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The Chloride Penetration Depth of Self-Compacting Concrete Using Scanning Electron Microscopy

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Abstract

Achieving a sustainable and durable concrete, with a minimum ecological impact is the current focus of the research in construction. Concrete durability design is based on the behavior of concrete in aggressive environments, one of which is the attack of chlorides. The main purpose of this paper is to test the resistance to chloride action of self-compacting concrete with fly ash addition, compared to self-compacting concrete with limestone addition. For this purpose, the colorimetric method and the scanning electron microscopy method are used, while evaluating the efficiency of the testing methods.

Rezumat

Obținerea unui beton performant, durabil, cu un impact ecologic cât mai mic este preocuparea actuală a cercetărilor din domeniul construcțiilor. Proiectarea durabilității betonului are la bază examinarea comportarii betonului în diferite medii agresive, unul dintre ele fiind atacul clorurilor. Această lucrare are ca obiectiv determinarea rezisteței la acțiunea clorurilor a betonului autocompactant cu cenuși zburătoare în comparație cu betonul autocompactant cu filer de calcar. În acest scop este utilizată metoda colorimetrică și metoda microscopiei electronice de baleiaj, evaluând totodată eficiența metodelor de determinare.

Keywords: *chloride penetration, self-compacting concrete, fly ash, scanning electron microscopy*

1. Introduction

A topical issue with regard to the durability of reinforced concrete structures is the resistance to chloride action. The most common sources of chlorides that can affect the concrete are deicing salt solutions or the marine environment. The penetrating chloride ions, in reinforced concrete elements, are a major danger to the reinforcement, producing corrosion of steel [1].

Permeability of concrete is belived to be the most important characteristic of concrete that affects its

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durability. At microstructural level, the chloride permeability is closely related to the pore structure of the cement-paste matrix. By reducing the water-cement ratio and replacing a part of cement with mineral additions, a less permeable concrete is obtained, which leads to higher durability [2]. The cause of high permeability is not limited to the composition of the concrete but also to poor concreting practice in terms of materials quality, mixing and casting the elements [3].

Self-compacting concrete, due to the pore structure and the very well-controlled production process, showed a better behavior to chlorides penetration than conventional concrete [2, 4, 5]. The use of fly ash as a mineral admixture improves the resistance to chlorides action, reducing the porosity of the concrete. The addition of fly ash causes the decrease of the number and size of voids as the fine fly ash particles fill better the gaps between the aggregates [6]. Due to the fineness and spherical shape of the ash particles, the fresh concrete properties are improved, reducing the water / cement ratio required for a certain workability. The puzzolanic effect of the fly ash, which will significantly elevate the long-term compression strength, is also to be mentioned. [2]

Since the penetration of chloride ions into the concrete elements is a slow process, many test methods have been developed in order to accelerate the penetration process and determine some specific parameters that indicate the resistance to chloride action [6]. A commonly used method is the colorimetric method, which indicates the penetration depth of chloride ions in samples or concrete elements using a silver nitrate solution as a colorimetric indicator [7,8,9]. The method is effective for measuring the depth, but in some cases, it is necessary to determine the chloride content of the concrete element at different depths. According to the *fib* Bulletin [1], the critical content of chlorides for reinforced concrete is very important in the service life prediction. In this respect, there is a test method described in ASTM C1152, which determines the amount of acid-soluble chlorides, equivalent to the total amount of chlorides in a concrete sample. In the case of special concretes containing organic additives, the results may be inconclusive [10].

In the last years, scanning electron microscopy (SEM) has been successfully used in the study of microstructure and chemical composition of reinforced concrete [11]. Using this technique, it is possible to evaluate the resistance of different types of concrete to chloride penetration by analyzing the amount of chlorides present in concrete at different depths. Quantification of chemical elements in the studied concrete samples can indicate the concentration of free chloride ions or the possibility of Friedel's salt formation in the presence of C_3A tricalcium aluminate [11, 12, 13,14].

In this paper are presented the experimental results obtained on samples and elements of self-compacting concrete with fly ash addition, respectively limestone filler addition, exposed to the action of chlorides. Chloride penetration depth was determined using the colorimetric method, and SEM analysis was used as an additional method for depth and concentration.

2. Experimental program

2.1 Materials

In order to obtain the self-compacting concrete compositions a CEM I 52.5 R cement type was used, according to SR EN 197-1 [15] and two types of mineral addition, fly ash, respectively limestone filler. Fly ash originates from Govora Power Plant, Vâlcea, with the following characteristics: density 1900 kg / m3, puzzolanic activity index at 28 days more than 75%, SiO2> 25%, CaO≤10%, Al2O3 + SiO2 + Fe2O3> 75%. Limestone filler is produced by Holcim Turda Grinding Plant, having the following characteristics: density 2670 kg / m3, particle size less than 0.125> 85%, CaCO3> 90%, chloride content 0.001%. The following types of river aggregates were used to produce self-compacting concrete; sand 0-4 mm, coarse aggregate 4-8 mm and 8-16 mm.

To improve workability, a superplasticizer (polyether carboxylate) Sika Viscocrete 20 HE was used.

2.2. Self-consolidating concrete mix proportions

The mix design method is based on the rational mix design method developed by Okamura and Ozawa [16], following the proportions indicated by The European Guidelines for Self-Compacting Concrete [17]. Two concrete compositions were designed, one with fly ash (SCC-CZ) and one with limestone filler addition (SCC-FC). The initial designed compositions were adjusted by laboratory trials, until the compositions corresponded the performance requirements of SCC. The final mixes of self-compacting concrete are detailed in Table 1.

Table 1**:** Final SCC mixes with fly ash addition, respectively limestone addition

Material		SCC-CZ*	SCC-FC**
Cement CEM I 52,5R	(kg/m^3)	350	410
Fly ash	(kg/m^3)	220	0
Limestone filler	(kg/m^3)	0	160
Water	(l/m^3)	220	150
HRWA	(l/m^3)	14	13
Total Aggregates	(kg/m^3)	1550	1550
Sand 0/4	(kg/m^3)	930	930
Gravel 4/8	(kg/m^3)	310	310
Gravel 8/16	(kg/m^3)	310	310
Water/Binder ratio	-	0.35	0.26
Cement replacement by mineral addition	(%)	63	39

* Self-consolidating concrete with fly ash addition

** Self-consolidating concrete with limestone filler addition

By setting the same total amount of powder (570 kg), two types of self-compacting concrete were obtained, one with a high volume of fly ash (63% of the cement) and one with limestone filler addition (39% cement).

2.3. Testing the workability of self-compacting concrete

The workability of final SCC compositions was evaluated by the slump-flow consistency, the T500 and V-funnel flow time and passing ability through the L box. The tests were done according to the indications of the European Guidelines for Self-Compacting Concrete [17].

2.4. Testing the compressive strength

The compressive strength was tested at 28, 72 and 120 days respectively for both types of SCC. Tests were made on 150 mm cubes according to SR-EN 12390: 2001 [18]

2.5. Testing the chloride penetration resistance

2.5.1 The colorimetric method

For the test, three cubes of 100x100x100 mm, both SCC with fly ash and SCC with limestone filler were cast. Samples were completely immersed in 3% sodium chloride (NaCl) solution for 90 days. From each type of SCC, a reference sample of the same size was left in plain water, under

laboratory conditions, of T=(20±2)^{o}C temperature, until testing.
At the end of the exposure period, the samples were split. A solution of silver nitrate (AgNO3) with a concentration of 1% was sprayed on the split surface of the sample. Chlorides bond with silver and produce silver-chloride, a white substance. In the absence of chlorides, silver bonds with the hydroxides present in the concrete, resulting a brown color [7]. As the chloride penetration is not uniform, it is recommended to perform seven measurements in every 10 mm, and the penetration depth is calculated as the average [9].

2.5.2 Scanning Electron Microscopy [SEM] method

The total chlorides content for the samples exposed to the action of sodium chloride was determined using scanning electron microscopy combined with Energy Dispersive X-ray Spectroscopy (EDX) analysis. An electronic microscope type JEOL-JSM 5600LV, equipped with an EDX spectrometer (Oxford Instruments, INCA 200 Software) was used for the analyses. SEM images were obtained by using the atomic number contrast obtained by recording backscattered electrons signal. Compositional analyses were obtained by recording the EDX spectrum at different depths of the sample, starting from the exposed surface. The analysis was performed on a flat surface for better accuracy of the results. The sampling and analysis methodology are described below. From the concrete samples exposed to chlorides action, 10x10x50 mm prismatic samples were taken from the core of the initial concrete samples (Fig.1)

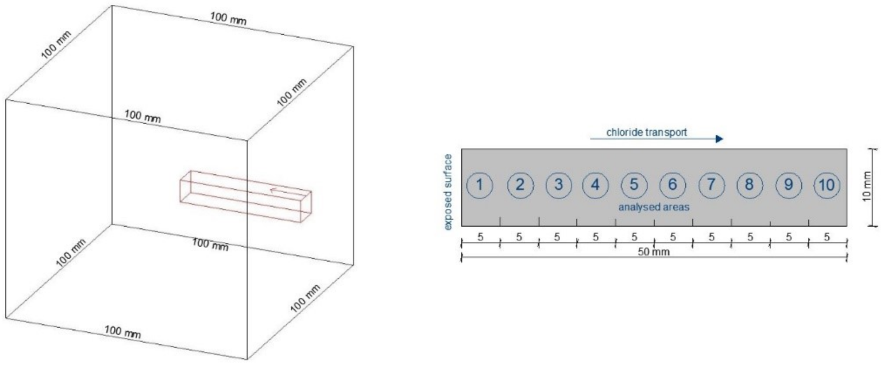

Figure 1. Sampling zone of prismatic samples and the analysed areas

The concrete surface analysis was made punctually, at a distance of 5 mm, following the penetration direction of the chlorides in the sample. Evaluating the concentrations of the chemical elements, especially the presence of chloride, we can estimate the chloride penetration depth as well as the percentage, mass and atomic quantity of Cl present in the concrete sample.

3. Results and Discussion

3.1. Workability of self-compacting concrete

The self-compacting ability of the designed compositions was evaluated, following the slump-flow consistency, the flow time, respectively the ability to pass through the L box bars. Table 2 gives the values of the experimental tests. For SCC with fly ash addition, a 690 mm slump-flow diameter, suitable for the SF2 consistency class, was obtained, and for SCC with limestone addition, a diameter of 750 mm, suitable for the SF3 class. Although the consistency and tendency of segregation is within the limits recommended by the European Guidelines [17], the flow time is high, indicating a higher viscosity than other SCC compositions [2,17,19]. The cause of the high viscosity may be the increased amount of superplasticizer additive used in SCC compositions.

Table 2**:** Final SCC mixes with fly ash addition, respectively limestone addition

SCC mixes	Slump flow (mm)	T500 flow time (s)	V-funnel flow time (s)	Passing ability using L-box (H2/H1)
SCC-CZ*	690	10	23	0.95
SCC-FC**	750	15	25	0,97

* Self-consolidating concrete with fly ash addition

** Self-consolidating concrete with limestone filler addition

3.2. Compressive strength

For both types of SCC, high strength classes were obtained. Self-compacting concrete with limestone filler addition has reached C60/75, and self-compacting concrete with fly ash addition C55/67. Although the compressive strength of SCC with fly ash is lower than SCC with filler, the fly ash SCC mix was obtained with 15% less cement than the filler SCC mix. Also, fly ash improved the compressive strength over time, as the increase from 28 days to 190 days was higher for SCC with fly ash (6.84%). The compressive strength obtained at 28, 72, and 190 days respectively can be observed in Fig. 2.

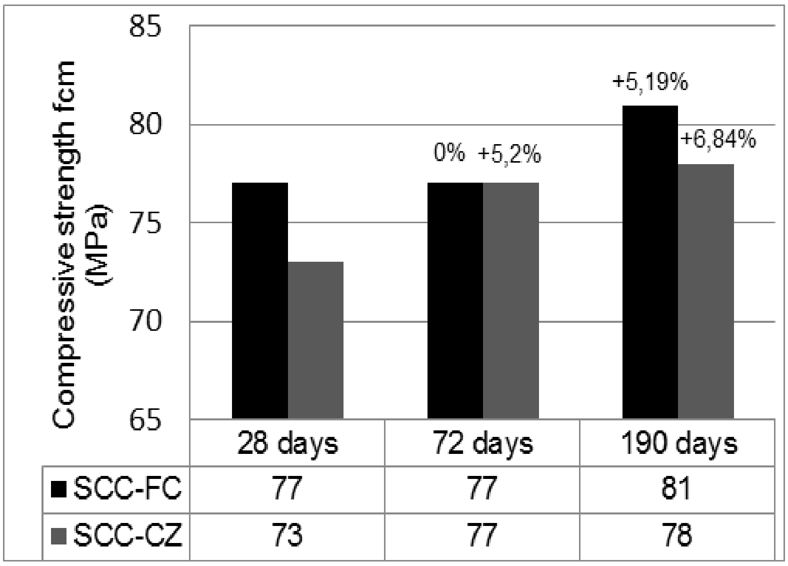

Figure 2. Time evolution of SCC compressive strength

Regarding to the high amount of mineral additions used and the high workability, high strength classes were obtained compared to other fly ash or limestone filler self-compacting concrete mixes [2,5,17,19]. Both concrete mixes can be classified as high strength concrete.

3.3. Chloride penetration resistance

The chloride penetration depth determined by the colorimetric method is 3 mm for SCC with fly ash and 5 mm for SCC with limestone filler. Areas affected by the presence of chlorides, and reference samples can be observed in Fig. 3 for SCC with fly ash, and in Fig. 4 for SCC with limestone filler.

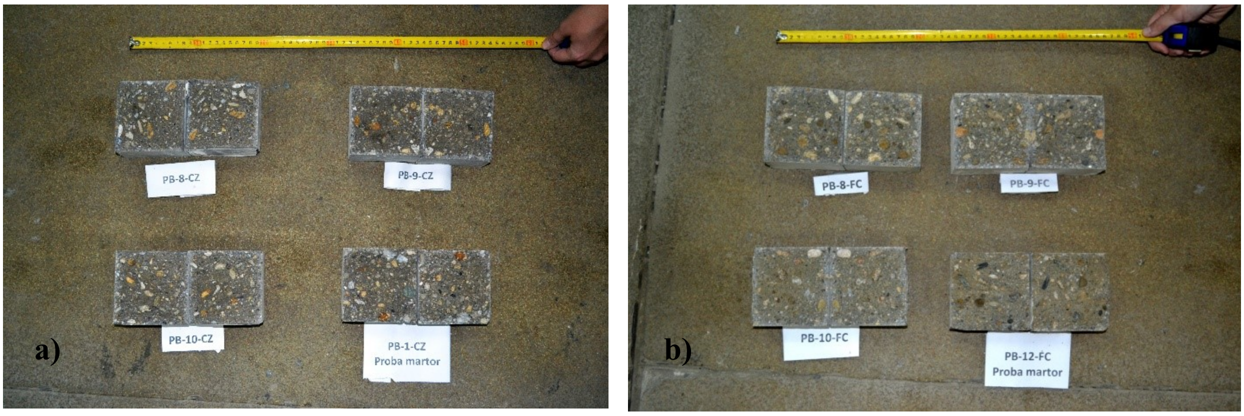

Figure 3. a) Split fly ash SCC samples, spayed with $AgNO_3$
b) Split limestone filler SCC samples, spayed with $AgNO_3$

The penetration depths measured for each concrete sample exposed to sodium chloride and reference samples are shown in Table 3.

Table 3**:** Chloride penetration depth for the self-compacting concrete samples

Sample code	Cube dimension (mm)	Penetration depth (colorimetric) (mm)	Penetration depth (SEM) (mm)
PB-8-CZ*	100x100x100	3	5...10
PB-9-CZ*	100x100x100	4	5...10
PB-10-CZ*	100x100x100	3	5...10
PB-1-CZ* (Ref)	100x100x100	0	0
PB-8-FC**	100x100x100	5	15...20
PB-9-FC**	100x100x100	4	15...20
PB-10-FC**	100x100x100	6	10...15
PB-12-FC** (Ref)	100x100x100	0	0

* Self-consolidating concrete with fly ash addition
** Self-consolidating concrete with limestone filler addition

Table 4**:** Chloride concentration for various depths using SEM analysis

Sample code	Cl concentration 0-5 mm (weight %)	Cl concentration 5-10 mm (weight %)	Cl concentration 10-15 mm (weight %)	Cl concentration 15-20 mm (weight %)
PB-8-CZ*	0,42	0,20	0,00	0,00
PB-9-CZ*	0,56	0,20	0,00	0,00
PB-10-CZ*	0,07	0,28	0,00	0,00
PB-1-CZ* (Ref)	0,00	0,00	0,00	0,00
PB-8-FC**	0,32	0,06	0,11	0,08
PB-9-FC**	0,14	0,26	0,16	0,11
PB-10-FC**	0,11	0,13	0,09	0,00
PB-12-FC** (Ref)	0,00	0,00	0,00	0,00

* Self-consolidating concrete with fly ash addition
** Self-consolidating concrete with limestone filler addition

By analyzing the chloride content with electronic microscopy technique, the total amount of Cl for the chloride exposed SCC samples was obtained. As the analysis of the samples was performed gradually, in depth, evaluating the presence or absence of chlorides and the depth of chloride penetration can be determined with higher accuracy. In the SCC samples with ash addition, the chlorides penetrated to a maximum depth of 10 mm, while in the case of SCC with limestone filler, the depth reaches up to 20 mm. The weight percentage of Cl found in each concrete specimen is given in Table 4.

By comparing the test methods for determining the chloride penetration depth in self-compacting concrete, a high precision can be achieved using electron microscopy. While the traditional method of measuring the chloride-affected area with silver nitrate shows a penetration of up to 5 mm for the limestone SCC, SEM analyses indicate the presence of chloride up to 20 mm deep. This difference is due to the fact that the colorimetric method only indicates the presence of free chloride ions, while the microscopic analysis indicates the total concentration of chloride (including chloride in chemical compounds) on the examined surface [19]. However, only the concentration of free chloride ions in the pore water of the hydrated cement paste controls the possible corrosion of embedded steel. [1]. Also, the result of the colorimetric method can be influenced by the type of cement and the mineral addition used, namely their ability to bind with chlorides. Chlorides bond with C3A and C4AF, Portland cement hydration products, so that a low aluminate content reduces the ability of cement to immobilize chloride ions [9].

Using the colorimetric method, the concentration of chloride concentration is very important to cause the chemical reaction of whitening the concrete in the presence of silver nitrate. The minimum percentage of chloride ions by the cement weight, to produce the white color is not indicated, with researchers obtaining different results: Otsuki (1993). 0,15%, Collepardi (1997) 0,01%, Andrade (1999) 1,14% -1,4%, etc. [9,20]. The microscopic analysis has detected chlorides at a greater depth than the colorimetric method because at greater depths, the free chloride ion concentration does not exceed the minimum concentration required to start the whitening reaction of the concrete sample. Also, chloride can diffuse over longer distances, where it forms chemical compounds.

With regard to the critical content of chloride, bound and unbound, recommended by *fib* Bulletin [1], the maximum value may vary between 0% and 1% of the cement weight. No concrete sample in this study reached the critical content of chloride recommended.

Another issue that may occur when using the colorimetric method is the simultaneous occurrence of carbonation. If the carbonation depth is greater than the chloride penetration depth, the results are unclear, according to Kim. (2013) [21]. For structures exposed at the same time to marine environment and CO2, it is necessary to associate the colorimetric method with other existing methods. In these exceptional cases, but also for greater precision in the amount of chlorides present in the concrete samples, it is preferable to use the scanning electron microscopy method. At the same time, the colorimetric method remains an efficient, fast, and practical method, involving minimal costs [9]. By obtaining the chloride penetration depth and the chloride concentration we can anticipate the corrosion of the steel by applying the probabilistic methods studied and proposed in the literature.

Unrelated to the testing method used, SCC with fly ash addition has shown a higher resistance to chloride action than SCC with limestone filler addition. Similar results were obtained with other experimental programs, which showed the positive influence of fly ash on the resistance to chloride ion penetration. By comparing the performance of a self-compacting concrete with filler addition to another with fly ash, there was a considerable decrease of the chloride penetration depth and the diffusion coefficient in the case of self-compacting concrete with fly ash [2]. Also, the self-compacting concrete, through low permeability and high strength class, has positively influenced the resistance to chloride action. Other experimental studies prove the results of the present study, that self-compacting concrete, has a better behavior to chloride than conventional concrete [2,4,5].

4. Conclusions

Through this experimental program, a high-performance, self-compacting, high-strength concrete has been achieved with a high volume of fly ash, reducing production costs, having a positive ecological impact on the environment. By performing a comparative study between self-compacting concrete with fly ash addition and self-compacting concrete with limestone filler addition, it can be concluded that the addition of fly ash had an important contribution to the cohesion and stability of the fresh concrete. Although limestone SCC showed a higher compressive strength at 28 days, fly ash favored the compressive strength evolution over time, up to 190 days.

Using two different methods of testing the chloride penetration depth, we can formulate some conclusions on the chloride resistance of self-compacting concrete with fly ash or limestone filler addition. Using the colorimetric method, we only obtained the chloride penetration depth, while using the microscopic method we obtained the chloride concentration in each concrete sample, but also more accurate penetration depth.

Although the SEM analysis method provides more information on the chloride penetration into concrete, the colorimetric method proves to be efficient, fast and inexpensive. Excluding exceptional situations, silver nitrate is a good indicator of the chloride penetration depth, especially for in situ concrete testing. When assessing or monitoring the state of a reinforced concrete construction, the action of chloride is often combined with other chemical or physical attacks. Concurrent occurrence of chloride penetration and carbonation is very common, so it is recommended to first measure the carbonation depth, then the depth of chloride penetration. When the carbonation depth exceeds the chloride penetration depth, the colorimetric method becomes insufficient. In this case, the electronic microscopy method can be used as an additional method. Using these test methods, we will achieve the chloride penetration depth and chloride concentration, important durability parameters in anticipating corrosion of the reinforcement. Both methods indicate a lower penetration depth for the fly ash SCC.

As a conclusion of this experimental study, fly ash has a positive influence on the resistance to chloride action and implicitly on the durability of self-compacting concrete. Regarding the efficiency of the test method, the advantages of using electronic microscopy are remarkable, but not to undermine the efficiency and practicability of the colorimetric method.

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