Replacement of Cement by Limestone Filler or Ground Granulate Blast Furnace Slag: the Effect on Chloride Penetration in Cement Mortars.

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ABSTRACT

This paper describes field trials carried out to examine the effect on the chloride penetration in cement mortar when a certain amount of the cement binder is replaced by limestone filler or granulate blast furnace slag. Limestone fillers produced from three different calcareous carbonates were used. The amount of replacement of cement by filler varied between 12 % and 24 %. The ground granulated blast-furnace slag (GBFS) used in the tests was a commercially available Swedish product, with replacement varying from 20 to 65 % of the binder content.

Key words: chloride diffusion. ground granulated blast-furnace slag. limestone filler.

1. INTRODUCTION

Alternative materials for partial replacement of Ordinary Portland Cement in concrete are widely used around the world, and are becoming more and more common. The reasons for using alternative materials are environmental, economic, or technical benefits. Common alternative materials include granulated blast furnace slag, silica fume, fly ash and limestone filler. The kind of alternative material that is used often depends on the availability and on the field of application.

Structures exposed to very harsh conditions are often made of concrete, due to the material's great durability. Examples of such harsh conditions are marine environments such as bridges, harbours or road environments where deicing salts are used. However, despite its great durability, concrete does deteriorate, and the cause is often due to chloride-induced reinforcement corrosion. This is a multifaceted phenomenon, where chloride penetration, chloride binding, and threshold values for corrosion initiation are detrimental factors.

This paper describes studies carried out to examine the effect on chloride penetration of mortars when a certain amount of the cement binder is replaced by limestone filler or granulate blast furnace slag. It is a part of a larger investigation where the other above-mentioned detrimental factors concerning chloride-induced reinforcement corrosion are studied. Chloride penetration data from accelerated laboratory experiments has previously been reported by the author [1,2]. This paper focuses on the measured chloride penetration profiles of mortar specimens submerged in seawater for up to three years.

2. MATERIALS

2.1 Constituent materials

The physical and chemical properties of the cement/additives/fillers used throughout the experimental program, as given by their producers, are shown in Tables 1 and 2. The aggregate used was CEN standard sand in accordance with EN 196-1 [3], and the cement was a CEM I 52.5 R product conforming to EN 197-1 [4].

Fillers produced from the three different qualities of natural calcium carbonate were used in this study, see Table 2. Type LL is a calcium carbonate filler manufactured from a high-purity white limestone from France. Type MA is a white marble powder with high purity from Austria, while type CH filler is a Danish calcium carbonate powder from a more recent origin than the two others, and can be defined as a fine microcrystalline sedimentary chalk. The size of the crystals is coarsest for the marble calcium and finest for the chalk. The calcium carbonate content of all three limestone qualities was $\geq$ 98 % by mass.

The ground granulated blast-furnace slag (bfs) used in the tests is a commercially available Swedish product called Merit-5000.

Table 1 – Chemical composition of the cement and slag

Chemical composition	Cement (%)	Slag (%)	Mineralogical composition of cement	(%)
CaO	64.1	31	C_3S	62.8
SiO_2	20.9	34	C_2S	12.4
Al_2O_3	3.8	13.1	C_3A	5.5
Fe_2O_3	2.7	0.2	C_4AF	8.3
SO_3	3.4	1.41		
MgO	2.8	17.0		
K_2O	1.1	0.52		
Na_2O	0.3	0.54		
Cl	0.02	0.01		

Table 2 - Physical characteristics of the cement, slag and limestone fillers used

Material	Designation	Mean particle size (µm)	Specific surface. BET (m^2/kg)
Cement	CEM	8	1760
Chalk	CH	2.3	2200
Limestone	LL	5.5	1000
Marble	MA	7.0	1500
Slag	BFS	8	470 (Blain)

Blaine fineness of the cement: 550 m^2/kg .

2.2 Mortars

Five different mortar mixtures were cast with Ordinary Portland Cement as the only binder, with water/binder-ratios ranging between 0.4 and 0.8. Another four different mortar mixtures were cast where a part of the Ordinary Portland Cement was replaced with limestone filler (binder = OPC + limestone). Finally, three different mortar mixtures were cast, where a part of the Ordinary Portland Cement was replaced with slag (binder = OPC + slag). The mixture compositions are shown in Table 3.

For all the mixes, the aim was to reach about the same consistency without using any chemical additives. This was accomplished by keeping the water content fairly constant and altering the cement content. The consistency was determined as described in European Standard test method EN 1015-3 [5].

The air contents, which were measured in accordance with Swedish Standard SS 13 71 24 [6], were relatively high, although no air entraining agents were used. This is probably a result of the fine-grained aggregate and the high paste volume. The variations between the different mixtures were small, with the air contents varying from 4.8 % to 6.0 % (except in one case). This indicates that variations of the air contents between the mixes do not influence the test results very much. The 28-days compressive strengths are also shown in Table 3, and were determined in accordance with European Standard EN 196-1 [3].

Table 3 – Mortar mix proportions used in the experimental study

Mortar	W/B	Cement	Limestone filler	Slag	Water	Aggregate	Air	Consistency	28 days compressive strength
		(kg/m^3)	(kg/m^3)	(kg/m^3)	(kg/m^3)	(kg/m^3)	(%)	(mm)	(MPa)
Cement									
OPC-0.4	0.40	702			281	1263		169	82.4
OPC-0.5	0.50	500			250	1500	4.9	170	66.7
OPC-0.6	0.60	413			248	1593		176	48.5
OPC-0.7	0.70	345			242	1666		168	42.2
OPC-0.8	0.80	319			255	1654		172	33.2
Cement and limestone filler									
LL12-0.5	0.50	440	60		250	1500	5.0	175	62.3
LL24-0.5	0.50	380	120		250	1500	4.7	180	48.6
MA24-0.5	0.50	380	120		250	1500	6.0	178	47.3
CH24-0.5	0.50	380	120		250	1500	4.8	173	49.8
Cement and slag									
BFS20-0.5	0.50	400		100	250	1500	5.3	185	58.7
BFS35-0.5	0.50	325		175	250	1500	6.0	184	65.0
BFS65-0.5	0.50	175		325	250	1500	5.3	195	57.3

3.   TEST PROGRAM

3.1   Specimens and exposure

The specimens for field exposure were cast in plastic moulds with an inner diameter of 145 mm and a length of 250 mm. 20 mm-thick slices were cut away from the ends of the specimens after about one month of water curing. The specimens, still in the plastic moulds, were then transported to the field exposure site and submerged in the sea in "open" plastic boxes, exposing the two newly cut surfaces to seawater, see Figure 3.
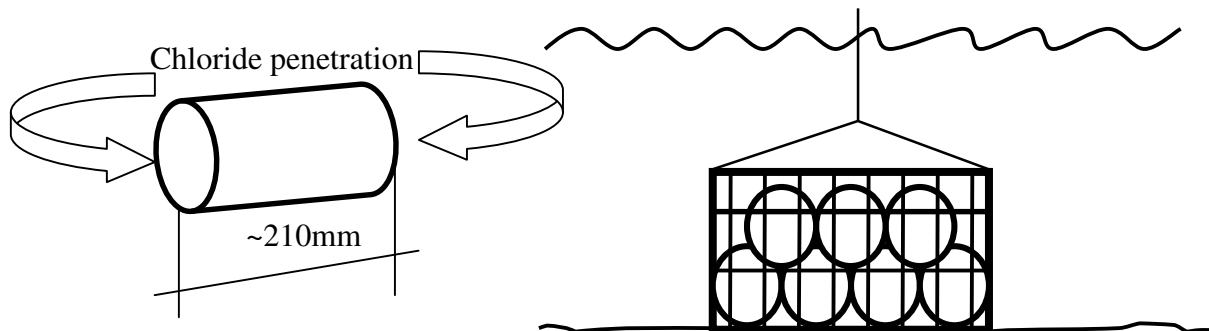

Figure 3 – Specimens, and the arrangement for immersing them in the sea.

The field exposure site is situated in Träslövsläge, on the south-western coast of Sweden. The exposure conditions at the site are well documented [7]. The chloride concentration in the seawater varies with time, from 10 to 18 g per litre, and the water temperature normally has an annual variation ranging between + 20 °C and + 2 °C.

3.2   Measurement of chloride profiles

After about three years submerged in the sea, two specimen of each kind of mortar were brought back to the laboratory for analysis. Each specimen was individually sealed in double-thickness plastic bags, and stored at room temperature for no longer than three weeks prior to measurement of chloride profiles. Cores with a diameter of 100 mm were taken from the centre of the specimens, and were then sawn in the middle. Three chloride profiles were determined.

For the measurement of chloride profiles, powder samples were taken by dry-grinding with a drill gradually from the exposed surface to a certain depth. Powder samples were taken at small depth intervals close to the exposed face, and thereafter the interval increased gradually. At least ten powder samples were taken for each profile, depending on the chloride ingress depth. The depth of each powder sample taken was measured manually with a sliding calliper with an accuracy of about 0.5 mm. From each depth, about 10 g of powder was ground, collected and stored in small sealed plastic bags until testing. Before testing, a sample of about 1 g from each depth was dried at 105 °C for 24 h and then tested for chloride content.

The acid-soluble chloride content in each sample was determined principally in accordance with AASHTO T260 [8], using potentiometric titration on an automatic titrator (Metrohm Titranor 716), with a chloride-selective electrode and an Ag/AgCl reference electrode. This method has shown good repeatability and reproducibility in round-robin tests, and in addition

the measured values agree very well with the expected "true" values [9]. After titration of chloride ions, the soluble calcium content of the same sample solution was determined in order to estimate the binder content. The method for determining the soluble calcium content is described in detail in [10].

The binder content was estimated, since the chloride content in concrete is often reported by many researchers as the mass percentage of binder, because of the heterogeneity of concrete and the limited sample size in this kind of measurement.

Because the aggregate consisted of only siliceous material (CEN NORMSAND EN 196-1) the binder content in the different powder samples could be determined through the soluble calcium content, using Equation 1.

$$Binder = \frac{CaO_{sample}}{CaO_{Binder}} \times 100 \tag{1}$$

3.3 Chloride profiles and curve-fitting parameters, D_{F2} and C_s

The chloride ingress model chosen to evaluate and describe the measured chloride profiles in this study is the frequently-used empirical model based on Fick´s 2nd law, expressed as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{2}$$

The analytical solutions for Eq. 2 depend on the boundary conditions. In this study, two types of boundary conditions occur: the semi-infinite boundary condition (single-sided penetration) and the case with limited thickness (double-sided penetration).

For the semi-infinite case, when the chloride ions did not penetrate the centre of the specimen, and with conditions:

$$C(x, t = 0) = C_i \qquad C(x = 0, t) = C_s$$

the analytical solution is [12] :

$$C(x,t) = C_i + (C_s - C_i)\left(1 - erf\left(\frac{x}{2\sqrt{D_{F2}t}}\right)\right) \tag{3}$$

Where $C(x,t)$ is the chloride concentration at depth x after exposure period t, C_i is the initial concentration in the mortars (in this study measured at around 0.05 mass% of binder for all mixtures), C_s is the chloride concentration at the exposure surface, D_{F2} is the chloride diffusion coefficient, and erf is the error function.

Because the chloride from the seawater could penetrate the specimens from both sides after three years of exposure, chloride ions had penetrated through the centre of some specimens. Equation 3 cannot be used in these cases, because the boundary is no longer semi-infinite.

Nilsson [11] suggested that, in these cases, Equation 4 can be used, which also is a solution to Equation 2, but for double-sided penetration, and can be found in Crank [12].

$$\frac{C(x,t)-C_i}{(C_s-C_i)} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp\left(-(2n+1)^2 \cdot \frac{\pi \cdot F_0}{4}\right)\cos\left(\frac{(2n+1)\pi}{2}\left(1-\frac{x}{L}\right)\right) \quad (4)$$

Where the Fourier number, F_0, is equal to:

$$F_0 = \frac{D_{F2}t}{L^2} \quad\quad\quad (4.1)$$

The rest of the parameters in Equation 4 correspond to the parameters in Equation 3, with the addition of parameter L, which is the half-thickness of the specimen.

A lot of theoretical issues can be highlighted when the above equations are used in chloride penetration models for mortars and concretes [13,14]. Nevertheless, curve-fitting of the measured chloride profiles to Eq. 3 or Eq. 4 was used to obtain the regression parameters, D_{F2} and C_S. These two parameters should not be seen as direct material properties, but as regression parameters, describing the chloride ingress under a specific exposure condition and after a specific exposure time [7].In the following of this article D_{F2} and C_S will be referred as the "apparent diffusion coefficient" respectively the "apparent surface chloride content", as suggested in [13, 14].

The curve-fitting procedure of measured chloride profiles is a very subjective matter. One of the reasons for this is the often irregular behaviour observed close to the exposure surface on measured chloride profiles. This irregularity occurs as a deviation of the measured profile compare to the fitting curves obtained from Equations 3 and 4, and is shown in Figures 2 and 3. The point from where the curve-fitting is started, and the amount of accessible measured points in this critical area, will have a huge influence on the regression parameters, D_{F2} and C_S.

For most measured chloride profiles, the deviation from an expected diffusion profile (from the solutions of Fick's 2nd law) seemed to occur at the same depth as that at which the parallel measured binder content had a tendency to decrease from the bulk quantity. This leaching of the binder content and the irregularity of the chloride profile can be seen in Figures 2 and 3. The majority of the regression analyses were therefore made with this certain depth as starting point. For the chloride profiles which did not fallow this pattern, the starting point was chosen by omitting the first one or two measuring points if the values significantly diverged from the expected diffusion profile.

Beside the regression parameters, D_{F2} and C_S, the depth, X_c from the exposure surface to the starting point of the curve-fitting, and the chloride ion concentration, C_x at that point, are presented in the results. Further, the correlation coefficient, R^2, for each curve-fitting is also specified. One or three sets of curve-fitting parameters for each mortar quality are presented in the result section, depending on, if double-sided (chloride ions had penetrated through the centre of the specimens) respectively single-sided penetration occurred.
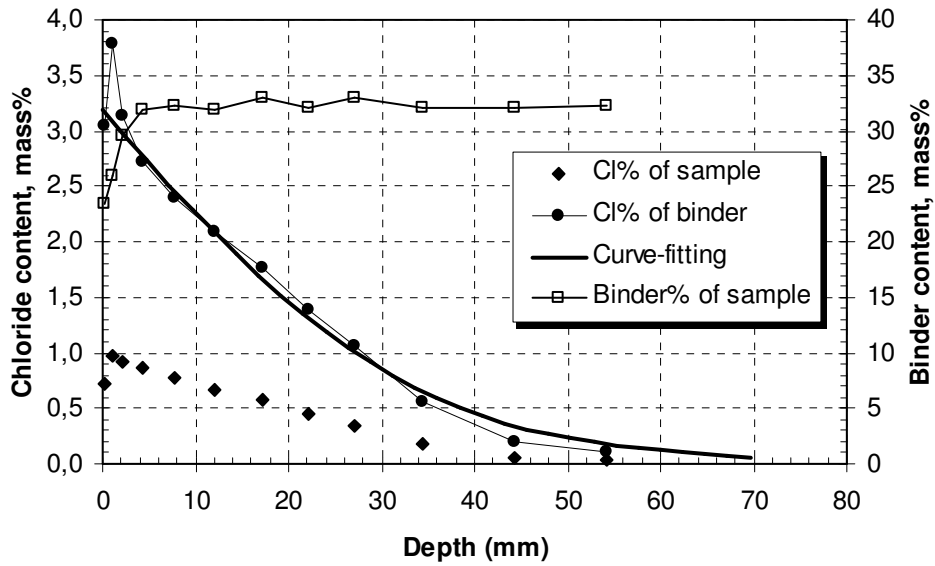
Figure 2-Curve fitting of the measured profiles to the error-function solution to Fick´s 2nd law (single-sided penetration).
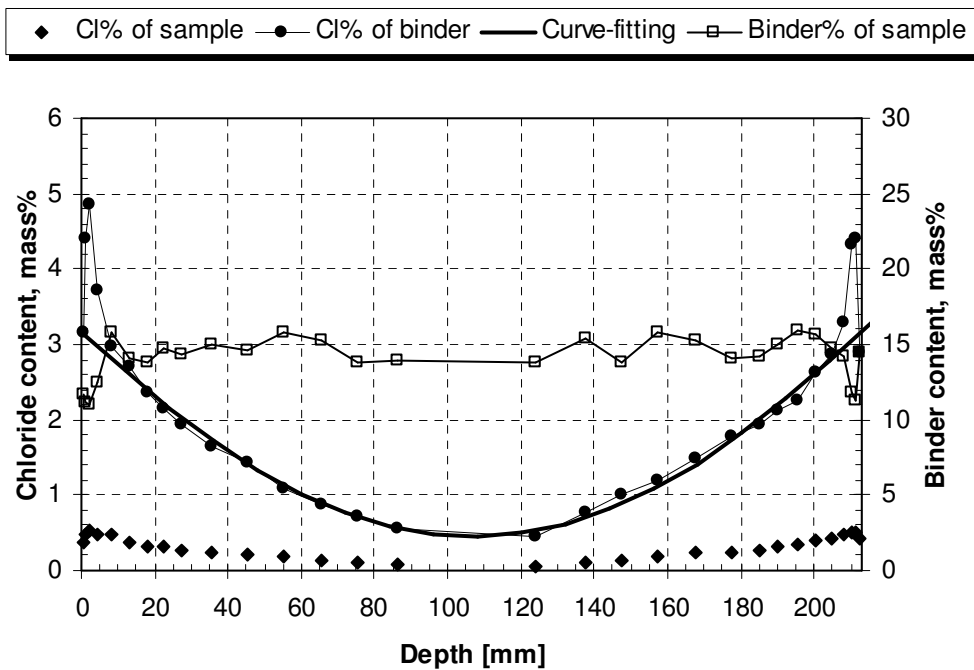

Figure 3-Curve fitting of the measured profiles to limited thickness solution (Eq 4) to Fick´s 2nd law (double-sided penetration).

4 RESULTS AND DISCUSSIONS

4.1 Ordinary Portland Cement

The results from the regression analysis for the mortars with Ordinary Portland Cement (OPC) are summarised in Table 4 and in Figures 4 and 5. For all mortars with OPC as the binder, the starting point for the regression analysis was chosen as the depth where the binder content was equal to the bulk binder content, and as close to the exposure face as possible.

Figure 4 shows the relationship between the "apparent diffusion coefficient", D_F, and water/binder ratio. As expected, the D_{F2} value increases with water/binder ratio, and the increase is almost linear, the results are in accordance with accelerated laboratory studies presented in [1, 15]. No relationship could be found between the "apparent surface chloride content", C_s, and water/binder ratio from Fig. 5.

Table 4 – Curve-fitted coefficients for OPC mortars after a field exposure of 1140 days

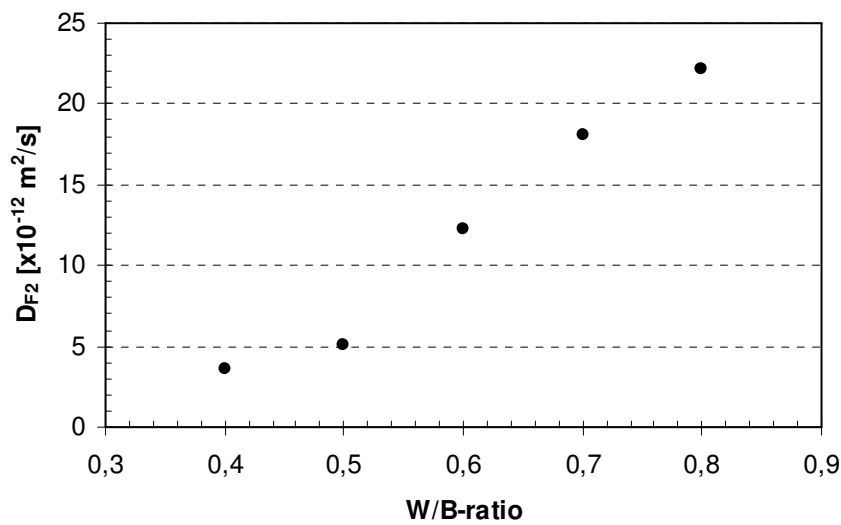| Mortar	D_{F2} ($*10^{-12}$ m^2/s)	C_s (mass % of binder)	X_c (mm)		C_x (mass % of binder)		R^2
OPC-0.4	3.53	3.19	4.35		2.70		0.99
	3.67	3.19	2.60		2.96		0.99
	3.66	3.23	4.50		2.78		0.99
mean	**3.62**	**3.20**					
OPC-0.5	4.80	2.09	1.85		1.95		0.98
	5.23	1.90	1.75		1.73		0.98
	5.36	2.68	2.70		2.54		0.99
mean	**5.13**	**2.22**					
OPC-0.6*	12.30	3.43	8.00	4.65	3.16	3.12	0.99
OPC-0.7*	18.10	3.43	8.00	4.60	2.98	3.41	0.95
OPC-0.8*	22.20	3.52	8.25	4.65	3.77	3.27	0.93

*Double-sided penetration

Figure 4 – The "apparent diffusion coefficient", D_{F2}, as function of water/binder ratio for mortars with Ordinary Portland Cement as binder.
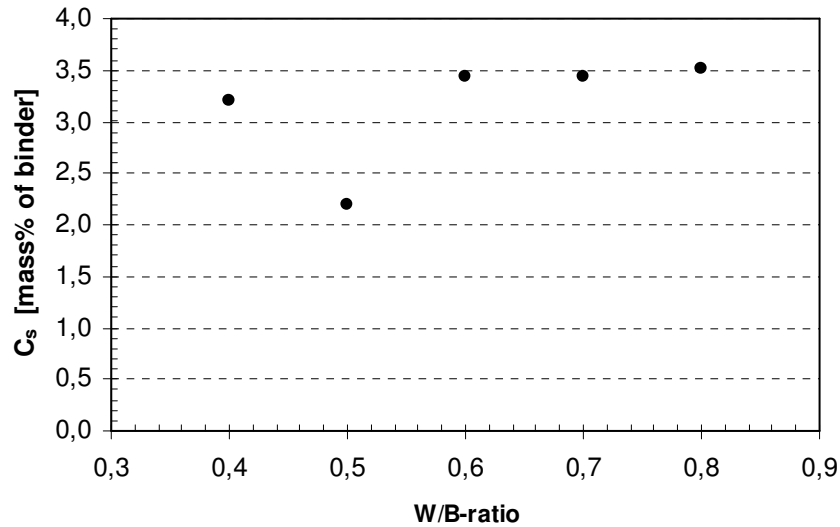
Figure 5 – The "apparent surface chloride content", C_S, as function of water/binder ratio for mortars with Ordinary Portland Cement as binder.

4.2 Limestone filler

The results from the regression analysis for the mortars with the combined binder OPC/limestone filler are summarised in Table 5 and Figures 6 and 7.

For all mortars, the starting point for the regression analysis was chosen on the same basis as for OPC mortars, except for mortar LL24-05. For this mortar, three measured points, closest to the exposed ends, were omitted to try to fit a realistic diffusion curve. The measured chloride profiles, for mortar LL24-05, showed different chloride penetration levels through respectively exposed ends of the same specimen, which can be seen in Table 5 as a low correlation coefficient (R^2) for the curve-fitting.

Table 5 – Curve-fitted coefficients for OPC/limestone filler mortars after a field exposure of 1140 days

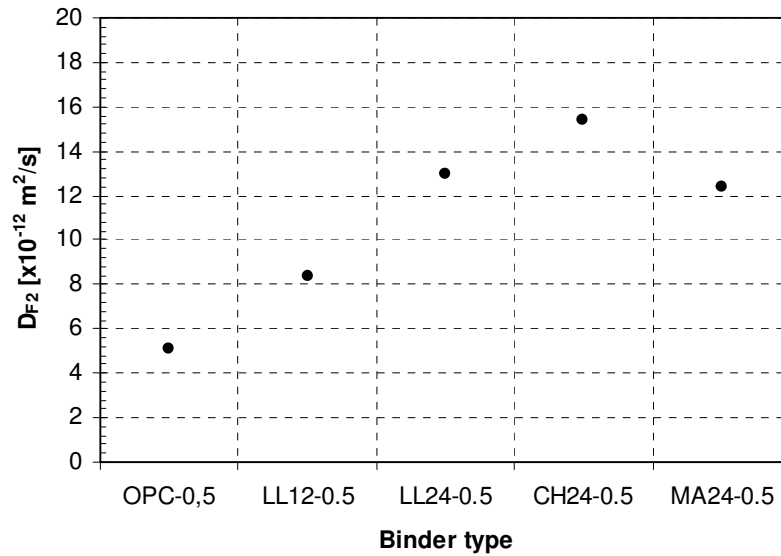| Mortar	D_{F2} ($*10^{-12}m^2/s$)	C_s (mass % of binder)	X_c (mm)		C_x (mass % of binder)		R^2
LL12-0.5	9.08	1.82	2.70		1.77		0.99
	9.17	1.36	1.10		1.30		0.97
	6.80	1.98	1.50		1.93		0.98
mean	**8.35**	**1.72**					
LL24-0.5*	13.00	1.68	4.85	8.25	1.16	1.78	0.54
CH24-0.5*	15.40	2.27	5.10	4.65	1.99	2.28	0.95
MA24-0.5*	12.40	2.66	8.20	8.45	2.53	2.40	0.94

* Double-sided penetration

Figure 6 – Relationship between the "apparent diffusion coefficient", D_{F2}, and binder type of OPC and OPC/limestone filler.

The effect of the replacement rate of OPC with limestone filler, and the effect of the limestone filler type, on the "apparent diffusion coefficient" is shown in Fig. 6. It can clearly be seen that an increasing rate of replacement of OPC with limestone filler means an increasing chloride penetration, similar that of an increased water/cement ratio, see Fig. 4. The type of limestone filler does not seem to have a profound influence on the chloride penetration, when comparing type LL24-05 with type MA24-05. However, it can be noticed that limestone quality CH24-0.5 has a somewhat enhanced D_{F2} compared with the two other qualities, this small discrepancy can not bee explained within the scope of this investigation.

No relationship could be found between "apparent surface chloride content" and the replacement rate from Fig. 7. Nor does Figure 7 show any relationship between the magnitudes of C_s and D_{F2} if compared with Fig. 6.
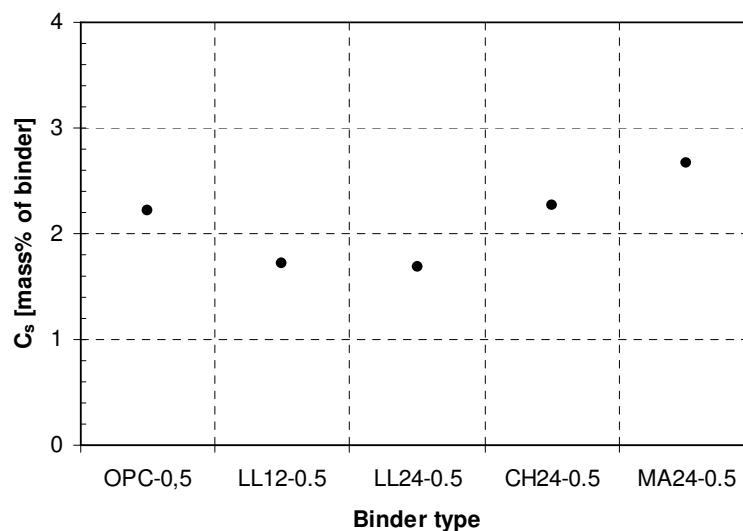

Figure 7 –Relationship between the "apparent surface chloride content", $C_{S,}$ and binder type of OPC and OPC/limestone filler.

4.3 Granulated blast furnace slag

The results from the regression analysis for the mortars with a combined binder of OPC/slag are summarised in Table 6 and Figures 8 and 9. For all mortars with a combination of OPC/slag as binder, only single-sided penetration occurred. The relationship between the chloride profile and the binder profile did not follow the previously mentioned pattern described in Section 3.3. The starting point for the curve-fitting for these mortars was therefore chosen by omitting the first two measuring points, because the values diverged from the expected diffusion profile.

Table 6 – Curve-fitted coefficients for OPC/slag-mortars after a field exposure of 1140 days

Mortar	D_{F2} ($*10^{-12}m^2/s$)	C_s (wt-%)	X_c (mm)	C_x (wt-%)	R^2
BFS20-0.5	2.12	3.29	5.25	2.55	0.99
	2.41	2.91	4.90	2.25	0.97
	1.44	3.03	3.90	2.38	0.99
mean	**1.99**	**3.08**			
BFS35-0.5	1.08	5.02	4.85	3.64	0.98
	0.79	3.67	4.55	2.53	0.98
	0.83	3.98	4.75	2.88	0.98
mean	**0.90**	**4.22**			
BFS65-0.5	0.53	5.63	4.25	3.66	0.98
	0.53	3.68	2.70	2.75	0.98
	0.52	4.17	2.55	4.17	0.99
mean	**0.53**	**4.49**			

Figure 8 shows the relationship between the "apparent diffusion coefficient", D_{F2}, and the slag content of the binder. In accordance with a lot of other investigations [16, 17, 18], an increased slag content resulted in a decreased D_{F2} value, implying an improved chloride resistance. For the OPC/ slag-mortars there seems to be a relationship between "apparent surface chloride content", C_s and D_{F2}, when comparing Fig. 9 with Fig. 8. The C_s increases with increased slag content, in contrast to D_{F2}, which has the opposite behaviour.
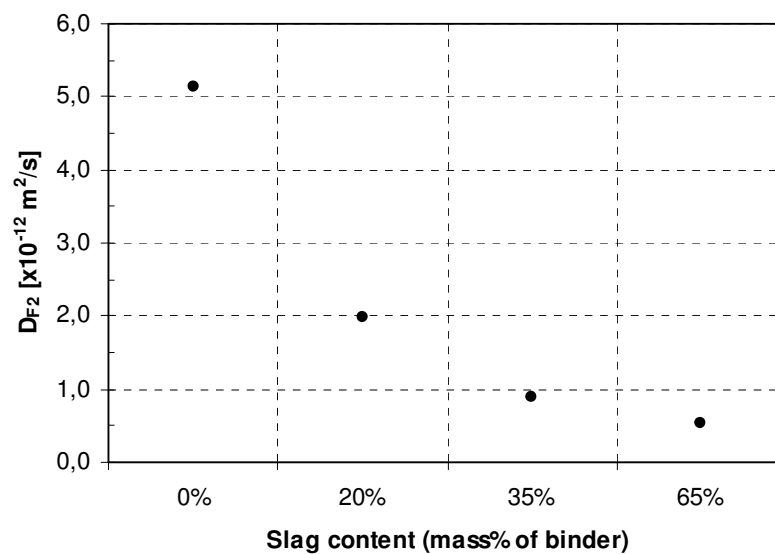

Figure 8 – Relationship between the "apparent diffusion coefficient", D_{F2}, and replacement rate of OPC with slag.
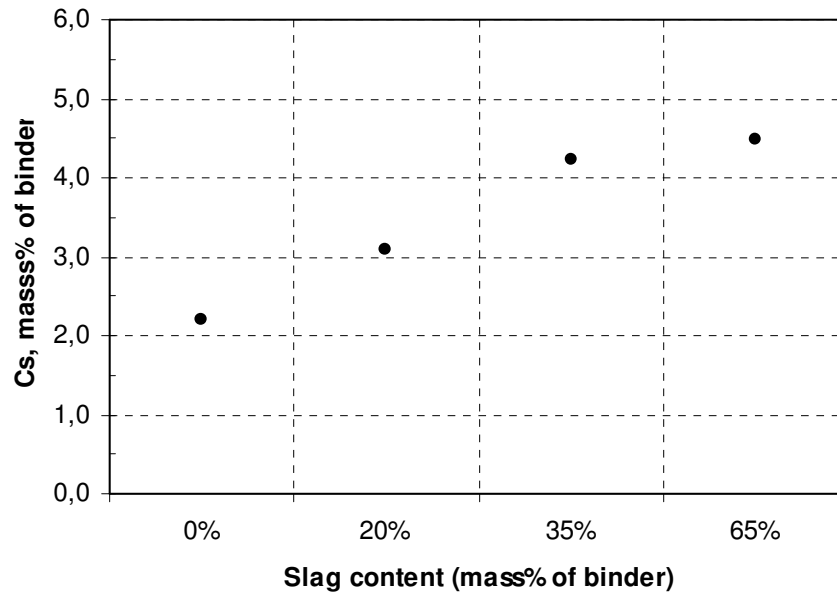
Figure 9 –Relationship between the "apparent surface chloride content", C_S, and replacement rate of OPC with slag.

5 CONCLUSIONS

It must be emphasized that the conclusions drawn from the results obtained in this study are primarily relevant for the type of materials and test procedures used in this study. The following conclusions can be drawn from the results presented in this paper:

- The "apparent diffusion coefficient", $D_{F2,}$ increases with increased water/binder ratio for OPC mortars.

- An increasing replacement rate of OPC with limestone filler produces an increasing "apparent diffusion coefficient".

- For mortars containing slag, the "apparent diffusion coefficient" was remarkably decreased compare with the other mortars, which implies a considerably improved chloride penetration resistance.

- For mortar with slag, there is a relationship between the "apparent diffusion coefficient" and the "apparent surface chloride content": the higher the "apparent diffusion coefficient", the lower the "apparent surface chloride content". This relationship is not apparent for the other mortar qualities.

6 ACKNOWLEDGEMENT

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