

Durability of mixtures containing calcium nitrite based corrosion inhibitor

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Abstract

The influence of calcium nitrite based corrosion inhibitor on the corrosion of reinforcing steel embedded in 14 different mortars is experimentally investigated in this work. Two Portland cements, NPC and SR (type I and V according to ASTM Standards) and 12 blended cements were used. The pozzolanic materials used were three lignite fly ashes, silica fume and one natural pozzolan (Milos' Earth). All blended cements were produced in the laboratory by grinding Portland clinker, gypsum and the appropriate pozzolanic material. One commercially available blended cement (CEM II/A-M 32.5N) was also used in this research. Mortar specimens (cylinders 100×40 mm) were prepared, according to DIN 1164 with and without calcium nitrite and used for measurements of carbonation and chloride-induced corrosion for a time period of 2 years. Chloride resistance was monitored according to ASTM C876 on specimens immersed in a 5% NaCl solution after an initial curing of 28 days. The carbonation depth was measured on cylinders cured in a severe environment using a spray indicator enabling the estimation of different pH values.

Results show that calcium nitrite has a beneficial effect in shifting the corrosion potential towards electropositive direction especially in the case of NPC and SR cements. The corrosion potential of blended mixtures was also shifted towards electropositive direction, but since the pozzolanic materials had a beneficial effect by themselves, the reduction was comparative smaller. The beneficial effect of calcium nitrite was also confirmed by the gravimetric weight loss measurements performed after 2 years of immersion in the 5% NaCl solution.

Carbonation depth of all mixtures was reduced or remained the same when calcium nitrite was used. Chloride permeability was not seriously influenced by the addition of calcium nitrite, as it is indicated by the total chloride measurements performed after 2 years of immersion in the 5% NaCl solution.

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1. Introduction

Reinforced concrete is the most commonly used construction material worldwide. In the absence of aggressive media such as chlorides and carbon dioxide, good quality concrete with sufficient cover is all that is needed for the structure to achieve its design life with little or no maintenance. Due to the presence of $\text{Ca}(\text{OH})_2$ in the pores of the cement matrix, the pH has an average value of 12.4 [1]. Under these circumstances a thin oxide layer is formed around the reinforcement bars helping them to remain uncorroded. Reinforcement

corrodes only if the protective layer deteriorates. This may be happen either due to the fall of the pH value of the pore solution—if the pH value falls below 11 the protective layer starts cracking, and it deteriorates totally when the pH falls below the value 9—or due to the great concentrations of chlorides around the reinforcement bar. Both phenomena—carbonation and chloride ingress—result in the corrosion of the reinforcement and the reduction of the designed service life of the structure.

The first step to increase the durability of steel reinforced concrete is to improve the quality of concrete. High quality concrete prevents corrosion, by reducing the chloride ingress and carbonation rate. Use of blended cements incorporating supplementary cementing materials such as silica fume, blast furnace slag, fly ash or natural pozzolan, is a solution that leads to mixtures

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with greater resistance against chlorides [2]. On the other hand, the carbonation depth of the mixtures usually increases, if the supplementary cementing materials replace the cement and decreases if they replace aggregates [2]. The chloride ingress reduction and the carbonation increase (or reduction) strongly depends on the material used for cement or aggregate replacement [2].

High performance concrete mixtures significantly increase the corrosion initiation time. It was reported [3] that the corrosion initiation due to carbonation may be significantly extended. However, there comes a time at which the corrosion of steel initiates.

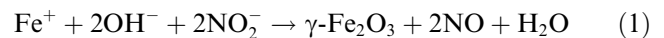
Tuutti [4] described the useful lifetime of a concrete structure in Fig. 1. This consists of two phases: The first phase corresponds to the time t_0 taken for chlorides and/or carbon dioxide to penetrate the concrete cover in sufficient amounts to break down the passive film. This phase is dependent on the chloride diffusion rate, D_{Cl^-} , the carbon dioxide diffusion rate, D_{CO_2} , the degree of chloride binding (and, consequently, the amount of chlorides remaining in solution, $C_{Cl(sol)}$), and the chloride threshold value, Cl_{TV} . All of these factors are influenced by the use of blended cements.

The second phase covers the period of active corrosion from t_0 to the time at which the products of corrosion will cause spalling, cracking and deterioration of the concrete. Since the corrosion products have a volume 2–4 times greater than the material they replace [1] the concrete cover suffers internal stresses resulting in cracking and spalling. Another problem arising at this phase is the load-bearing capability reduction of the rebar, due to the reduction of its nominal diameter. Since corrosion initiates, its rate is a function of oxygen ingress (D_{O_2}), the electrical resistivity of the concrete (ρ), the relative humidity (R.H.) and the temperature (T). It is reported [5] that diffusion of chloride ions dominates the generation of corrosion while the diffusion of oxygen dominates its rate.

However, in many cases in severe environments even good quality concrete cannot provide sufficient protection. Over \$20 billion of repair needed for the concrete

bridges in the US [6], with an estimate increase of \$500 million per year for additional necessary repair [7]. A number of additional corrosion protection systems such as corrosion inhibitors, epoxy-coated reinforcing steel, stainless steel, surface impregnation of concrete and cathodic protection are marketed therefore to address corrosion of steel in reinforced concrete. Among the corrosion protection systems the use of corrosion inhibitors as concrete admixtures is a very popular, easy and a relatively economical method.

An ideal corrosion inhibitor has been defined as “a chemical compound, which, when added in adequate amounts to concrete, can prevent corrosion of embedded steel and has no adverse effect on the properties of concrete” [8]. Calcium nitrite is now extensively used as a corrosion-inhibitive admixture in concrete [9]. Among the several hypothesis concerning steel passivation by nitrite [10] the mechanism of its action as an anodic inhibitor, due to formation of a stable passive film, is presented below [11]:



The influence of calcium nitrite on the corrosion of the embedded steel due to chloride ingress as well as its effect on the chloride binding capacity of the mixture is experimentally investigated in this work and related with the confined use of supplementary cementing materials.

2. Specimen's preparation—test procedure

The materials used were a Greek natural pozzolan of volcanic origin, Milo's Earth (ME) and two Greek lignite fly ashes, Megalopoli's fly ash (MFA) and Ptolemaida's fly ash (PFA). Ptolemaida's treated fly ash (PtFA) has also been used. PtFA has been treated in order to increase its fineness and to reduce the free CaO content of the material. MFA has a significant pozzolanic activity, whereas PFA and PtFA have pozzolanic as well as hydraulic activity [12]. The chemical composition of these materials, as well as the one of Portland clinker, CEM II32.5N cement (II32.5N) and sulfate resistant cement (SR), are presented in Table 1.

The mineralogical composition of the clinker used, as calculated according to ASTM C150 [13], is presented in Table 2.

The cements used for mortar mixtures were produced in the laboratory by mixing clinker, pozzolanic material and gypsum ($CaSO_4 \cdot 2H_2O$). The gypsum content was different for each mixing, in order to keep the total SO_3 content of the binder (clinker + gypsum) equal to 3.5%. All mixtures were produced according to DIN 1164 [14] using EN-196-1 [15] standard sand. The cementitious material:aggregate ratio was 1:3 and the water/cementitious material ratio was equal to 0.45 for each mixture. Different dosages of superplasticizer (Daracem 205)

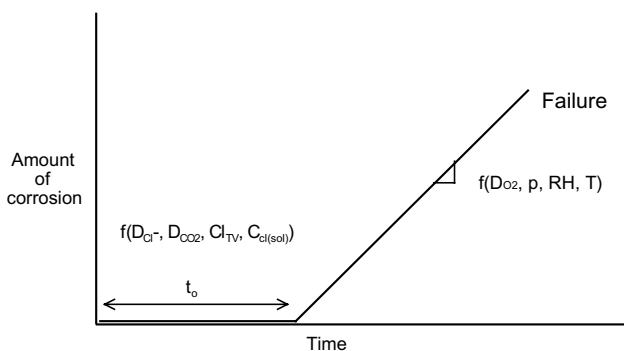


Fig. 1. Corrosion rate of reinforcing steel as a function of the lifetime of the structure (adapted from [4]).

Table 1
Chemical composition of the materials used

Oxide content (%)	Clinker	Commercial blended cement (CEM II32.5)	Type V (SR) cement	ME	MFA	PFA	PtFA	SF
SiO ₂	21.50	28	20.4	65.9	47.08	27.10	45.15	90.90
Active SiO ₂		–		23.21	15.69	–	22.58	–
Al ₂ O ₃	5.42	9	4.29	15.7	18.62	11.22	17.50	1.12
Fe ₂ O ₃	3.41	5.5	4.8	3.95	6.72	4.14	8.18	1.46
CaO	65.83	48.0	62.72	4.0	17.50	38.43	14.87	0.69
Free CaO				–	–	12.34	1.64	0.024
MgO	1.20	2.2	2.73	1.4	3.81	3.46	3.44	0.77
SO ₃	0.55	3.2	2.08	–	3.28	6.31	4.72	0.38
Na ₂ O	0.58	0.5	0.33	5.65	0.68	0.81	–	0.35
K ₂ O	0.80	1.5	0.37		1.52	0.54	–	0.57
Fineness (retained on 45 m sieve)	52.9	64	67	62.9	65.5	32	26	18 m ₂ /g (Bet)

Table 2
Mineralogical composition of clinker Portland according to [13]

Phase	Percentage
C ₃ S	61.74
C ₂ S	15.06
C ₃ A	8.59
C ₄ AF	10.38

were added in order to keep the flow constant. Calcium nitrite was added at a dosage of 20 l/m³. In this case the water/cementitious material ratio was properly reduced.

All cements prepared, as well as the SO₃ content of the mixture (clinker + gypsum) are presented in Table 3. The water/cementitious material ratio and the dosage of superplasticizer are presented in Table 4.

Compressive strength development was measured on prisms (40×40×160 mm) according to DIN 1164. Compressive strength measurements were performed at different ages up to 112 days (15 weeks) as the mean

value of six measurements. These values are presented in Table 5.

Carbonation depth and resistance against chloride-induced corrosion was also measured on cylinder (40×100 mm) mortar specimens. The carbonation depth was measured using a spray indicator enabling the estimation of different pH values provided by German Instruments, Denmark. The procedure described in [16] was followed for the estimation of resistance against chloride-induced corrosion. A 10 mm diameter bar was embedded in the middle of each mortar cylinder and half cell potential measurements (using calomel saturated electrode), according to ASTM C-876 [17], were performed up to 2 years after immersion in the corrosive solution.

Two series of cylinder (40×100 mm) specimens were produced from each mixture. All specimens were initially cured for 28 days in a curing room with relative humidity ≥95% and temperature 20±2 °C. After this age, specimens of the first series were placed in a curing

Table 3
Cements used for mortar production

Mix no.	Mixture	Cement type	SO ₃ content of the mixture clinker + gypsum (%)
1	NPC	93.58% clinker + 6.42% gypsum	3.5
2	II32.5N	CEM II32.5N	3.2
3	SR	SR (type V)	2.08
4	10% ME	10% ME + 84.24% clinker + 5.76% gypsum	3.5
5	30% ME	30% ME + 65.52% clinker + 4.48% gypsum	3.5
6	10% SF	10% SF + 85.31% clinker + 4.69% gypsum	3.5
7	15% SF	15% SF + 79.54% clinker + 5.46% gypsum	3.5
8	10% MFA	10% MFA + 84.78% clinker + 5.22% gypsum	3.5
9	30% MFA	30% MFA + 67.57% clinker + 2.43% gypsum	3.5
10	10% PFA	10% PFA + 84.94% clinker + 5.06% gypsum	3.5
11	30% PFA	30% PFA + 67.65% clinker + 2.35% gypsum	3.5
12	30% PtFA	30% PtFA + 66.18% clinker + 3.92% gypsum	3.5
13	40% PtFA	40% PtFA + 58.61% clinker + 1.38% gypsum	3.5
14	50% PtFA	50% PtFA + 49.36% clinker + 0.64% gypsum	3.5

Table 4
Water/cementitious material ratio, superplasticizer and corrosion inhibitor dosage of the prepared mortars

Mixture	W/binder ratio (wt% cem. materials)	Superplasticizer (wt% cem. materials)	Corrosion inhibitor (l/m ³)
NPC	0.45	1%	–
II35	0.45	1%	–
SR	0.45	Not used	–
10% ME	0.45	1%	–
30% ME	0.45	1%	–
10% SF	0.45	1%	–
15% SF	0.45	1%	–
10% MFA	0.45	1%	–
30% MFA	0.45	1%	–
10% PFA	0.45	1%	–
30% PFA	0.45	1%	–
30% PtFA	0.45	2%	–
40% PtFA	0.45	2%	–
50% PtFA	0.45	3%	–
NPC + CI	0.42	1%	20
II35 + CI	0.42	1%	20
SR + CI	0.42	Not used	20
10% ME + CI	0.42	1%	20
30% ME + CI	0.42	1%	20
10% SF + CI	0.42	1%	20
15% SF + CI	0.42	1%	20
10% MFA + CI	0.42	1%	20
30% MFA + CI	0.42	1%	20
10% PFA + CI	0.42	1%	20
30% PFA + CI	0.42	1%	20
30% PtFA + CI	0.42	2%	20
40% PtFA + CI	0.42	2%	20
50% PtFA + CI	0.42	3%	20

room with relative humidity 50–65% and temperature 21 ± 3 °C and used for carbonation measurements, while specimens of the second series were immersed until the middle of their height in a 5% NaCl solution and used for half cell potential and gravimetric weight loss measurements as well as for chemical analyses. Half cell potential (Figs. 2–7) and carbonation measurements (Table 6) were taken for a time period up to 2 years. Total and free chloride contents of each mixture as well as nitrite contents of CNI containing mixtures were also measured after 2 years of immersion in samples taken from cylindrical specimens according to the procedures described in [16] and [18] respectively. These measurements are presented in Table 8.

3. Results and discussion

3.1. Compressive strength development

As it is shown in Table 5 specimens produced with blended cements perform better compressive strength than the control's even from the age of 7 days. This finding is in accordance with other researchers [19–21] who attribute this fact at the development of pores with smaller diameter as well as at the greater amount of CSH produced from the hydration of blended cements [22]. Among the pozzolanic materials used Ptolemaida's

treated fly ash (PtFA) mixtures perform higher compressive strength values; the 30% PtFA mixture performs higher compressive strength values even from the silica fume specimens at the ages of 28, 60, 90 and 112 days. Addition of calcium nitrite slightly increased the compressive strength of all mixtures at the age of 7 and 28 days (Table 5).

3.2. Half cell potential

Results of ASTM C876 half cell potential measurements are an indication for the probability of rebar corrosion (Table 7). Half cell potential measurements presented here are the mean value of six measurements for each age. Among the mixtures examined, specimens produced with silica fume blended cements performed the best (Fig. 3). 30% PtFA specimens also had a very good performance (Fig. 7), almost equal to that of the 10% SF specimens. In this case it is noticeable that the protective effect of PtFA seems to be dramatically reduced as the cement replacement increases from 40% to 50%; an indication of severe corrosion initiation is clear after the age of 180 days (Fig. 7). MFA specimens (Fig. 5) perform satisfactory mainly when it replaces cement at high (30%) percentage. As the cement replacement decreases the protection ability decreases. On the contrary, PFA specimens in both percentages performed high corrosion risks (Fig. 6). Protection from chloride-

Table 5
Compressive strength (MPa) of the mixtures prepared

Mortar mixture	Hydration age (days)						
	7	14	21	28	60	90	112
NPC	37.55	42.08	–	55.33	–	55.63	57.81
NPC + CNI	39.82	–	–	56.90	–	–	–
II32.5N	35.68	46.61	50.79	54.00	61.52	64.00	66.50
II32.5N + CNI	36.85	–	–	55.18	–	–	–
SR	39.95	49.48	54.53	56.90	60.25	62.63	–
SR + CNI	41.68	–	–	57.82	–	–	–
10% ME	–	47.33	47.66	48.36	54.69	56.25	62.50
10% ME + CNI	–	–	–	49.68	–	–	–
30% ME	37.32	39.40	–	42.65	46.25	56.25	57.50
30% ME + CNI	38.49	–	–	43.15	–	–	–
10% SF	53.96	57.66	58.59	61.72	62.50	65.63	66.00
10% SF + CNI	55.06	–	–	62.47	–	–	–
15% SF	52.00	54.00	54.17	56.29	59.18	64.58	–
15% SF + CNI	53.57	–	–	57.76	–	–	–
10% MFA	50.94	51.45	52.19	54.00	56.25	58.33	63.00
10% MA + CNI	52.28	–	–	55.30	–	–	–
30% MFA	45.36	53.23	–	55.94	–	64.58	71.88
30% MA + CNI	47.02	–	–	57.26	–	–	–
10% PFA	38.96	50.78	59.01	60.43	61.68	63.54	66.88
10% PA + CNI	40.27	–	–	61.80	–	–	–
30% PFA	38.85	43.85	–	50.83	–	52.00	55.00
30% PA + CNI	39.78	–	–	52.45	–	–	–
30% PtFA	44.39	53.91	56.09	63.56	65.00	65.83	67.19
30% PtA + CNI	46.78	–	–	65.80	–	–	–
40% PtFA	43.83	53.79	53.80	57.40	61.25	64.96	66.63
40% PtA + CNI	45.69	–	–	59.89	–	–	–
50% PtFA	40.43	52.87	–	55.00	58.75	64.06	65.67
50% PtA + CNI	41.52	–	–	56.65	–	–	–

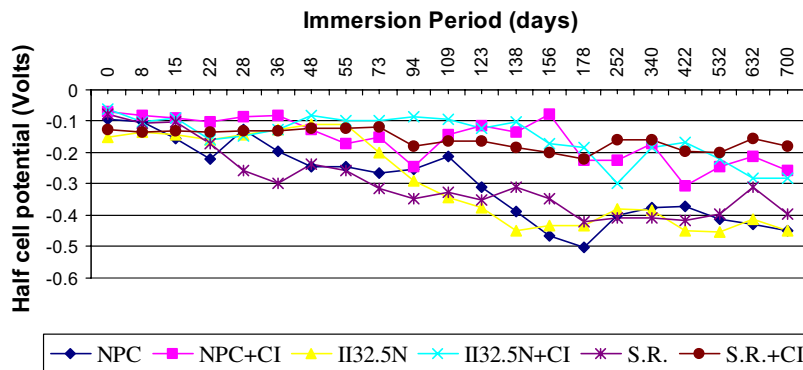


Fig. 2. Half cell potential measurements of NPC, SR and II32.5N mortars with and without corrosion inhibitor (CI) immersed in 5% NaCl solution for 2 years.

induced corrosion also decreases as the cement replacement increases in the case of ME (Fig. 4).

Among the mixtures tested in this research, NPC, SR, II32.5N, 50% PtFA, 30% PFA and 30% ME had the worst performance (Figs. 2, 4, 6, and 7). Those mixtures exhibited after 2 years of immersion potential values almost equal or lower than -0.426 V, which is an indication of high to severe corrosion (Table 7).

Use of calcium nitrite significantly reduces the corrosion risk in all mixtures by turning the half cell po-

tential to more positive values (Figs. 2–7). Although the addition of calcium nitrite has a beneficial effect in all cases, its contribution at the half cell potential is not always the same; the higher the corrosion risk of the mixture, the greater the influence of calcium nitrite. Thus, the potential shifting towards electropositive directions caused by calcium nitrite is greater in the case of 50% PtFA, SR, NPC, II32.5N and 30% ME mixtures (34.75%, 54.91%, 42.67%, 37.23% and 39.24% respectively) and smaller in the case of 15% SF mixture (only

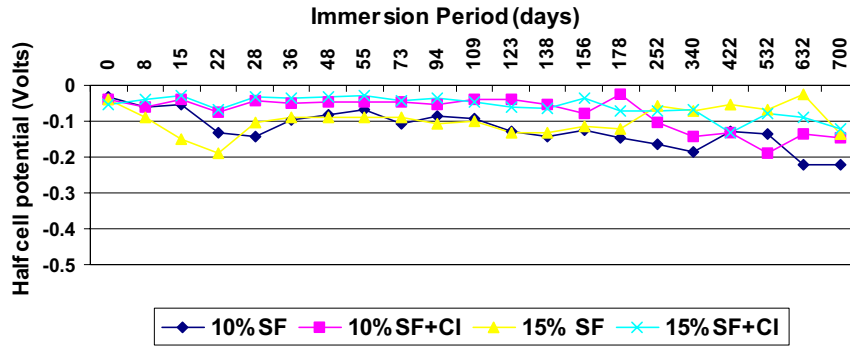


Fig. 3. Half cell potential measurements of 10% and 15% SF mortars with and without corrosion inhibitor (CI) immersed in 5% NaCl solution for 2 years.

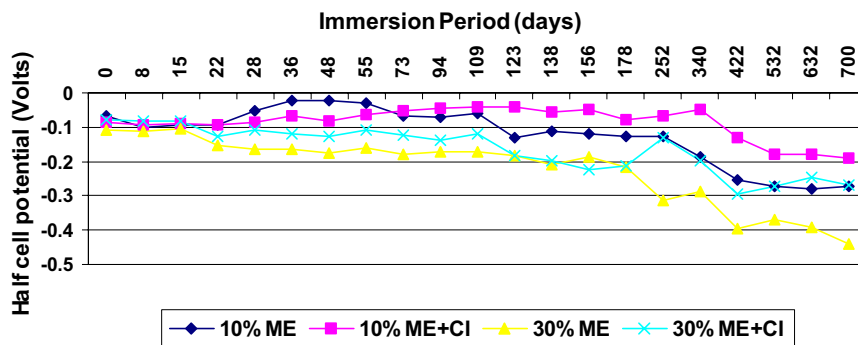


Fig. 4. Half cell potential measurements of 10% and 30% ME mortars with and without corrosion inhibitor (CI) immersed in 5% NaCl solution for 2 years.

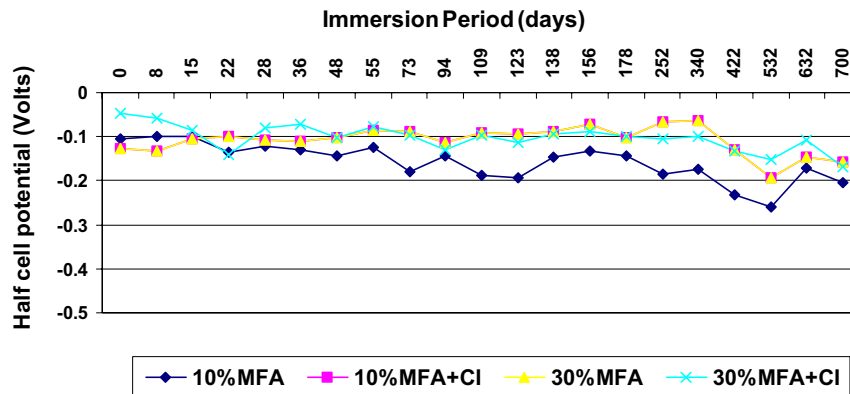


Fig. 5. Half cell potential measurements of 10% MFA and 30% MFA mortars with and without corrosion inhibitor (CI) immersed in 5% NaCl solution for 2 years.

9.11%). It is also noticeable that the corrosion risk turns from high to intermediate corrosion risk in the case of 50% PtFA, SR, NPC and II32.5N mixtures.

3.3. Gravimetric weight loss

Gravimetric weight loss of steel rebars was measured after 2 years of immersion according to the procedure

described in [16]. Results (mean value of six specimens) are presented in Fig. 8. Regarding the influence of cementitious materials on the protection of steel reinforcement, weight loss of steel rebars are in relative agreement with half cell potential measurements for the severe corrosion risk mixtures. Addition of calcium nitrite reduced the weight loss of steel rebars, but this reduction was lower than the one observed in half cell

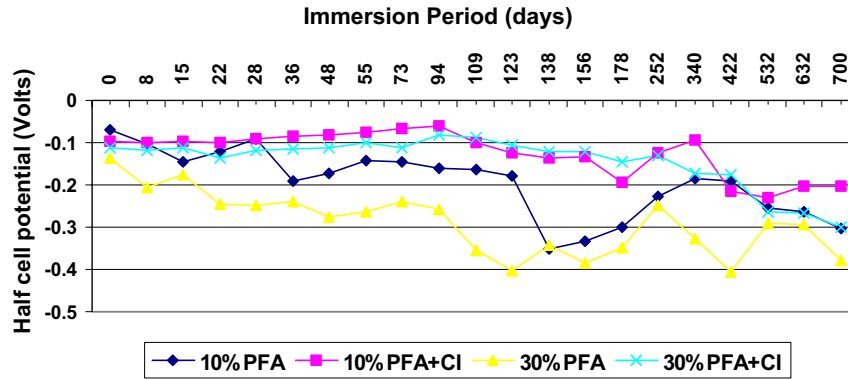


Fig. 6. Half cell potential measurements of 10% and 30% PFA mortars with and without corrosion inhibitor (CI) immersed in 5% NaCl solution for 2 years.

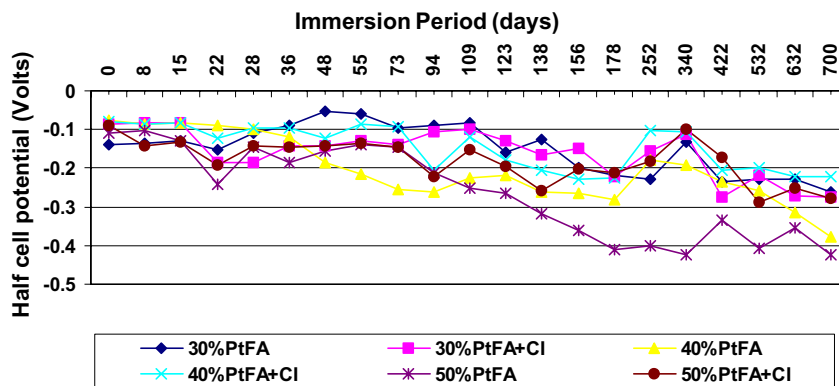


Fig. 7. Half cell potential measurements of 30%, 40% and 50% PtFA mortars with and without corrosion inhibitor (CI) immersed in 5% NaCl solution for 2 years.

potential. It is observed that this reduction was higher when the weight loss of the mixture without the inhibitor was relatively high (SR, 50% PtFA, NPC, II32.5N, 30% PFA) and lower when the weight loss was relatively low (10% SF, 10% MFA). The greater protection against the corrosion of steel rebars is offered by the combined use of calcium nitrite and high (30%) percentages of natural pozzolan (ME) or lignite fly ash (MFA or PtFA).

3.4. Carbonation depth

Carbonation measurements of all mixtures are presented in Table 6. The carbonation depth, as indicated with the phenolphthalein indicator ($\text{pH} < 9$), is for all blended mixtures greater or equal to the depth of the control mixture, especially at the age of 2 years. Since phenolphthalein solution changes color at pH values equal to 9, carbonation depth measured this way is rather an indication that corrosion has initiated, than it has not [1]. The really 'safe' area is the one with pH greater than 11. Those measurements are also presented in Table 6 as determined with the spray indicator mentioned above.

The front at which the pH changes to values less than 11, is for blended cement mixtures less or equal to the one of NPC in the case of 1 year exposure with the exception of 50% PtFA mixture. Although the $\text{Ca}(\text{OH})_2$ needed for the pozzolanic reaction decreases the pH of the pore solution, the formation of additional CSH leads to pores with smaller diameter resulting this way to less CO_2 permeable porosity. Among the materials tested in this research after 1 year's exposure SF, PFA and PtFA offer the greater protection against carbonation when they replace cement at percentages of 10%, 10% and 30% respectively. After exposure of 2 years 10% SF remains the best along with 10% ME and 10% MFA.

It seems that mixtures with calcium nitrite exhibit generally lower carbonation depth at both categories ($\text{pH} < 9$ and $\text{pH} < 11$), probably due to the greater amount of $\text{Ca}(\text{OH})_2$ formed when calcium nitrite is added [23].

3.5. Chloride and nitrite contents

Total and free chloride content as well as nitrite content of the produced mortars are presented in Table

Table 6
Carbonation measurements (mm) after exposure of 1 and 2 years

Mixture	Carbonation depth (mm)			
	Exposure period: 1 year		Exposure period: 2 years	
	pH < 9	pH < 11	pH < 9	pH < 11
NPC	3	5	4	6
NPC + CNI	3	4	4	5
SR	3	4	4	5
SR + CNI	3	4	3	4
II32.5N	4	5	6	8
II32.5N + CNI	3	4	5	6
10% ME	4	5	4	5
10% ME + CNI	3	4	4	5
30% ME	4	5	7	9
30% ME + CNI	3	4	5	6
10% MFA	3	5	4	5
10% MA + CNI	3	4	3	5
30% MFA	3	5	5	6
30% MA + CNI	3	5	4	5
10% PFA	3	4	6	8
10% PA + CNI	3	4	4	5
30% PFA	4	5	6	8
30% PA + CNI	2	3	4	5
30% PtFA	3	4	5	7
30% PtA + CNI	2	3	4	5
40% PtFA	5	5	6	8
40% PtA + CNI	4	5	5	7
50% PtFA	5	6	6	9
50% PtA + CNI	4	5	5	6
10% SF	3	4	4	5
10% SF + CNI	2	3	2	4
15% SF	4	5	4	6
15% SF + CNI	3	4	3	4

Table 7
Corrosion condition related with half cell measurements (calomel electrode)

Half cell potential	Corrosion condition
>−126 mV	Low (10% risk of corrosion)
−126 mV to −276 mV	Intermediate corrosion risk
<−276 mV	High (<90% risk of corrosion)
<−426 mV	Severe corrosion

8. Each measurement is the mean value of three specimens. Total chloride concentrations are quite high—in the range of 4.5–5.5 wt% of cementitious materials—for all mixtures except the 50% PtFA, 10% SF and 15% SF mixtures. The dense cement matrix formed in those cases resulted in lower chloride permeability. On the other hand, there are significant variations in the concentration of free chlorides, mainly because of the different chloride binding properties of the materials used.

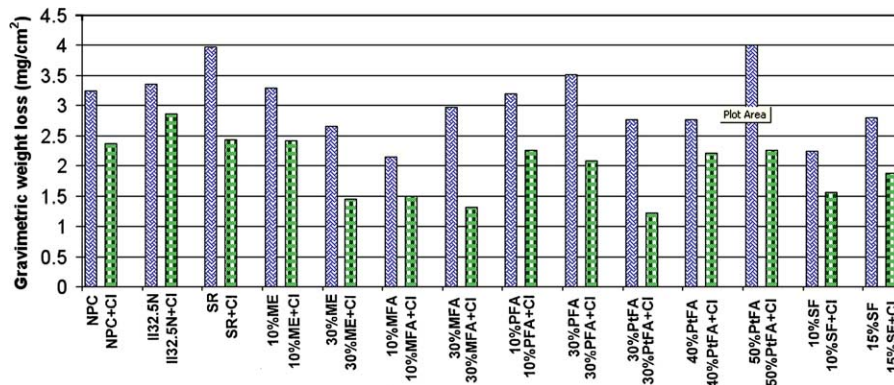


Fig. 8. Gravimetric weight loss of steel rebars after 2 years of immersion in 5% NaCl solution.

Table 8
Chloride and nitrite contents (wt% cem. materials) after two years of immersion in 5% NaCl solution

	Total Cl ⁻ content (wt% cem. materials)	Free Cl ⁻ content (wt% cem. materials)	NO ₂ ⁻ content (wt% cem. materials)	Total Cl ⁻ /NO ₂ ⁻ ratio	Free Cl ⁻ /NO ₂ ⁻ ratio
NPC	5.44	0.27			
rid NPC + CNI	5.07	0.27	0.51	9.91	0.52
II32.5N	4.58	0.33			
II32.5N + CNI	4.77	0.29	0.57	8.29	0.38
SR	4.94	0.80			
SR + CNI	5.12	0.75	0.56	9.2	1.35
10% ME	4.80	0.17			
10% ME + CNI	4.10	0.20	0.53	7.68	0.38
30% ME	5.57	0.41			
30% ME + CNI	5.09	0.48	0.76	6.68	0.63
10% MFA	4.31	0.24			
10% MA + CNI	4.25	0.26	0.67	6.36	0.39
30% MFA	5.44	0.14			
30% MA + CNI	5.48	0.25	0.64	8.55	0.40
10% PFA	4.54	0.10			
10% PA + CNI	4.60	0.24	0.70	6.54	0.35
30% PFA	5.36	0.22			
30% PA + CNI	5.69	0.27	0.55	10.41	0.49
30% PtFA	5.29	0.25			
30% PtA + CNI	5.30	0.35	0.71	7.41	0.50
40% PtFA	5.19	0.29			
40% PtA + CNI	5.27	0.47	0.63	8.29	0.74
50% PtFA	3.27	0.29			
50% PtA + CNI	4.07	0.58	0.65	6.29	0.90
10% SF	3.18	0.11			
10% SF + CNI	3.98	0.09	0.95	4.19	0.09
15% SF	3.47	0.19			
15% SF + CNI	3.12	0.17	0.98	3.18	0.17

As it was expected, SR mixture performed the higher free chloride concentration, due to its low C₃A content, while the lower free chloride content was measured on 10% PFA, 30% MFA and 10% SF mixtures.

No significant differences were observed between total chloride content of most mixtures with and without calcium nitrite. It seems therefore that addition of calcium nitrite does not influence the chloride permeability of the mixture, when the free water of the inhibitor is taken into account and the added water is properly reduced. On the contrary, free chloride content of calcium nitrite containing mixtures is usually increased in blended cement mixtures and in some cases (10% PFA and 50% PtFA mixtures) it is almost twice the concentration of the mixtures without inhibitor. Schießl and Dauberschmidt [24] have not noticed any difference in total and free chloride contents of different grade concretes prepared with and without calcium nitrite and I42.5N cement. In the case of Portland cement mixtures (NPC and SR) prepared with and without calcium nitrite there were also not found in this research any significant differences in total and free chloride concentration (Table 8). Tritthart and Banfill [25] investigated the binding properties of nitrite and chloride ions in mixtures prepared with different cements and different salt dosages. They concluded that nitrites and chlorides adsorb

competitively on cement and this is affected in a complicated way by the cement composition, the chloride concentration present and the type of nitrite salt (sodium or calcium nitrite). However, they also mentioned that adsorption is the main but not the only binding mechanism and there surely must be some influence of chemical binding. The increased free chloride content could be therefore partially explained due to the presence of nitrites, but further research is needed in order to point additional light on the phenomenon observed.

Nitrite contents were also measured in mortars containing calcium nitrite inhibitor. There were significant variations depending on the type of cement and consequently on the permeability of cement paste which enabled the leaching of nitrites. Consumption of nitrites for the formation of a γ -Fe₂O₃ layer according to Eq. (1) is another reason leading to the reduction of the nitrite content. The higher concentrations were measured in the case of SF mixtures whereas the lower concentrations were those of NPC, SR, II32.5N and 30% PFA mixtures (0.51%, 0.56%, 0.57% and 0.55% respectively). The nitrite content ranged between 0.63% and 0.76% in the rest blended mixtures.

Significant variations were also observed in the total and free chloride to nitrite ratios measured. Gianetti [26] suggests a maximum total chloride to nitrite ratio of

1.2–1.5 to ensure inhibition of steel corrosion. This is 2–7 times lower the values reported in this research. Corrosion has of course initiated in calcium nitrite containing mixtures, but sufficient inhibition is still offered for $\text{Cl}^-/\text{NO}_2^-$ ratios up to 8.55%. It is noticeable that SF mixtures do not performed the lowest weight loss, although they had the lower $\text{Cl}^-/\text{NO}_2^-$ ratios. On the other hand, sufficient protection was offered by the 30% PFA mixture, which had the highest $\text{Cl}^-/\text{NO}_2^-$ ratio measured. It seems therefore that there is a critical chloride/nitrite ratio for the initiation of corrosion, but after this point the propagation of the corrosion process depends strongly on the composition of cement.

The same observation is valid for the free chloride/nitrite ratios. It is also noticed that the lowest values were measured on SF mixtures, but not the lowest weight loss as well. However, mixtures with $\text{Cl}_{\text{free}}^-/\text{NO}_2^-$ ratios less than 0.40 have at general a weight loss less than 2 mg/cm². 10% PFA, 10% ME, II32.5N, 30% ME and 30% PtFA mixtures are the exception, with rebar weight loss of 2.26, 2.41, 2.86, 1.45, and 1.23 mg/cm² and $\text{Cl}_{\text{free}}^-/\text{NO}_2^-$ ratios of 0.35, 0.38, 0.38, 0.63 and 0.50 respectively. Therefore $\text{Cl}_{\text{free}}^-/\text{NO}_2^-$ ratios could probably be suggested as more reasonable to specify a limit value for the quantity of the steel mass lost due to corrosion especially in Portland and blended cements with low (<15%) pozzolanic content.

4. Conclusions

Chloride-induced corrosion resistance is generally increased by using blended cements. Among the supplementary cementing materials tested in this research, natural pozzolan, lignite fly ashes (MFA and PtFA) and silica fume offer the greatest protection; 30% ME, 10% and 30% MFA, 30% and 40% PtFA and 10% and 15% SF specimens perform steel rebar weight loss less than 3.0 mg/cm² after 2 years of immersion in the test solution.

Addition of calcium nitrite increases the chloride-induced corrosion resistance of all mixtures, but the protection offered strongly depends on the type of cement used. Best results were obtained under the combined use of calcium nitrite and high (30%) percent of natural pozzolan, MFA, PtFA, 10% MFA and 10% silica fume.

According to the findings of this research there is not good correlation between the $\text{Cl}_{\text{total}}^-/\text{NO}_2^-$ ratios and the extent of steel corrosion in blended cements. Use of $\text{Cl}_{\text{free}}^-/\text{NO}_2^-$ ratio could probably be suggested as more reasonable indication to specify limit values for the propagation of corrosion process, especially in Portland and blended cements with low (<15%) pozzolanic content. However, further research is needed to fully understand the mechanism of interaction between hydration of blended cements and changes in nitrite and chloride concentration.

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