

# **Antal Kerpely Doctoral School of Materials Science and Technology**



## **Improved Corrosion Resistance For Reinforced Concrete Using Inhibitors of Environmentally Friendly**

Thesis Booklet

By

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RECOMMENDATION FROM THE SUPERVISOR TO

**Shaymaa Abbas Abdulsada**

PhD Candidate at University of Miskolc Antal Kerpely Doctoral School of

Materials Science and Technology

Mrs. *Shaymaa Abbas Abdulsada* had joined our Kerpely Doctoral School at University of Miskolc bringing with her a quite well thought out research topic from her home workplace at University of Kufa, Materials Engineering Department, Najaf-Iraq. Upon her affiliation in our Doctoral School it also became possible to extend our former traditional chemical metallurgical research fields with a scientifically rather complex as well highly technology oriented novel one.


In the past years Mrs. *Shaymaa Abbas Abdulsada* has shown great progress both in pursuing her PhD study courses quite successfully and also in designing, managing and completing her mostly experimental research program. She was able to co-operate quite efficiently with supporting teams she found in the relevant regional industries (Wanhua BorsodChem Ltd., CRH Magyarország Kft.), and also in a leading domestic research institute Zoltan Bay Nonprofit Kft. as well as in several well equipped laboratories at the two most traditional Faculties of University of Miskolc.

As her research topic is a rather interdisciplinary one it was also necessary to initiate and built up several internal collaborations between the laboratories at the Institutes of Polymers and Ceramic Engineering and that of the Physical Metallurgy, Metal Forming and Nanotechnology in addition to the host Institute of Metallurgy with its Laboratory of Surface Treatments and Surface Technologies dealing also with metals corrosion studies.

At the Faculty of Materials Science and Engineering Mrs. *Shaymaa Abbas Abdulsada* could manage quite independently and progress well with her PhD research work. She was also studious and successful in publishing her results regularly in several scientific international journals and is still planning to present her research results at international conferences as, for example, at the EUROCORR 2021 event.

All in all, in my view, her overall achievements can be highly valued based on the requirements of the Antal Kerpely Doctoral School of Materials Science and Technology, and having observed through the years her persistent enthusiasm and persevering endeavors in further developing herself, I can only wish her reaching her goals both in the successful completion of her PhD studies and fulfilling her dreams in her future academic and personal life.

Miskolc, 5 April, 2021



Dr. Tamás I. Török

Professor Emeritus

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## Abstract

The breakthrough and diffusion of chloride ions into reinforced concrete structures is the major contributing factor for inducing corrosion of the steel reinforcement; therefore, this work focused on demonstrating the beneficial effects of green inhibitor (orange peels extract) and calcium nitrate on chloride-induced corrosion. Another reason for choosing and testing these types of inhibitors was to study their effectiveness in more depth by utilizing several distinct scientific approaches and using many different and highly sophisticated laboratory and materials testing techniques. In this way the chosen eco-friendly inhibitor (so-called green inhibitor) could also be compared with at least a less harmful inorganic one, namely calcium nitrate as that is also cheap and normally effective to mitigate the corrosion of iron in the given environment. Moreover, calcium nitrate can also be considered as a kind of replacement to the well-established nitrite inhibitor which latter one is also targeted by some toxicity concerns.

This work presented a study of the compressive strength and the porosity for concrete samples and focused on studying and analyzing the corrosion processes and the total chloride contents in concrete by testing electrical resistivity, half-cell potential, chloride ions concentration, and electrochemical polarization curves of concrete samples. The analysis was based on an experimental investigation of the samples with the time of immersion (during 18 months) in 3.5 wt.% NaCl aqueous solutions at room temperature according to European Standards. For this work, different mixtures of concrete were prepared by added corrosion inhibitors (orange peels extract and calcium nitrate) with concentrations of 1% and 3% by weight of cement to the concrete mix in addition to two different admixtures (superplasticizer admixture and water-resisting admixture). The results showed that low porosity, low chloride ion, and the more reduction in the chloride induced corrosion rate were observed in samples at 3 wt.% corrosion inhibitors (orange peels extract and calcium nitrate) with water-resisting admixture.

### 1. Introduction

The corrosion of steel reinforcement is one of the main causes of premature deterioration of reinforced concrete, leading to significant economic losses. Chloride ions in the marine zone or the use of thawing salts or carbonation in urban areas can cause rapid deterioration [1]. In general, for steel reinforcement, good quality concrete offers excellent protection. Because of the high alkalinity of concrete pore fluid, steel in concrete stays in a passive state initially and, in most instances, for long periods. Corrosion is initiated either due to a drop in alkalinity resulting from carbonation or the breakdown of the passive layer by chloride ion attack [2]. By using corrosion-resistant steels, cathode protection, fusion-bonded epoxy coatings, corrosion inhibitors, and admixtures, steel corrosion can be alleviated. Corrosion inhibitors are the most commonly used of these approaches, with high cost-effectiveness and easy use. Inhibitors prevent corrosion from occurring by increasing concrete pH or fixing harmful ions that can cause steel corrosion [3]. The inhibitors often form a hydrophobic film on the reinforcement surface by adsorbing inhibitor ions or molecules on the surface. It decreases reinforcement corrosion by blocking the cathodic or anodic reactions [4]. Concerning corrosion inhibitors, the environmental issues caused by most chemicals in general and those used in corrosion protection, in particular, have favored the production of so-called green inhibitors. Green inhibitors consist of chemicals and chemical processes intended to minimize or remove harmful impacts on the environment. Reduced waste materials, non-toxic elements, and increased performance may be involved in the use and processing of these chemicals [5]. The need to integrate a non-toxic and environmentally friendly inhibitor into concrete

structures to avoid rebar corrosion phenomena led to the study of nitrate-based compounds [6].

### **1.1 Knowledge gaps**

Studying the interactions between the corrosion inhibitors and admixtures (superplasticizer and water-resisting admixture) together because most of the researchers were just interested either in the effect of the corrosion inhibitors or that of the admixtures. Consequently, the recent dissertation's main topic was chosen to analysis the reinforced concrete samples' properties after mixing green inhibitor with water-resisting admixture and, for comparison, preparing also another mix with the same admixture (water-resisting admixture) and calcium nitrate inorganic inhibitor. Moreover, the construction of the previous procedure was repeated using superplasticizer admixture as well. In this way it became possible to draw new conclusions about the determinative effects of both types of admixtures (i.e. the selected two kinds of inhibitors combined with the two different admixtures). Finally, it also became possible to figure out each inhibitor's individual behavior with the two types of admixtures used in this work and describe their effectiveness in mitigating the risk of corrosion in reinforced concrete.

### **1.2 Major research aims**

The main objectives of the PhD research program are as follows:

**1-**Using orange peels extract or calcium nitrate as suitable and more environmental-friendly and less harmful to health type alternative inhibitors to the traditional chemical corrosion inhibitors.

**2-**Demonstrating the potential and advantages of using orange peel extract 'green' inhibitor in the prepared concrete mixtures to prove that certain kinds of food wastes as well can be transformed into useful engineering materials and so reducing the environmental pollution of our precious planet Earth.

**3-**Improving plasticity of fresh concrete mixes by using carefully chosen superplasticizer and water-resisting admixtures together with the selected two corrosion inhibitors.

**4-**Performing laboratory studies and material testing analysis on the ability of inhibitor containing hardened steel reinforced concrete mixtures' resistance to chloride induced corrosion in 3.5wt.% NaCl aqueous solution for 18 months at room temperature.

## **2. Experimental Work**

### **2.1 Materials**

#### **2.1.1 Cement**

Portland slag cement CEM II/A-S 42,5 R was used in this study conforming to the EN 197-1 [7] and it received from CRH Magyarország Kft. company in Miskolc, Hungary.

#### **2.1.2 Aggregate**

Aggregates was used according standard EN 12620 [8] and it received from CRH Magyarország Kft. company in Miskolc, Hungary.

#### **2.1.3 Water**

Tap water was used throughout this work for both making and curing the specimens.

#### **2.1.4 Corrosion Inhibitor**

##### **2.1.4.1 Green Inhibitor**

In this work were used orange peels as a green inhibitor. Fresh leaves of orange peels were washed under running water, shade-dried in a furnace at 50°C for 3 hours and ground into powder in the workshop of the Institute of Metallurgy. The extraction was carried out using the Soxhlet extraction process in Wanhua BorsodChem company in Hungary.

### 2.1.4.2 Inorganic Inhibitor

In this work were used calcium nitrate as inorganic inhibitor with the formula  $\text{Ca}(\text{NO}_3)_2$  and it is a colorless salt absorbs moisture from the air and is commonly found as a tetrahydrate.

### 2.1.5 Admixtures

In this work two types of admixtures according to EN 934-2 [9].

#### 2.1.5.1 Superplasticizer admixture

The superplasticizer that was used in this work (product name was Dynamon SR31 and it brown liquid) is an admixture based on modified acrylic polymers specially designed for ready-mixed concrete and it received from CRH MagyarországKft. company in Miskolc, Hungary.

#### 2.1.5.2 Water-resisting admixture

This admixture as a nanocement and it's effect mechanism is based on the changes in the chemical processes of concrete bonding which were examined on the level of physics (elemental level). Oxydron was used in this work it received from Bioekotech Hungary Kft.

### 2.1.6 Steel Reinforcement

Steel rebar samples (with diameter of 8 mm) were obtained from the ÓAM steel producing company operating in Ózd city, Hungary.

## 2.2 Concrete Mixes

Concrete mixes were designed in accordance with the European mix design method according to the EN 1990 [10]. The composition of the mix prepared for casting the specimens was as follows: Cement:  $400 \text{ kg/m}^3$  (CEM II/A-S 42.5 R), Water:  $172 \text{ kg/m}^3$ ,  $w/c = 0.43$  planned/targeted value, Admixtures:  $2.4 \text{ kg/m}^3$ , Aggregate:  $1815 \text{ kg/m}^3$  [(sand 0/4: 60%  $1089 \text{ kg/m}^3$ ) (gravel 4/8: 40%  $726 \text{ kg/m}^3$ )].

Ten types of concrete mixes were prepared throughout this study as shown in Table 1:

Table 1 The concrete mixtures (specimens) prepared for the experiments

Symbol of Mix	Type of Mix		
	Type of Admixture	% of Adding Orange Peels Extract Inhibitor	% of Adding Calcium Nitrate Inhibitor
A1=A3 Reference	Superplasticizer admixture	without	without
B1	Superplasticizer admixture	1% by weight of cement	-
C1	Superplasticizer admixture	3% by weight of cement	-
A2=A4 Reference	Water-resisting admixture	without	without
B2	Water-resisting admixture	1% by weight of cement	-
C2	Water-resisting admixture	3% by weight of cement	-
B3	Superplasticizer admixture	-	1% by weight of cement
C3	Superplasticizer admixture	-	3% by weight of cement
B4	Water-resisting admixture	-	1% by weight of cement
C4	Water-resisting admixture	-	3% by weight of cement

### 2.3 Preparation, Casting and Curing of the Test Specimens

The molds were thoroughly cleaned and oiled before casting to avoid adhesion with the concrete surface. Mixing of materials was done manually after that water was added to the mix with continued mixing, then the mix was put into the molds and it was homogenized. The test specimens were taken out from the molds after 24 hours of casting (as shown in Fig. 1) and then they were completely immersed in tap water for a period of 28 days aging. These specimens were then compressive strength tested (see Fig. 2). The reinforced concrete samples (prepared for the electrical resistivity testes, half-cell corrosion potential tests and linear polarization resistance tests) were partially immersed in 3.5% NaCl solution during 18 months, while the concrete samples prepared for the chloride ion ingress tests were completely immersed in 3.5% NaCl solution for one month, 3 months and 6 months (as in Fig. 3).

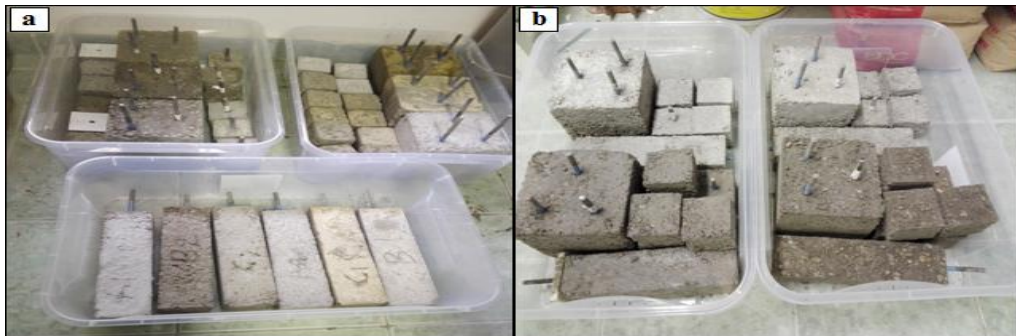


Figure 1 Specimens after taken out from the molds after 24 hours of casting a) samples with green inhibitor, b) with calcium nitrate

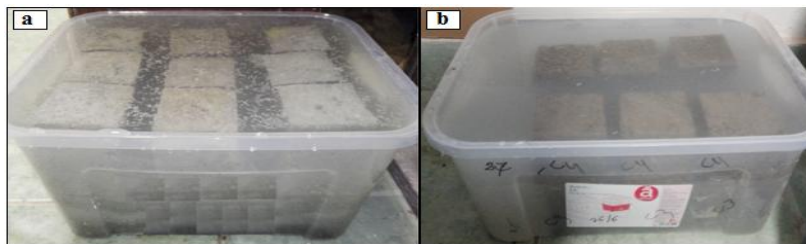


Figure 2 Curing of compressive strength specimens in tap water a) samples with green inhibitor, b) with calcium nitrate



Figure 3 Specimens of half-cell corrosion potential test and linear polarization resistance test immersed partially and specimens of chloride ion ingress test completely immersed in 3.5% NaCl solution a) samples with green inhibitor, b) with calcium nitrate

## 2.4. Concrete Testing

I did the following tests on concrete samples to detect their properties:

2.4.1 Chemical Composition Analysis of the Admixtures (both types of inhibitor + admixtures) and steel rebar

2.4.2 Compressive Strength Test

2.4.3 Porosity

2.4.3.1 Vacuum saturation porosity

2.4.4 Chloride concentration ( $\text{Cl}^-$  ions)

2.4.5 Electrical Resistivity Measurement

2.4.6 Half-Cell Corrosion Potential

2.4.7 Linear Polarization Resistance (Corrosion Current)

2.4.8 Studying corrosion products at the steel-concrete interface of the samples

2.4.8.1 SEM observation

2.4.8.2 Optical microscopy

2.4.8.3 XRD analysis

## 3. Results and Discussion

### 3.1 Analysis of the Chemical Composition

#### 3.1.1 Inhibitors and Admixtures

The chemical structure of the green inhibitor (orange peels extract) was determined by FTIR technique (as shown in Fig. 4).

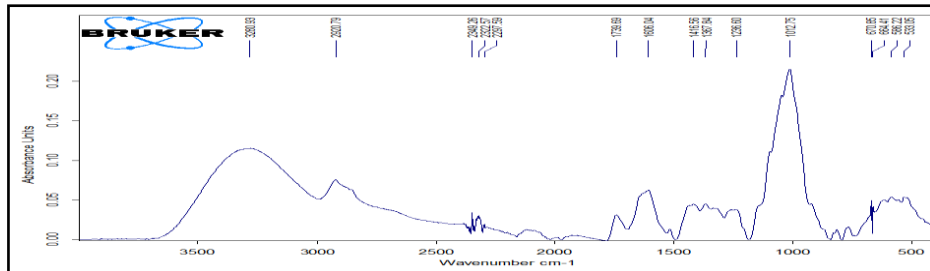


Figure 4 Fourier transform infrared spectrum (FTIR) depicting its IR absorbance peaks in the function of wave number with the most significant values indicated above the peaks for dry orange peels powder.

In the high energy region the peak at  $(3280.93)\text{cm}^{-1}$  is due to a large amount of OH groups of the carbohydrates and those of lignin. Also at  $(1045)\text{cm}^{-1}$  this peak corresponds to the link C–O–H or C–O–R (alcohols or esters) while the distinctive band at  $(2925)\text{cm}^{-1}$  is related to the presence of C–H stretching vibration together with bending vibrations around  $(1428)\text{cm}^{-1}$  of aliphatic chains ( $-\text{CH}_2-$  and  $-\text{CH}-$ ) forming the basic structure of this lignocellulosic materials. All of these compounds can form double bounds, triple ties and aromatic rings linkages with the surface of steel rebar causing the formation of a protective layer around it.



The chemical structure of calcium nitrate was determined by FTIR technique (as shown in Fig. 5).

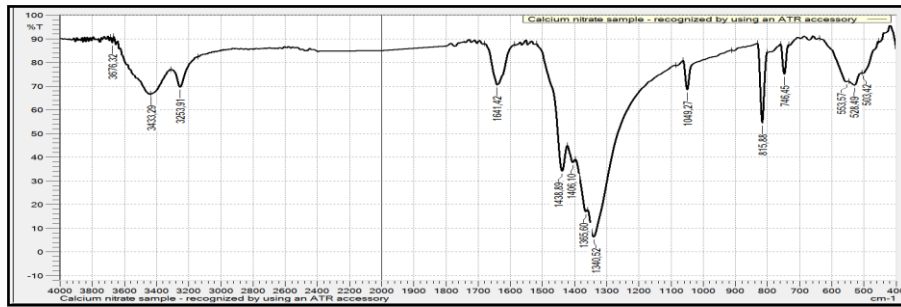


Figure 5 Fourier transform infrared spectrum (FTIR) depicting its IR absorbance peaks in the function of wave number with the most significant values indicated above the peaks for calcium nitrate inhibitor.

The relatively strong absorption band at  $\sim 3642\text{ cm}^{-1}$  corresponded to the OH stretching mode. The peak at  $\sim 1641\text{ cm}^{-1}$  was due to the  $\text{NO}_2$  symmetric stretching. The broad band centered at  $\sim 1438$  to  $1406\text{ cm}^{-1}$  refers to the deformation of C-H group. The peak at  $\sim 1365\text{ cm}^{-1}$  was due to the  $\text{NO}_3^-$  stretching. The peak at  $\sim 1340\text{ cm}^{-1}$  was due to the symmetric stretching mode of the N=O. All of these compounds can form double bonds, triple ties and aromatic rings linkages with the surface of steel rebar causing the formation of a protective layer around it.

From Fig. 6 it appears that the main component of the liquid superplasticizer admixture is a low molecular weight polyethylene glycol together with a smaller portion of a lower ester.

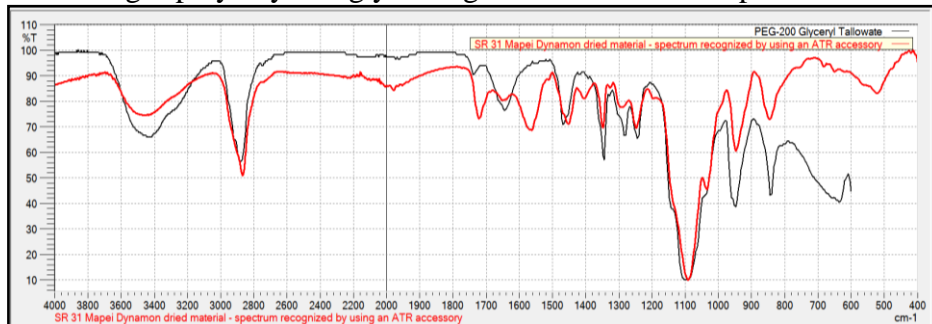


Figure 6 Fourier transform infrared spectrum (FTIR) depicting its IR absorbance peaks in the function of wave number with the most significant values indicated above the peaks for: Superplasticizer admixture.

ICP-OES and EDS analytical techniques were used to determine the major chemical elementary components of water-resisting admixture as given in Table 2. The solid water-resisting admixture consist of some mineral components such as calcium oxide, silicates and aluminates, so these components should also play important roles during the hydration of the freshly prepared concrete.

Table 2 The approximate chemical composition of water-resisting admixture (expressed as oxides) derived from two different chemical elementary analytical techniques.

Components (as oxides)	Composition in wt% and in at% (approximate values)		
	by EDS (using SEM) method, in wt%	by EDS (using SEM) method, in at%	by ICP-OES method, in wt%
<b>CaO</b>	61.8	57.2	58.0
<b>SiO<sub>2</sub></b>	27.3	27.1	21.4
<b>Al<sub>2</sub>O<sub>3</sub></b>	2.59	4.4	4.47
<b>MgO</b>	2.11	1.4	1.20
<b>Na<sub>2</sub>O</b>	0.83	0.85	0.31
<b>K<sub>2</sub>O</b>	0.91	1.4	0.78
<b>Fe<sub>2</sub>O<sub>3</sub></b>	1.31	3.5	2.67
<b>SO<sub>3</sub></b>	3.18	4.2	2.50
<b>TiO<sub>2</sub></b>	-	-	0.27
<b>ZnO</b>	-	-	0.14
<b>SrO</b>	-	-	0.09
<b>Mn<sub>2</sub>O<sub>3</sub></b>	-	-	0.05
<b>Cr<sub>2</sub>O<sub>3</sub></b>	-	-	0.006

### 3.1.2 Steel Rebar

The chemical composition (in% by mass) of steel rebar was determined by analytical analysis using ICP-OES technique and the result was presented in Table 3.

Table 3 The approximate chemical composition of steel rebar (concentration in wt%)

<b>C</b>	<b>Mn</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cr</b>	<b>Ni</b>	<b>Cu</b>	<b>Mo</b>	<b>Fe (calculated)</b>
0.19	0.78	0.24	0.027	0.035	0.11	0.11	0.27	0.02	98.22

### 3.2 Compressive Strength Test

Fig. 7 shows the results of compressive strength test at age 28 days for samples with green inhibitor (orange peels extract).

The results showed that:

1) For superplasticizer admixture in concrete there was not much reduction observed in the compressive strength. By using the orange peels extract as corrosion inhibitor in conc. 1% and 3% by weight of cement, it reduced the compressive strength considerably by 10.5% for 1% addition and 13% for 3% addition, respectively.

2) For water-resisting admixture with concrete causes reduction in compressive strength more than superplasticizer admixture in sample without green inhibitor. After using green inhibitor with 1% and 3% by weight of cement affect compressive strength with an increase 3.3% for 1% addition and 16.6% for 3% addition respectively.

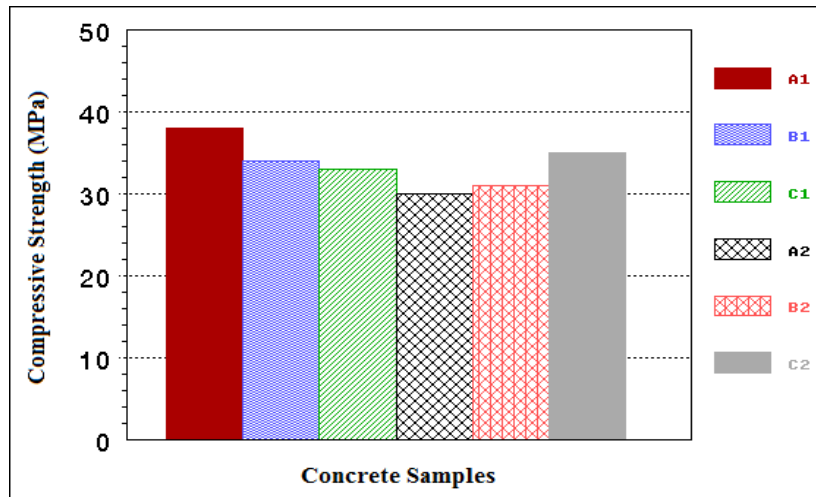


Figure 7 Compressive strength of concrete samples with green inhibitor after immersion in tap water for 28 days

After adding calcium nitrate as a corrosion inhibitor, the results of compressive strength (as shown in Fig. 8) showed that:

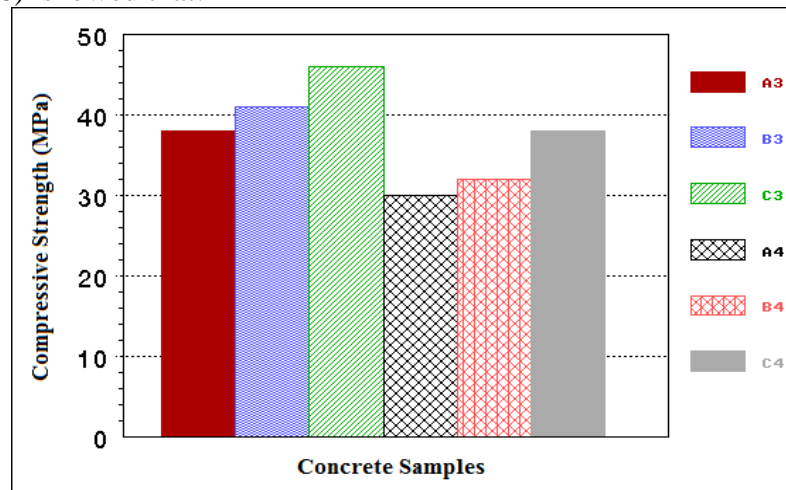


Figure 8 Compressive strength of concrete samples with calcium nitrate inhibitor after immersion in tap water for 28 days

(1) For superplasticizer admixture in concrete (without inhibitor) there was not much reduction observed in the compressive strength. (Without this admixture the given type concrete should have compression strength of C35/45 MPa at age 28 days.)

By using calcium nitrate as corrosion inhibitor in conc. 1% and 3% by weight of cement, it increased the compressive strength considerably by 8% for 1% addition and 21% for 3% addition, respectively. (2) For water-resisting admixture with concrete causes reduction in compressive strength more than superplasticizer admixture in sample without inhibitor. After using calcium nitrate inhibitor with 1% and 3% by weight of cement, affect compressive strength with an increase 7% for 1% addition and 27% for 3% addition respectively.

### 3.3 Porosity Measurement

Porosity is the sum of the entrained air pores and voids within the paste. By increasing the concentration of green inhibitor, porosity decreased as shown in Fig. 9.

The lowest porosity was obtained for the concrete with 3% green inhibitor and water-resisting admixture (sample C2). The maximum porosity of the samples tested was found with samples without inhibitor (A1, A2 ) but with high value in the sample with water-resisting admixture (A2).

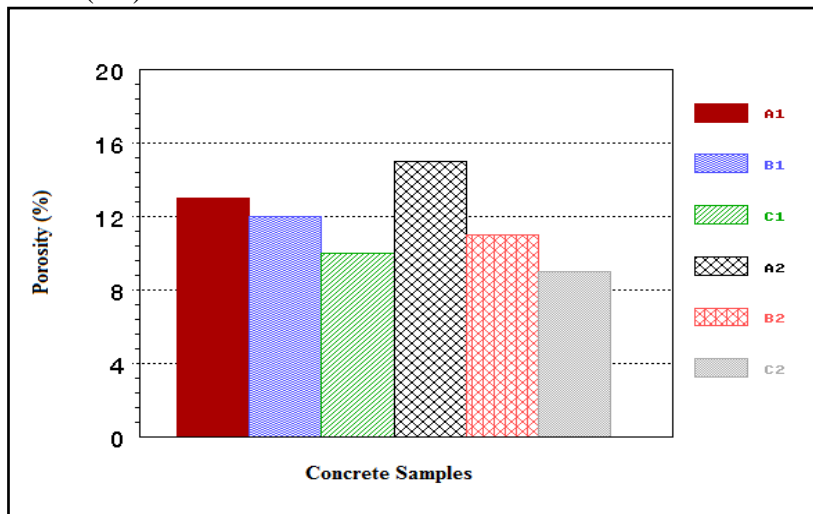


Figure 9 Variation in porosity for concrete samples with green inhibitor

Porosity did not change with 1% of the calcium nitrate inhibitor (particularly with superplasticizer admixture) but decreased with 3% of the same inhibitor as shown in Fig.10 for concrete samples.

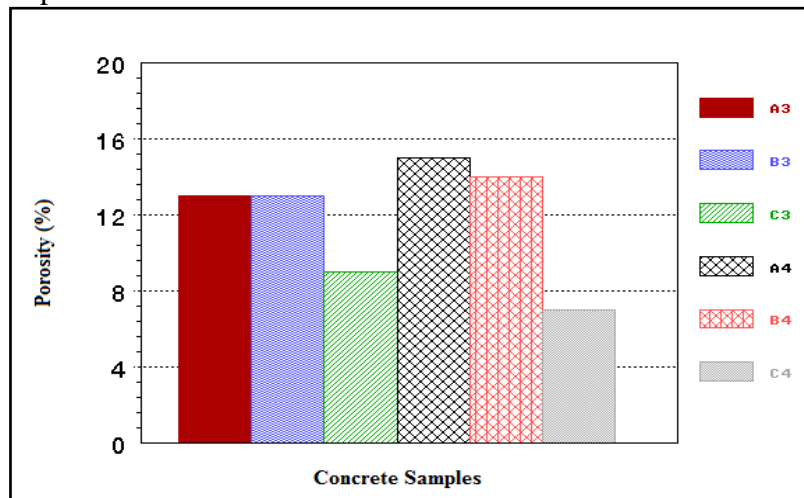


Figure 10 Variation in porosity for concrete samples with calcium nitrate inhibitor

For concrete with a 3% calcium nitrate inhibitor and water-resisting admixture (sample C4), the lowest porosity was obtained. The maximum porosity of the samples tested was found in samples without inhibitor (A3, A4), particularly in the water-resisting admixture sample (A4) and in high porosity samples with a 1% inhibitor.

### 3.4 Chloride Concentration (Cl<sup>-</sup> ions) Test

Figs.11 and 12 show the results of the chloride ions concentrations in concrete samples determined at the end of the different immersion periods of 1, 3, and 6 months, in 3.5% NaCl solution. The cut side and middle sections of the samples were analyzed in the laboratory of the BorsodChem company.

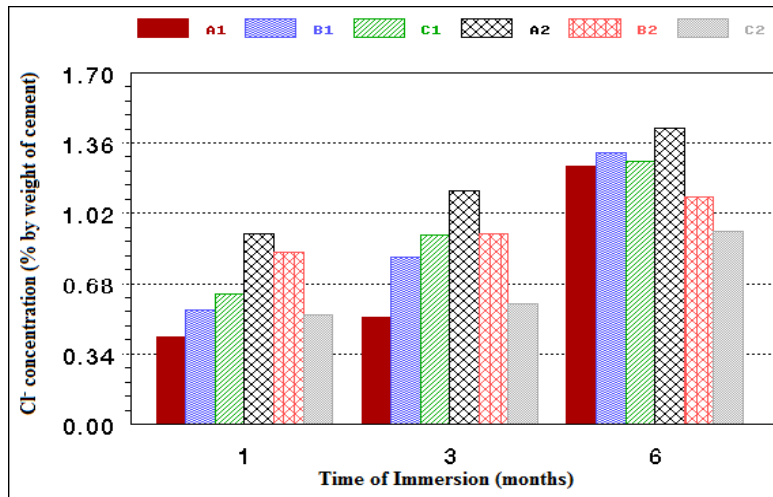


Figure 11 Cl<sup>-</sup> ions concentrations in the middle (from depths 1.75 to 3.5cm) of concrete samples with green inhibitor after immersion in 3.5%NaCl solution for different months

From the results of Cl<sup>-</sup> concentrations given in Figs. 11 and 12 for the samples immersed in 3.5%NaCl, it appear that all the samples after 6 months (only samples C1 it shows low value from the Cl<sup>-</sup> concentrations) show high risk of corrosion because the Cl<sup>-</sup> concentrations are higher than 1% by weight of the cement.

The sample C2 (both in the outer sides and the middle part) has the lowest concentrations of chloride ions after 6 months immersion in 3.5%NaCl. This sample had about 3% green inhibitor together with water-resisting admixture, hence, its many active groups and strong bonding ability must have reduced the porosity the most and reduced effectively the diffusion of chloride in the sample.

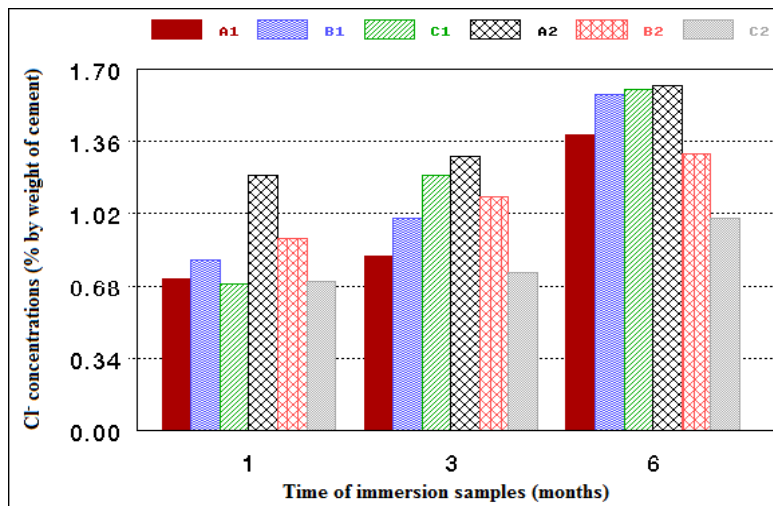


Figure 12 Cl<sup>-</sup> ions concentrations in the outer sides (from depths 0 to 1.75cm) of concrete samples with green inhibitor after immersion in 3.5%NaCl solution for different months

The results of Cl<sup>-</sup> concentrations in Figs. 13 and 14 for the samples with calcium nitrate inhibitor immersed in 3.5%NaCl, it appeared all the samples after 6 months have high risk for corrosion because the Cl<sup>-</sup> concentration more than 1% by weight of the cement.

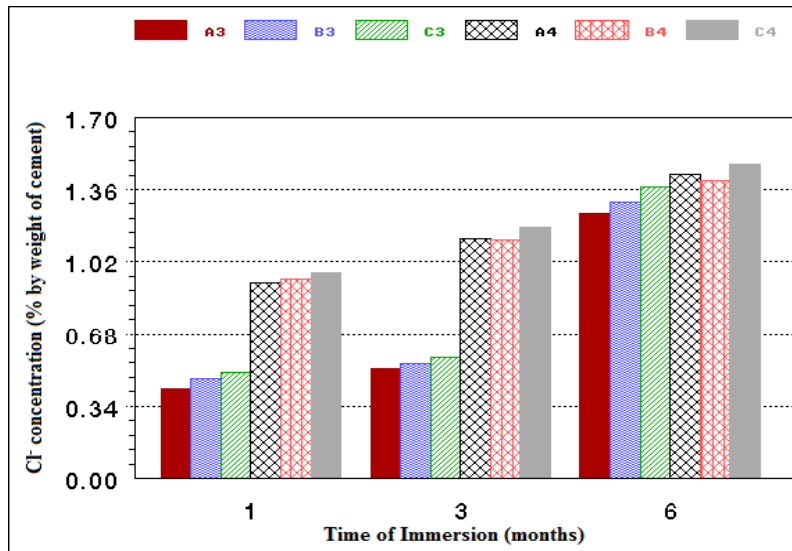


Figure 13 Cl<sup>-</sup> ions concentrations in the middle (from depths 1.75 to 3.5cm) of concrete samples with calcium nitrate after immersion in 3.5% NaCl solution for different months

Normally Cl<sup>-</sup> ions concentration in depths from 1.75 to 3.5cm (in the middle of the sample) less than in the depths from 0 to 1.75cm. The Cl<sup>-</sup> ions concentration increasing with increase the concentration of calcium nitrate, so the concrete samples with 3% calcium nitrate have the highest ratio from Cl<sup>-</sup> ions comparing with other samples and thereby slightly increases the risk of depassivation of the protective oxide layer on the embedded steel.

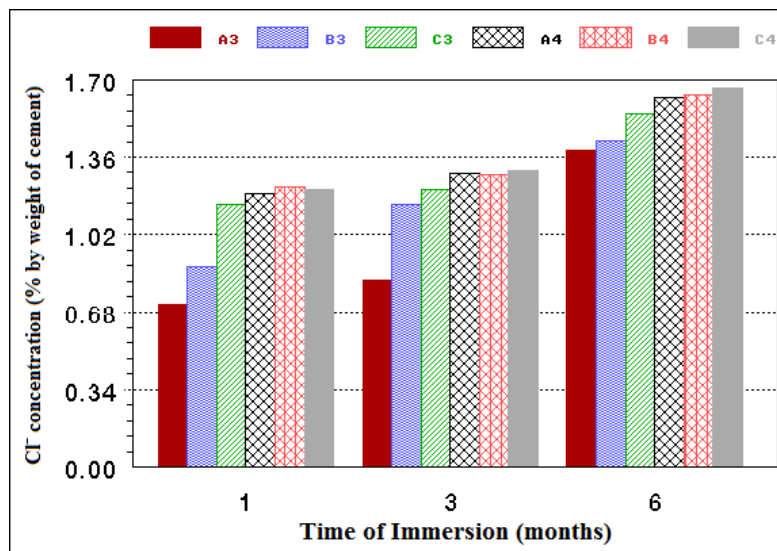


Figure 14 Cl<sup>-</sup> ions concentrations in the out sides (from depths 0 to 1.75cm) of concrete samples with calcium nitrate after immersion in 3.5% NaCl solution for different months

### 3.5 Electrical Resistivity Measurement

The results of our electrical resistance test for reinforced concrete samples with green inhibitor (in K.Ω) are shown in Fig. 15.

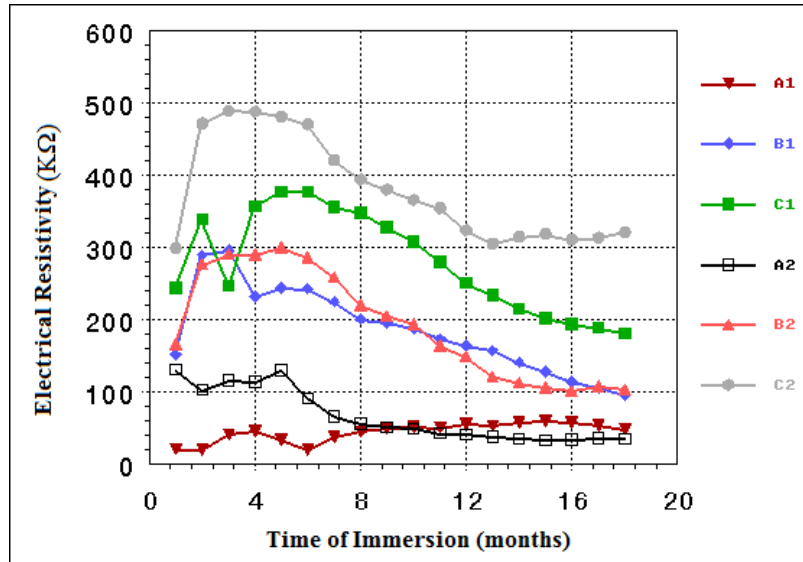


Figure 15 Electrical resistivity of concrete samples (with green inhibitor) with different time of immersion

Figure 15 sum up the electrical resistivity measured regularly during 18 months, after 18 months, and in this respect, the best sample showing the highest electrical resistivity was C2, first, because the chemical composition of the water-resisting admixture (with more active groups and forming stronger bounds), and second, together with C2 was containing the greatest admixing amount of green inhibitor (3%) could fill in well the pores and microcracks, and so increase considerably also the electrical resistivity in this sample. The average results of the electrical resistivity of the samples with calcium nitrate inhibitor (in K.Ω) were indicated in Fig. 16.

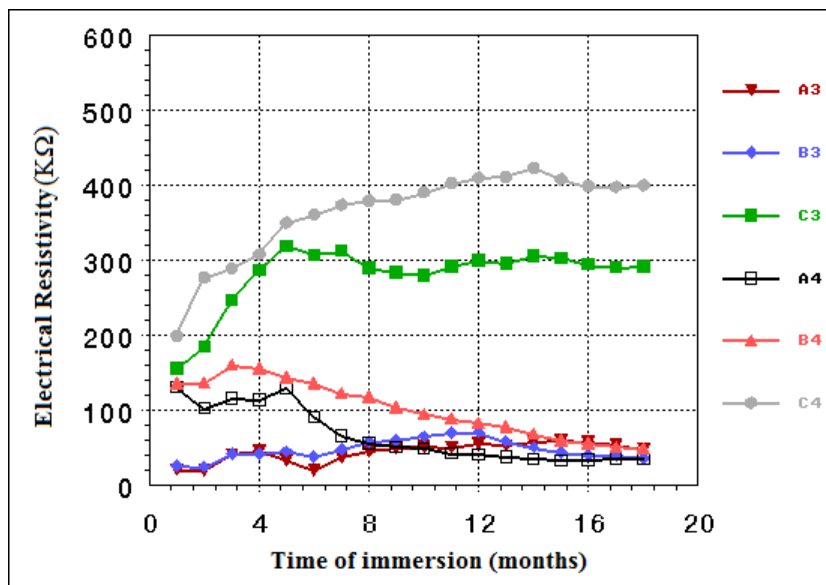


Figure 16 Electrical resistivity of concrete samples (with calcium nitrate) with different time of immersion

The samples with 3% calcium nitrate inhibitor showed increased electrical resistivity and it high values comparing with reference samples (A3, A4) but the electrical resistivity increased a little bit in the samples with 1% inhibitor because between 2 – 4% calcium nitrate of cement weight seems sufficient to protect the rebar against chloride-induced corrosion. Calcium nitrate in the samples C3 and C4 successfully stopped most of the

chloride-induced because calcium nitrate's corrosion inhibition is associated with the stabilization of the passivation film, which tends to be disrupted when chloride ions are present at the steel level. Electrical resistivity in the samples B3 and B4 showed not low resist to corrosion because it have only 1% calcium nitrate (less than 2%) so the chloride ion transport is driven by permeation through the pores since the samples and these chlorides have broken into the passive film on the steel rebar because the inhibitor can't make this passive film as a stable.

### 3.6 Half-Cell Corrosion Potential

Exemplary results of the half-cell potential measurements for samples with green inhibitor are shown in Fig. 17, on each sample, three half-cell readings were taken every test after that took the average for these reading.

It is clearly seen from Fig. 17 that the half-cell potential readings for all samples with green inhibitor (B1,B2 and C1,C2) are less negative (indicating greater resistance to corrosion) than samples without green inhibitor. In contradistinction to that the potential results obtained for samples A1 and A2 were more negative (between -200 to -350 mV) after 5-6 months immersion in 3.5%NaCl, which corresponds to a 50% probability that corrosion was occurring. Half-cell potential measurements became consistently less negative with increasing age for all six specimens.

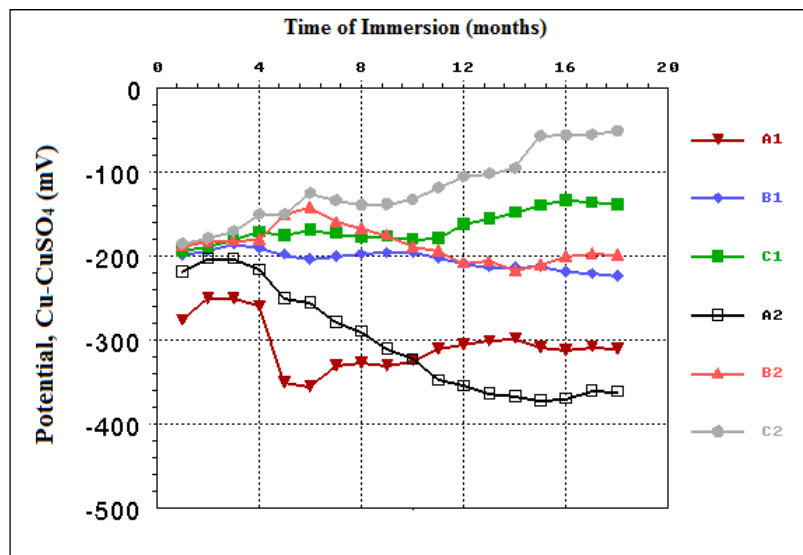


Figure 17 Corrosion potentials versus time for concrete samples with green inhibitor

Measurements of half-cell potential for samples with calcium nitrate after immersion in 3.5%NaCl for 18 months were shown in Fig. 18.

Fig. 18 showing that the half-cell readings for samples with 3% calcium nitrate inhibitor less negative (more resistance to corrosion) than samples with 1% and samples without calcium nitrate inhibitor. The potential results obtained for samples A3 and A4 were more negative (between -200 to -350 mV) after 18 months (especially after 5 months) from immersion in 3.5%NaCl, which corresponds to a 50% probability that corrosion was occurring. In samples B3 and B4 (1% calcium nitrate) the ratio is less than one (that is, there's more chloride than nitrate present) and this ratio will lead the chloride ions to react with the iron to begin the corrosion process. During the chemical reaction between the nitrate and iron, the supply of nitrate ions is depleted.



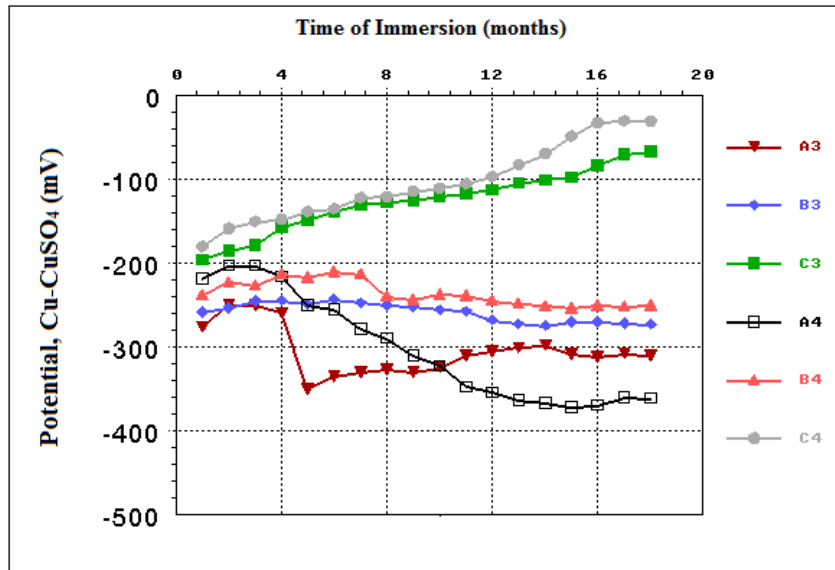


Figure 18 Corrosion potentials versus time for concrete samples with calcium nitrate

### 3.7 Linear Polarization Resistance

The observed electrochemical polarisation features and the calculated corrosion current densities in Fig.19a indicate the corrosion current densities of all the samples decrease with increase of concentration of the green inhibitor, which phenomenon can, with high probability, attributed to the formation of a protective layer around the surface of steel in contact with the inhibitor containing aqueous medium. During 18 months immersion the sample C2 which appeared the best sample with green inhibitor can resist corrosion.

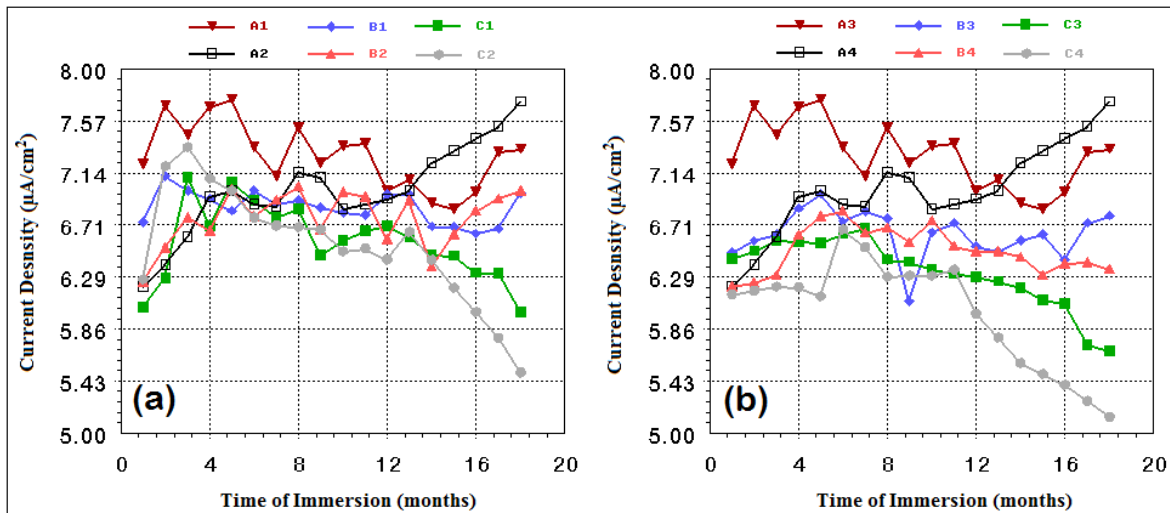


Figure 19 Current density obtained from the measured polarisation curves of concrete samples in 3.5% NaCl during 18 months at room temperature: a) with green inhibitor, b) with calcium nitrate inhibitor.

After 18 months immersion time of the concrete samples the corrosion current density in Fig.19b was increased with decrease in the electrochemical corrosion potential. Same tendency was found with the results extracted from the Tafel-plot type experiments. Samples with 3% calcium nitrate inhibitor (C3, C4) showed lower corrosion current density and this is an indication there's a stable protective layer was formed around surface of steel rebar by this inhibitor. Samples of A4, B4, and C4 indicate a remarkable changing

trend of the corrosion current densities, which are of smaller values than for the samples of A3, B3, C3).

### 3.8 Corrosion Rate

In our case a computer controlled (ZAHNER type potentiostat) was used to record the current – potential data which were then converted to corrosion rates according to standard procedures.

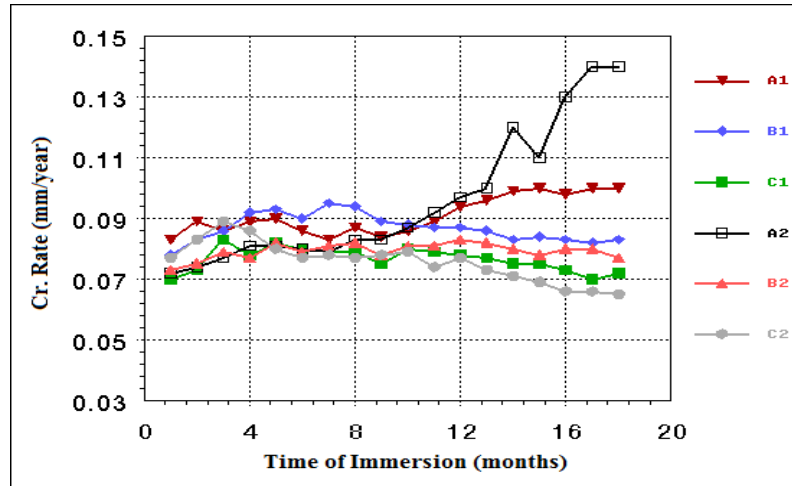


Figure 20 Corrosion rate for concrete samples with green inhibitor after immersion for 18 months in 3.5%NaCl solution

From Fig. 20 corrosion rates is increasing with time of immersion during the tested period of 18 months, and the rates are always somewhat lower in cases when the concrete samples contained the extract of the orange peel inhibitor with water-resisting admixture. It means that the inhibitive effect of the chosen and so tested green inhibitor is really plausible and promising especially together with water-resisting admixture.

The results of the corrosion rate for concrete samples with calcium nitrate were indicated in Fig. 21

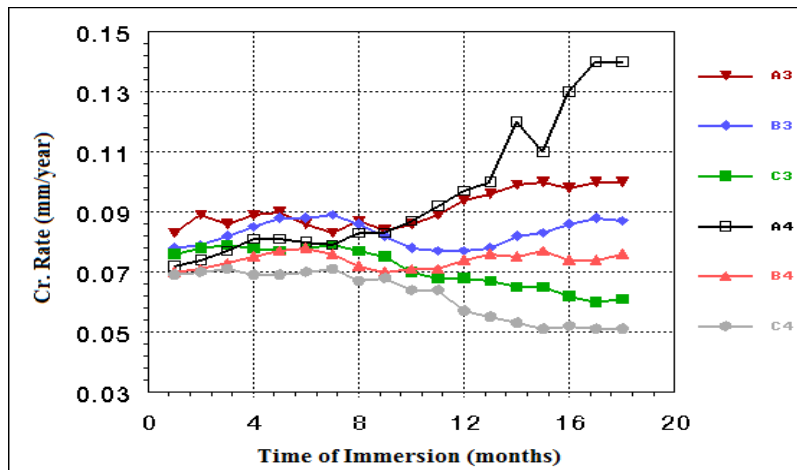
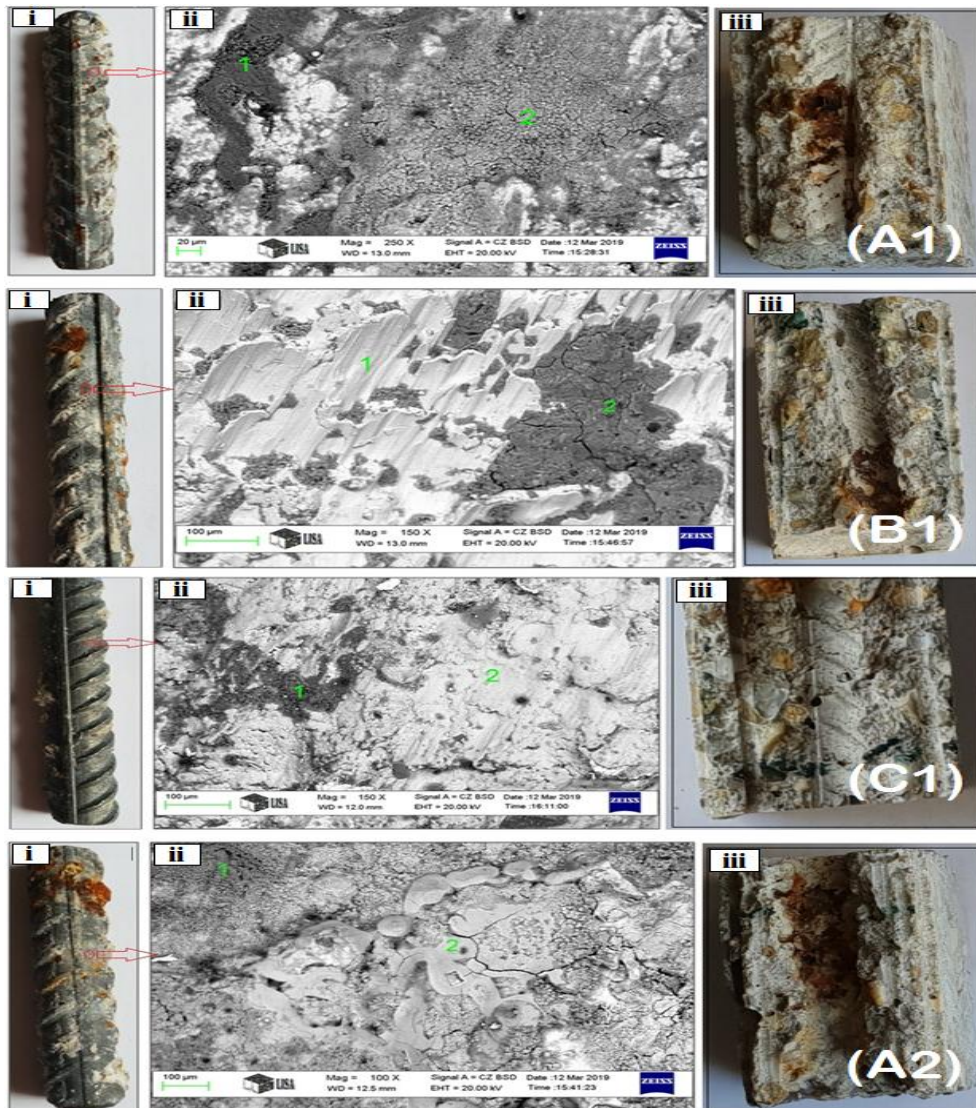


Figure 21 Corrosion rate for concrete samples with calcium nitrate after immersion for 18 months in 3.5%NaCl solution

As it is seen in Fig. 21, the tendency of the corrosion rates is increasing with time of immersion during the tested period of 18 months, and the rates are always somewhat lower in cases when the samples have calcium nitrate inhibitor at 3% and samples with water-resisting admixture. During 18 months the corrosion rate in samples C3 and C4 started decreasing with increasing the time of immersion but the samples with 1% inhibitor after 18 months have high increasing in corrosion rate because calcium nitrate have effective inhibition mechanism on chloride-induce corrosion of calcium nitrate at concentrations higher than 1% by weight of cement.

### 3.9 SEM-EDS Microstructural and Composition Analysis of the Steel Rebar Surface

For the microstructural SEM investigations the steel rebar specimens/rods first had to be removed from the concrete blocks which had previously been kept immersed in 3.5% NaCl solution for 18 months. After that the SEM-EDS analysis could be commenced and the results are presented in Figs. 22 and 23. The chemical elementary compositions determined at some selected surface points on the steel rebars (as marked clearly in Figs. 22 ii and 23 ii) were obtained by the EDS method being coupled to the scanning electron microscope (SEM) and are given in wt% in Tables 4 and 5.



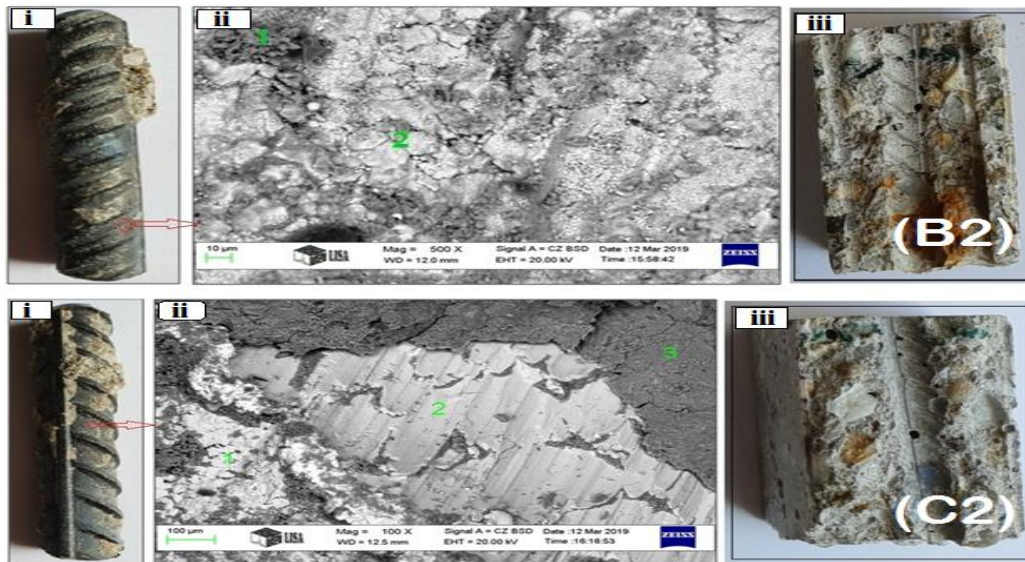


Figure 22 i) Close-up image of a steel rebar for sample after removal from the concrete, ii) SEM Micrograph of the section indicated in (i), iii) Representative image of a split concrete specimen with and without green inhibitor after removal of the steel rebar

Table 4 The approximate chemical composition (expressed as oxides) of some small selected surface areas (as indicated in Fig. 22i) of the steel rebars after removal from the concrete blocks by SEM-EDS

Components (as Oxides)	Composition by EDAX (ZAF correction) given in wt%, not normalised												
	A1		B1		C1		A2		B2		C2		
	Point 1	Point 2	Point 1	Point 2	Point 1	Point 2	Point 1	Point 2	Point 1	Point 2	Point 1	Point 2	Point 3
Na <sub>2</sub> O	0.13	0.46	3.61	1.38	2.36	1.40	0.14	0.35	13.6	6.01	3.61	6.45	0.61
MgO	0.00	0.30	1.42	4.13	2.29	2.26	1.16	0.25	3.13	2.31	3.15	0.50	4.28
Al <sub>2</sub> O <sub>3</sub>	0.19	0.95	1.21	10.9	5.62	1.22	1.26	0.59	2.35	1.32	2.39	0.57	2.77
SiO <sub>2</sub>	1.38	2.01	3.41	17.6	24.7	10.7	0.59	1.07	10.6	7.80	10.6	3.11	16.7
SO <sub>3</sub>	1.04	0.55	1.10	5.75	4.93	2.28	0.23	0.28	0.58	0.38	0.58	7.39	2.18
Cl <sub>2</sub> O	3.51	0.23	1.83	0.68	3.98	0.31	5.10	2.06	0.24	0.11	0.20	1.90	0.91
K <sub>2</sub> O	0.11	0.16	0.98	0.84	0.96	1.25	0.10	0.07	0.45	0.17	0.5	1.75	0.54
CaO	0.51	2.54	9.65	52.6	40.4	21.1	1.00	0.84	39.2	15.5	39.2	16.0	58.4
MnO	0.91	0.87	0.83	0.67	0.72	1.08	0.09	0.15	2.79	1.68	2.79	0.66	0.71
FeO	92.2	91.9	75.9	5.32	2.36	55.4	92.3	94.3	47.1	64.7	37.1	61.7	12.9

The observed microstructure (observed by SEM imaging technique and presented in Fig.22) and the EDS analysis for composition (Table 4) indicate the effects of the changing bulk and boundary materials properties, like the porosity and pore solution, as well as alterations at the metal/solution interfaces inside the concrete samples being immersed up to 18 months in 3.5%NaCl solution. The observed phenomena by the formation of porous corrosion products modifying the charge transfer resistance at the steel/solution interface. The results of the samples with calcium nitrate shown in Fig. 23 and Table 5 as the following:

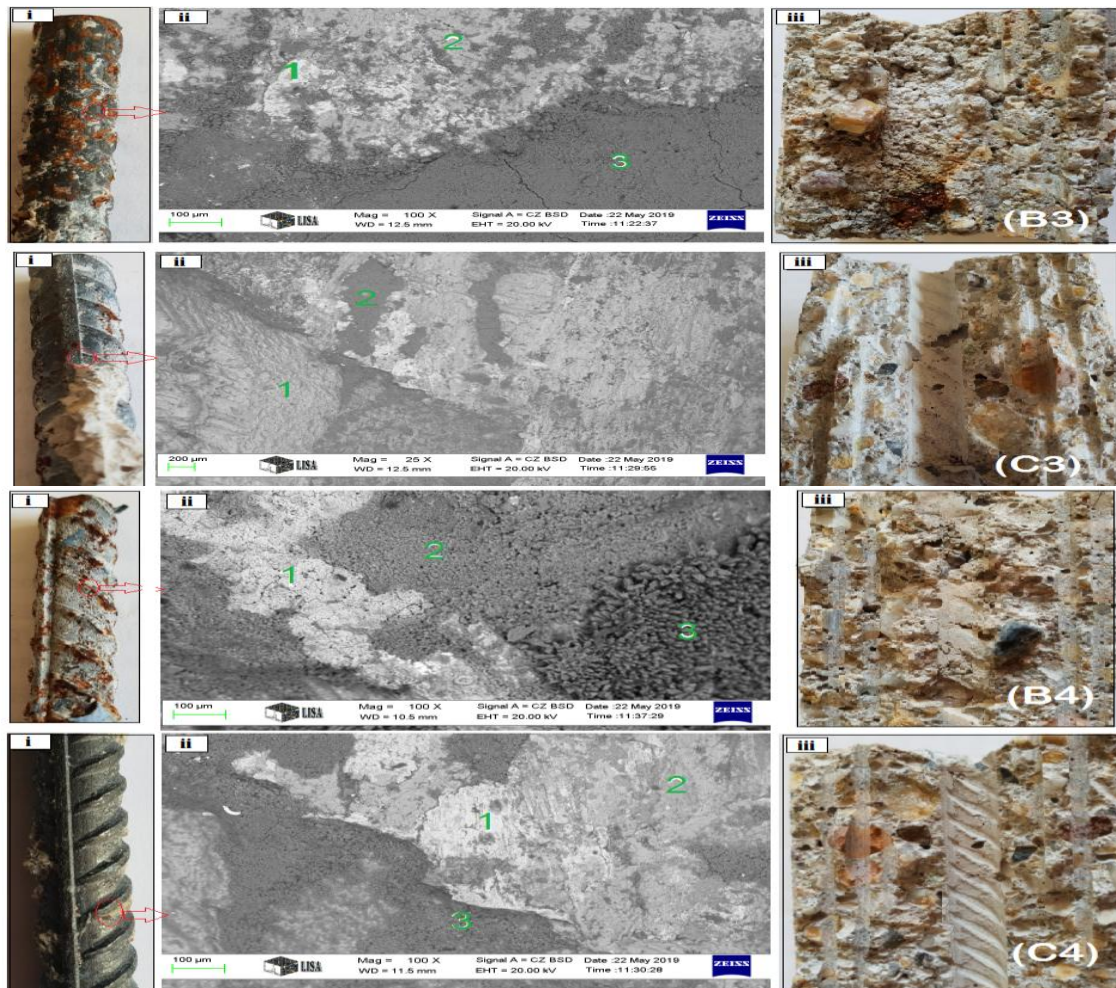


Figure 23 i) Close-up image of a steel rebar for sample after removal from the concrete, ii) SEM Micrograph of the section indicated in (i), iii) Representative image of a split concrete specimen with and without calcium nitrate inhibitor after removal of the steel rebar

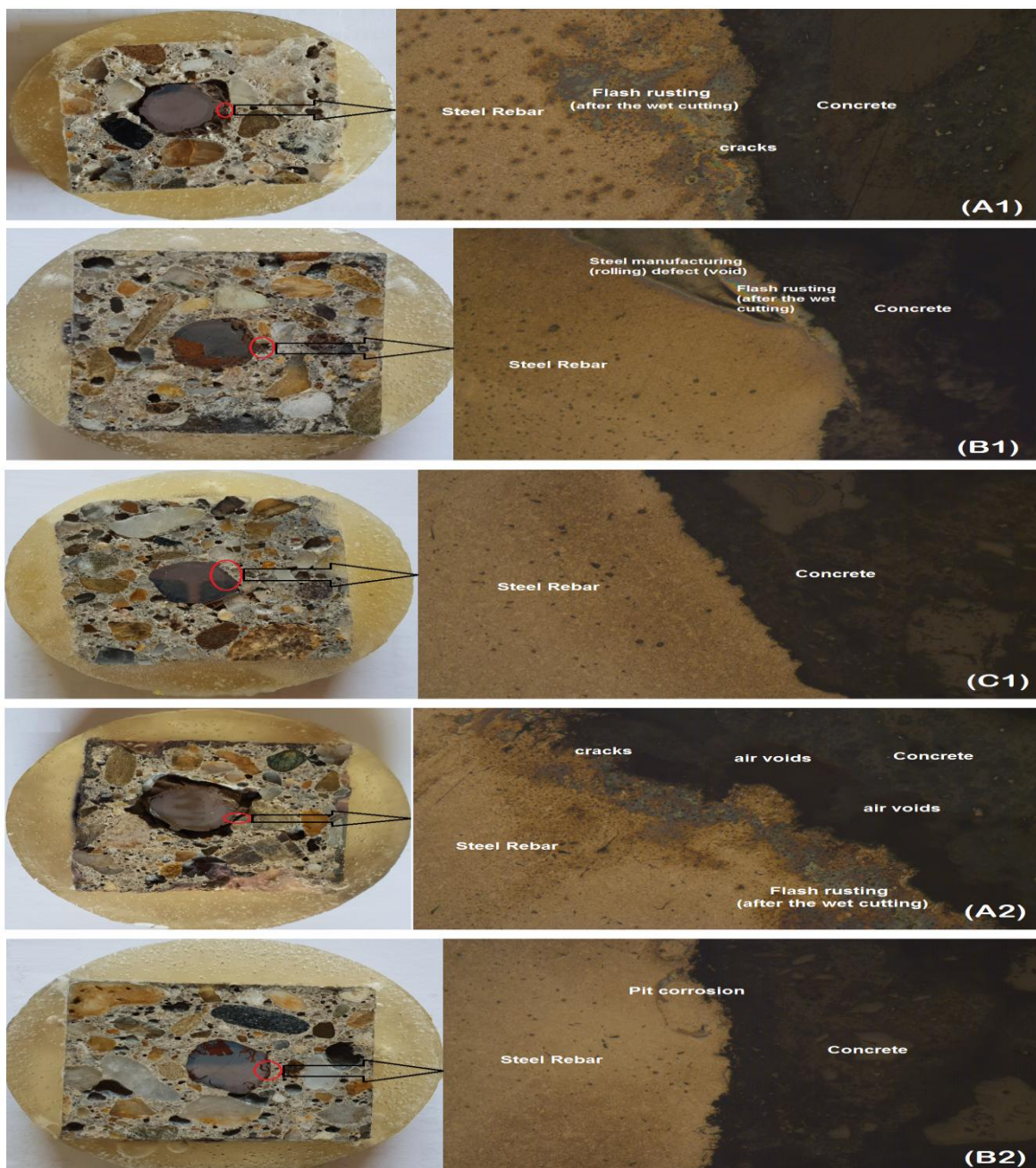
Table 5 The approximate chemical composition (expressed as oxides) of some small selected surface areas (as indicated in Fig. 23i) of the steel rebars after removal from the concrete blocks by SEM-EDS

Components (as Oxides)	Composition by EDAX (ZAF correction) given in wt%, not normalised										
	B3			C3		B4			C4		
	Point 1	Point 2	Point 3	Point 1	Point 2	Point 1	Point 2	Point 3	Point 1	Point 2	Point 3
Na <sub>2</sub> O	-	-	2.15	-	-	-	-	-	0.06	-	0.04
MgO	-	-	1.11	0.10	1.67	1.00	1.67	0.18	0.78	1.50	0.90
Al <sub>2</sub> O <sub>3</sub>	-	-	3.49	-	0.30	1.40	2.37	0.91	1.20	2.00	1.66
SiO <sub>2</sub>	0.98	1.68	14.20	10.37	20.27	4.89	15.99	0.61	23.61	10.44	8.19
SO <sub>3</sub>	-	-	-	3.36	0.29	-	-	-	2.45	3.50	2.57
Cl <sub>2</sub> O	4.01	-	3.1	-	-	4.00	-	5.54	-	-	-
K <sub>2</sub> O	-	-	1.61	-	-	-	-	-	-	-	0.78
CaO	2.23	5.81	72.29	9.65	31.54	2.10	76.65	1.71	30.56	35.65	76.5
MnO	0.14	1.49	0.00	0.83	1.20	0.49	0.74	1.28	3.15	3.80	1.86
FeO	92.7	91.02	2.56	75.9	46.29	86.13	2.58	90.77	38.39	43.91	8.32

From Figs. 22, 23 the increases in the corrosion (by formation oxidized areas) can mainly be related to the structural consequences of the hydration processes (so-called hardening) of the concrete bodies, that is the liberation of calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , and/or the formation of the well known cementitious compounds  $\text{C}_3\text{S}$  or  $\text{C}_3\text{A}$ , etc. The tested two admixtures (water-resisting admixture and superplasticizer admixture) added to the fresh concrete during the preparation step of the samples gave rise to reducing the water/cement ratio during the concrete blocks hardening, therefore there was not enough time for the formation of  $\text{Ca}(\text{OH})_2$  and/or  $\text{C}_3\text{S}$  and/or  $\text{C}_3\text{A}$ , .. etc. (which compounds cause greater capillary porosity in concrete and weaken the properties).

### 3.10 Optical Microscopy

Light optical micrographs for all concrete samples with and without green inhibitor are presented in Fig. 24.



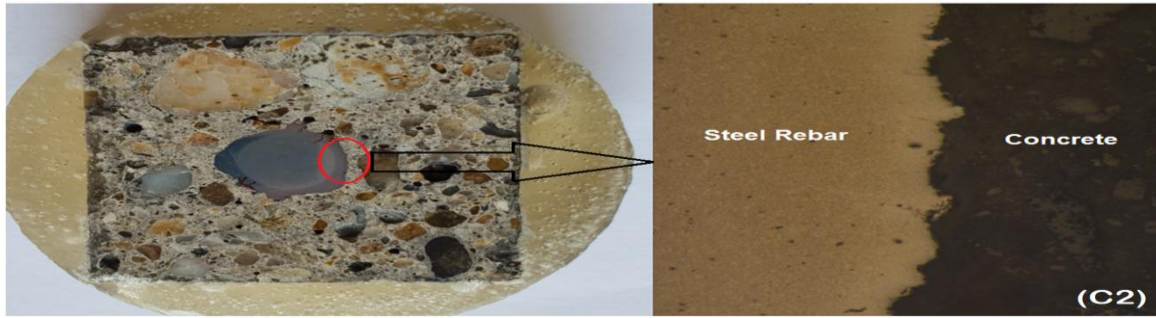


Figure 24 Light optical micrographs of the steel-concrete interface sections with magnification 50X of the concrete samples with and without green inhibitor showing the microstructure and the corrosion attack.

In Fig. 25 was shown the light optical micrographs of the steel-concrete interface sections for samples with calcium nitrate.

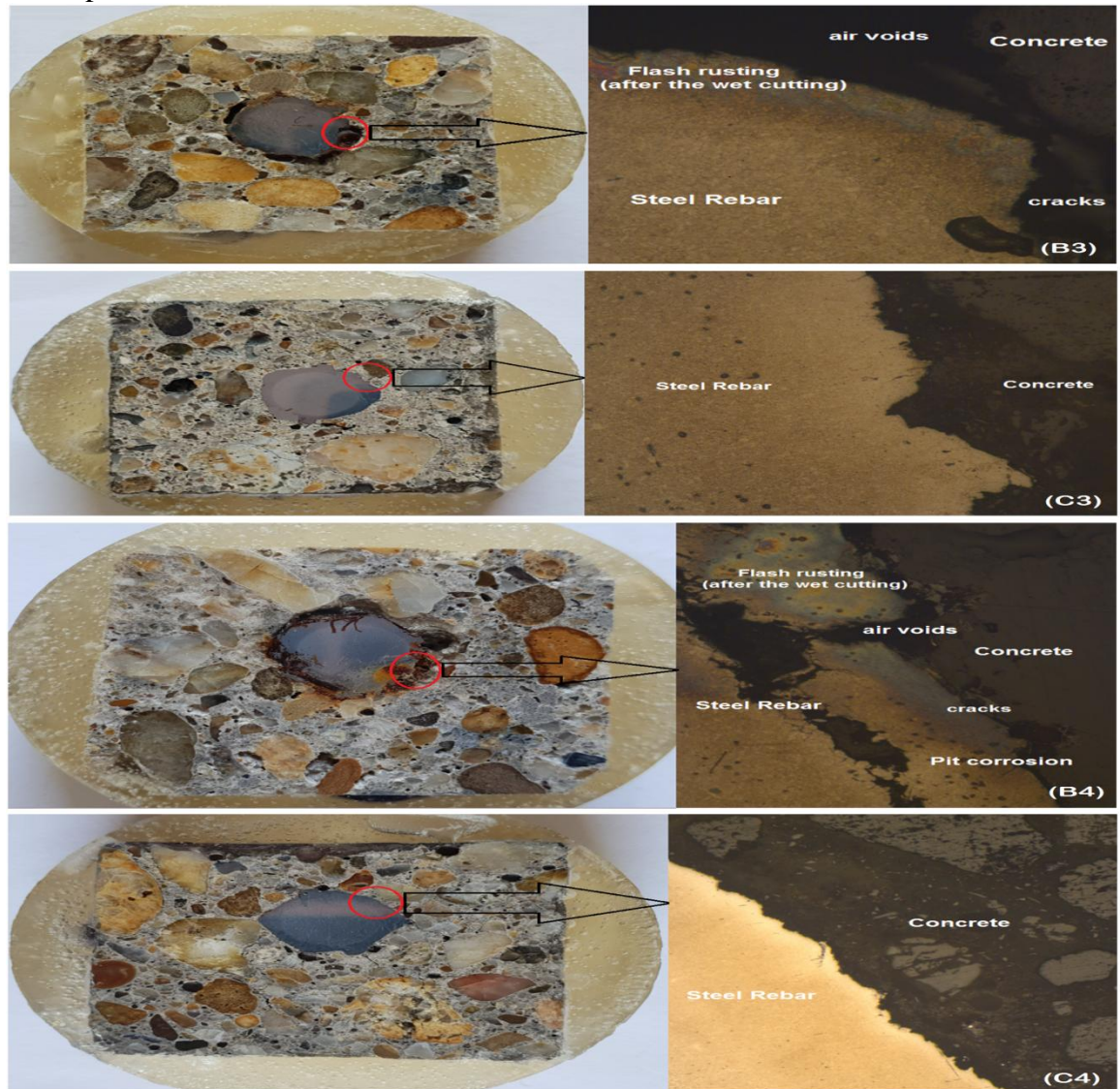


Figure 25 Light optical micrographs of the steel-concrete interface sections with magnification 50X of the concrete samples with and without calcium nitrate inhibitor showing the microstructure and the corrosion attack.

The visual examination revealed that in 75% of all cases, corrosion initiated between the rebar ribs or directly at the rib edge as shown in Fig. 24 in samples A1 and A2, and in Fig. 25 in samples B3 and B4. Some flash rusting stains (due to wet cutting of the 18-months-old blocks) can also be seen on some of the cut cross sections together with some cracks and air voids.

In Fig. 24 on the sample B1 there's a steel manufacturing (rolling) defect as well and some slight flash rusting areas (formed after wet cutting the specimen).

Inspection of the steel-concrete interface upon corrosion initiation typically revealed the presence of one distinct corroding spot, which in some cases was surrounded by significantly smaller corrosion pits, all of them within an area of maximum approximately 1 mm<sup>2</sup> as shown in Fig. 24 on the samples B2. The small corrosion pits were interpreted as sites where corrosion had initiated but was not able to reach stable pit growth (in contrast to the dominating corrosion site), these pits were typically covered with a crust of corrosion products, which occasionally remained even after the chemical cleaning process in inhibited hydrochloric acid. Inspection of the samples C1, C2 and C3, C4 showed there is no pits corrosion or cracks at the steel-concrete interface.

### 3.11 Composition Analysis of Corrosion Products by XRD test

The XRD records measured for the concrete samples with and without green inhibitor at their steel-concrete interfaces are collected and the analysis of the result were presented in Table 6. X-ray diffraction measurements detected the same products (Portlandite very low content and abundant content from calcite plus corrosion products (Brownmillerite, Biotite, Muscovite, Hydrocalumite, Ettringite, Chlorite) middle content), in concrete at its interface with concrete, as for free inhibitor samples. But the amount of calcite is lower and low or very low content amount of corrosion products in concrete samples containing inhibitor (samples with 1%, 3% green inhibitor and samples with 3% calcium nitrate only) than in the other specimens. Amorphous material was also detected, and is a product of corrosion and is made up by Fe-oxyhydroxides („rust”) and Ca-Al-silicate hydrates.

Table 6 The qualitative content of the main crystalline hydration products in samples with and without green inhibitor at concrete-steel interface by XRD analysis

Compound Name with Formula	Qualitative content of compounds					
	A1	B1	C1	A2	B2	C2
Portlandite [Ca(OH) <sub>2</sub> ]	+	+++	+++	+	+++	++++
Calcite [CaCO <sub>3</sub> ]	++++	+++	+++	++++	++	+++
Ettringite [Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O]	+++	+++	++	+++	+++	++
Hydrocalumite [Ca <sub>2</sub> Al(OH) <sub>6</sub> Cl·2H <sub>2</sub> O]	+++	+	++	+++	++	+
Biotite [K(Mg,Fe) <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(F,OH) <sub>2</sub> ]	+++	+	+	++	+	+
Brownmillerite [Ca <sub>2</sub> (Al,Fe) <sub>2</sub> O <sub>5</sub> ]	+++	++	++	+++	+++	+
Muscovite [KAl <sub>2</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(FOH) <sub>2</sub> ]	+++	No	No	+++	No	No
Chlorite [(Mg,Fe,Al) <sub>6</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub> ]	++	No	No	++	No	No

Notation: ++++: Abundant content; +++: Middle content; ++: Low content; +: Very low content; No: Absence.

Concrete samples with calcium nitrate their XRD records measured at steel-concrete interface and the analysis of the result were presented in Table 7.



Table 7 The qualitative content of the main crystalline hydration products in samples with calcium nitrate at concrete-steel interface by XRD analysis

Compound Name with Formula	Qualitative content of compounds					
	A3 (=A1)	B3	C3	A4 (=A2)	B4	C4
Portlandite [Ca(OH) <sub>2</sub> ]	+	+	+++	+	++	++++
Calcite [CaCO <sub>3</sub> ]	++++	++++	++	++++	+++	+
Ettringite [Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O]	+++	+++	++	+++	+++	+
Hydrocalumite [Ca <sub>2</sub> Al(OH) <sub>6</sub> Cl·2H <sub>2</sub> O]	+++	++	+	+++	+++	+
Biotite [K(Mg,Fe) <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(F,OH) <sub>2</sub> ]	+++	++	No	++	+++	No
Brownmillerite [Ca <sub>2</sub> (Al, Fe) <sub>2</sub> O <sub>5</sub> ]	+++	++	No	+++	+++	+
Muscovite [KAl <sub>2</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(FOH) <sub>2</sub> ]	+++	++	+	+++	+++	No
Chlorite[(Mg,Fe,Al) <sub>6</sub> (Si, Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub> ]	++	+++	No	++	No	No

Notation: ++++: Abundant content; +++: Middle content; ++: Low content; +: Very low content; No: Absence.

The XRD pattern (see Tables 6 and 7) for all concrete samples (with and without inhibitors) demonstrates the presence of strong peak is Quartz (SiO<sub>2</sub>, deriving from the sand grains in mortar) at about 2θ of 26.5°. The second clear and important peak is Portlandite (Ca(OH)<sub>2</sub>) at 2θ = 18° and 34° was created by the hydration of calcium silicates. Calcium hydroxide quantity precipitated at the steel surface is important in resist effect of corrosion. Calcite (CaCO<sub>3</sub>) of a small peak at 2θ of 29.5° is attributed to carbonation of hydrates on steel surface. The presence of these two last compounds can be explained by the fact that some traces of concrete materials could remain adhered to the rust during the sampling. Because all the samples were subjected to chloride ingress, the presence of Hydrocalumite (Ca<sub>2</sub>Al(OH)<sub>6</sub>Cl·2H<sub>2</sub>O) is justifiable and is confirmed by small peaks at 2θ = 11° and 21° in low and very low content for the samples with inhibitors and in middle content for samples without inhibitors. A little amount of Brownmillerite (Ca<sub>2</sub>(Al, Fe)<sub>2</sub>O<sub>5</sub>), Biotite (K(Mg,Fe)<sub>3</sub>(AlSi<sub>3</sub>O<sub>10</sub>)(F,OH)<sub>2</sub>), Muscovite (KAl<sub>2</sub>(AlSi<sub>3</sub>O<sub>10</sub>)(FOH)<sub>2</sub>), Ettringite (Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>·26H<sub>2</sub>O), Chlorite ((Mg,Fe,Al)<sub>6</sub>(Si, Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>8</sub>) as a corrosion products can be observed in different quantities in some of concrete samples as shown in Tables 6 and 7.

However, iron oxides (Hematite (Fe<sub>2</sub>O<sub>3</sub>) or Maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>)) cannot be clearly distinguished by this XRD pattern because their diffraction patterns are amorphous phases, only Iron(II) oxide (FeO) we distinguished by SEM-EDS technique.

Samples C2 and C4 has portlandite in high quantity this can explain the resistance of these samples to the attack of chlorides and very little corrosion products because the electrochemical mechanism of pitting corrosion confirms the inhibitive nature of OH<sup>-</sup> in the pore solution. The pH value of the pore solution in concrete is mainly maintained by the portlandite (Ca(OH)<sub>2</sub>) from the cement hydration and the alkaline ions (Na<sup>+</sup>, K<sup>+</sup>) in the pore solution. The inhibitive effect of OH<sup>-</sup> on pitting corrosion is enhanced by the concentrated distribution of Ca(OH)<sub>2</sub> on the concrete–steel interface. Samples A1, A2, B3, B4 have abundant content from calcite and because this component there's no ability to resist the effect of corrosion risk.

#### 4. Conclusions

After testing the XD3 reinforced concrete samples with or without corrosion inhibitors and two types of admixtures we can conclude the following points:

1. The concrete samples without any inhibitors had high porosity and lower corrosion resistance. Still, the samples prepared with admixing superplasticizer admixture (sample A1=A3) showed better resistance to corrosion than samples prepared with water-resisting admixture (sample A2=A4).
2. The lower concentration of infiltrated/ingressed  $\text{Cl}^-$  ions in the outer and depth samples were in samples C1, C2, C3, and C4 after immersion in 3.5 wt.% NaCl solution for six months to the other samples. Also, these samples showed lower porosity and the best corrosion resistance.
3. Electrical resistivity for all concrete samples (with both types of admixtures) increased with increased orange peels extract inhibitor concentration. In the case of calcium nitrate inhibitor, it increased only at a 3 wt.% concentration with two kinds of admixtures used in this work.
4. Half-cell potential became less negative values for concrete samples with increased the concentration of green inhibitor for both types of admixtures. It was also less negative values with samples containing 3 wt.% calcium nitrate with both kinds of admixtures used in this work.
5. Adding the orange peels extract inhibitor to the fresh concrete mixes showed a promising positive effect in corrosion resistance with water-resisting admixture (as in sample C2) than the superplasticizer admixture. The concrete samples with calcium nitrate became better to resist corrosion only at a 3 wt.% concentration from this inhibitor.
6. Calcium nitrate inhibitor, which was added by 1 wt.% to the samples B3 and B4, was not worked as an inhibitor and not improving any properties of concrete samples.
7. Corrosion products (containing iron oxides and chlorides) have been observed in rising quantities with decreasing inhibitor concentration by SEM-EDS and optical microscopy and also by XRD analysis on the steel rebar surface after removal from the concrete blocks (as at a 1 wt.% orange peel extract inhibitor and at a 1wt.% calcium nitrate inhibitor). The minimum amount of corrosion products was observed in the surface points tested at the samples C1, C2, C3, and C4 (these specimens often tended to be the least corroded (almost corrosion-free) surface by merely looking at the surface).

#### New Scientific Results

During 18 months testing period of the concrete samples immersed in 3.5 wt.% NaCl aqueous solution at room temperature the following novelties were found:

##### Claim 1:

High corrosion reduction rates were obtained with the concrete mix prepared with water-resisting admixture and 3 wt.% orange peels extract inhibitor, where the  $\text{Cl}^-$  induced corrosion rates were measured on the hardened samples immersed in 3.5 wt.% NaCl aqueous solution at room temperature for 18 months.

This comparison with all the other tested concrete mix compositions under the specified conditions is shown in the Figure.

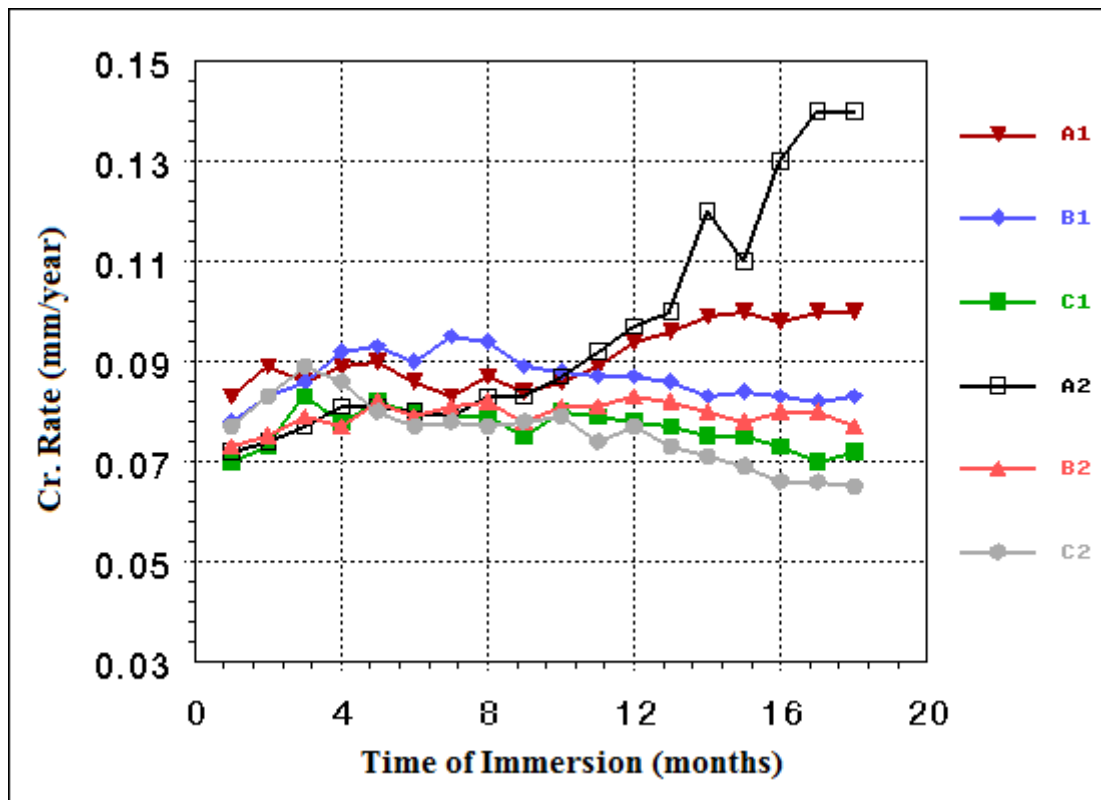


Figure to Claim 1: Corrosion rates of steel rebars in the reinforced concrete samples prepared with orange peels extract inhibitor and tested in 3.5 wt.% NaCl aqueous solution at room temperature, where A1: was prepared with superplasticizer and without orange peels extract inhibitor, B1: with superplasticizer and 1 wt.% orange peels extract inhibitor, C1: with superplasticizer and 3 wt.% orange peels extract inhibitor, A2: with water-resisting admixture and without orange peels extract inhibitor, B2: with water-resisting admixture and 1 wt.% orange peels extract inhibitor, C2: with water-resisting admixture and 3 wt.% orange peels extract inhibitor.

**Claim 2:**

The orange peels extract inhibitor can reduce the chloride induced corrosion rate more if it is applied together with water-resisting admixture in comparison to the case when it is applied only with superplasticizer admixture. As the water-resisting admixtures can alone reduce the porosity and so the ingress of chlorides towards the steel bars, this retardation effect becomes stronger when we apply it together with the orange peels extract inhibitor.

**Claim 3:**

Calcium nitrate inhibitor can work effectively as a corrosion reducing agent with two types of admixtures (superplasticizer and water-resisting admixture) at 3 wt.%, which was proved with the steel reinforced concrete samples immersed in 3.5% NaCl solution and tested for 18 months.

The Cl<sup>-</sup> induced corrosion rates reduction at 3 wt.% calcium nitrate inhibitor is shown in the Figure.

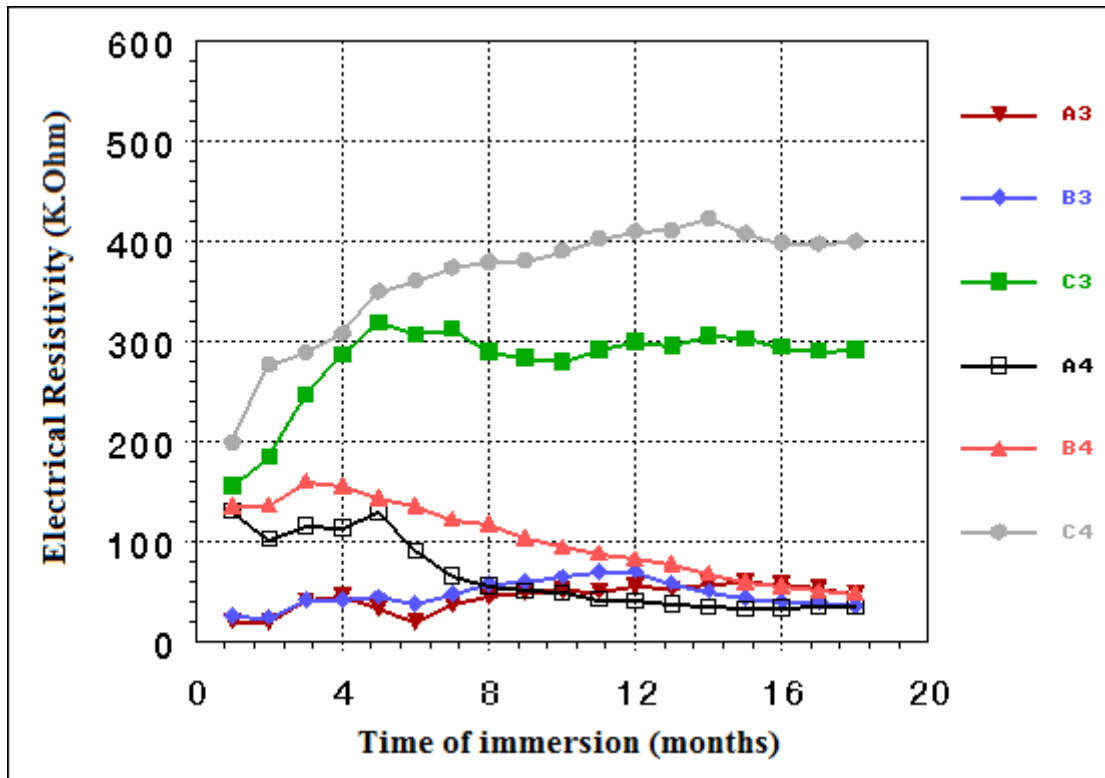


Figure to Claim 3: Electrical resistivity of steel rebars in the reinforced concrete samples prepared with calcium nitrate inhibitor and tested in 3.5 wt.% NaCl aqueous solution at room temperature, where A3: was prepared with superplasticizer and without calcium nitrate inhibitor, B3: with superplasticizer and 1 wt.% calcium nitrate inhibitor, C3: with superplasticizer and 3 wt.% calcium nitrate inhibitor, A4: with water-resisting admixture and without calcium nitrate inhibitor, B4: with water-resisting admixture and 1 wt.% calcium nitrate inhibitor, C4: with water-resisting admixture and 3 wt.% calcium nitrate inhibitor.

**Claim 4:**

Calcium nitrate inhibitor can work together with the water resisting admixture with better efficiency and can reduce the chloride induced corrosion rate more if we compare the test results obtained on the reinforced concrete samples prepared with the orange peels extract inhibitor and investigated up to 18 months immersion time in 3.5 wt.% NaCl aqueous solution at room temperature.

**Claim 5:**

At 3 wt.% concentration both orange peels extract inhibitor and calcium nitrate inhibitor were effective in mitigating the Cl<sup>-</sup> induced corrosion for the superplasticizer admixture and water-resisting admixture, which was demonstrated by the corrosion measurements and after comparing the results at 1 wt.% orange peels extract inhibitor and at 1 wt.% calcium nitrate inhibitor during 18 months time period of immersion the concrete samples in 3.5 wt.% NaCl aqueous solution at room temperature.

**References**

[1] M.L. Rivetti, J.S. Andrade, N.S. Amorim and D.V. Ribeiro, Corrosion Inhibitors for Reinforced Concrete: Corrosion Inhibitors, Principles and Recent Applications, IntechOpen, 2017.  
 [2] S.A. Abdulsada, R. Bak, A. Heczal, T.I. Török, Corrosion studies on XD3 reinforced concrete samples prepared by using calcium nitrate as inorganic corrosion inhibitor with different superplasticizers, Koroze a ochrana materiálu, 64, 11-18, 2020  
 [3] H.S. Ryu, S.H. Shin, C.G. Lim, T.W. Kang, S.Lim and H.T. Kim, Evaluation of Corrosion Resistance of Corrosion Inhibitors for Concrete Structures by Electrochemical Testing in Saturated

- Ca(OH)<sub>2</sub> Solutions with NaCl and Na<sub>2</sub>SO<sub>4</sub>, *Advances in Materials Science and Engineering*, Volume 2019, Article ID 8294360, 11 pages. <https://doi.org/10.1155/2019/8294360>
- [4] G.M. Akshatha, B.G. Jagadeesha and H. Pushpa, Effect of Corrosion Inhibitors in Reinforced Concrete, *International Journal of Innovative Research in Science, Engineering and Technology*, 4(8) 6794-6801, 2015. <https://doi.org/10.15680/IJIRSET.2015.0408013>
- [5] J. Damborenea, A. Conde, M.A. Arenas, 3-Corrosion inhibition with rare earth metal compounds in aqueous solutions, *Rare Earth-Based Corrosion Inhibitors*, Woodhead Publishing Series in Metals and Surface Engineering, 84-116, 2014.
- [6] Z. Marta, Effectiveness of Calcium Nitrate as Corrosion Inhibitor in Concrete, Master Thesis, Politecnico Di Milano, School of Industrial and Information Engineering, Department of Chemistry, Materials and Chemical Engineering, 2017.
- [7] European Standard EN 197-1, Cement - part 1: Composition, specifications and conformity criteria for common cements, 2000, European Committee for Standardization.
- [8] EN 12620, Aggregates for Concrete, European Standard was Approved by CEN National Members on September 2002.
- [9] EN 934-2, Admixtures for concrete, mortar and grout., European Standard was Approved by BSI on 30 June 2009.
- [10] European Standard EN 1990, Eurocode - Basis of structural design, 2010, European Committee for Standardization.

### List of papers

- [1] Abdulsada, S.A., Kristaly, F., Torok, T.I., Distribution of corrosion products at the steel-concrete interface of XD3 concrete samples, *Magazine of Civil Engineering*, 2020. 100(8). Article No. 10005. DOI: [10.18720/MCE.100.5](https://doi.org/10.18720/MCE.100.5)
- [2] S. A. Abdulsada, T. I. Török, Investigations on the resistivity of XD3 reinforced concrete for chloride ions and corrosion with calcium nitrate inhibitor and superplasticizers, *Cement Wapno, Beton*, 25 (2020) 330-343. <https://doi.org/10.32047/cwb.2020.25.4.7>
- [3] Abdulsada S. A., Bak R., Heczal A., Török T. I., Corrosion studies on XD3 reinforced concrete samples prepared by using calcium nitrate as inorganic corrosion inhibitor with different superplasticizers, *Koroze a ochrana materiálu* 64 (2020) 11-18. <https://doi.org/10.2478/kom-2020-0002>
- [4] S. Abbas Abdulsada, I. Tamás Török, Studying chloride ions and corrosion properties of reinforced concrete with a green inhibitor and plasticizers, *Structural Concrete*, WILEY, 21(5), 1894-1904, 2020. <https://doi.org/10.1002/suco.201900580>
- [5] S. Abbas Abdulsada, I. Tamás Török, Studying compression strength of XD3 concrete samples after addition of calcium nitrate inhibitor and superplasticizers, *építőanyag-Journal of Silicate Based and Composite Materials* 72 (2020) 16-19. <https://doi.org/10.14382/epitoanyag-jsbcm.2020.3>
- [6] S. Abbas Abdulsada, I. Tamás Török, Studying effect of addition green inhibitor on compression strength of reinforced concrete, *IOP Conference Series: Materials Science and Engineering* 613 (2019) 012024 <https://doi.org/10.1088/1757-899X/613/1/012024>
- [7] S. Abbas Abdulsada, É. Fazakas, I. Tamás Török, Corrosion testing on steel reinforced XD3 concrete samples prepared with a green inhibitor and two different superplasticizers, *Materials and Corrosion*, 70 (2019) WILEY, 1262-1272. <https://doi.org/10.1002/maco.201810695>
- [8] Shaymaa Abbas Abdulsada, Tamás I. Török, Measurements and Studying Corrosion Potential of Reinforced Concrete Samples Prepared with and without a Green Inhibitor and Immersed in 3.5%NaCl Solution, *Materials Science And Engineering, MultiScience - XXXII. microCAD International Multidisciplinary Scientific Conference, University of Miskolc, 5-6 September, 2018*, 44 (2019) 5–13.
- [9] S. Abbas Abdulsada, T.I. Török, É. Fazakas, Preliminary Corrosion Testing of Steel Rebar Samples in 3.5%NaCl Solution with and without a Green Inhibitor, *építőanyag-Journal of Silicate Based and Composite Materials* 70 (2018) 48-53. <https://doi.org/10.14382/epitoanyag-jsbcm.2018.10>
- [10] S. Abbas Abdulsada, É. Fazakas, T.I. Török, Corrosion studies of steel rebar samples in neutral sodium chloride solution also in presence of a bio-based (green) inhibitor, *International Journal of Corrosion and Scale Inhibition*, 7 (2018) 38-47. <http://dx.doi.org/10.17675/2305-6894-2018-7-1-4>