability and sorptivity of the different were measured using the Autoclamp permeability system [14]. For the air permeability, 3 tests per slab were carried out and the average results are reported in Table 4. It should be noted that the air permeability index could not be measured for 2B, 3A and 3B due to difficulties with the instrument. As the sorptivity test imparts water under pressure into the concrete, one test per slab is carried out.

4.2.1 Air Permeability

The air permeability values of the mixes are shown in Figure 13. A comparison of the OPC mixes (1A-C) clearly shows that the air permeability is least in the concrete with CN. This is considered to be due to the water reducing effect of CN which decreases the porosity and permeability of the concrete. This appears to be also true for the PFA concretes, albeit the same trend is difficult to confirm as there are no results for mix 2B. As only
Table 4  Air permeability and sorptivity indices of the various mixes

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Air permeability indices (ln(pressure)/min)</th>
<th>Sorptivity indices (m$^3$x10^{-7}/√min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>1.053</td>
<td>4.11</td>
</tr>
<tr>
<td>1B</td>
<td>0.511</td>
<td>0.965</td>
</tr>
<tr>
<td>1C</td>
<td>0.393</td>
<td>3.47</td>
</tr>
<tr>
<td>2A</td>
<td>1.171</td>
<td>8.48</td>
</tr>
<tr>
<td>2B</td>
<td></td>
<td>0.806</td>
</tr>
<tr>
<td>2C</td>
<td>0.313</td>
<td>6.80</td>
</tr>
<tr>
<td>3A</td>
<td></td>
<td>9.35</td>
</tr>
<tr>
<td>3B</td>
<td></td>
<td>1.96</td>
</tr>
<tr>
<td>3C</td>
<td>0.929</td>
<td>5.92</td>
</tr>
</tbody>
</table>

Figure 13  Air permeability indices of the various mixes

Figure 14  Sorptivity indices of the various mixes
one set of results available for the GGBs concrete (3C), no conclusion can be drawn on the performance. This is an area where further work is required to assess the performance.

4.2.2 Sorptivity

The sorptivity values of the mixes are shown in Figure 14. In all cases, it is clear that concrete with ELOTEX® COPRA900 (1B, 2B and 3B) have significantly lower sorptivity values than all other mixes. Unexpectedly, the results indicate that the CEM I concretes have better sorptivity properties than both the PFA and GGBS concrete with ELOTEX® COPRA900 and CN. These tests were undertaken at 49 days of age after 14 days of drying in an oven at 40°C for 14 days. It is expected, and has been shown previously [18] that the sorptivity values will reduce with age in those mixes with SCM’s due to the ongoing hydration and pozzolanic reactions over time. Comparing the two transport property findings, namely the air permeability and sorptivity it is clear that those concretes with ELOTEX® COPRA900 have a lower sorptivity than all others. In terms of corrosion resistance in a marine environment, a low sorptivity property can reduce the amount of chlorides that can then be transferred through the concrete via diffusion (under a concentration gradient) or by permeability (under a pressure gradient). ELOTEX® COPRA900 is originally proposed to improve the corrosion resistance property of concrete by surrounding the reinforcement with a protective layer. However, it is clear that it also improves the transport properties, particularly the sorptivity. Using the Autoclam instrument manual [14] which categorises the sorptivity readings into very poor, poor, good and very good [19, 20], the ELOTEX® COPRA900 mixes all rated very good.

4.3 Corrosion Monitoring

The average results from the weekly half-cell and macro-cell monitoring programme during ponding are shown in Tables 5 and 6. Half-cell potential measurement as a method to assess the likelihood of corrosion occurring has gained in confidence following the creation of ASTM standard C876 [16]. This standard provided guidelines (Table 7) to evaluate if corrosion is occurring. As may be seen, potentials greater than -350 mV have a high (90%) probability of corrosion occurring.
### Table 5  Half-cell results for various mixes

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Week Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
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<td>OPC</td>
<td>1A</td>
<td>86</td>
<td>276</td>
<td>250</td>
<td>266</td>
<td>275</td>
<td>269</td>
<td>303</td>
<td>323</td>
<td>430</td>
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<tr>
<td></td>
<td>1B</td>
<td>82</td>
<td>64</td>
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<td></td>
<td>1C</td>
<td>95</td>
<td>210</td>
<td>192</td>
<td>183</td>
<td>200</td>
<td>205</td>
<td>209</td>
<td>233</td>
<td>262</td>
</tr>
<tr>
<td>PFA</td>
<td>2A</td>
<td>99</td>
<td>256</td>
<td>276</td>
<td>322</td>
<td>310</td>
<td>360</td>
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<td>354</td>
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<td>86</td>
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<td></td>
<td>3C</td>
<td>113</td>
<td>181</td>
<td>179</td>
<td>193</td>
<td>202</td>
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</tbody>
</table>

### Table 6  Macro-cell results for various mixes

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Week Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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<tbody>
<tr>
<td>OPC</td>
<td>1A</td>
<td>0.010</td>
<td>0.0167</td>
<td>0.020</td>
<td>0.0233</td>
<td>0.0267</td>
<td>0.0300</td>
<td>0.0367</td>
<td>0.0367</td>
<td>0.040</td>
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<tr>
<td></td>
<td>1B</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
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</tr>
<tr>
<td>PFA</td>
<td>2A</td>
<td>0.010</td>
<td>0.0167</td>
<td>0.0167</td>
<td>0.020</td>
<td>0.0233</td>
<td>0.0300</td>
<td>0.0333</td>
<td>0.0367</td>
<td>0.0433</td>
</tr>
<tr>
<td></td>
<td>2B</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2C</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
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<tr>
<td>GGBS</td>
<td>3A</td>
<td>0.010</td>
<td>0.0167</td>
<td>0.0367</td>
<td>0.0433</td>
<td>0.050</td>
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<tr>
<td></td>
<td>3B</td>
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<td>0</td>
<td>0</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3C</td>
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<td>0</td>
<td>0</td>
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<td></td>
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</tbody>
</table>
Table 7

<table>
<thead>
<tr>
<th>Half-cell potential reading</th>
<th>Corrosion activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less negative than -200mV</td>
<td>90% probability of no corrosion</td>
</tr>
<tr>
<td>Between -200 and -350mV</td>
<td>An increasing probability of corrosion</td>
</tr>
<tr>
<td>More negative than -350mV</td>
<td>90% probability of corrosion</td>
</tr>
</tbody>
</table>

Half-cell results are coupled with the macro-cell corrosion current measurements to provide a comprehensive assessment if corrosion is occurring. Figures 15-17 present the half-cell and macro-cell readings for mixes 1A-C respectively. As may be seen, and somewhat expected, Mix 1A has higher half-cell and macro-cell results than mixes 1B and 1C. However, mix 1B has the lowest half-cell and macro-cell results with the half-cell readings remaining between 50-100mV throughout the weekly ponding regime. Mix 1C has higher readings than mix 1B with ELOTEX®COPRA900 and appears to be increasing over time, but less so than mix 1A. The results in Figure 20 are still less than that in Figure 18 which indicates that CN is reducing the corrosion rate.

The increase in half-cell results in those mixes with CN (Figures 18, 19 and 20) may not indicate that corrosion is occurring as CN increases the critical threshold of chlorides required before corrosion can begin. Also, no macro-cell current was recorded in these mixes.

In Figures 21-23, the half-cell and macro-cell results for the PFA mixes (2A-C) are presented. As may be seen, mix 2A has the highest rate of corrosion with an increasing rate of half-cell and corresponding macro-cell current. These results also appear to be increasing at a faster rate than mix 1A. It is anticipated that this rate of increase will reduce over time due to the ongoing hydration and pozzolanic reaction of the PFA over time.
Figure 15  Half-cell and macro-cell results for mix 1A

Figure 16  Half-cell and macro-cell results for mix 1B

Figure 17  Half-cell and macro-cell results for mix 1C
In Figure 16, the half-cell readings in mix 1B are reducing over time from -200mV to -75mV over the 7 week time period shown. As the sorptivity readings for this mix (Figure 14) are so low it is unclear as to why this reduction is occurring. One reason may be that the inclusion of a SCM reduced the half-cell potential over time as this effect is also occurring in mix 3B with GGBS. Over time due to the additional pozzolanic activity in these mixes coupled with the addition of ELOTEx®COPRA900 which surrounds the reinforcement, reduce the corrosion activity as may be seen.

![Figure 18](image1)

**Figure 18**  
Half-cell and macro-cell results for mix 2A

![Figure 19](image2)

**Figure 19**  
Half-cell and macro-cell results for mix 2B
The results for mixes 3A-C are shown in Figures 21-23. Again, it is clear that mix 3A has the highest rate of corrosion with both half-cell and macro-cell current increasing. The results for mix 3B (Figure 22) again demonstrate that the inclusion of ELOTEX®COPRA900 reduces the half-cell corrosion over time, at least within the time frame shown. Comparing the results with mix 2B with PFA, it appears that the decrease is less and is more similar to mix 1B with no SCM included. The inclusion of CN in mix 3C yields a slower rate of half-cell increase than that in mix 2C.
4.4 Freeze-thaw assessment

An accelerated freeze thaw test was carried on 3 cores per concrete mix and the transit time of each core was measured before and after the test. Increased transit times after testing would indicate the formation of micro-cracking from hydrostatic pressure caused by the expansion of water within the capillary pores due to the freeze-thaw cycles. Table 8 presents the transit time of the cores for mixes 1A-C and 2A-V before and after the tests and an average variation in transit was calculated for ease of interpretation. The weight of the dried residuals form the cores were also shown in Table 8. The cores from mixes 2A and 2C were severely deteriorated to the point where almost a third of the core had totally disintegrated. As a result, UPV readings were immeasurable.
Table 8  Freeze-thaw results

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Average weight of concrete removed (g)</th>
<th>Average transit time before test (µ sec)</th>
<th>Average transit time after test (µ sec)</th>
<th>Average variation of transit time (µ sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>49.9</td>
<td>17.97</td>
<td>34.47</td>
<td>16.5</td>
</tr>
<tr>
<td>1B</td>
<td>2.23</td>
<td>17.87</td>
<td>22.63</td>
<td>4.76</td>
</tr>
<tr>
<td>1C</td>
<td>51.63</td>
<td>16.97</td>
<td>27.87</td>
<td>10.9</td>
</tr>
<tr>
<td>2A</td>
<td>203.27</td>
<td>17.23</td>
<td>Unreadable</td>
<td>-</td>
</tr>
<tr>
<td>2B</td>
<td>1.5</td>
<td>20.67</td>
<td>24.27</td>
<td>3.6</td>
</tr>
<tr>
<td>2C</td>
<td>63.9</td>
<td>18.47</td>
<td>41.9</td>
<td>23.43</td>
</tr>
</tbody>
</table>

and are denoted “Unreadable” in Table 8. Figure 24 shows an image of a severely damaged core where UPV readings were unable to be measured against a core with relatively no freeze thaw damage that was readable. An increase in transit time was observed for all cores and is due to the disturbance of the ultra sonic pulse sent through the concrete as a result of micro cracking caused by the internal expansive pressures exerted on the microstructure of the concrete. Extremely high variations in transit time for mix 2A and 2C are a result of severe formation of micro cracking near the exposed surface of the core.

To assess the performance of the various mixes during the freeze-thaw cycles, the weights of the residual material that could be brushed off each core after the test was taken and are summarised in Table 8 and Figures 25. Figure 26 show the average transit time for the six mixes which indicate the formation of microcracks. It is clear that those concrete mixes containing ELOTEX®COPRA900 (1B and 2B) have performed better than all others in the study. It would also appear that ELOTEX®COPRA900 acts to discontinue the pore structure
Figure 24  Comparison between a severely damaged and a relatively undamaged core following the freeze-thaw analysis

resulting in a concrete that is less permeable.

Figure 25  Average weights (g) of concrete removed after freeze-thaw testing
4.8 Chloride ion migration

To assess the chloride diffusion of the near surface concrete the PERMIT ion migrations test was used (Figure 9a). Three tests were performed on separate CEM I slabs and the standard deviation of the $D_{mig}$ results was calculated as shown in Table 9 and Figure 27. The results demonstrate that the inclusion of ELOTEX® COPRA900 significantly improved the chloride diffusion of the concrete. [Reou, REF] found that the inclusion of CN increased the rate of chloride ion diffusion and this has been confirmed in the results here.
5. CONCLUSIONS

On the basis of the early age results obtained from this research work, the following conclusions have been drawn:

(1) ELOTEX®COPRA900 is an extremely effective corrosion inhibitor. Over the duration of this study incorporating accelerated corrosion regimes (ponding and freeze-thaw cycles), no evidence of corrosion was found using half-cell and macro-cell methods in those slabs containing it compared with slabs containing another well known corrosion inhibitor, namely CN.

(2) Following a series of air permeability, sorptivity and accelerated freeze-thaw tests, the concrete containing ELOTEX®COPRA900 was found to be less penetrable than other concretes in the study. This suggests that ELOTEX®COPRA900 alters the pore structure in such a way that the pores become discontinuous or a capillary blocking effect occurs.

(3) There was no evidence that the inclusion of ELOTEX®COPRA900 makes any significant difference to the performance of either PFA or GGBS in comparison with its performance within CEM I alone. However, the trends from other results containing the PFA used in this study suggest that they may be of poor quality and further investigation is warranted to confirm these findings.

(4) It has been demonstrated that the inclusion of ELOTEX®COPRA900 into the concrete in this study yields a decrease in its compressive strength of approximately 12 MPa in all concrete mixes at 7, 28 and 56 days. This may be due to the formation of oligomeric polysiloxane which forms a hydrophobic layer around the cement particles. Therefore, water may not be able to hydrate the cement particles. However, provided the cement particles are hydrated prior to the condensation reaction of siloxane takes place, strength development should satisfactory. Within the concrete mixes outlined here, 4% of ELOTEX®COPRA900 was used. This proportion of ELOTEX®COPRA900 would be slightly higher than normal with 2-3% more typical. If reduced proportions of ELOTEX®COPRA900 were used, it may reduce the effect on the strength loss see here.
6. **ACKNOWLEDGEMENTS**

The authors wish to acknowledge the assistance of the technical support and the facilities of School of Civil Engineering, The Queen’s University Belfast, Northern Ireland.

7. **REFERENCES**


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