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THE INFLUENCE OF CARBONATION AND AGE ON SALT FROST SCALING OF CONCRETE WITH MINERAL ADDITIONS

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Abstract
Resistance to salt frost scaling is tested by accelerated methods such as CEN/TS 12390-9 which originally were developed for Portland cement concrete. However, it has been shown that ageing and coupled deterioration mechanisms, like carbonation or leaching, alter the frost resistance. An example is concrete with high amount of slag where the frost resistance is reduced when the concrete is carbonated. Hence, modifications to the test methods have been proposed to take these effects into account and often an accelerated carbonation at an early age have been used. Though, it has been found that the accelerated tests show a much more negative effect than what is experienced in field conditions. This paper presents results from a laboratory study of concrete with mineral additions at different dosages and water/binder ratios which have been exposed to accelerated carbonation at 1% CO_2-concentration at different ages. The results show that exposing the specimens to accelerated carbonation at a young age will result in an increased scaling but that the carbonation depths corresponds to 10 year natural exposure. By increasing the age before the accelerated carbonation exposure the scaling is significantly reduced and the salt frost scaling resistance seems to correlate better with field observations.

1. Introduction

The resistance of concrete to salt frost scaling is tested by accelerated methods such as CEN/TS 12390-9 [1] and SS 137244 [2], which originally were developed based on the experience of Portland cement concrete [3] [4]. The testing regime is being under review, partly due to that it does not consider ageing effects, such as changes to pore structure, micro cracking, leaching and the effect of carbonation [3] [4] [5]. With increasing use of mineral additions, such as slag (GGBS) and fly ash (FA), for reducing the environmental footprint and improve resistance to reinforcement corrosion this type of test methods need to be modified so that it can safely and adequately be used for concrete with mineral additions. Moreover, the test results also need to be correlated with the performance in field conditions [6] [7].

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2. Experimental procedure

2.1 Materials and mix designs

The concrete mixture proportions are listed in Table 1; where the aggregate was a granitic type, the superplasticizer (SP) was polycarboxylate-based (PCE) with a dry content of 18%, and the air entraining agent was a synthetic surfactant with a dry content of 1.1%. For the experiments, two different Portland cements (CEM I, C2 & C3), one Portland-fly ash cement (CEM II/A-V, C5), one Portland-slag cement (CEM II/B-S, C6), one blast furnace cement (CEM III/A, C4), and two different GGBS (S1 & S2) were used. See Table 2 for properties of the cement and GGBS used. For the mixes with GGBS an efficiency factor (k-value) of 1.0 was used, i.e. comparison is made at equal water/binder (w/b) ratios.

Table 1: Concrete mix proportions, kg/m^3 (if not otherwise stated).

Binder (see Table 2)	*w/b*	Cement	GGBS	Aggregates	SP	AEA	Air content
C2	0.45	400		1 705	2.00	0.040	5.2 %
C3	0.45	400		1 703	2.00	0.040	5.6 %
C2+20%S1	0.45	320	80	1 699	2.00	0.040	4.9 %
C2+30%S1	0.45	280	120	1 696	2.00	0.040	5.1 %
C2+40%S1	0.45	240	160	1 693	2.00	0.052	5.0 %
C2+60%S1	0.45	160	240	1 687	2.00	0.040	5.8 %
C2+20%S2	0.45	320	80	1 687	2.00	0.040	5.8 %
C2+40%S2	0.45	240	160	1 703	2.00	0.040	5.5 %
C6	0.45	400		1 679	2.00	0.040	5.0 %
C4	0.45	400		1 688	2.00	0.040	5.1 %
C5	0.45	400		1 704	2.00	0.040	5.8 %
C5	0.40	425		1 708	2.55	0.053	5.7 %
C2	0.40	425		1 709	2.55	0.053	5.5 %
C2+20%S1	0.40	340	85	1 703	2.55	0.043	6.0 %
C2+30%S1	0.40	298	128	1 700	2.55	0.043	6.2 %
C1+40%S1	0.40	255	170	1 697	2.55	0.043	6.2 %
C4	0.40	425		1 690	2.98	0.036	6.3 %
C6	0.40	425		1 700	2.98	0.036	6.2 %

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Table 2: Materials.

ID	Type Acc. to EN 197-1	Density kg/m³	Blaine m²/kg	CaO M.-%	SiO₂ M.-%	Al₂O₃ M.-%	Fe₂O₃ M.-%	Na₂Oeqv M.-%
C1	CEM I 42,5 N SR3 MH/LA	3 200	330	64	22	3.7	4.5	0.51
C2	CEM I 42,5 N SR3 MH/LA	3 160	330	64	22	3.3	4.6	0.45
C3	CEM I 52,5 N	3 140	420	63	19	4.3	3.1	0.90
C4	CEM III/A 42,5 N/NA	3 000	450	52	28	8.9	1.2	0.70
C5	CEM II/A-V 42,5 N MH/LA	3 040	370					0.85
C6	CEM II/B-S 52,5 N	3 060	460	56	25	6.3	2.1	0.80
S1	GGBS	2 900	420	40	35	12		1.20
S2	GGBS	2 920	500	31	34	13		0.90

C4: Contains about 49% GGBS. C5: Is a Portland-fly ash cement with app. 14% and with the clinker of C1. C6: Contains about 33% GGBS

2.2 Freeze-thaw test procedure

The standard slab test procedure for freeze-thaw testing as described in CEN TS 12390-9 [1] and SS 137244 [2] were used to assess the salt-frost scaling resistance on a cut surface. Four different preconditioning regimes have been studied:

- **Standard procedure - 31d Std:** From demoulding (24±2 h) the cube is stored in water until the age of 7 days, and then stored in climate chamber (20±2°C and RH 65±5%) until a 50 mm thick specimen is cut at an age of 21 days. The slab is placed in a climate chamber (20±2°C and RH 65±5%) until it is 28 d old. At 28 d, 3 mm de-ionized water is poured on the top surface and the specimen is saturated for 72±2 h. At the age 31 d the freeze thaw cycles are started. This procedure is referred to as 31d Std.

- **Modified standard procedure – 31d C:** As standard procedure, but from the age 21 d until 28 d the cut specimen is placed in a climate chamber with 1.0 % CO_2-concentration (20±2°C and RH 65±5%). At 28 d, 3 mm de-ionized water is poured on the top surface and the specimen is saturated for 72±2 h. At the age 31 d the freeze thaw cycles are started. This procedure is referred to as 31d C.

- **45 d curing regime – 45d C:** From demoulding (24±2 h) the cube is stored in water until the age of 21 days. Then the cube is stored in a climate chamber (20±2°C and RH 65±5%) until specimen is cut at an age of 35 days. At the age 35 d the cut specimen is placed in a climate chamber with 1.0 % CO_2-concentration (20±2°C and RH 65±5%) until it is 42 d old. At 42 d, 3 mm de-ionized water is poured on the top surface and the specimen is saturated for 72±2 h. At the age 45 d the freeze thaw cycles are started. This procedure is referred to as 45d C.

- **87 d curing regime – 87d C:** From demoulding (24±2 h) the cube is stored in water until the age of 63 days. Then the cube is stored in a climate chamber (20±2°C and RH 65±5%) until specimen is cut at an age of 77 days. From the age 77 d until 84 d the cut specimen is placed in a climate chamber with 1.0 % CO_2-concentration (20±2°C and RH 65±5%). At 84 d, 3 mm de-ionized water is poured on the top surface and the

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specimen is saturated for 72±2 h. At the age 87 d the freeze thaw cycles are started. This procedure is referred to as 87d C and was only used for the mixes with GGBS.

For all specimens, the weights were recorded immediately before and after the saturation with de-ionized water to determine the water uptake. Moreover, on accompanying specimens, cured in the same manner as the specimens for freeze-thaw testing, the carbonation depth was determined after 7, 14 and 28 d exposure to 1.0% CO_2 by spraying a phenolphthalein solution on a freshly split concrete surface. In addition, the compressive strength of the concretes were determined at 28, 56, and 180 days.

3. Results

3.1 Compressive strength

The compressive cube strength (at age 28, 56, and 180 days for water cured specimens) for the concrete mixes are presented in Figure 1 (average of two specimens). For the mixes with higher amounts of GGBS the compressive strength at 28 and 56 days are lower. However, at 180 days the differences becomes smaller.
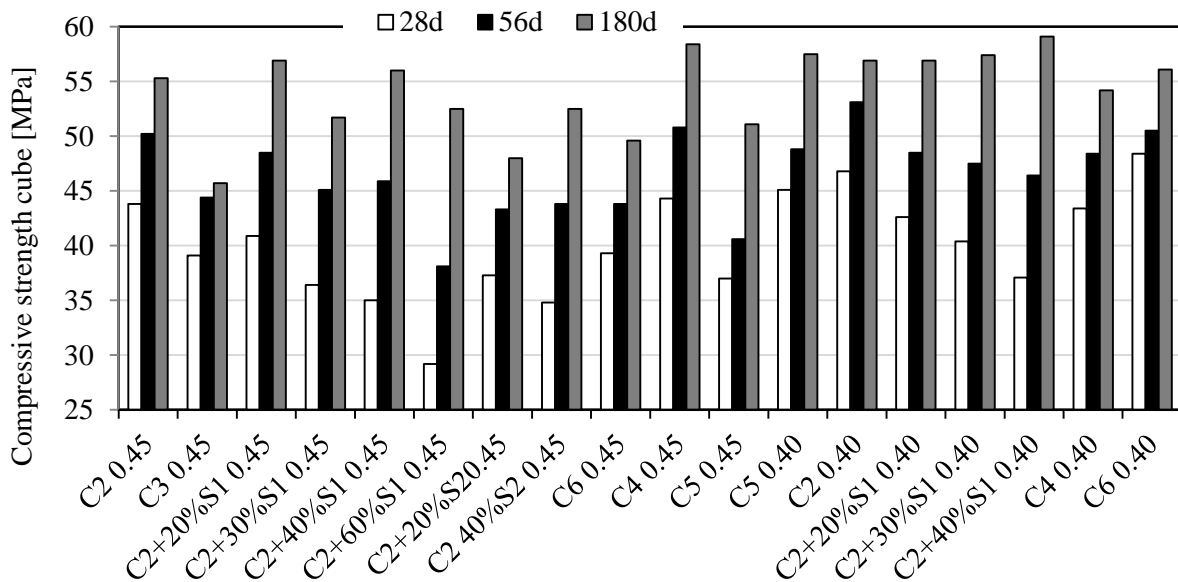

Figure 1: Compressive strength (water cured cubes) at 28, 56, and 180 days.

3.2 Carbonation, water uptake & pre-conditioning

In Figure 2 the carbonation depth for the different concrete mixes and curing conditions are presented. The carbonation depths are, as expected, influenced by the curing conditions and age at exposure and are lower for more mature specimens. Moreover, with increasing GGBS content the carbonation depth increase and with decreased w/b ratio it decreases and is considerably lower, especially for the more mature specimens (curing condition 87d C). In Figure 3 the water uptake (after 72±2 h saturation) for the different concrete mixes and curing conditions is presented. Compared with the standard curing condition (31d Std), almost all concrete mixes show an increased water uptake for the early carbonated specimens (31d C, start of carbonation at 21 d). For the curing condition 45d C (age 35 d when start of carbonation) the water uptake is reduced or almost unaffected for most of the mixes. The only deviation is for cement C5 (CEM II/A-V) which show an increased water uptake. Finally, for the curing

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condition 87d C (age 77 d when start of carbonation) the water uptake is reduced for all mixes. From these results it can be seen that the influence of hydration (age) is much more apparent for high GGBS contents.
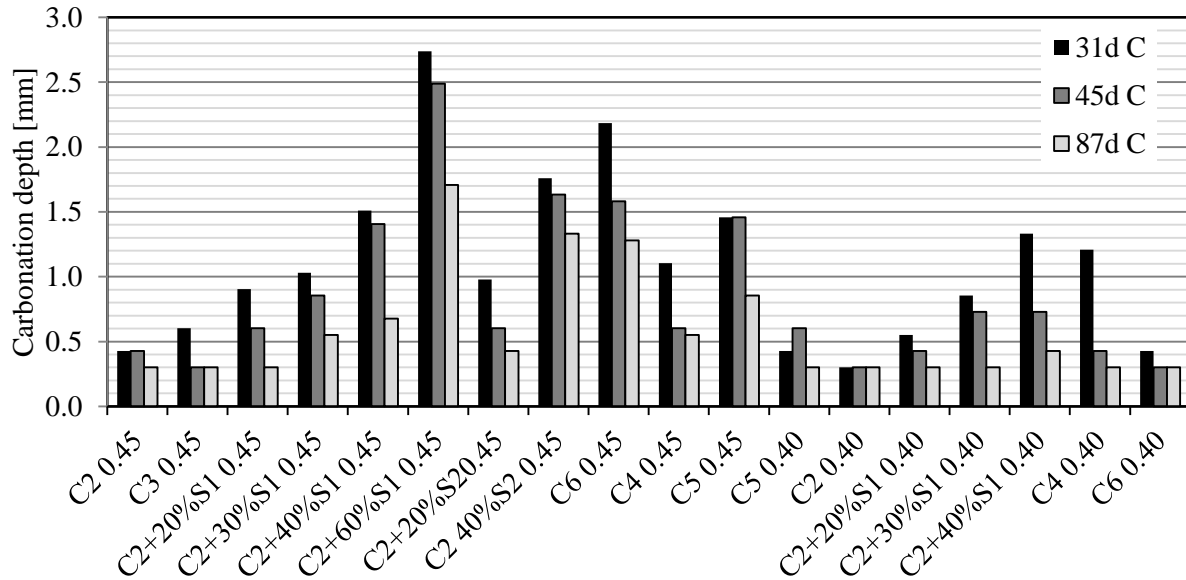

Figure 2: Comparison of carbonation depth after 1 week in 1% CO_2 for the different curing conditions.
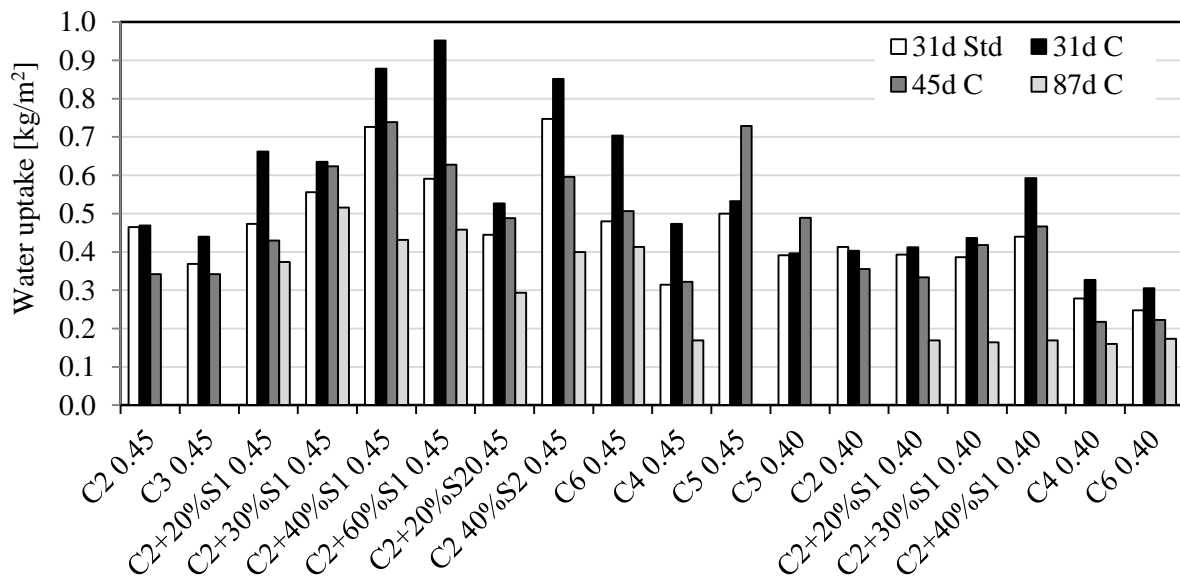
Figure 3: Comparison of the measured water uptake after 72±2 h surface saturation for the different curing conditions.

3.2 Surface scaling & pre-conditioning

The surface scaling after 56 and 112 cycles are presented in Figure 4 and Figure 5. The acceptance criteria for "good" frost resistance according to SS 137244 [2] is shown in the figures. As can be seen in the figures, in all cases the scaling compared with the standard procedure increased for the carbonated specimens independent of curing condition, with the

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exception of mix C2+20%S1 0.40 for 45d C and 87d C curing. The increase in scaling is generally highest for 31d C, i.e. when carbonation starts on specimens at an age of 21 d.
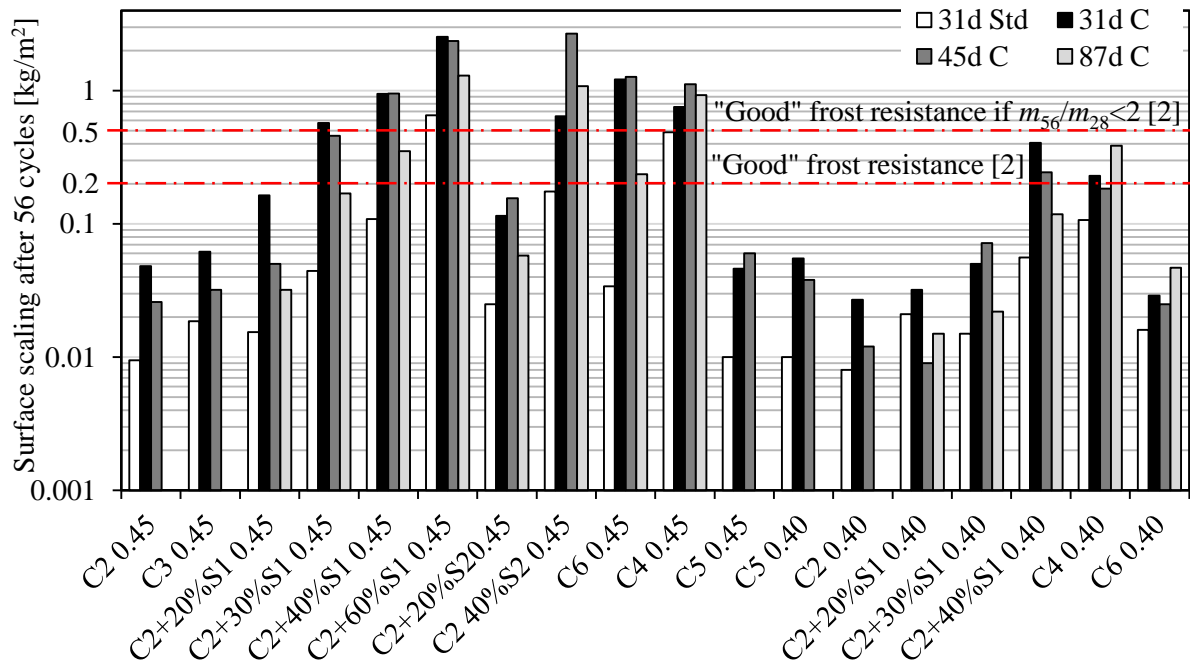

Figure 4: Comparison of the surface scaling (log scale) after 56 cycles for the different curing conditions. The ratio of the mass of scaled material after 56 cycles to 28 cycles (m_{56}/m_{28}) were for all tested concretes <2.0 except for C4 0.40 and C6 0.40 with curing condition 87d C.
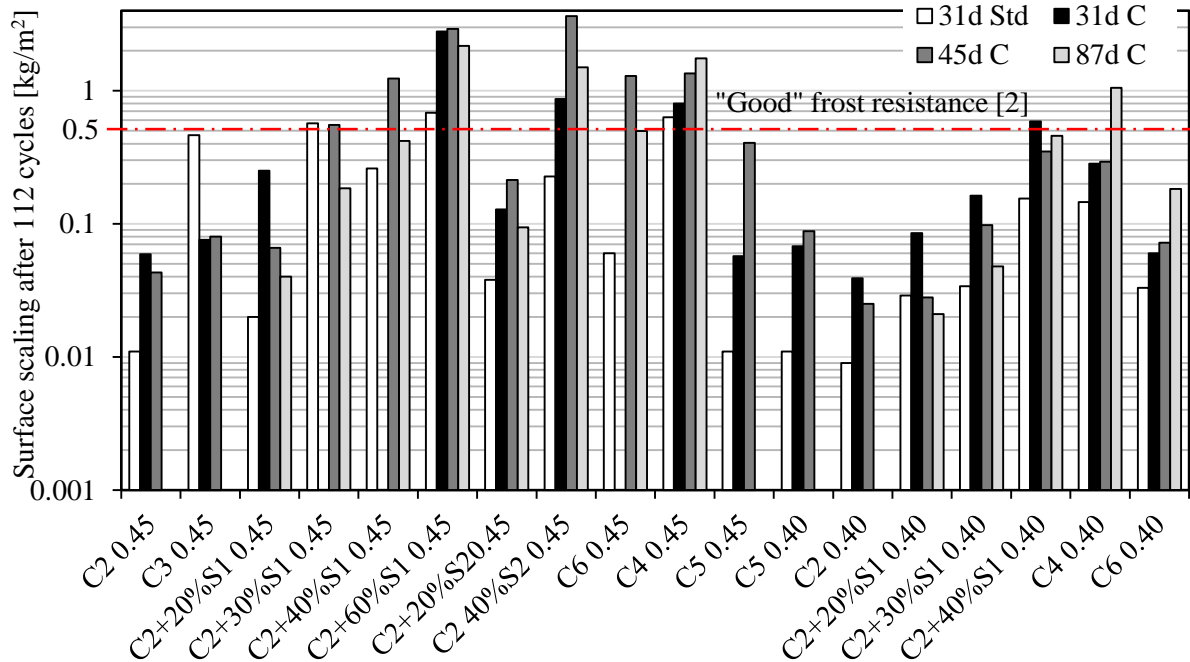
Figure 5: Comparison of the surface scaling (log scale) after 112 cycles for the different curing conditions. For some of the tested concretes the scaling for curing condition 31d C after 112 cycles could not be recorded due to large scaling and leakage problems.

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4. Discussion

As can be seen in Figure 4 and 5, the carbonation and age of the specimens has a big influence on the surface scaling. It has been known for a long time that with high amounts of GGBS the salt-frost scaling resistance is low and is negatively affected by carbonation [8] [3]. At what amount this negative effect starts to have influence have been said to be at about 30 to 40% GGBS of total binder content based on field data [9] [10]. Based on the results from this study, for the tested concrete mixes and materials, at approximately 30 to 40% GGBS of the total binder the negative effect starts to have influence; but it is dependent on *w/b* ratio and the properties of the GGBS. In Figure 6 the difference in behaviour between 20 and 40% GGBS for *w/b* ratio 0.45 is shown. In both cases there is a big difference for the early carbonated specimens (31d C). At the higher GGBS addition also the 45d C specimens show a large scaling. What is interesting is that the major part of the scaling, for 40% GGBS, occurs during the first 7 days. Moreover, for the more mature specimen, 87d C (carbonation started at 77 days) there is only a moderate increase in the scaling. For the mixes with 20% GGBS, all meet the requirement for "good" frost resistance according to [2]. With 40% GGBS it is only the standard procedure (31d Std) and the 87d C that meets the requirement for "good" frost resistance according to [2] with GGBS S1. For GGBS S2 the criteria is met at 30% GGBS but not at 40%. However, there is a difference between GGBS S1 and S2, where S2 have a larger carbonation depth at dosage 40% compared to S1. This could be due to the different chemistry of the GGBS with a lower Ca/Si ration for S2 which could promote more rapid carbonation.
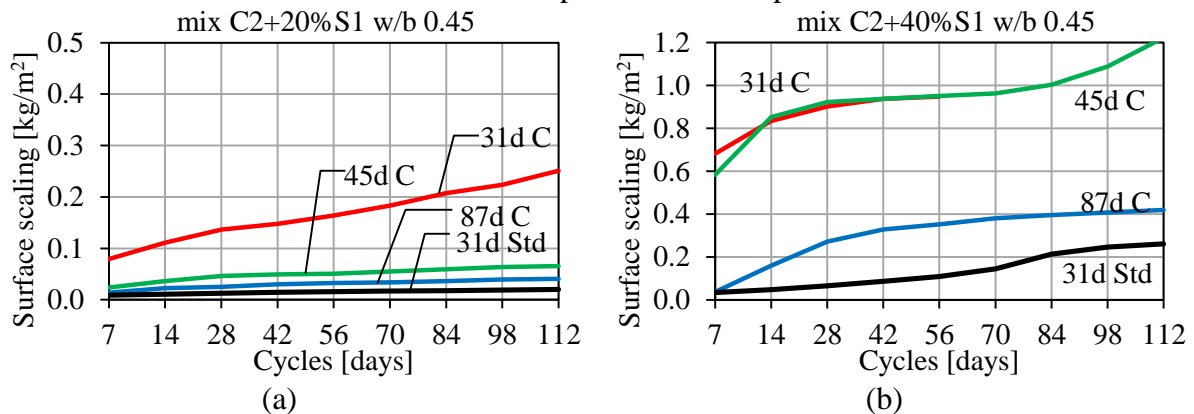

Figure 6: Example of surface scaling and the effect on curing conditions at different amounts of GGBS (note the different scales on the y-axis). (a) For mix C2+20%S1 *w/b* = 0.45 and (b) for mix C2+40%S1 *w/b* = 0.45.

In Figure 7 a comparison is made for a GGBS addition of 30% at *w/b* ratio of 0.45 and 0.40. Also here it can be seen that at *w/b* 0.45 that the scaling is much higher for 31d C and 45d C. But at *w/b* 0.40 difference are smaller and all meet the requirement for "good" frost resistance, while at *w/b* 0.45 it is only the standard procedure (31d Std) and the 87d C that meets the requirement. Figure 8 shows the results for two mixes with CEM II cements (C6 and C5) where an accelerated scaling occurs after a number of cycles for the more mature specimens. The reason for this type of behaviour is not clear but it could either be due to the prolonged water curing, giving rise to an increased water saturation, or due to that the concrete becomes more dense with prolonged curing and age, which could lead to increased hydraulic pressure.
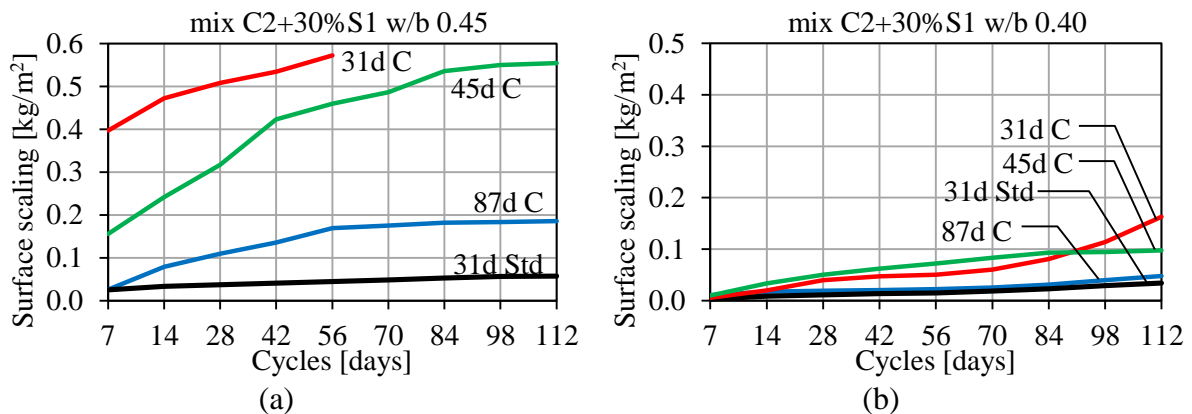
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Figure 7: Example of surface scaling and the effect on curing conditions and *w/b* ratio (note the different scales on the y-axis). (a) For mix C2+30%S1 *w/b* = 0.45 and (b) for mix C2+30%S1 *w/b* = 0.40.
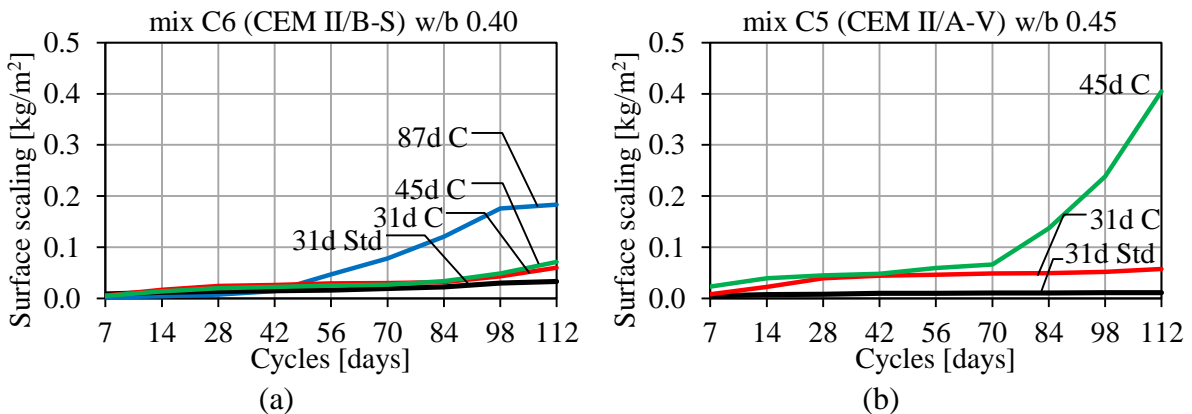

Figure 8: Example of surface scaling and the effect on curing conditions on late accelerated scaling for mature specimens. (a) For mix C6 *w/b* = 0.40 and (b) for mix C5 *w/b* = 0.45.

It has been suggested that the amount of scaling after carbonation correlates to the carbonation depth [8] and also that the carbonation will cause a coarsening of the pore structure leading to a higher water absorption for concrete with GGBS [3]. In Figure 9(a) the scaling at 56 cycles have been plotted against the carbonation depth for all mixes with GGBS and in Figure 9(b) the water uptake has been plotted against carbonation depth. The general trend is that scaling increase with increasing carbonation depth, but the correlation is only high (R^2 0.7 to 0.9) for the scaling and carbonation depth for 31d C ($R^2 = 0.83$) and 45d C ($R^2 = 0.75$). For 87d C the correlation is much lower. For the water uptake, there is trend indicating a higher water uptake with increased carbonation depth, but the correlation is moderate (R^2 0.5 to 0.7) or low (R^2 0.3 to 0.5). With respect to the measured carbonation depths for the accelerated carbonation (7 days in 1% CO_2) the measured depths (see Figure 2 and 9) should be compared to what is expected in field conditions (exposure conditions corresponding to XF4). Data from specimens exposed to atmospheric CO_2 during 11 year exposure at a field stations [10] showed a carbonation depth of about 1.1 mm with 30% GGBS at *w/b* 0.50 and 3.8 mm for a CEM III/B at *w/b* 0.50. At *w/b* 0.40 the carbonation depths were approximately 0.7 mm respectively 2.1 mm.

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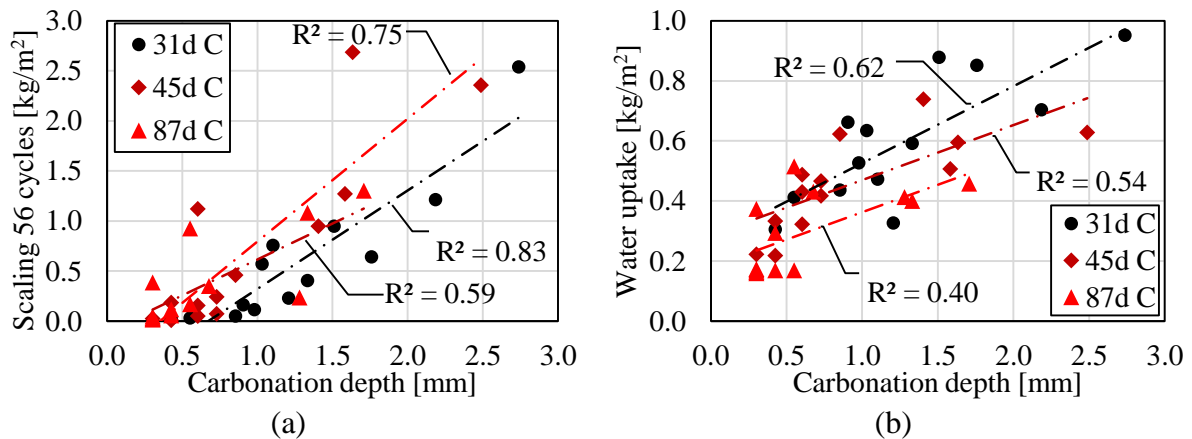22-24 August 2016, Technical University of Denmark, Lyngby, Denmark

Figure 9: Correlation between scaling after 56 cycles and carbonation (a) and between water uptake and carbonation (b) for all mixes containing GGBS.

In general, the coupled effect of carbonation and frost and ageing is complex. In this study all the tested concretes hade a larger scaling for specimens exposed to carbonation, this was also the case for the pure Portland cement and the fly ash cement, but the increase was rather small. For the concrete mixes with GGBS the increased scaling for carbonated specimens was dependent on the amount of GGBS and at low dosages (20%) and at low w/b the increase was small. In the literature there are different opinions and results reported with respect to ageing, [3] [5] [11], both positive and negative effects of ageing have been reported for concrete with Portland cement as well as for concrete with fly ash and GGBS. In light of the results from this study and what has been reported in the literature it seems plausible that the main mechanism(s) causing a change in the salt-frost scaling resistance is related to the coarsening of the pore system caused by carbonation at high GGBS amounts [3]. Prolonged curing or lowering the w/b ratio reduces the thickness of the carbonated layer and the scaling. However, it cannot be ruled out that there also could be a chemical effect. It has been reported that decomposition of monsulfate to ettrengite, due to carbonation or due to partly transformation into monochloride, can occur during the freeze-thaw cycles [12].

5. Conclusions

The effect of accelerated carbonation, 1 week in an atmosphere with 1% CO_2-concentration, on salt-frost scaling and the influence of different curing conditions has been studied. With the materials used and w/b ratios investigated it is clear that at 20% GGBS of total binder there is very little effect of carbonation on the frost resistance. Even with early accelerated carbonation at age of 21 days (31d C) all the tested concretes meet "good" scaling resistance or better after 112 cycles. For higher amounts of GGBS the early accelerated carbonation lead to increased scaling and especially at high amounts of GGBS (>40%). With prolonged curing the scaling generally decreased, but at higher GGBS content there was not that big difference between 31d C and 45d C (21 or 35 days when starting carbonation). For the longest curing time 87d C (77 days when starting carbonation) the scaling was lower and GGBS contents of 30% achieved good frost resistance and this was also the case for some of the mixes with 40% GGBS, but the scaling was higher. But it should also be pointed out that for the mixes with a higher slag content the compressive strength was much lower as an efficiency factor (k-value) of 1.0 was used. The following conclusions can be made:

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- The correlation between carbonation depth and scaling was high for specimens exposed early at the age of 21 and 35 days but lower for the specimens exposed at 77 days.
- With 20% GGBS of the total binder it was found that carbonation did not have a significant effect on the salt-frost scaling, even at early age carbonation.
- A GGBS content of about 30 to 40% is reasonable with respect to the salt-frost scaling resistance, but the testing and carbonation should not be done to early as this will produce a carbonation depth corresponding to more than 10 years natural carbonation.
- A prolonged curing regime before commencement of carbonation is needed if the test results should be realistic. In this study an age of 77 days when starting carbonation and 87 for start of frost cycles seems to have given reasonable results.

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