Investigation of the Mechanical Properties and Durability of Concretes Produced with Microsilica and Crystalline Admixtures

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Abstract. In order to enhance the durability of reinforced concrete structures and their protection against corrosion, the addition of various durability enhancing concrete admixtures to the composition of the mixtures is a catalytic factor, in addition to proper concrete mix design and correct execution of the concreting process. This durability enhancing concrete admixtures include permeability reducing admixtures, such as crystalline admixtures, as well as silica fume (microsilica). Crystalline admixtures reduce permeability, which is one of the key factors leading to premature concrete wear and corrosion of the reinforcement, sealing capillary pores and cracks through the crystal growth mechanism under the presence of moisture. Correspondingly, microsilica as a strong pozzolanic material has the ability to reduce porosity and create a denser structure in hardened concrete, acting equally beneficial on long-term durability. The durability testing of the specimens of the first experimental part was carried out through appropriate laboratory tests involving the determination of the compressive strength of each mixture, the depth of penetration of water under pressure and the deterioration of concrete, either due to carbonation or due to chloride ingress. Results indicate that addition of crystalline admixture enhances the durability of concrete against carbonation and chloride induced corrosion. These durability indicators are further enhanced when crystalline admixtures are used in combination with silica fume.

Keywords: Concrete · Durability · Service Life of Concrete · Crystalline Admixtures · Microsilica · Corrosion

1 Introduction

Reinforced concrete is undoubtedly the most widely produced and used material in the world. This can be attributed to the simple materials of which it is composed, the ease of the production process, its satisfactory mechanical properties and its affordable price. Of course, as ideal as it may sound as a building material, it has many vulnerabilities, which are mainly due to its interaction with the environment, resulting in a deterioration in its quality. The subject of many studies in recent years has been the phenomenon of durability of reinforced concrete structures. The loss of functionality and premature wear

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of concrete is due to the corrosion mechanisms, i.e. the result of physical and chemical actions that occur between the concrete components and the corrosive substances of the environment to which the concrete is exposed. Therefore, the ultimate goal of the construction industry is to ensure to the maximum extent possible the service life for which reinforced concrete structures are designed.

In order to enhance the durability of reinforced concrete structures and their protection against corrosion, the addition of various durability enhancing concrete admixtures to the composition of the mixtures is a catalytic factor, in addition to proper concrete mix design and correct execution of the concreting process. These durability enhancing concrete admixtures include permeability reducing admixtures. Permeability of concrete is the movement of water due to a pressure gradient, such as water in contact with a concrete structure installed underground [2], and is one of the key factors leading to premature concrete wear and corrosion of the reinforcement.

As it is stated in ACI212.3R-16, a class of materials referred to as permeability-reducing admixtures (PRAs) have been developed to improve concrete durability through controlling water and moisture movement [10] as well as by reducing chloride ion ingress [3–8] and permeability [9]. According to ACI212.3R-16 [2], admixtures intended to reduce water ingress split into two subcategories: PRAs for concrete exposed to nonhydrostatic conditions (PRAN) and PRAs for concrete exposed to hydrostatic conditions (PRAH) [2]. Crystalline admixtures are classified as PRAH's products, sealing capillary pores and cracks through the crystal growth mechanism under the presence of moisture. Correspondingly, microsilica as a strong pozzolanic material can be considered as a durability enhancing concrete admixture due to its ability to reduce porosity and create a denser structure in hardened concrete, acting equally beneficial on long-term durability [5].

Based on the above findings and data on the issue of durability, the subject of this research is to investigate the effect of crystalline admixtures and silica fume (microsilica), as well as their combined action on mechanical properties and durability of concrete of strength class C20/25 and C30/37, under conditions of highly corrosive environment. More specifically, it studies the possible protection that the above admixtures can offer separately but also in combination against corrosion.

The experimental part of the research is divided into two sections. The first part of the experiments involves the preparation of three mixtures of unreinforced concrete of the same composition, the only difference being the presence or absence of crystalline admixture and microsilica. More specifically, specimens of conventional concrete, which are characterized as reference concrete specimens, specimens with the addition of crystalline admixtures at a percentage of 0.8% per weight of cement and specimens with the addition of crystalline admixtures at a percentage of 0.8% per weight of cement and microsilica at a percentage of 2% per weight of cement were prepared.

The second part involves the preparation of reinforced concrete specimens of three mixtures of the same composition, the only difference being the individual use of crystalline admixture and silica fume. In particular, specimens of conventional concrete, specimens with the addition of crystalline admixtures at a percentage of 0.8% per weight of cement and specimens with the addition of microsilica at a percentage of 5% per weight of cement were prepared.

The durability testing of the specimens of the first experimental part was carried out through appropriate laboratory tests involving the determination of the compressive strength of each mixture, the depth of penetration of water under pressure and the depth of the corroded zone of concrete, either due to carbonation or due to chloride ingress. The durability of the reinforced specimens of the second experimental part was tested by measuring the corrosion potential of the reinforcements to assess their condition against corrosion. In addition, specific parameters for the reinforced concrete specimens were taken into account in order to assess their effect on the corrosion phenomenon. Thus, the coating thickness as an inhibitor of the progression of reinforcement corrosion was additionally studied, as well as the activity of crystalline admixtures depending on the degree of activation of the crystals. The laboratory tests that were carried out to obtain data are listed below:

1. Compressive strength of concrete
2. Water permeability of concrete
3. Permeability of concrete to chloride ions by calculating the chloride diffusion coefficient, according to NT BUILD 492
4. Carbonation of concrete, by testing mixtures under accelerated carbonation conditions (insertion of specimens in the accelerated carbonation chamber) and natural carbonation (exposure of specimens to environmental conditions)
5. Measurement of corrosion potential of steel

The research concludes with an extensive analysis and commentary of the results of each experiment.

2 Experimental Program

The research was divided in two phases. During the first phase of this research three concrete mixtures were produced - one conventional, one with added crystalline admixtures and one with added crystalline admixtures in combination with silica fume (microsilica). Concrete mixtures were of C25/30 and C30/37 strength class, according to EN206-1 [1]. CEM II 32.5 (B-M) N cements were used to produce the mixtures. Aggregates were of limestone origin with a maximum grain diameter of 31.5 mm. Appropriate doses of retarder and polycarboxylate superplasticizer were used to achieve the desired cohesiveness and workability of the fresh concrete.

The purpose of designing these compositions is to create a comparative situation between mixtures containing no additives and those containing one or both additives. In Composition 1, no admixture of any kind is used, as it was prepared to be used as a reference mix, mainly for the purpose of comparing results, and is therefore characterized as reference mix (REF). In Composition 2, only crystalline admixtures were used at a percentage of 0.8% per weight of cement, while in Composition 3, crystalline admixtures were added at a percentage of 0.8% per weight of cement in combination with microsilica at a percentage of 2% per weight of cement. Composition 2 is reported as 0.8%PRAH, while Composition 3 is reported as 0.8%PRAH-2%MS. The mixing ratio as well as the properties of the fresh concrete mixtures (determination of workability through concrete slump test at 0 and 30 min) are shown in Table 1.

Table 1. Mixing ratio of concrete mixtures (1st Phase).

kg/m^3		C25/30			C30/37		
		REF	0.80% PRAH	0.80% PRAH - 2% MS	REF	0.80% PRAH	0.80% PRAH - 2% MS
Cement	CEM II/(B-M) 32.5N	300	300	300	350	350	350
Aggregates	Sand	1145	1145	1145	1115	1115	1115
	Gravel	300	300	300	295	295	295
	Coarse	445	445	445	445	445	445
Superplasticizer		1.85	1.85	1.85	2.5	2.5	2.5
Retarder		0.6	0.6	0.6	0.7	0.7	0.7
Water		180	180	180	175	175	175
W/C		0.6	0.6	0.6	0.5	0.5	0.5
PRAH		–	2.4	2.4	–	2.8	2.8
MS		–	–	6	–	–	7
Concrete Slump Value S_0 (cm)		21	18	13	17	20	17
Concrete Slump Value S_{30min} (cm)		17	14	9	14	14	13

Cubic specimens of 150 × 150 × 150 mm and cylindrical specimens of 100 × 200 mm were prepared. All samples were maintained in a curing chamber (T = 20 °C, RH > 98%) until the test age. Cylindrical specimens with dimensions of 60 × 100 mm were also used for measuring the carbonation depth.

The 150 mm cubes were used to measure the compressive strength at the age of 28 days as well as to determine the water absorption. Resistance to chloride penetration of concrete was measured in cylindrical specimens with a diameter of 100mm and a height of 50mm cut off from the 100 × 200 mm specimens. These specimens were maintained as above until the age of 28 days. The chloride diffusion coefficient Dnssm was then evaluated according to the procedure described in NT Building 492 [3].

Carbonation resistance was measured in cylindrical specimens 60 × 100 mm. These specimens were maintained in the above-mentioned curing chamber for 7 days and then remained in a laboratory environment until the age of 28 days. After this age some of the specimens were inserted into the accelerated carbonation chamber (RH = 55–60%, T = 20 °C, CO_2 = 1%) where they remained for 56 days. The rest of them were transferred to the outdoor space of the laboratory, where they remained for 6 months exposed to all weather conditions in order to investigate the natural carbonation of concrete.

The second phase of the research investigates the corrosion degree of the reinforced concrete specimens when exposed in a highly corrosive chloride environment. It includes the preparation of three mixtures of strength class C25/30 and C30/37 and focuses on the impact of three parameters that possibly affect the protection against reinforcement corrosion and overall durability of concrete.

More specifically, the first parameter is related to the ability of the concrete composition, in terms of admixture action, to ensure the desired durability. The second parameter focuses on the activation of PRAH's crystal growth mechanism. Crystalline PRAH's contain Portland cement, silica sand and various active chemicals, which react with the water contained in the fresh concrete and the by-products of cement hydration process, forming a network of insoluble crystals inside the pores. Therefore, the more moisture there is in the mass of concrete, the greater the action of the crystals, resulting in the continuous reduction of the porosity of the hardened concrete. Some specimens were placed in the concrete water impermeability apparatus for 3 days and others for 28 days, in order to determine the extent to which the ability of chloride penetration into the concrete is reduced depending on the period of accelerated crystal growth. The third parameter studies the importance of the reinforcement coating in ensuring durability. The reinforcements of the specimens were placed with a coating thickness of 15 mm, 25 mm and 35 mm.

Table 2. Mixing ratio of concrete mixtures (2^{nd} Phase).

kg/m^3		C25/30			C30/37		
		REF	0.80% PRAH	5% MS	REF	0.80% PRAH	5% MS
Cement	CEM II/(B-M) 32.5N	300	300	300	350	350	350
Aggregates	Sand	1145	1145	1145	1115	1115	1115
	Gravel	300	300	300	295	295	295
	Coarse	445	445	445	445	445	445
Superplasticizer		1.85	1.85	1.85	2.5	2.5	2.5
Retarder		0.6	0.6	0.6	0.7	0.7	0.7
Water		180	180	180	175	175	175
W/C		0.6	0.6	0.6	0.5	0.5	0.5
PRAH		–	2.4	2.4	–	2.8	2.8
MS		–	–	15	–	–	17.5

The same components were used to prepare the reinforced specimens as in the first phase of the research (e.g. Table 2), the only difference being the individual addition of crystalline admixtures at a percentage of 0.8% per weight of cement and microsilica at a percentage of 5% per weight of cement. In addition, Φ12 ribbed reinforcing bars were used. The specimens were maintained in the curing chamber until the age of 28 days. The concrete mix designs for the second experiment were: Composition 1. REF, Composition 2. 0.80%PRAH, Composition 3. 5% MS (Fig. 1).

Fig. 1. Reinforced concrete specimens before immersion in NaCl- solution in the laboratory environment.

The above specimens were partially immersed in a tank containing sodium chloride solution immediately after the end of their curing process for a period of 6 months, except for the 0.8% PRAH 3 Days and 0.8% PRAH 28 Days mixtures in which the accelerated activation of the crystals was preceded.

The behaviour assessment of the reinforced concrete in a corrosive environment was carried out by the half-cell potential testing method [7] at specific times with the aid of an electrode, according to ASTM C876-91 [6].

3 Experimental Results and Discussion

3.1 Compressive Strength

The compressive strength was measured for all concrete mixtures at the age of 28 days. These values are shown in Table 3.

Table 3. Compressive strength of concrete mixtures (MPa).

(MPa)	C25/30			C30/37		
	REF	0.80% PRAH	0.80% PRAH - 2%MS	REF	0.80% PRAH	0.80% PRAH - 2%MS
28 days	39.5	46.2	49.3	50.3	51.9	52.9

C25/30 0.8%PRAH - 2%MS and C25/30 0.8%PRAH yielded improved compressive strength than the reference mix, with C25/30 0.8%PRAH - 2%MS showing the highest compressive strength values. The highest percentage increase in compressive strength up to the age of 28 days was shown by the C25/30 0.8%PRAH mixture, with a percentage of 36%, followed by the C25/30 0.8%PRAH-2%MS mixture with a percentage increase of 27%.

All C30/37 specimens, throughout their hydration process, showed a common compressive strength progression. At the critical age of 28 days, the C30/37 reference mix has the lowest value, as expected, but there is no significant difference, as the compressive strength ranged between 50–53 MPa. The highest percentage increase in compressive strength up to the age of 28 days was shown by the C30/37 0.8%PRAH–2%MS mixture, with a percentage of 32%, followed by the reference mixture with a percentage increase of 26%.

The implication of these analyses is, that the crystalline admixtures both individually in a composition and synergistically with microsilica, contribute positively and to a satisfactory degree to the compressive behavior of the concrete.

3.2 Water Permeability

Cubic specimens of 150 mm were placed in the concrete water impermeability apparatus for 3 days, where controlled pressure was applied to the surface of the specimens. The depth of water penetration was measured, after the testing period, by breaking the specimen in half (Table 4).

Table 4. Water permeability depths of concrete mixtures.

(mm)	C25/30			C30/37		
	REF	0.80% PRAH	0.80% PRAH - 2% MS	REF	0.80% PRAH	0.80% PRAH - 2% MS
28 days	17.67	16.00	11.67	11.30	4.00	3.50

At the age of 28 days the C25/30 REF mixture was highly porous. However, the mixture with crystalline admixtures presented a relatively greater water penetration depth, at around 16mm. On the contrary, the C25/30 0.8%PRAH - 2%MS mixture showed much better behavior in the water permeability test compared to the other mixtures.

The C30/37 reference mix performed lower penetration depth since it was produced with lower w/c and higher cement content (Table 2), resulting this way to a denser microstructure. The mix with crystalline admixtures showed significantly better water permeability behavior as the maximum water penetration depth reached only 4 mm. The combined action of crystalline admixtures and microsilica performed even better as the water penetration depth of the C30/37 0.8%PRAH-2%MS mixture was further reduced to 3.5 mm.

3.3 Chloride Penetration Coefficient

Chloride resistance is determined by the value of the chloride penetration coefficient in concrete, Dnssm, according to the procedure described in NordTest Build 492 [3]. The higher the value of Dnssm, the greater the permeability of concrete, as it allows chloride ions to penetrate from the external environment to the inner concrete mass, resulting in a significant decrease in durability (Table 5).

Table 5. Dnssm chloride penetration coefficient.

(10^{-12}m/s)	C25/30			C30/37		
	REF	0.80% PRAH	0.80% PRAH - 2% MS	REF	0.80% PRAH	0.80% PRAH - 2% MS
28 days	29.54	6.26	5.12	11.45	3.92	3.53

The C25/30 0.8%PRAH - 2%MS mix gave the most desirable protection against chloride penetration, as it had the lowest Dnssm coefficient, 83% lower than the reference mix and 18% lower compared to the C25/30 0.8%PRAH. The C25/30 REF mix is characterized as unsuitable for aggressive environments against chlorides.

Based on the results, the reference mix had the highest chloride penetration coefficient. In contrast, the C30/37 0.8%PRAH's Dnssm coefficient was 66% lower than that of the reference mix. The C30/37 0.8%PEN-2%MS mix's Dnssm coefficient was shown to be reduced by 69% compared to the reference mix and by 10% compared to the mix with crystalline admixtures. Activation of crystals reduced the chloride permeable porosity thus reducing the Dnssm coefficient.

3.4 Carbonation Depth

The assessment of concrete carbonation under natural and accelerated carbonation conditions was based on the phenolphthalein test [4]. The carbonation depth of all mixtures of the first phase is shown in Table 6. It should be noted that the carbonation depth of the specimens placed in the accelerated carbonation chamber was expected to be greater than that of the specimens exposed to natural environmental conditions.

Table 6. Carbonation depth of concrete mixtures.

(mm)	C25/30			C30/37		
	REF	0.80% PRAH	0.80% PRAH - 2%MS	REF	0.80% PRAH	0.80% PRAH - 2%MS
Accelerated Carbonation (56 days)	9.7	5.8	5.5	5.4	3.4	3.8
Natural Carbonation (6 months)	3.8	2.7	2.9	1.2	0.6	0.9

The C25/30 mixtures with crystalline admixtures and microsilica, both in accelerated and natural carbonation, were much more resistant as they showed low carbonation depths. In particular, from the test carried out in the outdoor environment of the laboratory, the C25/30 0.8%PPRAH mix showed better resistance to CO_2 invasion in the concrete because the corrosion depth was 11% less than the C25/30 0.8%PRAH-2%MS mix.

Similarly for the C30/37 mixtures, greater carbonation depths, both under accelerated and natural carbonation, were observed in the reference mixture. In particular, the average carbonation depth, under accelerated carbonation conditions, of the reference mixture is 59% greater than the C30/37 0.8%PRAH mixture and 42% greater than the C30/370.8%PRAH-2%MS. The minimum carbonation depth was that of the C30/37 0.8%PRAH mix, with a value of 3.4 mm. From the test carried out in the outdoor environment of the laboratory, a slightly better behavior was shown by C30/37 0.8%PRAH mixture with a carbonation depth of 0.60 mm, followed, increased by 50%, by the C30/37 0.8%PRAH-2%MS mixture. The greatest carbonation depth, increased by 100% compared to C30/37 0.8%PRAH, was that of the reference mixture with a value of 1.2 mm. Once again activation of crystals reduced the porosity of PRAH produced mixtures thus increasing their carbonation resistance.

Half-cell potential

Below are the results of the corrosion potential grouped by coating thickness. In each graph, four (4) areas were delineated according to the Standard [6]. Depending on the area where the reinforcement is located based on its corrosion potential, conclusions are drawn about its corrosion probability. The boundaries of these areas and the degree of probability of corrosion of the reinforcement in each area are listed below:

Zone I. Corrosion probability of 10% for corrosion potential values Ecorr > -150 mV.

Zone II. Uncertain reinforcement condition for corrosion potential values of -150 mV $>$ Ecorr > -350 mV.

Zone III. 90% corrosion probability for corrosion potential values of -350 mV $>$ Ecorr > -450 mV.

Zone IV. Definite corrosion of reinforcement for corrosion potential values Ecorr $<$ -450 mV.

As it is discussed in the literature, these values are an indication for the corrosion probability of the steel reinforcement but not be considered as fixed boundaries in term of corrosion probability, because they are subject to the influence of several factors (Figs. 2 and 3).

The reference mixtures for all coating thicknesses in both strength classes show the highest corrosion potential values.

Based on the graphs, the best behavior against chloride attack for the C25/30 concrete strength class was shown by the 35mm C25/30 0.8%PRAH (28 days) specimens followed by the 35mm C25/30 0.8%PRAH (3 days) specimens. In fact, these mixtures remained until the end of the experiment in Zone III. However, the C25/30 5%MS and C25/30 0.8%PRAH mixtures with a coating thickness of 35 mm entered Zone IV after 155 and 188 days immersed in sodium chloride solution. On the other hand, the coating thickness of 15 mm was not enough to protect the specimens against corrosion, as the

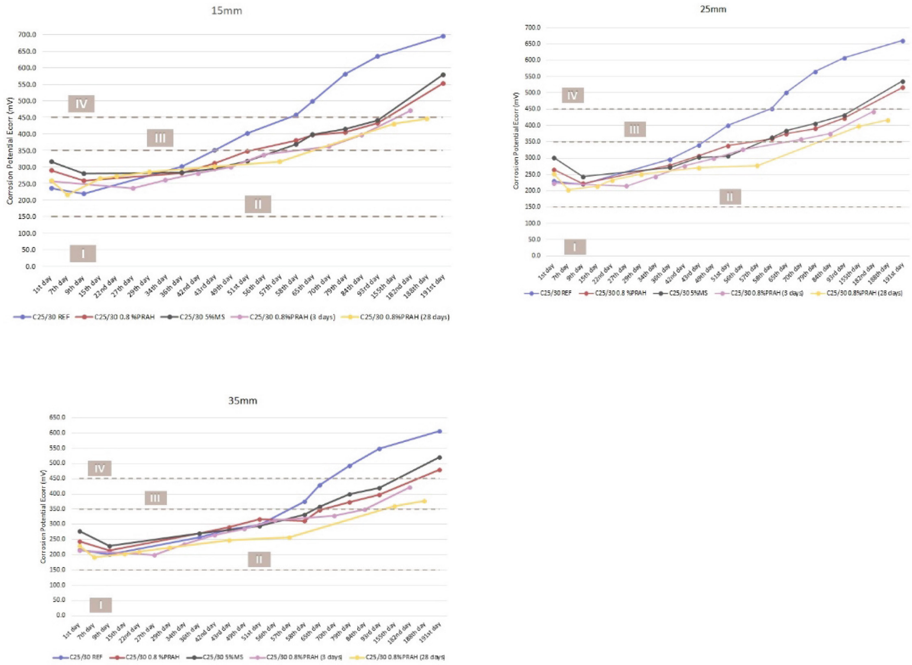

Fig. 2. Corrosion potential of reinforcing steel in C25/30 concrete with coating thickness of 15 mm, 25 mm and 35 mm.

reinforcements corroded in a short time. Regarding the coating thickness of 25 mm, only the specimens of the C25/30 0.8%PRAH (28 days) mix managed to remain in Zone III, while the probability of corrosion of the reinforcement of the other specimens was classified as 100%. In the C25/30 5%MS mix, complete corrosion of the reinforcement started at 130 days, i.e. 25 days faster corrosion compared to the 35 mm coating thickness.

All the above observations apply to mixtures of strength class C30/37. In particular, all specimens with a 35 mm reinforcement coating thickness showed lower corrosion potential values than the corresponding specimens with 15 and 25 mm coating thickness. The greater decrease was mainly observed in the mixes with crystalline admixtures subjected to water permeability testing for 3 and 28 days. The specimens of C30/37 0.8%PRAH (28 days) with a 35 mm coating thickness entered Zone III at the end of the experiment, i.e. 191 days after being placed in the sodium chloride solution, while the specimens with a 15 and 25 mm coating remained in Zone III until the end of the experiment. The next best behavior was shown by the specimens left for 3 days in the water permeability apparatus, as all specimens of the mixture were in Zone III at the end of the experiment and only the specimens with a 15 mm coating thickness entered the lower limit of zone IV.

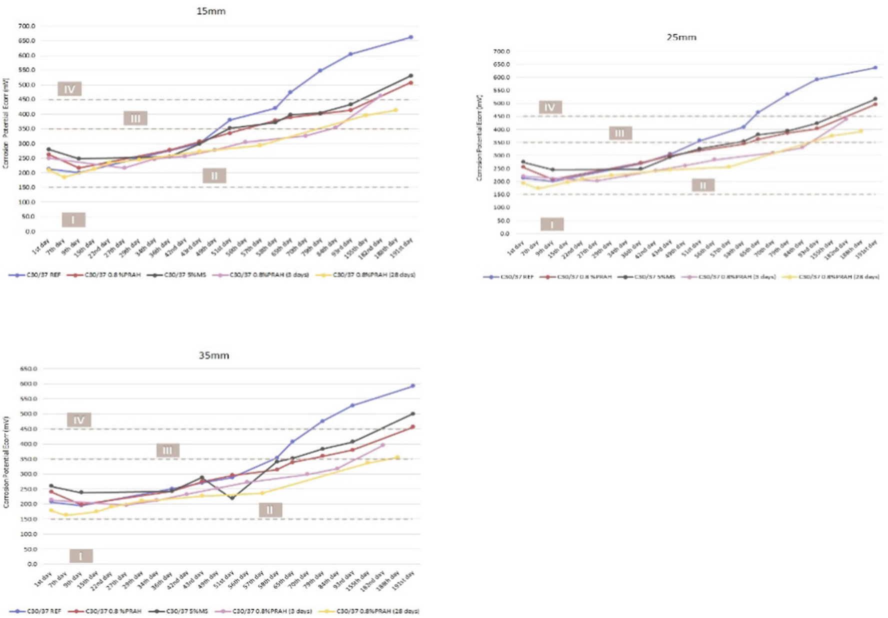

Fig. 3. Corrosion potential of reinforcing steel in C30/37 concrete with coating thickness of 15 mm, 25 mm and 35 mm.

4 Conclusions

The use of crystalline admixtures in concrete significantly increases its durability. The addition of crystalline admixtures at a rate of 0.8 wt% of the cement significantly reduces the carbonation depth as well as the chloride penetration coefficient in the concrete, greatly increasing the service life of reinforced concrete structures against carbonation and chloride induced corrosion.

The simultaneous addition of crystalline admixtures and silica fume to the concrete further reduces the chloride penetration coefficient very slightly, while increasing the carbonation depth due to the consumption of $CA(OH)_2$ by the Microsilica.

Both the addition of crystalline admixtures at a rate of 0.8% wt. of cement as well as the addition of Microsilica at a rate of 5% wt. of cement protect the concrete reinforcement to the same degree against corrosion due to chloride penetration. The protection against corrosion of the steel is significantly increased after partial or total activation of the crystals. Full activation of the crystals closes the pores and makes it difficult for chlorides to penetrate inside the concrete, significantly delaying the onset of reinforcement corrosion and thus extending the service life of reinforced concrete structures, even for low coverage.

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