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Salt-Frost Scaling of Concrete with Slag and Fly Ash - Influence of Carbonation and Prolonged Conditioning on Test Results

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ABSTRACT

According to Swedish experience the slab method in CEN/TS 12390-9 is successful in predicting the salt-frost resistance of Portland cement concrete. However, doubts have been raised whether the same can be said when used on concrete with supplementary cementitious material, e.g. fly ash or ground granulated blast furnace slag (GGBS). Test results from concrete mixes with up to 35 % fly ash 65 % GGBS, with two different Portland cements and a water-to-binder ratio of 0.45 are presented in this paper. The tests were carried out with the standard method and with five modifications concerning the pre-conditioning of the specimens before freeze-thaw cycling. The age of the specimens at sawing was increased, the time in 65 % RH was prolonged and exposure to 1 % CO₂-environment was used. The results show that for air-entrained concrete with fly ash or GGBS both prolonging the exposure to 65 % RH and exposure to CO₂ diminishes the salt-frost resistance. The influence increases with increasing amount of fly ash or GGBS. However, the type of cement also has a certain influence. The influence of exposure to CO₂ on the salt-frost resistance of concrete without entrained air was totally different from the influence on concrete with entrained air.

Key words: Concrete, salt-frost resistance, freeze-thaw, carbonation, scaling, slag, GGBS, fly ash

1. INTRODUCTION

1.1 General

In Sweden requirement levels with regard to salt-frost resistance of concrete is set with the use of the slab method in CEN/TS 12390-9 [1]. This method was originally developed for Portland cement (CEM I) concrete and, according to more than 20 years of experience, has proven to be a useful tool to distinguish CEM I-concretes with a good salt-frost resistance from those which perform poorly. However, pure CEM I concrete is becoming less frequently used, since the use of supplementary cementitious materials (SCM), such as fly ash and ground granulated blast furnace slag (GGBS), to replace CEM I in concrete is steadily increasing. The question then arises, whether this method for evaluating the salt-frost resistance also gives results relevant for concretes with SCM. Some test results have shown that for instance aging and CO₂ exposure influence the salt-frost resistance of concrete containing GGBS to a much larger degree than CEM I concrete [2], [3] & [4].

A project was initiated in order to evaluate if the slab method gives reliable results also with concretes containing GGBS and fly ash or whether changes to the test procedures are needed when these materials are included, in order to predict the performance in field. In the project the method in CEN/TS 12390-9 and five modified versions of it have been used on 13 concrete mixes, containing different amounts of GGBS and fly ash. The modifications all concerned the pre-conditioning of the specimens before exposure to freeze-thaw cycling, and they were aimed to represent the influence of aging factors, such as concrete age, carbonation and desiccation.

In order to correlate results from laboratory tests with field exposure, specimens from the same mixes were also placed at the highway field site at RV40 in Borås, where de-icing salts are used. However, no results from the field exposure are included in this paper.

2. EXPERIMENTALS

2.1 Materials

Since this project was mainly aimed at validating the use of the method for exposure class XF4 according to EN206 [5], i.e. a road environment where de-icing salts are used, the main Portland cement (CEM I) used in this study is one commonly used in Swedish bridges, a CEM I 42.5 N - SR3 according to EN 197-1 [6] with a low alkali content (max 6 %), in the following named A-cement. In some mixes an ordinary rapid hardening CEM I, 52.5 R [6] was used, here called R-cement. In one case a CEM II/A-V [6] with about 16 % fly ash was used, here called B-cement. The Portland cement clinker in this cement was from the same source and had the same chemical composition as in the R-cement. All three cements came from the Swedish cement producer Cementa AB.

The ground granulated blast furnace slag (GGBS) was Merit 5000 from Merox conforming to EN 15167-1 [7] and the fly ash came from Norcem and was conforming to EN 450-1, Category

A [8]. The coarse aggregate consisted of 8/16 mm crushed granite, and the fine aggregate of natural graded deposits 0/8 mm. The superplasticizer used was Sika Visco Crete RMC-520PB and the air entraining agent was Sika AirPRO.

2.2 Concrete compositions and specimens

According to the Swedish application standard to the European concrete standard, SS 137003 [9], the requirement on maximum equivalent water-to-cement ratio, including the use of k -factors for the SCM:s (Type II additions according to EN 206 [5]), in exposure class XF4 is 0.45. This was therefore chosen as water-to-binder ratio for all the mixes, i.e. a $k = 1$ was used for the SCM:s. The decision to use $k = 1$ was based on that the k -factor for the same material differs, not only between countries but also within the same country, depending on local regulations, see for example [9]. Moreover, the concept of k -factors is not used when the same material is a constituent of a factory made cement, where the SCM:s are regarded as a constituent equal to Portland cement clinker.

The proportions between the CEM I and the GGBS or fly ash were chosen to reflect the limits between different cement types according to EN 197-1. In all cases except one, mix B(16F) where the B-cement containing fly ash was used, the CEM I and the GGBS or fly ash were mixed in the concrete mixer. The total binder content in all mixes was 400 kg/m³.

An air content of 5.0 % was aimed at for mixes with entrained air. Three mixes without entrained air were also included. A superplasticizing agent was used in all mixes to obtain a slump around 150 mm, and the measured slump in the mixes varied between 120 mm and 170 mm.

Table 1 – Composition of mixes

Designation	Cement type	Cement		GGBS		Fly ash		Air entraining agent
		kg/m ³	% ¹⁾	kg/m ³	% ¹⁾	kg/m ³	% ¹⁾	
AU	A-cement	400	100					No
A20SU	A-cement	320	80	80	20			No
A20FU	A-cement	320	80			80	20	No
A	A-cement	400	100					Yes
A20S	A-cement	320	80	80	20			Yes
A20F	A-cement	320	80			80	20	Yes
A35S	A-cement	260	65	140	35			Yes
A35F	A-cement	260	65			140	35	Yes
R	R-cement	400	100					Yes
R35S	R-cement	260	65	140	35			Yes
R35F	R-cement	260	65			140	35	Yes
R65S	R-cement	140	35	260	65			Yes
B(16F)	B-cement	400	100				(16) ²⁾	Yes
¹⁾ % of the total binder content								
²⁾ Included in the cement								

From the mixes 150 mm cubes were cast for the determination of the compressive strength, analysis of the air pore structure and for the salt-frost resistance test.

2.3 Tests - Properties of the fresh and hardened concrete

The density of the fresh concrete was determined according to EN 12350-6 [10] and the air content of the fresh concrete according to EN 12350-7 [11].

The compressive strength was determined in accordance with EN 12390-3 [12] on water cured cubes at 2, 28 and 91 days age. The reported results represent the average compressive strength of three cubes per age and mix.

The air pore structure was analysed on one specimen per mix in accordance with EN 480-11 [13].

2.4 Test - Salt-frost resistance

The test procedure for the slab method according to CEN/TR 12390-9 (here called 21-Bas) was used as a basis. In addition to the standard procedure five modifications of it were also used. The modifications all concerned the pre-conditioning of the specimens before subjecting them to freeze-thaw cycles. No changes to the freeze-thaw cycles were made.

The six pre-conditionings used in this study were:

- 21-Bas: According to CEN/TR 12390-9, slab method with salt
- 21-CO₂: According to CEN/TR 12390-9, slab method with salt, with the exception that after the pre-conditioning of the sawn half cubes in 65 % RH, they were placed in a climate chamber with 65 % RH and 1 % CO₂ for seven days.
- 21-3-RH: According to CEN/TR 12390-9, slab method with salt, except for the pre-conditioning of the sawn half cubes in 65 % RH which was prolonged from one week to three weeks.
- 21-11-RH: According to CEN/TR 12390-9, slab method with salt, except for the pre-conditioning of the sawn half cubes in 65 % RH which was prolonged from one week to eleven weeks.
- 91-Bas: According to CEN/TR 12390-9, slab method with salt, with the exception that the cubes were sawn at the age of 91 days instead of at 21 days age.
- 91-CO₂: According to 21-CO₂, With the exception that the cubes were sawn at the age of 91 days instead of at 21 days age.

A schematic representation of the six pre-conditionings can be seen in Figure 1.

The evaporation rate in the climate chamber used for CO₂ exposure (21-CO₂ and 91-CO₂) chamber was 95 g/(m²·h), which is higher than the 45 ±15 g/(m²·h), which is the requirement on climate chamber for slab test according to CEN/TS 12390-9.

All specimens with entrained air were exposed to 112 freeze-thaw cycles, in order to make sure that no sudden changes in the behaviour occur after 56 cycles. For the specimens without entrained air, exposure to 56 freeze-thaw cycles was assumed to be sufficient to result in scaling much larger than normally accepted limit values. At such high levels of scaling there is a risk that the method

no longer gives reliable results, due to disintegration of the specimens. The results show that this assumption was correct.

Detailed information of the experimental set-up can be found in [14].

Figure 1 – Schematic representation of the procedures of the six different pre-conditionings.

3. RESULTS AND COMMENTS

3.1 Air content, quality of the air pore system, density and compressive strength

The measured properties, other than salt-frost resistance, measured on the fresh and hardened concrete for all mixes are given in Table 2.

Table 2 – Air content, density and compressive strength for the mixes

Mix	Fresh concrete		Pore structure analysis		Hardened concrete			
	Density	Air content	Air content	Spacing factor	Density ¹⁾	Compressive strength		
	[kg/m ³]	[%]	[%]	[mm]	[kg/m ³]	2 d	28 d	91 d
AU	2393	2.0	-	-	2393	35.0	68.4	78.2
A20SU	2368	2.0	-	-	2373	20.2	54.1	61.7 ²⁾
A20FU	2340	2.3	-	-	2353	18.1	45.6	52.8 ²⁾
A	2289	5.9	5.8	0.160	2283	20.1	41.3	48.6
A20S	2270	5.8	4.5	0.147	2305	14.2	42.7	51.1
A20F	2271	5.4	8	0.052	2273	15.9	36.4	49.5
A35S	2271	5.5	5.0	0.157	2310	10.9	43.5	54.2
A35F	2253	5.0	5.3	0.077	2290	10.8	29.5	46.7
R	2326	4.9	3.1	0.255	2350	48.5	59.3	68.1
R35S	2288	5.2	3.6	0.164	2310	27.0	50.1	56.3
R35F	<i>n.a.</i> ³⁾	4.5	4.1	0.124	2327	31.9	46.7	57.7
R65S	2260	5.5	5.4	0.155	2280	10.5	40.6	50.3
B(16F)	2280	5.2	4.7	0.220	2290	33.7	47.5	56.7

¹⁾ Determined on specimens for compressive strength at 2 days age (average of 3).
²⁾ Determined at the age of 48 days
³⁾ Not available

The air content of the air entrained mixes measured on the fresh concrete is between 4.5 and 5.9 %. This is within the limits expected for these mixes, when taking into account acceptable tolerances according to EN 206 [5].

The microscopical pore structure analysis that was carried out on one specimen from each mix with entrained air, indicates a considerably lower air content in mix R than the one measured on the fresh concrete. Also, the mixes R35S and R35F show values lower than the 4.5 % pre-supposed as minimum value for this study.

There are no limits for air content for XF4 in the SS 137003 [9], since the salt-frost resistance shall be determined by testing. According to SS 137003, an air content of 4.5 % would be needed for these mixes in order to fulfil the requirement for exposure class XF3 and XF2 without frost testing. The tolerance for this value is 0.5 percent units, giving a minimum of 4.0 % air. Mixes R and R35F and, as anticipated, the mixes without entrained air have air contents below this value.

From the microscopical analysis one can deduce that the pore structure of all mixes with A-cement show acceptable air contents and a satisfactory space factor (< 0.2 mm), irrespective if the binder is only CEM I or with GGBS or fly ash. This indicates that the choice of air entraining agent was well adapted to this cement type. The mixes with R-cement have overall lower air contents than those with A-cement, and the difference is larger the more CEM I the mix contains. This observation is also supported by the measured densities of the mixes. Thus, the choice of air entraining agent was not optimal for mixes with the R-cement.

Figure 2 – Strength development of water cured cubes from mixes with and without GGBS.

The strength development for the water cured specimens with and without GGBS is shown in Figure 2 and can for the mixes with and without fly ash be found in Figure 3. The mixes without entrained air have higher compressive strengths at all ages than the mixes with entrained air and the same binder composition, which is quite natural since they have lower ratio between (water + air) and binder. For the mixes with A-cement and GGBS, which all have about the same air content, GGBS gives lower compressive strength at 2 days age but at 28 days and 90 days age the strength is comparable to those of the mixes without GGBS. When A-cement is combined with fly ash, the strength gain is lowered at 28 days, and it is not until after 90 days that the same level of compressive strength as for concrete mixes without fly ash is reached.

Figure 3 – Strength development of water cured cubes from mixes with and without fly ash.

The influence of GGBS and fly ash in mixes with R-cement is not as easily detected as for A-cement, due to the variation in air content. Mix R has higher strength values at all ages than would be expected if the air content had been around 5 %, which supports the observations of considerably lower air content in this mix. However, the form of the strength development curves indicates that the influence of GGBS and fly ash with R-cement is more or less similar to what was observed with A-cement.

3.2 Scaling

Classification

When evaluating the salt-frost resistance in the following the Swedish traditional classification, which can be found in SS 137244 [15] is used, which in a simplified form can be described as follows (m_{xx} is the scaling after xx freeze-thaw cycles):

Very good salt-frost resistance: $m_{56} < 0.1 \text{ kg/m}^2$

Good salt-frost resistance: $m_{56} < 0.2 \text{ kg/m}^2$ or
 $m_{56} < 0.5 \text{ kg/m}^2$ and $m_{56}/m_{28} < 2$ or
 $m_{112} < 0.5 \text{ kg/m}^2$

Acceptable salt-frost resistance: $m_{56} < 1 \text{ kg/m}^2$ and $m_{56}/m_{28} < 2$ or
 $m_{112} < 1 \text{ kg/m}^2$

Not acceptable salt-frost resistance: when the criteria above are not met

The scaling levels 0.1, 0.2, 0.5 and 1.0 kg/m^2 are marked in the figures, as relevant.

Concretes without entrained air

Three mixes without entrained air are included in the test series, all with the A-cement and with and without 20% GGBS and fly ash. These were subjected to maximum 56 freeze-thaw cycles and the scaling was extensive. All the six different pre-conditionings lead to larger scaling after 56 cycles than 1 kg/m^2 , which is the limit for acceptable salt-frost resistance according to SS 137244. Towards the end of the freeze-thaw cycling the scaling consisted of loose concrete

pieces and aggregate particles. In some cases, there was no salt solution left on the surface at cycles higher than 28 due to leakage, which has given less scaling than if the surface had been covered with salt solution constantly. Therefore, only the scaling values after 14 and 28 days for all pre-conditionings will be analysed here (Figure 4).

Figure 4 – Accumulated scaling after 14 and 28 cycles for mixes AU, A20SU and A20FU, all pre-conditionings.

Generally, the mix with 20 % GGBS shows the lowest amount of scaling closely followed by the pure CEM I mix while the mix with 20 % fly ash shows at least two times larger scaling for all pre-conditionings than the other two mixes.

Comparing 21-Bas and 91-Bas one can see that, as expected, the strength development has only a marginal effect on the scaling of the GGBS and the pure CEM I mix, while the scaling diminishes considerably for the fly ash mix.

CO₂-exposure has generally a positive influence on the scaling, both at higher and lower ages, but especially on the pure CEM I mix. The lowest scaling is for all three mixes achieved when the specimens are sawn at the age of 91 days and are then exposed to CO₂. However, the positive influence of CO₂-exposure is somewhat smaller for GGBS concrete than for the fly ash and pure CEM I concrete.

When studying the results from the tests with differing lengths of the pre-conditioning period in 65 % RH, one has to be aware of that not only the moisture condition of the surface is changed but also the degree of carbonation of the surface and the strength of the specimen has increased.

In this study, the differences between the scaling of the pure CEM I mix after one week (21-Bas), three weeks (21-3-RH) and eleven weeks (21-11-RH) are small.

For the mix with 20 % fly ash two weeks further conditioning in 65 % RH increases the scaling. Presumably, the concrete strength is not enough increased, and the pore structure is still not well developed, which makes the specimen sensible to drying. After 11 weeks pre-conditioning the fly ash concrete is more mature and less sensible to drying, and the scaling decreases.

As regards the mix with GGBS the largest scaling is achieved after 11 weeks of pre-conditioning in 65 % RH. This indicates that drying has a certain negative effect on the scaling, and carbonation does not give the same positive effect on the scaling of GGBS concrete as for the other two mixes.

Concretes with entrained air - without GGBS or fly ash

Scaling after 28, 56 and 112 cycles for the two mixes with pure CEM I with entrained air is shown in Figure 5.

Figure 5 – Accumulated scaling after 28, 56 and 112 cycles for mixes A and R, all pre-conditionings.

Generally, the scaling is larger for mix R than for mix A, which is anticipated since the air-pore system in mix R is not optimal. Mix A fulfils the requirements for very good salt-frost resistance according to SS 137244 for all pre-conditioning alternatives except 21-CO2, where it though clearly fulfils the requirement for good resistance. The salt-frost resistance of mix R is surprisingly good despite a non-optimal air pore system, and it fulfils the requirement for good salt-frost resistance for all pre-conditionings except 21-11-RH, where it fulfils the requirement for acceptable salt-frost resistance. Both mixes fulfil the requirement that the scaling shall not accelerate between 28 and 56 cycles for all pre-conditionings. The accumulated scaling during the whole test period for the different pre-conditionings of mix R is given in Figure 6. For all pre-conditionings there is an accelerating trend towards the end of the test. This trend starts at 42-56 cycles for 21-Bas and 91-Bas, while it appears later for the other pre-conditioning alternatives. Since the air content in this concrete is lower than expected, this may be due to that the air pores during the cycling at this point have been filled with so much water that a critical degree of water saturation in the concrete has been exceeded. It is probable that this tendency would not have been observed during the test if the air content had been higher.

As for the concrete without entrained air, increasing age at sawing has a positive influence on the salt-frost resistance for both mixes.

The effect of carbonation on the scaling of air entrained pure CEM I concrete is opposite to what is observed in concretes without entrained air. The scaling increases when the specimens have been exposed to CO₂ before the test with a factor between 2 and 3, both when sawn at 21 days

age and at 91 days age, but the scaling remains at a very low level. However, it must be noted that the very low scaling makes it difficult to draw any certain conclusions. The differing evaporation rate in the climate chambers and the doubled exposure period to 65 % RH may also influence the scaling.

Prolonged pre-conditioning in 65 % RH has only a marginal effect on mix A (NB that the scaling is so small that it is close to the measuring uncertainty). However, mix R shows a clearly increased scaling when the pre-conditioning period is 11 weeks. The increase appears at a very early stage of the freeze-thaw cycling (up to 28 cycles) which can be seen in Figure 6. After this point the scaling proceeds at approximately the same rate as for the other pre-conditionings.

Figure 6 – Accumulated scaling for the six pre-conditionings for mix R.

Concretes with entrained air - with and without GGBS

For the mixes with GGBS and entrained air the accumulated scaling after 28, 56 and 112 cycles are given in Figures 7 and 8 for the different pre-conditionings and mixes. However, the analysis is focused on the values after 56 cycles. Note that the vertical scale differs in Figure 7 and Figure 8.

From Figure 7 one can conclude that if 20 % GGBS is combined with an A-cement and is salt-frost tested without any pre-conditioning with CO₂ the scaling is approximately the same as for CEM I-concrete, irrespective if the sawing is carried out at 21 or 91 days age. If the amount of GGBS is increased to 35 % when combined with A-cement, the scaling increases for all pre-conditionings. However, the mixes still show good or very good salt-frost resistance for the pre-conditionings without CO₂-exposure. On the other hand, when 35 % GGBS is combined with the R-cement the increase of scaling is only marginal for pre-conditionings 21-Bas and 91-Bas.

Figure 7 – Accumulated scaling after 28, 56 and 112 cycles for mixes A, A20S, A35S, all pre-conditionings.

Figure 8 – Accumulated scaling after 28, 56 and 112 cycles for mixes R, R35S and R65S, all pre-conditionings.

If the specimens are exposed to CO₂ during the pre-conditioning the scaling increases, more the higher the GGBS content. The influence is larger when the CO₂ exposure starts at 28 days ages than at 91 days age. When the specimens are sawn at 21 days age CO₂ exposure increases the scaling after 112 cycles with a factor between 5 and 8 and when sawn at 91 days age the factor is between 3 and 5. However, if the GGBS content does not exceed 20 % the criteria for good salt-frost resistance are still fulfilled. The mix with 65% GGBS does not fulfil the criteria for acceptable salt-frost resistance after exposure to CO₂ in any case.

As can be seen in Figures 7 and 8 the scaling increases with increasing amount of GGBS when the pre-conditioning period is prolonged for all mixes with entrained air, but not as much as when the specimens are exposed to 1 % CO₂ for seven days.

Since the different scales in Figures 7 and 8 make comparison between mixes with different cements difficult, the values for the two mixes with 35 % GGBS is shown in Figure 9 for all pre-conditionings. It appears that when R-cement is combined with 35 % GGBS less scaling occurs

than when the same amount of GGBS is combined with A-cement, although the air content is somewhat lower. For the pure CEM I mixes the situation was opposite (Figure 5). Mix R has a lower air content, but that A-cement when used alone has a positive influence on the salt-frost resistance has also been shown in studies by Fagerlund [16]. The only pre-conditioning which leads to a larger scaling for 35 % GGBS in combination with R-cement than with A-cement is the one with long pre-conditioning time in 65 % RH, (21-11-RH).

Figure 9 – Accumulated scaling after 28, 56 and 112 cycles for mixes A35S and R35S, all pre-conditionings.

When comparing scaling after 56 cycles (21-CO2/ 21-BAS and 91-CO2/91-Bas) for A35S and R35S, one can conclude that the influence of CO₂-exposure on the scaling is at the same level for the two cement types in mixes (with 35 % GGBS).

Concrete with entrained air - with and without fly ash

Mix B contains a factory-made cement with about 16 % fly ash and with the same type of clinker as in the R-cement. Mix R can therefore be used as a fly ash free reference also for this mix.

The mixes with up to 20 % fly ash showed for all pre-conditionings scaling under 1 kg/m² after 56 freeze-thaw cycles while those with 35 % fly ash experienced scaling at a totally different level, with scaling up to 5.5 kg/m². Scaling for the mixes with maximum 20 % fly ash is shown in Figure 10, while scaling for mixes with 35 % fly ash can be seen in Figure 11.

A fly ash substitution of maximum 20 % does not lead to more than marginally increased scaling when tested according to the standard (21-Bas). Sawing at a higher age (91-Bas) reduces the scaling somewhat. However, the scaling is very small for all specimens tested according to Bas procedures making it difficult to draw any clear conclusions. Since fly ash leads to a slower strength development a significant difference between 91-Bas and 21-Bas was expected. The tendency can be seen but for these concrete qualities with high scaling resistance when tested according to the standard procedure (21-Bas) no large improvement as a result of prolonged pre-conditioning is observed.

After exposure to 1% CO₂ the scaling increases with a factor between 3 and 4 for the mixes with maximum 20 % fly ash while the increase is much smaller for those without fly ash. In all cases the mixes with maximum 20 % fly ash fulfil the requirement for acceptable or good salt-frost resistance after CO₂ exposure. For exposures 21-Bas and 91-Bas the requirements for very good or good salt-frost resistance are fulfilled.

The slow strength and structural development up to 90 days age in fly ash concrete leads to that the concrete is more sensitive to drying during this period. This which becomes evident when comparing 91 Bas and 21-11-R in Figure 10, where the specimens have the same age at the start of freeze-thaw cycling but are stored under different ambient conditions. The scaling of A20F clearly increases when the pre-conditioning in 65 % RH is prolonged. For the mixes with the more rapid R-cement, the scaling is not significantly increased when pre-conditioning 21-3-RH is applied. But when 21-11-RH is used, the fly ash mix (B16F) shows considerably more scaling than the mix without fly ash (mix R).

If the amount of fly ash substitution is increased to 35 % the scaling becomes much greater, as can be seen in Figure 11. When the scaling is as large as for these mixes, there is a large risk that the surface of the specimens has not been kept moist during the entire cycling due to leaching of the salt solution caused by disintegration of the specimens, and scaling at later cycles may be misleading. Therefore, the comparisons are based on the scaling after only 28 and 56 cycles.

Figure 10 – Accumulated scaling after 28, 56 and 112 cycles for mixes A, AS20F, R and B(16F), all pre-conditionings.

The mix with R-cement has generally a lower scaling than the mix with A-cement. The only pre-conditioning that leads to any changes worth mentioning is to let the specimens age to 91 days before sawing and freeze-thaw cycling (91-Bas). In that case mix R35F fulfils the requirement for acceptable salt-frost resistance, while mix A35F lies just above the limit. For all

other pre-conditionings the scaling is much higher than the limit for acceptable salt-frost resistance.

No clear influence of the length of the pre-conditioning period can be seen for these mixes with 35 % fly ash. Neither has exposure to CO₂ any clear influence when it is carried out at early age (21-CO₂). However, when it is carried out later (91-CO₂) it increases the scaling substantially compared to for 91-Bas. However, the scaling is still at about the same level as the minimum level of the rest of the pre-conditioning alternatives.

After three weeks in 65 % RH all these mixes with low fly ash contents fulfils the criteria for good salt-frost resistance and after eleven weeks in 65 % RH the criteria for acceptable salt-frost resistance are fulfilled.

Figure 11 – Accumulated scaling after 28, 56 and 112 cycles for mixes A35F and R35F, all pre-conditionings.

5. DISCUSSION

The results from the salt-frost testing show that there is a clear difference of the influence of type of binder, carbonation and desiccation on the salt-frost resistance on concretes with and without entrained air.

5.1 The importance of air pores and the capillary pore system for the salt-frost resistance

In concrete without entrained air the salt-frost resistance mainly depends on the pore-size distribution and its connectivity (gel and capillary pores) and the amount of freezable water in the pores, i.e. its water-to-binder ratio, age, type of binder, self-desiccation and degree of pore filling. For all types of binders, the concrete remains salt-frost resistant if the water-to-binder ratio

is sufficiently low and it has reached a high enough degree of hydration [17]. At what water-to-binder ratio and age this occurs depends on the binder composition. At very low water-to-binder ratios the concrete self-desiccates and it has such a low permeability that the pore volume which is emptied from water due to self-desiccation will not be filled with water even after long term exposure to external water.

Introduction of air pores increases the salt-frost resistance radically. However, the influence of air pores also varies with several parameters, among others the water-to-binder ratio and the binder composition. The salt-frost resistance of concrete with entrained air depends on the contribution to the salt-frost resistance of the concrete pore structure (capillary and gel pores) and on the contribution of the entrained air pores. The contribution of the air pores is in certain cases dominating and in other cases of minor importance. In order for the air pores to be effective, it is necessary that the air content is sufficient, the air pores are of appropriate size and that they are well distributed in the cement paste. Additionally, it is important that the air pores are surrounded by a cement paste with an appropriate pore-size distribution, which enables an effective use of the extra space for expansion that the air pores provide. If the capillary pore structure is too dense the transport of water to these pores during freezing is obstructed and they can not be fully exploited. If the capillary pore structure is too coarse, the air pores do no longer function as isolated air-filled bubbles providing room for expansion. In [18] it was shown that the influence of air pores on the salt-frost resistance is largest in the water-to-binder interval 0.45 - 0.65.

5.2 Influence of GGBS and fly ash on scaling at salt-frost testing

On concrete mixes without entrained air

The tests of concrete mixes without entrained air in this project has only been performed on three compositions, all with A-cement and at water-to-binder ratio of 0.45. The mixes had 20 % fly ash, 20 % GGBS and no additions, respectively. In these tests the mix with GGBS showed the least scaling, closely followed by the CEM I mix. Fly ash had a clear negative effect on the salt-frost resistance. At this water-to-binder ratio level neither of them provided an acceptable salt-frost resistance in any of the six pre-conditioning alternatives.

A number of compositions without entrained airs and with different binders (but none with fly ash) and water-to binder ratios were tested in [17] with the same test method as in this project. Ggbs leads to a higher salt-frost resistance, even at as high contents as 70%. Of the cements, the same A-cement as in this project, gave most scaling while CEM I with smaller grain size showed better salt-frost resistance. As in this project, no binder composition achieved acceptable salt-frost resistance at a water-to-binder ratio of 0.45. For CEM I mixes and mixes with low amounts of additions the water-to-binder ratio had to be lowered to around 0.3 in order to obtain acceptable salt-frost resistance. With 70 % GGBS this could be achieved at a water-to-binder ratio of 0.35.

On concrete mixes with entrained air

Figure 12 shows the difference in scaling after 28 cycles between mixes without and with entrained air, for the preconditioning alternatives 21-Bas and 91-Bas. From this figure it becomes clear that the effect of the air pores is highest for the mix with 20 % fly ash, and least for the mix with 20 % GGBS.

Figure 12 – Difference in scaling after 28 freeze-thaw cycles between mixes without entrained air and mixes with entrained air (AEA = air entraining agent).

The study in [17] also comprises tests on the same compositions but with entrained air. The target value for the air content was 4.5 %. The striking feature of these test results compared to those without entrained air is that the influence of binder type is reversed. A-cement has the best salt-frost resistance while finer cements and increasing amounts of GGBS give more scaling. One can conclude that the effectivity of the air pores is highest for the A-cement. At GGBS contents of 30 % and higher the air pores are not at all as effective. With 70% GGBS, entrained air gives hardly any contribution at all at water-to-binder ratio 0.5 and below. The observation in [17] agrees well with the trends in the present study.

In the project presented in this paper, only one type of GGBS has been used, which limits the possibility to draw conclusions which are valid for all GGBS that fulfils EN 15167. Löfgren and co-workers [19] have tested concrete mixes with partly different binders (among others three different CEM I and two different GGBS) with water-to-binder ratios 0.40 and 0.45 and GGBS contents up to 70 % with the same salt-frost testing method, and with somewhat differing variations of pre-conditionings than in this project. The results of that project show that GGBS with different origins give somewhat differing scaling. The same GGBS as was used in this project gives somewhat higher scaling than another GGBS which has a lower MgO content. It is also evident that a lowering of the water-to-binder ratio to 0.4 gives better salt-frost resistance for mixes with GGBS. In the study in [19] only two mixes with fly ash were studied where the fly ash content was as low as around 16 % and the salt-frost resistance was only affected marginally. This is in line with the findings of the present study.

Another project in which the salt-frost resistance of concrete mixes with different binder compositions was investigated is presented in [20]. It includes mixes with water-to-binder ratios between 0.35 and 0.44 which all contained 4 % silica fume and between 17 and 50 % fly ash, and 48 or 75 % GGBS respectively. The same tendencies as regards the influence of GGBS and fly ash on the salt-frost resistance as in this project were experienced in that project.

Influence of carbonation on the scaling at the salt-frost testing

When a concrete carbonates CO_2 reacts with $\text{Ca}(\text{OH})_2$ in the cement paste. The $\text{Ca}(\text{OH})_2$ may come from portlandite or from the CSH gel, see [18]. Irrespective of the origin of the $\text{Ca}(\text{OH})_2$ one water molecule of chemically bound water is released in this reaction. The total pore volume diminishes somewhat, since the volume of the reaction product is greater than the volume of the involved $\text{Ca}(\text{OH})_2$. What influences the moisture properties more is the fact that the gel water decreases with the same amount of water as the chemically bound water released in the carbonation reaction [14]. In [14] it is also shown that the capillary and gel pore structure is coarsened by carbonation. This diminishes the hygroscopicity of the concrete, i.e. the capability to bind non-evaporable water in the pore system. The pore volume in the non-hygroscopic range (above 98 % RH), which will only be filled with water when the specimen is surrounded by free water, increases.

The decreased hygroscopicity of the concrete due to carbonation may be the reason why the specimens without entrained air show better salt-frost resistance after long-time field exposure than when tested in laboratory [21]. The surface may dry and carbonate intermittently during the exposure and when the surface is again exposed to water only the outermost surface layer is water filled. At testing according to the laboratory test method, the surface is exposed to liquid almost continuously.

On the other, carbonation diminishes the salt-frost resistance of air entrained concrete for all mixes. In this case the changes in the gel- and capillary pore structure clearly diminishes the effectivity of the air pores. As shown in [18] the changes in the pore structure due to carbonation is largest when GGBS is incorporated in the mix, somewhat less extensive with fly ash and least in CEM I mixes. However, if the scaling without exposure to CO_2 is as low as 0.2 kg/m^2 after 56 freeze-thaw cycles or below, the concrete normally still exhibits good salt-frost resistance after CO_2 exposure (scaling less than 0.5 kg/m^2).

One week of exposure to 1 % CO_2 in addition to the standard test method was also used in the projects [19] and [20] discussed in the previous section, however not in exactly the same way as in the present project. The scaling after 56 cycles increased in these three studies with a factor between 2.3 and 4.7, when one week of exposure to 1 % CO_2 was added. The average increase when the specimens were sawn at 21 days age in the present project, was at approximately the same level as the increase reported in [22] for specimens conditioned at atmospheric CO_2 -levels for one year before testing compared to when tested according to the standard procedure.

Exposure to 65 % RH during longer periods also causes a coarsening of the capillary pore structure, however without diminishing the gel water content. The degree of coarseness of the capillary pore structure depends on several factors, it varies with the fineness of the cement, and addition of fly ash and GGBS. For all air entrained mixes prolonging the pre-conditioning in 65 % RH causes an increase in scaling. CEM I mixes are not particularly affected, but R-cement is more sensitive than A-cement. With increasing amount of GGBS the scaling increases with increasing exposure time. If the amount of GGBS does not exceed 35 % the scaling after 11 weeks pre-conditioning is still on an acceptable level. However, this is not valid with 65 % GGBS.

There is a decisive difference between the test method and what happens in real structures. In the method the surface is all the time covered with liquid and no carbonation or drying takes place during the freeze-thaw cycling, only during the pre-conditioning. In field, periods of freeze-thaw cycles alternate with periods when the surface can dry and carbonate. Which type of carbonation

and exposure to 65 % RH that represents what happens in field can only be decided when field tests of the same mixes are evaluated. Such field tests of mixes from this project are on-going.

6. CONCLUSIONS

The results from the salt-frost testing show that there is a clear difference of the influence of type of binder, carbonation and desiccation on the salt-frost resistance between concretes with and without entrained air.

In concrete without entrained air the salt-frost resistance mainly depends on the pore-size distribution and its connectivity (gel and capillary pores) and the amount of freezable water in the pores, i.e. its water-to-binder ratio, age, type of binder, self-desiccation and degree of pore filling. These parameters also influence the salt-frost resistance of concrete with entrained air, but the most important factor for providing salt-frost resistance is then the quality of the air pore system (size and distribution of the air pores). However, the efficiency of the air pores also seems to depend on the properties of the gel and capillary pore structure and the denseness of the surrounding mortar. For concrete with entrained air, mechanisms that lead to changes in the gel and capillary pore structure also alter the salt-frost resistance even if the air pore system remains intact. Use of SCM, carbonation and desiccation change the gel and capillary pore structure, which influences the effectivity of the air pore system and leads to differing salt-frost resistances.

The salt-frost resistance of concrete without entrained air and with a water-to-binder ratio of 0.45 is affected positively by replacing 20 % of the CEM I with GGBS, while the effect of 20 % fly ash is clearly negative. However, in all concretes without entrained air the scaling is far beyond what is considered to represent acceptable salt-frost resistance.

Limited amounts (maximum 20 %) of GGBS and fly ash only affect the salt-frost resistance of concrete with entrained air and water-to binder ratio 0.45 marginally. Good salt-frost resistance (scaling maximum 0.5 kg/m² after 56 cycles) can be achieved even after carbonation and eleven weeks of exposure to 65 % RH. With 35 % fly ash and 65 % GGBS the scaling is extensive and the salt-frost resistance poor.

Exposure to CO₂ prior to the freeze-thaw cycling has a negative effect on all air entrained concretes. The influence increases with increasing amount of GGBS and fly ash, and it is particularly large for mixes with GGBS. However, if the scaling without exposure to CO₂ is as low as 0.2 kg/m² after 56 freeze-thaw cycles or below the concrete normally still exhibits good salt-frost resistance after CO₂ exposure (scaling less than 0.5 kg/m²). The effect of CO₂ exposure on concrete without entrained air is on the contrary positive.

The salt-frost resistance of concrete with entrained air and higher amounts of fly ash or GGBS is decreased when the specimens are exposed to 65 % RH for extended periods before the freeze-thaw cycling, however not to the same extent as after CO₂ exposure.

The influence of longer exposure to 65 % RH on concrete without entrained air and with maximum amount of GGBS or fly ash of 20 % is only marginal

Sawing the specimens and starting the freeze-thaw cycling later gives better salt-frost resistance for all mixes, with or without entrained air, with or without GGBS or fly ash. The positive effect is particularly large for concrete with 35 % fly ash.

The cement type (CEM I) also influences the salt-frost resistance. The more coarsely ground A-cement, which is sulfate resistant and has a low alkali content, provides better salt-frost resistance than the more rapid hardening ordinary R-cement when used as the only binder. But in combination with GGBS or fly ash the R-cement gives less scaling than the same combinations with A-cement

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