International RILEM Conference on
Materials, Systems and Structures in Civil Engineering 2016

segment on
Electrochemistry in Civil Engineering
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RILEM, The International Union of Laboratories and Experts in Construction Materials, Systems and Structures, is a non profit-making, non-governmental technical association whose vocation is to contribute to progress in the construction sciences, techniques and industries, essentially by means of the communication it fosters between research and practice. RILEM’s activity therefore aims at developing the knowledge of properties of materials and performance of structures, at defining the means for their assessment in laboratory and service conditions and at unifying measurement and testing methods used with this objective.

RILEM was founded in 1947, and has a membership of over 900 in some 70 countries. It forms an institutional framework for co-operation by experts to:

- optimise and harmonise test methods for measuring properties and performance of building and civil engineering materials and structures under laboratory and service environments,
- prepare technical recommendations for testing methods,
- prepare state-of-the-art reports to identify further research needs,
- collaborate with national or international associations in realising these objectives.

RILEM members include the leading building research and testing laboratories around the world, industrial research, manufacturing and contracting interests, as well as a significant number of individual members from industry and universities. RILEM’s focus is on construction materials and their use in building and civil engineering structures, covering all phases of the building process from manufacture to use and recycling of materials.

RILEM meets these objectives through the work of its technical committees. Symposia, workshops and seminars are organised to facilitate the exchange of information and dissemination of knowledge. RILEM’s primary output consists of technical recommendations. RILEM also publishes the journal *Materials and Structures*, which provides a further avenue for reporting the work of its committees. Many other publications, in the form of reports, monographs, symposia and workshop proceedings are produced.
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Lisbeth M. Ottosen

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PRO 113: Concrete with Supplementary Cementitious materials

PRO 114: Frost Action in Concrete

PRO 155: Fresh Concrete

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Preface

The conference “Materials, Systems and Structures in Civil Engineering – MSSCE 2016” is part of the RILEM week 2016, which consists of a series of parallel and consecutive conference and doctoral course segments on different topics as well as technical and administrative meetings in several scientific organizations. The event is hosted by the Department of Civil Engineering at the Technical University of Denmark and the Danish Technological Institute and it is held at the Lyngby campus of the Technical University of Denmark 15-29 August 2016.

This volume contains the proceedings of the MSSCE 2016 conference segment on “Electrochemistry in Civil Engineering”. The conference segment is organized by the E-KIN Research team at Department of Civil Engineering, Technical University of Denmark. The proceedings contain full papers and abstracts presented at the conference segment. The papers are organized in alphabetical order in both categories. All contributions have been peer reviewed.

The various topics of the proceedings are within reinforcement corrosion (Corrosion mechanisms and propagation, modelling of service life, and corrosion prevention), electrochemical assessment methods (in both construction and geotechnical materials), electrochemical repair techniques (stopping corrosion, crack closure and desalination for heritage conservation) and electrochemical upgrading of waste for use in construction materials (concrete or ceramics).

Lisbeth M. Ottosen

August 2016, Lyngby, Denmark
Welcome

Were you aware that a part of your daily language is likely to be in Danish? A thousand years ago the Danish word “Vindue” came along with the Vikings to England. Several hundred years later it reached North America, and from there – just two to three decades ago – almost every person in the world learned to understand and pronounce this word: “Windows”, which etymologically means “an eye to the wind”.

As a child your career as construction professional may have started with LEGO, and before you went to bed, your mother told you the unforgettable fairytales of H.C. Andersen. You may have grown up with the delicious taste of Lurpak butter on your bread, and though you might find it strange that “God plays dice with the Universe”, hopefully your school teacher told you that on this topic Einstein was flat out wrong and Niels Bohr was right. Right now you may prefer to be sitting in the sun with a chilled Carlsberg beer in your hand, enjoying the iconic view of the Sydney Opera House. All of it is Danish made, and many things around you at home, if not made in Denmark, were probably brought to you by Maersk, the world’s largest shipping company, the modern Danish Viking fleet.

Though Denmark is one of the world’s smallest countries, yet it stands – along with your country – among the greatest. On top of a thousand years of outreach from Denmark, your visit to the Danes is most welcome. On your approach to Copenhagen airport you had a view to wind turbines harvesting green energy, you saw record breaking bridges, and perhaps you got a glimpse of the island Ven where the nobleman Tycho Brahe literally speaking changed our view of the world through perfection of astronomical observations with his naked eye. In Copenhagen you may appreciate a walk in the fairytale amusement park TIVOLI, and in the Copenhagen harbour you may have a rendezvous with a Little Mermaid.

Of all things in Denmark you will surely enjoy the conference and doctoral courses Materials, Systems and Structures in Civil Engineering, MSSCE 2016 which are held in conjunction with the 70th annual RILEM week. On this occasion RILEM celebrates its 70 years birthday and thus maintains generations of experience. However, new activities and the in-built diversity keep RILEM fresh and dynamic like a teenager.

The event takes place in northern Copenhagen, Lyngby, at the campus of the Technical University of Denmark, 15-29 August 2016. MSSCE 2016 aims at extending the borders of the RILEM week by including doctoral courses, by involving a palette of RILEM topics in the conference and workshop activities, and by collaborating with other scientific organizations. The insight and outlook provided by this event make it RILEM’s technical and educational activity window.

It is a pleasure to share with you what is unique to RILEM and Denmark!

Ole Mejlhede Jensen, Technical University of Denmark
Honorary president of RILEM 2016, Chairman of MSSCE 2016
CONCRETE ELECTRICAL RESISTIVITY TO EVALUATE REINFORCEMENT SERVICE LIFE

Carmen Andrade

(1) Institute of Construction Sciences “Eduardo Torroja” IETcc – CSIC-Spain

Abstract

Current codes have requirements for the durability design of concrete based on compressive strength and provisions related to cement content and water – cement ratio. For reinforcement corrosion the codes also specify the maximum flexural crack widths. However, modern trends prefer to specify the performance rather than the concrete characteristics. This performance approach demands to define a durability controlling parameter, such as the chloride diffusion coefficient, with its corresponding test and the model to predict the time to steel corrosion. This paper describes the use of the concrete electrical resistivity to be used as durability performance parameter and also the complementary information that the resistivity can provide as it is: the setting period, the mechanical strength and the degree of curing. Also is explained how to design the concrete mix to obtain a target resistivity.

1. Introduction

Concrete electrical resistivity was measured comparatively early with respect to the application of other electrochemical techniques in concrete because studies are reported from the 40-50’s [1-2] related to the characterization of concrete as an electrical insulator to be used in train sleepers and because it was applied to non-destructive measurement of cement setting [3]. It is in the decade of the 60’s when reinforcement corrosion was started to appear as an important potential distress and electrochemical techniques started to be applied, in particular polarization curves [4-6].

However, its role in these electrochemical experiments was not appraised until Polarization Resistance technique, R_p, was used to measure the instantaneous corrosion rate [7-8], because their values could be very much affected by the ohmic drop if not removing resistive component from the recorded value. The systematic measurement of the ohmic drop affecting R_p measurements enabled the evidence that the concrete resistivity is a direct function of concrete porosity and its degree of water saturation [9-11] and then, the corrosion rate results a direct function of resistivity with the consequence that ohmic control is the key rate controlling mechanism of reinforcement corrosion.
It is in the decade of the 90’s when the interest on resistivity arises again when the relation between chloride diffusion and concrete resistivity is demonstrated [12]. To explore this relation was not appreciated and instead, most of the researchers focused to develop models and tests on chloride migration [13-14]. However, the author of this communication has been attracted by the potential numerous applications of concrete resistivity and in particular has identified that it is the key parameter linking microstructure with transport ability of concrete and has studied in depth the fundamentals of resistivity in particular the possibility to predict the reinforcement service life from its characterization [15-16]. In present work some the microstructural bases of the resistivity as universal parameter controlling transport processes in concrete as porous medium are described as well as the relation between reinforcement corrosion and degree of saturation which makes to vary concrete resistivity.

2. Concrete resistivity

Concrete electrical resistance, R, is the relation between the voltage drop, V, applied to a conductive body and the current, I, induced by it.

\[ R = \frac{V}{I} = \rho \frac{l}{A} \]  

(1)

This Resistance if standardized to a regular geometry enables to know the resistivity through Ohm’s law which is given in equation 1 (l= the distance between electrodes and A is the cross section area in figure 1).

The most common method of measurement of resistivity is shown in figure 1 (left). Two electrodes are placed in two parallel faces of a concrete specimen or disc and voltage is applied. The other common method is that known as “four points or Wenner method” shown right in the same figure.

2.1 Relation of Resistivity with concrete microstructure

Concrete is a porous body in which the solid phases are non-conductive being the pores filled with a solution which is the conductive phase. Then the resistivity/conductivity of the concrete will depend on the total pore volume and on its pore size distribution. As higher is the porosity, lower is the resistivity providing the concrete is water saturated. If the concrete is not saturated then, the resistivity is an indication of concrete degree of saturation [11-12]. This relation can
be expressed through a modification of Archie’s law [17], where $\rho_0$ is the resistivity of the pore solution, $W$ is the volumetric fraction of water and $\tau$ is the tortuosity factor, $\tau$:

$$\rho = \rho_0 W^{-\tau}$$

Regarding the influence of the chemical composition of pore solution, $\rho_0$, its impact in the total resistivity following equation 2 is small providing the concrete remains alkaline. If concrete is carbonated then the value of $\rho_0$ is much higher.

3. Relation between corrosion rate and resistivity

As indicated the electrical resistivity decreases as concrete water saturation increases [8, 11, 16]. Figure 2 shows the resistivity isotherms of four concrete types with the decrease of the resistivity for values of RH>85% where capillary condensation is started.

![Figure 2](image)

Figure 2 Values of resistivity in function of the RH of four concretes.

It is precisely this dependence with moisture of the resistivity which explains the relation between it and the reinforcement corrosion rate which is illustrated with the graph $I_{corr}$-resistivity [9, 10] of figure 3, in which it is illustrated the average relation and some values of a particular test. The inclined line in the figure 3 represents the expression:

$$I_{corr} (\mu A/cm^2) = \frac{26}{\rho (K\Omega/cm)}$$

This relation has open the door to several practical developments and to establish that below a RH of 65% the corrosion practically stops while it is above 85-90% RH when the carrion increases due to the capillary pores are starting to be filled with evaporable water.
Figure 3. Graph $I_{corr} - \rho_{et}$ which indicates the relation between the $I_{corr}$ and the degree of concrete saturation. The symbols are examples of site measurements.

4. Relation between resistivity and diffusivity

On the other hand resistivity is related to the ionic transport ability of concrete through Einstein laws which relates the movement of electrical charges to the conductivity of the medium [13, 18] as represented in figure 4 in a log-log graph:

$$D_e = \frac{F}{\rho_{et}} = F \cdot \sigma$$

Where:
- $D_e$ = effective diffusion coefficient
- $F$ = a factor, which depends on the external ionic concentration
- $\rho_{et}$ = “effective” resistivity (in this case of concrete saturated with water)
- $\sigma$ = conductivity (inverse of resistivity)

A value of $k_{Cl}$ of $20 \times 10^{-5}$ can be used for external chloride concentrations of 0.5 to 1 M.

With respect to the influence of temperature, it has an important effect on resistivity, which only can be generalized if the $p$ values are standarized to a reference temperature that it is proposed to be 25°C. Other possibility is the use of Arrhenius law, however it has been detected that the Activation energy depends on the degree of saturation and a single value seems not exiting. However the final effect of temperature in the corrosion initiation and propagation periods is controversial as an increase in temperature may produce an evaporation, which in turn would effect by slowing both, $D$ and $V_{corr}$. Therefore, the incorporation of temperature effects on models is very premature and more results are needed.
5. Evolution of resistivity during setting and hardening

When water is mixed with the cement powder the paste formed is very fluid and then the resistivity is very low (figure 5), however as soon as the paste is setting, the resistivity increases following cement hydration [3]. The increase continues during hardening as porosity evolves with cement hydration. This increase with time serves to monitor the “aging factor of hydration” which will be addressed later.

6. Relation resistivity and mechanical strength

The increase of resistivity with time is parallel to that of mechanical strength due both parameters depend on concrete resistivity. In figure 6 is shown their relation for numerous concretes which indicates that the resistivity may be used to predict mechanical strength when the specimens are of the same type and cured in standarized conditions.
7. Service life model based in the resistivity measurements

As has been mentioned, the ability of resistivity to quantify diffusivity is based in one of the Einstein laws, which relates the movement of electrical charges to the conductivity of the medium [13, 15, 16, 19] (see equation 4). This expression only accounts for the transport of the chloride ions through the pore network which is insufficient to characterize the transport through concrete where reaction of chlorides takes place and this reaction and the hydration make to evolve the porosity. Then some factors have to be applied to equation 3 to account for these effects together with the value of the k factor which takes into account the concentration of the chloride or aggressive substance.

The factors introduced in the equation 3 have been:
- $k$ has been named “environmental factor”. It depends on chloride concentration and in the case of carbonation, on the concrete moisture content [13, 16]
- $r_n$ “retarder or reaction factor” [20] which multiplies the resistivity to account for the “retarder” effect of chloride binding during penetration of chlorides. It can also be applied to the case of carbonation. This is due to carbonation progresses when the concrete is partially saturated. That is, as higher is the porosity or the empty pores due to dry conditions, higher the carbonation depth will be but a certain moisture level is necessary for teh carbonation reaction to proceed.
- Finally, the “aging factor” $q$ [21] which accounts for the evolution with time of the porous microstructure.

These factors have been quantified in order to introduce them in an expression linking resistivity with time that will be described later.

**Environmental factor $F$**
The environmental factors $F_C$ and $F_{CO2}$ depend on the exposure conditions [13, 16]. Table 1 presents values that were calculated by inverse analysis of test results obtained on real structures.
Table 1. Values of environmental factors, $k_{Cl}$ and $k_{CO2}$, following the exposure classification of EN206

<table>
<thead>
<tr>
<th>Exposure class</th>
<th>$F \text{ (cm}^3\Omega/\text{year)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X0,XC1,XC2</td>
<td>200</td>
</tr>
<tr>
<td>XC3 moderate humidity</td>
<td>1000</td>
</tr>
<tr>
<td>XC4 cycles wet and dry</td>
<td>3000</td>
</tr>
<tr>
<td>XS1 (d &gt; 500 m distance to the coast line)</td>
<td>5000</td>
</tr>
<tr>
<td>XS1 (d &lt; 500 m distance to the coast line)</td>
<td>10000</td>
</tr>
<tr>
<td>XS2 submerged</td>
<td>17000</td>
</tr>
<tr>
<td>XS3 tidal</td>
<td>25000</td>
</tr>
</tbody>
</table>

Reaction factor $r_b$

The reaction factors $r_{Cl}$ and $r_{CO2}$ [20] depend on the type and amount of cement and therefore on the reaction of the penetrating substance with the cement phases. Equation 3 can be expressed as:

$$D_{CO2} = \frac{F_{CO2}}{r_{CO2}}$$

The values can be calculated either by direct measurement, or indirectly by measuring the relation between the effective and apparent diffusion coefficients, or by calculation based on the cement composition. Table 2 presents examples of $r_{Cl}$ values that were calculated based on test results obtained by comparing steady and non-steady diffusion coefficients.

Table 2. Examples of values of the reaction factor of chlorides, $r_{Cl}$, for 3 types of cement

<table>
<thead>
<tr>
<th>Cement</th>
<th>$r_{Cl}$</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I</td>
<td>1.9</td>
<td>1.3</td>
</tr>
<tr>
<td>CEM I + silica fume</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>CEM IIA (with pozzolan and fly ash, in ≤ 20%)</td>
<td>3.0</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Aging Factor $q$

It accounts for the refinement of the concrete pore system results in an increase of resistivity with time [21]. The resistivity evolves with time due to the progression of hydration, the combination of the cement phases with the chlorides or carbon dioxide which usually decreases the porosity and by the concrete drying out (depending on the environment. It can be calculated through the expression 5, [24] (see figure 3 right):

$$\rho_t = \rho_0 \left( \frac{t}{t_0} \right)^q$$

Where:

- $\rho_t$ = resistivity at any age $t$
- $\rho_0$ = resistivity at the age of the first measurement $t_0$
Values of $q$ found for different cement types are given in table 3.

<table>
<thead>
<tr>
<th>Cement</th>
<th>$q$</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.22</td>
<td>0.01</td>
</tr>
<tr>
<td>II/A -P</td>
<td>0.37</td>
<td>0.06</td>
</tr>
<tr>
<td>II/A-V</td>
<td>0.57</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The relation between $q$ and the aging factor $n$ of the diffusion coefficient gives the expression [24]:

$$q = 0.8n$$  \hspace{1cm} (7)

8. Service life model: relation between resistivity and time to corrosion

The model proposed is based on the measuring of electrical resistivity for its use as the main parameter for determining both $t_i$ and $t_p$ periods. In order to predict the corrosion onset it is necessary to have an equation in which the resistivity could be the rate determining parameter in function of the time. For estimating the penetration of the aggressive front, it is assumed the simplest equation of the “square root of time”, or “time lag” expression.

$$x_i = V_{CO_2,Cl} \sqrt{t}$$ \hspace{1cm} (8)

Where $V_{CO_2,Cl}$ is proportional to the square root of the diffusivity and is then the inverse of the resistivity:

$$V_{t,CO_2} = \sqrt{D = \frac{F_{t,CO_2}}{\rho \cdot \tau_{t,CO_2}}}$$ \hspace{1cm} (9)

In the case of considering the propagation of corrosion ($t_p$), taking into account the loss in rebar diameter, or pit depth, ($P_{corr}$) as the limit corrosion attack, the service life of structure can be written by the expression [25]:

$$I_{corr} (\mu A/cm^2) = \frac{K_{corr}}{\rho_{ef}(Kohm.cm)}$$ \hspace{1cm} (10)

The relation for the service life prediction can be then formulated as follows:

$$t_i = \frac{P_{corr} \cdot \rho_{ef} \left( \frac{t}{t_0} \right)^q \cdot W_s}{K_{corr} \cdot 0.00116}$$ \hspace{1cm} (11)

Where:

$P_{corr}$ = steel cross section reached at the time $t_p$
\( \rho_{ef} = \text{resistivity at 28 days in saturated conditions} \)

\( q = \text{aging factor of the resistivity (Table 4)} \)

\( \xi = \text{environmental factor of the corrosion rate (it can be of 10±2 for carbonation and 30±5 for chlorides)} \)

\( K_{corr} = \text{constant with a value of 26 μA/cm}^2 \cdot \text{kΩ·cm} = \text{to 26 mV/cm relating the resistivity and the corrosion rate I} \)

Then, the final expression of the service life model based on resistivity is:

\[
t_i = t_i + t_p = \frac{x^2 \cdot \rho_{ef} \left( \frac{t}{t_0} \right)^q}{V_{Cl,CO_2}} + \frac{P_{corr}}{V_{corr}} = t_i = \frac{1}{F_{Cl,CO_2}} \cdot r_{Cl,CO_2} + \frac{P_s \cdot \left( \frac{t}{t_0} \right)^q}{K_{corr} \cdot 0.00116}
\]

(12)

8.1. Example of application

For the initiation period the application of the above theory can be shown by way of example, assuming a concrete with a cover depth of 4 cm made with cement type I with silica fume (reaction factor = 1.5 and aging factor = 0.22) to be placed in exposure class XS3 (tidal and splash conditions). Considering a service life of 100 years, the values of the reaction, as well as the environmental and aging factors are presented in Table 4. The calculations indicate that the resistivity needed at 28 days of age, measured in saturated conditions, is 215 Ω·m.

Table 4. Input data for a calculation of the concrete resistivity

| Cement type I with silica fume | \( t_{Cl} = 1.85 \) |
| Exposure class (XS3) | \( F \ (cm^2 \cdot \Omega \cdot \text{year}) = 25000 \) |
| Service life | \( t \ (\text{years}) = 100 \) |
| Cover depth | \( X_{Cl} (cm) = 4 \) |
| Ageing factor during 10 years | \( q = 0.22 \) |

\[
4 = \left[ \frac{25000}{100} \cdot \left( \frac{100}{0.0767} \right)^{0.22} \cdot 1.5 \right] \cdot 100 \implies \rho_s (\Omega \cdot cm) = 21497 \implies \rho_s (\Omega \cdot m) = 215
\]

With this resistivity the length of the propagation period following Table 5 is:

Table 5. Input data for the propagation period

| Limit Diameter loss, \( P_{corr} \) | 100 μm = 0.01 cm |
| \( \rho_{ef} \) at 28 days | 21.5 Kohm.cm |
| \( q \) applied during 100 years | 0.22 |
| \( W_s \) in saturated conditions | 1 |
This propagation period may be included in the 100 years or considered apart as an additional safe time until cracking is produced.

9. Production of concrete for a specified apparent resistivity

Once known the resistivity which is needed to reach a nominal service life, it remains to describe how the concrete producer can design a mix to fulfil the service life specification. This can be done [22] by considering a modification of Archie’s law linking resistivity and porosity:

$$\rho_{28d} = \rho_c \cdot \varepsilon^{-\tau}$$  \hspace{1cm} (13)

where $\rho_{28d}$ is the resistivity of concrete under saturated condition at 28 days, $\tau$ is the tortuosity coefficient which is estimated by fit to the experimental data, and $\varepsilon$ is the total porosity.

The coefficient $\tau$ depends on the concrete composition which is identified to the tortuosity, and could be determined from type or family of cement type by means of measuring the porosity and the resistivity. The values found in present research are. For type I cement $\tau=1.9$, for type II-AV $\tau=2.3$ and for type II AP $\tau=1.6$.

From the specified resistivity the paste porosity can be obtained and through Power’s relation on porosity and w/c ratio

$$\varepsilon_p(\%) = \left(\frac{w}{c}\right)^{-0.36\alpha} \times 100$$  \hspace{1cm} (14)

In order to use $\rho_p$ in the model based on Archie’s law, it must convert the porosity of the paste ($\varepsilon_p$) to porosity of the concrete ($\varepsilon$). For this, it is applied a simple method based on multiply the percentage of capillary porosity of the paste to the volume of paste ($\gamma$) in the concrete.

$$\varepsilon = \varepsilon_p \cdot \gamma$$  \hspace{1cm} (15)

It is feasible to prepare a mix with the needed effective resistivity at 28 days, providing the consideration of the type of cement and its retarder factor. The concrete producer should verify by testing the reaching of the specified resistivity while the cement producer should give the retarder factor of his cements.

So, the following concrete design methodology based on Archie’s law model is proposed to achieve the prescribed value $\rho_{28d}$.
1. Select a type of cement. It fixes the values of reaction factor $(r)$ and tortuosity $(\tau)$ are defined.
2. Select a w/c ratio and calculate porosity of the paste following Powers’ model
3. Then calculate the expected resistivity through $\rho = \rho_o \cdot \left(\varepsilon_p \cdot \gamma\right)^r$.

10. Final comments

It has been summarized some of the possible applications of the concrete electrical resistivity values. Its main advantage is that the measurement is non-destructive and the concrete can be monitored [23]. Concrete Resistivity is able to inform on:
- Porosity
- Degree of water saturation
- Degree of curing
- Cement setting time
- Concrete mechanical strength
- Reinforcement Corrosion rate
- Gas and water permeability

In present work has been summarized the model for service life prediction based The in Einstein law relating electrical resistance or conductance with the diffusion coefficient. Making certain assumptions this basic law can be applied to the advance of carbonation front or chloride threshold, and to the representation of steel corrosion propagation. This model can be used for calculating cover thicknesses from actual resistivity values or the minimum resistivity for a certain cover thickness.

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References


Abstract

The European countries have a great number of reinforced concrete bridges and many of them are suffering from corrosion. Prior to define a repair strategy, a precise and reliable diagnosis of the corrosion state of the reinforcing bars is mandatory. In order to carry out this inspection, many challenges remain especially for the RC structures exposed to a marine environment. The assessment strategy is based on the choice of Non Destructive Techniques taking into account their precision, location, number of measurements, the environmental conditions and duration. Currently, more empirical approaches are used by structure's owners and we propose to implement statistical methods as well as data mining for a more reliable and optimal diagnosis.

Within the DéCoF-Ré project, the diagnosis tools and the evaluations made afterwards are established from data obtained on different piers of a real bridge, based on NDT such as visual inspection of the degradations, rebar's localization, half-cell potential mapping, electrical concrete resistivity mapping and corrosion rate measurements performed in 2015. The first results are presented. They concern the effect of environment on the reliability of diagnosis. An additional durability study based on the analysis of durability indicators (such as chloride profiles) will be conducted in 2016.

1. Introduction

Corrosion of steel rebar in concrete is the main cause of degradation of reinforced concrete (RC) structures [1, 2]. In new structures, steel is in a passive state due to the high alkalinity of the concrete (pH~13). However, with time, full carbonation of the concrete cover or chloride...
ions penetration up to the rebar level can induce an active corrosion of the steel. At the steel/concrete interface, the formation of iron oxides which volume can be 2 to 6.5 times higher than the iron itself, internal stress occurs which can induce cracks, delamination or even spallings in concrete [3]. The reinforcement corrosion can also lead to a reduction of the steel cross section that will modify the carrying capacity of the structure, reducing its service level, and even its service life and eventually ending up to the structure’s collapse [1-3].

For reinforced concrete structures exposed in a marine environment, steel reinforcement corrosion is mainly due to the chloride penetration in the concrete cover. Chloride contamination can affect bridge elements submerged in sea water, in the tidal zone, in the splash zone above high tide and in the atmospheric zone [4-7].

For steel structures, different exposure zones had already been defined: atmospheric, splash, tidal and submerged zones [8] from two interreg projects (Medachs and Duratinet). Literature on corrosion of RC structure due to chloride contamination mainly comes from laboratory tests [9-13] or accelerated marine exposure under controlled climatic conditions. Investigations on corrosion’s state of RC structure exposed to a marine environment for a long time are scarce [14-16]. Therefore, in order to improve the understanding of the real corrosion behaviour, “on-site” studies are needed.

This paper presents preliminary results on half-cell potential measurements performed on a bridge in a marine environment in France and proposes a numerical treatment of the data that will highlight the tide effect.

2. Materials and methods

2.1 Description of the multi-span bridge

Figure 1 : Description of the île de Ré bridge.

The île de Ré bridge is located in the French Atlantic coast. It was built in 1987-1988 to provide an access to the Ré Island from La Rochelle mainland. The bridge has a total length of 2928.5 meters, a width of 15 meters and a maximum height of 30 meters above the sea. Among its 28
piers, 24 piers (P4 to P27) are in the sea as illustrated in Fig.1. Piers were raised using a concrete composition based on a CPJ 45 RPM cement that today would correspond to a CEM II/B cement (Tab. 1).

### Table 1: Concrete mix composition (in kg/m³).

<table>
<thead>
<tr>
<th>Cement</th>
<th>Water</th>
<th>w/c</th>
<th>Sand 0/3 mm</th>
<th>Gravel 6/20 mm</th>
<th>Additive Pozzolith 200N</th>
</tr>
</thead>
<tbody>
<tr>
<td>370</td>
<td>185</td>
<td>0.5</td>
<td>830</td>
<td>1200</td>
<td>0.74</td>
</tr>
</tbody>
</table>

#### 2.2 Investigated zones
Corrosion diagnosis was performed on 15 piers (14 in seawater using a vessel and 1 on the beach). The measurements presented in this paper are those that were carried out on the most exposed side of the investigated piers (Fig. 2) meaning dominant winds (WSW for La Rochelle with 30 km/h mean speed), daily sunshine and strongest wetting/drying cycles. Measurements were performed during the rising tide, thus allowing the concrete to dry and to oxygenate. The investigated area’s dimensions are: height 3m and width 1.85m. Measurements were performed for the same height between +3.95 and +6.95 m CD (where water heights are expressed relative to Chart Datum (CD) corresponding to La Rochelle – La Pallice harbour in France). The investigated area, as shown on Fig. 3, includes 3 exposure zones (tidal, splash and atmospheric) which boundaries are defined by tidal coefficients according to corrosion of steel structures [8], one of the objective of the paper is to analyse is this discretization is convenient for RC structures also:

- Mean High Water Springs (MHWS) is defined by a tidal coefficient of 95 for water height of +6.00 m CD;
- Mean High Tide (MHT) is defined by a tidal coefficient equal to 70 for water height of +5.45 m CD.

#### 2.3 Corrosion diagnosis methodology
Corrosion diagnosis methodology was divided in six steps. The first step consisted in finding the general bridge’s information from the archives. The following steps were then realised using a vessel. The second step consisted in a visual inspection of the piers to obtain a general degradation state (rust spots, leachings, cracks, etc.). The third step aimed at locating the reinforcements (horizontal and vertical rebars) using a ground penetrating radar (EasyScan 1.6
GHz, GSSI®). In the fourth step, concrete electrical resistivity was measured using a Wenner probe (Resipod 5 cm, PROCEQ®). The fifth and sixth steps were dedicated to the electrochemical measurements, respectively half-cell potentials (Canin⁺ (copper/saturated copper sulphate electrode (CSE, +318 mV vs NHE), PROCEQ®) and corrosion rates (GalvaPulse, Germann Instrument®). The half-cell potential method is the most common non-destructive measurement used in corrosion diagnosis [7, 11-13]. In this paper, only the measurements performed along the horizontal reinforcements with a 5 cm spacing (meaning 36 readings per horizontal) are presented. Depending on the piers, 14 to 16 horizontal reinforcements are present in the three meters high investigated area.

3. Results and discussion

3.1 Potential data and interpretation

Corrosion evaluation by using half-cell potential measurements is the most typical procedure for the inspection of RC structures. However the interpretation of the measurements is not straightforward.

The ASTM C876-91 standard [12] indicates a direct correlation between fixed potential values and the probability of corrosion (this standard has been massively discussed and a new version was published in 2009 [13]). Potential values less than -350 mV/CSE are attributed to a high probability of corrosion (>90%). Assuming this interpretation, from the whole measurements realised on the bridge, the pier's zones with heights lower than +4.95 m CD would present a 90% probability of corrosion. However this conclusion is not confirmed by the visual inspection observations.

In a COST-509 document published in 1997 [17], for large surveyed areas, potential values were represented as frequency distributions (10 to 20 mV class) or cumulative probability. A first estimation of the corrosions state was made by looking at the potential gradients: potential differences greater than 150 – 200 mV indicate corrosion of the area with lower potentials. However no dimensions of the "large area" were mentioned. Assuming this interpretation, a high risk of corrosion is observed for all the piers with potential differences between 340 and 555 mV considering the whole inspected area (3x1.85m). For pier B, presented on Fig. 4a, the difference is equal to 515 mV (max=-115 mV, min=-630 mV). If the considered large area is divided in 3 horizontal zones of 1x1.85m, potential differences for each zone become equal to: 140 mV for Zone 1 (bottom), 170 mV for Zone 2 (middle) and 330 mV for Zone 3 (top). As expected, risk of corrosion depends on the dimensions of the considered area.

In 2001, the RILEM technical committee 154 [11] recommended an interpretation which consisted in considering larger gradients ΔE/Δx based on the potential maps (for example an equicontour line plot with a maximum potential interval of 50 mV) in order to locate areas of corroding reinforcement. However no value of the "larger gradients" was mentioned. But in the literature, a larger gradient of 8mV/cm is generally used to indicate a high risk of corrosion [15, 18]. Equicontour larger gradient plot for pier B is presented on Fig. 4b, gradient is superior at 8mV/cm only on the top right corner. Moreover in the RILEM recommendations, potential mapping results should be combined in a useful way with other non-destructive methods such as resistivity mapping. However, in the case of this bridge, the resistivity values were not so useful regarding the reinforcement and its corrosion risk because of the rather thick concrete cover (>8cm).
The equicontour potential line plot of Pier B, which is considered as a passive one, (Fig. 4a) shows that the potentials are less and less negative with increasing heights. Considering the bottom part of the investigated area, potentials are in the range -700 to -650 mV (+3.95 and +4.30 m CD). These low values can be explained because the reinforced concrete is in the tidal zone meaning that the concrete is saturated of seawater and lacks of oxygen [11-13, 18-21]. For the top part of the investigated area, potentials are in the range -150 to -100mV (+6.60 and +6.95 m CD) because concrete is dry and oxygenated.

![Equicontour potential line plot (a) and equicontour potential gradients ΔE/Δx plot (b).](image)

Figure 4: Half-cell potential maps of pier B, equicontour potential line plot (a) and equicontour potential gradients ΔE/Δx plot (b).

From literature data it has been proved that potential readings can be very negative without significant presence of corrosion [7, 11]. This phenomenon can be induced by concrete cover, concrete resistivity and oxygen availability [11, 19-21]. This latter is very likely in marine environment for elements in submerged or in tidal zones. Therefore, the observations of the vertical potential gradient may not be due to the corrosion process but to the environment. In the next section of this paper, a model to characterize the tide’s effect on the potentials is proposed.

### 3.2 Modelling method

First, using a criterion of no damage from visual corrosion, four piers (upon 15) have been selected as "reference" piers. For each of these four piers, the mean value ($\mu_{\text{corr}}$) and the standard deviation ($\sigma_{\text{corr}}$) have been calculated for each horizontal reinforcement (in the three meters high investigated zone, there are 14 rebars and 36 measures were performed per rebar). In order to delete the outliers values from the main trend, the absolute potential values which were not included in the range defined by $\mu_{\text{corr}} + 3 \sigma_{\text{corr}}$ [22], were deleted of the dataset (~3% of the original values were removed). Then, the mean trend for the bridge was defined for each horizontal rebar taking into account the four reference piers by calculating the mean...
potential value and the standard deviation. The curve presented in Fig. 5 is representative of the tide’s effect on the corrosion potential values.

In a second step, the different behaviours visually observed on Fig. 5 were distinguished using a mathematical approach: the slope between two potential values was computed by accounting its uncertainty. These mathematical results are presented on Fig. 6. The slope range corresponding to the Behaviour 1 is defined by considering the extreme value on the left as the lower value. Once a slope value is lower than this extreme value a behaviour modification is considered. The same method is used to define the slope range corresponding to the Behaviour 3, the extremal value on the right as the highest value. Other slopes values correspond to the Behaviour 2. Boundaries between two different behaviours are represented by two vertical lines.

In a third step, a linear regression is used to fit each of the three behaviours and the error of measurement ($\xi_C$) which is the sum of the statistical error ($\xi_{CStat}$) and the repeatability error ($\xi_{CRep}$) is included. The statistical error is negligible as the mean potential value is calculated upon 144 experimental values for each horizontal rebar. The repeatability error is unknown for
on-site measurement, but at least the device error (+/-5 mV for the Canin’s bar electrode), noted \(\xi_C\) Canin, was considered. The error of measurement is just considered equal to the device error. Results are presented on Fig. 7. Solid line corresponds to the fit using experimental data, dashed line corresponds to the fit taking into account the error of measurement. Grey straights (solid or dashed) represent potential evolution into the boundaries between two different behaviours. The parameters of the linear regression are given in Tab. 2. Coefficients of determination \(R^2\) are very good in each case, excepted for Behaviour 3 with a value of 0.21 that corresponds to a horizontal line.

Figure 7: Mean corrosion potential with the error of measurement, tide’s effect law and change in slope corresponding to a change in the exposure zone versus water height.

<table>
<thead>
<tr>
<th>Behaviour</th>
<th>Number of experimental points</th>
<th>Slope (mV/m)</th>
<th>Y-intercept (mV)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Behaviour 1</td>
<td>4</td>
<td>235.9</td>
<td>-1522.8</td>
<td>0.9897</td>
</tr>
<tr>
<td>Behaviour 2</td>
<td>3</td>
<td>125.4</td>
<td>-939.3</td>
<td>0.9112</td>
</tr>
<tr>
<td>Behaviour 3</td>
<td>5</td>
<td>12.4</td>
<td>-297.1</td>
<td>0.2108</td>
</tr>
</tbody>
</table>

3.3 Discussion
Tab. 3 resumes the boundaries results found in the previous section together with the theoretical ones defined for steel structures [8] (Fig. 3). Boundaries between two different behaviours can be correlated to the water height and associated tidal coefficient. Boundaries between splash/atmospheric zones are very close to the theoretical ones. But they are quite different for tidal/splash zones. Those boundary differences may be explained by: first, theoretical boundaries have been defined for steel structures, corrosion behaviour may be different for RC structures. Second, theoretical boundaries have been defined for a very calm sea and ideal climatic conditions, but those particular environmental conditions are very rare. Sea level depends on several parameters, for example wind creates waves and a low atmospheric pressure provokes an increase of sea level and inversely.
Table 3: Boundaries between 2 exposures zones in meters CD and associated tidal coefficient.

<table>
<thead>
<tr>
<th></th>
<th>Tidal and Splash zones</th>
<th>Splash and Atmospheric zones</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water height</td>
<td>Tidal coefficient</td>
</tr>
<tr>
<td>Theoretical</td>
<td>5.45</td>
<td>70</td>
</tr>
<tr>
<td>Modelling</td>
<td>4.83 - 5.03</td>
<td>42 - 52</td>
</tr>
</tbody>
</table>

Pier A  Pier B  Pier C

Figure 8: Half-cell equi-potential map for 3 piers before modelling (at the top) and after modelling (at the bottom).
In order to check the validity of the found mathematical law which supposed to represent the tide’s effect on the corrosion potential, 3 piers have been selected and were inspected at the same exposed face (Fig. 2): 2 of them (Piers A and B) are supposed to be passive whereas the third one (Pier C) presents an important anodic area. These piers have been selected visually, using the equicontour potential line plot from the raw potential data, which are presented at the top of Fig. 8. The anodic area on the Pier C is easily recognizable, but no one of the standard or recommendations prove it. Reference corrosion potential, calculated from found mathematical law, are subtracted to every experimental potential values, 36 per rebar. At the bottom of the Fig. 8 the equicontour potential line plot after using the mathematical law are represented.

Based on the COST-509 [17] interpretation, conclusions from gradient potentials are different: from raw data, the 3 piers rather indicate a high risk of corrosion state with potential gradients for Piers A, B and C respectively equal to 435, 515 and 505 mV. After correction, gradient potentials of Piers A and B are respectively 177 and 183 mV meaning no risk of corrosion while for Pier C, the 463mV gradient potential confirms an active corrosion state.

4. Conclusions and outlooks

This paper presents a modelling method used to take into account the tide effect on the corrosion potential. Half-cell potential’s measurements of horizontal reinforcement of 4 bridge’s piers without visual damage and without electrochemical anomalies (like anodic area) have been used as reference. From these results, the following conclusions can be drawn:
- 3 zones with a different corrosion potential behaviour have been identified, boundaries between these zones correspond to the values used to describe the different exposure zones (tidal, splash and atmospheric zones);
- The tide effect has been deleted from original data. Modified maps highlight anodic and cathodic areas and COST-509’s recommendation can be used to determine the corrosion’s risk of a pier, which was not possible before modelling of the tide effect.

The outlooks of future work is:
- In order to study the tide effect on half-cell potential values, the measurements will be performed during the falling tide and compared to those obtained for rising tide;
- The influence of exposure conditions (wind and sun) will be studied based on the half-cell potential measurements performed on two opposite sides of the pier taking into account the impact of falling / rising tide;
- This modelling method will be applied to others NDT measurements (concrete electrical resistivity and corrosion rate);
- This modelling method would be useful to compare the corrosion state of different structures on the Atlantic coast.
Acknowledgments

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MATHEMATICAL LAW OF STEEL THICKNESS LOSS VERSUS TIME APPLIED TO REINFORCED CONCRETE CONTAMINATED BY CHLORIDES – FIRST RESULTS

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Abstract
In civil engineering constructions, one of the major factors responsible for the deterioration of reinforced concrete (RC) structures such as bridges for example is the corrosion of the rebars. In order to evaluate the durability of RC structures, the corrosion in its propagation phase needs to be ascertained.
In this study, chloride contaminated reinforced concretes (chlorides were either added in the mix (G) or have penetrated by wetting/drying cycles (I)) have been exposed to different environmental conditions: outdoor and six controlled conditions based on two temperatures (20°C and 45°C) and three relative humidities (60%, 80% and 92%). Within a five years study, rebar corrosion was evaluated four times a year, using electrochemical measurements (half cell potential, linear polarization resistance, Nyquist impedance) and corrosion rate was calculated. These latter values were converted in steel thickness loss (stl) versus time (t) in order to propose a mathematical law for simulating/predicting corrosion.
A mathematical power law (stl=at with α>1) fitted the experimental points better than a linear law. Moreover, the results obtained at 20°C and 80% RH were very close to those obtained outdoor for I specimens. Finally, crack behaviour depended on the chloride contamination type, the environmental condition and the time.

1 INTRODUCTION

Corrosion is known as the main degradation of reinforced concrete structures [1-4]. Corrosion can be induced by chloride ions or carbonation. Damages can consist in rust leaching, cracks, loss of reinforcement section, loss of bond between reinforcement and concrete and spalling of concrete. Therefore a loss of serviceability and structure safety can be feared.
In the laboratory, electrochemical characterization of a reinforced concrete sample is based on three main measurements: half-cell potential, impedance and linear polarisation resistance using a potentiostat. Then a corrosion rate can be calculated. The measurements can be performed frequently. On site, portable equipments are used to carry out: half-cell potential mapping, resistivity mapping and corrosion rate measurements. Usually the prediction of a bridge service life is based on only one corrosion diagnosis and considering a linear law. The aim of this paper is to propose a mathematical law of corrosion in the propagation phase expressed as steel thickness loss versus time in the case of chloride contaminated reinforced concrete samples exposed to controlled conditions in the laboratory and to outdoor conditions.

2 EXPERIMENTAL SECTION

2.1 Concrete states
Reinforced concrete slabs (300x300x50mm with 5 parallel rebars) were casted according to the composition given in Table 1. This concrete composition was chosen with a water to cement ratio equal to 0.7 because it is representative of old reinforced concrete structures and in order to achieve chloride contamination in a reasonable time. Slabs were casted and/or aged to study three different states: slabs "T" were reference reinforced concrete, slabs "I" contained chlorides that have penetrated by wetting and drying cycles (salted pond NaCl 35g/L, during 12 months) and slabs "G" were contaminated with 5% of NaCl by weight of cement added in the mix.

Table 1: Concrete composition (kg/m3), cement is CEM I 52.5 N CE CP2 NF.

<table>
<thead>
<tr>
<th>Composition</th>
<th>275</th>
<th>192</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palvadeau</td>
<td>149</td>
<td>277</td>
</tr>
<tr>
<td>(size mm)</td>
<td>0/0.315</td>
<td>0.315/1</td>
</tr>
</tbody>
</table>

2.2 Reinforced concrete prisms
Specimens of the study were reinforced concrete prisms that were sawed from the slabs described previously (10 prisms per slab). The prisms T, I and G (which dimensions were 150x50x50 mm) contained a central rebar (200 mm length and 6 mm diameter) with an uninsulated steel surface equal to 18.8 cm². More details for describing the specimens can be found in [6]. Total [7] and free [8] chloride contents (in g% by weight of cement) were respectively equal to 4.8 and 3.1 for prism n°664-I and to 2.7 and 1.4 for prism n°639-G.

2.3 Environmental conditions
Six controlled environmental conditions were considered based on two temperatures (20°C and 45°C) and three relative humidities (60%, 80% and 92%). The natural outdoor condition consisted in the suburb of Paris where temperature, relative humidity and precipitations recorded from September 2008 to January 2014 respectively varied within a range of -10 to
+30°C, 29 to 91%RH and 0 to 4cm/day except for 20th December 2009 (12cm). These ranges were coherent with the French climate (except for the high precipitations in December 2009). For each environmental condition, five prisms per concrete state were investigated (meaning 140 prisms).

2.4 Measurement termed points
Corrosion rebar characterizations were carried out 4 times a year from 2008 to 2014 except for 45°C and 80% RH where measurements were stopped approximately after 2 years because of the delamination of the prisms.

2.5 Electrochemical tests
In order to calculate the corrosion rate of the prism's rebar, three non-destructive techniques were performed using a multichannel potentiostat (VMP2Z model from BioLogic): half cell potential (HCP) monitoring, electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR). The experimental test details can be found in [6]. Corrosion rate was calculated from the Stern and Geary equation [9]: \( i_{corr} = B/Rp.S \) where B is a constant (considered as 26 mV [10], \( R_p \) the polarization resistance (ohm) taking into account the ohmic drop and S the steel surface (18.8cm² in this study)). For each concrete state (T, I and G) corrosion rate was calculated as the average of the five prisms per environmental conditions (or less if autopsy or delaminated prisms) and analysed considering the four levels of corrosion suggested by the RILEM [11]: negligible (\( i_{corr} < 0.1 \mu A/cm² \)), low (0.1-0.5\( \mu A/cm² \)), moderate (0.5-1\( \mu A/cm² \)) and high (\( i_{corr} > 1 \mu A/cm² \)).

3 RESULTS AND DISCUSSION

3.1 Electrochemical results
For a 20°C temperature and for three different relative humidities (60%; 80% and 92%), the evolution of half-cell potential, resistance and corrosion rate of the reinforced concrete prisms T, I and G versus measurement termed points in a five years period are respectively represented in Figure 1, Figure 2, and Figure 3. As a remark, the electrochemical characterizations of the prisms before being exposed to a given environmental condition (time equal to zero in the graphs) cannot be directly compared with the ones obtained after. Therefore these particular values were represented with a different color bar on the histograms.

The ranges of \( E_{corr} \) values (mV, SCS) for the reinforced concrete samples were respectively -150 to +100 for the sound T prisms, -600 to -200 for the reinforced concrete I with chlorides coming from wetting/drying cycles and -500 to -150 for the mix chloride contaminated G prisms. These ranges are in accordance with those cited in table 1 in [12]. The influence of humidity was significantly observed between 60% and 80% RH for chloride contaminated concretes: the higher the humidity the more negative were the \( E_{corr} \) values. However, going from 80 to 92% RH did not significantly change the \( E_{corr} \) values.

The ranges of \( R_e \) values (ohm) for the reinforced concrete samples were respectively 1 000 – 10 000 for the sound T prisms, 200 – 3 000 for I prisms and 500 - 8 000 for G prisms. At 20°C,
the order of Re values (ohms) with concrete states was I<G<T. This result can be explained by the ionic species which contributes to a smaller resistance and therefore chloride contaminated concrete has smaller resistances than sound concrete [13]. As expected, the Re values decreases with increasing relative humidity as it appears clearly from 60 to 80 and to 92% RH. No influence of the exposure’s time on the Re values could be noticed.

Concerning the corrosion rates, T prisms, with icorr values lower than 0.01 μA/cm², remained passive through the three years study whatever the conditions [11]. Both chloride contaminated reinforced concretes (I and G) were corroding for relative humidities higher than 60%. This result shows that the corrosion process does not only respond to a chloride content (which is quite high (§2.2)) but also to an environmental condition and these two parameters need to be considered together. At 20°C, moderate and high levels of corrosion were observed for 80 and 92% RH. The icorr values of chlorinated reinforced concretes depended on the measurement termed points and rather indicated an increase followed by a plateau.

Increasing temperature from 20°C to 45°C lead to a more severe corrosion and earlier cracks (results not presented here). More results can be found in [6, 14, 15].

Figure 1: Half-cell potentials (a), resistances (b) and corrosion rates (c) of T prisms exposed to a 20°C temperature and relative humidity (60%, 80% and 92%) versus measurement termed points. (Horizontal dotted lines represent the corrosion levels as indicated in [11]).
Figure 2: Half-cell potentials (a), resistances (b) and corrosion rates (c) of I prisms exposed to a 20°C temperature and relative humidity (60%, 80% and 92%) versus measurement termed points. (Horizontal dotted lines represent the corrosion levels as indicated in [11]).
Figure 3: Half-cell potentials (a), resistances (b) and corrosion rates (c) of G prisms exposed to a 20°C temperature and relative humidity (60%, 80% and 92%) versus measurement termed points. (Horizontal dotted lines represent the corrosion levels as indicated in [11]).

Figure 4 presents the results of half cell potential, resistance and corrosion rate versus measurement termed points for T, I and G prisms exposed to outdoor conditions. For the reference reinforced concrete T prisms, no corrosion of the steel rebar was observed during the five years study: half-cell potential values were in the range +20 to -100 mV, resistance values were in the range 500 to 4 000 ohms and corrosion current densities were in the nano-ampere range. For the chloride contaminated reinforced concrete I and G prisms, the electrochemical results were very similar in between them: potential values were indicative of a likely corrosion (-300; -450 mV for I prisms and -400; -550 mV for G prisms); resistance values were in the range 200 to 2 000 or 500 to 2 000 ohms respectively for I and G prisms. Finally, i_corr values from 0.5 to almost 3 μA/cm² confirmed the active corrosion state [11].
3.2 Mathematical law of corrosion in the propagation phase

Usually, prediction of reinforced concrete structure service life is based on a single \( i_{corr} \) measurement and the assumption of a linear corrosion for decades of years. In this work, the proposal is to consider the whole \( i_{corr} \) values determined every four months during five years (meaning an assumption of a linear \( i_{corr} \) for a three months period). The objective is to determine a mathematical law of corrosion in the propagation phase expressed as steel thickness loss (stl) versus time.

As an example, Figure 5 presents the results obtained for I prisms exposed to outdoor conditions. Firstly, considering a single \( i_{corr} \) value and a linear law: for the minimum \( i_{corr} \) value (0.53\( \mu \)A/cm\(^2\)) obtained for 6 months) the steel thickness loss would be equal to 31\( \mu \)m after 5 years and equal to 62\( \mu \)m after 10 years; Respectively for the maximum \( i_{corr} \) value (2.56\( \mu \)A/cm\(^2\) at 36 months) the steel thickness loss becomes 152\( \mu \)m and 300\( \mu \)m after 5 or 10 years. Secondly, considering the whole \( i_{corr} \) values of the five years study, it is possible to fit the experimental points with a mathematical linear law \((stl=at \text{ with } a=0.0467; R^2=0.9859)\) or power law \((stl=bt^a \text{ with } b=0.003 \text{ and } a=1.3827; R^2=0.9881)\). Both laws are satisfactory to simulate the corrosion evolution upon the five years period, with steel thickness loss values of 85\( \mu \)m or 97\( \mu \)m according to respectively the linear or the power law. Comparing the results obtained from one single measurement or the whole series of experimental points it is obvious that the first method could lead to under-estimation or over-estimation of the corrosion process as mentioned in [16]. Therefore, in order to increase the reliability of the results, it should be mandatory to follow the corrosion process frequently or even monitoring it. This work is still ongoing in order to find which law is the most reliable for longer periods.
As a second example, Figure 6 presents the results for I prisms exposed to the controlled conditions (20°C and 60, 80 or 92% RH) together with the fitting curves representative of the mathematical laws linear (a) or power (b). Comparing both results, the power law fits the whole series of experimental points more satisfactorily than the linear law.

Figure 6: Fitting the whole series of values for I prisms, exposed to 20°C and 60, 80 or 92% RH, with a mathematical linear law (a) or power law (b). Results for I prism exposed outdoor are also indicated in (b).
3.3 Determination of the steel thickness loss responsible of cracks

Another result from this extensive study is the determination of the steel thickness loss that induces cracks using both the visual inspections and the mathematical power laws. Figures for I prisms are given in Table 2. This parameter is important because as soon as the concrete cover is cracked the corrosion process should become different (not only propagation but also penetration of the aggressive species to the rebar).

Table 2: Determination of the steel thickness loss that induces cracks based on visual inspections and mathematical power law for I prisms.

<table>
<thead>
<tr>
<th>Environmental conditions</th>
<th>First crack (months) from visual inspections</th>
<th>Steel thickness loss (μm) calculated with the power law</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outdoor</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>20°C, 60%RH</td>
<td>45</td>
<td>12</td>
</tr>
<tr>
<td>20°C, 80%RH</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>20°C, 92%RH</td>
<td>18</td>
<td>11</td>
</tr>
</tbody>
</table>

4 CONCLUSIONS

This intensive experimental 5 years study (based on 140 reinforced concrete prisms, 3 concrete states, 7 environmental conditions, measurements performed 4 times per year) aimed at proposing a mathematical law which simulates the corrosion in its propagation phase and which can be useful for further predictions. It was found that a mathematical power law (steel thickness loss versus time) fitted the experimental results better than a linear law. The alpha power value was higher than one as if the propagation in the case of chloride contamination was catalytic alike. Moreover, results demonstrate that considering the whole series of corrosion rate values lead to a more reliable steel thickness loss, otherwise the results could be under or over estimated (particularly for reinforced concrete exposed to outdoor conditions). Finally, an evaluation of the steel thickness loss that induced concrete cracks was determined.

The study continues in order to validate the conclusions over longer periods.

REFERENCES


ELECTRO-DESALINATION OF GLAZED TILE PANELS – DISCUSSION OF POSSIBILITIES

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Abstract
Glaze is lost from tiles in tile panels due to presence of soluble salts and this means loss of important heritage. The present paper discusses the possibility to apply electro-desalination. An in-situ test has not been performed yet, but encouraging results have been obtained with different parts of the system. Single tiles, a variety of porous stones and the mortar on the back of a tile have all been electro-desalinated successfully in laboratory scale. Thus individually, all parts of the wall with tile panel can be electro-desalinated. The interface between mortar and tile can be problematic. In the few experiments conducted on tiles with attached mortar, the mortar was desalinated to a higher degree than the biscuit and successful desalination of the biscuit through the mortar requires further research.

In-situ pilot scale tests were performed on highly salt-contaminated walls without tiles by placing electrodes at the same side of the wall. Thus it may be possible to desalinate tile panels, without any physical damage of the fragile glaze, by placing electrodes on the back of the wall or by removing some tiles, placing electrodes in their spaces, and extracting the salts from there before the tiles are placed back again.

1. Introduction

Ceramic tiles, azulejos, are an important Portuguese cultural heritage. They have been used continuously during five centuries. Regrettably many tiles are lost due to decay. The Portuguese tiles applied in panels are designed for surface continuity, so the width of joints does not interfere with the image. Their sides are bevelled and, when mounted together to form a panel, their edges contact [1]. This may constitute a problem in cases the tiles are wet for a long period causing swelling and subsequent crack and damaged glazing. Today many degraded tile facades are in urgent need of maintenance [2]. Soluble salts are a major cause of decay, and aside from human actions, are likely the most important cause of decay and loss of single tiles as well as
whole panels [1]. The damage caused by soluble salts is generally due to their accumulation and phase transition at or near the surface of the object, or between layers, as a result of moisture transfer processes [3]. The salts can enter the tiles from rising groundwater in the wall to which they are attached. Rain water may also be introduced through the roofs of ancient buildings [4]. Tiles are applied after being soaked so that they are dilated, in order that further (thermal or hydric) expansion does not cause cracking. But afterwards, they contract. Therefore, the joints may be slightly open when rain hits the panel. This will influence the distribution of salts in the wall. Mimoso et al [1] visited different monuments around Portugal aiming to assess decay patterns, particularly when caused by salt crystallization. They concluded that the durability depends largely of the tile being defect-free and mounted on dry walls. Tiles with manufacturing defects (glaze partially cracked or delaminated) thus offer easy routes for moisture propagation and salt crystallization.

In-situ treatment options for removal of salts are few. Poultice technique (a poultice is applied to the surface and salts are transported out from the tile by diffusion and/or advection) suffers from the need for the poultice to be applied to the often fragile glazed surface, thus physical damage may be hard to avoid. Also, in areas where glaze is intact transfer is nil.

The present paper deals with development of electro-desalination for in-situ treatment of tile panels. A discussion of possibilities and limitations of the method for desalination of tile panels is given on basis of already published work with results ranging from desalination of single tiles to wall sections (without tiles).

Tiles are placed on the wall on a bed of mortar (figure 1). It is important to remove salts from all parts during the in-situ electro-desalination, otherwise the tiles will soon be salt infected again from salts entering from mortar and wall. In this paper electro-desalination of the different parts: wall, tile bed, ceramic biscuit and glaze are first discussed separately. Influence from interfaces between the different materials/parts is then discussed and finally the possibility for in-situ electro-desalination of tile panels is evaluated, focusing on the possibility to place the electrodes around the panel to avoid any further damage.

![Figure 1: Cross section of tile panel.](image)

This paper discusses electro-desalination of the four single parts followed by a discussion of in-situ treatment of tile panel and support

## 2. Principles of electro-desalination

The main transport mechanism for salt ions in a moist, porous material under application of an electrical potential gradient is electromigration, which electro-desalination is based on. During the process, the concentration of dissolved salts will decrease in the porous material as the
dissolved ions concentrate around the electrode of opposite polarity. The overall principle of electro-desalination is shown in figure 2. The electrode compartments consist of an inert electrode placed in a clay poultice. The electrode compartments are placed on the surface of the porous material to be desalinated. The optimal placement is determined by several factors, which are discussed later in this paper.

The dominating electrode processes are electrolysis of water: \( \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 (g) + 2e^- \) (at the anode) and \( 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 (g) \) at the cathode. When the removed chloride ions reach the anode they can be oxidized to \( \text{Cl}_2 \) from the electrode process: \( 2\text{Cl}^- \rightarrow \text{Cl}_2 (g) + 2e^- \). Electrolysis influences the pH around the electrodes. It is necessary to neutralize acidification at the anode in order to prevent decay of the material to be desalinated. Hendrix et al [5] underlined how important it is to avoid acidification, as in experiments without pH neutralization the stones were severely damaged close to the anode. This was confirmed by [6] who reported that buffering of the acid produced at the anode was important to avoid decomposition of the stone (seen as increased porosity due to dissolution of calcite) in case no buffering system was used. In addition, they reported gypsum formations in the region closest to the anode both with and without poultice, but a higher degree of gypsum was seen in the setup without poultice. Also in order to obtain sufficient desalination pH neutralization can be crucial. Kamran et al. [7] showed that without neutralization at the electrodes, the desalination process in bricks stopped due to formation of a sharp transition zone between the acidic and alkaline region. This zone resulted in a large electrical potential gradient due to a local depletion of ions here. So for different reasons, the metallic electrodes should not be placed directly on the material to be desalinated.

Carbonate rich clay poultice can be placed between the electrodes and the stone for neutralization of pH changes. Calcareous clay for brick production or a mixture of kaolinite and calcite both efficiently neutralized the acid [8]. The acid was neutralized by the \( \text{CaCO}_3 \) in the poultices. In the cathode poultice and in the porous material there may be precipitation of \( \text{Ca(OH)}_2 \) in the material as a result of the alkalisation from the cathode [9]. Over time \( \text{Ca(OH)}_2 \) reacts with \( \text{CO}_2 \) from the air and forms \( \text{CaCO}_3 \). Neither \( \text{Ca(OH)}_2 \) nor \( \text{CaCO}_3 \) are considered damaging, because aqueous solutions of calcium hydroxide (limewater) have been used for many centuries to protect and consolidate limestone. In addition to neutralizing the acid, the poultice also gives good electrical contact between metallic electrode and stone, and it serves as sink for removed ions. When the clay poultices are removed after the desalination, the ions of the salts are removed with it.
3. Electro-desalination of the different parts in a tile panel

In this chapter the experimental results with the different parts of the tile panel shown in figure 1 are discussed separately.

3.1 Single tiles – biscuit and glaze

Experiments have been reported with electro-desalination of single tiles in the laboratory [10-12]. The experimental setup of these is illustrated in figure 3a. The tiles were placed with the glaze down and because they had dried out during indoor storage, water was sprayed on the back side before placing the electrode compartments (poultice and inert electrode mesh) as far apart as possible. The tile and electrode compartments were wrapped in plastic to hinder evaporation of water, which would hamper the passage of electric current. A constant current was then applied to the electrodes. Moist pores are needed in order to be able to have passage of current through the biscuit. In cases, where salt decay is problematic, waster must be present at least during some periods and it is assumed that it is not neither necessary to add extra water or cover the wall as in the laboratory atmosphere with very low RH.

The first results reported on electro-desalination of single tiles were obtained with XIX century tile segments spiked with NaCl [10]. Removal efficiencies of 96% Cl was reached in less than 6 days. Following this good result, experiments with spiked tiles, experiments were conducted with 18th century tiles, which had been removed from Palacio Centeno (Lisbon) during renovation due to damage of the glazing from the presence of salts. These tiles were severely contaminated with both chlorides and nitrates. The charge transfer in the electro-desalination experiments was too low in the experiments to obtain full desalination, but promising results were obtained as significant decreases (>81% Cl, ~ 59% NO3 and ~ 22% SO42-) were seen. In Ottosen et al [12] the duration of the experiments was long enough to obtain sufficient desalination (2-3 month). There is neither a common European nor a Portuguese guideline on acceptable levels for salt in building stone. To evaluate the salt concentrations, the only accessible threshold values are from the Austrian ÖNORM B 3355-1 [13] and these are chosen as a first approach here, though these limiting values are much debated. In relation to the ÖNORM the concentrations of Cl (9900 mg/kg) and especially NO3 (30,600 mg/kg) were very high in the tiles (exceeding the concentrations where desalination is advised). After the electro-desalination the concentrations of both Cl and NO3 were well below the lower level of the ÖNORM (which are respectively 300 mg Cl/kg and 500 mg NO3/kg), so the desalination of the biscuit was successful.

Figure 3: (a) Experimental setup for desalination of single tile; (b) 20th century tile used in lab experiment.
Large parts of the glaze and parts of the biscuit were lost in the Palácio Centeno tiles, presumably due to salt decay. The most severe damage was seen from the outer edges towards the centre of the tile [1]. Salt crystals (NaCl) were clearly identified under the lifted glaze by SEM-EDX, but after electro-desalination no crystals were found under the glaze. Thus this important interface was successfully desalinated [12]. Salt crystals cannot directly be reached by the electric field as they carry no electric charge. During electro-desalination salt crystals must have been dissolved into ions in the pore solution, likely by the penetration of water from the wet poultice, hereby mobilizing them for electromigration. When free ions are removed, equilibrium will change towards dissolution of more crystallized salts and the new ions can subsequently be removed by electromigration, so a low and harmless concentration of salt was obtained over time. It must be investigated, if the water in salt damaged tile panels is sufficient for such dissolution of salt crystals over time.

The fraction of the applied current carried by Cl\(^-\) and NO\(^3-\) during the desalination was very high meaning a high current efficiency. During the desalination Cl\(^-\) and NO\(^3-\) were removed at the same rate. The initial sulphate concentration was low, but when the more mobile chloride and nitrate were removed to a low level removal of sulphate started [12].

An experiment with electro-desalination of a Portuguese 20th-century tile (figure 3b) has also been conducted (not previously published). The average initial concentrations were 700 mg Cl\(^-\)/kg and 930 mg SO\(_4^{2-}\)/kg and thus the salt contamination was much less than the older tiles from Palacio Centeno. After 3 weeks with 1 mA applied 76% Cl\(^-\) and 87% SO\(_4^{2-}\) were removed. Hereby it was shown that also this biscuit type can be desalinated.

3.2 Tile bed and interface between tile bed and tile

Lime mortars have been used since ancient times in masonry, renders, plasters, and also as adhesive agents for tiles, namely between 16th and mid. 20th centuries. This type of mortar is known to be compatible with old masonry and ancient ceramic tiles [14].

Brammer & Sveegaard [15] and Ferreira et al [16] reported laboratory results with electro-desalination of three tiles from different centuries. Mortar was attached to the tiles in these investigations (see figure 4). Each of the three tiles was broken. The tiles were: 17th-century tile from the Alentejo Region (mortar very hard and unfortunately not considered original), 18th-century tile from Palacio Centeno, Lisbon (mortar very porous and loose, considered original) and 20th-century tile of unknown origin (mortar was hard, but is considered original). Initial samples were taken from both tile and mortar prior to the desalination experiments. From the first two tiles it was only one sample from both. The 20th-century tile was separated into two pieces where one was used to find the initial salt concentration and the other for the desalination experiment.

As in the experiments with single tiles, the tiles were placed with the glaze down. Water was sprayed on the mortar, which was now the upper part and the electrode compartments were placed on the mortar surface. The overall conclusions from the electro-desalination experiments with tile and mortar attached were:

*17th century tile:* The glazing of the tile did not show sign of salt decay and the concentrations in the initial samples were also very low 93 mg Cl/kg and 130 mg NO\(_3^{-}\)/kg in the mortar and 53 mg Cl/kg and 42 mg NO\(_3^{-}\)/kg in the biscuit. Still it was decided to see if the salt content could be lowered by electro-desalination, which was the case. The removal after 7 days with about 1 mA applied were in average 51% Cl and 83% NO\(_3^{-}\)/kg in the mortar and 15% Cl and 64% NO\(_3^{-}\) in the biscuit. Thus even at such low concentrations salt was removed in the applied electric...
field. The highest decrease was obtained in the mortar, but the concentration was also decreased in the biscuit [15].

18th century tile: Very high initial concentrations in both mortar (6600 mg Cl⁻/kg and 14,000 mg NO₃⁻/kg) and biscuit (6600 mg Cl⁻/kg and 14,000 mg NO₃⁻/kg) were found. During the 24 days of experiment the current was gradually increased from 5 to 10 to 20 mA as the voltage (reflecting the overall resistivity) was very low. From the mortar was removed 91% Cl⁻ and 84% NO₃⁻ and from the biscuit 42% Cl⁻ and 9% NO₃⁻ [15-16]. The desalination was not completed in this experiment as too high concentrations remained, however, as the voltage was still low at the end of the experiment and as the concentrations of salt ions continuously increased in the poultice the desalination could have progressed longer [17]. The percentages of salt removal from the mortar were significantly higher than from the biscuit in this experiment.

20th century tile: Compared to the Önorm neither of Cl⁻, NO₃⁻ and SO₄²⁻ exceeded the limiting value were salt removal is advised. However, the average SO₄²⁻ concentrations were high both in mortar and biscuit and the concentration varied considerably, so it was decided to perform electro-desalination even if the adapted upper limiting values from the ÖNORM were not exceeded (the concentration level falls within the category where individual evaluation is advised). This because some sulphate salts are known to be highly damaging. In the reference piece the average concentrations with standard deviation were: mortar 1540 ± 1490 mg SO₄²⁻/kg and biscuit 650 ± 590 mg SO₄²⁻/kg. After electro-desalination the concentrations were: mortar 150 ± 83 mg SO₄²⁻/kg and biscuit 120 ± 32 mg SO₄²⁻/kg. This corresponds to a removal on average of 90% from the mortar and 82% from the biscuit.

Figure 4: experimental tiles with mortar. Top: 17th century tile from Alentejo (PT); middle: 18th century tile from Palacio Centeno, Lisbon; bottom: 20th century tile of unknown origin.
The interface between mortar and tile can be problematic for in-situ electro-desalination in cases where the tile is partly loosened and there is air-filled space between them. Then passage of current is not possible in this zone. In all three tiles the salt ions were removed better from the mortar than tile, but this may reflect that the electrodes were placed on the mortar and not the biscuit. Salt ions were removed over the interface in all cases. The adhesion mechanism between tile and mortar is ruled partially by physical forces, such as Van der Walls and the suction of fresh binder by the tile, and partially by chemical links. Thus, the chemical and mineralogical composition of the bonding agent, i.e. the mortar, may be critical for an appropriate bond [14]. The interface can be very weak and experiences focusing on mapping interface properties, where the interface is limiting the electro-desalination process of the tile through the mortar must be obtained from experimental work, followed by finding a method where these situations can be found while the ties are still in place.

3.3 Brick and natural stone

Electrochemical desalination of different porous matrices has been tested in the laboratory, namely baked clay bricks (Handcrafted red bricks for renovation purposes [18-19], yellow brick [20], and red bricks [21]) and natural stones (posta and cotta sandstones [22], Gotlandic Sandstone [6], Nexø sandstone [23], and granite [24]). Electro-desalination was successful in every case, and thus the success for desalination of a tile panel is not considered to be dependent on the porous material of the wall itself. The influence on electro-desalination of the interface between wall and mortar must be investigated similarly to the interface between tile and mortar. However, no such experiments have been conducted yet.

4. Pilot tests with masonry without tile

Ottosen and Hansen [25] summarize results from four small (2-6 electrode units) and one larger (74 electrode units) in-situ pilot scale tests for electro-desalination of masonry (natural stone and brick masonry). In every case, the electrodes were placed at the same side of the wall and with alternating polarity. When the electrodes are placed like this, the electric field is strongest close to the surface, but will distribute into the wall as shown schematically in figure 5a. When the electrodes are at the same side, the salt concentration decreases closest to the electrodes first and over time the desalination progresses into the depth of the material [18]. Figure 5b is an example of a pilot scale plant for electrodesalination. Neither of the pilot scale tests can be regarded as the final proof of concept, as full desalination has not been obtained yet. Every test was unfortunately stopped before full desalination due to limited project-duration. However, when they were stopped, the transference number for the target ion was still high, and desalination could have progressed further if the experiment had been prolonged. The large pilot scale plant covered about 25 m² surface of a limestone wall of a historic warehouse. The wall was highly contaminated with NaCl (7300 mg Cl/kg). A total of 3.8 kg chloride (6.3 kg NaCl) was removed during 390 days [8]. A small pilot scale experiment was close to full desalination. The main pollutant was NaCl (initial levels: 1400 –4000 mg Cl/kg. The Cl concentration in the masonry below the cathode and between the electrodes was decreased to a sufficient level in 10 cm depth. The concentration below the anode was decreased to a level of 1800 mg Cl/kg, which was still too high compared to the ÖNORM (300 mg/kg).
5. Discussion on possible in-situ desalination of tile panels

For in-situ electro-desalination of tile panels the electrodes should not be placed on the surface with the fragile glaze. As the overall transport mechanism for the salt removal is electromigration advantage can be taken of the electric field lines to distribute over a certain volume. The electric field will be strongest where the conductivity is highest, and this must be expected to be close to the surface where the salt damage also develops. In laboratory experiments using bricks [18] it was clearly shown that the part of the brick closest to the electrodes was desalinated before the middle part, which was again desalinated before the lowest part of the stone. In sandstones cut in irregular shapes, parts of the stone not directly between the electric field were also desalinated, though later than the part between the electrodes [26]. These two studies show that electrodes do not necessarily need to be on each side of the object to be desalinated. This can be utilized when desalinating tile panels. In case there are no air cavities between wall-mortar-tile, it is likely that the desalination can be achieved by electrodes placed on the surface of the wall opposite to the tiles. Another option is to remove already loose tiles and place electrodes on the mortar where they were removed. The removed tiles should be desalinated ex-situ (e.g. by submersion) before placed in the tile panel again after electro-desalination.

There are several open questions, which need to be researched and answered. For example, the walls can be more than 1 m thick. This may limit the option of placing the electrodes at each side as the electrical resistance may be very high, and also the wall may not be in hydraulic contact all through. An option may here be to place the electrodes at the same side and focus on desalinating the wall closest to the tiles only. The solubility of the salts is a determining factor for electro-desalination. All damaging salts are soluble as it is the cycles between solubilized and nucleated which causes the decay. However, if solubility is very low, electro-desalination will be very slow (years). We may need to wet the wall in periods with low RH or, alternatively cover the wall during treatment to keep the moist and hinder evaporation. In the pilot scale plants performed so far on walls without tiles, wetting was not necessary. When the supply of moisture and salts remains active after electro-desalination, as in the case of rising damp, salt induced decay will reappear over. A suggestion might be to estimate the rate at which the salts are supplied into the masonry again and plan for a new desalination action before a damaging level reappears.
ELECTROCHEMICAL INVESTIGATION OF CARBON-BASED CONDUCTIVE COATINGS FOR APPLICATION AS ANODES IN ICCP SYSTEM OF REINFORCED CONCRETE STRUCTURES

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Abstract
Carbon-based conductive coatings are complex composites, consisting of an organic or inorganic binder and conductive carbon components, for application as anodes in impressed current cathodic protection systems of reinforced concrete structures. The electrochemical properties of three coatings at different humidity and in saturated calcium hydroxide solution were studied by electrochemical methods, such as electrochemical impedance measurement, measuring of open circuit potential over time and galvanostatic polarization.

1. INTRODUCTION
Carbon based conductive coatings (CBCC) are complex composites, consisting of an organic or inorganic binder and conductive carbon components, for application as anodes in impressed current cathodic protection systems (ICCP) of reinforced concrete structures. These mixtures can be painted as paste or aqueous dispersion at the prepared concrete surface. For current supply of the rectifier to the coating (secondary anode) different materials like wires made of platinised titanium, copper or mixed metal oxide coated titanium (primary anode) are used. The negative pole of the rectifier is connected to the reinforcing steel (cathode) and the positive pole to the primary anode (figure 1). By supplying a protective current between anode and cathode, the potential of the reinforcing steel should be lowered below -720 mV (versus Ag/AgCl/0.5 M KCl) into an electrochemical inactive range [1]. An industrial research project in cooperation between the Bundesanstalt für Materialforschung und -prüfung (BAM, Berlin) and the Institute of Building Materials and Research (RWTH-Aachen University) should assess the applicability of three commercial carbon-based conductive coatings as secondary anode in ICCP systems.
As part of this research project, extensive electrochemical and morphological investigations of carbon based conductive coatings were carried out to determine important parameters such as applied current density, pH value of the electrolyte solution, humidity and, type of binder and their influence to the degradation behaviour of these coatings. The coatings differ from each other both in binder and the type of electrically conductive pigments, as well as in surface roughness and porosity. The characteristic properties of the used coatings are represented in the table 1.

<table>
<thead>
<tr>
<th>samples</th>
<th>CBCC 1</th>
<th>CBCC 2</th>
<th>CBCC 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder</td>
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<td>aluminosilicate polymer</td>
<td>acrylic resin</td>
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<td>graphite powder</td>
<td>graphite powder</td>
<td>graphite NiCCF</td>
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<td>1.20-1.33</td>
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<tr>
<td>solids content [%]</td>
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<td>48</td>
<td>50</td>
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<tr>
<td>electric resistance [Ω·cm]</td>
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<td>&lt;1.0</td>
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<tr>
<td>porosity [%]</td>
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<td>1-5</td>
<td>10-20</td>
</tr>
</tbody>
</table>

2. ELECTROCHEMICAL INVESTIGATIONS

The electrochemical properties of the CBCC’s in saturated calcium hydroxide solution were studied by electrochemical methods, such as electrical impedance measurement, measuring of open circuit potential over time and galvanostatic polarisation. For the galvanostatic polarisation with in situ pH-value measurements we designed a special corrosion-measurement-cell (figure. 2).
The dissolved organic and inorganic carbons in electrolyte solution were quantified by using a photometric method [2]. The structures of the coatings were investigated before and after the electrochemical investigations by microscopy and SEM/EDX analysis.

3. PRACTICAL APPLICATION

The conductive coatings are also investigated by an application at real practical structures. The electrochemical characters from the CBCC’s are validated against a standard anode system made of mixed metal oxide (mmo) mesh (figure.3).

Figure 2: Measurement cell for polarisation experiments at conductive coatings

Figure 3: left: conductive coating with spacers for the concrete cover reinforcement; right: application of a mmo mesh as classical ICCP-system
For the validation the applied current, instant off potential and clamping voltage are recorded by the ICCP-system [3]. For the practical application of the anode systems, just two of the investigated carbon anode systems were used.

ACKNOWLEDGEMENTS

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REFERENCES

6. Conclusions

Electro-desalination of tile panels has not been tested yet, but different experiments in laboratory and pilot scale have been encouraging in relation to develop the method for this purpose. Single tiles have been desalinated and both the biscuit and the interface between glaze and biscuit were desalinated successfully. Mortars, several types of natural stones and baked clay bricks have been successfully desalinated with the method, too. In fact, all types of porous stones have been successfully treated by electro-desalination. The coming research must focus on interfaces between the materials and how these influence the desalination. In-situ electro-desalination has been conducted at different salt-infected walls without tiles. The final proof of concept has not yet been reached, i.e. full desalination of the wall due to a too short duration, but the salts were removed at a high efficiency of the applied current. The electrodes were placed at the same side in these experiments, which could also be a solution for tile panels, either to conduct the desalination from the back side of the wall (opposite to the tiles) or by removing few tiles and place electrodes in the wholes. These ideas however remain to be tested.

Acknowledgements
Joao Mimoso (LNEC) is acknowledged for getting the idea and suggesting electro-desalination to be tested on tiles and providing the first tile. Ivo Férin and colleagues (Loubet and Isabel) for providing the salt contaminated tiles.

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REMEDIATION OF AS - COMPARISION OF TWO DIFFERENT ELECTRODIALYTIC CELLS AND APPLICABILITY OF TREATED SOIL IN BRICK MATERIALS

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Abstract
An electrodialytic process (ED) was applied to clean-up an industrial soil from wood preservation polluted with arsenic (As). Two different cell-conditions were tested, in a 2-compartment cell set-up, using stirred soil suspensions. The experiments were carried out during 14 days, applying a constant current intensity of 5 mA. In addition, after ED a possible reuse of the soil for clay bricks was tested. The best result in the removal of As from suspended soil was obtained when suspended soil was placed in cathode compartment and the pH of the anolyte. In the other setup the soil suspension was kept in anode compartment and the pH of the catholyte was maintained acid. This setup only achieved 3% of As removal towards the catholyte. These results showed that alkaline conditions favored the As desorption from soil to water and that the main transport mechanism was electromigration through the anion exchange membrane towards the anolyte. The treated soil proved to be an option to be used in bricks, which is also an advantage in the management process of soil residue.

1. Introduction

Arsenic (As) is one of the elements of major environmental concern due to its highly toxicity to all forms of the life [1]. Arsenic is a natural element with features intermediate between metals and non-metals [2]. Arsenic contamination has been reported worldwide and is cited as the most hazardous substance by the USA Agency for Toxic Substance and Disease Registry [3] and is considered one of the priority pollutants by the US EPA and the EU. The sources of As can be natural (i.e. through dissolution of As compounds adsorbed onto pyrite ores into the water by geochemical factors) and anthropogenic (i.e. through use of insecticides, herbicides, phosphate fertilizers, mining and smelting, industrial processes and coal combustion) [2]. These sources of As can damage the health of the surrounding environments and increase the risk of
soil, a serious environmental hazard. According to the U.S. Environmental Protection Agency the permissible limit of As in soil is 24 mg kg⁻¹.

Electrokinetic remediation (EKR) is a technique used to clean up waste matrices under the influence of an electric field generated between electrodes which induces different transport mechanisms (electroosmosis, electromigration and electrophoresis) and electrochemical reactions (electrolysis and electrodeposition) [4,5]. Electrodiolytic remediation (EDR) adds the electrodialysis to the process, by the use of ion exchange membranes that act both as physical and chemical barriers. By the use of ion exchange membranes, the main direction for the electromigration within the polluted matrix is determined to be out of the soil. The EDR was developed at the Technical University of Denmark in 1992, was patented in 1995 (PCT/DK95/00209), and has proven to be efficient in removing a wide range of contaminants, such as heavy metals [6], polycyclic aromatic hydrocarbons [7] and polychlorinated biphenyls [8] from suspended soils. The success of EDR is reported to be dependent on the specific site conditions, including the type and amount of contaminant, soil characteristics, organic content, as well as experimental conditions such as stirring and pH [5,9].

In the present study, the ED process was applied to a soil contaminated with As in a two-compartments cell design (2C). The feasibility of inserting the soil suspension in the anode or cathode compartment together with pH adjustment (alkaline in anolyte and acid in catholyte). The potential reuse of EDR treated soil in brick was also assessed.

2. Materials and methods

2.1 Experimental soil
The soil used in the present study was sampled from Collstrop site, located in an industrial area in Denmark. Collstrop soil is highly polluted with As provided by wood preservation activities.

2.2 Soil characteristics
The soil was analyzed for the following parameters: As concentration, pH, conductivity, carbonate and organic matter content. Laser and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) analysis was also carried out.

Arsenic concentration was determined according to the Danish Standard 259 [10]. Briefly, 1 g of dry soil was extracted with 20 mL HNO₃ and heated at 200 kPa (120 ºC) for 30 minutes. The liquid phase was separated from the solid particles by vacuum filtration (0.45 μm filter) and diluted till 100 mL. Arsenic concentration was determined by inductively coupled plasma - atomic emission spectrometer (ICP-AES).

Soil pH was measured by suspending 5 g of dry soil in either 20 mL 1 M KCl or in distilled water and measured using a Radiometer pH electrode. Conductivity was measured using a CMD2010 conductivity meter after suspending 10 g of dry soil with 25 mL of distilled water followed by 30 min of agitation on a shaking table.

Carbonate content was determined volumetrically by the Scheibler method (2.5 g of soil reacting with 20 mL of 10% HCl). The amount was calculated and all the present carbonate
was assumed as calcium carbonate. Organic matter was determined by loss on ignition after 1 h at 550 °C.

SEM analysis was performed on the untreated and treated soil.

2.3 Desorption of heavy metals as a function of pH
The effect of pH in As desorption was assessed by suspending 2.5 g dry soil in 25 mL of HNO₃ or 25 mL NaOH with concentrations ranged between 0.01 M to 1.0 M followed by shaking during one week. The samples were made in duplicate. Extractions in distilled water were made as reference. After desorption tests, samples were filtered (0.45 μm), pH measured and As determined by ICP-AES.

2.4 Experimental setup
A two compartment cell set-up (2C) was tested varying the position of contaminated soil (Figure 1A and 1B). The cells were made from polymethyl methacrylate. The compartment where the suspended soil was placed had a L=10 cm and the electrolyte compartment a L=5 cm. Each cell had an internal diameter of 8 cm. Ion exchange membranes separating the central compartment from the electrode compartments were from Ionics, anion exchange membrane (AEM, AR204 SZRA B02249C) and cation exchange membrane (CEM, CR67 HUY N12116B). The electrodes were platinized titanium bars, with a 3 mm diameter (Bergsøe Anti Corrosion A/S, Herfoelge, Denmark). A power supply (Agilent E3612A) was used to maintain a constant current. The fresh electrolyte (500 mL of 10⁻² M NaNO₃) was circulated in a closed system (“Pan World” magnetic pumps from Plastomec Magnet pump model P05). The electrolyte was conditioned at the beginning of the experiment, and whenever necessary, to achieve an acidic (pH=2) or alkaline pH (pH=10), depending on the applied treatment.
Figure 1 - Schematic presentation of the laboratory 2C cell used in experiments: A) soil suspension in the anode compartment, CEM, and catholyte pH adjusted to 2; B) soil suspension in the cathode compartment, AEM, and anolyte pH adjusted to 10.

2.5 Electrodialytic experimental conditions

Two electrodialytic experiments were performed (Table 1). One cell compartment was filled with 50 g of soil and 350 mL of distilled water corresponding a liquid/solid ratio of 7. In treatment 1 (T1) the suspended soil was kept in the anode compartment, a CEM was used to separate compartments, catholyte pH was adjusted to 2 throughout the treatment (Figure 1A). In treatment 2 (T2) the suspended soil was kept at the cathode compartment, an AEM was used to separate compartments, and anolyte pH was adjusted to 10 (Figure 1B).

The voltage between working electrodes, conductivity and pH of both cell compartments were measured twice a day. The pH of the electrolytes was adjusted whenever needed by addition of HNO₃ (1:1) and NaOH (6M).

At the end of the ED experiments, the suspended soil was drained using filter paper aiming to separate the solid from the liquid phase. The water content was measured. The soil solution was then filtered (0.45 μm) and the solid phase dried until constant weight (105 °C), crushed by hand and extracted (analysis description in section 2.2). Membranes and electrolytes were soaked in 1 M and 5 M HNO₃, respectively, for 24 h to release metals and the liquid phase filtered (0.45 μm). The As concentration in the different parts of the cell (soil, soil solution, electrolyte, membrane, electrodes) was then determined by ICP-AES.
2.6 Brick pellets
Pellets were made with EDR treated soil (T2) in order to study the suitability for further reuse in ceramics. Different amounts of soil were joined with pure clay (yellow wienerberger from soft-molded bricks) to test the stability of the pellets. The samples had a total weight of 2 g and 10 % of distilled water was added. Brick pellets (2 cm in diameter) were made in a form and pressed to pellets in an Instron 6022 tester at 3.14 kN. The wet pellets were weighted before being heated at a furnace with a gradual temperature increase (until 1025 °C) where they were kept by 1 h. After cooling to room temperature, the fired pellets were weighted and characterized by porosity, density and leaching (Section 2.6.1.).

2.6.1 Parameters of brick pellets
Aiming to determine porosity and density, the brick pellets were placed in a desiccator under vacuum for 3 h (100 N m⁻²). After this time, the desiccator was filled with deionized water and pellets left for 1 h. The desiccator was then opened to the air during 1 day. The pellets were weighed over and under the water [11]. The leaching of As was also tested according to DS/EN 12457-3 [12]. The fired pellets were crushed and distilled water was added, liquid/solid ratio of 2. The suspension was agitated for 16 h and the liquid phase separated from the solid particles by vacuum filtration (0.45 μm). As concentration was determined by ICP-AES.

3. Results and discussion
3.1 Soil characteristics
The characteristics of the soil are listed in Table 2. The soil has a sandy loam texture. The initial concentration of As was 594 mg/kg. Like was expected according with literature [13], the pH of the soil in distilled water was of 6.3 whereas pH in KCl was of 5.4. The conductivity of the soil was of 0.2 mS/cm.

Table 2: Initial characteristics of Collstrop soil.

<table>
<thead>
<tr>
<th>Type of soil</th>
<th>As (mg/kg)</th>
<th>pH_{KCl}</th>
<th>pH_{H2O}</th>
<th>Conductivity (mS/cm)</th>
<th>Carbonate content (%)</th>
<th>Organic matter (%)</th>
<th>Grain size distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandy Loam</td>
<td>594 ± 100</td>
<td>5.4 ± 0.05</td>
<td>6.3 ± 0.3</td>
<td>0.2 ± 10</td>
<td>2.2 ± 0.04</td>
<td>19 ± 1</td>
<td>6 43 51</td>
</tr>
</tbody>
</table>
3.2 Desorption of As as a function of pH

The concentrations of As extracted from soil at different pH values is shown in Figure 3. In distilled water 61 mg/kg of As was extracted.

The results showed that As is desorbed from soil under highly acid (0.1<pH<0.4) and alkaline (8<pH<13) pH values. The lower pH values (0.1-0.4) released ≈514 mg/kg of As whereas the higher pH (=13) released 533 mg/kg.

![Figure 3 - Arsenic desorption as a function of pH.](image_url)

3.3 SEM analysis

Figure 2 shows the differences in soil particles before and after EDR treatments. The largest changes in shape/morphology occurred in T2 where the suspended soil remained in cathode. This means that higher pH values may have influenced particles distribution. In T2, the small particles are adsorbed onto the surface of the largest ones forming aggregates (Figure 2 iii) whereas before EDR treatment (Figure 2 i) or in T1 (Figure 2 ii) the small particles are separated from the other particles.

![SEM images](image_url)
3.4 Electrodialytic experiments
3.4.1 General results
The voltage, conductivity and pH of the soil suspension during the EDR experiments are shown in Figures 3, 4 and 5, respectively.

Both treatments presented a similar behavior in voltage. From the beginning of the treatment until day 8, the voltage gradually dropped followed by a stabilization tendency. This pattern is probably because ions from electrolysis at the electrodes (H⁺ or OH⁻) decreased the conductivity in the suspension in the first phase.

Figure 2 - SEM picture of Collstrup soil before EDR (i) and after EDR treatments under acid, T1 (ii) and alkaline, T2 (iii) conditions.
The electrical conductivity (Figure 4) increased in both treatments, corroborating voltage decrease due to a decreased electrical resistance (e.g. due to $\text{H}^+$ and $\text{OH}^-$ produced from water electrolysis).

The pH in the soil suspension is shown in Figure 5. When the soil suspension was placed in the anode (T1) the pH decreased until \( \approx 2 \) whereas when placed in the cathode (T2) it increased to \( \approx 11 \). The pH changes are due to water electrolysis, resulting in the formation of $\text{H}^+$ in the anode and $\text{OH}^-$ in the cathode compartment.
3.4.2 Electrodialytic arsenic removal

An overview of As removal after EDR treatment is given in Table 3. The removed As is defined as the element found in the electrolyte compartment and in the ion exchange membrane. The removal percentage is calculated dividing the mass of element removed (electrolyte + membrane) by the final mass found in it (soil + soil solution + electrolyte + membrane). The mass balance ranged between 77% and 99%. The As distribution in the different parts of cell after the ED process is shown in Figure 6. Also, the distribution pattern of As differed significantly when compared with acid and alkaline pH cell-conditions.

Table 3: Overall results of EDR of soil.

<table>
<thead>
<tr>
<th>Treatments (T#)</th>
<th>Removal efficiency (%)</th>
<th>Amount removed (mg/kg)</th>
<th>Mass balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>3</td>
<td>31</td>
<td>99</td>
</tr>
<tr>
<td>T2</td>
<td>74</td>
<td>502</td>
<td>77</td>
</tr>
</tbody>
</table>

The EDR with acid cell-conditions (T1) resulted in 3% of As removal, corresponding to 31 mg/kg whereas the in the presence of alkaline cell-condition (T2) 74% of As were removed towards the anode compartment corresponding to 502 mg/kg of As.

The soil suspension in the anode compartment (T1) was subject to oxidizing conditions and due to the CEM, only the movement of cations towards the catholyte was allowed which, in turn, was acidic due to pH adjustment (neutralization of OH⁻ by H⁺ addition). At the final pH achieved in anode compartment of T1 (pH 2), As presented a weak soil desorption (see Figure 6) but also the typical negative charge at this pH (H₃AsO₄ + H₂O ⇌ H₂AsO₄⁻ + H₃O⁺, pKₐ=2.20) limits its migration through CEM towards catholyte, as the prevailing As species is uncharged. Arsenic desorption is highly dependent on pH and redox potential conditions which influences
its chemistry and composition [14]. Arsenic is a metalloid, which the primary forms in soils are arsenate-As(V) (H$_2$AsO$_4$) in oxidizing environment and arsenite-As(III) (H$_3$AsO$_3$) in reducing environments [15]. The experiments made so far were conducted in open laboratory cells with stirring and As(V) is expected to be the primary form and the main stable specie in an oxidizing environment. At neutral to acidic pH, the uncharged specie (H$_3$AsO$_3$) is expected to be present and therefore it will not be able to electromigrate [14]. From the 10% of As desorbed from soil to water (at pH 2), only 3% was able to pass through the CEM towards the catholyte. Ottosen et al. (2000) [14] reported that the efficiency of EDR treatment increased for As removal at low pH by adding an enhancement solution in order to desorb As from the soil.

The T2 treatment showed high (74%) As removal which is explained by the high As desorption at the pH achieved in the cathode compartment (pH 11). The presence of the AEM allowed the migration of As towards the anolyte, due to its negative charge under this chemical conditions. During the ED process, NaOH was added to the anolyte to keep the pH alkaline (=10) at both sides of the membrane.

Despite the 74% of As removal in T2, the EDR treated soil still contained approximately 150 mg/kg of As. The application of this soil in construction material was tested aiming to optimize the re-use of industrial contaminated soil.

![Figure 6 - Distribution of As after EDR treatments under acid, T1, and alkaline, T2, conditions.](image)

### 3.5 Brick pellets

Figure 7 shows the brick pellets made with different amounts of soil. Due to the insufficient particle aggregation observed in pellets constituted by 100% of treated soil, clay was joined at different amounts (50%, 75% and 90%). Clay minerals brought plasticity to the bricks showing consistence for all the tested percentages (50, 75 and 90%). Also, the brick pellets showed a different appearance (e.g. color) in accordance to the amount of clay.
The suitability of the brick pellets to be used as a constructed material was defined by porosity, density and As leachability (Section 3.4.1.; Table 4).

![Figure 7 - Brick pellets with different amounts of soil (100 %, 50 %, 25 % and 10 %).](image)

Porosity, which is directly related to the amount of water present, increased (between 27% to 34%) with the addition of clay to the brick pellets. This is explained by carbonates that decompose during sintering with gas releases conducting to pore formation in bricks [16]. Higher amount of pores means higher water absorption, which can reduce the brick resistance and durability. Regarding to dry matter density, the bricks showed to be very similar.

Leaching tests proved that As present in EDR treated soil was not released from the bricks. That means the use of treated soil as building material does not represent a risk to the environment, open a path to use this soil also for construction materials.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Amount of soil (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (%)</td>
<td>50 25 10</td>
</tr>
<tr>
<td>27 ± 1</td>
<td>32 ± 1</td>
</tr>
<tr>
<td>34 ± 1</td>
<td></td>
</tr>
<tr>
<td>Density (mg/m³)</td>
<td>2.6 ± 0.1</td>
</tr>
<tr>
<td>2.7 ± 0</td>
<td></td>
</tr>
<tr>
<td>2.7 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>Leaching (mg/kg)</td>
<td>ud</td>
</tr>
<tr>
<td>ud</td>
<td></td>
</tr>
<tr>
<td>ud</td>
<td></td>
</tr>
<tr>
<td>ud: under value</td>
<td></td>
</tr>
</tbody>
</table>

4. Conclusions

This work showed that the electrode compartment where the contaminated soil is located, is determining the As removal due to the prevailing pH changes. The set-up with suspended soil in the cathode compartment showed 74% of As removal towards the anolyte. The high pH of the cathode compartment promotes As desorption followed by electromigration through the AEM. The EDR treated soil may be further reused in ceramic bricks (together with clay) without risk of As leachability.

Acknowledgement

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CHANGES IN ELECTRICAL RESISTIVITY USED AS MONITORING TOOL DURING THE ELECTROKINETIC TREATMENT OF CLAYEY SOILS

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Abstract
Electrokinetic, or Electrochemical treatment, is one of the possible techniques to decontaminate impervious soils such as clayey soils. Real time monitoring of the electrical resistivity of a soil can be a useful tool in controlling and assessing the removal of water and ions during decontamination using this technique. Field conditions were simulated in laboratory environment using a Perspex box of dimensions 350 x 100 x 150 mm\(^3\) filled with compacted soil. Two tests were performed on compacted kaolin samples with void ratio of 0.9: one mixed with tap water and other with a 0.5 M NaCl solution. After the saturation, the soils were electrokinetically treated under constant voltage gradients. Electrical resistivity was measured during the course of the treatment. Properties like electrical conductivity and pH of the pore fluid were also measured. The profiles of these properties are indirect measurements of the amount of ions exchanged. They allowed to quantify changes in NaCl concentration during the course of EKT. The results show an efficient removal of water and salt from the soils, in particular in the areas close to the electrodes.

Keywords: Decontamination, Monitoring, Electrical resistivity, Clayey soils

1. Introduction

Electrokinetic Treatment (EKT) is an efficient technique for decontamination and dewatering especially in fine grained soil such as clays. This is because of the electroosmotic drag of ions and water molecules in the soil due to the application of electrical current, and also because electroosmotic permeability is larger than saturated hydraulic permeability, and for this reason water percolates faster than if only a hydraulic gradient would be applied [1,2,3,4]. This technique has proven to be efficient for the removal of salts from soil and also from other construction materials [5,6].
Electrical resistivity of a soil is related to the presence and amount of ions, which affect also the electrical conductivity of the pore fluid. For this reason, its evolution during the course of the treatment can be used as a real time monitoring tool to track the progress on decontamination. Factors like changes in temperature, pH and conductivities of the soil caused due to precipitations and chemical reactions affect the resistivity readings, hence these factors should also be taken into consideration in order to analyse the results efficiently [7].

This principle was used in the study performed using a laboratory scale setup for EKT, which is presented in this paper. Two tests were performed on compacted kaolin mixed with tap water and with a 0.5 M NaCl solution, to which constant voltage gradients were applied. Real time monitoring of EKT was done by measuring electrical resistivity in the soil, and pH and electrical conductivity (EC) of the pore fluid. These measurements allowed indirect monitoring of NaCl concentration after comparison the values measured in these experiment with those measured in the test where the soil was prepared with tap water.

2. Material and Experimental Setup

Two EKT tests were performed with white kaolin, compacted using different fluids: tap water and NaCl solution (0.5 M). The clay was mixed with the fluid to achieve a moisture content of 25% and compacted at a void ratio of 0.9. Kaolin clay was used in the research for better understanding of the electrokinetic processes during the EKT. The material was supplied in powder, with 68% in mass of grains with silt size (diameters between 0.075 mm and 0.002 mm) and 31% with clay size (diameters smaller than 0.002 mm). Solid volumetric weight is 26.1 kN/m³.

Liquid limit is 52% and plasticity index is 22%, therefore the material classifies as highly plastic silt (MH) according to the Unified Soil Classification System. The soil prepared with NaCl (0.5 M) shows a liquid limit of 48% and plasticity index 23%. The coefficient of electroosmotic permeability of kaolin measured with distilled water is $1 \times 10^{-9} \text{m}^2/\text{V/s}$.

The electrical resistivity of kaolin with the compaction water content is $33 \Omega \cdot \text{m}$ and decreases to $25 \Omega \cdot \text{m}$ after the saturation with distilled water. The zeta potential value (ZP) for this soil decreases for acidic pH whereas it increases for basic pH. It values -22 mV for pH=7 [8].

The laboratory scale setup developed for EKT is shown in Fig. 1. The setup comprises of a soil cell of dimension 350 x 100 x 150 mm³, with 2 electrode chambers attached to the ends of the cell (Perspex material), a power source Aim-TTi EX354RD 280W (0-35 V and 0-4 A), graphite as anode and steel as cathode. Electrical resistivity of the soil was measured using electrodes inserted in the entries followed by the measurement of pH and electrical conductivity of the pore fluid collected from the entries was measured during all the EKT tests. The electrodes used are made of Nickel coated Stainless Steel with 4 mm diameter and 100 mm length.

The laboratory scale setup developed for EKT is shown in Fig. 1. The setup comprises of a soil cell of dimension 350 x 100 x 150 mm³, with 2 electrode chambers attached to the ends of the cell (Perspex material), a power source Aim-TTi EX354RD 280W (0-35 V and 0-4 A), graphite as anode and steel as cathode. Electrical resistivity of the soil was measured using electrodes inserted in the entries followed by the measurement of pH and electrical conductivity of the pore fluid collected from the entries was measured during all the EKT tests. The electrodes used are made of Nickel coated Stainless Steel with 4 mm diameter and 100 mm length.

The clay was compacted into the EKT equipment perspex box. After compaction, it was saturated by promoting the percolation of the fluid (same as that used at compaction) through the application of variable water head, by filling one of the electrode reservoirs. The electrical resistivity of the soil was measured during the saturation phase in order to check the degree of saturation. The soil was assumed to be saturated after stable readings, even though very few air bubbles were trapped. This also simulates the field conditions. Detailed plan of the test is shown in Tab. 1.
Current intermittence (CI) and Enhanced treatment (Et), were used to reduce the power consumption and increase EKT efficiency [9]. CI consists in applying voltage at a predetermined on/off intervals instead of continuous DC supply. In Et, the fluid in the electrode chambers is replaced by normal tap water in regular intervals in order to maintain the pH near the electrodes to 7. The same enhancement, which is also called conditioning, can also be done by the addition of acid and base buffer solutions or by use of membranes.

Table 1: Plan of the EKT tests conducted on Kaolin.

<table>
<thead>
<tr>
<th>Pore Fluid</th>
<th>Subtest</th>
<th>Duration Hr</th>
<th>V/cm</th>
<th>Fluid in Electrode Chambers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>1A</td>
<td>72 (CI)</td>
<td>1</td>
<td>Tap water</td>
</tr>
<tr>
<td></td>
<td>1B</td>
<td>72</td>
<td>2</td>
<td>Tap water</td>
</tr>
<tr>
<td></td>
<td>1C</td>
<td>72</td>
<td>2</td>
<td>Tap water (Et)</td>
</tr>
<tr>
<td>NaCl Solution (0.5 M)</td>
<td>2A</td>
<td>2.5 (CI)</td>
<td>1</td>
<td>NaCl (0.5 M)</td>
</tr>
<tr>
<td></td>
<td>2B</td>
<td>96 (CI)</td>
<td>1</td>
<td>Tap water (Et)</td>
</tr>
<tr>
<td></td>
<td>2C</td>
<td>24 (CI)</td>
<td>2</td>
<td>Tap water</td>
</tr>
</tbody>
</table>

CI – Current Intermittence; Et – Enhanced treatment

Factors such as CI against the continuous supply of voltage, Et against the unenhanced treatments and different voltage gradients were studied in the EKT tests on soil mixed with tap water and 0.5M NaCl solution. Every subtest was planned in accordance to the features discussed above. Each subtest was conducted for at least three continuous days and the soil was left to stabilize for the next 3-4 days to avoid the history effects of the previous subtest on the
new sub test. The duration was not changed unless harmful circumstances were observed. Such is the case of subtests 2A and 2C, which were extremely reactive tests and were terminated before the time. Based on that it can be suggested a voltage gradient of 1V/cm or less for treating the soils having high amount of Salt concentrations. Higher voltage gradients accelerate the dissolution speed of the Na⁺ and Cl⁻ ions, which causes increase in temperature. The temperature rise from 22 to 38°C in the electrode chamber was observed just within the first few hours of subtests 2A and 2C. In this paper temperature effects were not considered. Only the electrical resistivities measured were analysed to determine the effect of EKT on the ionic concentrations in the soil.

As shown in Fig. 1, for data treatment the soil was vertically divided into four zones named A, B, C, D starting from the Anode. Each zone has 3 entries on each of its sidewalls with vertical spacing of 40 mm, further dividing the soil in 3 levels. The horizontal spacing between the entries in each zone is 100mm. The entries on both sidewalls are identified as A1, A2, A3, B1, B2...D3 (shown in Fig. 1) and A1’, A2’, A3’, B1’, B2’...D3’ (in the back).

3. Results and Discussions

3.1 Longitudinal Electrical Resistivity of Soil

The longitudinal resistivity \( \rho_{\text{long}} (\Omega \cdot m) \) was measured along the length of the soil cell using Wenner method [10]. A current (I) of 10 mA was applied between the outer electrodes of both the sidewalls A1-D1, A1’-D1’, A2-D2, ... and A3’-D3’ and the resistance between the inner two electrodes B1-C1, B1’-C1’, B2-C2 and B3’-C3’, respectively, was determined by balancing the bridge circuit. Eq. (1) was used to calculate the resistivity, where \( V \) is the voltage measured. The resistivity electrodes were inserted to a depth of 30 mm in the soil through the entries which are at a distance (d) of 100 mm. The average of the resistivity values from both sidewalls along the duration of the tests for tap water and NaCl solution can be seen in Fig. 2.

\[
\rho = \frac{2 \pi V}{I} \cdot d
\]

There is an overall decrease in \( \rho_{\text{long}} \) values for all the subtests where tap water was used. It is believed to be due to flushing of the water into the soil structure under the electrical gradient. There was a sudden drop in the \( \rho_{\text{long}} \) values in the first 3-4 hours and then it becomes stable till the end of the test except for a slight rise in 1A and 1B.

Since Et was not applied for 1A and 1B, the pH at the end of the test rose to 3.3 at anode and 11.3 at cathode. The rapid dissociation and association with water molecules leads to a high diffusion coefficient. The ionic mobility for H⁺ and OH⁻ ions controls the chemistry across the soil structure when EKT is not enhanced. Since the ionic mobility of H⁺ is more than OH⁻ ions, the stronger acidic front flows from Anode to Cathode and decreases the charge of the soil thus reducing its electroosmotic permeability. Acidic pH is generated due to H⁺ which reduces the zeta potential (ZP) of the soil and impedes the EKT, whereas basic pH can help in the formation precipitating compounds which sometime can also create impedance in EKT. Therefore, both the acidic and basic conditions need to be avoided during the EKT, which can be done by introducing Et.
Figure 2: Longitudinal resistivity $\rho_{\text{long}}$ for tap water (left) and NaCl solution (right).

On the other hand, for the NaCl solution the $\rho_{\text{long}}$ values found increased along time. This indicates the decrease in the amount of ionic concentration in the soil because the values are becoming closer to those measured in the test where the soil was prepared with tap water. There was a distinct increase in the $\rho_{\text{long}}$ values from the end of 2B to the beginning of 2C. In between the subtests for a period of around 72 hrs, the electrode chambers are filled with tap water. This creates a gradient in NaCl concentration between the soil and the tap water in the chambers. Due to this ionic diffusion during the post EKT effects [11], there is an increase in the rate of the movement of ions caused by the chemical gradient and for this reason resistivity increased.

3.2 Lateral Electrical Resistivity for NaCl

The longitudinal resistivity values previously presented in Fig. 2 correspond to the overall resistance of the soil in between zones B and C. In order to track the changes in the resistivities in every zone, electrical resistivity was measured in the direction perpendicular to the length of the soil cell. By this manner data in the entire volume of the soil can be found.

The lateral electrical resistivity $\rho_{\text{lat}}$ (\(\Omega\cdot\text{m}\)) was measured transverse to the direction of the electrical flow along the length of the soil. To do this, a voltage (V) of 5 V was applied between A1-A1’, B1-B1’, etc. The current (I) flowing between the soil area (A) around the entry was measured in mA unit. The tip to tip distance (L) of the two electrodes in the transverse direction is 60 mm. Using Ohms law, the lateral electrical resistivity was calculated using Eq. (2). An average value of the three entries (A1-A1’, A2-A2’ and A3-A3’) was used for that zone.

$$\rho = \frac{V}{I \cdot L} \tag{2}$$

The $\rho_{\text{lat}}$ values for all the zones during the EKT of NaCl are shown in Fig. 3. As expected, distinct difference in the values of resistivity for different zones can be seen. In 2A, on application of EKT there was a tremendous supply of Na⁺ and Cl⁻ ions to the soil because the same fluid was used in the chamber. Thus a slight decrease in the resistivity values is noticed.
along the time. Tap water was used in the chambers for 2B and 2C, so on the application of
EKT, the Na⁺ and Cl⁻ ions start migrating to Cathode and Anode. A pungent odour of Cl gas
was felt near the Anode chamber.
Particularly in the zones A and D, the \( \rho_{\text{lat}} \) values increases along the time whereas the changes
in the values in zones B and C was very less. While the Na⁺ and Cl⁻ ions are flowing towards
the opposite direction during the most time of the test, the middle zones of the soil are congested
with the ions flowing from both the sides, plus the ion already present in it. Thus it can be said
that, the amount of ions play a vital role in the electrical resistivity values.

![Figure 3](image-url)  
Figure 3: Lateral Resistivity values for the subtests (a) 2A, (b) 2B and (c) 2C.

### 3.3 Electrical Resistivity Calibration Curve

As the resistivity value is strongly related to the concentration of ions in the pore fluid, the
values can be correlated to the NaCl concentration present at that instant during the EKT test.
A calibration curve for Electrical resistivity of kaolin was determined for decreasing
concentrations of NaCl in solutions used for its compaction. These samples were prepared with
voids ratio and moisture contents identical to those adopted for the EKT tests and were saturated
with the same solution to keep salt concentration constant. The electrical resistivity test was
performed as described by [12], in which Wenner method was used in small samples (having 25 mm diameter and 60 mm length) prepared inside PVC tubes and to which steel nails were inserted as electrodes.

Because of the difference in the method of measuring the resistivity for the calibration curve and the lateral resistivity measured in the EKT test according to section 3.2, a conversion factor was used to convert the values from the original calibration curve. This conversion factor was obtained by comparing two techniques of measuring resistivity with different fluids (further details in [13]). The final calibration curve is shown in (Fig. 4) and the best fit for the range of 0.01 to 0.5 M of NaCl.

The calibration curve can now be used to find the distribution of NaCl in the soil during EKT, by considering the values measured. Resistivity ($\rho$) can be converted to the respective NaCl concentrations in Molarity (M) using Eq. (3).

$$M = 1.67 \rho^{-1.31}$$

The values are presented in Fig. 5. The least molarities of 0.06 and 0.12 M was observed in zone A and D, respectively, during the subtest 2C. The resistivity values in these samples are directly affected by the amount of NaCl ions concentration in the soil.

After the application of current, there is flow of ions into the inner two zones B and C from both the ends of the soil, which makes it conductive because of the high concentration of ions. The speed of Na$^+$ and Cl$^-$ ions also affects the conductivity of the pore fluid. The ionic mobility of Na$^+$ is lesser than Cl$^-$ ions [14]. Therefore, Cl$^-$ ions from the zone A travels faster to the Anode, which reduces the total amount of ionic concentration in that zone. Thus the resistivity of zone A is expected to be the least amongst all.
3.4 pH and Electrical Conductivity (EC) of Pore Fluid
During EKT there is continuous changes of pH and EC of the pore fluid. These values were measured in the different zones and are shown in Fig. 6 and Fig. 7, respectively for pH and EC. Only the values found for the test where the soil was prepared with the NaCl solution are presented.
Figure 7: Electrical Conductivity of the pore fluid at the end for the subtests.

It can be seen (Fig. 6) that the acidic and basic fronts are equally moving towards opposite electrodes (H+ concentration near the anode, Zone A, and OH- concentration near the cathode, Zone D). On the other hand, the trend of the EC of the pore fluid (Fig. 7) show to be similar to that of the NaCl concentration (Fig. 5). However, the values found in both cases are not equal because the data obtained from the EC of the pore fluid gives the exact amount of salt concentration present in larger pores of the soil. But, since the ions are also present in micro pores of the clayey soil, the results obtained from the electrical resistivity values will be more reliable than the EC of pore fluid itself.

4. Conclusions

The following conclusions can be made on the experimental study of the EKT performed on the kaolin soil mixed with tap water, as well as with the 0.5 M NaCl solution:

- Using EKT for the removal the salts is very efficient, however the factors such as formation of strong acids/bases, evolution of gases and increase in temperature must be kept in consideration.
- Tap water contains less amount of salt therefore the electrical resistivity values increase and reflect the amount of the water and the voids in the soil.
- The reliability of monitoring the saturation or decontamination of the soil by measuring its electrical resistivity can be further increased by considering the evolution of pH and conductivity of the pore fluid.
- Changes in pH and their effect on zeta potential must be considered to correct the value of electroosmotic permeability, and therefore the rate of EKT.

To conclude, real time monitoring of the decrease in the salt concentration using the electrical resistivity values can be a deciding factor during the EKT as it allows to control or change the working parameters of the on-going test. It can be used as decision making tool, for instance to stop the test when the desired minimum and safe level of contamination is achieved due to EKT.
Acknowledgements
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References
QUANTITATIVE EXPRESSION OF AN ORGANIC CORROSION INHIBITOR (PCI-2014) FOR REPAIRING STEEL BARS IN CONCRETE CONTAMINATED WITH CHLORIDE

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(1) Yantai University, Yantai, China

Abstract
A numerical relation of a permeable organic corrosion inhibitor (marked PCI-2014) for repairing steel bars in concrete with different chloride content was studied. The corrosion current density ($I_{corr}$) of steel bar in chloride-contaminated concrete after absorbing PCI-2014 was measured by linear polarization resistance (LPR) tests. The inhibitor concentration at steel and concrete interface after painting PCI-2014 was calculated by a proposed MCI transport model. Then the correlation equation among $I_{corr}$ of steel bar, MCI concentration at the surface of steel and the free chloride content in concrete was established by statistical analysis. So the minimum MCI requirements for repairing the corroded steel bars in concrete can be calculated. The expression can be used to guide the application of PCI-2014 inhibitor for durability improvement of concrete structure.

1. Introduction
Steel bar corrosion is the key reason of premature deterioration for concrete structure in chloride conditions, which may cause huge economic losses [1–4]. How to repair the corroded steel bar in chloride-contaminated concrete structure in service has become more and more important. Among the measures for repairing the corroded bar in damaged concrete structure, surface painting MCI has drawn much attention due to its characteristics such as nondestructive, economic and efficient [5–10]. However, the quantitative expression and the repair standard for the application of MCIs were few reported, which hindered the MCI application in engineering. In this paper, the influence law of a new MCI marked PCI-2014 to corrosion current of steel bars in concrete with different chloride contents was studied. A relationship among the MCI concentration at steel-concrete interface, free chloride content and corrosion current of steel bar was proposed.
2. Experimental program

2.1 Test preparation
The selected bars as work electrode were machined, polished, washed with ethanol and dried carbon structural steel with 7 mm diameter and 70 mm in length, whose ends were masked with epoxy resin. The roughness of steel bars was less than 3.2μm. Connect wires with one end of the specimens and embed the steel electrode into concrete (cover 31.5mm). Mortars used in this study were ordinary portland cement with strength grade 52.5 MPa, clean fine aggregate and potable city water. The size of mortar specimens is 70.7×70.7×70.7mm³. The water to cement ratio of mortars is 0.45, 0.55 and 0.65, respectively. The specimens with same W/C ratio were separated into four groups with adding 0.25%, 0.5%, 0.75% and 1.0% NaCl (wt.) of the cement respectively. The mortar specimens were cured until 28 days in standard curing room. Then the two bottoms of specimens were initially sealed and then dried in an oven at 60°C until a constant mass was obtained. After the specimens cooling down to room temperature (about 20°C), four side faces of the specimens were exposed to PCI-2014 sources.

2.2 Absorption test of MCI in concrete
The gravimetric method [11] was used to measure the volume of absorbed PCI-2014 after the different immersing time such as 1d, 2d, 3d, 4d and 5d. The absorbed PCI-2014 content (Wₐ, g/kg) in mortar specimens were estimated according the following equation:

\[ W_\alpha = \frac{m - m_d}{m_d} \]  

(1)

Where, \( m \) is the weight of specimen at different absorption time; \( m_d \) is the initial weight of dried specimen.

2.3 The test of free chloride content
The free chloride ion content in mortar was measured according to the ‘hydraulic concrete test procedures SL352-2006’ [12]. The extract of mortar specimen was grinded, soaked and filtered. Then a certain amount of the solution was titrated by silver nitrate standard solution. Potassium chromate was acted as the indicator in titration process. The free chloride ion content can be calculated when brick-red precipitate was generated. The porosity values of specimens are tested by using water absorption test method.

2.4 Test of steel bar \( I_{corr} \)
LPR was measured by using PARSTAT 2273 after immersion in the inhibitor until 1d, 2d, 3d, 4d and 5d. The corrosion current was calculated by the Stern-Geary relationship [13]:

\[ I_{corr} = \frac{B}{R_p} \]  

(2)
where $R_p$ was the measured polarization resistance. $B$ was the Stern–Geary constant. The value of $B$ for steel bars in concrete was typically considered as 26 mV for active and 52 mV for passive corrosion.

3. Results and discussion

3.1 Free chloride ion

The test results of free chloride ion content (to cement, wt.) and the calculated binding rate of chloride ion are shown in Table 1. As seen in Table 1, a lower water cement ratio in concrete would bring a relatively larger C-S-H hydration products. So a stronger combination ability of the chloride ion and a lower free chloride ion content would produce [14].

<table>
<thead>
<tr>
<th>W/C</th>
<th>NaCl (%)</th>
<th>Total Cl (%)</th>
<th>Free Cl- in mortar (%)</th>
<th>Binding rate of Cl- (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>1# 0.25</td>
<td>0.038</td>
<td>0.016</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>2# 0.5</td>
<td>0.076</td>
<td>0.033</td>
<td>56.2</td>
</tr>
<tr>
<td></td>
<td>3# 0.75</td>
<td>0.114</td>
<td>0.054</td>
<td>52.4</td>
</tr>
<tr>
<td></td>
<td>4# 1</td>
<td>0.152</td>
<td>0.068</td>
<td>55.3</td>
</tr>
<tr>
<td></td>
<td>5# 0.25</td>
<td>0.038</td>
<td>0.018</td>
<td>52.4</td>
</tr>
<tr>
<td></td>
<td>6# 0.5</td>
<td>0.076</td>
<td>0.037</td>
<td>50.9</td>
</tr>
<tr>
<td>0.55</td>
<td>7# 0.75</td>
<td>0.114</td>
<td>0.057</td>
<td>49.9</td>
</tr>
<tr>
<td></td>
<td>8# 1</td>
<td>0.152</td>
<td>0.075</td>
<td>50.9</td>
</tr>
<tr>
<td></td>
<td>9# 0.25</td>
<td>0.038</td>
<td>0.022</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>10# 0.5</td>
<td>0.076</td>
<td>0.04</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>11# 0.75</td>
<td>0.114</td>
<td>0.071</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>12# 1</td>
<td>0.152</td>
<td>0.092</td>
<td>39.3</td>
</tr>
</tbody>
</table>

3.2 MCI concentration at interface of concrete-steel

Based on previous study [15], the concentrations of PCI-2014 in concrete versus absorbing time can be calculated by MCI transport model for reactive inhibitors. According to this MCI transport model, the absorbing mass of PCI-2014 can be calculated at different time and at various points. The comparison between experimental and numerical calculation results of PCI-2014 mass in concrete with different water to cement ratios were shown in Fig.1. From Fig.1 we can see that the test results were consistent with numerical results well, manifesting that the MCI transport model mentioned above was reasonable to analysis the transport process of PCI-2014 in mortar.

Therefore, the PCI-2014 mass concentrations at steel-concrete interface could be calculated by the MCI transport model. Table 2 shown the PCI-2014 mass concentrations at steel-concrete interface and porosity values of specimens with different W/C in 5d.
Fig. 1 PCI-2014 content calculated by transport model and by test in mortars

Table 2 The PCI-2014 mass concentrations at steel-concrete interface and porosity values of specimens with different W/C in 5d

<table>
<thead>
<tr>
<th>No.</th>
<th>Porosity (%)</th>
<th>PCI-2014 concentration at steel-concrete interface (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1d</td>
</tr>
<tr>
<td>1#</td>
<td>8.4</td>
<td>0.007</td>
</tr>
<tr>
<td>2#</td>
<td>8.2</td>
<td>0.006</td>
</tr>
<tr>
<td>3#</td>
<td>7.7</td>
<td>0.006</td>
</tr>
<tr>
<td>4#</td>
<td>7.3</td>
<td>0.005</td>
</tr>
<tr>
<td>5#</td>
<td>9.8</td>
<td>0.008</td>
</tr>
<tr>
<td>6#</td>
<td>9.3</td>
<td>0.008</td>
</tr>
<tr>
<td>7#</td>
<td>8.8</td>
<td>0.007</td>
</tr>
<tr>
<td>8#</td>
<td>8.6</td>
<td>0.007</td>
</tr>
<tr>
<td>9#</td>
<td>12.6</td>
<td>0.013</td>
</tr>
<tr>
<td>10#</td>
<td>12.2</td>
<td>0.012</td>
</tr>
<tr>
<td>11#</td>
<td>11.3</td>
<td>0.011</td>
</tr>
<tr>
<td>12#</td>
<td>11.1</td>
<td>0.010</td>
</tr>
</tbody>
</table>
3.3 Corrosion current of steel bars in concrete

The $I_{\text{corr}}$ of steel bars in concrete with different content of NaCl at different absorbing time were shown in Fig. 2. The $I_{\text{corr}}$ of steel bars in specimens with 0.75% NaCl declined to 0.1$\mu$A cm$^{-2}$ after immersed in PCI-2014 for 1d, indicating the electrodes were in passivation state [16]. Even in concrete with 1.0% NaCl, the $I_{\text{corr}}$ of steel bars was reduced to a slightly corrosion state. The corrosion current has a tendency to decrease.

![Graph showing $I_{\text{corr}}$ of steel bars in concrete with NaCl vs. PCI-2014 absorption time]

Fig.2 $I_{\text{corr}}$ of steel bars in concrete with NaCl vs. PCI-2014 absorption time

3.4 Establishment of relationship

$I_{\text{corr}}$ of steel bar is defined as the dependent variable. The concentration of water-soluble chloride ion ($C_{\text{cl}}$) and PCI-2014 content at steel-concrete interface ($C_{\text{in}}$) are defined as the independent variables. The relationship between the three variables was analyzed by nonlinear regression analysis software [17]:

$$I_{\text{corr}} = 4.794 \times C_{\text{cl}}^{1.11} - 5.018 \times C_{\text{cl}}^{1.398} \times C_{\text{in}}^{0.2871}$$  \hspace{1cm} (3)

The coefficients in the equation were calculated by the Least Squares. The determination coefficient [18] $R^2 = 0.932$, suggesting that $I_{\text{corr}}$, $C_{\text{cl}}$, and $C_{\text{in}}$ were in high correlation with each other. Fig.4 was the three-dimensional image of the relationship among them. As it shown in Fig.4, when the chloride content in concrete was low, the requirement of PCI-2014 concentration to repair the steel bar (suppose 0.1$\mu$A cm$^{-2}$) was small accordingly. Water-soluble chloride ion content in concrete increased significantly with the $I_{\text{corr}}$ of steel bar.
increase. The more serious of the steel bar corrosion degree was, the more amount of PCI-2104 was needed to repair the steel in concrete.

Fig.3 Graphical representation of the regression equation

4 Conclusion

The steel corrosion current density with time after absorbing PCI-2014 in concrete was measured to obtain the change of steel bar corrosion degree in chloride-contaminated concrete. The correlation equation among the steel corrosion current, free chloride content and PCI-2014 concentration at steel-concrete interface was established by statistical software. The equation determination coefficient was 0.932, suggesting that the steel corrosion current, water-soluble chloride ion content and PCI-2014 concentration were in high correlation with each other. So the amount of surface applied PCI-2014 to repair the steel bar in chloride-contaminated concrete can be calculated given some parameters. The research provides support for application of MCI to rehabilitate the corroded steel bars in chloride-contaminated concrete structure future.

Acknowledgements

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References

Abstract

In this contribution, the possibility of nanoparticle injection by electromigration, as a novel approach for concrete repair, is presented. The electromigration was employed to inject nanosilica particles and an organosiliconate into normal Portland cement concrete. Several different concentrations of solutions were tested. Incorporation of nanosilica to inner pore system and the effect on the densification were studied by means of SEM-EDS and accelerated chloride penetration tests on treated and control samples. It was found that nanosilica can penetrate a few millimeter zone in a reasonable time and further block chloride penetration. The effect is higher if a higher concentration of nanoparticles is used. Large decrease in chloride concentration in outer parts of concrete later exposed to accelerated chloride penetration test was achieved on samples treated with both nanosilica and organosiliconate solution. Several issues still remain open like particles agglomeration or the change in the subsequent chloride profile in the sample compared to natural diffusion or accelerated migration.

1. Introduction

Traditionally, electrochemical methods are used in concrete industry to solve problems of steel reinforcement corrosion caused primarily by chloride penetration [1]. These methods that are based on electrode potential shift and ionic exchanges can be used e.g. for cathodic protection of steel [2], chlorides extraction or for injection of corrosion inhibitors towards steel rebars [3-5]. Other methods are used for injection of healing substances, e.g. realalkalisation agents, to concrete. Some of the methods like extraction of chlorides and injection of healing agents can be done simultaneously and positive and negative ions transported in concrete against each other [6,7]. All the methods are used as temporary and non-destructive treatments that may lead to the decrease in chloride concentration in concrete.
In this contribution, novel approaches of electrochemical methods used for injection of nanoparticles [8,9] and an organosilicone hydrophobic agent are presented. Depending on the particle/ion charge they can be transported by an electrical field. Nanoparticles are dispersed in colloids and typically bear a negative surface charge. The negative charge is also characteristic for hydrophobic agents. Their transport is limited to one direction that unluckily coincides with the chloride flow. The use of anionic healing agents is, therefore, limited to cases where chlorides are absent or already extracted from the concrete before the nanoparticle or the organosilicone treatment.

2. Materials

2.1 Healing agents
Colloidal nanosilica (NS) particles are known for their beneficial role when incorporated into concrete [10,11]. In this study, NS particles are used as healing agents that are transported in concrete via electrical field. Nanosilica particles are commercially produced in the range of diameters from 5 to 200 nm with varying specific surface from 50 to 250 m²/g. SiO₂ is dispersed in the colloid as particles with anionic surface charge with [-O]- termination stabilized by Na⁺ or NH₄⁺ counter-ions dispersed in water. The pH of the NS solution is typically 9-11. Due to its surface charge the negatively charged particles can be moved by an electrical field towards anode. As another anionic agent, sodium methylsiliconate (SMS) is tested. The pH of SMS is 13-14, thus compatible with concrete. The SMS is a hydrophobic agent that has a water-repelling action when used on outer or inner surfaces of concrete. It is water soluble, it has a small molecular mass ~116 g/mol and its chemical composition is CH₆NaO₃Si.

2.2 Concrete samples
Normal strength concrete specimens were prepared from Portland cement type I (Holcim), quartz sand, gravel and water in the ratio of 415/831/831/182 kg/m³. Water to cement ratio was 0.44. No plasticizer or further admixture was added to the mixture. Samples were cast into cylindrical moulds having 100 mm in diameter and 200 mm in height. The resulting concrete bulk density reached 2360 kg/m³. After 24 hours the samples were demoulded, placed into water and cured until testing. Samples were tested at the age of 40-80 days. Before the tests, 50 mm thick slices were cut from the cylinders and placed into an electromigration chamber.

2.3 Methods
One of the methods for testing the concrete susceptibility to chloride penetration, the rapid chloride penetration test (ASTM C1202), measures the total charge passed through the sample placed in an electromigration unit. The unit comprises of two compartments (upstream and downstream) and can serve for ionic exchange in lab samples. The methodology was adopted in this work for injection of nanoparticles and an organosilicone into concrete using an externally applied electrical field (Fig. 1).
Each compartment contains stainless steel mesh electrode attached to a DC power source with constant electric potential (20 V in our case). Tests were conducted in the lab temperature of 25°C.

Several types of tests have been conducted. The upstream compartment was filled with different concentrations of nanosilica 15-50 wt. %. The samples were labeled hereafter as NS-x. Alternatively, the upstream compartment was filled with sodium methylsiliconate, labeled as SMS-x (see Tab. 1). The downstream compartment was always filled with 0.3N NaOH and the test duration was set to 48 hours for all cases. After the treatment, samples were dried for 24 hours at 50°C to allow bonding of nanoparticles/SMS on inner pore surfaces.

Subsequently, the effect of the treatment was measured in an accelerated chloride penetration test conducted in the electromigration unit. In this test, samples were exposed to injection of 3% NaCl placed in the upstream compartment. Again, the downstream compartment was filled with 0.3N NaOH. The effectiveness of the nanosilica/organosiliconate treatment was checked in this test by measuring the chloride concentration profile in the sample. The total (acid soluble) Cl⁻ concentration with respect to concrete mass was assessed by ion selective electrodes from powder collected in different sample depths.

Table 1: Nanoparticle and organosiliconate properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration [wt.%]</th>
<th>Specific surface [m²/g]</th>
<th>Particle size range [nm]</th>
<th>pH</th>
<th>Molecular weight [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS-1</td>
<td>15</td>
<td>234²</td>
<td>5-50</td>
<td>9-11</td>
<td>-</td>
</tr>
<tr>
<td>NS-2</td>
<td>30¹</td>
<td>198-250¹</td>
<td>undeclared</td>
<td>8.6⁻</td>
<td>116.12</td>
</tr>
<tr>
<td>NS-3</td>
<td>50¹</td>
<td>50²</td>
<td>19-156²</td>
<td>9-11</td>
<td>-</td>
</tr>
<tr>
<td>SMS-1</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>13</td>
<td>116.12</td>
</tr>
<tr>
<td>SMS-2</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>13</td>
<td>116.12</td>
</tr>
</tbody>
</table>

¹Data taken from product sheet, ²Data taken from [12]
3. Results

3.1 Nanosilica and SMS penetration

Detection of the penetration front of nanosilica into concrete was monitored with element analysis in electron scanning microscope (SEM-EDS) by increased concentration of Si in the concrete surface layer. Line scans were performed at several arbitrary positions. An increased concentration was detected in the surface layer with the thickness of about 3 mm (Fig. 2). Therefore, the effect of Si deposition and sealing of the pores was justified. However, it is worth to note that tests were conducted as voltage controlled with the duration of 48 hours meaning the current changed (decreased) over time. Thus, the effective injection of nanosilica also changed already from the beginning as the sample resistance increased in time with the treatment and the NS injected volume was lowered. This was manifested also by the agglomeration of SiO₂ between the sample surface and cathode. The most likely reason for this behavior is that the mobility of newly injected particles decreases with time as the pores are sealed and blocked by already injected particles. The sample resistance increases during the test leading to the decrease of an electrical current which in turn lowers the amount of NS injected. The evolution of the current passed through the sample during different kinds of tests is depicted in Fig. 3.

![Figure 2: Increased concentration (cps=count per seconds in X-ray diffraction) of Si at the surface (the green line) on a nanosilica injected sample.](image-url)
Fig. 3 Time course of the charge passed through the sample during nanosilica injection.

It can be seen in Fig. 3 that in the control sample (upstream chamber was filled with chloride solution) the current is slightly decreasing with time. The current is almost constant in the case of SMS treatment meaning SMS bears the charge equally or even better than chlorides. There is a significant decrease of the current in the case of NS injection for reasons already mentioned (yellow curve in Fig. 3). An interesting situation happens if the chlorides are injected through already NS treated sample. The current increases in the first third of the process and than it stabilizes having the trend similar to non-treated samples. The accelerated migration test clearly demonstrates that NS acts as an efficient barrier to chloride transport, although the effect is limited in time. After one third of the test time chlorides break a barrier and start to flow more easily.

3.2 Chloride penetration

The effectiveness of the treatment was measured in accelerated chloride penetration tests. Chloride profiles evaluated after the tests can be seen in Fig. 4. The red line in Fig. 4 shows a typical concentration profile as received on untreated (control) samples. The NS and SMS treatments cause a significant decrease in the concentration at surface and subsequent layers. It shows a positive effect of both NS and SMS treatments. The most prospective treatment in terms of the largest decrease in Cl concentration was found to be NS-3, i.e. the sample treated with 50% nanosilica solution. The concentration decrease is very notable, about 75% (Fig. 4). On the other hand, the profiles show some increase of concentrations in deeper parts of the sample, again for all treatments. The reason for this behavior can lie in the accelerated procedure itself. When concrete is exposed to an electric field all free ions from the pore solution are moved towards electrodes with an opposite charge. It might happen that some leaching of e.g. Ca$^{2+}$ ions can cause an increase of the open porosity. Later, this can lead to easier penetration of chlorides in an accelerated test.
4. Conclusions

It was shown in the paper that the injection of nanoparticles and a hydrophobic agent into concrete by the electromigration technique is feasible. Surface concrete layers can be effectively improved by nanosilica or silicate and more than 70% decrease in subsequent accelerated chloride penetration tests can be achieved on samples treated with 50% nanosilica solution. Nanosilica works as densifier and blocks capillary pores inside the specimen. Similar, but not as high, decrease in the chloride concentration was achieved by sample treatment with an organosilicate. Due to the anionic character of all tested agents, the treatments are limited to cases where the initial chloride concentration is zero or to concretes from which chlorides have already been extracted. To avoid such limitation other than anionic agents are considered for future investigations.

Acknowledgement

Financial support of the Czech Science Foundation (project 16-11879S) is gratefully acknowledged. Supplying of nanosilica samples by AkzoNobel is thankfully acknowledged as well.

References

ELECTROCHEMICAL CHLORIDE EXTRACTION: EFFICIENCY AND SIDE EFFECTS WITH DIFFERENTS MINERAL ADMIXTURES

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(1) Eduardo Torroja Institute (IETcc), Spanish National Research Council (CSIC)

Abstract

Deterioration of concrete structures occurs mainly because of contamination caused by salts or other agents that provoke the penetration of ions, such as Cl\(^-\) through concrete. In addition, electrochemical chloride extraction (ECE) is used as a technique for mitigating chloride-induced corrosion of the reinforcing bars in concrete structures. However, the mechanisms of ion migration, as well as the passivation process are still not well understood. The main objective of this paper is to evaluate the effectiveness of the Electrochemical Chloride Extraction (ECE) process in mortar specimens with various mineral admixtures, evaluating accumulative charged density, free chloride and total chloride content and electrochemical measurements such as I\(_{corr}\) and E\(_{corr}\) the in all the specimens. To demonstrate the feasibility of applying this technique on full-sized concrete structures and to identify needed improvements to the technology, this research work was tried on four chloride contaminated mortar typologies with different mineral admixtures such as silica fume, fly ash, and slag. For all specimens, an anode system consisting of felt-sandwiched catalyzed titanium mesh kept wet by an electrolyte was used. An electrical charge was applied between the anode and the steel bar for different periods on time depending on the admixture.

In the specimens fabricated with CEM I with an 8% of replacement in silica fume or fly ash, and CEM I without any additions, the majority of the chloride ions were removed from the concrete at the depth of the steel bars and the re-passivation of the steel was detected by non-destructive electrochemical techniques while the treatment was still connected. For the case of CEM III (with high amount of slag), even after the treatment was applied and the test time was much longer than in the other specimens, free and total chloride content was higher than the allowed in the standards.

1. Introduction

Electrochemical chloride extraction (ECE) is an effective way to extract chlorides which have infiltrated or been mixed into reinforced concrete by means of electrochemical instrument which supplies an external electric field between concrete rebars (cathode) and an exterior metal electrode (anode). Under the force of electric field the chloride ions in concrete will be transferred through the pore solution to the exterior electrolyte in contact with the anode. Coincidentally, the electrochemical reactions occurring at the steel surface provide the evolution of hydroxyl ions by the reduction of oxygen and water. This process alkalises the concrete in the vicinity of the rebar.
The purpose of chloride extraction is to rehabilitate a reinforced concrete part from corrosion activity and to provide long term corrosion protection of steel reinforcement in concrete which has been affected by chloride and to re-establish self-protection ability. The duration of treatment is from several weeks up to as much as several months, depending on the amount of accumulated chloride, the permeability of the concrete, the layout of the reinforcement and other factors. The decision to terminate the application should be made according to the specific requirements detailed in the technical specification [1]. In this way, the ECE process will remarkably decrease the chloride concentration near reinforcements, keeping the reinforcements from further corrosion, therefore the reinforced concrete structure will be effectively protected and its service life will be prolonged [2][3].

Even thought the relation between electrochemical migration and diffusion coefficient of Cl$^-$$^-$ ion through concrete has been more and more closely discussed by the scientific community [4][5][6][7], the effects of mineral admixtures on chloride extraction efficiency have not been enough investigated [8][9]. From this viewpoint, in this work the influences of silica fume, fly ash and slag have been evaluated on the ECE treatment.

As is illustrated in [1], there is no explicit, single criterion for the termination of the treatment. Because of the uneven conditions in the concrete, no specific correlation with electrical measurement values can be given. The decision when to terminate the application shall be made according to more than one of the following: Chloride content, accumulative charged density and $I_{corr}$ & $E_{corr}$ values. In a previous work, that was carried implementing ECE treatment in two of contaminated OPC mortars: one contaminated with 2.5% of Cl$^-$$^-$ (as NaCl) and another contaminated with 5% of Cl$^-$$^-$ (as CaCl$_2$) [10], other alternative indicators able to be monitored during the treatment were proposed, and the application of these monitoring techniques in other mortar typologies is now under study.

The main objective of this paper is to evaluate the effectiveness of the Electrochemical Chloride Extraction (ECE) in mortars with mineral admixtures, evaluating accumulative charged density, free chloride and total chloride content and electrochemical measurements such as $I_{corr}$ and $E_{corr}$.

2. Experimental procedures

Prismatic mortar specimens (size 7x7x7 cm) of the mixture proportions given in Table 1 were cast with three embedded steel rebars. A substitution of 8% of cement (CEM-I) was applied in the dosage of the mixes identify as FA (fly ash) and SF (silica fume). In the case of SLAG typology, a CEM III is used (as is specified in the table). The amount of 5.0% chlorides by mass of cement were added as NaCl to the mixing water. All specimens were demoulded after 24 h and were cured for 28 days at a 100% relative humidity, RH, chamber. Fresh concrete properties are given in Table 2.

<table>
<thead>
<tr>
<th>MATERIALS</th>
<th>CEM I</th>
<th>FA</th>
<th>SF</th>
<th>SLAG</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEMENT*</td>
<td>675 gr</td>
<td>621 gr</td>
<td>621 gr</td>
<td>675 gr</td>
</tr>
<tr>
<td>SAND</td>
<td>2025 gr</td>
<td>2025 gr</td>
<td>2025 gr</td>
<td>2025 gr</td>
</tr>
<tr>
<td>NaCl</td>
<td>55,70 gr</td>
<td>55,70 gr</td>
<td>55,70 gr</td>
<td>55,70 gr</td>
</tr>
</tbody>
</table>

Table 1: Mixture proportions and exposure regimes of the mortar specimens.
Table 2: Fresh state characterization: Density, occluded air and mortar fluidity tests.

<table>
<thead>
<tr>
<th>SPECIMEN</th>
<th>Density Kg/dm³</th>
<th>Ocl air %</th>
<th>Ø final cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLAG</td>
<td>2.08</td>
<td>7.2</td>
<td>23</td>
</tr>
<tr>
<td>CEMI</td>
<td>2.05</td>
<td>9</td>
<td>22.5</td>
</tr>
<tr>
<td>SF</td>
<td>2.02</td>
<td>9.9</td>
<td>19.5</td>
</tr>
<tr>
<td>FA</td>
<td>2.12</td>
<td>6.1</td>
<td>23</td>
</tr>
</tbody>
</table>

Table 3 depicts Electrical resistivity values at early age state and after 28 days, which reflect the different characteristic of the various mineral admixtures because of their hydration capacity. Its demonstrates that the resistivity measurement can imply the different chemical and physical behaviour of different mineral admixtures in cementitious materials [11][12].

Table 3: Electrical Resistivity at the age of 24 hours and 28 days.

<table>
<thead>
<tr>
<th>SPECIMEN</th>
<th>24 hours (ΩKΩcm)</th>
<th>28 days (ΩKΩcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLAG</td>
<td>0.036</td>
<td>12.937</td>
</tr>
<tr>
<td>CEMI</td>
<td>0.080</td>
<td>0.520</td>
</tr>
<tr>
<td>SF</td>
<td>0.069</td>
<td>0.377</td>
</tr>
<tr>
<td>FA</td>
<td>0.057</td>
<td>0.446</td>
</tr>
</tbody>
</table>

2.1 Electrochemical evaluation before ECE treatment

The electrochemical parameters evaluated in the specimens before ECE treatment were:
- Electrical resistance, Re
- Half-cell potential, Ecorr, vs. Ag/AgCl/3M KCl reference electrode placed on the specimen surface.
- Polarization Resistance, Rp, using the three-electrode arrangement (linear swept rate 10 mV/min).

When stable corrosion rate values were obtained using the Rp method, the ECE treatment was applied.

2.2 ECE treatment application
To detect the influence of the electro-remediation treatment, only two of the three rebars (Sb and Sc) were connected to the protection system, leaving the third rebar (Sa) without connection to the current that results in ion migration.

The Titanium mesh (TiMMO) made by coating titanium with a combination of metal oxides that are electrically conductive, was placed below the underside of prims, as anode. The total area covered by the anode was 49 cm². A wet sponge was placed between the specimen and the mesh, assuring permanent electrolytic contact between the anode and cathode as Figure 1 depicts. Ag/AgCl textile repositionable electrode (3M™Red Dot™) has been used to monitor the electric potential of the different steels during the treatment constantly.

The ECE treatment was applied potentiostatically. The initial voltage applied was 12 V. This value was increased in three steps during the tests according to the total accumulated electric charge density reached, σ (calculated in each specimen according to the specimen area covered by the anode, 49 cm²):

- When the accumulated charge reached 1500 Ah/m², the voltage was increased to 16 V.
- The maximum voltage applied was 20 V and it was applied when the accumulated charge was 2000 Ah/m².
- The treatment was stopped when reaching 4500 Ah/m²

This methodology was applied in all the cases except for the slag typology, as will be shown in the results.

The same electrochemical parameters that were measured before the current application were evaluated twice a week during the whole ECE treatment (current on). The only difference was that in this case, \( R_p \) measurements were carried out in two different ways: one using the disconnected steel as the working electrode and the other one using the two steel rebars connected to the ECE treatment as the working electrode. The counter electrode used for these measurements was an external stainless steel mesh placed in the concrete surface (face parallel to the anode).

Once a week, the current was disconnected and electrical resistance, depolarized potential, and \( R_p \) after 24 h of depolarization were also taken on the three steel rebars. \( I_{corr} \) was calculated from \( R_p \) values using the Stern Geary equation.
2.3 After the ECE treatment

The corrosion rate, $I_{corr}$, was also calculated from $R_p$ after the end of the treatment. Approximately, 3 months after the end of the treatment, the specimens were broken. Chloride profiles in mortar were determined by chemical analysis to check the real percentage of chlorides in the cement matrix. On the one hand, total chloride content was determined at different depths in the covering of each steel. On the other hand, free chlorides were also determined to know the proportion of chlorides that were not combined with the alkali cement phases. These “free chlorides” are the ones that are able to migrate through the concrete cover provoking the rebar corrosion.

3. Results and discussion

3.1 Accumulative Charged Density

First parameter analysed is accumulative charged density. This parameter together with chloride content after ECE treatment and $I_{corr}$ & $E_{corr}$ are the most frequently used parameters to determine the efficiency of the treatment [1]. Enough efficiency is usually assumed if a certain total electrical charged density $\sigma$ (Ah/m²) has been passed [13]. However, previous results [14], show that due to the different micro-structural characteristics of the different cement types (indicated by the resistivity) and their different binding ability, this parameter is not reliable enough to inform on the re-installing of passivity. In present experimentation, a total electrical charged density of 4500 Ah/m² was reached for CEM I, SF and FA typologies (Figure 2). Treatment time varies from 70 up to 120 days depending on the specimen properties and the wetting conditions. In the case of SLAG typology, the total charge density reached after more than 350 days of test was 1800 Ah/m², which is under the limit of 2000 Ah/m² that the standards recommend. This difference is due largely to the high electrical resistivity of this dosage, as is shown in Table 3.

![Figure 2: Accumulated charged density.](image-url)

3.2 Monitoring $I_{corr}$ values (through LPR) and $E_{corr}$, before, during and after the ECE treatment.

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Figure 3 shows the evolution of $E_{corr}$ & $I_{corr}$ values (Vs Ag/AgCl) before, during and after treatment in some examples of the different types of mortar under study. The values during ECE treatment shown in these figures correspond to periods measured system disconnect (after 24h depolarization). These values assessed during treatment not appear to provide reliable information regarding the effectiveness.

About $E_{corr}$ values, the tests performed on specimens CEM I show values before starting ECE treatment of around -600 mV vs Ag/AgCl electrode, that is, high probability of corrosion according to ASTM C876-09. These values descended drastically after the end of treatment to low corrosion risk values in the two steels embedded that are connected to the treatment (Sb and Sc) (-180 mV vs Ag/AgCl), remaining in high probability of corrosion values in the non connected steel (Sa) (-400 mV vs Ag/AgCl). The behaviour of SF and FA is similar than the one registered in CEM I. $E_{corr}$ values are more negative than -500 mV before starting treatment. After treatment it have not been reached values less negative than -300 mV in the not connected steel (Sa) values, which indicate corrosion risk in these cases. In the other hand, steels which have been connected to treatment reach values below the threshold set in ASTM C876-09[15] as low corrosion risk. SLAG samples have values between -450 and -650 mV before treatment. The peculiarity of this type, with high resistivity values, increases treatment time without turning to $E_{corr}$ values under the high corrosion risk threshold.

About $I_{corr}$ values, this parameter after completion of treatment and stabilization value (several weeks after disconnection) is considered to determine the quantitative reduction of corrosion in steel [16][17][18]. Figure 3 show $I_{corr}$ values evaluated before, during and after the ECE treatment. Values during treatment, despite being recorded in the periods of disconnection, 24h after depolarization, do not indicate the state thereof as shown in the graphs.

In the study in CEM I specimens, a decrease of $I_{corr}$ from 1 μA/cm² to values below 0,2 μA/cm² for treatment connected steels (Sb and Sc) it was observed while the Sa steel, not connected, showed values indicative of active corrosion (higher than 0,2 μA/cm² according to[1]). This is in concordance with the previous study cited before [14]. In the case of FA and SF, note that, even thought the tendency is similar than in CEM I, the differences after treatment between steel Sa (not connected) and connected (Sb and Sc) are smaller in the case of FA and SF than in CEM I. In all cases the not connected steel (Sa) shows values above the threshold depassivation (active corrosion), although values are about one order of magnitude higher in the case of CEM-I than in FA and SF. With regarding to SLAG typology, as has been shown in Figure 3, the test was stopped before reaching enough charge density to repassivate the steels.
3.3 Quantitative analysis of chloride profiles at the end of treatment

When stable $E_{corr}$ and $I_{corr}$ values were reached after the end of the treatment, specimens were broken and chloride content was determined. After acid attack, quantitative determinations were made by the potentiometric method. Both, free chlorides and total chlorides (uncombined with cement phases and therefore soluble in water and liable to diffuse through the concrete pores) following the recommended procedures RILEM TC 178-TM were determined [1].

It can be outlined that in SF & CEM I specimens have suffered a reduction of chlorides below the marked in the Spanish structural concrete standard [19] by the maximum limit of chlorides in the site work concrete ($0.4\% \text{Cl}^-$ total related to the cement mass) in the rebars vicinity. Notably, despite having made the extraction towards a single face of the specimen, the chloride reduction was greatly reached.

In this essay, The CEM I typology has values well below the limits set by the EHE for both total and free in every rebar and at all depths, except in the area near the anode. It is observed increasing concentration values in the area near the anode.

In the case of SF, a reduction below the threshold established by the EHE is met in the vicinity of the rebars connected to the treatment, although the quantity increase in chloride concentration in the vicinity of the anode is observed and a reduction in treatment efficiency in the area beyond the cathode (rebar). Not connected rebar presents lowest percentages of reduction.
For FA, note, that the % reduction in this type are lower than those obtained in SF and CEM I, not getting itself to values below the threshold set by the EHE in the case of some of the probes. As in the case of SF, chloride accumulation in the area beyond the cathode is observed, (Figure 4). The analysis of this parameter in the SLAG type specimens shows that total chloride content is in all the cases over the limit established by the Spanish regulation, but it is remarkable to mention that both free and total chloride content determined close to the central steel connected to the treatment is lower than the values obtained in the external rebars. However, electrochemical results from Figure 4 show corrosion rate values indicating active corrosion in the central steel (Sb), and in Figure 2, charge density graph shows a deficient progress of the treatment. So, the treatment is not effective for this mineral admixture.

Besides, in general, mineral admixtures are improving the combination of chloride with the cement phases, in some cases (FA, SF) see how although the total chloride remain high (as a result of the high degree combination) free chloride content decreased with treatment. Trying to correlate the results provided by the nondestructive electrochemical techniques evaluation after the treatment (quantification of the corrosion rate), coincidences are clear for rebars connected to treatment, showing low $I_{corr}$ values consistent with negligible levels of chloride ion concentration.
4. Conclusions

The conclusions drawn from this preliminary study carried out in specimens fabricated with CEM I, CEM I with a substitution of 8% in FA and SF, and CEM III (high slag content) contaminated with chlorides, show that the behaviour of these admixtures in relation to an ECE treatment is different depending of the additions.

Examples of the monitoring of four different mixes (FA&SF&CEMI&SLAG) during ECE by different electrical and electrochemical techniques are shown. In the case of using CEM III (slag), no steel repassivation reached. In the cases of SF, FA the repassivation of the steels connected to treatment were reached in the same way than in plain CEM I specimens, which means that a substitution of 8% in SF of FA do not affect drastically to the treatment efficiency.

It is noted as the different combination of chlorides (total and free chlorides) affects the four types of concrete studied. Besides, in general, mineral admixtures are improving the combination of chloride with the cement phases, in some cases (FA, SF) total chloride remain high (as a result of the high degree combination) while free chloride content decreased with treatment. Notably, electrical resistivity values at early age state and after 28 days, which reflect the different characteristic of the various mineral admixtures because of their hydration capacity, affects to the ECE treatment. Both factors (combination of chlorides and electrical resistivity) are those that have most affected the development of treatment.

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References


EFFECT OF PHASE DISTRIBUTIONS ON THE CORROSION OF QUENCHED AND SELF-TEMPERED (QST) STEEL REBARS

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Abstract
Quenched and Self-Tempered (QST) steel reinforcing bar (rebar) has a composite phase microstructure with ductile core of ‘ferrite-pearlite (FP)’ and hard peripheral ring of ‘tempered martensite (TM)’. Typically, a good quality QST rebar will have a peripheral TM ring with uniform thickness and constituting about 25% of the cross-sectional area (CSA). This continuous TM microstructure at the periphery is expected to provide good corrosion resistance. However, a separate two-year laboratory study observed higher than expected rates of chloride-induced corrosion for QST rebars. This paper presents the research performed to find the reason behind this high corrosion rates of QST rebars. The variations in the distribution of TM and FP microstructure of rebars (8, 12, and 16 mm diameter) collected from India, Germany, Hungary, Italy and Russia were studied. Etching of rebar cross-sections using 5% Nital solution, revealed the discontinuous peripheral TM ring and the presence of exposed FP at the periphery of some rebars. Then, the possibility of corrosion-cell formations at these peripheral TM-FP interfaces was investigated. Five small coupon specimens each of FP and TM phases were extracted from the rebar and metallographic specimens were prepared. Then, a series of Open Circuit Potential (OCP) and Linear Polarization Resistance (LPR) tests were performed on these specimens immersed in simulated concrete pore solutions with various chloride concentrations. In general, the FP phase is found to be more vulnerable to chloride-induced corrosion than TM phase – indicating a high probability of localized corrosion in QST steel rebars with incomplete TM ring. Therefore, there is a need for better quality control in the manufacturing to ensure that complete TM ring is formed at the periphery of the QST rebars.

1 INTRODUCTION

Corrosion of steel is an inevitable global issue in the reinforced concrete construction industry in the present century. The technology and skills in the industry constantly try to address a cost of corrosion of approximately 2.4 trillion US Dollars [1] worldwide (as per the statistics from World Corrosion Organization in 2010) to maintain the reinforced concrete, steel, and steel-composite structural systems. This cost is more than 3% of global GDP from 2010 and almost the same as India’s GDP in 2015. The concrete reinforcing bar (rebar) production per year has grown worldwide from 131 million metric tons to more than double (280 million metric tons) the total production in just ten years [2]. This scenario calls for a better understanding of the types of corrosion in the steel used in regular construction industry. The
current construction industry includes a specially processed Quenched and Self Tempered (QST) steel rebar with a dual phase microstructure. The dual phase composition gives good strength and better ductility for QST steel rebar when compared to the conventional bars (Cold-Twisted Deformed (CTD) steel, mild steel etc.). Thus, now-a-days, QST steel serves as a primary option for reinforcement in concrete construction and has been widely employed for more than a decade.

The QST steel rebars have a composite microstructure with a continuous peripheral ring of ‘tempered martensite’ (TM) and a core of ‘ferrite-pearlite’ (FP) phases, as shown in Figure 1 (a). Well-controlled quenching and tempering processes are necessary to achieve this cross-section.

![Figure 1 Cross-sections of good and poor quality QST rebars](image)

In general, the QST steel bars are expected and marketed as a better corrosion resistant steel than the conventional Cold-Twisted Deformed (CTD) steel rebars. However, based on a two-year laboratory study, Karuppanasamy and Pillai (2016) [3] reported that the chloride-induced corrosion rates for QST rebars are statistically similar to that of CTD steel rebars. Based on a subsequent study, Nair and Pillai (2015) [4] observed discontinuities in the peripheral TM ring and exposed FP phases on several QST steel rebars, as shown in Figure 1 (b). The presence of such discontinuous peripheral TM phases and/or exposed FP phases could be the reason for the high corrosion rates observed by [3]. The electrochemical behavior of these FP and TM phases in QST steel rebars and their impact on the corrosion of rebar with discontinuous TM phase is not well-reported in literature and is the focus of this paper. This paper is a continuation of Nair and Pillai (2016) [5], which presented preliminary work on the microstructure variations and possible localized corrosion of QST rebars exposed to chloride environments.

Literature generally agrees that QST steel rebars have better corrosion resistance than CTD rebars. This is on the basis of electrochemical tests on steel alone, or steel embedded in concrete/ mortar. Pradhan and Bhattacharjee (2007, 2009a) [6, 7] studied QST steels manufactured by two different technologies (Thermex™ and Tempcore™). Tempcore™ QST was found to perform better than Thermex™ QST rebars. Both Thermex™ and Tempcore™ were found to be better corrosion resistant than the CTD steel rebars embedded in different cementitious systems. Pradhan and Bhattacharjee (2009b) [8] also found that Tempcore™ QST steel has a higher chloride threshold and longer corrosion initiation period when compared to
the other steel rebars under the scope. The reason for this performance is attributed to the outer ring made of TM. It is claimed to be a well-established fact that the TM microstructure is more corrosion resistant than FP in Mohanty and Jha (1998) [9]. But, Al-rubaiey et al. (2013) [10] reported that FP is more resistant to average general corrosion than TM and that both FP and TM exhibit statistically similar resistance against localized corrosion due to chlorides. This could pose to be an issue in the case of poor quality QST rebars with discontinuous TM rings. On the other hand, Karuppanasamy and Pillai (2016) observed statistically similar corrosion rates for both QST and CTD steel rebars. The mixed opinions on the corrosion resistance for QST steel rebars could be the result of an unexpected corrosion mechanism - possibly a corrosion-cell formed between the exposed phases of TM and FP on the surface of QST rebars used in concrete structures - which is not well-reported in literature. This paper tries to address this special case by studying the electrochemical characteristics of individual TM and FP phases isolated/extracted from QST rebars that are used in regular concrete construction industry.

2 MATERIALS AND METHODS

The study is divided into two stages: 1) microstructure phase distribution study and 2) corrosion characteristics of QST steel rebars. The scope of the study is limited to 8, 12 and 16 mm diameters with yield strength grade of 500 N/mm². The steels were manufactured in Italy, Germany, Hungary, Russia (and collected from Germany) and India. Stage 1 was executed with around 50 steel specimens and Stage 2 with 10 steel specimens (5 each from TM and FP phases).

2.1 Stage 1 - Microstructure phase distribution study

The primary objective in this stage was the identification of cross-sectional phase distribution by etching of steel rebar cross sections. The etching was done using 5% Nital solution (ASTM E407) [10]. The etched cross sections are photographed and analyzed for the area constituted by TM and FP separately. The Area Ratio for TM (AR_TM) is defined as the percentage of the TM phase in the total cross-sectional area of the rebar. The AR_TM is quantified by analyzing the photographs using Image J™, a free open source image analysis software.

2.2 Stage 2 – Electrochemical/Corrosion Characteristics

This study investigates the electrochemical response of FP and TM in Simulated Pore Solution (SPS) environment with different chloride concentrations. Repeated measurements of OCP and LPR were obtained on same metallurgical coupon specimens after exposing to SPS with different chloride concentrations. The coupons used on these specimens were cut from a 36 mm QST steel rebar. As shown in Figure 2, the TM and FP coupons were extracted from the mother rod by Electron Discharge Wire (EDW) cutting under water at 20°C. The area of each steel coupon is approximately 1.5 cm². The actual area was used in the calculation of corrosion rates. As shown in Figure 3 and Figure 4, these steel coupons were hot and pressure mounted in bakelite powder with a mould diameter of 25 mm and connected to electrical lead wires. The hot mounting was done at a temperature of 150°C and pressure of 160 bars. The specimens were first exposed to Chloride-Free SPS and then to chloride-contaminated SPS as described next.
2.2.1 Passivation period

The specimens were immersed in chloride-free SPS for 7 days so that a stable passive layer, as in the case of reinforced concrete systems, would form on the surface of coupons. The SPS was prepared by mixing 0.3g Ca(OH)$_2$, 10.4g NaOH and 23.23g KOH in 967g of distilled water. Poursaeed and Hansson (2007) [12] has recommended a minimum of 3 days of immersion in SPS for the formation of stable passive film on steel surfaces. In this study, the Open Circuit Potential (OCP) was monitored at an interval of 12 hours for 7 days and the formation of a stable passive film was confirmed based on the stable OCP values observed. Figure 5 shows the experimental setup (corrosion cell and potentiostat) for corrosion measurements.
2.2.2 Response in chloride environment

After immersion in chloride-free SPS for 7 days, the passivated specimens were immersed in chloride-contaminated SPS (concentration starting from 0.5 to 2.2 %Cl⁻ by weight of total solution; at an increment of 0.1 %Cl⁻). In order to allow sufficient time for the chloride-induced corrosion, if any, to initiate and propagate, an immersion period of 8 hours was maintained for each level of chloride. At the end of 8 hours, the OCP and LPR tests were performed and the polarization resistance (Rp) was determined. For the LPR test, the potential sweep was ±10 mV (with respect to OCP) and the sampling rate was 0.1667 mV/s. The Rp was calculated using the corrosion current (I_corr) and the Stern-Geary equation. The Stern-Geary coefficient was assumed to be 26 mV.

3 RESULTS AND DISCUSSION

3.1 Microstructural phase distributions

As mentioned earlier, etching with 5% Nital can reveal the TM and FP phases with a dark grey outer ring (TM) and a lighter grey core (FP), respectively. The results from the etching test is given in Figure 6. Most of the QST steel rebars collected from various countries (A to E) showed a complete/continuous TM ring at the periphery. However, there were a few specimens with discontinuous TM rings, especially with 8 and 12 mm diameter rebars (say, Country C). A general observation is that the chances for the presence of discontinuities decrease with increasing rebar diameter. This is probably because the TM ring thickness decreases in rebars of lower diameters and may become difficult to control in the manufacturing line, unless proper quenching methods are adopted.
As shown in Figure 6, the grey-shaded images/photographs were obtained from around 50 steel specimens subjected to etching. The analysis of these grey-shaded images provided the quantitative estimates of the area of TM ($A_{TM}$) in these 50 specimens, see Figure 7. The data shows that $A_{TM}$ lies approximately between 25 to 47% (average of 34.5%) of the total cross section area. $A_{TM}$ is observed to increase with the diameter of the steel bar. This indirectly suggests that more quality control is needed during the manufacturing of lower diameter rebars since the thickness of TM is very less when compared to that in rebars of larger diameters. Hence, sufficient control will be required in the manufacturing line to avoid TM discontinuities in QST steel rebars with small diameters (say, less than or equal to 12 mm).

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<td>16</td>
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</table>

Figure 6: Cross-sections of QST steel after etching

Figure 7: TM area ratio variation
3.2 Electrochemical/corrosion responses

As mentioned earlier, a series of LPR tests were conducted on the test specimens and $I_{\text{corr}}$ (with respect to the increasing chloride concentrations) were determined and are given in Figure 8. It can be observed that the corrosion rates of FP (hollow markers) are higher than that of TM (dark markers). This indicates that different areas can corrode at different rates when discontinuous TM phases (i.e., discontinuous TM ring) and exposed FP phases are present. Thus, the systems with QST steel rebars could fail to meet the expected or design life in the presence of discontinuities TM phases at the periphery. Note that the Specimen TM4 started to malfunction at around 1.3 %Cl$. In TM1, corrosion was visible on the face of the steel specimen which shows the sudden increase in the corrosion rate. FP1 seem to start at a lower rate of corrosion at 0.6 and 0.7 %Cl$ and drastically increase at 0.8. In general, it can be concluded that the FP phase observed on QST steel rebars is more vulnerable than the TM phase.

![Figure 8: Corrosion rate ($I_{\text{corr}}$) as a function of Cl- concentration in SPS](image)

One of the major challenges faced in the slow degradation of bakelite (mould material) in the SPS solution – resulting in coupon specimen getting detached from the mould. Therefore, long exposure study (say, more than 10 days) is difficult. However, further tests are ongoing on specimens (molded at higher temperature and pressure) with enhanced resistance against alkaline environment.

4 SUMMARY AND CONCLUSIONS

This paper presented data on the variation in the area of ‘ferrite-pearlite’ (FP) phase and ‘tempered martensite’ (TM) phase in the typical QST steel rebars that are i) manufactured and collected from India and ii) manufactured in Italy, Germany, Hungary, Russia and collected from Germany. The observations on etching the rebar cross sections have shown that the poor
quality control measures during the manufacturing/quenching can lead to discontinuous TM phase at the periphery. The TM phase constitutes an area of approximately 25 - 45% of the total cross-sectional area and ATM decreases with decreasing diameter of the rebar.

The corrosion tests on TM and FP specimens isolated from a QST steel rebar shows that FP is more vulnerable to chloride-induced corrosion than TM. This could result in a differential and faster chloride-induced corrosion than expected in the rebars with discontinuous TM phase at the periphery. The study strongly recommend to enhance the quality control measures in the manufacturing/quenching process and introduce quality check measures (standard etching/Nital test) to ensure that the QST steel rebar satisfies the expected cross-sectional phase distribution. Such a measure could enhance the durability for concrete structures exposed to marine/chloride environments.

5 ACKNOWLEDGMENTS

The authors acknowledge the financial support from the Ministry of Human Resources Development (MHRD) through the Department of Civil Engineering, Indian Institute of Technology Madras, Chennai, India. The authors are thankful to Prof. Christoph Gehlen of Technical University of Munich (TUM), Munich, Germany and Prof. Frank Dehn of Leipzig University, Leipzig, Germany for providing the steel specimens from various countries. The authors appreciate the assistance from the staff and fellow students in the Building Technology and Construction Management Division, Department of Civil Engineering at IIT Madras.

6 REFERENCES


Abstract
The repair strategy for reinforced concrete structures in marine environment suffering from chloride-initiated corrosion usually includes cathodic protection. Three major coastal bridges are located in the sea south of Funen. During the period 2008 to 2015, several cathodic protection systems (CP-systems) have been designed and installed on the structures of these bridges. The CP-systems used are impressed current cathodic protection (ICCP) for girders and bridge piers above water and galvanic anode cathodic protection (GACP) for the submerged parts of bridge piers.

The ICCP anode systems include titanium anodes with mixed metal oxide coating shaped as mesh, rods and ribbons all embedded in concrete or mortar, and the GACP anodes are aluminium alloy. The systems are automatically operated and access for monitoring and adjustment is carried out remotely via the internet.

This paper presents considerations regarding the cathodic protection designs, the challenges during installation and evaluation of the performance of the cathodic protection systems seen from the Consultant’s point of view.

1. The bridges

The three bridges are all part of highway no. 9, and the bridges link the island of Funen to the island of Langeland via the islands of Tåsinge and Sio. The bridges are named Svendborgsund Bridge, Siøsund Bridge and Langeland Bridge. The bridges were opened for traffic in 1966, 1960 and 1962 respectively. The substructures of the three bridges are constructed in reinforced concrete and the superstructures are pre-stressed box girders.

The Svendborgsund Bridge is a high bridge with a total length of 1220 m. The navigation span has a length of 90 m with a height of 33 m. The superstructure of the approach spans comprises pre-stressed concrete box girders with 3 boxes, and the approach spans comprises pre-stressed slabs. All spans are simple supported by reinforced concrete bridge piers (foundation with two
columns) and two abutments. The Søsund Bridge is a low bridge with a total length of 558 m. The navigation span has a length of 25 m with a height of 4.6 m. The superstructure comprises 25 m long pre-stressed concrete box girders with six boxes. All spans are simple supported by 21 reinforced concrete bridge piers and two abutments. Finally, the Langeland Bridge is a high bridge with a total length of 774 m. The navigation span consists of a 91 m long concrete arch and has a height of 26 m. The superstructure of the approach spans comprises 34 m long pre-stressed concrete box girders with five boxes. All spans are simple supported by 20 reinforced concrete bridge piers and 2 abutments.

Figure 1. The three bridges

The reinforced concrete structures for all three bridges have been suffering from chloride initiated reinforcement corrosion. The bridge girders and/or pier tops have been exposed to chlorides from deicing salt from the road leaching through the construction joints. The piers are exposed to chlorides from the seawater (approx. 2 percentage salt). The Langeland Bridge was already in the 70ies suffering from corrosion due to chloride ingress. Traditional concrete
repairs were carried out on the piers at the end of the 70ies and in the beginning of the 80ies, however, special inspections in the beginning of this millennium revealed that new corrosion had initiated in the piers.

For all three bridges, cathodic protection was chosen as repair strategy. This method was chosen either because the deterioration was still relatively limited and the removal of "intact" concrete could be minimized, or because removal for the chloride contaminated concrete was not an option. For the Svendborgsund Bridge, this was the only strategy because extensive removal of chloride-contaminated concrete on the plinths was not feasible. Economical calculations for an additional service life of 50 years showed for all structures, that cathodic protection was the optimum strategy. The installation of the cathodic protection system has been supplemented with traditional concrete repairs in order to prepare the structures for the CP-systems. Furthermore, for all three bridges the construction joints have been replaced and the leaching of chloride contaminated water has been stopped.

Table 1: CP-systems installed.

<table>
<thead>
<tr>
<th>Bridge</th>
<th>Number of CP-systems</th>
<th>Structure (installation period)</th>
<th>Number of anode zones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langeland</td>
<td>3</td>
<td>Top of bridge piers (2008-2013)</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bridge piers incl. foundation to top of granite cladding (2009-2013)</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Box girders bottom plate, cell 2 and 4 (2010-2013)</td>
<td>22</td>
</tr>
<tr>
<td>Siøsund</td>
<td>2</td>
<td>Top of bridge piers (2006-2008)</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Remaining bridge piers incl. foundations (2014-2015)</td>
<td>40</td>
</tr>
<tr>
<td>Svendborgsund</td>
<td>1</td>
<td>Box girders and slabs at construction joints (2011-2013)</td>
<td>20</td>
</tr>
</tbody>
</table>

In the period 2015-2016, CP-systems will be installed for the bridge piers of the Svendborgsund Bridge - an ICCP system as well as a GACP system - the latter on the part of the substructure located below water level due to chloride induced reinforcement corrosion as mentioned earlier.

2. Design considerations

When designing a CP-system several parameters have to be taken into account, among others:

- The Owner's requirements
- Condition of the structures
- The accessibility of the structure, the entire bridge as well as the relevant structural elements.
- The CP-system (performance criteria, anode system, monitoring, power supply and control and monitoring system)
2.1 The Owners requirements

Today the Bridge Owner "The Danish Road Directorate" requires that cathodic protection shall be taken into account as a repair method when choosing the optimum repair strategy for bridges suffering from reinforcement corrosion.

For the Owner the following topics have been of great importance when choosing the cathodic protection systems:

- Minimizing traffic disruptions during installation
- Minimizing installation costs
- High efficiency and long service life of the system
- Well known system (references) and long track record
- Minimizing operation and maintenance costs

For both the Svendborgsund Bridge and the Langeland Bridge, the major challenge has been to gain access to the internal part of the box girders. In order to work in such narrow spaces rules from the Danish health and safety legislation had to be followed, which include requirements to the distance to access points as well as maximum working hours within the girders. In order to follow the rules, access holes in the bridge's top plate to the girders became part of the project. Access to the bridge piers was established by scaffolding with access from the sidewalk.

Bullet point 3, 4 and 5 have been included in the design of the anode system and choice of control and monitoring system.

2.2 Condition assessments

Operation and maintenance of the three bridges includes regular general inspection with a frequency according to the condition, followed by special investigations to evaluate the severity of any findings. As basis for the cathodic protection design, data was available about the structural condition based on visual inspection, chloride content, measurements of concrete cover, half-cell potential and electrical continuity, as well as corrosion condition of reinforcement evaluated in break-ups, and finally petrographic analysis on concrete cores revealing deterioration state as well as cause. However, these data are only samples and surprises were found during repair and installation.

2.3 Protection criteria

The design of the cathodic protection for the reinforced concrete structures has been carried out in accordance with EN ISO 12696 [1] and DNV-RP-B401 [2], the latter for the GACP system. The protection criteria is in accordance with EN ISO 12696, i.e. for reinforced concrete structures in atmospheric exposure, which is 100 mV depolarisation in 24 hours, and for submerged exposure an instant off potential of -720 mV vs. Ag/AgCl/0.5M KCl shall apply.

As regards the overprotection criteria, the potential shall not be more negative than -1100 mV vs. Ag/AgCl/0.5M KCl. However, for the pre-stressed box girders the overprotection criteria is -900 mV vs. Ag/AgCl/0.5M KCl. The latter criterion is to avoid any risk of hydrogen embrittlement of the pre-stressed steel.
2.4 Anode systems
Due to the requirements to the anode systems (well-known, durable, long service life and limited maintenance during the service life) titanium with mixed metal oxides (MMO) was chosen as material for the ICCP anodes. This is the traditional well-proven anode material used for 25+ years in other of the Danish Road Directorate's CP-systems. Aluminium alloy has been chosen as galvanic anode material, which is the most commonly used material for GACP of marine structures. Another important parameter when choosing the anode system has been the very difficult access to the bridge structures, so repair or replacement of the anode system should be avoided during the service life of the system. Both access to the piers and access to the girder through the access holes leads to traffic disturbance.

Several shapes of the titanium anodes with MMO are commercially available, where the most commonly used types are mesh, ribbons and rods. The anode types installed on the different structures vary. The basis for the decision of anode type can be seen in Table 2. The often-used anode mesh gives a uniform current distribution, which is preferred for large "normal" reinforced surfaces, whereas the anode rod and anodes ribbons are used for smaller surfaces or localized protection. Anode rods are also very useful where deeper reinforcement layers need protection. All the anode systems are designed for a current of 20 mA/m² steel surface area and a design life of 20 years. The design current corresponds to that reinforcement corrosion is already initiated, so the CP installations are all for repair purpose.

For the piers and bottom plate in the girders on the Langeland Bridge, trial installations have been carried out before the design in order to evaluate different systems. For the piers, both anode mesh and conductive mortar had been tested, however, the mortar was rejected due to minor current output and limited track record. For the girders both mesh and ribbons were tested, however, due to ease of installation mesh were preferred. For the surface mounted anode mesh, the bonding to the substrate is crucial. If de-bonding occurs, the current will not be distributed to the reinforcement in delaminated areas. In order to avoid de-bonding due to shrinkage, casting of the overlay was sectioned.

Experience from the first CP-system installed on the Siøsund Bridge on the pier tops has shown that both the anode ribbons and the anode rods are sensitive to direct moisture load. When the top of the anode rod is exposed to water, most of the current will pass through the outermost active anode surface and thereby produce so much hydrogen gas, that the anode rod may be teared apart. In order to avoid anode disruption in areas at risk of direct moisture exposure, the anode tops have been drilled deeper into the concrete structure and covered entirely by a reasonable mortar cover. The anode ribbons had a similar problem with direct moisture exposure, which lead to an uneven current distribution resulting in a heavy acid production locally leading to premature failure of the embedment mortar (disintegrated). In order to minimise the risk of direct moisture exposure, it is a requirement, that the ribbons are completely embedded and the joint between the mortar and the original concrete is without cracks. Sealing has been required for special sensitive details. The anode system on the pier tops has been replaced in 2014-2015.
Table 2: Anode systems.

<table>
<thead>
<tr>
<th>Bridge</th>
<th>Anode system</th>
<th>Basis for anode shape/remarks</th>
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<tr>
<td><strong>Langeland Bridge</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Girder, bottom plates</td>
<td>Anode mesh and concrete overlay</td>
<td>Large surface areas, easy to install.</td>
</tr>
<tr>
<td>Pier shafts</td>
<td>Anode mesh with shotcrete overlay and additional horizontal anode rods (400 mm) in drilled holds. Rods embedded in mortar</td>
<td>Large surface areas, easy to install. Shotcrete overlay carried out in sections to avoid delamination due to shrinkage. Additional anode rods to fulfill higher current demand at pier top.</td>
</tr>
<tr>
<td>Foundations</td>
<td>Anode mesh with shotcrete overlay</td>
<td>Large surface areas, easy to install. Shotcrete overlay carried out in sections to avoid delamination due to shrinkage.</td>
</tr>
<tr>
<td>Foundations (2 nos.)</td>
<td>Vertical anode rods (3000 mm long) in drilled holes. Rods embedded in mortar</td>
<td>In order to protect behind large rock fillings around the foundation the anode system was installed from the top of the foundations.</td>
</tr>
</tbody>
</table>

| **Siøsund Bridge**  |                                                                               |                                                                                               |
| Pier top            | Horizontal anode ribbons in slots and additional anode rods in drilled holes both anodes embedded in mortar | Localized need for protection at pier top.                                                      |
| Pier shaft          | Vertical anode ribbons in slots. Ribbons embedded in mortar                  | Localized need for protection due to discrete steel profile reinforcement in pier shafts.       |
| Foundation above water line | Vertical anode rods (1200 mm long) in drilled holes. Rods embedded in mortar | Easier to get behind granite cladding and in order to avoid water influence on the anode.       |
| Foundation below water line | Aluminium alloy galvanic anodes                                               | Galvanic anodes are chosen, as there is some uncertainty about the electrical continuity in the reinforcement |

| **Svendborgsund Bridge** |                                                                               |                                                                                               |
| Girder locally at construction joints | Horizontal and vertical anode rods (150 to 900 mm long) in drilled holes. Rods embedded in mortar. | In order to protect the rebars in the huge structures below the bearing. With the anode rods it is possible to protect the rebars at larger depth from the surface. |
The distribution of the anodes is designed to fulfil the current demand according to calculations of the actual reinforcement surface area, including surface area of any other metallic items that may drain the current. The primary current distributor to the anode systems is either titanium ribbon or titanium wire. The embedment mortar or concrete shall have a suitable resistivity according to the manufactures recommendation, usually less than 15,000 ohm cm.

2.4 Monitoring
Monitoring of the performance of the cathodic protection systems is based on a number of reference electrodes, type Mn/MnO$_2$, located within the structures to be protected. The monitoring location is designed as follows:

- Critical points with high probability of under-protection (furthest point from current distributor) or excessive protection (close to current distributor)
- Representative locations

The pre-stressed bridge girder is monitored due to the risk of hydrogen embrittlement of the pre-stressed reinforcement in case of overprotection. The substructure of each bridge consists of a number of uniform structures. In order to have a reasonable amount of reference electrodes in the structures, a number of piers were chosen for monitoring of each system. The philosophy is that the results of the control measurements of monitored piers are disseminated to the corresponding uniform structures, and the system is adjusted accordingly for all piers.

2.5 Power supply and control and monitoring system
All CP-systems on the three bridges are powered from the end of the bridges, i.e. all cables are led centrally in the box girders to the abutment, where the power supplies for all the anode zones, transformer-rectifiers, measuring modules and computers for control and monitoring are located. Each system has a main computer, which performs automatic measurements on the anode zones, collects the measuring data and sends the data to a management system via the internet. The central location for the power supplies and the control and monitoring system has
been chosen due to the difficult access to the box girders in the operation phase of the CP systems. As operational cost are important for the lifecycle cost of the systems and the bridges are located on smaller islands, remote operation and control of the systems minimizes the operational costs considerably. The cathodic protection system is managed remotely via an external server, where a CP-management system is installed (The Danish Road Directorate has a CP-management system, which includes management of all systems on all their bridges).

3. Installation

In general, all the CP-systems have been installed as intended, however, some lessons were learned.

3.1 Electrical continuity in reinforcement

The installation of the CP-systems has given some challenges, among others the prerequisite for cathodic protection – continuity in the reinforcement – was not fulfilled for all structures. For the Langeland Bridge the reinforcement in the plinths on the pier top was lacking continuity and similarly for the reinforcement above and below the granite on the foundations. The continuity on the plinths was carried out by welding the reinforcement together, while the reinforcement above and below the granite was made continuous by installing an external connection on the foundation. On the Siøsund Bridge, the results of the continuity were not clear. However, as the CP-system consists of galvanic anodes, the risk of stray currents to reinforcement not in continuity is limited, and there is no risk for increased corrosion rate compared to the original state.

3.2 Installation of anode mesh

Another challenge on the Langeland Bridge was delamination of the shotcrete overlay on the anode mesh at the bottom of the pier tops. This was due to a combination of shrinkage at the free edge and a surface roughness that was not sufficient. The method for roughening was improved, which reduced the risk of delamination.

3.3 Installation of anode rods

For the Svendborgsund Bridge, the drilling of holes for installation of anodes rods turned out to be a challenge as the Contractor had difficulties in determining where the reinforcement was located at larger depths, due to the huge structures with several layers of reinforcement, and as a consequence quite a lot of holes were drilled to find a suitable hole. In addition, the sidewalk was reinforced. This led to much reinforcement and in order not to cause short circuit between the reinforcement and the anodes, the rod anodes had to be embedded in mortar (cylindrical shape) before installation. As mentioned before, the anode rods shall not be exposed to water. On the abutments for the Svendborgsund Bridge, water was leaching through the water proofing membrane. In order to avoid the moisture ingress to the anode rods, all the rods were sealed on top with water resistant material.

3.3 Installation of anode ribbons

On the Siøsund Bridge, when installing anode ribbons in 2014-2015, focus has been on the embedment of anode ribbons as well as cracking in joints. In order not to have cracks in the
joints between the embedment mortar and the original concrete, curing compound was used on the vertical ribbons (pier shafts). For the anode ribbons in the pier top, the joints were sealed in order to avoid moisture load, if the construction joint in the future should be leaching, e.g. due to damaged sealing tape. The tightness of the joint (no cracking) as well as the full embedment of the anode ribbons in mortar were checked by drilling cores through the joint and ribbons. All cores fulfilled the requirement.

3.4 Installation of power supply and control and monitoring system

For the CP-system on the girders at the Langeland Bridge, depolarisation values over 24 hours showed positive IR-drops. This turned out to be due to the coupling of anode zones where more than one anode zone were coupled to the same measuring module, i.e. the measuring connections of the anode zones were coupled, and when the current was turned off, residual currents flow between the anode zones. The problems were solved when the measuring connections were separated.

4. Evaluation of performance

On the Langeland Bridge, the monitoring results show that the CP-systems on the pier tops and the remainder pier shafts interfered with each other. This was not a surprise since the systems are not synchronised. In order to avoid the mutual interference, the systems have to be synchronized or the influencing system shall be turned off during depolarization measurements. This does not apply for the Siøsund Bridge as the reinforcement in the pier shafts is comprised of single steel profiles that are not continuous with the "normal" reinforcement in the pier tops, i.e. the two CP-systems have no influence on each other.

4.1 CP-management system

The operation and performance data for all the CP-systems are available in the CP-management system. The system is developed especially for management of the Road Directorate's CP-systems. The basis for the management system was a requirement to optimize the operation of all the CP-systems in order to minimize the cost of operation without compromising the quality. With the management system it is easy to follow up on the operation, i.e. the functionality as well as the performance of the CP-systems. This also allows for a quick response when a fault on a CP-system has been detected. It provides enhanced continuous operation. The control and monitoring system of the individual CP-systems automatically initiates and logs data for the control measurements, i.e. current and voltage output for each anode zone, electrochemical potentials measured "on", "instant off" and "24 hours off" and impedance of the reference electrodes. The depolarization measurements are carried out for each system once a month, whereas the other values are measured on a daily basis. The generated data files are sent automatically twice a day from the CP-systems' main computer to the server with the management system. If one or more of the parameters are outside the set limits (user defined), or if data has not been received, an alarm is sent to the responsible for the operation of the actual CP-system.
5. Conclusion

Our experiences from the design, installation and operation of several CP-systems on the three coastal bridges are among others:

- Cathodic protection as repair method has proven to be effective to protect the reinforcement from corrosion by fulfilling the performance requirements.
- The best choice of CP system is dependent on the construction and local conditions (not necessarily linked to the corrosion).
- Design and installation of cathodic protection for pre-stressed concrete structures is safe due to the close follow up on operation via the CP-management system.
- Small details in installation of the anode system can compromise the anode system and lead to premature failure of the CP-system.
- The CP-management system is a major advantage in the operation phase due to the easy access to data, and fast intervention in case of system failure due to alarm.

6. References

CORROSION PROCESSES AND ECE TREATMENT IN A BOTH CARBONATED AND CHLORINATED REINFORCED CONCRETE

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Abstract

Civil engineering structures and historical buildings can suffer from corrosion of the embedded reinforcing steel once the concrete cover is totally carbonated and/or when chloride ions reached the steel/concrete interface. On field, these two types of contamination can be encountered separately or combined requiring implementation of proper repair methods.

In this study, both chlorinated and carbonated reinforced concrete specimens were followed by three main analysis means: Raman microspectroscopy, electrochemical characterization and scanning electron microscopy. They were first characterized during the two-step aging process, chlorides addition and complete cover carbonation. Electrochemical chloride extraction was then performed as a repair treatment (1A/m² of steel surface during 8 weeks). Its efficiency and its impact on the specimen interface and cement matrix were studied.

Study of rebar’s electrochemical characteristics during the aging notably showed an increase of corrosion rate from negligible value of 0.1 μA/cm² after fabrication to above 10 μA/cm² after carbonation. SEM observations confirmed this phenomenon with the identification of a corrosion layer on most of the concrete/steel interface after carbonation. The ECE efficiency was put in evidence by a decrease of Cl- concentration below the theoretical threshold value of 0.4 % mass of cement after two weeks. Simultaneously a realcalinisation was observed around the reinforcement bar which reached about 1 cm in 28 days.

1. Introduction

Complete cover carbonation and chloride ions penetration until the steel/concrete interface are the two main causes of reinforced concrete degradation induced by corrosion. These two types of contamination can be encountered separately or combined on civil engineering structures as well as on historical buildings requiring implementation of proper repair methods.
This study aims to characterize the corrosion processes then the electrochemical chloride extraction (ECE) treatment in a both carbonated and chlorinated reinforced concrete. For this purpose, four series of specimens based on two cements and two aging processes were casted. In this paper the study’s complete protocol is presented. First results obtained on one series of specimens during the aging then during the treatment are presented and discussed in a second time. SEM-EDS analyses and Raman microspectroscopy were used to characterize the corrosion product layer at the steel/concrete interface. SEM-EDS gave information about corrosion products distribution, morphology and elements of composition while Raman microspectrometry allowed the identification of crystallized corrosion phases formed. Electrochemical characterization (non-destructive-testing (NDT)) was used to follow the evolution of the state of corrosion of the rebar (active/passive).

2. Methodology

In this section the specimens’ characteristics and the experimental program established to follow the evolution of corrosion state during the aging and during the electrochemical treatment are presented.

2.1 Specimens formulation and design

Design and composition of specimens used for this study must allow and facilitate chemical reactions within the concrete cover (high W/C ratio and limited vibration). To achieve this, cylindrical specimens of reinforced concrete of 10 cm in height and 4 cm in diameter (Figure 1) were casted using the composition already used in Tong’s thesis [1] that allows on a reduced scale to stay close to the granular distribution of a concrete (Table 1).

<table>
<thead>
<tr>
<th>siliceous Palvadeau aggregates (kg/m³)</th>
<th>Cement (kg/m³)</th>
<th>Water (kg/m³)</th>
<th>W/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/0.315</td>
<td>387</td>
<td>251.55</td>
<td>0.65</td>
</tr>
<tr>
<td>0.315/1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5/1</td>
<td></td>
<td></td>
<td></td>
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<tr>
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<tr>
<td>229</td>
<td>387</td>
<td>251.55</td>
<td>0.65</td>
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</table>

Two types of cement were selected:
- CEM I (52.5 N CP2; Holcim, Lumbres factory) is a usual Portland cement which will allow results comparisons. The specimens were named type 1.
- CEMIII/A (52.5 L PM ES CP1 NF; Lafarge, Le Havre factory), is a cement frequently encountered on concrete historical monuments. Furthermore, the use of this cement which contains blast furnace slag is promoted for the construction of new structures because of its lower impact on environmental issue (less CO₂ produced). Therefore, the results will help improve knowledge about the behavior of reinforced structure using this cement. The specimens were named type 3.

Rebar is a smooth round steel type S 235JR of 5mm in diameter with an active surface of 10 cm². The open porosity measured after curing (28 days for CEM I cement and 90 days for CEM III cement) was about 18 % ± 1%.
2.2 Experimental set-up

A specific set-up was designed (Figure 2) in order to study, in a first step, the corrosion of a both carbonated and chlorinated reinforced concrete and then, in a second step, the efficiency and impact of the electrochemical repair (during the treatment and after its end).

Two different aging procedures were studied:
- Chloride addition to the mix (5 % of cement mass of NaCl) (M0) and then carbonation until complete carbonation of the concrete cover (50 % CO₂; 70 % HR) (M1). The specimens were named type G.
- Carbonation until reaching the concrete/steel interface (50 % CO₂; 70 % HR) (M1) and then chloride penetration by wetting/drying cycles (five days in a solution of 35 g/L NaCl and two days in the laboratory at room temperature) (M2). The specimens were named type I.

Evolutions of carbonation and chloride contamination by wetting/drying cycles were followed thanks to colour indicators, respectively phenolphthalein (0.5 % in ethanol which is not a CMR reagent at this concentration) and silver nitrate solutions (0.1 N).
After the aging step, the electrochemical chloride extraction treatment was then conducted on 37 specimens of each series (G1, I1, G3 and I3). The treatment principle is presented on Figure 3. As indicated in the NF EN 14038 part 2 standard [2], a current density of 1 A/m² of steel was applied between the rebar and a titanium/platinum grid (counter-electrode) during 8 weeks. The electrolyte used was a disodium tetraborate solution (25 g/L of Na₂B₄O₇·10H₂O) to promote ionic exchanges and facilitate chloride ions entrapment. The treatment monitoring was performed controlling and/or following the room temperature, the applied current, the voltage of each specimen and the voltage of the whole specimens on a one hour frequency base. Three control specimens were taken from the treatment after 3, 7, 14, 28 and 56 days, 56 days corresponding to the end of the treatment. These times were selected as several authors observed that the extraction of chloride ions is more efficient during the treatment’s beginning [3-6]. Electrolyte was renewed at each term (except 3 days) to avoid a loss of treatment efficiency due to the increase of chloride ions concentration into the electrolyte. Regarding the chloride extraction evolution, concrete’s free and total chloride concentrations were measured on two of the control specimens by AgNO₃ potentiometric titration (on the first centimetre around the rebar and on the 0.75 cm of external cover). Moreover the electrolyte chloride titration was also performed. Phenolphthalein test was performed on the surface of part c (Figure 1) of the two same control specimens. The third control specimen was kept to perform an electrochemical characterization after depolarisation.

After treatment, the electrochemical characteristics of the reinforced specimens will be checked every month to verify rebars are depolarized (storage at 60%HR and 20°C). Then cycles of relative humidity will be performed electrochemical characteristics followed to ensure the durability of the treatment.

Simultaneously to the treatment, two specimens (which are not submitted to the current) were used to observe lixiviation phenomenon. They were immersed in the tetraborate solution and Cl⁻ titration was performed after 28 days and 56 days of treatment.

![Figure 3: Simplified principle of electrochemical chloride extraction](image)

2.3 Analysis means
To study the corrosion process of the rebar, three main analyses means were used on different parts of the cylinder (Figure 1):
- A Jobin-Yvon Horiba (LABRAM) Raman spectrometer was used. Spectra were obtained with a helium-neon red laser (0.1 mW for these measurements). For these study acquisitions a x50 objective was used to focus laser light and collect spectra for duration of 600 seconds. Specific designed cells were prepared from the regular one after the aging step to follow the concrete/steel interface “in-situ” during the corrosion initiation and propagation and then during the treatment by Raman microspectroscopy. After cutting as presented Figure 1, a thin glass slide was pasted on the polished surface to isolate the steel/concrete interface from a direct contact with the external environment. After preparation, these samples were immerged in a 25g/L Na₂B₄O₇·10H₂O solution. Regular observations at a magnification of 50 were made until the detection of pitting corrosion. Raman spectra were then acquired in different areas of interest. The same areas were followed during the ECE treatment and after treatment.

- A JEOL 5600LV scanning electron microscope (SEM) equipped with a micro-analyzer X in dispersal of energy Oxford Link Pentalet was used to observe corrosion at the concrete/steel interface. Two types of samples were examined: polished cross sections to evaluate corrosion layers evolution and fractured samples to observe both corrosion crystallised phases’ morphology and eventual modifications of the cement matrix.

- An electrochemical characterization was performed with a VMP2Z potentiostat (5 pathways) at each step of the process. The half-cell potential (E<sub>corr</sub>), the linear polarization resistance (LPR) and the electrical concrete resistance (Re) were measured and the corrosion rate i<sub>corr</sub> (μA/cm²) was calculated according to the formula (1).

\[
i_{\text{corr}} = \frac{B}{R_p S}
\]

With: B =26 mV, Rp (ohm) the linear polarization resistance and S (cm²) the active steel surface (10 cm² in this study)

3. Results and discussion

In this section results obtained on G1 specimens casted with CEMI cement and NaCl addition to the mix and then carbonated are presented.

3.1 Corrosion processes

Corrosion products characterization

- Raman Spectroscopy

Trials of corrosion in-situ following were made on a specimen type G1 before carbonation. Chlorinated green rust (Figure 4) was the predominant phase found (main Raman bands at 434 cm⁻¹ and 506 cm⁻¹ and a chloride presence characteristic band around 320 cm⁻¹) [7] which evidenced the presence of chloride into the corrosion processes. Moreover, green rust oxidation into FeIII oxyhydroxyde did not occur which proved the good isolation of the interface from a direct exposure to oxygen from the air.
After casting, the steel/concrete interface was mostly characterized by an absence of corrosion (Figure 5-a). Figure 5-b shows a representative area of the interface after carbonation with about 5 μm of corrosion products on the steel and 5 μm migration within the concrete. After carbonation, the corrosion layer thickness could vary from 5 to 20 μm and if the penetration of corrosion products within the concrete was mostly of 5 to 15 μm, it could reach up to 250 μm in few areas. The observation on fracture after carbonation (Figure 6-a) showed numerous areas of corrosion in the rebar print. The crystallisation morphology of corrosion products mainly containing Fe, O and Cl is presented on Figure 6-b.
Electrochemical characterization

Fig 7, 8, and 9 respectively present the half-cell potential, the resistance and the corrosion rate of the G1 specimens at two different times. M0 is related to the corrosion state after curing (+3 days) while M1 is related to the corrosion state after carbonation (24 weeks after curing including a month of preconditioning and 14 weeks of accelerated carbonation).

From Fig 7, G1 specimens potentials measured after curing were in the range -230 mV to -579 mV with a mean value of -457 mV and a standard deviation (based on the 70 samples) of 84 mV while after carbonation, the average value and the standard deviation were respectively -550 mV and 14 mV (based on 57 samples). This indicates that after carbonation, the potential specimen values became more electronegative and more homogeneous.

From Fig 8, the average value and the standard deviation of the resistance were respectively 193 ohm and 16 ohm after curing and 97 ohm and 13 ohm after carbonation. The decrease by a 2 factor is rather unexpected as the carbonation process induces a reduction of the porosity. However both values (at M0 and M1) are still very low (some hundreds) and usually a significant evolution for the reinforced concrete is rather a thousand.

Finally, the corrosion rate after curing (Figure 9) was below 0.1 μA/cm² thus indicating a negligible level of corrosion according to the Rilem [8]. After carbonation a drastic increase of corrosion rate (values higher than 10 μA/cm²) demonstrated a high level of corrosion [8].
3.2 Electrochemical treatment on G1 specimens

ECE treatment implies several phenomena particularly corrosion products transformations, chloride ions extraction, OH⁻ formation and ionic migration. This part aims to study these different effects.

**Corrosion products characterization**

- **Raman Spectroscopy**

During ECE treatment, regular Raman acquisitions (every day) were performed to follow the phases transformations induced. After two days of polarization, the main phase detected was magnetite (main Raman band at 670 cm⁻¹) (Figure 10). This phase remained stable during 2 weeks of polarization after which the treatment was ended. Further experimentations will be done for a Raman microspectroscopy following of a specimen both chlorinated and carbonated.
- Scanning electron microscopy

SEM observations and EDS acquisitions will be performed at the end of the treatment (not presented in this paper).

**Chloride titration**

Figure 11 shows the evolution of chloride concentration during the ECE treatment as well as the alkaline evolution at the rebar level. The chloride threshold for preventing corrosion on new structures from the EN206 standard [9] has also been added.

Regarding the chloride extraction, the evolution of chloride ions extraction was in good agreement with the increasing chloride ions concentration titrated into the electrolyte. After 3, 7, 14 and 28 days the chloride ions extraction was respectively of about 52 %, 67 %, 89 % and 92 % in the external cover and 27 %, 70 %, 92 % and 96 % in the first centimetre around the rebar. The extraction was faster during the seven first days of treatment which is in accordance with literature results [3-6]. Results show that the free chloride concentration became less than the EN206 chloride threshold of 0.4 % mass of cement after 7-14 days of treatment. Figure 11 also highlights that the difference between total and free chloride ion concentrations decreased with the duration of treatment which could mean that bounded chloride ions can be electrochemically extracted.

Regarding the pH evolution (Figure 11), observed realalkalisation was probably due to the hydroxyl ions formation around the rebar and the cations migration towards the rebar. Based on results obtained and the standard [10], concerning realalkalisation the minimum treatment duration required is either 28 days to obtain a 10 mm realalkalised concrete zone around the rebar or a range of 7 to 14 days considering the experimental rebar diameter (5 mm).

![Figure 11: Evolution of chloride concentration and layer thickness (pH>9) during ECE treatment](image)

Figure 11: Evolution of chloride concentration and layer thickness (pH>9) during ECE treatment
4. Conclusion

In this experimental work, the set-up design adopted to study, first the corrosion process on both chlorinated and carbonated reinforced concrete specimens, and second, the electrochemical cathodic treatment were presented.

First results obtained on G1 specimens allowed to establish the following conclusions:
- Chloride contaminated G1 specimens showed a negligible corrosion 30 days after curing as indicated by corrosion rates less than 0.1 μA/cm².
- After the carbonation process, as expected, corrosion increased rather drastically as evidenced by corrosion rates higher than 10 μA/cm². SEM results confirmed this behaviour with the observation of corrosion products on most of the interface (5-20 μm on the rebar and up to 250 μm of penetration within the concrete).
- Efficiency of the electrochemical treatment based on chloride extraction as well as realkalisation of the concrete around the reinforcement was demonstrated. Two weeks of treatment were needed to obtain a Cl⁻ concentration below the threshold value of 0.4 % mass of cement while 28 days of treatment lead to one centimeter of realkalisation.

The following of treatment durability and Raman spectroscopy results will complete the experimental work on G1 specimens. Comparison with 3 other types of specimens will give a larger view on this subject.

References

ELECTROMIGRATION OF Li IONS INTO CEMENTITIOUS MATERIALS AS OBSERVED BY NMR

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Abstract

Alkali-silica reaction (ASR) is a chemical reaction between the hydroxyl ions present in the pore solution and reactive silica. An efficient method to prevent ASR is by introducing Li ions into the system which will form a non-expansive gel. LiOH is the most efficient salt to inhibit long-term ASR expansion. The most effective way to drive Li into a sample is by electromigration. However, previous investigations did not provide specific information that can reveal and describe the lithium transport mechanism under an electric field gradient. We developed a numerical model that can describe the lithium ions transport mechanism in concrete. To verify the model, we have measured the Li profiles non-destructively by Nuclear Magnetic Resonance (NMR). This NMR method gives us the possibility for real-time monitoring of transport processes during migration experiments. In particular, it was found that significant amount of lithium ions introduced into the mortar are removed from the pore solution due to binding to the cement matrix during the first days of the experiment. Based on the obtained experimental data we propose a physical model for the lithium transport process during electromigration in mortar and predictions are made on the effectivity.

Key-words: Alkali-silica reaction, Nuclear Magnetic Resonance, lithium, electromigration, binding.

1. Introduction

Alkali-silica reaction (ASR) is known as one of the major causes of the deterioration mechanisms of concrete structures. ASR is a chemical reaction between hydroxyl ions the alkalis (sodium and potassium) present in the pore solution and the silica present in the aggregates. The reaction product is an alkali-silica gel. This gel reaction absorbs water from the cement paste and starts to swell. The expanding gel creates tensile forces, causing the concrete to crack. Due to cracking, the permeability of the material will increase. Therefore, external alkalis can penetrate the concrete more quickly and hence increase damage due to ASR. As a result, the concrete will also become more vulnerable to other deterioration mechanisms. In Figure 1 shows a schematic representation of the various steps of ASR in the concrete.
Step 1: The hydroxyl ions (OH\textsuperscript{-}) and alkali elements (Na\textsuperscript{+} and K\textsuperscript{+}) react with reactive silica

Step 2: ASR gel formation

Step 3: ASR gel absorbs water from the surrounding pore solution that leading to expansion and cracking

Figure 1: A schematic representation of ASR steps

Lithium compounds can help to reduce and control the deleterious expansions in concrete caused by ASR [1]. When lithium is it starts to form a Li-Ca-Na-K-Si gel and Li-Si crystals [2] which are non-expanding. Figure 2 shows the schematic diagram of ASR in the present of lithium.

The lithium ions (Li\textsuperscript{+}) with ASR gel form Li-Ca-Na-K-Si gel

Li-Si crystals formation

Figure 2: A schematic representation of ASR in the present of Li ions.

2. Experimental

To measure the Li transport during electromigration experiments, we have used NMR. A home-built NMR scanner with a static magnetic field of 0.78T and a static magnetic field gradient of 0.2 T/m was used to measure lithium ions distribution burying. The material used in this study is a mortar made from a standard Portland cement type I. The mortar had water to cement ratio of 0.6 and sand-to-cement proportion 1: 3 with a final porosity
Mortar specimen were cast in blocks with a size of 10x10x100 cm and placed in water for two years.

Anode: \[ 2HO^- + 2e^- \rightarrow H_2O + \frac{1}{2}O_2(g) + 2e^- \]

Cathode: \[ 2H_2O + 2e^- \rightarrow 2HO^- + H_2 \]

In the experiment both the anode and cathode reservoir cells were filled with the saturated LiOH and Ca(OH)₂ solutions, respectively. Both solutions are very basic of alkaline. The saturated Ca(OH)₂ solution has a pH of 12.5 pH which is equal to pH in a concrete pore solution. Therefore, the both solutions are used for migration experiments will not change the pH of the concrete [8].

The applied electric field promotes the cations attraction to the cathode, and anions move through the porous material towards the anode, supporting Li⁺ ions migration into the concrete and at the same time removing Na⁺ and K⁺ ions. The average temperature of the samples during treatment was constant and equal to the room temperature of 21°C.

During the migration experiment, the sample was taken out of the electrokinetics set-up and measured in the NMR setup for 40 min. The concentration of lithium ions was determined in the mortar specimen using the NMR. After scanning, the sample was placed back into the electrokinetic set-up in order to continue the experiment. The profiles were obtained with a scanning resolution of 1.3 mm.

3. Numerical model

In concrete, the pore solution consists of a mix of many ionic species including hydroxyl, sulphate, sodium, potassium, calcium, etc. The hydroxyl has the highest concentration in the pore solution, followed by sodium and potassium. The transport process of ions in a saturated concrete is mainly by diffusion and migration processes. Therefore, the transport of an ionic species during electromigration through a porous medium can be expressed by the Nernst-Planck equation. The one-dimensional average ionic flux density is given by:

\[
I_i(x, t) = -D_i \left[ \frac{\partial C_i(x, t)}{\partial x} + \frac{z_i F}{RT} C_i(x, t) \frac{\partial \varphi(x, t)}{\partial x} \right],
\]

where for each ions species \(i\), \(I_i\) is the ionic flux \([\text{mol m}^{-2} \text{s}^{-1}]\), \(D_i\) is the effective diffusion coefficient \([\text{m}^2 \text{s}^{-1}]\), \(C_i\) is the concentration in pore solution \([\text{mol m}^{-3}]\), \(z_i\) is the valence of ionic species, \(x\) is the space position \([\text{m}]\), \(t\) is the time \([\text{s}]\), \(F\) is the Faraday constant (96484.6 \(\text{C mol}^{-1}\)).
\[ R \text{ is the ideal gas constant (8.3143 [J mol}^{-1} \text{ K}^{-1}), } T \text{ is the absolute temperature [K] and } \phi \text{ is the electrical potential in the direction of } x. \text{ The mass balance for each ion species is defined as:} \]

\[ p \frac{\partial C_i}{\partial t} = - \frac{\partial f_i}{\partial t}, \tag{2} \]

where \( p \) is the total water-permeable porosity of concrete [%].

Substituting Eq. (1) and (2) the governing equation leads to:

\[ p \frac{\partial C_i(x, t)}{\partial t} = D_i \left( \frac{\partial^2 C_i(x, t)}{\partial x^2} + \frac{z_iFE}{RT} \frac{\partial C_i(x, t)}{\partial x} \right) = 0, \tag{3} \]

where \( E \) is electrical field.

The all ionic species considered here must satisfy a local electroneutrality condition, which can be written as [9, 10]:

\[ \sum_{i=1}^{N} z_i C_i = 0. \tag{4} \]

Previous researchers have shown that between the ions in a liquid state and the surface of the pore wall, i.e., ions are bound the pores-surface of the solid matrix. Therefore, the total ion concentration can be written as:

\[ C_{Ti} = C_{bi} + C_f, \tag{5} \]

where \( C_{Ti} \) is the total ions concentration [mol m\(^{-3}\)], \( C_{bi} \) is the concentration of bound ions [mol m\(^{-3}\)], and \( C_f \) is the free ions concentration [mol m\(^{-3}\)].

Freundlich isotherm can describe the relation between the amount of bound lithium ions on the cement based material and free ions. This assumption is made based on that Freundlich isotherm is an empirical model developed for the heterogeneous material, such as concrete. The Freundlich isotherm is governed by the following equation:

\[ C_{bi} = K_b C_i^n, \tag{6} \]

where \( K_b \) and \( n \) are empirical parameters determined experimentally. The mass transfer rate can be written as [11]:

\[ r = k \left[ C_i - \left( \frac{C_{bi}}{K_b} \right)^{1/n} \right]. \tag{7} \]

As a result, the transport model for the free ions can be described by:
whereas for the bound ions we find:

\[ (1 - p) \rho_s \frac{\partial C_{bi}(x, t)}{\partial t} = k \left[ C_i - \left( \frac{C_{bi}}{K_B} \right)^{1/n} \right], \]

(9)

where \( \rho_s \) specific density of concrete [g dm\(^{-3}\)].

The initial and boundary conditions are by:

\[ C_i(x = 0, t) = C_i^0 \quad \text{and} \quad C_{bi}(x, t = 0) = C_{bi}^0, \]

(10)

where \( C_{bi}^0 \) is the initial concentration of the solution and \( C_{bi}^0 \) is the initial concentration of bound ions.

In this work, we only consider the bonding of lithium ions.

**4. Input Data for the Model**

From the model described in the previous section, it is possible to simulate the electromigration experiment. The input parameters used in the numerical model are given in Table 1.

<table>
<thead>
<tr>
<th>Diffusion coefficient ([m^2 , s^{-1}])</th>
<th>Pore solution concentration ([\text{mol} , \text{m}^{-3}])</th>
<th>Anodic solution concentration ([\text{mol} , \text{m}^{-3}])</th>
<th>Cathodic solution concentration ([\text{mol} , \text{m}^{-3}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+) (3.2 \times 10^{-12})</td>
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<td>4900</td>
<td>0</td>
</tr>
<tr>
<td>Na(^+) (2.3 \times 10^{-12})</td>
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<td>0</td>
</tr>
<tr>
<td>K(^+) (3.4 \times 10^{-12})</td>
<td>360</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ca(^{2+}) (1.4 \times 10^{-12})</td>
<td>0</td>
<td>0</td>
<td>230</td>
</tr>
<tr>
<td>OH(^-) (9 \times 10^{-12})</td>
<td>460</td>
<td>4900</td>
<td>460</td>
</tr>
</tbody>
</table>

The remaining parameters used for this model are:

\( \rho_s = 2200 \, [\text{kg} \, \text{m}^{-3}], \, p = 0.15\% , \, k = 1.39 \times 10^5 \, [\text{s}^{-1}], \, K_B = 0.361 , \, n = 1 \) and \( L = 0.05 \, [\text{m}] \).
5. Results

We first have determined the binding isotherm for Li. Here we look at the absorption of the Li on crushed mortar particles. Based on the experimental procedure [12], that is used to obtained the binding isotherm. That is one determines the decrease of the Li concentration as materials is introduced into the solution and ions start to be bound. The relation between the free and the bound ions is measured when an equilibrium is reached. In order to decrease the time to reach an equilibrium a crushed sample is used. The solution was analysed using an ion chromatograph (IC).

By performing experiments with different initial values of the Li concentration, a point-wise function $C_b = C_b(C_f)$ can be obtained, which is the ion binding isotherm. From the obtained data the bound lithium content was calculated, and the binding isotherm was plotted. Figure 5 shows the binding isotherm obtained by using IC for absorption method on crushed mortar samples.

![Figure 5: The measured Lithium binding isotherm of mortar measured by IC for absorption method.](image)

In fact, the proposed binding method based on the assumption that lithium has direct contact with every small grain material. However, in a real specimen the interior pore surface where the material matrix is accessible to the lithium can be less than the total surface of a crushed sample. The lithium binding capacity can be then affected by many other factors such as the change in the porous structure and pore distribution. Therefore, the result obtained by the proposed method can be considered as an absolute upper limit to the real lithium binding capacity.

The free lithium ions distribution was measured across the sample during electromigration experiment by NMR. As anode reservoir cells were filled with the 4900mol m$^{-3}$ of LiOH solution with and 230mol m$^{-3}$ Ca(OH)$_2$, respectively. The measured Li profiles with time in the sample during the treatment with an applied electrical potential between the electrodes of 40V are shown in Figure 6a. As can be seen, the Li concentration near the electrode increases in time, whereas at the same time Li is penetrating into the sample.
A numerical model that describes the transport of ions during electromigration was implemented in COMSOL Multiphysics. The 1D model shows the behavior of lithium, sodium, potassium and hydroxide ions that dominated the in pore solution. The simulation results have been computed with same initial and physical parameters for the experiment. Figure 6b presents the simulated lithium concentration profiles as a function of position and time.

Figure 6: Free lithium ions concentration as a function of time and position from a) experimental data and b) simulation results. The time between subsequent profiles is one day.

As can be seen, the simulations compare well with the obtained results and show the mean features of the Li moving into the sample, but also the slow increase near the boundary due to binding. In Figure 7 we have plotted the simulated bound Li content as a function of time.
Figure 7: The simulation results of bound lithium ions concentration as a function of time and position. The time between subsequent profiles is one day.

This simulation shows that the binding has a large influence on the Li penetration. The simulation result can also provide information on the behavior of other ionic species studied here: sodium, potassium, and hydroxide. Figure 8 shows the ionic species concentration distribution as a function of position and time.
As can be seen, both sodium and potassium ions leave the sample as Li is penetration the sample. The hydroxide ions penetrate the sample from the cathodic solution to the sample.

5. Conclusion

In the present study, the transport of Li ions in the pore solution was studied by NMR. The NMR technique is able to reveal detailed information about lithium distribution in the sample relatively quickly and non-destructively. This method has been used in conjunction with electromigration tests. The experiments have been performed on mortar mixture with the saturated LiOH anolyte and Ca(OH)$_2$ catholyte solutions, respectively. Additionally, a one-dimensional model was introduced that describes the transportation of ions during migration through the mortar in order to predict the efficiency of electromigration. The provided results for electromigration test help to understand the way of lithium migration to the porous media. The proposed electromigration model of multi-species ions in not only description tool but also an important part in the design of the ASR prevention.

References


POLARIZATION RESISTANCE OF STEEL BAR EMBEDDED IN ENGINEERED CEMENTITIOUS COMPOSITE UNDER DIRECT CURRENT EXERTION

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Abstract
The corrosion of steel bar in concrete structure has always been a serious issue compromising the durability of concrete structure because corrosion could reduce the cross section area of rebar, compromise the bond between rebar and concrete, and induce cover cracking. In recent years, Engineered Cementitious Composite (ECC) has been developed as a replacement of traditional concrete because of the advantages in high ductility, strain hardening effect, environmental friendliness, etc. However, the corrosion resistance performance of ECC has rarely been studied. Therefore, this paper covers an experimental study on the corrosion resistance of R/ECC system using linear polarization resistance (LPR) techniques. Steel rebars were embedded in two cylinders made up of Mortar and ECC. Corrosion process had been speeded up by applying direct current. The corrosion behavior of the steel rebar was monitored by LPR techniques periodically. The testing results obtained from LPR measurements indicated that the polarization resistance of ECC was larger and evolved slower than that of Mortar. The determination of instantaneous corrosion rate proved that ECC had slower corrosion processes than Mortar. This experiment provides quantitative evidence that ECC is superior to Mortar in terms of corrosion resistance.

1. Introduction
The corrosion of steel bar in concrete structure has always been a serious issue compromising the durability of concrete structure. The corrosion of rebar will reduce the cross section area of rebar. Corrosion will damage the bond between rebar and concrete, which is made up of chemical adhesiveness, friction and mechanical interlocking. The corrosion of steel rebar will damage the
interface between rebar and concrete, as a result of which adhesiveness and friction is being impaired. The corrosion may destroy the ribs on the deformed rebar so the mechanical interlocking is being damaged. Corrosion product has higher volume ratio than steel icon. Its expansion will generate inner circular stress which could lead to cover cracking. The surface of original steel bar in concrete is closely adhered by thin passivation layer, which is mainly composed of iron oxide constituent $Fe_2O_3$ in very condense form [1]. The formation and maintenance of stable passivation layer highly depends on the high alkalinity (PH > 11.5) of the concrete [2]. However, the penetration of airborne $CO_2$ from environment will lower down the alkalinity of concrete. The passivation layer could be damaged by $CO_2$. Besides, the infiltration of chloride ion $Cl^-$ from deicing salt, seawater and other sources could initialize and speed up the corrosion of steel rebar especially when rebar lose the protection of passivation layer [1, 3]. Mehta [4] found that the permeability of concrete plays a fundamental role in causing the corrosion issues. The penetration of aggressive chemicals from the environment and the porosity of concrete material makes the corrosion of steel rebar hard to prevent.

The corrosion processes of steel bar can be divided into two half-cell reactions, anodic reaction and cathodic reaction, shown in Eq. (1) and Eq. (2). Anodic reaction will produce iron ion $Fe^{2+}$ and cathodic reaction will produce hydroxide $OH^-$. While iron ion and hydroxide could form $FeO$ and $Fe_{2}O_{3}$, which is generally known as rust, as illustrated in Eq. (3). Linear polarization resistance (LPR) is also frequently used to study the corrosion current and corrosion rate of system by using Stern-Geary equation [5, 6]. LPR provides a very direct measurement of the velocity of corrosion process. LPR techniques could help imply which stages the corrosion processes have entered or whether the cover had cracked through its potential-current diagrams. In recently decades, LPR techniques has proved to be most efficient methods to investigate the corrosion behavior of steel bar.

Anodic reaction: $Fe \rightarrow Fe^{2+} + 2e^-$

Cathodic reaction: $O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$

Rust formation: $2Fe^{2+} + O_2 + 4OH^- \rightarrow nFeO \cdot mFe_{2}O_{3} \cdot OH + H_2O$

In the early 1990’s, Engineered Cementitious Composite (ECC) has been invented as a replacement of tradition concrete because of the advantages in high ductility, strain hardening effect, environmental friendly, etc. [7]. Sahmaran, Liet al [8] discovered that the mass loss of rebar in ECC was much lower than in mortar under the same accelerated corrosion time. Even though several researches have been focused on the corrosion of steel bar in tradition concrete or fly ash added concrete or ECC, there is no specific research focusing on the corrosion mechanism of Rebar-ECC (R/ECC) system using electrochemical techniques. Therefore, this paper covers an experimental study on the corrosion of R/ECC system using LPR techniques. R/Mortar is also investigated as control sample. This study has uncovered the differences in LPR experimental results of R/ECC system in the contrast with R/Mortar system. LPR analysis results confirms that the corrosion rate of R/ECC is smaller than that of R/Mortar in the whole corrosion cycle.
2. Experiment program

Two circular cylinder specimens were manufactured in accordance with the standard techniques. The dimension and details of specimens are identical. As shown in Fig. 1, it is in cylindrical shape with a diameter of 75 mm and a height of 250 mm. The plain steel rebar is 13 mm in diameter and has no ribs. The surface of the steel rebar is polished in order to get rid of the small rust and then it is kept in the dry cabinet until casting. The top and bottom end of the rebar are coated with epoxy resin, and only 100 mm the middle part are exposed. The raw materials in the mixture of specimens include ordinary Portland cement, class F fly ash, silica sand (the average size of sand is around 110 micrometers), oil coated PVA fiber (12 mm long), water, superplasticizer. The cementitious materials (binder) are cement and fly ash. No coarse aggregate is used. Tab. 1 shows the material mix proportions of mixture. In specimen ECC, the binder is composed of 30% cement and 70% fly ash by weight; the water/binder ratio is 0.27; sand/binder ratio is 0.36; the mix has 2% of PVA fiber by volume.

![Fig.1. The dimension and details of specimen](image)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Cement</th>
<th>Fly ash</th>
<th>Sand</th>
<th>Water</th>
<th>PVA</th>
<th>SP</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECC</td>
<td>370</td>
<td>862</td>
<td>443.7</td>
<td>333</td>
<td>26</td>
<td>5</td>
</tr>
<tr>
<td>Mortar</td>
<td>377</td>
<td>880</td>
<td>450</td>
<td>339</td>
<td>0</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 1: The Mix proportion of specimen ECC and Mortar (kg/m3)
Accelerated corrosion method was used to speed up the corrosion process of steel bar in specimen. The corrosion of steel rebar develops at much higher speeder than natural corrosion under electrical current exertion. Fig. 2 shows the schematic plan of accelerated corrosion experiment setup. The specimen was kept in 3.5 wt. % sodium chloride solution. A constant potential was exerted on the rebar of the specimen to electrically accelerate the corrosion process. A cyclic accelerated corrosion plan was used. The current at a constant voltage was sustained for 24 hours. Afterwards LPR measurements were conducted. After measurement, another round of accelerated corrosion and testing begun. The first cycle was only 17 hours because of miscalculation. The accelerated corrosion cycle proceeded until clear major cracks had been observed or the solution in the container had turned to be yellow.

A three-electrode measurement system was set up to examine the R/ECC and R/Mortar system, as illustrated in Fig. 3. The steel rebar, the steel wire mesh, the saturated calomel was used as working electrode, counter electrode, and reference electrode respectively. Linear polarization resistance (LPR) measurement were conducted on each specimen using Versa Studio equipment produced by Princeton Applied Research. In LPR measurements, the initial potential was -10 mV and the final potential was 10 mV. The scan rate was 0.125 mV/s.
3. Discussion of experimental results

The polarization resistance, corrosion current, linear correlation factor, corrosion rate at different corrosion duration have been calculated and presented in Tab. 2 and Tab. 3. The linear correlation factor shows the strength of linear association between the potential and current of polarization curve in specimen under electrical signal. The linear correlation factor makes a suitable indicator of how easy the chemical could penetrate into the cover. The bigger the linear correlation factor, the easier the penetration of chemicals. When linear correlation factor is 1, it means chemical could penetrate into specimen thru solution without physical obstruction, which is also the case when cover has cracks from inside to outside surface. Tab. 2 and Tab. 3 demonstrates that the linear correlation factor of R/Mortar is bigger than that of R/ECC at the corrosion duration of zero. It may result from the fact that Mortar has higher porosity than ECC. As displayed in Tab. 2, the linear correlation factor rises from 0.578 to 1 as accelerated corrosion duration increases. And the linear correlation factor of specimen R/Mortar also rises from 0.75 to 1, shown in Tab. 3. The time when linear correlation index become one was at 209 hours for R/ECC and 113 hours for R/Mortar. For both specimen, the time when linear correlation factor becomes 1 was also the time when the corrosion-induced cover cracking in the cylinder have been observed and some rust had seep out and made solution yellow. The linear correlation factor and experimental observation proves that the cover cracking in cylinder ECC occurred at a much later time than cylinder Mortar. This may
be attributed from the strain-hardening and multi-cracking features of ECC material. ECC has higher ability to sustain the expansion of corrosion products because the fiber in the matrix could distribute the internal circular stress.

Fig. 4 shows the evolution of polarization resistance $R_p$ of cylinder ECC and Mortar with the accelerated corrosion time. Before accelerated corrosion experiment, polarization resistance $R_p$ of ECC and Mortar are quite similar. As accelerated corrosion proceeds, $R_p$ of both specimens decreases. But $R_p$ of Mortar decreases faster than that of ECC. Exponential function is used to fit the $R_p$ of both. The follow equation expresses the exponential fitting line of $R_p$ in cylinder ECC:

$$R_p(ECC) = 82.6e^{-0.02t}$$

The follow equation expresses the exponential fitting line of $R_p$ cylinder Mortar:

$$R_p(Mortar) = 92.3e^{-0.043t}$$

Eq. (1) and Eq. (2) shows that power index of exponential fitting function of cylinder Mortar doubles that of cylinder ECC. The descending speed of $R_p$ of Mortar is twofold in logarithmic scale. Based on Stern-Geary equation [9], polarization resistance is related to corrosion current $i_{corr}$, as following equation.

$$i_{corr} = \frac{B}{R_p}$$

where constant $B$ is $0.026 \sim 0.052$ [3], $i_{corr}$ is corrosion current.

The corrosion current ($i_{corr}$), generated by the flow of electrons from anodic to cathodic sites, could be used to compute the corrosion rate by the application of a modified version of Faraday's Law [9]:

$$C = \frac{i_{corr}E}{Ad} \times 128.67$$

where $C$ is corrosion rate in "mils per year" (mpy), $E$ is equivalent weight of the corroding metal (g), $A$ is area of corroding electrode (cm$^2$), $d$ is density of corroding metal (g/cm$^3$)

Fig. 5 shows the variation of corrosion rate as a function of corrosion duration. The corrosion rate of ECC experiences abrupt rise at 209 hours, while the sudden rise of corrosion rate of Mortar occurs at 89 hours. The threshold values are also around the time when cover crack inside out and linear correlation index becomes 1. The cover cracking opens a channel for the chemical to go in
specimen and engage in contact with steel rebar. In overall the corrosion rate in Mortar is higher than that in ECC. Therefore, LPR have provided a non-intrusive method to quantify the corrosion rate. These experimental results confirm that ECC has better corrosion resistance than Mortar.

<table>
<thead>
<tr>
<th>Duration (hours)</th>
<th>Linear Correlation Index</th>
<th>Rρ</th>
<th>Icorr</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>65.0</td>
<td>0.33</td>
<td>0.014</td>
</tr>
<tr>
<td>17</td>
<td>0.58</td>
<td>60.4</td>
<td>0.36</td>
<td>0.015</td>
</tr>
<tr>
<td>41</td>
<td>0.50</td>
<td>57.0</td>
<td>0.38</td>
<td>0.016</td>
</tr>
<tr>
<td>65</td>
<td>0.58</td>
<td>34.2</td>
<td>0.64</td>
<td>0.027</td>
</tr>
<tr>
<td>89</td>
<td>0.76</td>
<td>8.2</td>
<td>2.65</td>
<td>0.111</td>
</tr>
<tr>
<td>113</td>
<td>0.86</td>
<td>3.9</td>
<td>5.54</td>
<td>0.232</td>
</tr>
<tr>
<td>137</td>
<td>0.66</td>
<td>7.9</td>
<td>2.75</td>
<td>0.115</td>
</tr>
<tr>
<td>185</td>
<td>0.88</td>
<td>2.9</td>
<td>7.51</td>
<td>0.314</td>
</tr>
<tr>
<td>209</td>
<td>1.00</td>
<td>1.1</td>
<td>19.51</td>
<td>0.816</td>
</tr>
<tr>
<td>233</td>
<td>1.00</td>
<td>0.6</td>
<td>35.81</td>
<td>1.498</td>
</tr>
<tr>
<td>257</td>
<td>1.00</td>
<td>0.4</td>
<td>48.94</td>
<td>2.047</td>
</tr>
<tr>
<td>269</td>
<td>1.00</td>
<td>0.4</td>
<td>53.32</td>
<td>2.230</td>
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<tr>
<td>281</td>
<td>1.00</td>
<td>0.2</td>
<td>111.97</td>
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</tr>
<tr>
<td>293</td>
<td>1.00</td>
<td>0.2</td>
<td>99.50</td>
<td>4.162</td>
</tr>
<tr>
<td>305</td>
<td>1.00</td>
<td>0.2</td>
<td>96.93</td>
<td>4.055</td>
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</table>
Table 3: LPR results of cylinder Mortar

<table>
<thead>
<tr>
<th>Duration (hours)</th>
<th>Linear Correlation Index</th>
<th>$R_p$ (kohms)</th>
<th>$I_{corr}$ (uA)</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.75</td>
<td>66.6</td>
<td>0.33</td>
<td>0.014</td>
</tr>
<tr>
<td>17</td>
<td>0.81</td>
<td>33.0</td>
<td>0.66</td>
<td>0.028</td>
</tr>
<tr>
<td>41</td>
<td>0.87</td>
<td>20.3</td>
<td>1.07</td>
<td>0.045</td>
</tr>
<tr>
<td>65</td>
<td>0.84</td>
<td>23.2</td>
<td>0.94</td>
<td>0.039</td>
</tr>
<tr>
<td>89</td>
<td>0.97</td>
<td>1.7</td>
<td>13.07</td>
<td>0.547</td>
</tr>
<tr>
<td>113</td>
<td>1.00</td>
<td>0.3</td>
<td>77.58</td>
<td>3.245</td>
</tr>
<tr>
<td>137</td>
<td>1.00</td>
<td>0.2</td>
<td>141.49</td>
<td>5.918</td>
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<tr>
<td>149</td>
<td>1.00</td>
<td>0.1</td>
<td>185.78</td>
<td>7.771</td>
</tr>
<tr>
<td>161</td>
<td>1.00</td>
<td>0.1</td>
<td>225.71</td>
<td>9.441</td>
</tr>
<tr>
<td>173</td>
<td>1.00</td>
<td>0.1</td>
<td>247.13</td>
<td>10.337</td>
</tr>
</tbody>
</table>

Fig. 4: The evolution of $R_p$ with the accelerated corrosion time
4. Conclusion

This paper describes an experimental program on using LPR to study the corrosion resistance of ECC material. LPR results had confirmed that ECC has higher polarization resistance, higher ability to sustain the expansion of corrosion product. The corrosion rate rises suddenly when cover cracks inside out. At the same accelerated corrosion duration, the corrosion rate of ECC is much lower than Mortar. This experiment provides quantitative evidence that ECC is better than Mortar in terms of corrosion resistance.

References

INCORPORATION OF TREATED STRAW AND WOOD FLY ASH INTO CLAY BUILDING BRICK

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Abstract
High Cd content in straw and wood fly ash, generated from biomass-fired power plants, prohibits its recycling as fertilizer spreading on the landfilled. To improve and alter the current mainstream of fly ash treatment by landfilling, different approaches were tried for treatment of straw and wood fly ash, such as washing with water to quickly recover the highly soluble salts (mainly K and Cl), and treatment of the washed fly ash with elevated heavy metal content resulted from washing by electrodialytic remediation (EDR). The finding that SiO2 (quartz) accounted for a significant portion in the treated ash, suggests the possibility of the ash reuse in sintered clay bricks. In this study, the straw and wood fly ash treated by washing and EDR was incorporated into yellow clay bricks at different substitution rates. The properties of the clay-ash bricks were studied in terms of shrinkage, water absorption, porosity, density, compressive strength and leaching behavior, and compared with the 100% clay bricks. It’s promising to use the treated ash as a secondary building material.
ELECTROKINETIC POLYMERIZATION OF POLYMETHYL METHACRYLATE IN HARDENED CEMENT PASTE

Henry Cardenas(1), Nayeem Nasser(2), Xi Xie (1)

(1) Louisiana Tech University, USA
(2) Weyerhauser Corp., USA

Abstract
This study investigated the electrosynthesis of polymethyl methacrylate within the porous network of hardened cement paste (HCP). Anticipated benefits included the enhancement of tensile strength and the reduction of porosity. Methyl methacrylate, being slightly water-soluble, also exhibited the tendency to carry a slightly negative charge. It was driven toward titanium wire anodes embedded within cylindrical specimens of HCP. The tensile strength of the treated specimens was increased 60%. Raman Spectroscopy conducted on solid residuals obtained from extracted pore fluid indicated the presence polymethyl methacrylate (PMMA) that had formed within the pores. It was estimated that the electrosynthesized PMMA appeared to exhibit a significantly higher tensile strength than typically observed for bulk PMMA. Interestingly, the porosity of the HCP was not significantly altered. These observations guided the discussion of a possible mechanism of polymerization that would be expected to exhibit a relatively low yield of polymer that is forming primarily along the positively charged walls of the capillary pores within HCP.
ELECTROKINETIC NANOPARTICLE TREATMENT FOR CRACK REPAIR IN CONCRETE

Henry Cardenas(1), Israel Popoola(1)

(1) Louisiana Tech University, USA

Abstract
Subgrade areas of concrete structures can suffer from water penetration through foundation cracks. In many cases cracks can be sealed using a non-shrinking grout. Unfortunately, the interface between the grout and the crack surfaces tends to exhibit relatively poor strength. In difficult cases the ingress of water may continue along the interface. This study examined the use of nanoscale pozzolonic particles that were electrophoretically driven toward the crack repair interface. Mixed-metal-oxide coated titanium electrodes were embedded in the grout that was used to seal the cracks. The transport process concentrated the particles along these electrodes. Lab studies revealed that significant strength was developed at the repair interface. A field study is also presented in which a 3 m foundation crack located 10 m below grade was similarly treated. The study elucidated a number of practical considerations while successfully sealing the crack. At the time of the repair the floor crack was permitting a groundwater inflow rate of approximately 1 liter per hour. A 30-day follow up examination of the repair site revealed no continued water ingress despite an historic flooding event in which ~60 cm of rain fell in the vicinity during a 5-day period.
LABORATORY AND IN-THE FIELD EXPERIENCES ON THE MEASUREMENT OF SPONTANEOUS POTENTIAL IN MASONRY AFFECTED BY RISING DAMP

Elisa Franzoni(1), Simone Bandini(1), Gabriela Graziani(1)

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Abstract

Rising damp is a severe problem in historic masonry structures all over the world, as it jeopardises the indoor comfort and causes several deterioration processes in building materials, such as frost damage, salt crystallisation cycles, etc.. Among the technologies proposed for fighting rising damp, electro-osmosis has found several applications in real buildings, but its effectiveness can be considered still under investigation. In fact, although this method is based on electrokinetic principles that are already widely exploited in different fields, the electrokinetic processes taking place in historic masonry walls have not been fully elucidated yet.

In this paper the results of the measurement of spontaneous electric potential in fired-clay brick walls affected by rising damp are reported, as a contribution towards a better knowledge of the electrokinetic process in masonry. The testing was performed firstly in small-scale masonry models built in the lab with different bricks and subjected to capillary rise of water and saline solutions. Then, some brick masonry walls of heritage building affected by rising damp were tested with the same methodology used in the lab, in order to detect the presence of spontaneous electric potentials also in real materials and conditions.
ELECTROKINETICS TO MODIFY VOLUME CHANGE CHARACTERISTICS OF EXPANSIVE SOILS: A LABORATORY BASED INVESTIGATION

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Abstract
Volume change characteristics of expansive soils can cause significant structural damages to built infrastructure, particularly significant in long term performance of road pavements. The objective of this study was to investigate the potential of electrokinetic processing techniques to stabilise volume change characteristics of expansive soils. The investigations were carried out in the laboratory using soil collected from Horsham, Victoria, Australia, a well-known region for highly reactive soils, causing significant damages to road pavements. A layer of soil was placed in glass tanks and compacted to a known density and water content typical of field conditions. Using electrodes inserted into the soil, a direct current was passed across the soil under different voltage gradients varying between 0.25 to 2.0 V/cm for periods of 7, 14, 30 & 60 days. After electrokinetic processing, soil specimens were tested for volume change properties using soil reactivity indicators such as consistency limits, linear shrinkage, free swell index, shrink-swell index and activity. The test results show that with electrokinetic treatments, the volume change potentials of the experimental soil reduced to a greater or lesser degree depending on the magnitude of the voltage gradient and processing time. Under certain voltage gradients and treatment durations, experimental soil transformed from extremely reactive status to a slightly or almost non-reactive condition. In general, higher voltage gradients produced more rapid results in reducing volume change potentials however, they also lead to detrimental processes such as excessive drying, shrinking and cracking of soil, thus devaluing the merit of the treatment. The experimental results suggest the potential of developing electrokinetic treatment technique to stabilise volume change properties of expansive soils effectively and efficiently.
REPLACEMENT OF 5% OF OPC BY FLY ASH AND APC RESIDUES FROM MSWI WITH ELECTRODIALYTIC PRE-TREATMENT

Cátia Magro\textsuperscript{(1,2)}, Gunvor Kirkelund\textsuperscript{(2)}, Paula Guedes\textsuperscript{(1)}, Pernille Jensen\textsuperscript{(2)}, Lisbeth Ottosen\textsuperscript{(2)}, Alexandra Ribeiro\textsuperscript{(1)}

\textsuperscript{(1)} CENSE, Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, Portugal
\textsuperscript{(2)} Department of Civil Engineering, Technical University of Denmark, Lyngby, Denmark

Abstract

Fly ash (FA) and air pollution control (APC) residues are waste products from Municipal Solid Waste Incineration (MSWI). They are classified as hazardous waste due to the content of leachable heavy metals (HM), salts and/or dioxins.

An electrodialytic (ED) process was applied to FA and APC residues as pre-treatment prior to incorporation in mortar, aiming to stabilize and remove HM and chlorides. Eight ED experiments were performed for 7 days with a L/S ratio of 3.5. The number of compartments (2 or 3) and current density (0.1 or 1.0 mA cm\textsuperscript{-2}) varied. After ED treatment the heavy metals left in the ash were not leached to the same extent as in the original ash.

In mortar 5\% of Ordinary Portland Cement was replaced by FA and APC residues (raw and ED upgraded). The studied parameters: compressive strength, HM leachability, and Cl content.

The ED pre-treatment resulted in a decrease in both leaching of HM and the Cl content. The compressive tests presented comparable values to the reference mortars. This study suggests that the characteristics of FA and APC residues from MSWI after pre-treatment allows them to be reused in building materials, giving a new edge to waste management.
ELECTRO-DESLATION OF SANDSTONE CONTAMINATED WITH SODIUM SULPHATE

Lisbeth M. Ottosen(1)

(1) Department of Civil Engineering, Technical University of Denmark

Abstract

Cultural heritage stone monuments are lost all over the world due to salt induced decay. When water accesses the pore network of a stone, the water may carry various salts in solution. Several mechanisms can subsequently cause crystal growth and crystallization-dissolution cycles, which can result in severe stone damage.

The damaging effect varies between salts and salt mixtures, and not all salts are equally harmful, e.g. [1] showed that evaporation from a saturated Na2SO4 solution caused more damage in limestone than evaporation from a saturated NaCl solution, because Na2SO4 easily forms supersaturated solutions, which is a mechanism for the generation of stress [2]. According to [3], at 20°C Na2SO4·10H2O is the stable form of sodium-sulphate at relative humidity (RH) between 71 % and 93 %. Na2SO4·10H2O occupies a 314 % larger volume than the anhydrous salt. Thus, the volume of sodium-sulphate changes significantly with changes in RH, which is likely to be a major factor involved in the development of crystal pressure. The topic of the present communication is removal of Na2SO4 from carbonaceous sandstone by electro-desalination (ED) in order to stop the decay.

ED is based on application of an electric potential gradient and electromigration of the ions from the damaging salts out from the stone. During ED electrodes are placed externally on the surface of the salt infected stone. The electrodes are placed in a poultice in which the ions from the salts concentrate during the treatment. When removing the poultices after the desalination, the ions of the salts are removed with them.

At both electrodes there are pH changes due to electrolysis reactions. The pH decreases at the anode and increases at the cathode. It is necessary to neutralize the pH changes in the poultice to prevent pH changes of the stone itself. Herinckx et al. [4] underlined the importance of avoiding stone acidification, as in experiments without pH neutralization; the stones were severely damaged next to the anode. Calcite rich clay poultice can be used for neutralization of the pH changes at the electrodes [5]. The calcite buffers the pH changes and the clay gives good workability, so the poultice can have optimal contact to the surface of the stone to be desalinated. When the calcite buffers the acid from the anode, Ca\(^{2+}\) ions are released. If these
ions do not precipitate with anions in the poultice, they are transported into the limestone by electromigration, and can possibly precipitate with dissolved $\text{SO}_4^{2-}$ as shown in numerical-chemical modelling by [6]. The precipitation would happen in the stone closest to the anode. Should this happen, it may hamper the desalination and the formation of calcium-sulphates may even contribute to further salt weathering.

Compiling experimental results from various ED experiments it is evident, that chlorides and nitrates are removed faster than sulphates. This has most often been ascribed the generally lowest solubility of the sulphates. In case the acidification from the anode is not buffered in the poultice, sulphate is accumulating in the part closest to the anode in a calcareous sandstone during ED, and although accumulation was also seen in a similar experiment with poultice, the latter was less pronounced. Over time, the sulphate concentration decreased again in the stone closest to the anode [7]. Overall, from the experiments conducted, gypsum formation in the stone seems not to hamper sulphate removal by ED from different stones.

References

[2] Steiger, M.; Asmussen, S., 2008, Crystallization of sodium sulfate phases in porous materials: The phase diagram $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and the generation of stress, Geochimica et Cosmochimica Acta, 27, 4291-4306
USING GEOELECTRICAL METHODS TO ASSESS CORROSION OF REBAR AND PREFERENTIAL FLOW PATHS IN DAMS

André Revil (1)

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Abstract
The first part of the talk is related to the use of a passive geophysical method to non-intrusively assess the corrosion of buried metallic objects. Indeed, large amplitude (>100 mV) negative electrical potential anomalies are generally observed close to buried metallic objects. In order to explain the mechanisms generating such signals, a controlled laboratory experiment has been carried out involving two metallic cylinders buried with vertical and horizontal orientations in the capillary fringe within a sandbox. 2D and 3D self-potential data were collected at several time steps along with collocated pH and redox potential measurements. Large dipolar self-potential and redox potential anomalies developed in association with the progressive corrosion of the vertical metallic bar, while no anomalies were observed in the vicinity of the horizontal bar. This difference is due to the orientation of the metallic bars with the vertical bar subjected to a significantly larger redox potential gradient. The self-potential data were inverted to recover the causative source current density field using a deterministic least-squares 4D (time-lapse) finite element modeling approach. These results were then used to retrieve the 3D distribution of the redox potential along the vertical metallic cylinder and associated with the corrosion. The results of the inversion were found to be in excellent agreement with the measured distribution of the redox potential. This experiment indicates that passively recorded electrical signals can be used to non-intrusively monitor corrosion processes [1].

The second part of this talk is dealing with the use of the self-potential technique to assess preferential flow path in Earth dams using the electrokinetic approach. The electrokinetic approach is based on the streaming current density associated with the drag of the excess of electrical charges existing in the diffuse layer coating the surface of the grains and by the flow of the pore water. This current density generates an electrical field that can remotely measured using a set of non-polarizing electrodes connected to a multichannel voltmeter. A field experiment is here used to show how passive seismic and electrical data can be combined together to detect a preferential flow path associated with internal erosion in an Earth dam. Continuous monitoring was performed during a 7-day full-scale earthen embankment failure test. Spatially coherent acoustic emissions events and the development of a self-potential anomaly associated with induced concentrated seepage and internal erosion phenomena were
identified and imaged near the downstream toe of the embankment, in an area that subsequently developed a series of concentrated water flows and sand boils, and where liquefaction of the embankment toe eventually developed. I will discuss a novel 4D grid-search algorithm for acoustic emissions localization in both time and space, and the application of the localization results to add spatially varying constraints to time-lapse three-dimensional modeling of self-potential data in the terms of electrokinetic source current localization (see [2] for details). Seismic signal localization results are utilized to build a set of time-invariant yet spatially varying model weights used for the inversion of the self-potential data. This approach to geophysical monitoring of earthen embankments provides an improved approach for early detection and imaging of the development of embankment defects associated with concentrated seepage and internal erosion phenomena [2, 3]. The same approach can be used to detect various types of hydromechanical disturbances in civil engineering.

References


ELECTROKINETICS INDUCED CEMENTATION IN OFFSHORE SOILS

Julie Q. Shang (1)

(1) Department of Civil and Environmental Engineering, The University of Western Ontario, London, ON, Canada, N6A 5B9

Abstract

The research on electrokinetics induced cementation in offshore soils is presented. Experimental data and theoretical analysis demonstrate that significant cementation of offshore sediment and calcareous sand after electrokinetic treatment is attributed to electrochemical reactions with natural occurring carbonates, which is independent of electroosmotic consolidation. An innovative approach for soil improvement is developed based on the discovery, i.e. the combined electrokinetic and chemical treatment. Marine sediment samples mixed with chemical admixtures, including sulphate resistant cement, quicklime and coal fly ash, are subjected to the electrokinetic treatment. The effectiveness of the combined treatment is evaluated in terms of the soil shear strength and compressibility, as well as soil characteristics such as the water content, Atterberg limits, and water chemistry. The operational parameters such as the electric current density, applied voltage gradient and treatment time, are also discussed. The study demonstrates that with solid understanding of electrochemistry principles, the electrokinetic treatment may be applied in engineering practice for increasing the soil shear strength, reducing soil compressibility, modifying soil plasticity and enhancing load carrying capacity. The treatment is most effective in the vicinity of electrodes, which makes it especially attractive for increasing the bearing capacity of embedded anchors, caissons, sheetpiles and skirted foundations.
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This volume contains the proceedings of the MSSCE 2016 conference segment on “Electrochemistry in Civil Engineering”. Electrochemistry is important to different branches within civil engineering, including both the unintended electrochemical reactions as reinforcement corrosion and the intended reactions driving electro-desalination of construction materials. The proceedings emphasizes the application of electrochemistry to technological development as well as testing and fundamental understanding within the interdisciplinary area between electrochemistry and civil engineering.

The various topics of the proceedings are within reinforcement corrosion (Corrosion mechanisms and propagation, modelling of service life, and corrosion prevention), electrochemical assessment methods (in both construction and geotechnical materials), electrochemical repair techniques (stopping corrosion, crack closure and desalination for heritage conservation) and electrochemical upgrading of waste for use in construction materials (concrete or ceramics).

All contributions have been peer reviewed.

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