論文 Combined Effects of Carbonation and Chlorides on Steel Corrosion in Ecocement Mortars

Kwasi Osafo AMPADU *1, Kazuyuki TORII *2, Takashi KUBOTA *3, Takuya ECHIGO *4

ABSTRACT

In this study, the corrosive behaviours of steel bars embedded in the mortars of two types of ecocement; a high chloride type and a portland cement type were investigated. Two sets of specimens were prepared and each subjected to a different environmental conditions. The first set was subjected to an accelerated carbonation followed by wetting and drying whilst the second set was subjected to only wetting and drying. Electrochemical and physical measurements were conducted on the specimens and the results discussed in a complementary manner.

Keywords: Ecocement, carbonation, wetting and drying, electrochemical measurements, A.C. Impedance, weight loss, corroded area

1. INTRODUCTION

Ecocement is a new type hydraulic cement produced using incinerator ashes as part of the raw materials, in addition to limestone and clay that are also used in the production of ordinary portland cement. The New Energy and Development Organization (NEDO) developed the technology of its manufacture [1]. The first type of ecocement that was produced contains large amounts of chlorides, which may accelerate corrosion of steel bars if used in reinforced concrete structures. Earlier studies performed in this regard proved that to be the case [2]. Its use has therefore been limited to street pavements, concrete drains, sea defence blocks and other mass concrete structures. As a result of the high chloride content of the first type of ecocement, researchers at Taiheiyo cement corporation of Japan has developed a second type that has low amount of chloride content [3].

In this experiment, the combined effects of carbonation and chlorides on the corrosion of mild steel bars embedded in the mortars of both types of ecocement were studied.

2. EXPERIMENTAL PROCEDURES

2.1 Materials mix proportions and specimen preparations

Table 1 shows the chemical compositions of both types of ecocement. It is seen that type I contains more sulphate and more chloride than type II. The chloride content of type I exceed the limit allowed in most specification.

Table 2 shows the mix proportions of the mortars used in this experiment. Mortar specimens were prepared at water to cement ratios of 0.45, 0.55 and 0.65.

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TABLE 1 Chemical compositions of ecocement type I and II (% by weight)

<table>
<thead>
<tr>
<th></th>
<th>Ig. loss</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ecocement Type I</td>
<td>0.5</td>
<td>14.9</td>
<td>10.5</td>
<td>2.5</td>
<td>56.7</td>
<td>1.7</td>
<td>9.2</td>
<td>0.8</td>
<td>0.01</td>
<td>0.80</td>
</tr>
<tr>
<td>Ecocement Type II</td>
<td>0.6</td>
<td>18.0</td>
<td>8.8</td>
<td>2.5</td>
<td>62.1</td>
<td>1.7</td>
<td>3.7</td>
<td>0.3</td>
<td>0.01</td>
<td>0.08</td>
</tr>
</tbody>
</table>

TABLE 2 Mixture proportions of mortar specimens (kg/m³)

<table>
<thead>
<tr>
<th>Type of ecocement</th>
<th>W/C</th>
<th>Water</th>
<th>Cement</th>
<th>Sand</th>
<th>Retarder</th>
<th>Chlorides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>0.45</td>
<td>293</td>
<td>651</td>
<td>1302</td>
<td>4.56</td>
<td>5.21</td>
</tr>
<tr>
<td>(High chloride content)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.55</td>
<td>336</td>
<td>611</td>
<td>1222</td>
<td>2.44</td>
<td>4.89</td>
</tr>
<tr>
<td></td>
<td>0.65</td>
<td>374</td>
<td>576</td>
<td>1152</td>
<td>1.73</td>
<td>4.61</td>
</tr>
<tr>
<td>Type II</td>
<td>0.45</td>
<td>293</td>
<td>651</td>
<td>1302</td>
<td>—</td>
<td>0.52</td>
</tr>
<tr>
<td>(Low Chloride content)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.55</td>
<td>336</td>
<td>611</td>
<td>1222</td>
<td>—</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>0.65</td>
<td>374</td>
<td>576</td>
<td>1152</td>
<td>—</td>
<td>0.46</td>
</tr>
</tbody>
</table>

The fresh mortars were placed in a 180 mm by 100 mm by 60 mm rectangular prismatic mould with a 10mm diameter by 160 mm length mild steel and a stainless steel bar embedded at a cover depth of 10 mm. External stainless steel plugs were connected to one end of the rods to serve as contact points for electrical connection. The moulds were removed at 7 days after casting. All but the surface of the specimens close to the embedded steel bars were then coated with an epoxy. Two sets of specimens were prepared. One set was placed in an environmental chamber and subjected to a wetting and drying cycle. In this chamber, a mist of water was sprayed onto the surface of the specimens for a period of 3 days followed by a 4-day dry period in an alternate cycle. The temperature and relative humidity in the environmental chamber were maintained at 40 °C and 95% during the wet period and 20°C and 50% respectively during dry period.

The second set of specimens was also placed in an environmental chamber, which is designed for an accelerated carbonation test but can also double as wetting and drying chamber. This chamber has a built in microprocessor and as such all the desired environmental conditions were simply input at the control panel for an automatic execution. 5% of CO₂ was circulated through the environmental chamber, which was maintained at a relative humidity of 50% and a temperature of 40 °C. The CO₂ was circulated until the neutralization depths of most of the specimens reached the surface of the embedded steel bars (10mm cover) after which the environmental conditions were changed to that of wetting and drying cycle. During this phase of the experiment, the environmental chamber was reprogrammed to spray a mist of water unto the surface of the specimens for a period of 3 days followed by a 4-day dry period in an alternate cycle. A relative humidity of 95% and 50% was maintained during the wet and dry periods respectively. The temperature was however maintained at 40°C throughout both wet and dry periods.

2.2 Measurements of specimens

In the measurement of the carbonation depth, a piece of the specimen is cut, split into two pieces and then 1% solution of phenolphthalein is sprayed onto the freshly split surface. The depth of the colourless zone is measured as the carbonation depth.

The 3-electrode configuration technique was used for the half cell potential and linear polarization resistance (LPR) measurements. A saturated calomel electrode (SCE) was used as a reference electrode whilst the embedded normal steel and stainless steel bars served as a working and auxiliary/counter electrode respectively. The corrosion current density, Icorr in μA/cm², was calculated using the Stern-Geary equation, \[ I_{corr} = B/(A\cdot R_p) \] [4], where B, the Tafel constant, of 26 mV was used. The AC impedance method was also used to monitor the corrosion of the steel bars.
embedded in the mortars. The experimental set up was similar to that of the LPR. An AC signal of 20 mV amplitude was impressed to the normal steel (working electrode) through the stainless steel (counter/auxiliary electrode) with a frequency range of 5 mHz to 10 kHz.

3. RESULTS AND DISCUSSION

3.1 Carbonation depth

Fig. 1 shows the graph of the carbonation depth with the square root of the exposure time for the mortar specimens of both types of ecocement. It is seen that in both cements, the higher the w/c ratio the higher the neutralization or carbonation depth. The figure also shows that the carbonation depths of the Type I specimens are larger than the corresponding values of type II specimens. This is because the calcium hydroxide content of the hydrated paste of ecocement type I is much lower than that of the type II [5]. Thus, when the type I mortars are exposed to carbon dioxide, their calcium hydroxide content soon depletes in a neutralization reaction to form calcium carbonate. That is, for the same amount of carbon dioxide consumed in a neutralization reaction, the carbonation front would progress into deeper depths in the type I mortars than that of the type II. Thus, the fact that the carbonation depths in the type I mortars are larger than that of the type II does not necessarily imply that the former is more porous than the latter. Another important observation is that, the carbonation depth varies linearly with the square root of the exposure time, however the parameters of the linear equation are different for each specimen. From the above results, it can be inferred that ecocement type I mortars are more susceptible to carbonation than that of type II.

3.2 Corrosion current

Fig. 2 shows the variation of the corrosion current with exposure time of the steel bars embedded in the mortars subjected only to wetting and drying. It is seen that in the case of the type I specimens, the corrosion current of the steel bar embedded in the mortar with w/c of 0.45 was high during the initial stages but reduced to the noble region towards the end of the experiment. On the other hand the corrosion current of the specimens with w/c of 0.55 and 0.65 increased suddenly about 52 weeks of exposure, indicating a break down of passivity leading to corrosion initiation and propagation. The reason may be that the cement content and for that matter the inherent chloride content of mortar of the specimen with w/c of 0.45 is the highest among the specimens, resulting in a higher corrosion current during the initial stages. However, as hydration progresses microstructure improves and also additional calcium hydroxide is formed, resulting in a restoration of the passive layer on the surface of the steel bar embedded in the mortar with low w/c. In the case of the steel bars embedded in the mortars with w/c of 0.55 and 0.65, the effect of the wetting and drying aids in the transport of moisture and oxygen through their porous microstructure unto the surface of the embedded steel bar, leading ultimately to corrosion. In the case of the type II specimens, the corrosion current of all the specimens remained practically within the noble zone throughout the exposure period. The corrosion current of the steel bar embedded in the mortar with w/c of 0.65, however shot above 0.1 μA/cm², indicating low corrosion, at about 82 weeks of exposure.

Fig. 3 shows the graph of the corrosion current versus exposure period for the specimens that were subjected to accelerated-carbonation followed by wetting and drying. The figure shows that in the case of the type I specimens, during the period of exposure to CO₂, the corrosion current of all the specimens increased rapidly to the severe zone. After 30 weeks of exposure, the corrosion current of
with w/c of 0.45 remained practically within the noble zone throughout the exposure period because the carbonation depth in this specimen did not reach the surface of the embedded steel bar. The figure also shows that the corrosion current of the type II specimens with high w/c is higher than that of the corresponding type I specimens even though one would expect an opposite result due to the high chloride content of the type I ecocement. While this is difficult to explain, the immobilization of the chloride in the type I ecocement to form Friedel's salt during hydration may be a contributing factor. Both XRD and DSC analysis of the type I mortars confirmed the formation of Friedel's salt.

Fig. 4 shows the corroded area versus w/c for the specimens subjected to accelerated-carbonation followed by wetting and drying in comparison to that subjected only to wetting and drying. For the type I specimens, it is seen that in the case of the specimens subjected to carbonation followed by wetting and drying, the corroded areas of the steel bars embedded in the mortars remained independent of w/c whilst in the case of the specimens subjected only to wetting and drying, the higher the w/c the higher the corroded area. For the type II specimens, the corroded areas are higher in the specimens subjected to carbonation followed by wetting and drying than that of the specimens subjected only to wetting and drying.
Fig. 4 Corroded area versus water to cement ratio of steel bars embedded in the two sets of specimens

Fig. 5 Weight loss versus water to cement ratio of steel bars embedded in the two sets of specimens

Fig. 5 shows the weight loss versus w/c for the specimens subjected to accelerated-carbonation followed by wetting and drying in comparison to that subjected only to wetting and drying. It is seen that in both cases the higher the w/c, the higher the weight loss, for the type I specimens. The figure also shows that the weight loss of the specimens subjected to carbonation followed by wetting and drying is higher than that of the specimens subjected only to wetting and drying.

Fig. 6 shows the graph of the weight loss obtained from physical measurements versus that calculated from the corrosion current using Faraday's law. It is seen that there is a linear correlation between their logarithms, however the parameters of the relationship is different in both experimental conditions. In particular it is seen that whereas in the case of the specimens subjected only to wetting and drying, the values obtained from the physical measurement is almost equal to that calculated from the electrochemical measurement, in the case of the specimens subjected to carbonation followed by wetting and drying, the two quantities are different and as such some form of calibration is required. Thus, one has to be cautious in the interpretation of electrochemical measurements in carbonated-induced corrosion in reinforced concrete structures.

3.3 AC Impedance spectrum

Figs. 7 and 8 show the impedance plane plots obtained from the AC impedance measurements as at the end of the exposure period. A closer look at the figures together with Figs. 2 and 3 show that the impedance plane plots of the non-corroded steel bars gave a straight lines in the low frequency region whilst that of the corroded steel bars gave small diameter arcs. In the AC impedance method for the monitoring of corrosion, the diameter of the arc obtained in the impedance plane plot is equivalent to the polarization resistance and as such a large diameter arc indicates a low corrosion current or a passive system whilst a small diameter arc indicates a corroding system.
4. CONCLUSIONS

From the results discussed above, the following conclusions could be drawn.

(1) Under wetting and drying conditions, steel bars embedded in mortars of type I ecocement is more susceptible to corrosion than that of type II ecocement.

(2) Carbonation accelerates corrosion of steel bars embedded in the mortars of both types of ecocement.

(3) Electrochemical measurement yields a good result in the monitoring of corrosion of steel bars embedded in cement mortars.

(4) In both types of ecocement, the extent and severity of the corrosion of the embedded steel bars depend on the w/c, the higher the water cement ratio, the greater the severity of corrosion.

ACKNOWLEDGEMENTS

The authors give thanks to the ecocement project team of Taiheiyo Cement Corporation Ltd. for supplying the cement for the experiment and providing useful advise.

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