Freeze thaw resistance of non-ferrous slag concrete

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Abstract. The objective of this work is to study the freeze thaw resistance of supplementary cementitious materials (SCM) based concrete made from non-ferrous slag (NFS) benchmarked with CEM I 52.5 N and CEM III 42.5 B concrete. NFS is synthesized during the production of Cu metal from Cu scraps. The freeze thaw resistance of NFS concrete containing 70% CEM I 52.5 R and 30% NFS (w/b = 0.45) as binder, as well as of CEM I 52.5 N and CEM III 42.5 B concrete was tested following CEN TR 15177 (2006). The analysis was based on a calculation of the relative dynamic elastic modulus determined by ultrasonic measurements and a determination of the water absorption by mass in function of the number of freeze thaw cycles. Furthermore the relative tensile strength loss after 56 cycles was considered and a microstructural analysis was performed. All concrete mixes showed a relative tensile strength after 56 freeze thaw cycles lower than 100% of the initial value, whereas the CEM III 42.5 B concrete showed the highest strength loss of around 15% followed by 11% for NFS concrete. NFS concrete also showed highest water uptake of around 4% whereas CEM I 52.5 N and CEM III 42.5 B concrete showed values of 1.2% and 2.2% respectively.

Keywords: Non-ferrous slag, freeze thaw resistance, ultrasonic measurement, sustainability & circular economy

1 Introduction

Based on the expected evolution of the population and demand, the IEA CSI cement technology roadmap predicts that the global cement production is set to grow by 12-25% by 2050 [1,2]. However, by considering the usage of supplementary cementitious material (SCM) based cement in high volume, the huge increase in the cement production units can be reduced. SCM based cements are used widely in concrete application for implementing the principle of sustainability and circular economy. A commonly used SCM material is blast furnace slag (BFS), a by-product from ferrous metallurgy and used for the synthesis of BFS cements. In contrast non-ferrous slag (NFS) is only used in limited volumes due to the presence of higher iron contents and low calcium contents in the slag chemistry. Moreover, the availability is lower compared to ferrous slags such as BFS.

In the work of Hallet et al [3], the impact of slag fineness on the reactivity of blended cements with high volume NFS (replacing Portland cement (PC) with 30, 50 and 70 wt% NFS) was investigated. The authors stated that NFS with increased fineness showed similar reactivity as siliceous fly ash. In addition, Feng et al [4] studied the pozzolanic activity of granulated copper (Cu) slag with the help of calorimetry, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The final findings stated that the blended cements with 30% granulated Cu slag with CaO addition showed increased reactivity after 7 days compared to the 100% PC system. Moreover, in the recent work of Sivakumar et al [5], reactivity of one kind of NFS was evaluated by the novel R^3 method. The assessment showed that the NFS acts as a reactive pozzolanic material with an acceptable performance in heat release, bound water content and calcium hydroxide (CH) consumption.

Studies with respect to the freeze thaw resistance of BFS concrete are abundantly available while no studies corresponding to the freeze thaw resistance of NFS as SCM binder could be found. The laboratory studies reported in [6–9] proved that the replacement of cement by BFS showed poor freeze thaw resistance (with/without deicing salts). However, certain optimizations can be carried out in the concrete composition to improve the freeze thaw resistance. Deja et al [9] studied the freezing and deicing salt resistance of concrete containing 57% BFS in presence of air entraining agents and microfibers. The final finding stated that the concrete with an air content above 5% improved the freeze thaw scaling resistance. Moreover, the age of the BFS concrete is crucial. Chidiac et al [10,11] investigated the scaling resistance of the BFS concrete as a function of age. One of the interesting findings stated that the BFS concrete cured for a period of 2 years showed improved scaling resistance compared to the sample cured for 28 days. In addition to the age and air content, carbonation shrinkage and interfacial transition zone also play a vital role in the scaling resistance of BFS concrete [12].

The principal aim of this research was to investigate the freeze thaw resistance following CEN TR 15177 (2006) of the novel binder with NFS as SCM and compare the performance with that of traditional binders as PC and blast furnace slag cement.

2 Materials and methodology

2.1 Materials

Patented NFS (designated as Modified Ferro Silicate slag) from Metallo Belgium was used as the SCM to prepare concrete together with CEM I 52.5 R. Traditional cement used in the study was a Portland cement type CEM I 52.5 N and a blast-furnace slag cement type CEM III 42.5 B. Natural sand 0/1 mm and 0/8 mm together with gravel

4/16 mm and 4/32 mm were used as the aggregates. Polycarboxylic ether based superplasticizer was used to improve the workability of the concrete.

2.2 Characterization of raw materials

Wavelength-dispersive X-ray fluorescence spectrometry was used to analyse the chemical composition of the starting materials. X-ray diffraction with 10% internal standard (crystalline ZnO) was used to investigate the mineralogy of the NFS slag and PC. Rietveld analysis was used to quantify the diffractogram.

2.3 Concrete composition, slump and air content

Reference concrete was designed with a strength class of C35/45 fulfilling the requirements for an environmental class EE4 (humid interior environment or outer environment with frost and de-icing salts) according to the standard NBN EN 206 + NBN B 15-001. Concrete containing 30% NFS and 70% CEM I 52.5 R was bench marked against CEM III 42.5 B and CEM I 52.5 N. Table 1 shows the three concrete compositions. After casting, the samples were stored at a temperature and relative humidity of 20°C and 95% respectively. Demolding was carried out after 24 h. Slump and air content were determined 15 min after mixing with respect to the norm NBN EN 12350-2 (2009) and NBN EN 12350-7 (2009) respectively.

Table 1. Concrete mix design (kg/m^3)

Component	CEM I 52.5 R + NFS	CEM III 42.5 B	CEM I 52.5 N
Sand 0/1	88	84	84
Sand 0/8	719	681	683
Gravel 4/16	170	161	161
Gravel 4/32	930	880	883
CEM I 52.5 R	273	0	0
CEM I 52.5 N	0	0	390
CEM III 42.5 B	0	390	0
NFS	117	0	0
Superplasticizer	1.287	1.287	1.560
Water	175	175	175

2.4 Freeze thaw experiment

Ten prisms with dimensions 400 x 400 x 100 mm^3 were made per mixture to investigate the freeze thaw internal damage resistance. The freeze thaw test was carried out on the basis of the standard CEN / TR 15177 (2006). The standard prescribes the test pieces to be stored in plastic foil for 6 days after demolding. The plastic wrap was removed when the test specimens were 7 days old. Subsequently, the test specimens were stored under water for 21 days. After this, the freeze thaw test was carried out in a freeze-thaw cabinet for 56 cycles. According to the standard NBN B15-100 (2016), 5 test specimens per concrete type must be subjected to a splitting test before exposure to the freeze-thaw cycles. After 56 cycles, another 5 exposed test specimens must be subjected to a splitting test. The splitting test was performed according to the standard NBN EN 12390-6 (2010). Relative strength loss (Δf) was calculated by (tensile strength before frost-thaw – tensile strength after frost-thaw) / tensile strength before frost-thaw. CEN / TR 15177 (2006) states that the degradation of test pieces must be monitored by determining the relative dynamic elastic modulus (RDM). The measurements were taken using the Proceq Pundit Lab Ultrasonic Instrument. The degradation as a function of the number of freeze-thaw cycles (0, 8, 14, 28, 42, 56) was determined on the basis of the ultrasonic pulse velocity . Eq. (2) defines the calculation of RDM, where V_n and V_0 are the longitudinal velocity (m/s) after n and 0 freeze-thaw cycles respectively.

$$RDM\ (\%) = V^2{}_n/V^2{}_0\ .\ 100 \tag{1}$$

The water absorption is expressed in % with respect to the mass after 35 days and as a function of the number of freeze thaw cycles. The final value of water uptake is then calculated as the average after 56 freeze thaw cycles per sample. The water absorption was calculated as per the equation 2, where m_{56F} and m_{35d} are the mass of the specimen after 56 freeze thaw cycles and mass of the specimen after 35 days in grams.

$$Water\ absorption(\%) = (m_{56f}\text{-}m_{35d})/m_{35d}\ .\ 100 \tag{2}$$

2.5 Fluorescence microscopic analysis

Fluorescence microscopic analysis was carried out only on the freeze thaw exposed NFS slag concrete. 50 mm diameter cores were vacuum impregnated with fluorescent epoxy. After hardening, the samples were sawn in longitudinal direction. The sawn samples were then glued onto 30 mm x 50 mm glass plates, cut to a thickness of 10 mm and plane ground. Later, the samples were cleaned and placed under vacuum for 2 h after which they were impregnated with fluorescent epoxy. Afterwards, the impregnated concrete samples were ground to remove excess epoxy. Subsequently, the ground surface was glued onto an object glass and further ground to a thickness of 20 µm. Afterwards, a cover glass was glued onto the sample with UV hardening glue.

3 Results and discussion

3.1 Characterization of raw materials

Table 2 shows the chemical composition of the raw materials. The main constituents of NFS used in this work are Fe_2O_3 and SiO_2. XRD analysis showed the presence of around 92 wt% amorphous phase (= glass) and 8 wt% crystalline phase, mainly spinel. NFS was milled in the similar range of particle size with respect to the PC.

Table 2. Chemical composition of the starting materials in wt%

Component	CEM I 52.5 N	CEM I 52.5 R	CEM III 42.5 B	NFS
SiO_2	18.3	18.0	25.8	32.3
Fe_2O_3	4.0	4.1	2.6	40.9
Al_2O_3	5.2	5.2	8.2	11.0
CaO	64.3	64.1	52	3.9
Others	8.2	8.6	11.4	11.9

3.2 Slump , air content and compressive strength

Table 4 shows the consistency of the three different mixes. All three mixes showed a desirable slump class S4. CEM I 52.5 N showed an air content of 1.5% whereas the CEM III 42.5 B and CEM I 52.5 R + NFS showed an air content of 1.3% and 1.2% respectively. Table 4 also shows the 28 days compressive strength of the synthesized concretes.

Table 4. Slump and air content of the concrete

Binder	Slump (mm)	Air content (%)	Air to paste (%)	Compressive strength (28 d)
CEM I 52.5 N	180	1.5	5.1	58.6
CEM III 42.5 B	190	1.3	4.4	51.5
CEM I 52.5 R+ NFS	200	1.2	4.1	52.1

3.3 Freeze thaw resistance

Relative Tensile strength loss

Figure 1a) shows the splitting tensile strength of the CEM I 52.5 N, CEM III 42.5 B and CEM I 52.5 R + NFS concrete before/after freeze thaw exposure. All samples showed a decreased splitting tensile strength compared to the initial value. The decrease in strength is explained by internal damage due to freeze thaw cycles, as further discussed in section 3.4. Figure 1b) shows the relative strength loss of the concrete caused by the freeze thaw mechanism and is calculated based on the mean of 5 values per mix before/after freeze-thaw attack. A relative strength loss of 15% for CEM III 42.5 B was obtained whereas the CEM I 52.5 N and CEM I 52.5 R + NFS showed a relative strength loss of around 11%.

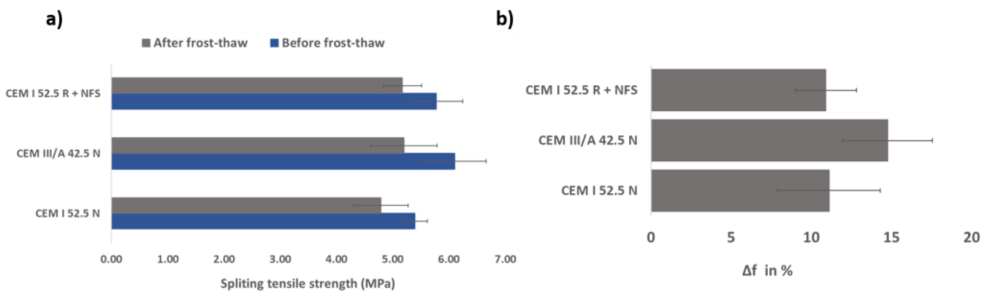

Fig. 1. Splitting tensile strength a) splitting tensile strength before/after freeze thaw b) relative strength loss

Water absorption

Figure 2 shows the water uptake calculated according to formula 2. NFS slag concrete showed an increase in mass of around 4% after 56 freeze thaw cycles whereas CEM I 52.5 N and CEM III 42.5 B concrete showed values of 1.2% and 2.2% respectively.

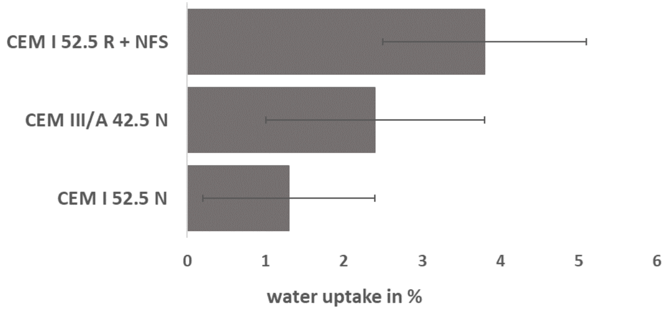

Fig. 2. Mass change (water uptake) after 56 cycles

Relative dynamic elastic modulus

Figure 3 shows the mean RDM values determined on the basis of the ultrasonic measurements after 0, 8, 14, 28, 42 and 56 freeze thaw cycles. CEM I 52.5 N concrete samples showed around 4% reduction in their mean RDM after exposure to 8 freeze thaw cycles whereas CEM III 42.5 B and CEM I 52.5 R + NFS concrete samples showed around 7% and 6% reduction in mean RDM to its initial value. CEM III 42.5 B and CEM I 52.5 R + NFS showed a decrease in the RDM from 93% to 90% and 94% to 92% between 8 and 14 cycles whereas CEM I 52.5 N showed only a slight decrease from 96% to 95%. After 14 cycles, CEM I 52.5 N showed a constant decrease losing only an additional 1% after 28 and 42 cycles. CEM III 42.5 B showed a decrease of 13% and 15% whereas CEM I 52.5 R + NFS showed a decrease of 10% and 12.5% after 28 and 42 cycles with respect to its initial value. After 56 cycles, CEM III 42.5 B showed the highest loss of 18% followed by 15% for CEM I 52.5 R +

NFS. CEM I 52.5 N showed only 8.5% loss of RDM outperforming both CEM III 42.5 B and CEM I 52.5 R + NFS.

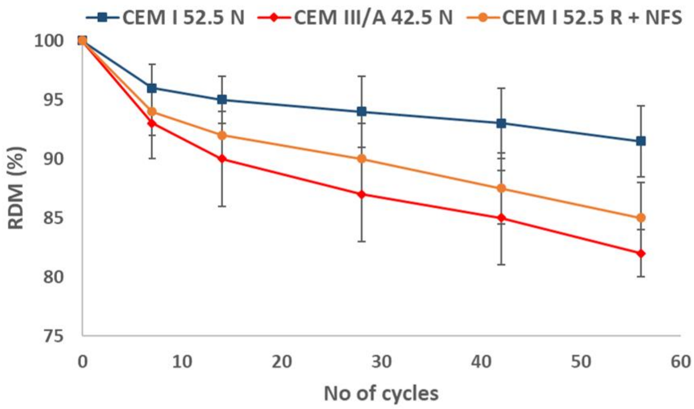

Fig. 3. Relative dynamic elastic modulus calculated by ultrasonic measurement

3.4 Relative dynamic elastic modulus vs relative tensile strength loss

While comparing the results between the RDM (Figure 3) and relative tensile strength (Figure 1b) of the different mixes before and after frost thaw attack, contradictory behaviour can be found. Relative tensile strength loss measured by the tensile strength difference for CEM III 42.5 B concrete showed a decrease of 15% whereas the RDM results showed a higher decrease of 18%. Moreover, similar co-relation can also be seen in the CEM I 52.5 R + NFS where RDM results showed higher decrease value (15%) compared to the relative tensile strength loss of 11%. However, CEM I 52.5 N concrete showed lower decrease of RDM value (8.5%) compared to relative strength loss of 11.1%.

3.5 Fluorescence microscopic analysis – General observations

Figure 4 shows the binder matrix (yellow region) and aggregate (black region) of the CEM I 52.5 R + NFS concrete exposed to the freeze thaw cycles. Figure 4a) shows the porous structure of the ITZ whereas the Figure 4b) shows the presence of cracks which are mainly propagating via the ITZ. The ITZ tends to become wider, weaker and it can be considered as the weakest link in the concrete [13]. The possible cause (wide & weak ITZ) could lead to an increase in liquid transport rate creating larger pores while freeze thaw cycles are causing loss in tensile strength. This behaviour could be observed in the Figure 4a and 4b as well as in Figure 1 (relative tensile strength loss). Figure 5 mainly shows the binder matrix of CEM I 52.5 R + NFS concrete after freeze thaw cycles. In Figure 5a), cracks can be seen clearly in the binder matrix. Figure 5b,c show the presence of voids/pores in the binder matrix. As one of the interesting findings, Figure 5c) shows the cracks generating from the pores. This could be possibly explained due to the thermal expansion coefficient difference between ice and concrete. Since, these voids are filled with water and resulting in the formation of ice crystals during freeze cycles, the expansion and shrinkage of ice exerts tensile stress resulting in cracks.

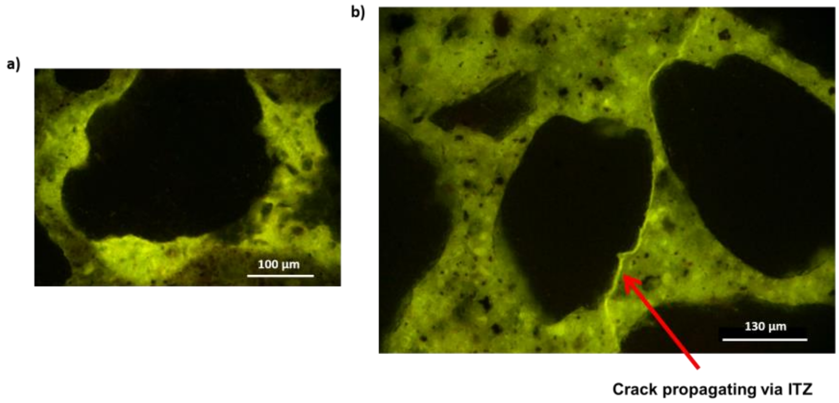

Fig. 4. Fluorescence microscopic analysis a) porous ITZ b) crack in ITZ

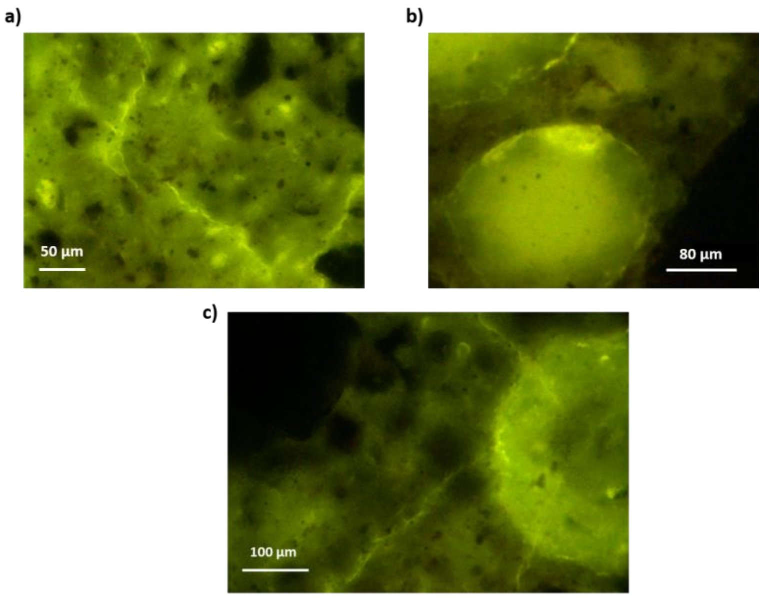

Fig. 5. Fluorescence microscopic analysis a) binder matrix b) voids in binder matrix c) cracks originating from voids

4 Conclusion

In this study, concrete containing 30% NFS and 70% CEM I 52.5 R was prepared and bench marked against CEM III 42.5 B and CEM I 52.5 N to investigate the freeze thaw resistance according to CEN TR 15177 (2006).

Following can be stated as the important findings:

1) All three tests showed that CEM I 52.5 N performed best
2) Performance of CEM III 42.5 is in all tests worse in comparison to the CEM I 52.5 N. Although based on the splitting tensile strength tests the performance of CEM I 52.5R + NFS is comparable to that of CEM I 52.5N; the other tests show a an increased water uptake and increased loss in RDM
3) Fluorescence microstructural analysis showed cracks along the ITZ suggesting that the ITZ could be the weakest link in concrete.

As further investigation, NFS concrete with air entraining agent should be produced to examine the influence of entrained air voids against freeze thaw resistance. Moreover, curing regime and period are important factors influencing freeze-thaw resistance, Freeze thaw resistance of NFS concrete with different curing period should also be investigated as a further study.

Acknowledgments

The work has been financed by the SIM MARES program, grant number HBC.2017.0607. The author would like to thank the industrial partner Van Pelt for producing concrete. The authors would also like to thank Hanne Vanoutrive (KU Leuven) for assisting with the freeze thaw measurements.

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