

# Corrosion studies on XD3 reinforced concrete samples prepared by using calcium nitrate as inorganic corrosion inhibitor with different superplasticizers

Abdulsada S. A.<sup>1</sup>, Bak R.<sup>2</sup>, Heczal A.<sup>2</sup>, Török T. I.<sup>1</sup>

<sup>1</sup> Faculty of Materials Science and Engineering, University of Miskolc, Hungary

<sup>2</sup> Department of Surface Technology, Bay Zoltán Nonprofit Ltd. for Applied Research, Budapest, Hungary

E-mail: qkosha86@uni-miskolc.hu

*This research paper presents an analysis of the corrosion properties of steel-reinforced concrete samples during immersion in 3.5 wt. % NaCl aqueous solution by measuring their response both cathodic and anodic polarization in order to determine the corrosion rates in the function of their calcium nitrate inhibitor content. This cheap inorganic inhibitor was added to the concrete mix in concentrations of 1% and 3% by weight of cement in addition to two different superplasticizers (MapeiDynamon SR 31 and Oxydtron). The compressive strengths of the so prepared samples were also checked according to the relevant European standard and were within the acceptable limits, so this inhibitor does not weaken this important property of the concrete samples.*

*The test results on steel reinforced samples immersed in 3.5 wt. % NaCl aqueous solutions at room temperature showed promising corrosion mitigating effects just after 6 months testing period. After 6 months the lower corrosion currents (i.e. better corrosion resistance) for both types of superplasticizers were observed with those samples which contained 3% calcium nitrate inhibitor. The best result was observed with sample C4 (in this case 3% calcium nitrate was added to the mixture of cement+Oxydtron superplasticizer). The advantageous inhibition mechanism of nitrate anions is also discussed and interpreted.*

## INTRODUCTION

The corrosion of steel reinforcement is one of the main causes of premature deterioration of reinforced concrete, leading to significant economic losses. Rapid deterioration can be caused by chloride ions in a marine zone or due to the use of thaw salts or by carbonation in urban zones [1]. In general, good quality concrete provides excellent protection for steel reinforcement. Due to the high alkalinity of concrete pore fluid, steel in concrete initially and, in most cases, for sustained long periods of time, remains in a passive state. Initiation of corrosion occurs either due to a reduction in alkalinity arising from carbonation or the breakdown of the passive layer by the attack of chloride ions [2].

In countries like the United States, Canada, and Europe, when ice accumulates on bridges during cold weather, salt is usually used to melt the ice. And, when the concrete structures become and have been exposed to such chemically aggressive agents such as chloride ions, originating either from deicing salts or marine environment or chloride contaminated aggregates, in presence of chloride, the protective passive layer of steel will be locally destroyed and so the unprotected steel areas can and will start dissolve [3-7].

The corrosion of the steel reinforcement of a reinforced concrete structure is an electrochemical process (as shown in Fig. 1) and occurs when there is difference in the concentration of dissolved ions inside the concrete, creating electrochemical potential cells or corrosion cells, characterized by a flow of electrons and ions between the cathodic and anodic regions [1].

Corrosion of steel can be alleviated by using corrosion-resistant steels, cathodic protection, fusion-bonded epoxy coatings, corrosion inhibitors, and admixtures.

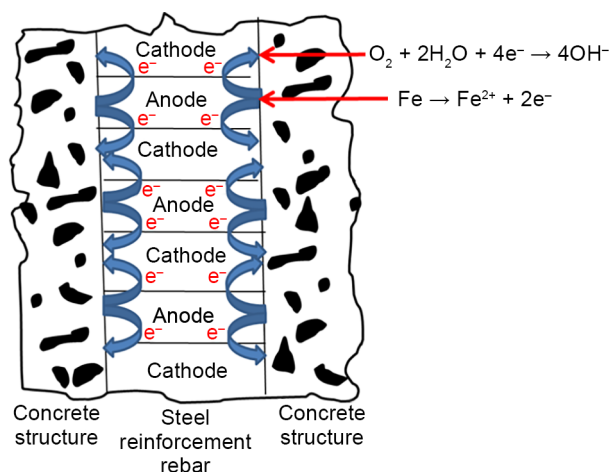


Fig. 1. Representation of the corrosion process [1]

Among these methods, corrosion inhibitors are the most widely used, with high cost-effectiveness and convenient usage. Inhibitors prevent the onset of corrosion by increasing the concrete pH or by fixating harmful ions that can cause the corrosion of steel [8].

Also the inhibitors form a hydrophobic film on the surface of reinforcement by adsorbing either ions or molecules of inhibitors on the surface. It reduces the corrosion of reinforcement by blocking cathodic or anodic reaction. The use of inhibitors is simple and economical with good inhibiting effect [9].

Frequently used corrosion inhibitors include inorganic and organic inhibitors. The investigation of a new class of corrosion inhibitors to replace the effective calcium nitrate inhibitor caught on in the late 1980s, when European regulations started to limit its application because of toxic issues and environmental requirements. As alternative to overcome these drawbacks, organic and inorganic inhibitors were studied. The requirement to incorporate into concrete structures a non-toxic and environmental-friendly inhibitor to prevent rebars corrosion phenomena, led to the study of nitrate-based compounds [10].

The main purpose of this paper is to present an experimental study pursued by linear polarization resistance measurements to monitor and evaluate corrosion processes in the steel rebar used in reinforced concrete with calcium nitrate inorganic inhibitor and two types of superplasticizers.

## MATERIALS AND METHODS

### Materials used

All materials were used in this work conformed to the European Standards starting with cement – Portland slag cement CEM II/A-S 42.5R conforming to the EN 197-1 [11] (this type of cement chosen because it is very workable, has a progressive increase in its initial strength, has very good cement density and its resistance to chemical reactions is high, the chemical composition of this cement was:  $\text{SO}_3$  content (3.5-3.7 %), Cl content (0.04-0.07 %) – and then aggregates (fine and coarse according standard EN 12620 [12]). Steel rebar samples selected with diameter of 8mm for this work. Tap water was used for both making and curing the specimens (because as a general in preparing concrete structure using tap water (easier and cheaper than distilled water), the chemical composition of tap water that used in this work consist from the following compounds:  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ).

Used three types from admixtures during preparing concrete samples, one of these admixtures was calcium nitrate as inorganic inhibitor, the other two admixtures were Mapei Dynamon SR 31 and Oxydtron (nanocement) as a superplasticizers.

### Samples preparation

The European mix design method type XD3 class was used to preparing concrete mixes. The cover depth of concert we select the structure class type S2 with depth 35 mm have service life of 10 to 25 years. The composition of the mix prepared for casting the specimens was as follows in Table 1:

Tab. 1. Composition of concrete mixture

Component (units)	Amounts per 1 m <sup>3</sup> of fresh concrete
Cement (kg) (type CEM II/A-S 42.5 R)	400
Water (L) (w/c = 0.43 planned/targeted value)	172
Admixtures (kg)	2.4
Additive (kg) [(sand 0/4: 60 % / 1089 kg m <sup>-3</sup> ) and (gravel 4/8: 40 % / 726 kg m <sup>-3</sup> )]	1815

The samples were prepared (with the two different plasticizers) containing calcium nitrate inhibitor as well in 0 %, 1 %, 3 % as shown in Table 2.

Tab. 2. The concrete mixtures (specimens) prepared for the experiments

Type of Mix		
Symbol of mix	Type of admixture	% of adding calcium nitrate inhibitor
B3	Dynamon SR 31	1 % by weight of cement
C3	Dynamon SR 31	3 % by weight of cement
B4	Oxydtron	1 % by weight of cement
C4	Oxydtron	3 % by weight of cement

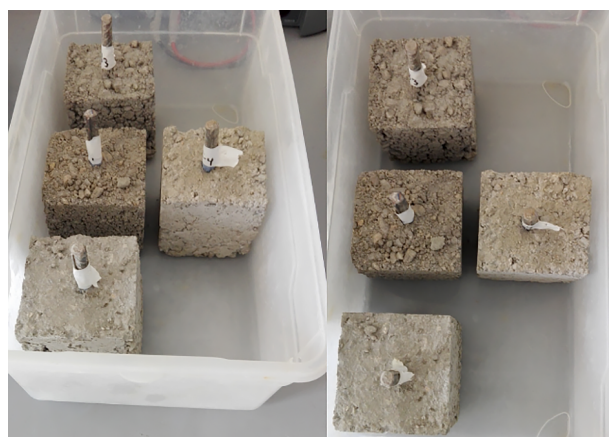


Fig. 2. Specimens after taken out from the molds after 24 hours of casting

The reinforced concrete cubes so prepared for electrochemical polarization testing had dimensions of  $70 \times 70 \times 70$  mm and each concrete cube was reinforced with one (8 mm diameter) straight steel wire.

For electrochemical polarization test was prepared cubes with dimensions  $70 \times 70$  mm and each concrete cube was reinforced with one (8 mm diameter) straight steel wire.

After casting the concrete samples and hardening for 24 hours, the specimens were taken out from the molds as shown in Figure 2, then were immersed partially in 3.5 wt. % NaCl solution.

### Linear polarization resistance (corrosion current)

Corrosion current was determined through recording the Tafel plots by using a programmed electrochemical polarizing device. The examination was implemented upon the steel bars embedded in concrete specimens, exposed to 3.5 % NaCl solution, in addition to specimens that were subjected to accelerated corrosion testing program. For this purpose, the three electrodes of the device were used differently. The calomel electrode was used as the reference electrode, the platinum electrode as the auxiliary electrode, and the steel bars that were embedded in concrete were used as working electrode. The device was programmed to polarize the potential of the steel up to  $\pm 120$  mV from/to the value of open circuit potential (OCP) in both directions (cathodic and anodic). Afterwards, the program would draw a relationship between the potential and current through semi-logarithmic scale. Accordingly, the corrosion current intensity can be calculated then by dividing the corrosion current ( $i_{\text{corr}}$ ) by the surface area of the rebar, which part was embedded in concrete and was exposed to the solution. Each sample was tested two time, Figure 3 shows the way of connecting the electrodes to measure corrosion current of reinforcing steel.

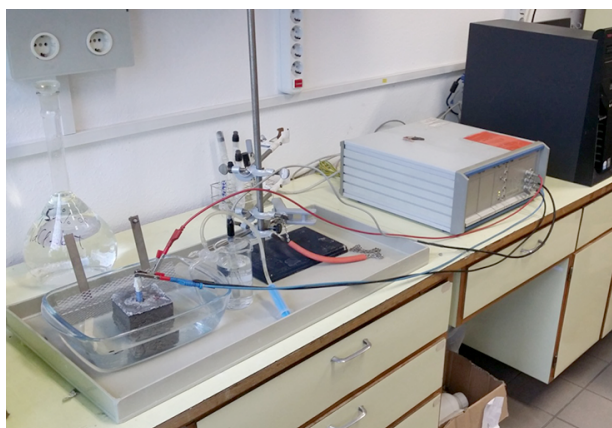


Fig. 3. Linear polarization resistance test setup with a specimen and the measuring circuit

## RESULTS AND DISCUSSION

### Linear polarization resistance

The electrochemical polarization curves of reinforcing steel samples imbedded in samples of concrete blocks (without and with calcium nitrate inhibitor) and kept immersed in 3.5 % NaCl solution were determined and are graphically represented in Figures 4 to 9. The corrosion current densities and corrosion potentials obtained from the electrochemical polarization measurements on the concrete samples are given in Tables 3 to 8. The variation in polarization curves of reinforced concrete samples after immersion for one month in 3.5 % NaCl represents in Figure 4. The corrosion current densities (Tab. 3) of the samples with inhibitor decrease with increase of concentration of calcium nitrate inhibitor, which phenomenon can, with high probability, be attributed to the formation of a protective layer around the surface of steel in contact with the inhibitor containing aqueous medium.

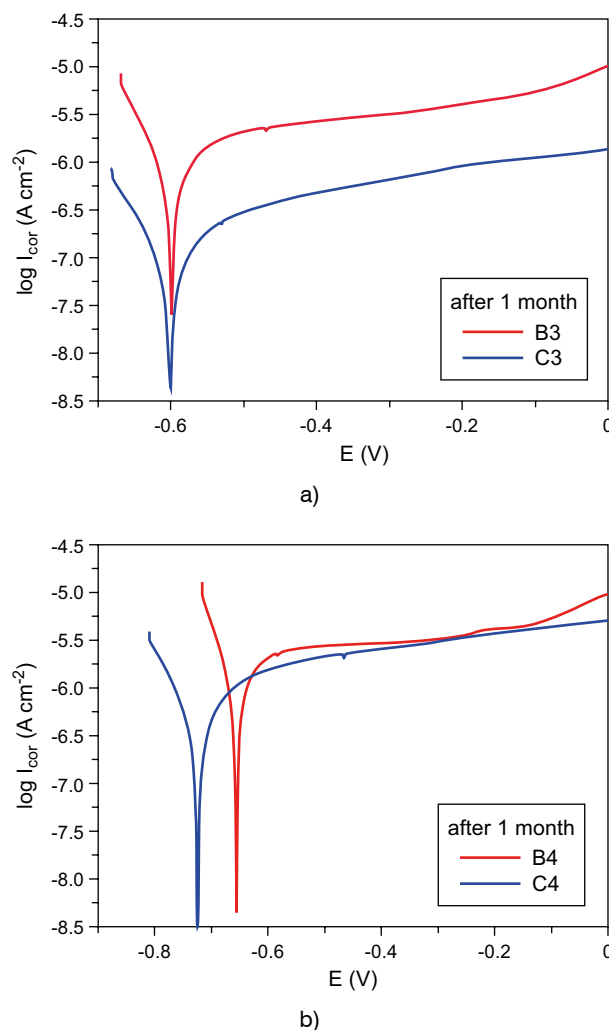


Fig. 4. Polarisation curves recorded: a) for B3, C3 samples, b) for B4, C4 samples after immersion concrete samples in 3.5% NaCl solution for 1 month

Tab. 3. Test results obtained from the measured polarisation curves of steel in 3.5% NaCl after 1 month

Sample	E (V)	$i_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )
B3	-0.599	6.491
B4	-0.655	6.208
C3	-0.598	6.437
C4	-0.723	6.143

Tab. 4. Test results obtained from the measured polarisation curves of steel in 3.5% NaCl after 2 months

Sample	E (V)	$i_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )
B3	-0.611	6.585
B4	-0.627	6.242
C3	-0.681	6.503
C4	-0.591	6.175

Figure 5 and Table 4 shows that the corrosion current densities for all samples increase a little bit after two months due to the chloride attack.

After three months of immersion time of the concrete samples kept in chloride solution (as it is seen in Fig. 6 and Tab. 5) the corrosion current density for all samples continues increasing. Samples with 3 % calcium nitrate inhibitor (C3, C4) show smaller values increasing than the samples with 1% inhibitor (B3, B4), from

which trends it is also clearly seen that samples with Oxydtron (B4, C4) resist corrosion better than samples MapeiDynamon SR 31 (B3, C3).

Figure 7 shows the values of corrosion current density for all samples after 4 months (see Tab. 6) increased except samples C3, C4 (started to resist corrosion).

After five and six months immersion time of the concrete samples the corrosion current density was increased with decrease in the electrochemical corrosion

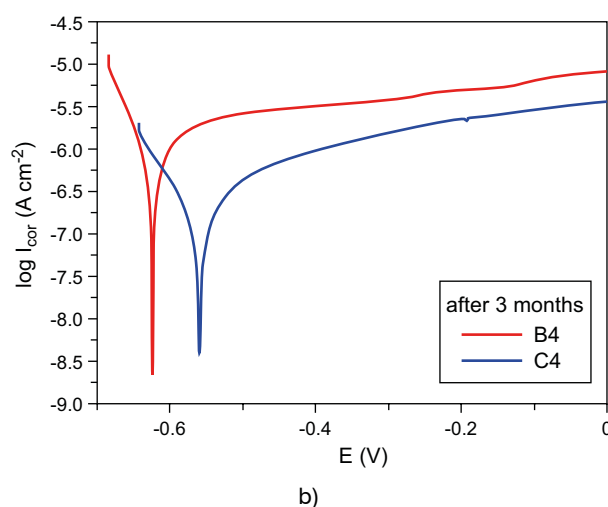
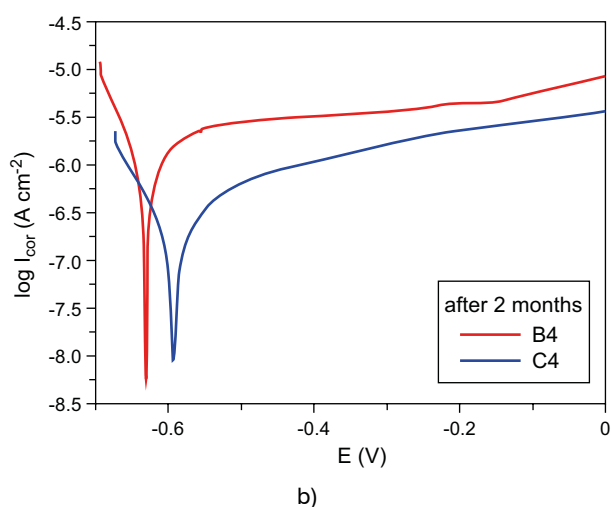
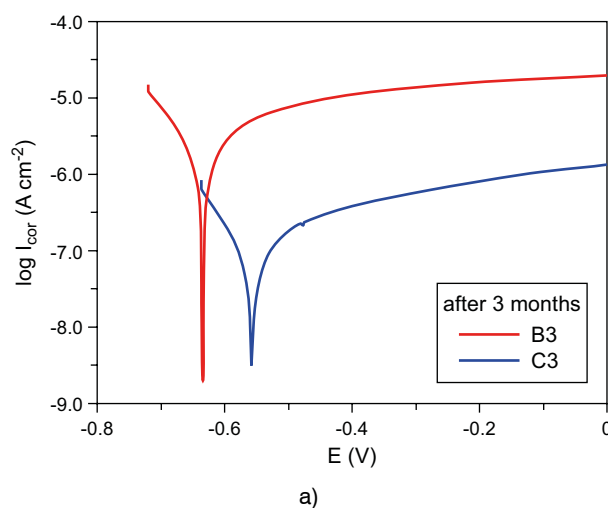
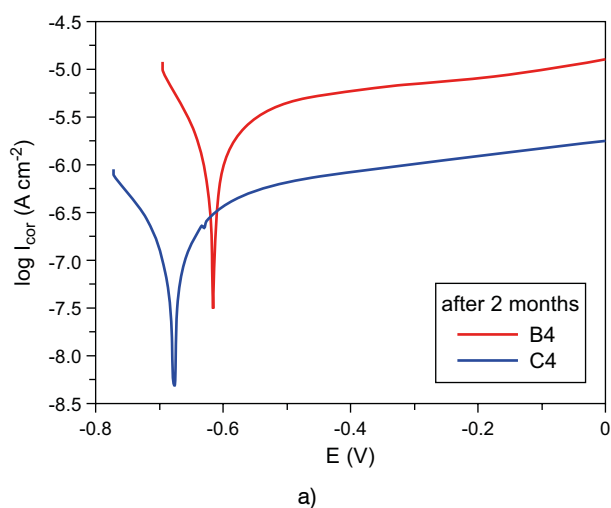


Fig. 5. Polarisation curves recorded: a) for B3, C3 samples, b) for B4, C4 samples after immersion concrete samples in 3.5% NaCl solution for 2 months

Fig. 6. Polarisation curves recorded: a) for B3, C3 samples, b) for B4, C4 samples after immersion concrete samples in 3.5% NaCl solution for 3 months

Tab. 5. Test results obtained from the measured polarisation curves of steel in 3.5% NaCl after 3 months

Sample	E (V)	$i_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )
B3	-0.633	6.637
B4	-0.622	6.304
C3	-0.557	6.585
C4	-0.559	6.206

Tab. 6. Test results obtained from the measured polarisation curves of steel in 3.5% NaCl after 4 months

Sample	E (V)	$i_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )
B3	-0.643	6.852
B4	-0.641	6.634
C3	-0.527	6.575
C4	-0.526	6.203

potential (as show in Fig. 8, Tab. 7 and Fig. 9, Tab. 8). 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 is a stable protective layer formed around the surface of steel rebar by this inhibitor.

Samples of B4, and C4 indicate a remarkable changing trend of the corrosion current densities, which are of

smaller values than for the samples of B3, C3). It should be the consequence of an unfolding physico-chemical protection developing due to pozzolanic reactions and associated chemical passivation (i.e. higher resistance against corrosion) of the embedded steel rebars in the concrete blocks (B4, C4 samples) prepared with the Oxydtron admixture.

Calcium nitrate inhibitor at 3% worked as a good protector for steel rebar from attack of chloride ions due

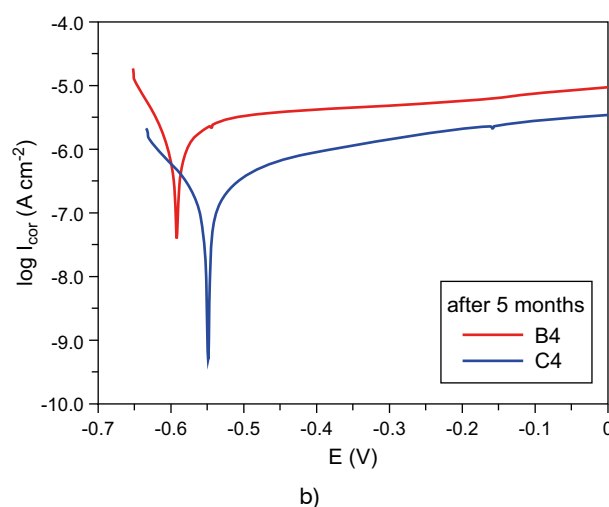
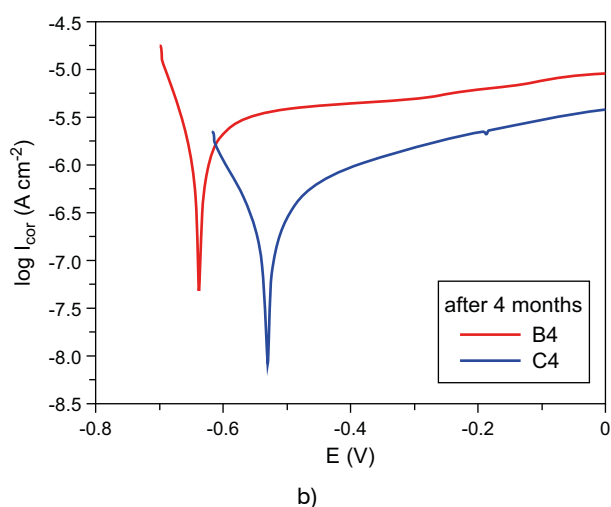
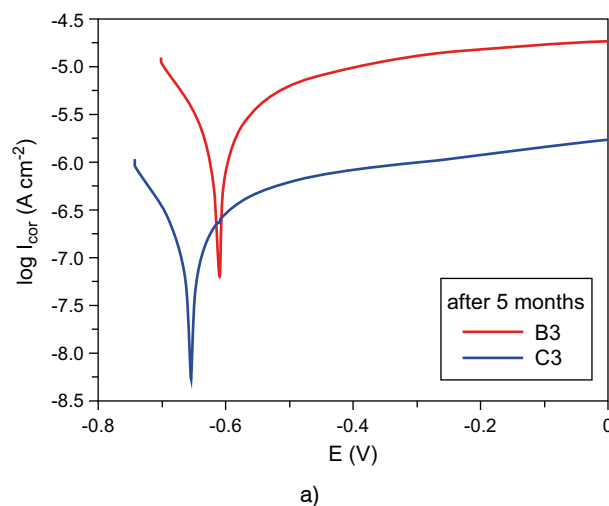
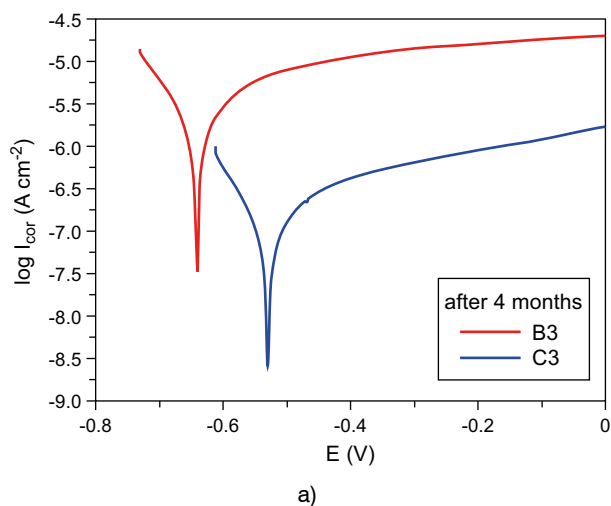


Fig. 7. Polarisation curves recorded: a) for B3, C3 samples, b) for B4, C4 samples after immersion concrete samples in 3.5% NaCl solution for 4 months

Fig. 8. Polarisation curves recorded: a) for B3, C3 samples, b) for B4, C4 samples after immersion concrete samples in 3.5% NaCl solution for 5 months



Tab. 7. Test results obtained from the measured polarisation curves of steel in 3.5% NaCl after 5 months

Sample	E (V)	$i_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )
B3	-0.610	6.972
B4	-0.591	6.791
C3	-0.653	6.567
C4	-0.550	6.127

its effective stabilization influence on the passive layer, but at 1% there appeared lower resistance to corrosion as after 3 months chloride ions must have accumulated in such a high level at the metallic surface of steel that the nitrate anions re-passivation power could not counteract the chloride ions corrosion pit initiation potential.

Otherwise, this kind of interpretation of the inhibiting mechanism of calcium nitrate against the corrosion of steel in concrete was first suggested by Justnes [13].

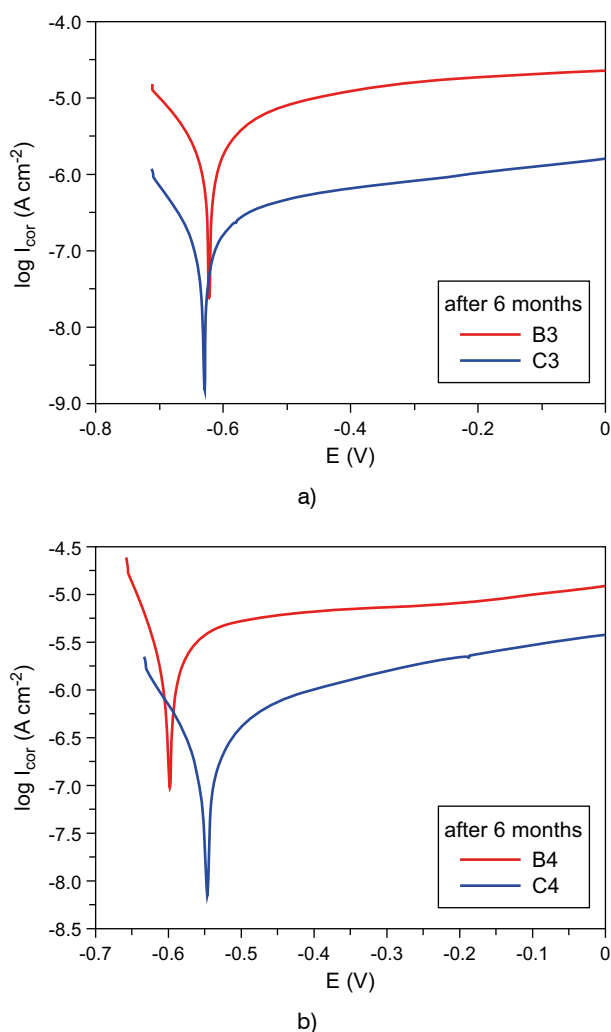


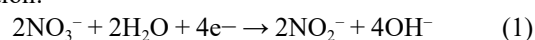
Fig. 9. Polarisation curves recorded: a) for B3, C3 samples, b) for B4, C4 samples after immersion concrete samples in 3.5% NaCl solution for 6 months

Tab. 8. Test results obtained from the measured polarisation curves of steel in 3.5% NaCl after 6 months

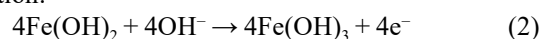
Sample	E (V)	$i_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )
B3	-0.625	5.847
B4	-0.595	5.832
C3	-0.623	6.985
C4	-0.545	6.842

He assumed that the oxidation action of nitrate is the consequence of its easy reduction to nitrite. In alkali aqueous environment such as the pore solution's pH in the young age of this type of concretes, one can illustrate the re-passivation redox reactions taking place between the iron (Fe)/iron-oxide-hydroxide( $\text{Fe}(\text{OH})_2$ ) and the solution interface as two electrochemical half-reactions as shown below:

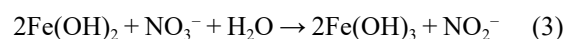
Reduction:



Oxidation:



Then they can be combined to give the total reaction:

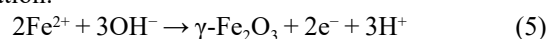


However, somewhat in contrast to Justnes, the authors P. Saura, E. Zornoza, C. Andrade, and P. Garcés [14] considered the formation of another iron(III) oxide compound, namely the creation of  $\gamma\text{-Fe}_2\text{O}_3$ . In this case the corresponding two half reactions are as follows:

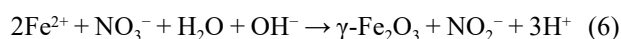
Reduction:



Oxidation:



And, they as well can be combined to give the total reaction:



The above mechanism was assessed in simulating concrete pore solution and the  $\gamma\text{-Fe}_2\text{O}_3$  formed layer was proved to be stable in alkaline environments, inducing a strong protective effect on the steel surface [13].

### Corrosion rate

The corrosion rate (Cr. rate) or corrosion velocity,  $V$ , represents the volumetric loss of metal on unit area in unit time. In the present recommendation it is expressed in mm/year, although other units may also be used. Cr. rates expressed in mm/year were obtained from the corrosion currents, (either  $i_{\text{corr}}$  or  $I_{\text{corr}}$ ) in  $\mu\text{A cm}^{-2}$  through

Faraday's law and the density of the metal. For the steel,  $1 \mu\text{A cm}^{-2}$  is equivalent to a corrosion rate of  $0.0116 \text{ mm/year}$  for uniform attack [15].

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.

In a previous published worked [3] studied concrete samples without inhibitors (A3 (=A1) with Mapei Dynamon SR 31 superplasticizers and A4 (=A2) with Oxydtron (nanocement) superplasticizers) as a references samples and the calculated corrosion rate for the samples after immersion during 6 months in 3.5% NaCl solution was  $0.086 \text{ mm/year}$  for A3 sample and  $0.08 \text{ mm/year}$  for A4 sample.

As it is seen in Figure 10 and Table 9, the tendency of the corrosion rates is increasing with time of immersion during the tested period of 6 months, and the rates are always somewhat lower in cases when the samples have calcium nitrate inhibitor especially at 3% and samples with superplasticizer type Oxydtron (because the Oxydtron consist of some mineral components such as calcium oxide, silicates and aluminates, so these components play important roles during the hydration of the freshly prepared concrete). After 3 months the corrosion rate of samples C3 and C4 started decreasing with increasing time of immersion but the samples with 1% inhibitor after

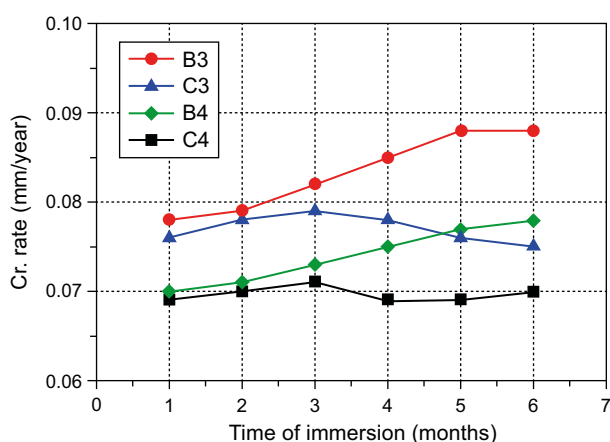


Fig. 10. Corrosion rates for concrete samples after immersion for different time in 3.5% NaCl solution

Tab. 9. Corrosion rate of concrete samples

Symbol of sample	Corrosion rate (mm/year) for concrete samples after immersion in 3.5% NaCl solution for every month					
	1 month	2 months	3 months	4 months	5 months	6 months
B3	0.078	0.079	0.082	0.085	0.088	0.088
C3	0.076	0.078	0.079	0.078	0.076	0.75
B4	0.070	0.071	0.073	0.075	0.077	0.078
C4	0.069	0.070	0.071	0.069	0.069	0.070

3 months still show increasing corrosion rates because calcium nitrate have effective inhibition mechanism on chloride-induced corrosion only at concentrations higher than 1% by weight of cement [16].

## CONCLUSION

After testing the XD3 type concrete samples containing inorganic calcium nitrate inhibitor with embedded steel wire probes we can conclude the following points:

- The resistance against the steel rebar corrosion increases with increasing concentration of  $\text{Ca}(\text{NO}_3)_2$  inhibitor but this increase was very little with 1% inhibitor (B3 and B4), because it could probably help form only a very weak passive layer, however at a rather higher  $\text{Ca}(\text{NO}_3)_2$  inhibitor concentration of 3% it showed better corrosion inhibition (C3 and C4) due to the higher (re)passivation capacity/potential of the nitrate anions.
- During the immersion period of 6 months when the samples were kept in 3.5% NaCl solution the corrosion properties of Samples C3 and C4 were not effected significantly more by the  $\text{Cl}^-$  ions ingress/diffusion, as these samples were prepared with 3% calcium nitrate inhibitor and that much inhibitor content could effectively modify the steel rebars surface via the so-called passivation or re-passivation mechanism. So that calcium nitrate acted as an effective inhibitor against chloride-induce corrosion at concentrations higher than 1% by weight of cement in the tested steel reinforced XD3 concrete blocks.

## Acknowledgement

We would like to thank everyone who helped us to complete this research in the department of surface technology, Bay Zoltán Nonprofit Ltd. for Applied Research, Budapest, Hungary. We must also not forget the efforts of the Institute of Metallurgy, University of Miskolc in providing all the possibilities available to us in order to make the research successful.

## 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. <http://dx.doi.org/10.5772/intechopen.72772>
2. M. Adamu, L. E. Umoru, O.O. Ige, Effect of Calcium Nitrate and Sodium Nitrite on the Rebar Corrosion of Medium Carbon Steel in Seawater and Cassava Fluid. *Journal of Minerals and Materials Characterization and Engineering* **2014**, 2, 223-229. <http://dx.doi.org/10.4236/jmmce.2014.23027>
3. S. A. Abdulsada, É. Fazakas, T. I. Török, Corrosion testing on steel reinforced XD3 concrete samples prepared with a green inhibitor and two different superplasticizers, *Materials and Corrosion* **2019**, 70, 1262-1272. <https://doi.org/10.1002/maco.201810695>
4. S.A. Abbas, 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* **2018**, 70, 48-53. <https://doi.org/10.14382/epitoanyag-jsbcm.2018.10>
5. S.A. Abbas, 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*, 2018, 7, 38-47. <http://dx.doi.org/10.17675/2305-6894-2018-7-1-4>
6. M.A. Quraishi, D.K. Nayak, R. Kumar and V. Kumar, Corrosion of Reinforced Steel in Concrete and Its Control: An overview, *Journal of Steel Structures and Construction* **2017**, 3, 1-6. <https://doi.org/10.4172/2472-0437.1000124>
7. S. A. Abdulsada, A.I. Al-Mosawi and A.A. Hadi, Studying the Effect of Eco-addition Inhibitors on Corrosion Resistance of Reinforced Concrete, *Bioprocess Engineering* **2017**, 1, 81-86. <http://doi.org/10.11648/j.be.20170103.14>
8. 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* **2019**, Article ID 8294360, 11 pages. <https://doi.org/10.1155/2019/8294360>
9. 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* **2015**, 4 (8), 6794-6801. <https://doi.org/10.15680/IJIRSET.2015.0408013>
10. 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.
11. EN 197-1, *Cement – Part 1: Composition, specifications and conformity criteria for common cements*, 2000.
12. EN 12620, *Aggregates for Concrete*, 2002.
13. H. Justnes, *Concrete Corrosion Problems solved by Calcium Nitrate*, in 25<sup>th</sup> Conference on Our World in Concrete and Structures, 349–356, 2000.
14. P. Saura, E. Zornoza, C. Andrade, and P. Garcés, Steel corrosion – inhibiting effect of sodium nitrate in simulated concrete pore solutions, *Corrosion* **2011**, 67, 075005-1-075005-15. <https://doi.org/10.5006/1.3613642>
15. C. Andrade and C. Alonso with contributions from J. Gulikers, R. Polder, R. Cigna, Ø. Vennesland, M. Salta, A. Raharinaivo and B. Elsener, Test methods for on-site corrosion rate measurement of steel reinforcement in concrete by means of the polarization resistance method, *Materials and Structures* **2004**, 37, 623-643. <https://doi.org/10.1007/BF02483292>
16. P. Montes-Garcia, H. Z. López-Calv, and T. W. Bremner, Effectiveness of calcium nitrate inhibitor (CNI) in cracked concrete, *Revista Ingeniería de Construcción* **2009**, 24, 233-244. <http://dx.doi.org/10.4067/S0718-50732009000300002>