THE INFLUENCE OF CARBONATION ON DEICER SCALING RESISTANCE OF BLAST FURNACE SLAG CONCRETE (BFSC)

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Abstract

Blends of BFS/OPC concretes with slag binder ratios (s/b = 0, 0.5, 0.7) were initially wet cured and stored for 7 days at 20 °C and RH > 95%, followed by 21 days dry storage at 20 °C and 65 % relative humidity. Afterwards, several samples were exposed to accelerated carbonation under 10 % CO_2 and 60 % R.H. while others were kept in laboratory controlled condition and natural CO_2 exposure. Carbonated concretes were exposed to freeze and thaw cycles under deicing salt according to CEN/TS 12390-9 standard. Samples were analysed utilizing optical and scanning electron microscopy to determine the structure left after carbonation and associate its influence in concrete's de-icing resistance. The carbonation front was determined by spraying phenolphthalein on a freshly split surface. Open porosity of samples were determined after drying at 40 °C and 105 °C according to NBN B05-201.

Optical microscopy shows an irregular arrangement of tiny bright calcium carbonate minerals spread in the concrete paste for the BFS concrete. This pattern was also observed by SEM, a technique which shows more details of what is believed to be a porous leached paste zone co-existing next to a calcium salt enriched deposition sector. OPC concrete remains insensitive to carbonation maintaining the same scaling resistance with time, while carbonation in the blended concretes increases and scaling resistance decreases with higher BFS content.

1   INTRODUCTION

There are many advantages in the usage of blended cement concrete where high amounts of blast furnace slag (BFS) replace ordinary Portland cement (OPC). Among these benefits are improvements on concrete's workability, reduced heat production, and if cured properly they develop good chemical and mechanical resistance. The inconvenience found in using high amounts BFS is that this last property is a condition difficult to assure specially if construction practice requires that structures are put to work in very short time and are deprived of the required curing time for concrete. Gruyaert et al. determined by image analysis of BSE-images [1] that (BFC) blast furnace cement pastes with slag/binder ratio of 0, 0.5 and 0.85 cured for 28 months reached a degree of hydration of 74%, 94% and 91% respectively for the Portland cement fraction while hydration of the slag fraction was 72% for the lower replacement and 39 % for the higher. Utton [2] who studied a cement paste with relatively more slag, BFS:OPC (9:1), found only 45 % for the overall degree of hydration after two years at 20 °C.

It is recognized that BFS concretes perform worse compared to OPC concretes when exposed to freeze and thaw cycles combined with de-icing salts, a deleterious process supposedly principally of physical nature due to the freezing of water in the capillary pore system of concrete. From these findings one should assume an important contribution of the hydration behaviour of the BFS on concrete's de-icing salt scaling resistance, regarded that paste microstructure is shaped by this process. However, in addition a cautious analysis has to be done of the influence of carbonation on the initial pore structure since it might be altered by CO_2 attack. Several tests have been performed in this research in order to elucidate in what manner carbonation modifies the microstructure of concretes and how this affects the de-icer scaling resistance of BFS concrete.

2   EXPERIMENTAL PROCEDURE

Three concrete mixtures were proposed for this research, as presented in table 1.
The aggregates were siliceous gravel and a natural sand. Portland cement was used, type CEM I 52.5 N according to European Standards, with no special durability property. A (ground granulated) blast furnace slag addition was also used to replace 50 and 70 % by weight of the Portland cement. In order to improve the fresh concrete properties (slump between 160-210 mm) a super plasticizer (polycarboxilate based) was used in amounts between 0.2 – 0.4 % by weight of total binder.

Table 1: Mix design, kg/m3 , w/b = 0.45, Slump S4 (160-210 mm)

Material type	S_o	S_{50}	S_{70}
Cem I 52.5 N	350	174	102
BFS	0	174	238
Water	158	157	154
Sand 0/4	781	777	759
Gravel 2/8	619	616	601
Gravel 8/16	480	477	466

The chemical composition of OPC and BFS are presented in Table 2

Table 2 : Cement and slag chemical composition (LOI = loss on ignition)

	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$	MgO	K$_2$O	CO$_2$	Na$_2$O	Cl$^-$	Sulphide	Ins. Resid.	LOI
OPC (%)	63.37	18.90	5.74	4.31	3.34	0.89	0.73	0.50	0.47	-	-	0.41	1.51
BFS (%)	41.24	36.37	9.83	0.26	1.62	7.41	0.41	0.90	0.28	0.02	0.79	0.43	1.30

After mixing, concrete was cast in cylindrical molds (Ø 100 mm, h 50 mm). All cylinders were compacted on a vibrating table. Subsequently, they were stored for 7 days at 20 °C and RH > 95%. Afterwards, the cylinders were removed from the molds and maintained for an additional 21 days at 20 ± 2 °C and 60 ± 5 % RH . This condition of curing simulates more closely the real curing situation at field site.

After the initial curing, the external cylinders surfaces were covered with adhesive aluminum foil, leaving only 2 faces (top and bottom faces) uncovered, this is to permit CO$_2$ ingress without restriction for these two opened faces.

As shown in fig. 1, half of the samples were exposed to a 10 % CO$_2$ concentration in a carbonation chamber, while the other half were exposed to natural carbonation, at CO$_2$ concentration of 0.03 % in a climate controlled room. For both exposure conditions, the samples were maintained at 20 ± 2°C and 60 ± 5 % RH until the time for testing.
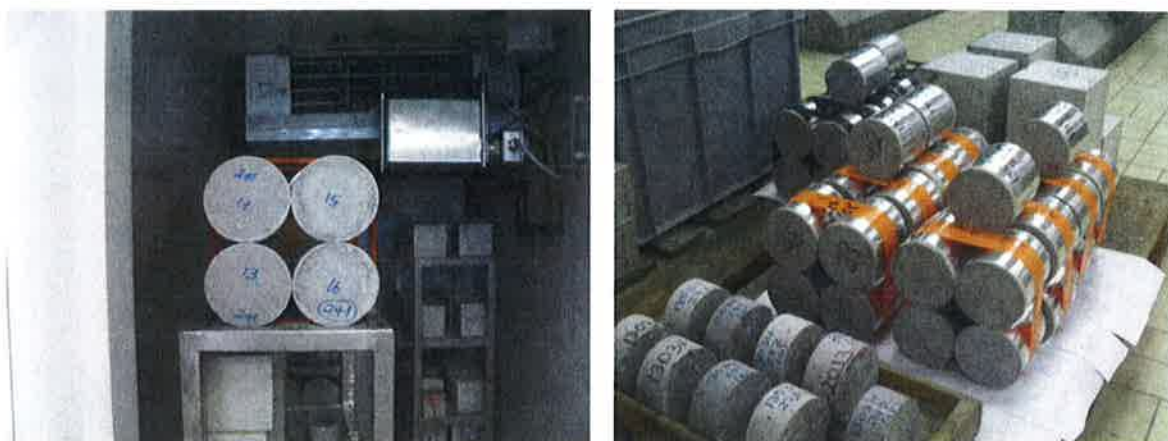

Fig. 1: Accelerated and natural CO$_2$ exposures.

The cylinders were tested at the age of 0, 2, 4, 8, 11, 15, and 19 weeks. For each testing age, cylinders were taken out from the curing place (accelerated and normal carbonation), sawn into 2 half cylinders (Ø 100 mm, h 50 mm) and the aluminum foil was removed. Then 3 half cylinders representing each type of mix, were tested on the trowelled carbonated surface side (top face) for deicing scaling resistance according to the temperature cycle prescribed in CEN/TS 12390-9 Standard "Testing hardened concrete-Part 9:Freeze-thaw resistance-Scaling", Fig. 2.
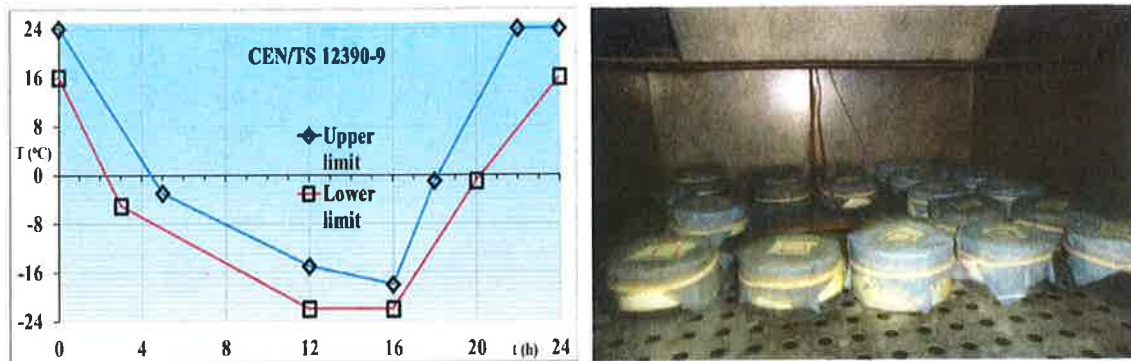
Fig. 2: Temperature T ($^{\circ}$C) vs. time t (h) cycle in the center of the freezing medium.

The other carbonated samples were utilized to measure the concrete's open porosity after drying at 40 $^{\circ}$C and 105 $^{\circ}$C according to NBN B05-201 and also to determine concrete's carbonation depth by using 1% phenolphthalein in 70% ethyl alcohol on a freshly split surface.

Several exposed concrete samples were chosen to prepare thin sections for optical microscopy analysis and Scanning electron microscopy techniques.

3   OBTAINED RESULTS AND INTERPRETATION

3.1   Carbonation depth

The carbonation was measured on the sample's freshly split surface, spraying a solution made of 1% phenolphthalein in 70% ethyl alcohol. The carbonated surface is colourless while the non-carbonated zone turns purple due to the presence of free calcium hydroxide (Portlandite) which yields a pH $\geq$ 8.3. The obtained results (median of ten measurements) for accelerated 10% CO_2 exposure taken from 3 specimens representing 1 sample are shown in Fig. 3.
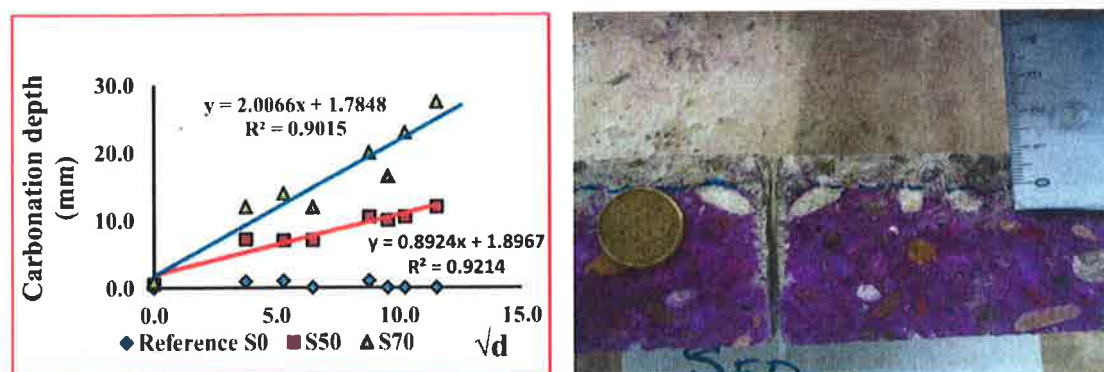

Fig. 3: Carbonation depth of concrete exposed to accelerated 10% CO_2 vs. the square root of time.

In the graph the carbonation depth "y" (mm) is plotted against the square root of the CO_2 exposure time "d" (days), in order to obtain the carbonation coefficient "A" which is the slope of the straight line and y_o is the initial carbonation depth at the beginning of the carbonation exposure employing equation (1),according to Borges et al. [3].

$$y = y_o + A \sqrt{d} \tag{1}$$

The accelerated tests were run using a CO_2 concentration (10 %) which is about 33 times higher than the one found in Urban Cities (0.3 %) and 333 times higher than the one found in rural areas (0.03 %), Tam et al. [4].
To establish a correlation between depths 'y_{ac}' and 'y_n' (accelerated and normal), we shall consider the corresponding CO_2 concentration according to equation (2).

$$y_{ac} / y_n = (CO_{2\,ac} / CO_{2\,n})^{0.5} \tag{2}$$

The results shown that concrete's sensibility to carbonation increases with increasing slag replacement content, while the reference concrete (with slag/binder ratio s/b = 0) during the test period has zero carbonation coefficient which means that its carbonation rate is very slow. Concretes with s/b = 0.7 (S_{70}) have a carbonation coefficient 2.2 higher than concrete with s/b = 0.5 (S_{50}).
To compare the two types of concretes with slag replacement, and have an indication of what is expected regarding the natural carbonation progress (0.03% and 0.3% CO_2) with time, some calculations were made using the found results utilizing equation (2), and synthetized in table 3.

Table 3. Expected carbonation depth (mm) of BFS concretes (s/b = 0.5, 0.7) for CO_2 concentration 0.03% for rural areas, 0.3% for urban Cities.

Mix	Carbonation depth mm (CO_2 = 0.03 %)				Carbonation depth mm (CO_2 = 0.3 %)			
S_{50}	0.1	4.8	6.7	8.2	9.4	0.3	15.1	21.2	25.9	29.9
S_{70}	0.1	10.6	14.9	18.3	21.1	0.3	33.5	47.3	57.8	66.7
t (years)	0	25	50	75	100	0	25	50	75	100

From the previous table it can be inferred that for the same environmental condition, the carbonation depth of concrete with 70% BFS replacement, progresses 2.2 times deeper than that achieved by concrete with 50% BFS.

3.2 Open porosity

Carbonated samples, half cylinders (Ø 100 mm, h 50 mm) were oven dried at 40 °C and 100 °C until constant mass (< 0.1 % @ 24h) before vacuum saturation according to NBN B05-201 paragraph 6.1 (1976), the corresponding porosity was then calculated by hydrostatic weighting (air & water), the obtained results are shown in Fig. 4.
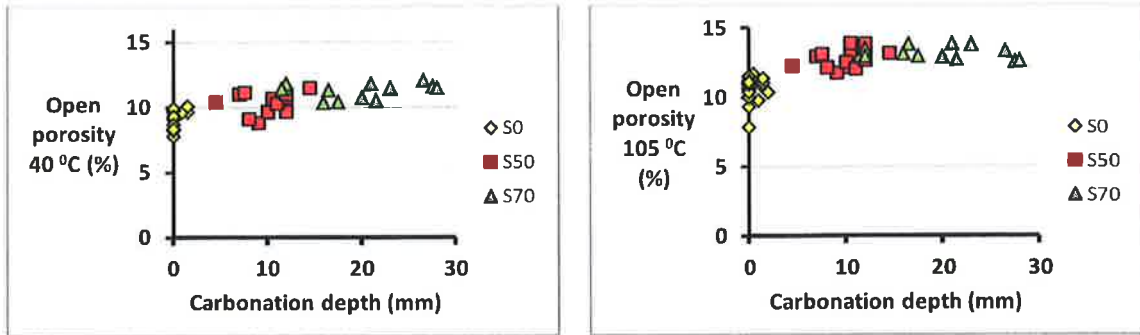
Fig. 4: Open porosity of BFS concretes (s/b = 0, 0.5, 0.7) subjected to 10% CO_2 as function of the carbonation depth , determined after drying at 40 °C (left) or 105 °C (right).

The open porosity at 40 °C gives a rough estimate of what is happening with capillarity after the samples are exposed to accelerated carbonation, thus capillary porosity tends to increase after CO_2 exposures for samples S_{50} and S_{70}, while average porosity for S_o concrete has remained almost unchanged. On the other hand, overall concrete porosity at 105 °C, seems to remain unaltered in all the samples.

3.3 Scanning electron (SEM) and thin section microscopy

With the purpose of exploring the carbonated microstructure of OPC and BFS concretes, several thin sections were studied under petrographic microscope, and under scanning electron microscope.

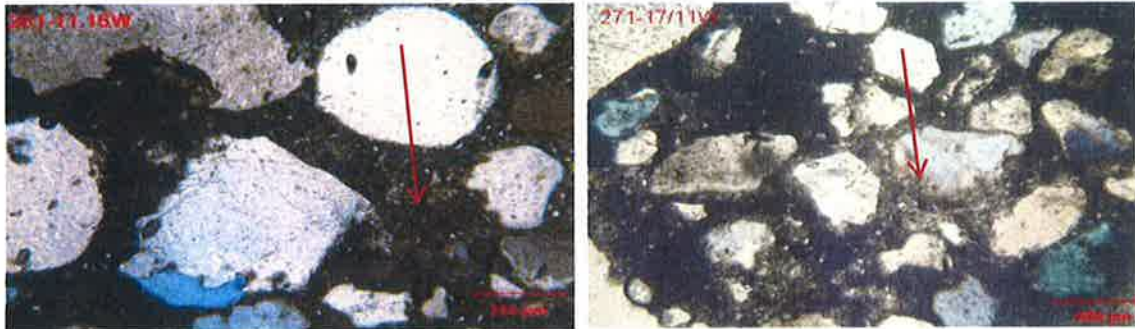Fig. 5 shows a photograph of carbonated BFS concretes (S50 & S70) under parallel light.

Fig. 5: S_{50} & S_{70} concretes after being exposed to 10% CO_2 for 15 & 11 weeks, carbonated paste is brownish colored surrounding quartz aggregates (parallel light).

An incompletely carbonated paste composed of tiny dull and bright crystals was observed between aggregates. It was also noticed that the calcium carbonate minerals on S_{50} concrete seem to develop a more dense structure than that found in S_{70} pastes.

With the intention of having a closer look at the carbonated microstructure, the same thin sections were investigated using SEM. Fig.6 shows the pore structure of carbonated BFS S_{70}.
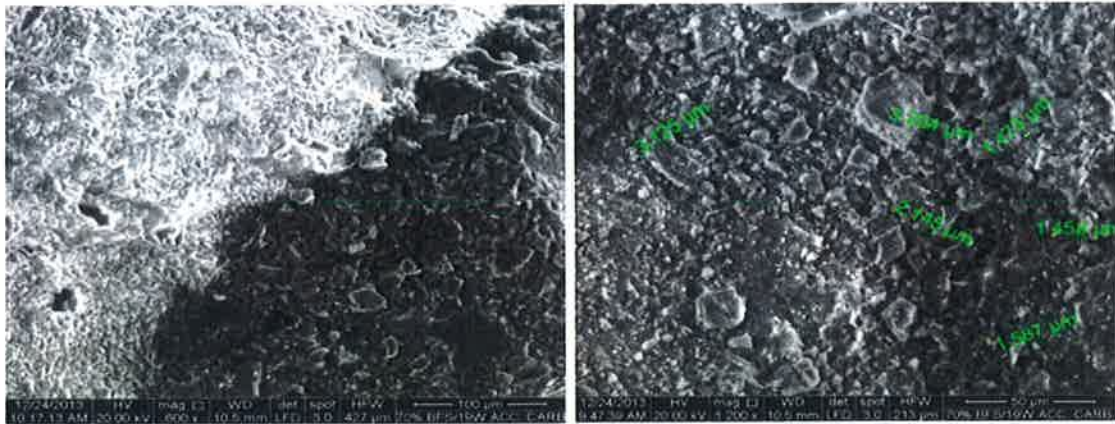
Fig. 6: S_{70} 19 weeks (10% CO_2) carbonated paste showing a leached porous paste coexisting with a deposition zone of sponge-like carbonate salts white deposit (left), pore size shown (right).

Although the porosity of the concrete paste was not quantified, an increase of the void system was noticed as the slag replacement rises in the concrete. This can be expected if it is considered that concretes have been exposed to short wet curing times (7 days), followed by 21 days at relatively dry environment (60 % R.H.), before the carbonation exposure, which has contributed to poor OPC/BFS hydration specially at the surface, leaving a free way to CO_2 ingress that also continues with porosity creation by leaching action.

3.4 Freeze and thaw with deicing salt

Fig. 7. shows the results of freeze and thaw cycles (56) of carbonated half cylinders (Ø 100 mm, h 50 mm).

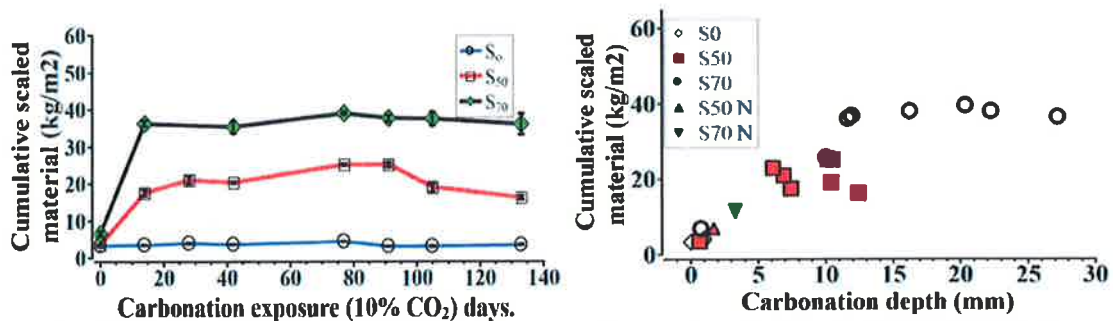Fig. 7: Scaling resistance of BFS concretes (s/b = 0, 0.5, 0.7) with 3% NaCl solution (CEN/TS 12390-9), after 10% CO_2 exposure and environmental CO_2 exposure (S_{70N}, S_{50N}).

From these results it is concluded that carbonation does not have any significant influence on the de-icing resistance of pure OPC concrete. For the concretes made with BFS/OPC blends and cured as in this investigation, carbonation has a deleterious influence. The harmful effect increases with carbonation depth until a maximum is reached. Beyond that point there is not further increase of the deleterious action of carbonation. This behaviour could be

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explained by the decrease in porosity with increasing depth into the surface found by Battaglia et al. [5] in the carbonated zone of BFS concretes, while inversely, porosity of OPC concretes increased continuously with distance from surface.

Summarizing our results it can be said that S_{50} reaches its maximum rate of scaling after 6 mm of carbonation depth while S_{70} needs about 12 mm to reach it.

Compared to that of OPC concrete, the average rate of scaling for S_{70} and S_{50} are 11 and 5 times higher respectively, while S_{70} has a rate that is about twice the one found in S_{50}.

4   CONCLUSIONS

- While the freeze and thaw performance of BFS concretes is considered good, its resistance in the presence of de-icing salts can be qualified as poor, especially when concretes are carbonated.
- Carbonation is a complex process which depends not only on the nature of materials used to prepare the concrete, but also on the amount and proportions utilized, curing conditions and the amount of CO_2 the concrete is exposed to.
- The purpose of this research is to acquire information from BFS concrete de-icer scaling resistance when subjected to unfavourable conditions for hydration and the best situations for carbonation, such as a short period of wet curing, followed by a long and steady period of intermediate relative humidity. In such circumstances BFS consumes part of the produced $Ca(OH)_2$ for its hydration and competes with CO_2 in its depletion. In this scenario and when CH is not available, carbonation of CSH is started [5] giving as a result a leached microstructure, the progress of hydration is reduced. Porosity and permeability are increased enabling the ingress of more CO_2 to the system continuing the damage.
- The augmented BFS concrete's porosity and permeability driven by carbonation in the concrete microstructure, provides the most unfavourable condition for its deicer scaling resistance.

ACKNOWLEDGEMENTS

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