Iqbal, Ahsan; Ojala, Teemu; Al-Neshawy, Fahim; Punkki, Jouni

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Effect of Slag Content and Carbonation/Ageing on Freeze-Thaw Resistance of Concrete

Ahsan Iqbal
M.Sc.
Department of Civil Engineering, Aalto University
Rakentajanaukio 4 A, 02150 Espoo, Finland
email: ahsan.iqbal@aalto.fi

Teemu Ojala
M.Sc.
Department of Civil Engineering, Aalto University
Rakentajanaukio 4 A, 02150 Espoo, Finland
email: teemu.ojala@aalto.fi

Fahim Al-Neshawy
Ph.D., Staff Scientist
Department of Civil Engineering, Aalto University
Rakentajanaukio 4 A, 02150 Espoo, Finland
email: fahim.al-neshawy@aalto.fi

Jouni Punkki
Ph.D., Professor of practice
Department of Civil Engineering, Aalto University
Rakentajanaukio 4 A, 02150 Espoo, Finland
email: jouni.punkki@aalto.fi

ABSTRACT

The construction industry is pursuing the reduction of CO_2 emissions and the development of low-carbon concrete. LOIKKA research project was initiated in Finland with the aim to reduce the CO_2 emissions of concrete manufacturing by 50%. The use of blast furnace slag was seen as the most competitive way to significantly reduce CO_2 emissions of concrete. However, incorporating slag in concrete can lead to durability complications, particularly concerning salt freeze-thaw resistance. This study investigates the effects of slag content, carbonation/ageing, and pre-curing conditions on the freeze-thaw and salt freeze-thaw resistance of concrete. Additionally, it evaluates the compressive strength development and porosity differences of test concretes. Slab tests were conducted to determine the surface scaling and internal damage resistance of concrete specimens. The results showed that high slag content and carbonation reduced salt freeze-thaw resistance. The incorporation of 50% slag content as the cement clinker replacement is considered critical. An increase in slag content led to a decrease in the compressive strength at 7 days due to the low reactivity of slag but achieved the highest compressive strength at 91 days with 70% slag content. These insights contribute to our understanding of the durability properties of concrete incorporating slag.

Key words: Concrete, blast furnace slag (GGBFS), surface scaling, internal damage, carbonation, pre-curing, CO_2 emissions.

1. INTRODUCTION

1.1 Background

Concrete is one of the most abundantly used construction materials around the globe. It is used for the construction of buildings and infrastructure and its annual production accounts for more than 4Gt, which is expected to grow in the future [1]. Cement being the primary and most important constituent in the concrete mix, it produces about 5–8% of global CO_2 emissions [1,2]. A single ton of cement is observed to release on average 0.7–0.8 tons of CO_2 around the globe [3,4]. The three major contributing sources to CO_2 emissions of cement are, production of cement clinker, energy consumption for production purposes, and raw materials processing, i.e. limestone [5].

LOIKKA is a joint project between Aalto University and the Finnish construction industry aiming to reduce the concrete CO_2 emissions. The goal of the project is to reduce the CO_2 emissions from concrete production by 50%. The aim is to achieve this target by 2028. The most effective way to minimise CO_2 emissions of concrete is to reduce the amount of cement clinker in cement, as the production process (calcination) of the clinker is accountable for almost 60% of the total CO_2 emissions compared to emissions originating from the combustion of fossil fuels for energy generation throughout the process [5].

Concrete structures are designed for long service lives, ranging from 50 to 100, or even 200 years. The long service life is crucial for sustainability, minimising the need for frequent replacements and reducing overall environmental impact. It is important to optimise mix designs, including the use of low-carbon concrete, that can balance the need for reduced CO_2 emissions with maintaining or even enhancing the durability of concrete structures. When comparing different concrete mix compositions, it should incorporate differences in strength, durability, and service life [6]. Thus, it is important to point out that service life should not be sacrificed because of the CO_2 emissions.

LOIKKA project primarily focuses on the utilisation of ground granulated blast furnace slag (GGBFS). Slag is an effective admixture that can be used in the concrete in large quantities, which can significantly reduce the emissions of concrete production. Also, slag fulfils the requirements of the European cement and concrete standards [7]. Slag has been used in European concrete for around 100 years and its effects on the durability of concrete are quite well known. However, the addition of slag in the freezing environments, has raised some concerns [8]. Nearly one third of the concrete volume that is cast in the Nordic countries must exhibit adequate freeze-thaw resistance [9]. Slag has clear effects on the freeze-thaw resistance of concrete. In general, 50% slag content is considered a critical limit value in terms of salt freeze-thaw resistance [8]. This is also the case in the Finnish Transport Agency's instructions for the manufacture of infrastructural concrete[10].

In the case of freeze-thaw and salt freeze-thaw attack, two concrete damage mechanisms are mainly distinguished: internal damage and surface scaling, respectively [9,11,28]. Internal damage in concrete occurs as microcracks form throughout the concrete body due to water expansion upon freezing, leading to loss of mechanical properties and, ultimately, to complete destruction of concrete [9,11,28,31]. Surface scaling arises from the interaction between the ice layer and the concrete surface in the presence of salt. This phenomenon leads to superficial, progressive damage to the concrete, characterised by the removal of small flakes from the material's surface [12,28]. In the experiments, internal damage is primarily associated with freeze-thaw attack, whereas in salt freeze-thaw attack, scaling is considered the dominant damage phenomenon. This is attributed to the fact that moderate salt concentrations significantly increase scaling intensity, and also air-entrained concretes are utilised for high salt scaling resistance. Air-entrained concrete mixes are effective in reducing the damage due to scaling and even more effective against internal damage. Therefore, internal damage is rarely observed in air-entrained concretes [28]. In general, air-entrained concrete showed little to no internal damage, regardless of slag content. However, other factors proved critical in measuring internal damage, including w/b ratio, exposure to salt environments, and testing age [16,26,28].

Another important parameter to consider is the effect of carbonation or pre-conditioning/ageing on the freeze-thaw and salt freeze-thaw resistance of concrete incorporating slag. The ageing effect of freeze-thaw resistance of concrete containing high slag content is explained by either physical or chemical effect or combination of both [28]. The physical explanation is that carbonation causes a coarsening of the pore structure, leading to increased capillary porosity and freezable water content, which in turn leads to surface scaling [13–15,28]. It must be noted that the age at the start of the freeze-thaw test is different for non-carbonated and carbonated specimens. The freeze-thaw resistance is affected not only by carbonation, but also by other factors such as drying and age (degree of hydration) [15].

Furthermore, it is well known that the air-entrained concrete mixes are effective in reducing surface scaling. However, exposure of air-entrained concrete to carbonation has a negative effect on the surface scaling resistance [13,16,17]. It has been reported in [17] that the negative effect begins to influence prominently when the percentage of slag in the total binder content reaches approximately 30 to 40% by mass. Another reason for the coarsening of the capillary pores is the prolonged exposure to 65% RH. For air-entrained concretes, increasing the pre-conditioning time in 65% RH leads to increased surface scaling, especially for high slag content [13,18]. On the contrary, for prolonged water curing (protection from exposure to CO_2 and 65% RH) before the start of freeze-thaw test, the scaling generally decreases. Moreover, [28] states that the prolonged protected curing from CO_2 reduces thickness of carbonated surface layer and the scaling.

Furthermore, carbonation depth is also influenced by curing conditions, i.e., relative humidity, CO_2 concentration, and composition of the concrete mix. The rate of carbonation is found to be highest at intermediate relative humidities, i.e. between 50% and 80% RH [28]. Exposure to accelerated carbonation tend to increase the carbonation rate that in turn increases the scaling and carbonation depth with high slag content. Accelerated carbonation testing usually produces exaggerated carbonation depth values that correspond to approximately 10 years of natural exposure [17].

2 EXPERIMENTAL PROCEDURE AND METHODS

2.1 Materials and concrete mix design

The research consisted of two distinct phases. In Phase I, nine concrete mixes were tested with various binder types. Phase II focused on CEM I type cement with 0, 40, and 70% slag additions. The binder types used in both phases are shown in Table 1. All the binders/cements used during the tests were produced by Finnsementti Oy, Finland, except Akmenes – CEM III/B that was produced by Akmenes Cementas, Lithuania. To enable comparison between both phases, the water-to-binder ratio was kept constant at 0.45. The target concrete slump and air content were set at 150 ± 25 mm and 5 ± 1%, respectively. These values were achieved by modifying the concrete consistency and air content using additives, i.e., superplasticiser (SP) and air-entraining agent (AEA).

According to [7,32], the recommended efficiency factor for slag additions to the concrete mix ranges between 0.4 to 1.0. In this study, the efficiency factor of slag was assumed to be equal to 1.0 (k = 1). The decision to use k = 1 was based on the fact that this study was a comparative analysis of concrete mixes with different binders with varying slag contents. Therefore, it was critical to maintain the amount of total binder (cement + slag) and w/b ratio constant for all the mixes. Moreover, according to [13] the concept of efficiency factor is not used when the material serves as a constituent of factory-made cement, where the SCMs are considered as an equal constituent to Portland cement clinker.

Table 1 – Binder types and total slag content used in Phase I and Phase II.

Test phases	Concrete codes	Binder types	Total slag content (%)
Phase I	CEM I	CEM I 52.5 R	0
	CEM II/A	CEM II/A-LL 42.5 R	0
	CEM II/B	CEM II/B-M (S-LL) 42.5 N	17
	CEM II/B + 25% slag	CEM II/B-M (S-LL) 42.5 N + (25% slag)	38
	CEM III/A	CEM III/A 52.5 L	42
	CEM II/B + 50% slag	CEM II/B-M (S-LL) 42.5 N + (50% slag)	59
	FS – CEM III/B	CEM III/B 42.5	69
	Akmenes – CEM III/B	Akmenes CEM III/B 32.5 N	70
	CEM II/B + 75% slag	CEM II/B-M (S-LL) 42.5 N + (75% slag)	80
Phase II	CEM I	CEM I 52.5 R	0
	CEM III/A	CEM I 52.5 R + 40% slag	40
	CEM III/B	CEM I 52.5 R + 70% slag	70

Natural aggregates with maximum aggregate size of 16 mm were used and all concrete mixes in Phase I were produced using the same aggregate gradation. Concrete mixes for Phase I were prepared at the concrete laboratory, Aalto University. The detailed concrete mix composition is presented in Table 2. Ready-mix concrete was ordered from concrete production plant for Phase II. Detailed composition from the concrete plant was not provided due to policy matters. However, it was made sure to keep the air content and slump values within the target range, similar to Phase I. The measured slump and air content values are shown in Table 3.

Table 2 also shows the CO_2 emissions of the concrete mixes in Phase I. The CO_2 emissions were calculated in terms of GWP (Global Warming Potential) emissions with the BY low carbon calculator available at [19], approved by the Finnish Concrete Association. The calculation covers binders (cement and admixtures), aggregates, additives, and water as raw materials. The emissions also include the transport of the raw material, and electricity and heat energy consumption during the production process of concrete. The emissions are calculated individually for each concrete mix based on the target values of the composition of the mix. The calculation accounts for the quantity of admixture i.e., slag in the mix. It should be noted that the emission values only refer to the concrete, and not, for example, to reinforcement of the concrete structures, transport of concrete, concrete products, and other worksite activities. The emission value of the concrete can be utilised in the emission calculations of buildings, provided it is kept in mind that the emission value only covers the concrete material. Detailed information of the low carbon concrete classification can be found in [19].

Table 2 – Mix proportions and calculated CO_2 emissions of concrete mixes during Phase I.

Concrete code	CEM I	CEM II/A	CEM II/B	CEM II/B+25 % slag	CEM III/A	CEM II/B+50 % slag	FS–CEM III/B	Akmenes CEM III/B	CEM II/B+75 % slag
Water and cement									
Cement (kg/m^3)	430	430	430	323	430	215	430	430	107
Slag (kg/m^3)	0	0	0	107	0	215	0	0	323
Water (kg/m^3)	195	195	195	195	195	195	195	195	195
w/b	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Aggregates (kg/m^3)									
Filler 96	115	115	115	115	115	115	115	115	115
0.1/0.6 mm	164	164	164	164	164	164	164	164	164
0.5/1.2 mm	214	214	214	214	214	214	214	214	214
1 /2 mm	214	214	214	214	214	214	214	214	214
2/5 mm	263	263	263	263	263	263	263	263	263
5/10 mm	296	296	296	296	296	296	296	296	296
8/16 mm	378	378	378	378	378	378	378	378	378
Admixtures									
SP (kg/m^3)	1.505	0.774	0.774	0.516	0.430	0.294	0	0	0
AEA (kg/m^3)	0.430	0.430	0.430	0.430	0.430	0.430	0.430	0.430	0.430
Air (dm^3/m^3) as per 5% vol.	50	50	50	50	50	50	50	50	50
Fresh properties									
Slump (mm)	150	160	170	170	170	165	170	140	170
Air content (%)	4.8	4.9	5.0	5.2	4.9	5.5	5.2	4.1	5.5
CO_2 emissions (Kg-CO_2-ekv/m^3)	383	369	291	231	248	171	145	145	111

Table 3 – Binder types, measured slump, and air content of concrete mixes in Phase II. The w/b ratio 0.45 was fixed for all the concrete mixes.

Binder types	Slump (mm)	Air content (%)
CEM I 52.5 R	160	4.70
CEM I 52.5 R + 40% slag	175	5.40
CEM I 52.5 R + 70% slag	170	5.10

2.2 Preparation of test specimens

The 100-mm cubes were cast from the concrete mixes to determine the compressive strength. The compressive strength of water cured specimens was determined at the age of 7, 28, and 91 days in accordance with EN 12390-3 [20]. For the air-void analysis, a 50-mm thick specimen was sawn from the core of a 500-mm beam with a cross-section of 100-mm^2. The air-void analysis was performed on a single specimen from each concrete mix in Phase I. Furthermore, the carbonation depth specimens were prepared in both phases according to EN 12390-12 [23].

Freeze-thaw resistance of concrete was investigated using the slab test. The test procedure and the preparation of specimens was according to the test standards CEN/TS 12390-9 [21] and CEN/TR 15177 [22] for the surface scaling and internal damage, respectively. Four 150-mm cubes from each concrete mix were cast for the slab test. All test specimens were sawn surfaces taken from the cores of the cubes as instructed in [21,22]. Surface scaling and internal damage were measured from the same four specimens cast from each concrete mix. In addition to the standard procedure, the specimens were pre-conditioned before exposure to the freeze-thaw cycles to investigate the influence of carbonation/ageing and other pre-curing conditions (e.g., water curing and plastic wrapping) on the freeze-thaw resistance. The carbonation/ageing and pre-curing conditions in Phase I and Phase II are presented in Table 4. The illustration of binder types, pre-curing/ageing period and conditions in Phase II are presented in Figure 1.

Table 4 – Carbonation/ageing, and pre-curing conditions and duration in Phase I and Phase II.

Test Phases	Pre-conditionings
Phase I	1. Surface scaling and internal damage measurements with and without chlorides, as per standard procedure CEN/TS 12390-9 [21] and CEN/TR 15177 [22], respectively. 2. Surface scaling and internal damage measurement with and without chlorides, with the exception that the test specimens were cured in the carbonation chamber for 2 months, exposed to CO_2 concentration (3.0 ± 0.5%), as per EN 12390-12 [23], before freeze-thaw cycles. 3. Surface scaling with chlorides, with the exception that test specimens were cured in the climate room (65% RH and +20ºC) for 1 year, exposed to CO_2 concentration (0.04 ± 0.001%), as per EN 12390-10 [24], before freeze-thaw cycles.
Phase II	1. Surface scaling with chlorides, as per standard procedure CEN/TS 12390-9 [21]. 2. Surface scaling with chlorides, with the exception that the cubes were sawn after underwater curing for 3, 6, and 12 months, before freeze-thaw cycles. 3. Surface scaling with chlorides, with the exception that test specimens were cured in the climate room (65% RH and +20ºC) for 3, 6, and 12 months, exposed to CO_2 concentration (0.04 ± 0.001%), as per EN 12390-12 [23], before freeze-thaw cycles. 4. Surface scaling with chlorides, with the exception that test specimens were plastic wrapped to protect from carbonation and cured in the climate room (65% RH and +20ºC) for 3, 6, and 12 months, before freeze-thaw cycles.

No changes to the freeze-thaw cycles were made for the measurement of the surface scaling and internal damage. All the specimens were exposed to a maximum of 56 freeze-thaw cycles. A single freeze-thaw cycle composed of 24 hours. The average freeze-thaw temperature variation in the freezing chamber was set between +20ºC and -20ºC. The detailed information of the experimental procedure and setup can be found in [21] and [22].

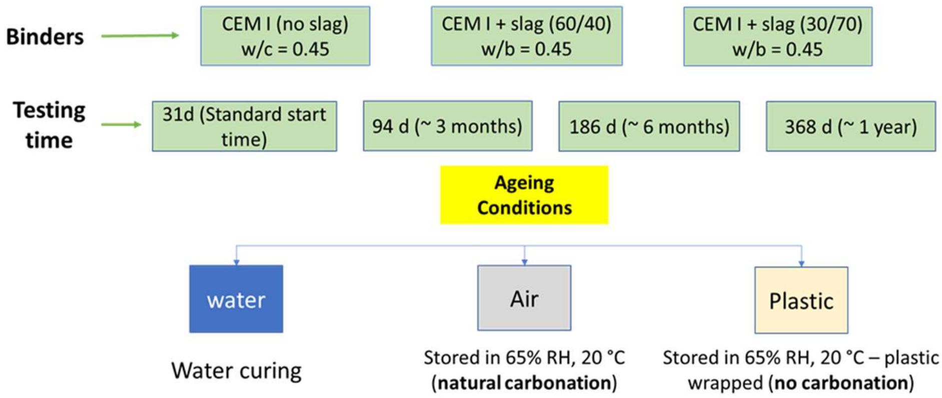

Figure 1 – Illustration of binder types, pre-curing/ageing period and conditions (Phase II).

3. RESULTS AND DISCUSSION

3.1 Freeze-thaw resistance with chlorides

In the exposure classes XF2 and XF4, freeze-thaw damage takes place in the presence of chlorides, where the failure is seen as scaling on the surface of the concrete specimen [7]. The scaling limit criteria of 0.1, 0.2, 0.5 and 1.0 kg/m^2 after 56 cycles for freeze-thaw resistance are considered among different countries [13]. For salt freeze-thaw resistance evaluation, the mean scaling and internal damage values were analysed using four parallel specimens from each concrete mix. No leakage of the salt solution from the test surface of the slabs was observed, therefore, the scaling and internal damage values after 56 cycles for all concrete mixes will be presented.

Surface scaling of non-carbonated concretes using slab test (Phase I)
Nine concrete mixes with varying slag content were subjected to a maximum of 56 freeze-thaw cycles. The test results in Figure 2 show that the surface scaling increased with the increasing slag content. Concrete mixes with slag content higher than 50% led to larger scaling than 0.5 kg/m^2 after 56 cycles. All concrete mixes showed surface scaling below 1.0 kg/m^2, except for concrete containing CEM II/B (80% slag). Between the two types of concrete mixes, scaling resistance was lower in mixes with additional slag incorporation than in those with blended slag within binders. This reduction can be due to slower strength development for such mixes with increasing slag content.

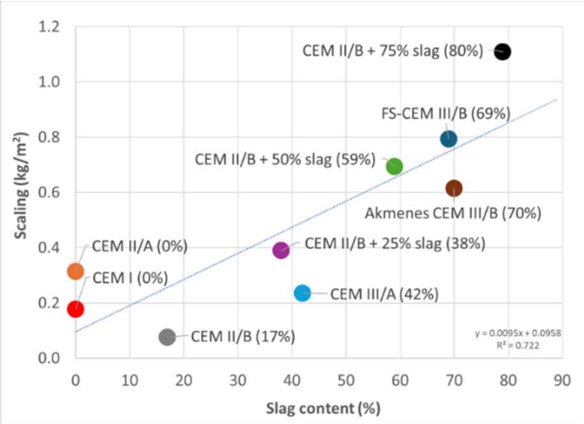

Figure 2 – Effect of slag content on the surface scaling of non-carbonated concretes using slab test with 3% NaCl solution after 56 cycles.

The scaling rates of the concrete mixes over the complete testing (56 cycles) are shown in Figure 3. The scaling curves showed a phase of initial high rate between 0 and 14 cycles, followed by a phase of relatively lower scaling. It was suspected that the initial rapid scaling was influenced by the carbonation of the concrete surface. It must be noted that the 'non-carbonated' specimens were also subjected to normal laboratory air for one week, as per standard procedure [21], which probably led to carbonation of the test surface. Furthermore, according to [8], slow reactivity of slag in concrete mixes causes higher surface scaling during the initial freeze-thaw cycles.

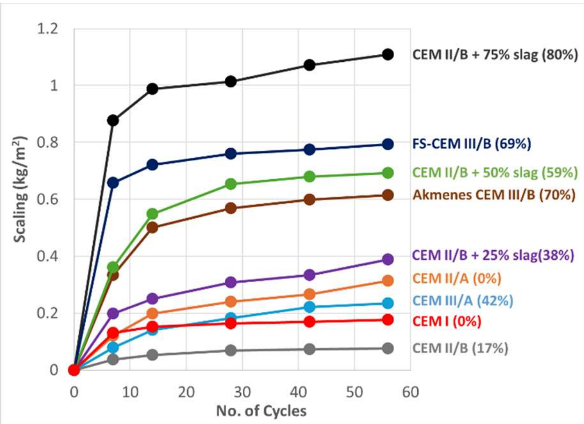

Figure 3 – Scaling rates of non-carbonated concretes over complete (56) testing cycles with 3% NaCl solution.

Surface scaling of carbonated concrete mixes using slab test (Phase I)

The scaling results of the concrete mixes after 56 cycles, pre-cured in the carbonation chamber for two months with (3.0±0.5%) CO_2 concentration are presented in Figure 4. The scaling values increased by a factor of 6 to 8 compared to non-carbonated specimens. All the concrete mixes exceeded 1.0 kg/m^2, except the concrete with CEM II/A (no slag). Above 1.0 kg/m^2, the test surfaces of concrete mixes with slag content were totally broken. For the concrete with slag content, the decrease in salt freeze-thaw resistance as a result of carbonation is because of the significant coarsening of the pore structure [15]. Furthermore, the results confirm that carbonation diminishes the salt freeze-thaw resistance of air entrained concrete mixes. The effectiveness of air pores are diminished by the changes in the gel and capillary pores [13,16]. Additionally, the decrease in salt scaling resistance is also attributed to the carbonated surface layer, especially for concrete with slag [28].

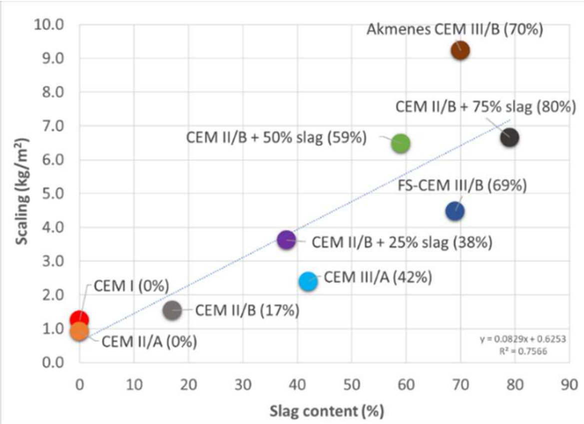

Figure 4 – Effect of slag content and carbonation (3.0±0.5%) CO_2 *on the surface scaling using slab test with 3% NaCl solution.*

The results of scaling rates over 56 cycles in Figure 5 showed an increasing trend of scaling in concrete specimens with CEM II/B (38 – 80% slag) and especially in Akmenes-CEM III/B (70% slag). According to [15], the high rate of scaling is attributed to the carbonated surface layer. There is a significant correlation between the carbonated volume and the volume of scaling during the rapid deterioration. It is thus the carbonated material that is scaled off during the rapid scaling. After the layer is scaled off, the scaling rate reduces and becomes comparable to non-carbonated concrete. However, rapid scaling can be observed in the concrete mixes with high slag content even after 56 cycles. This can be the effect of exposure to high CO_2 concentration (3.0±0.5%). Other concrete mixes with lower slag content (CEM I-0%, CEM II/A-0%, and CEM II/B-17% slag) showed reduced scaling rate after 14 cycles.

Figure 6 shows the surface scaling of the concrete specimens exposed to the natural carbonation (0.04±0.001%) CO_2 concentration in the climate room 65% RH, for 12 months (1 year). All concrete mixes containing 17–80% slag exceeded the scaling value of 1.0 kg/m². Studies [13,28] showed that in air-entrained concrete mixes, extended pre-curing at 65% RH increased surface scaling with increasing slag content. Exposure to 65% RH for longer durations also causes coarsening of the capillary pore structure, however without diminishing the gel water content. The extent of coarseness of the capillary pore structure depends on factors such as binder fineness, and slag content.

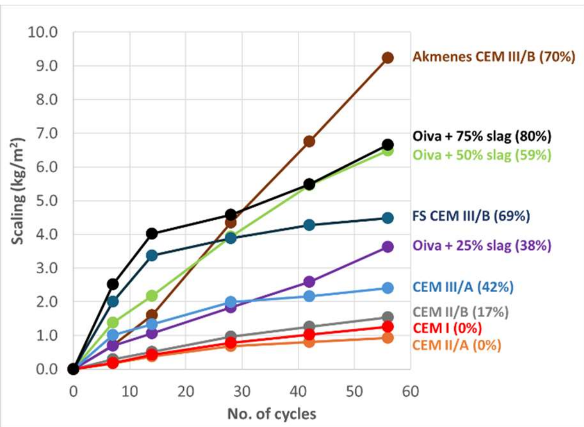

Figure 5 – Scaling rates of the carbonated concrete mixes (3.0±0.5%) CO_2 *over 56 testing cycles of slab test with 3% NaCl solution.*

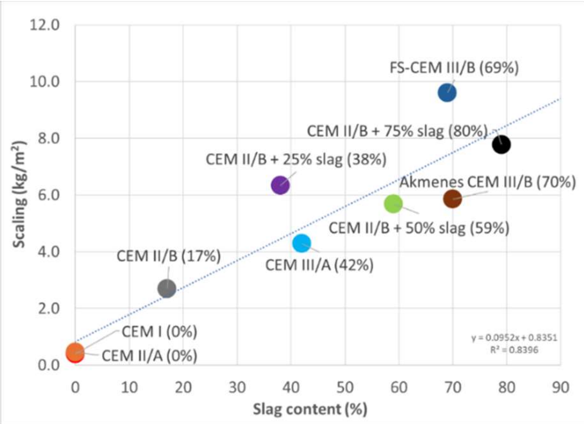

Figure 6 – Effect of slag content and natural carbonation (0.04±0.001%) CO_2 concentration, on the surface scaling using slab test with 3% NaCl solution.

Effect of carbonation on surface scaling in the slab test (Phase I)

Comparison of the surface scaling results after 56 freeze-thaw cycles between the different carbonation/ageing conditions are shown in Figure 7. The pre-curing conditions before starting the slab test are presented in Table 4. For non-carbonated specimens, the scaling for all the concrete mixes remained below the scaling value of 1.0 kg/m², with the exception of CEM II/B (80% slag). In contrast, under accelerated carbonation conditions, all the concrete mixes exceeded the scaling limit compared to the non-carbonated concrete mixes, except for CEM II/A (0% slag). Natural carbonation exposure at 65% RH caused all concrete mixes containing 17–80% slag to exceed the scaling limits. Notably, exposure to both accelerated carbonation and natural carbonation at 65% RH resulted in approximately similar maximum scaling of just above 9.0 kg/m^2. The scaling values were 8 to 10 times larger than those observed in non-carbonated specimens. The largest surface scaling after both carbonation periods were observed in concrete mixes with CEM III/B (69% and 70% slag). However, it is difficult to compare the effect of accelerated and natural carbonation on the large scaling between the individual binders with increasing slag content. As mentioned in [15], it should be noted that the age (degree of hydration) and drying time at the start of the freeze-thaw varied significantly between the non-carbonated, accelerated and natural carbonated specimens. The results in [13,15,18] affirm that the effect of ageing at 65% RH leads to a significant decrease in salt freeze-thaw resistance, particularly in concrete mixes with slag content. However, the primary reason of the increased surface scaling due to pre-curing/ageing is the result of the pore structural changes caused by carbonation and not the degree of hydration and drying.

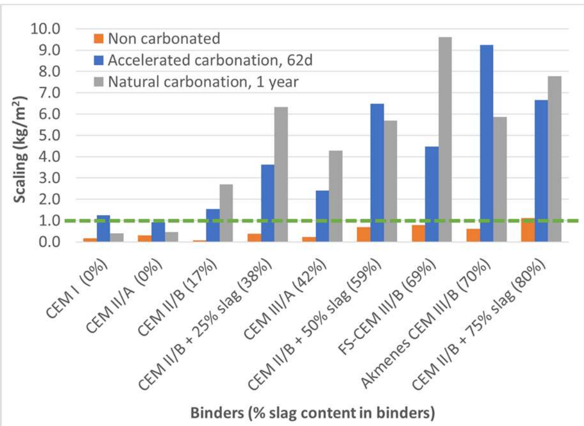

Figure 7 – Effect of slag content, and carbonation conditions on scaling with 3% NaCl solution (Phase I).

Effects of curing conditions and testing age on the surface scaling in slab test (Phase II)
Three concrete mixes having 0, 40, and 70% slag content were tested. Starting age of the salt freeze-thaw test and storing conditions varied to study the effect of ageing and curing conditions. Figure 8 shows that the ageing of specimens exposed to natural carbonation (0.04±0.001%) at 65% RH increased the surface scaling by a factor of 5, independent of slag content and binder type. However, the scaling intensity increased with increasing slag content. The scaling values for CEM III/A (40% slag) exceeded 1.0 kg/m² when salt freeze-thaw test started after six and 12 months. For CEM III/B (70% slag) scaling exceeded 1.0 kg/m² after all testing ages except for standard procedure (28d).

Water cured and plastic wrapped test specimens had high freeze-thaw resistance due to minimal air exposure in all three concrete mixes. With binders having 40% and 70% slag content, longer curing time, i.e., 28–91 days water curing and plastic wrapping reduced scaling by 50%. In addition, the results show that starting the slab test after 91 days curing or later gave low scaling values for non-carbonated concrete mixes independent of the slag content. CEM I exhibited clearly the lowest scaling values at all the testing ages and curing conditions. The scaling results of water cured, and plastic wrapped specimens largely coincided for all the testing ages. This validate the results in [15,28] that the increased surface scaling due to ageing in 65% RH is primarily because of the change in total porosity and the changes in pore size distribution caused by carbonation and not by other ageing effects, i.e., drying and age (degree of hydration).

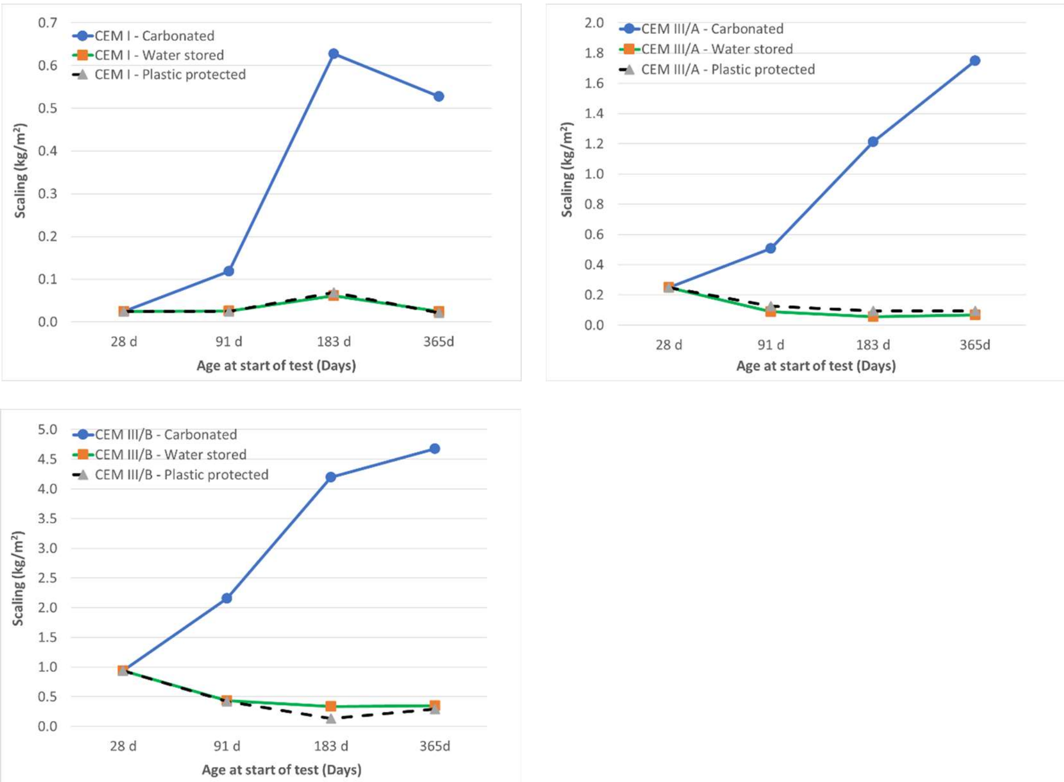

Figure 8 – Effect of curing conditions, age at testing start, and slag content on surface scaling with 3% NaCl solution. Left to right: a) CEM I (0%); b) CEM III/A (40%); c) CEM III/B (70%).

Effect of carbonation on the internal damage (Phase I)
The internal damage of nine concrete mixes exposed to the salt freeze-thaw test in Phase I was also measured on the same specimen used for measuring the surface scaling. Figure 9 shows the comparison between RDM values after 56 cycles for non-carbonated and carbonated concrete

specimens with varying slag content. The pre-curing conditions before starting the slab test are presented in Table 4. Internal damage caused by freezing and thawing contributes to a reduction in the dynamic modulus of elasticity (RDM). In Finnish standard SFS 7022 [25], no minimum limit value of RDM is provided in case of salt freeze-thaw resistance. However, a minimum critical limit 75% RDM for the exposure class XF3, 50 years design working life is marked in Figure 9. The results show no indication of internal damage with varying slag content, except for non-carbonated concrete with CEM II/B (80% slag). According to [26,28], the internal damage is observed only for concrete mixes without air entrainment. Furthermore, pre-curing in the carbonation chamber with (3.0±0.5%) CO_2 concentration and (57±3%) RH caused a slight increase in resistance to internal damage, except for CEM I (0% slag) and CEM III/B (69% and 70% slag). [29] affirms the result as, carbonation could lead to drying of concrete specimens, which helps resist internal cracking during freeze-thaw cycles. This means a reduced ultrasonic pulse transmission time (UPTT) across the concrete specimens, resulting in high RDM measurements.

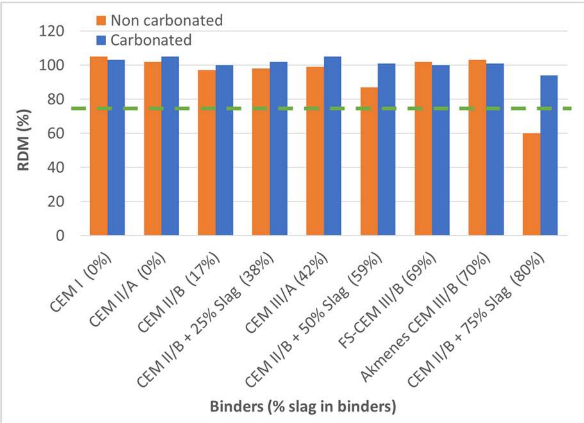

Figure 9 – Effect of carbonation and slag content on the internal damage using slab test with 3% NaCl solution.

3.2 Freeze-thaw resistance without chlorides

In exposure classes XF1 and XF3, the freeze-thaw damage takes place in the absence of chlorides and the failure mechanism as internal damage is considered critical [7]. However, according to [25], the conformity should be demonstrated both for internal damage (modulus of elasticity) and scaling, where both requirements must be met. The freeze-thaw resistance of concrete with regard to the internal damage is performed according to CEN/TR 15177 [22]. Finnish standard SFS 7022 [25] provides the minimum critical values of (≥ 75%) and (≥ 85%) RDM for the XF3 exposure class, based on the design working life of 50 and 100 years, respectively. Moreover, [26] also suggested the minimum critical limit of (≥ 70%) RDM for the outer panels of concrete building facades. In this study, the internal damage limit of (≥ 75%) RDM is assumed.

Surface scaling of non-carbonated concretes using slab test with de-ionised water (Phase I)
The scaling rates of the non-carbonated concretes over the complete testing cycles (56) are presented in Figure 10. The results show that the accumulated scaling values of concrete specimens after 56 freeze-thaw cycles are significantly smaller and well below the scaling value of 0.1 kg/m^2. A common trend of reduced scaling rate after 14 cycles can be observed among all the concretes, except CEM II/B (80% slag). The increasing slag content does not correlate clearly with the surface scaling. Moreover, the results support the findings in [12] where the scaling is

clearly observed in the presence of salt in the ice layer while little or no scaling occurs in the case of a pure ice layer on the top of concrete.

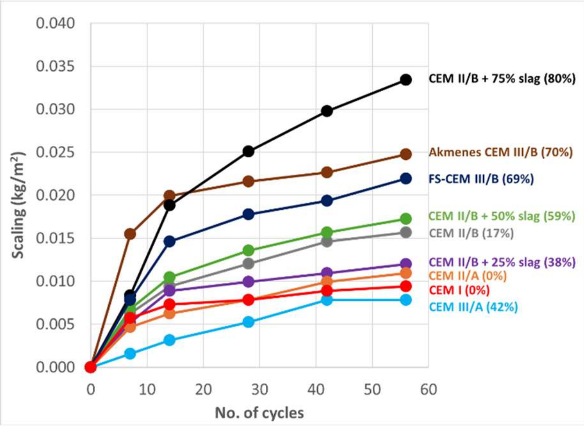

Figure 10 – Scaling rates of non-carbonated concretes over complete (56 cycles) with de-ionised water.

Surface scaling of carbonated concretes using the slab test with de-ionised water (Phase I)
The findings related to the scaling rates of carbonated concretes for the complete freeze-thaw cycles are shown in Figure 11. After 56 freeze-thaw cycles, the accumulated scaling values indicate strong freeze-thaw resistance for all the tested concretes, with scaling values less than 0.1 kg/m^2. Despite this, a consistent upward trend in surface scaling was observed following each freeze-thaw cycle. According to [15], the high rate of scaling is attributed to the carbonated surface layer. The relationship between slag content and scaling is less apparent among the concretes, except for CEM II/B (80% slag), which experienced the highest scaling.

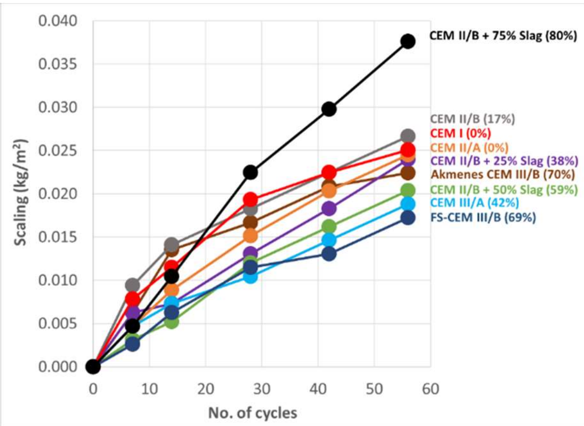

Figure 11 – Scaling rates of the carbonated concretes over complete (56 cycles) with de-ionised water (Phase I).

Effect of carbonation on surface scaling in the slab test with de-ionised water (Phase I)
Figure 12 presents the comparison in the surface scaling after 56 cycles between non-carbonated and carbonated concretes. According to [12,28], internal damage is primarily associated with freeze-thaw attack without chlorides, as for surface scaling the interaction between the ice layer and the concrete surface in the presence of salt. However, the increase in surface scaling can be observed from the results with increasing slag content, except for concrete mixes with CEM II/B (38% slag) and CEM III/A (42% slag). Furthermore, both non-carbonated and carbonated concretes tested exhibited high resistance to scaling. Carbonation resulted in slight increase in surface scaling, except for concrete mixes with CEM III/B (69% and 70% slag). The maximum

observed scaling was just above 0.03 kg/m² for non-carbonated and carbonated concretes with CEM II/B (80% slag), which remained well below the scaling value of 0.1 kg/m².

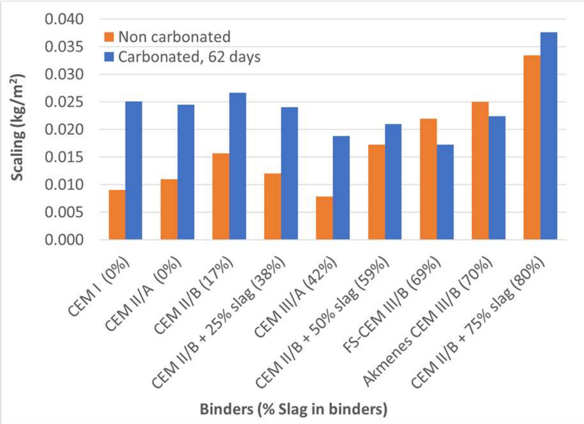

Figure 12 – Scaling comparison values of non-carbonated and carbonated test specimens, deionised water (Phase I).

Effect of carbonation on internal damage in the slab test with de-ionised water (Phase I)

Figure 13 shows the changes in dynamic modulus of elasticity (RDM) after 56 freeze-thaw cycles between non-carbonated and carbonated concrete mixes exposed to carbonation with 3.0±0.5% CO_2 concentration for two months with varying slag content. With de-ionised water all the concrete types exhibited high RDM values than the critical minimum limit of 75% (XF3 – 50 years), showing no signs of internal cracking. On contrary to the surface scaling, carbonation resulted in a slight increase in internal damage resistance, except for concretes with CEM I (0%) and CEM III/B (69% slag). Carbonation of concrete could lead to drying of concrete specimens, which helps resist internal cracking during freeze-thaw cycles [29]. Furthermore, internal damage is observed most of the time for concrete mixes without entrained air, and high w/b ratio [26,28]. The high RDM values also suggest that the concrete mixes with adequate air-entrained pore structure minimises damage caused by freezing and thawing in concrete [26].

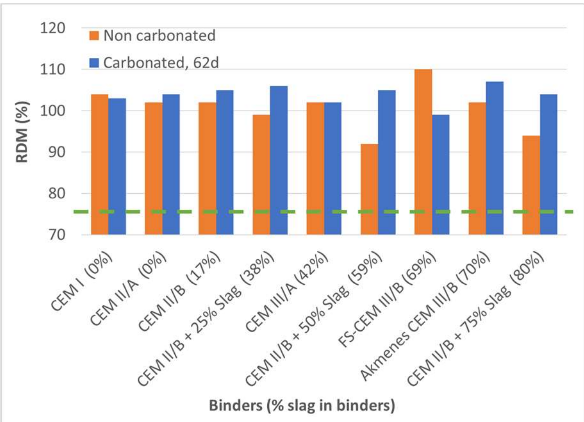

Figure 13 – Effect of carbonation and slag content on the internal damage using slab test with de-ionised water (Phase I).

3.3 Carbonation depth

Figure 14 shows the carbonation depth results of concrete specimens exposed to 3.0±0.5% CO_2 concentration for two months in the carbonation chamber (57±3% RH) in phase I. The results show that the carbonation depth increased with increase in slag content, except in CEM III/A (42% slag) which had the CO_2 penetration approximately similar to concrete mixes without slag. Concrete with CEM II/B (80% slag) exhibited twice the carbonation depth compared to CEM I (0% slag). The average carbonation depth measured between the test concrete mixes with varying slag content was 14 mm. According to [30], the increase in carbonation depth with slag content compared to the pure cement is a consequence of the differences in the pore structure and transport properties due to the varying binder composition, testing age, curing methods and conditions of the concrete. For instance, the highest carbonation depth was found for concrete specimens stored in 65% RH. Moreover, the rate of carbonation for concrete is also usually highest in 50 to 80% RH [28]. For accelerated carbonation testing, longer curing periods are in the most cases recommended to obtain a more realistic and representative microstructure before subjecting to high CO_2 levels. However, in the current study, the curing period before exposure to carbonation was not prolonged (21 days), which resulted in high carbonation depth.

Furthermore, a correlation was found by comparing the depth of carbonation with the amount of scaling (expressed as scaling depth) after 56 freeze-thaw cycles, as shown in Figure 15. In general, the trend in Figure 15 shows that with the increase in slag content, the surface scaling resistance was relatively lower in the carbonated surface layer compared to non-carbonated material below this layer. However, at equal carbonation depths, scaling depths varied among concrete mixes. The results also show that only a small portion of the carbonated material had scaled off. In concrete mix with the highest slag content CEM II/B (80% slag), only 17% of the carbonated layer was scaled off. As discussed earlier, the physical explanation is the coarsening of the pore structure resulting in an increase in capillary porosity and increase in freezable water content as a result of carbonation, which in turn exhibit surface scaling [13–15,28]. However, [29] concludes that the increase in capillary porosity caused by carbonation could not be the main cause, because the surface scaling without salt did not increase significantly in the carbonated zone. In this research, the results of scaling resistance without salt coincide with this argument. [29] also mentioned that the negative effect of carbonation on the salt scaling resistance was because of a chemical effect. The investigation of chemical effects is however beyond the scope of this research.

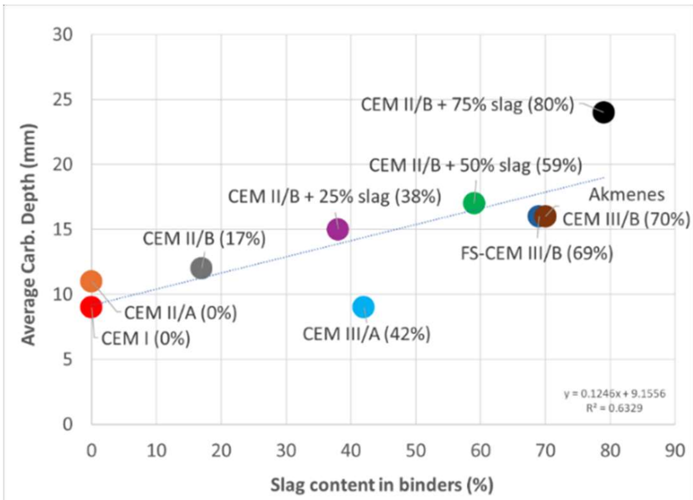

Figure 14 – Effect of slag content in binders on carbonation depth in Phase I.

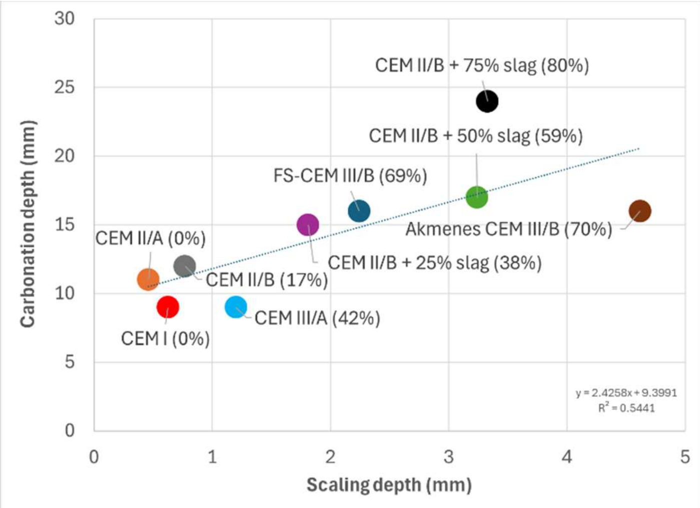

Figure 15 – Depth of carbonation as a function of the depth of scaling after 56 cycles (Phase I)

In Phase II, three concrete mixes were exposed to natural carbonation having CO_2 concentration 0.04±0.001% and 65% RH. Other concrete specimens from the same concrete mixes were placed under the similar conditions, wrapped in plastic to minimise air contact. The carbonation depth was measured after three, six, and twelve months. Contrary to Phase I, carbonation depths in Figure 16 were minimal due to exposure to natural carbonation at 65% RH. The concrete with the highest slag content (70%) exposed to CO_2 for twelve months had the highest carbonation depth of 4 mm. No CO_2 penetration occurred in plastic-wrapped concretes at any age.

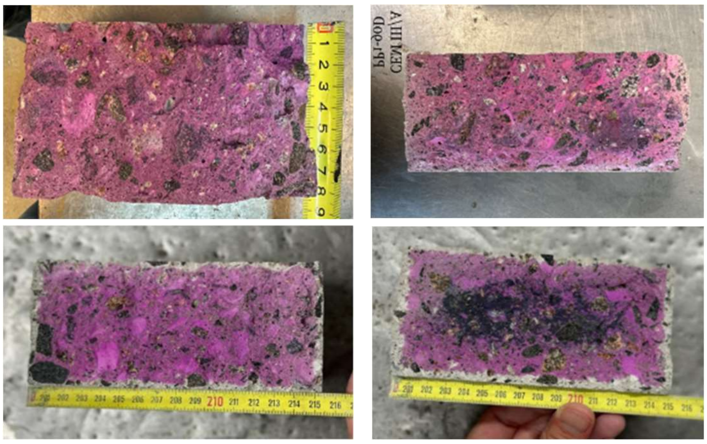

Figure 16 – Effect of slag content, curing conditions and duration on carbonation depth in Phase II. Left to right top row: a) CEM I (90d, plastic wrapped); b) CEM I-40% slag (90 d, plastic wrapped). Left to right bottom row: c) CEM I-70% slag (180 d, carbonated); d) CEM I-70% slag (365 d, carbonated).

3.4 Air-void analysis (Phase I)

Assessment of freeze-thaw resistance can be evaluated through indirect air-void analysis using concrete thin-sections. However, in Finland in case of infrastructural concretes, thin-section or air-void analysis cannot be used to evaluate salt freeze-thaw resistance. In this project, however, to ensure the quality of the pore structure of the concrete, thin-section analysis was performed. Spacing factor is considered as the best parameter from air-void analysis to evaluate frost resistance of concrete [10]. The results in Table 5 gave very low spacing factor (≤ 0.16 mm), and high specific surface area (> 25 mm^2/mm^3) for all concretes. In practice, this means that the protective pores were very small, and it is possible that part of the protective pores become filled with water in chlorine environment. The results show that the spacing factors correlate poorly with the surface scaling in the slab test. At high slag content, scaling was high even though the spacing factor remained low. The results affirm [29], that the concrete mixes with high slag content improved air-void parameters compared to pure cement concrete. This further indicates that the negative effect of carbonation on salt scaling resistance with high slag content cannot only be because of physical effect.

Table 5 – Results of air-void analysis

Binders	Protective pores, (%)	Compaction pores, (%)	Spacing factor, (mm)	Specific surface area (mm^2/mm^3)
CEM I	4.6	1.3	0.14	40
CEM II/A	5.0	0.7	0.11	47
CEM II/B	5.0	0.7	0.10	50
CEM II/B + 25 % slag	5.1	0.2	0.12	42
CEM III/A	3.9	1.0	0.10	55
CEM II/B + 50 % slag	5.7	1.4	0.11	47
FS - CEM III/B	3.1	0.4	0.16	38
Akmenes - CEM III/B	3.4	1.9	0.13	47
CEM II/B + 75 % slag	5.8	1.3	0.13	40

3.5 Compressive strength (Phase I)

An increase in slag content led to a decrease in the compressive strength at 7 days due to the slow reactivity of slag as shown in Figure 17. The compressive strength decreased at 7 and 28 days with an increase in slag content when the additional slag was added. Except for CEM III/A, CEM III/B and Akmenes-CEM III/B binders, which exhibited improved compressive strength development due to the production process, where clinker and slag were grinded together. The highest compressive strength was achieved with CEM III/A (42% slag) and Akmenes-CEM III/B binder (70% slag) at 28 and 91 days, respectively. The comparison of compressive strengths is also affected by the different standard strengths of the cements, which ranged from 32.5 to 52.5 MPa.

Furthermore, the compressive strength of concrete with additions depends on the activity index of the addition. The slow rate of strength development of concrete with slag content can be countered by using efficiency factor concept [7,32]. In addition, the compressive strength of concrete highly depends on the w/c ratio. Therefore, one way to achieve the same strength when using slag is to decrease the w/b ratio. Moreover, to achieve similar compressive strength for the same water content, the mass of addition used must be larger than the mass of cement that is replacing it, i.e., $k < 1$ [7,8,32]. However, for the purpose of comparative analysis in this research, the overall quantity of binder and the w/b ratio were kept constant in all the concrete mixes, i.e., $k = 1$.

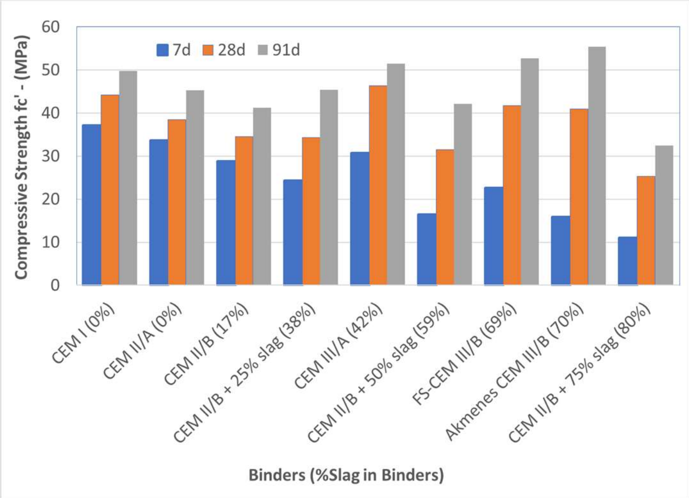

Figure 17 – Effect of binders incorporating slag on compressive strength of concrete at 7, 28, and 91 days.

4. CONCLUSIONS

Within the limits of this work, the following conclusions can be drawn:

- Slag had a clear effect on the surface scaling in the slab test with chlorides. The results confirm the slag content of 50% to be a critical value for acceptable freeze-thaw resistance.
- Exposure to carbonation before the slab test has an increasing effect on the surface scaling with chlorides. All the concrete mixes incorporating slag content, exposed to accelerated carbonation and atmospheric level CO_2 at 65% RH exceeded the surface scaling value of 1.0 kg/m^2 in the presence of chlorides.
- Ageing, curing conditions, and slag content had a clear effect on surface scaling with salt. Prolonged exposure to atmospheric CO_2 at 65% RH increased surface scaling by five times. In contrast, ageing of plastic wrapped, and water cured specimens reduced surface scaling, i.e., 28–91 days of curing reduced scaling by 50%. Hence, level of carbonation before the testing is critical for surface scaling.
- Freeze-thaw resistance without chlorides appeared to be high for all the tested concrete mixes. The dynamic modulus of elasticity (RDM) of all the concretes exceeded the critical minimum limit of 75% (XF3 – 50 years). The surface scaling results were also well below the maximum limit. For exposure classes XF1 and XF3, the internal damage failure mechanism is considered critical.
- Carbonation had a slightly positive effect on the internal damage resistance of concrete mixes subjected to freeze-thaw cycles with and without chlorides. However, no clear correlation between slag content and dynamic modulus of elasticity (RDM) values was observed.
- Carbonation of concretes at higher CO_2 concentration (3.0±0.5%) for two months increased the carbonation depth by five times compared to natural carbonation (0.04±0.001%) for one year. Plastic wrapping reduced the carbonation depth by minimising contact with air. Incorporation of slag also increased the CO_2 penetration.
- Air-void analysis was performed using thin-section analysis method. Results support the observation that spacing factor is not a reliable parameter to evaluate freeze-thaw resistance with chlorides for slag concrete.

- With increasing slag content, the results showed a reduction of compressive strength at 7 days but achieved the highest strength at 91 days with 70% slag content.
- CO_2 emission calculations made for concretes show the effectiveness of slag usage in reducing emissions. However, slag should be used with care, especially in structures exposed to salt freeze-thaw loadings.

5. FURTHER RESEARCH

The effect of carbonation on the salt freeze-thaw resistance of concrete incorporating slag content is critical. However, it is difficult to replicate the natural atmospheric conditions in the laboratory, i.e., CO_2, temperature, and RH fluctuations. Hence, it is crucial to study the impact of carbonation on the existing concrete structures and its effects on freeze-thaw resistance.

ACKNOWLEDGEMENT

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