Composition and Morphology of Product Layers in the Steel/Cement Paste Interface in Conditions of Corrosion and Cathodic Protection in Reinforced Concrete

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The present study explores the formation of corrosion products on the steel surface in reinforced concrete in conditions of corrosion and subsequent transformation of these layers in conditions of cathodic protection (CP). Of particular interest was to investigate if the introduced pulse CP (as cost-effective alternative of CP) will lead to similar (or even better) transformation of the product layers on the steel surface, compared to conventional techniques. Qualification and quantification of the studied layers was performed using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray analysis (EDAX), visualization of morphology and products distribution was achieved using environmental SEM (ESEM).

It was found out that the product layer, formed on the steel surface in reinforced concrete is inhomogeneous and composed of variety of products, differing in crystallinity and composition, comprising an inner layer with similar to Fe\textsubscript{3}O\textsubscript{4} and an outer layer, composed of iron (oxy)hydroxides and iron (oxy)hydroxy-chlorides (i.e. a combination of \(\alpha\)-, \(\beta\)-, \(\gamma\)-FeOOH, Fe(O,OH,Cl) and Fe\textsubscript{2}O\textsubscript{3}). The product layer in corroding specimens is a combination of low valent oxides and iron-oxy(hydroxy)chlorides and exhibits a rough morphology. The product layers in the protected specimens are far more compact. Cathodic protection reduces salinity around the steel bars, hence the inner product layer (mostly Fe\textsubscript{2}O\textsubscript{3}+Fe\textsubscript{3}O\textsubscript{4}) remains more uniform whereas the outer layer exhibits much lower crystallinity. The transformation phenomena are found to be more apparent under pulse CP conditions, attributed to the obviously beneficial effects of pulse CP in terms of enhanced chloride withdrawn from the steel surface and minor influence (less side effects) on the bulk concrete microstructure.

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Introduction

The most common and important causes for reinforcement corrosion are either localized depassivation of the steel surface due to chloride ingress or more uniform corrosion due to acidification of the pore solution as result of carbonation of the cement paste. Cathodic protection (CP) has been found to be one of the most useful techniques for inhibiting chloride-induced corrosion in reinforced concrete [1]. The fundamental mechanisms underlying the efficiency of CP techniques are strongly correlated to the morphology and transformations of product layers on the steel surface. This paper pursues to explore the formation, distribution and morphological alterations of corrosion products in reinforced concrete in conditions of corrosion and CP. Moreover, the study aims to reveal the advantages of an improved alternative of conventional CP, denoted in the paper as pulse CP, in terms of favorable structure of the product layers formed under pulse CP conditions, compared to those observed under the conventional techniques of protection.

In a simplified way, corrosion of reinforcing steel in concrete can be represented by two electrochemical reactions: dissolution of iron at anodic sites (Eq.1) and the corresponding oxygen reduction at local cathodes, using the electrons generated by the metal dissolution (Eq.2)

\[
\begin{align*}
2Fe_{(s)} & \rightarrow 2Fe^{2+}_{(aq)} + 4e^{-} \quad (1) \\
O_{2(g)} + 2H_{2}O_{(l)} + 4e^{-} & \rightarrow 4OH^{-}_{(aq)} \quad (2)
\end{align*}
\]

The products of the above reactions normally interact and in a final stage transform into a stable protective film on the steel surface. The protective properties of the formed layer depend on pH, oxygen availability, cement chemistry. The protective layer is additionally supported by the presence of Ca-rich outer layer, which adheres to the steel as well. The calcium rich layer provides only limited protection, the inner layer of iron oxide/hydroxides is the one passivating the steel [2]. In general pH in concrete is about 12.5 - 13 and oxygen availability is comparatively restricted in case of sound concrete layer on the steel surface. Consequently the passive layer could be stable with time. However, in the presence of aggressive substances, moisture and microcracks, which favore oxygen and aggressive substances penetration to the vicinity of the steel surface, breakdown of passivity occurs and corrosion is initiated. The passive layer breakdown mechanisms were extensively studied by numerous authors [3-6] and number of models are already proposed and described, for example: adsorption-displacement mechanism, chemico-mechanical mechanism, migration-penetration mechanism.

Whatever the mechanism of protective film breakdown, the final stage is exposure of small areas of fresh metal surface to the electrolyte (in this case to the pore solution). The metal dissolution in these areas creates locally increased concentration of metallic ions in addition to aggressive ions migrating from the bulk solution to the steel surface i.e. mass transport perturbation occurs in the diffuse layer on the metal surface. By all means, once corrosion is initiated and film transformations or formation of new product layers occur, there are several possibilities for the formation sequence of these layers, depending on the environmental conditions. In conditions of CP, transformations of the product layers occur as well, mainly in terms of lowering the products cristallinity and leading to the formation of a more compact layer on the steel surface. The favourable conversions are more pronounced under pulse CP conditions compared to conventional CP and are attributed to the beneficial effects of pulse in reducing pore water salinity and favorable physico-chemical and microstructural alterations in the bulk cement paste.
Materials and methods

The materials used in the present study were reinforced concrete cylinders, cast from OPC CEM I 32.5, w/c ratio 0.6, with dimensions: H=25cm, D=12 cm, embedded construction steel (d=12mm). Aiming at initiation of corrosion before applying CP, the specimens were maintained in salt spray chamber (5% NaCl, 25 to 35°C) for 460 days after curing for 28 days. The CP was employed in 2 regimes (conventional and pulse), using DC current in the range of 5 to 20 mA/m² steel surface, duty cycle for the pulse regime was 12.5% to 50 % at 1kHz frequency.

Cathodic protection was applied after corrosion was initiated, at certain intervals for different cell-couples. The results in the present study are for specimens on which CP was applied at 120 days of age i.e. in the time of applying protection, corrosion was already in an advanced stage. The microstructural characterization in this study is for 270 days of age, when conditioning of the specimens was interrupted for investigation. The composition and morphology of product layers on corroding and protected steel surfaces were investigated, using optical microscopy (for visual inspection), XRD, XPS and EDAX analysis (for quili- and quantification) and morphology determination by scanning electron microscopy, using environmental SEM (ESEM Philips XL).

Experimental results and discussion

1. Optical microscopy investigation

Fig.1 presents the observed product layers on the steel surface of a protected specimen (pulse CP)(Fig.1 top) and a corroding specimen (Fig.1 bottom), along with the relative “print” in the cement paste (middle column).

Higher magnification (6.4x) of the deposits (Fig.1, right column) reveals dark-brown to black color of the products for the protected specimen, attributed to hematite/magnetite
formation and orange to light-brown color of the product deposits for the corroding specimen, denoted to iron oxy(hydroxy)chlorides and oxyhydroxides.

Samples of the steel surface from all specimens were investigated further, using the above mentioned techniques (XRD, XPS, ESEM, EDAX), immediately after removing the concrete layer, surrounding the steel bars i.e. conditions for atmospheric influences were avoided. The microstructural analysis of the steel surface in conditions of corrosion and protection will be presented in what follows.

2. X-ray diffraction analysis.

The study focuses on the difference in chemical composition and morphological aspects of corrosion products between corroding and protected specimens. In addition, the comparison among the protected specimens (under pulse CP and conventional CP) aims at revealing the beneficial effects of the pulse technique in terms of favourable transformations of product layers on the steel surface.

![X-ray diffraction patterns](image)

Fig. 2 X-ray diffraction patterns for corroding specimen (up), protected specimen under pulse CP (middle) and protected specimen under conventional CP (bottom), using CuKα radiation: C-calcite, G-goethite, MG – magnetite, MG – maghemite, L – lepidocrocite, Q – quartz, W – wustite, Ar – aragonite, P – portlandite, A – akaganeite, H – hematite, S – siderite.

The peak intensity in the XRD diffractograms is generally corresponding to the amount of specific corrosion products, thus rendering possible a qualitative comparison between different specimens. The common products on the steel surface, in the conditions under study, include iron oxides, iron (oxy)hydroxides and oxy(hydroxy)chlorides in the presence of chlorides. Wustite (FeO), Hematite (Fe₂O₃), Magnetite/Maghemite (Fe₃O₄) are categorized in the group of oxides, while the iron oxyhydroxides vary in crystal structure (α-,β-,γ-,δ- FeOOH) or in composition in the case of akaganeite ([Fe³⁺OOHCl]). Goethite (α-FeOOH) and Lepidocrocite (γ-FeOOH) are prominent corrosion products in rust layers, akaganeite has been identified only in layers
formed through corrosion of steel in chloride environment (as in the present study). These products are present in both corroding and protected specimens, however CP is expected to induce changes in proportions and morphology of the product layers.

The main characteristic differences in the XRD patterns for the three specimens are:

1. The patterns for the protected specimens (Fig.2 middle and bottom) present more magnetite (MG, MH), corresponding to peaks 2θ 35.5°, 43°, 57°, 62.5° and 67° respectively.

2. Compared to the protected specimens, the corroding specimen (Fig.2 top pattern) shows relatively high amount of wustite (W) at 2θ 42°, presence of lepidocrocite (L) and goethite (G) at 2θ 36.5°(overlapping partly with magnetite) and a characteristic peak for akaganeite (A at 2θ 56°). Siderite and aragonite (S, Ar) are present in the corroding specimen, which along with L, G and A are barely detected in the protected specimens.

3. The proportions of high valent oxides, particularly magnetite for the protected specimens are much higher. With this respect and compared to conventional CP, the specimens under pulse CP show favorable composition of the product layers, evidenced by the sharper peaks for magnetite at 2θ 35.5° and 2θ 62.5°, in addition to the absence of a distinguished peak for goethite at 2θ 37° and sharper peaks for portlandite at 2θ 34.2° and 2θ 46.5°.

Hence, the pulse CP brings about favourable modifications of the corrosion products in terms of higher amounts of protective and adhering to the steel surface Fe₃O₄, which along with the Ca-rich layer (evidenced by adhered portlandite) and non detectable by XRD oxy(hydroxy) chlorides, denotes for better efficiency compared to the conventional CP.

3. X-ray photoelectron spectroscopy

The XPS analysis supports the findings from XRD in terms of amounts and composition of corrosion products. The XPS spectra are presented on Fig.3 below, the identified compounds are summarized in Table.1. The fitting of O1s, Ca2p and C1s spectra revealed the presence of CaCO₃ in all specimens (the energy scale is corrected to the C1s - peak maxima at 285 eV). Iron oxyhydroxides and iron oxides are present in different amounts as well, the former enriching the product layers in corroding specimens and conventionally protected specimens (IIIN and VIDC), the latter (the iron oxides) more pronounced in specimens under pulse CP (VIIpDC).
As seen from Fig.3 a) there is a high energy broadening of the O1s spectrum for the corroding specimen (IIIN) at binding energy of 531.87 eV, which is due to higher chloride concentration and formation of more hydrated iron compounds, hence the amount of iron oxyhydroxides (FeOOH) in the corroding specimen is higher, as identified by XRD.

Such distribution is also reported by [7] for similar systems, where the presence of chlorides results in thicker films in which the contents of FeOOH and water tend to increase. Moreover, the binding energy of 531.87 eV for the corroding specimen (Fig.3 a) is attributed to OH-M bonds, while binding energies 530.26 eV and 530.46 eV for the protected specimens (pulse CP and CP respectively) are attributed to O-M bonds. Hence the presence of Fe$_2$O$_3$ and Fe$_3$O$_4$ in protected specimens is more pronounced.

### Table 1. Compounds according Fe2p, O1s, Ca2p and C1s spectra and relevant binding energy.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fe (2p) eV</th>
<th>O (1s) eV</th>
<th>Ca (2p) eV</th>
<th>C (1s) eV</th>
</tr>
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<tbody>
<tr>
<td>Fe$_2$Si</td>
<td>707.5</td>
<td>528.27</td>
<td>344.8</td>
<td>FeCO$_3$</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>708.1-708.2</td>
<td>529.1</td>
<td>346.1</td>
<td>Fe(CO)$_3$</td>
</tr>
<tr>
<td>Fe$_2$O$_4$</td>
<td>709</td>
<td>529.4</td>
<td>346.7</td>
<td>NaCO$_3$</td>
</tr>
<tr>
<td>FeO</td>
<td>709.3-709.6</td>
<td>529.5-529.8</td>
<td>346.7</td>
<td></td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>709.6, 709.9</td>
<td>FeOOH</td>
<td>529.7</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td>Fe/SiO$_2$</td>
<td>709.9</td>
<td>Fe$_2$O$_4$</td>
<td>529.8</td>
<td>CaSiO$_3$</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>710.2-710.4</td>
<td>Fe$_3$O$_4$</td>
<td>530.1</td>
<td>Ca(ClO)$_2$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>710.3</td>
<td>Ca(OH)$_2$</td>
<td>531.2</td>
<td>Ca(ClO)$_2$</td>
</tr>
<tr>
<td>Fe$_3$Al(SiO$_4$)$_3$</td>
<td>710.7</td>
<td>CaCO$_3$</td>
<td>531.2-531.3</td>
<td>CaO</td>
</tr>
<tr>
<td>FeOOH</td>
<td>712.0</td>
<td>Fe(OH)$_2$</td>
<td>531.4</td>
<td>Ca(OH)$_2$</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>723.5</td>
<td>CaSiO$_3$</td>
<td>531.5</td>
<td></td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>724</td>
<td>FeOOH</td>
<td>531.7</td>
<td></td>
</tr>
<tr>
<td>FeOOH</td>
<td>724.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Fe2p spectra (Fig.3b) reveals the following: for corroding specimen (IIIN), binding energy 709.3 eV and 709.6 eV correspond to FeO and Fe$_2$O$_3$ respectively; for the protected specimens, binding energy 710.2 eV and 710.4 eV correspond to Fe$_3$O$_4$ and 712 eV to FeOOH. Fe$_3$O$_4$ is most likely more pronounced in specimen under pulse CP (higher intensity of the peak at the relative binding energy – VIIpDC), while FeOOH is most likely in higher amounts in the corroding specimen and the protected specimen VIDC as they depict wider peaks, with larger surface area at this relevant binding energy (712 eV).

### 4. Morphological and microstructural observations – ESEM and EDAX

SEM imaging was employed for evaluating the morphology of product layers and their distribution in the vicinity of the steel/cement paste interface. The investigations were performed on cross sections of the specimens, which visualize the characteristic changes relevant to bond strength and mechanical properties respectively. Longitudinal sections of the steel surface and the corresponding “steel prints” on the cement paste were investigated as well. The analysis was coupled with energy dispersive X-ray (EDAX) for evaluation of the chemical composition of corrosion and cement hydration products.

Fig.4 presents the cross section of the steel/cement paste interface of the corroding specimen (left) is clearly visible along with shrinkage cracking of the cement paste. The microcracking is a result from the volume expansion of the corrosion products.
which at first occupy the restricted space around the steel bar, fill in cracks and voids and penetrate further into the bulk material. In contrast, the protected specimen presents a compact steel/paste interface (Fig. 4 right), with no visible significant damage, although CP was applied at 120 days of age i.e. after corrosion was certainly initiated on the steel surface taking into consideration the extreme environmental conditions.

The corrosion process on the steel surface of the protected specimens was obviously arrested and no further growth of corrosion products occurred, resulting in a dense layer, enriched in calcium (Fig.5 right), in contrast to the cracks and voids as consequence from corrosion products growth and further penetration into the bulk material, as observed in the corroding specimens at the same age (Fig.5 left).

Longitudinal sections of corroding and protected specimens (steel surface) are presented on Fig.6. The severe corrosion damages on the steel surface of the corroding specimen are evident (Fig.6 left), whereas the steel surface of the protected specimens (Fig.6 middle and right) is comparatively uniform. Comparing specimens under pulse CP (Fig.6 middle) and specimens under conventional CP (Fig.6 right) it is seen that for the specimen under pulse CP a more adherent layer of cement paste (enriched in calcium)
covers the steel surface. The observation is consistent with the higher amounts of portlandite, detected by XRD analysis (section 1 above). Of course the distribution of calcium-rich layers (e.g. CaO and Ca(OH)$_2$) is not uniform, however, cement paste layers more adhered to the steel surface mean lower amount of corrosion products which normally increase the bond degradation process.

![Fig.6 Longitudinal sections of the steel surface in corroding (left), pulse CP protected (middle) and conventional CP protected (right) specimens – overview.](image)

The cement paste, adhered or in the vicinity of the steel surface, in all conditions was investigated for chemical composition and morphology of the cement hydration products. Relevant to the present study, the chloride concentration around the steel bar, as corrosion determining factor, is of most interest.

![Fig.7 Morphology of the cement paste layers, adhered to the steel surface (top) and EDAX analysis (bottom) in corroding specimen (left), presenting a complex of NaCl and CaCl$_2$ incorporated in the cement matrix and protected specimen (right), presenting typical globular morphology of the calcium-silica-hydrate, ettringite needles and the platy morphology of calcium-chloro-aluminates (bound chlorides).](image)

Fig.7 presents the morphology of the cement paste layer adhered to the steel surface in corroding specimen (left) and in protected specimen (right). The cement paste for corroding specimen contains high amounts of chlorides (NaCl and CaCl$_2$), while the
chlorides in the protected specimens are reduced as consequence of the protection current. The amounts still present are found to be chemically bound in the form of calcium-chloro-aluminates with platy morphology as seen on Fig. 7(right).

Fig. 8 Different dimensions of $\gamma$-FeOOH in the corroding specimen (left), grown on a flat layer of magnetite, showing significantly higher cristallinity (crystal length about 17.5 $\mu$m) compared to the small residue of $\gamma$-FeOOH (crystal length about 8 $\mu$m) , nested in the magnetite layer of a protected specimen (right).

As mentioned, the CP was expected to bring about changes in crystallinity and morphology of product layers on the steel surface. The findings from the XRD and XPS analysis were confirmed with microscopical observations of these layers, revealing higher amounts and crystalinity of the corrosion products in corroding specimens, compared to protected specimens, both at same age of 270 days. The observations are supported by energy dispersive X-ray analysis, results of the latter for the most relevant compounds are summarized in Table 2.

Table 2. Summarized data from EDAX analysis of the corrosion products, depicted on the micrographs (the w.% do not equal 100% as the table contains only compounds, relevant to the discussion).

<table>
<thead>
<tr>
<th>Fig. No.</th>
<th>Products</th>
<th>Composition (most relevant compounds), w.%</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Cl$_2$O Fe$_3$O$_4$ (iron oxides and hydrous) CaO</td>
</tr>
<tr>
<td>Fig.9 (left)</td>
<td>Akaganeite [Fe$^{3+}$(O,OH,Cl)]</td>
<td>3.56</td>
</tr>
<tr>
<td>Fig.10 (&quot;pit&quot;)</td>
<td>Inner product</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>Outer layer (pit wall)</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>Adjacent flat (carbonated layer)</td>
<td>0.86</td>
</tr>
<tr>
<td>Fig.11(left) (&quot;pit&quot;)</td>
<td>Inner product</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Outer adjacent layer (Magnetite)</td>
<td>0.20</td>
</tr>
<tr>
<td>Fig.11 (right)</td>
<td>Geothite ($\alpha$-FeOOH)</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>Lepidocrocite ($\gamma$-FeOOH)</td>
<td>0.67</td>
</tr>
<tr>
<td>Fig.12 (flat regions)</td>
<td>Magnetite (Fe$_3$O$_4$)</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Fig.8 presents layers of lepidocrocite ($\gamma$-FeOOH) in the corroding specimen (left) and the protected specimen (pulse CP) (right). Fig.9(left) presents the needle-like cristallinity of akaganeite, identified in the corroding specimen only. The presence of akaganeite supports the hypothesis for high salinity in the corroding specimens as it is found only in chloride containing environments [8-10].
Akaganeite is mainly responsible for micro-cracking in reinforced concrete as it is less adherent and not accommodating in rust layers [8], thus impeding the formation of a film with good protective properties. It’s found to grow in the weak zones of the paste/gravel or the steel/paste interfaces (Fig.9 right), which along with its typical needle like structure additionally promotes microcracking. The microstructural observations are supported by the XRD analysis with the characteristic pick for akaganeite at $2\theta$ 56°, corresponding to planner distance $d=1.64 \text{ Å}$.

![Fig. 9 Needle like morphology of akaganeite (left) in the corroding specimen, growing preferentially in voids or weak zones, as cement paste/aggregate, thus causing significant debonding and microcracking (right)](image)

![Fig. 10 Localized corrosion on the steel surface in the corroding specimen, products locally grow in the form of a “pit” surrounded by a carbonate-enriched layer (left) and higher magnification of the local region (right)](image)

Certain product morphology is observed on the surface of the corroding specimens in the regions of localized corrosion. Fig.10 (left) shows local corrosion (circled region), grown on a layer enriched in carbonates (leaf-like morphology on the right side of the image). Fig 10 (right) presents higher magnification of the local corroding area, revealing the growth of corrosion products (most likely akaganeite and lepidocrocite) outwards of the formation, surrounded by a perpendicularly grown amorphous layer of oxy(hydroxy)chlorides, initially formed on the steel surface.
Fig. 11 Micrographs (4000x) presenting “healed” local damage on the surface layer (magnetite) of protected specimen (left), “flower”-like morphology of $\alpha$-FeOOH and relatively flat “needle”-like layer of $\gamma$-FeOOH (right).

In contrast, such local damages in the protected specimens reveal completely different morphology and composition of the products filling in the “pits” (Fig. 11 left). Local disruptions of the product layers in the protected specimens were expected as cathodic protection was applied at 120 days of age, however as seen from Fig. 11 (left), these local areas are significantly reduced in surface area, are filled in with Ca-rich products and there is no product growth as in the corroding specimen (Fig. 10 left), hence due to the changed cement chemistry as consequence from the cathodic current, these local areas in the protected specimens are “healing”. Fig. 11 (right) depicts the “flower”-like
morphology of goethite (α-FeOOH), detected in the protected specimens and “foam”-like flat layer of low crystalline lepidocrocite (γ-FeOOH).

Finally, a comparison of crystallinity of corrosion products in corroding, protected (pulse CP) and protected (conventional CP) is presented on Fig. 12. It is obvious that the crystallinity of corrosion products (namely nested lepidocrocite and goethite in the relatively flat layers of magnetite) for the protected specimens is much lower in the specimen under pulse CP (Fig.12a), compared to the conventionally protected specimen (Fig.12b). Of course, the crystallinity of the same products in the corroding specimen is much higher (crystal length of at least 12 µm -Fig.12c).

As supported by the XRD and XPS analysis, the specimen under pulse CP presents higher amounts of relatively flat magnetite. Small residues (circled regions Fig.12a) of iron-(oxy)hydroxides (crystal length about 2 to 5 µm) are detected nested in the adhered magnetite layers, while the specimens under conventional CP are characterized by higher amounts of (oxy)hydroxides with higher crystallinity (crystal length about 10 µm – Fig.12b). The different crystallinity, morphology and distribution is denoted to the more favourable cement chemistry under pulse CP conditions, as supported by EDAX analysis as well – Fig.13.

**Conclusions**

The present study reveals the close dependence of product layers formation, conversion, amounts, morphology and crystallinity on the cement chemistry in reinforced concrete systems. The product layer in corroding specimens is a combination of mainly low valent oxides and iron-oxy (hydroxy)chlorides, exhibits rough morphology and
higher cristallinity. Cathodic protection reduces salinity around the steel bars, hence the product layers are more uniform and compact, exhibit lower crystallinity and are composed predominantly of high valent iron oxides, consequently a more adhered and protective layer is formed. The transformation phenomena are found to be more apparent under pulse CP conditions, hence the pulse regime is able to arrest corrosion as efficient as the conventional CP technique on one hand, and is more favourable for the steel surface and cement chemistry in terms of morphology and microstructure on the other.

References: