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PREDICTING CHLORIDE INDUCED DEPASSIVIATION AND MINIMUM CONCRETE COVER WITH DIFFERENT BINDERS

Ingemar Löfgren [1 & 2], Tang Luping [1], Oskar Esping [2] & Anders Lindvall [2]

(1) Chalmers University of Technology, Gothenburg, Sweden
(2) Thomas Concrete Group, Gothenburg, Sweden

Abstract

Corrosion of steel reinforcement represents the major cause affecting durability of reinforced concrete structures in road and marine environments. To assure durability, standards attempt to provide specifications for long-term performance by simple deemed-to-satisfy rules for approximate environmental classification. This paper presents results from a study of modelling of chloride ingress in concrete with fly ash and ground granulated blast-furnace slag. Chloride threshold values for corrosion initiation are discussed. A physical model, ClinConc, was employed to calculate the chloride ingress profiles after exposure under marine (submerged) and road environments for 100 years. The model was validated using field data after exposure in the Swedish seawater for about 20 years. The results show that the addition of mineral additions in general increases the resistance of concrete to chloride ingress and allows smaller concrete cover thicknesses. However, one critical parameter is the chloride threshold value. In consideration of both the chloride resistance and the alkalinity, which influence the critical chloride threshold value, the concrete with mineral additions still reveals sufficient margin to allow a significantly lower chloride threshold for initiation of corrosion of reinforcement steel in concrete.

1. Introduction

Chloride induced reinforcement corrosion is still a big durability problem of reinforced concrete structures such as bridges and tunnels in road infrastructures. At the present, the specification of durability is mainly based on the establishment of various constraints to the mixture proportions of the concrete, such as cement type and water/binder (*w*/*b*) ratio, together with requirements on the cover thickness as function of the severity of the exposure. This approach does not consider the actual performance of concrete materials with different types of cement and mineral additions added to the cement or directly to the concrete. With the help of more sophisticated durability models safer structures can be designed with expected service life and reduced consumption of materials. This paper intends to evaluate the service life of reinforced concrete with binders blended with fly ash (FA) and ground granulated blast furnace slag

(GGBS) regarding chloride-induced corrosion of reinforcement steel, based on the current knowledge and models, see [1]. Moreover, the aim is to provide recommendations with respect to requirements on minimum concrete cover for different concrete compositions, with main focus on bridges and tunnels with a service life of 100 years.

2. Experiments

For the experiments, three different Portland cements (CEM I), one Portland-fly ash cement (CEM II/A-V), one Portland-slag cement (CEM II/B), one blast furnace cement (CEM III/A), two different GGBS, and one type of FA were used in the study, see Table 1 for properties. For the concrete mixes granite type of aggregates were used (maximum aggregate size 16 mm) and for all the mixes the air content was 5 to 6% by volume. For the mixes with mineral additions an efficiency factor (*k*-value) of 1.0 was used, i.e. comparison is made at equal *w*/*b* ratios.

Table 1: Materials.

ID	**Type**	**Density**	**Blaine**	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**Na_2O_{eqv}**
	Acc. to EN 197-1	kg/m^3	m^2/kg	M.-%	M.-%	M.-%	M.-%	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
FA	Fly ash	2 100						2.40

C4: Contains about 49% GGBS.
C5: Is a FA cement with app. 14% FA and with the clinker of C1.
C6. Contains about 33% GGBS.
FA: The FA had a fineness of 16% (<45 μm) and a loss on ignition of 2%.

The compressive cube strength and the chloride migration coefficient was measured for all mixes. The chloride migration coefficient was determined according to NT BUILD 492 [2]. The compressive strength (water cured cubes) and chloride migration coefficient at 28, 56 and 180 days are presented in Table 3. As can be seen there are variations in the performance of the different materials with respect to the chloride migration coefficient, e.g. difference between GGBS S1 and S2, is probably due to their different fineness and/or chemical composition.

Table 3: Compressive strength (cube) and chloride migration coefficient of concrete.

Binder & *w/b*	**amount**	**Comp. strength [MPa]**			**Chloride mig. [$\cdot 10^{-12}$ m^2/s]**		
(See table 1)	[kg/m^3]	28 days	56 days	180 days	28 days	56 days	180 days
C1 0.45	400	45.2	52.2	58.2	17.6	14.5	13.9
C2 0.45	400	46.9	53.7	59.2	20.0	14.9	14.6
C3 0.45	400	42.8	48.6	50.1	10.9	9.0	8.6
C2+20%S1 0.45	400	45.6	54.1	63.5	11.4	8.7	6.1
C2+30%S1 0.45	400	39.4	48.8	56.0	11.5	7.2	4.3
C2+40%S1 0.45	400	37.5	49.1	59.9	15.2	6.5	2.9
C2+60%S1 0.45	400	37.0	48.3	66.6	8.9	4.7	2.5
C1+20%S1 0.45	400	45.5	52.7	58.4	9.4	6.4	4.7
C1+40%S1 0.45	400	36.8	46.3	55.5	7.6	4.1	3.8
C6 0.45	400	47.0	52.4	59.4	8.6	6.2	5.8
C4 0.45	400	50.4	57.8	66.4	5.0	3.3	2.3
C2+20%S2 0.45	400	48.6	57.8	63.2	12.0	8.5	5.6
C2 40%S2 0.45	400	38.7	49.1	57.9	11.1	6.1	3.6
C5 0.45	400	45.8	50.2	63.2	15.5	11.5	4.8
C1+20%FA 0.44	419	38.8	46.7	-	22.8	14.0	6.2 [1)]
C5 0.40	425	50.7	54.8	64.6	12.5	8.6	4.0
C1+20%FA 0.40	438	45.8	53.7	-	16.9	8.9	3.0 [1)]
C1+25%FA 0.39	465	49.1	58.4	-	16.4	9.3	3.6 [1)]
C2 0.40	425	50.5	57.4	61.5	19.0	14.9	13.1
C2+20%S1 0.40	245	50.0	57.0	66.8	12.9	7.8	5.7
C2+30%S1 0.40	425	48.4	56.8	68.7	10.4	5.5	4.5
C2+40%S1 0.40	425	45.6	57.0	72.6	9.3	5.3	3.5
C4 0.40	425	54.7	61.0	68.3	4.7	3.5	2.9
C6 0.40	425	59.2	61.7	68.6	6.3	4.5	4.4

[1)] Estimated from the data measured at 28 and 56 days using exponent time-dependent relationship.

3. Corrosion initiation

3.1 Chloride ingress modelling

Based on recent validation results from concrete specimens after over 20 years' exposure in the Träslövsläge harbour [3] and 10 years field exposure in road environment [4] in Sweden, the

ClinConc model [5] revealed the best agreement with the field data. Therefore, this model was used for modelling of chloride ingress in this study. The ClinConc model consists of two main procedures, see [5]: 1) Simulation of free chloride penetration through the pore solution in concrete using a genuine flux equation based on the principle of Fick's law with the free chloride concentration as the driving potential, and 2) Calculation of the distribution of the total chloride content in concrete using the mass balance equation combined with non-linear chloride binding. The ClinConc model uses free chloride as the driving force and takes non-linear chloride binding into account, thus describing chloride transport in concrete in a more scientific way than the empirical or semi-empiric models. The free chloride concentration in the concrete at depth, x, is determined using the following equation:

$$\frac{c-c_i}{c_s-c_i}=1-\operatorname{erf}\left(\frac{x}{2\sqrt{\dfrac{\xi_D D_{6m}}{1-n}\cdot\left(\dfrac{t_{6m}}{t}\right)^n\cdot\left[\left(1+\dfrac{t_{ex}}{t}\right)^{1-n}-\left(\dfrac{t_{ex}}{t}\right)^{1-n}\right]\cdot t}}\right) \qquad (1)$$

where: c, c_s and c_i = the concentration of free chlorides in the pore solution at depth x, at the surface of the concrete and initially in the concrete, respectively; D_{6m} = the diffusion coefficient measured by the RCM test, e.g. NT BUILD 492 [1], at the age of t_{6m}; ξ_D is the factor bridging the laboratory measured D_{6m} to the initial apparent diffusion coefficient for the actual exposure environment; n is the age factor accounting for the diffusivity decrease with age; t_{ex} is the age of concrete at the start of exposure and t is the duration of the exposure.

Different from the empirical models, the factors ξ_D and n in the ClinConc can be calculated based on the physical properties of concrete including cement hydration, hydroxide content, water accessible porosity, time-dependent chloride binding, and the environmental parameters such as chloride concentration and temperature. The detailed descriptions of the factors ξ_D and n are given in [6].

The total chloride content is basically the sum of the bound chloride, c_b, and free chloride, c, expressed as (as mass % of binder):

$$C=\frac{\varepsilon\cdot(c_b+c)}{B_c}\times 100 \qquad (2)$$

where: ε is the water accessible porosity at the age after the exposure; B_c is the cementitious binder content, in kg/m^3 concrete; and c_b, is the bound chlorides expressed in the same unit as free chloride.

In the modelling of the marine environment a chloride ionic concentration of 14 g/l and an annual mean water temperature of +11°C was used. For the road environment a chloride ionic concentration of 1.5 g/l and an annual mean air temperature of +10 °C were applied. For the initial chloride content 0.1% of binder was assumed, even though the actual values in the tested mixes were lower. Examples of calculated chloride profiles for marine environment (submerged, XS2) are shown in Figure 1. The chloride profiles for all mixes are not shown as there were minor differences for some of the mixes, e.g. with the different slags. Moreover, for the mixes with GGBS the difference in chloride ingress between *w*/*b* 0.45 and 0.40 were in many cases very small because their chloride migration coefficient were similar.

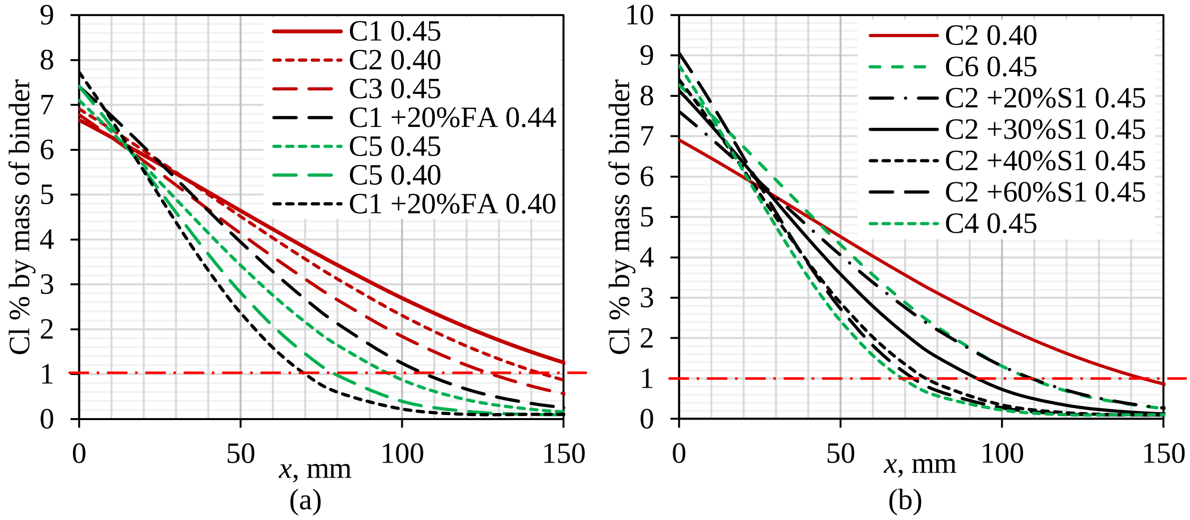

Figure 1: Comparison of calculated chloride profiles for marine environment (submerged, XS2) after 100 years exposure. (a) For CEM I and mixes with FA and (b) for some of the mixes with GGBS or GGBS cements.

3.2 Chloride-induced corrosion and minimum concrete cover

It is generally accepted that the active corrosion (depassivation) occurs when the chloride concentration reach a certain critical level, referred as the chloride threshold value C_{cr} [7] [8]. The chloride threshold value depends on many parameters. Comprehensive literature reviews on the subject [8] [9] show large scatter in the reported chloride threshold values with one order of magnitude, from 0.1% up to around 2% by mass of binder. One of the decisive factors is the pH value of the pore solution which is dependent on the type of binder [7] [8], because the passive film is formed and maintained under the alkali condition or the concentration of hydroxide ions. For reinforcement steel embedded in concrete additional factors such as moisture content, temperature, oxygen availability, defects on the concrete-steel interface are also important. Usually C_{cr} is expressed as the total or acid soluble chloride. In this case, the chloride binding capacity of cementitious hydrates has to be taken into account.

It is conventionally believed that the mineral addition in concrete results in lower chloride threshold value because of the pozzolanic reactions which consume $Ca(OH)_2$ from the cement hydration, resulting in a lower pH value in the pore solution [10]. This is still questionable, because the initial pH (13-14) of the pore solution is mainly attributed to the alkaline oxides K_2O and Na_2O, as expressed by equivalent $[Na_2O]_{eqv}$ in the binder whilst the long-term pH is dependent on the existence of portlandite in the hardened cement paste. It has been reported that for GGBS contents of ≤ 40% the concentration of alkali in the pore solution is within the range of pure CEM I but high amounts (>75%) can have a strong influence on the alkalinity [11]. However, it has also been reported [12] [13] that even at a GGBS content >75% there is still portlandite remaining in 20 year old samples. At about 50% GGBS more than 9% portlandite by mass of binder remained after hydration for 3 and 20 years, see [13] [14] [15]. The same has been reported for concrete with FA [149 [15]; when FA <30% there is still portlandite remained. It is known that calcium leaching is a process much slower than chloride ingress. If there is no carbonation, very little amount of portlandite can keep the pH value of solution about 12.5 due to its low solubility (0.023 mol/l).

On the other hand, the higher chloride binding capacity, lower diffusivity and finer pore structure of concrete with mineral addition positively contribute to the resistance of concrete against corrosion initiation, as indicated in a study of reinforced concrete specimens after over 20 years' exposure in the Träslövsläge harbour [3]. According to [3], the estimated chloride threshold value from the field exposure is about 1% by mass of binder for most types of concrete with Portland cement and silica fume whilst the concretes with FA and GGBS did not show a corrosion tendency at a chloride content even higher than 1% by mass of binder. Therefore, the conventional opinion of low C_{cr} for the concrete with mineral additions due to its lower alkalinity is questionable, because on one side there is no sufficient evidence of a significant lower pH value in the pore solution and on the other hand the improved microstructures in such types of concrete may prevail the weakness of low alkalinity, if it is.

Assuming a service life of t_L = 100 years, the minimum cover thickness x_c can be estimated from the following equation in the ClinConc model, if the free chloride threshold value c_{cr} is given:

$$x_c = 2\sqrt{\frac{\xi_D D_{6m}}{1-n}\cdot\left(\frac{t_{6m}}{t_L}\right)^n\cdot\left[\left(1+\frac{t_{ex}}{t_L}\right)^{1-n}-\left(\frac{t_{ex}}{t_L}\right)^{1-n}\right]\cdot t_L}\cdot \mathrm{erf}^{-1}\left(1-\frac{c_{cr}-c_i}{c_s-c_i}\right) \quad (3)$$

In this study for estimation of the minimum cover thickness the value of 1% total chloride by mass of binder was used as criteria for concrete exposed under the marine environment and 0.4% total chloride by mass of binder for concrete exposed under the road environment due to the high availability of oxygen and possible carbonation. The corresponding free chloride threshold value c_{cr} used in equation (3) can be inversely obtained from equation (2).

The calculated minimum concrete cover required under the marine environment and for the road environment is presented in Figure 2. As can be seen, in the marine environment the minimum concrete cover predicted is 70 mm for C4 (CEM III/A) and those mixes with 60% GGBS. With lower GGBS content the required cover increase and becomes about 80 mm with 40%, 90 mm with 30% and 100 to 110 mm with 20%. For the mixes containing FA (with 15 to 20%), 100 to 110 mm is required at *w*/*b* 0.45 and 70 to 80 mm at *w*/*b* 0.40. The largest concrete cover is required for the sulfate resistant Portland cement (C1 and C2), with 160 mm at *w*/*c* 0.45 and 140 mm at *w*/*c* 0.40. In comparison, the ordinary Portland cement requires 130 mm at *w*/*c* 0.45. For the road environment the concrete mixes with GGBS or FA require 35 to 50 mm cover at *w*/*b* 0.45 and 35 to 45 mm at *w*/*b* 0.40. In comparison, the ordinary Portland cement requires 65 mm at *w*/*c* 0.45 and the sulfate resistant Portland cement a cover of 70 mm at *w*/*c* 0.40. In general, the required covers in the marine environment are much higher than the recommended values in EN 1992-1-1 [16] but are in line with the recommended value of 100 mm by the Norwegian road authorities [17].

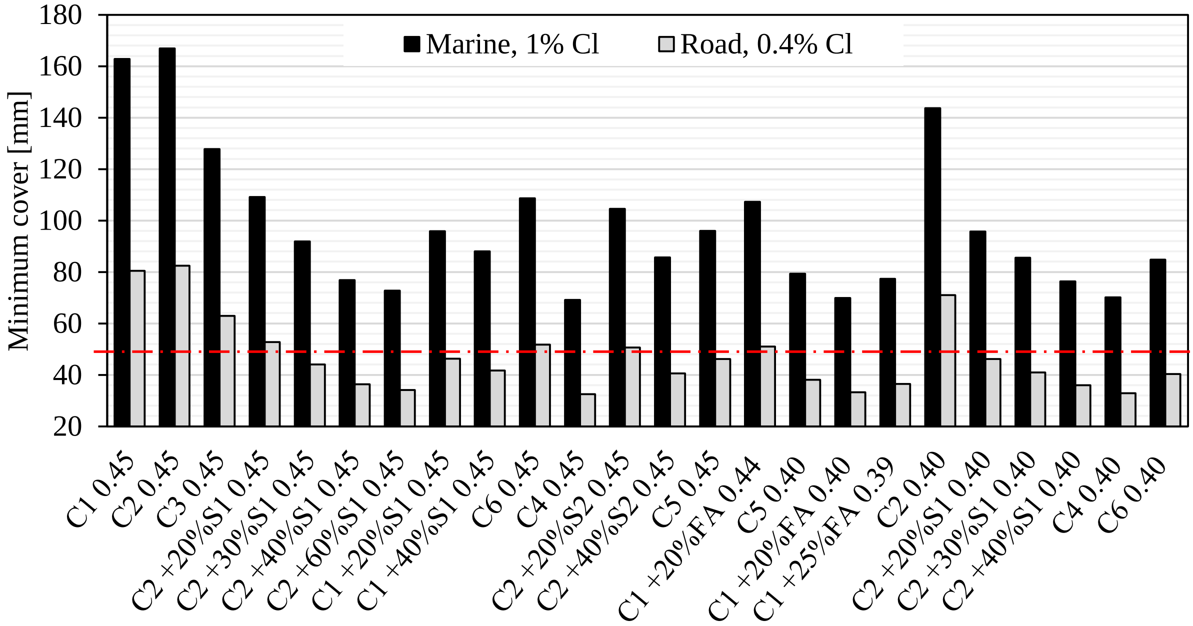

Figure 2: Calculated minimum concrete cover for marine (XS2) and road environment (XD3) for a service life of 100 years.

3.3 Allowable low limit of chloride threshold

So far it is still lack of actual chloride threshold value for concrete, especially for those with mineral additions, due to the absence of standard test method for the threshold value. Under the assumption of the same service life and cover thickness as concrete based on the mixes with C1 and C2 (sulfate resistant Portland cement), a chloride content at the cover depth in concrete with mineral additions can be calculated with the help of the ClinConc model. Thanks to the higher resistance of concrete with mineral additions to chloride ingress, this calculated chloride content will be lower than the chloride threshold for the reference concrete (with C1 or C2) and can thus be considered as a theoretical allowable low limit of chloride threshold for concrete with mineral additions. In this study, a cover thickness of 100 and 70 mm, and a chloride threshold value of 1% and 0.4% by mass of binder were assumed for the marine and road environment respectively. The results are illustrated in Figure 3. From Figure 3, it can be seen that under the marine and road environment, the theoretical low limit of threshold for all the other types of concrete with mineral additions is considerably lower than the reference threshold for concrete with C1 and C2 (sulfate resistant Portland cement). For the marine submerged condition the chloride threshold value could be allowed to be as low as 0.1% to 0.2%, 10 to 20% of that of a sulfate resistant Portland cement. This means that concrete with mineral additions, due to the improved resistance to chloride ingress, are expected to have more than sufficient margin to protect reinforcement steel from corrosion.

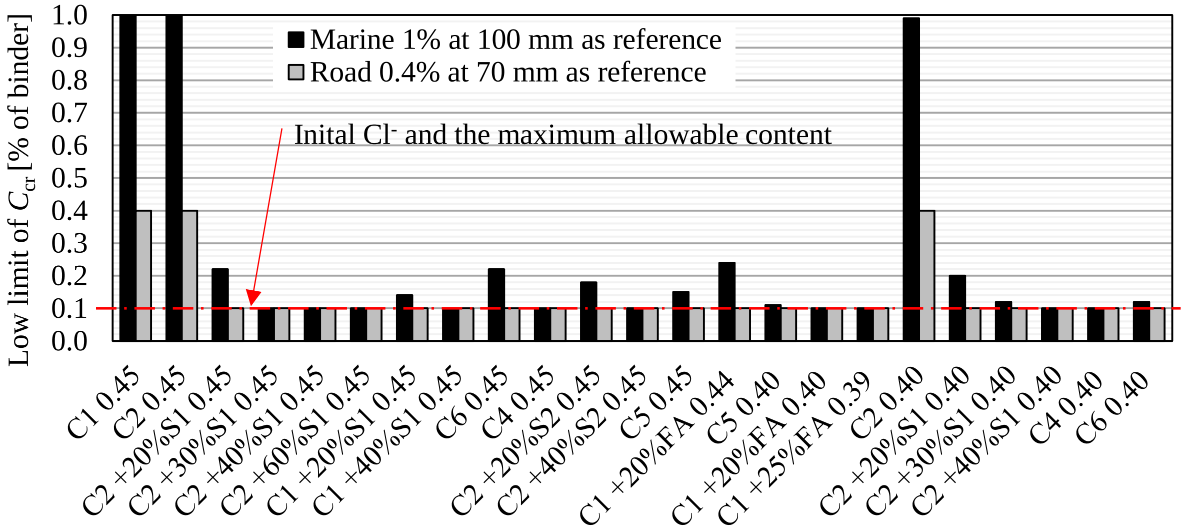

Figure 3: Allowable low limit of the chloride threshold value for the same concrete cover and service life compared with the concretes with cement C1 & C2 (CEM I 42.5N SR3 MH/LA).

4. Discussion

The results from the above modelling together with the limited field data after exposure in the Träslövsläge harbour for 20 years have given a certain evidence showing the positive contribution of mineral addition to the resistance of concrete to chloride ingress. For the addition of GGBS up to 60% in this study (75% for the field exposure), the chloride resistance increases with the addition level. Similarly, fly ash at an addition of 15 to 25 % increased the chloride resistance significantly. With respect to chloride threshold values, the field data from Träslövsläge harbour seem to indicate that 1% can be used for mixes with Portland cement as well as for mixes with GGBS or moderate amount of fly ash. In the literature mineral additions, such as fly ash and slag, have been reported to give rise both higher and lower threshold values [8]. But it has also established that the most influencing parameters are the steel-concrete interface (e.g. presence of defects) and the steel potential [8] which makes results from literature difficult to interpret.

Given the uncertainty regarding the chloride threshold value a possible low limit of chloride threshold was determined. The result from this back-calculation show that by reducing the chloride migration coefficient to one third compared to a mix with CEM I (sufate resistant) the low limit threshold can be as low as 0.1 to 0.2 % of binder if 1.0% is assumed for CEM I in submerged marine environment. In consideration of both chloride resistance and alkalinity, the concrete with mineral additions (at moderate amounts) still reveals sufficient margin to allow a significantly lower chloride threshold for initiation of corrosion of reinforcement steel in concrete. Most reported chloride threshold values for concrete with slag or fly ash [8] [9] do not indicate such low threshold values at moderate amount of mineral additions (up to 25% fly ash and 50% GGBS). The reduction in threshold value, for the cases where this has been found, reported is generally not more than 50% [18]. Hence, the improved resistance to chloride ingress, where moderate amount of mineral addition can reduce the chloride migration to one third compared to a CEM I, overcomes the potential negative effect on the chloride threshold value.

With the help of models, like ClinConc, rapid chloride test methods such as NT BUILD 492 [2] can be used for specification and verification by a performance based approach. As can be seen in Figure 2 there is a big variation in required concrete covers. With a prescriptive approach such variations are difficult to handle. Moreover, there is also variation in the performance of the different materials with respect to the chloride migration coefficient which also cannot be considered with a prescriptive approach. This variation can, however, be considered with the performance based approach although it still requires a reliable test method to quantify chloride threshold values. Moreover, for large concrete covers the effects of more stable internal climate and less oxygen availability may have positive impact on the chloride threshold values and corrosion rate which needs to be considered.

5. Conclusions

The ClinConc model was used to model chloride ingress in concrete with Portland cement and with various mineral additions with the measured chloride migration coefficient as the key input parameter. Some limited field data measured from concrete exposed in the Träslövsläge harbour for about 20 years [3] and 10 years exposure in a road environment [4] were used for validation of the modelled results. From both the literature review and the experimental and modelling results [1] it can be concluded that, for the mineral additions:

- The chloride resistance of concrete increases with mineral addition. For GGBS, the higher the addition level (up to 60% GGBS in this study), the better the resistance is, whilst for FA, the addition level in the range of 13% and 25% reveals similar resistance.
- The alkalinity of concrete with GGBS may not necessarily be low because both the alkaline components in GGBS and the reduced porosity contribute to a high concentration of hydroxide ions in the pore solution. It is only at high addition levels that this might be a concern.
- The alkalinity of concrete with FA is proportionally reduced with the addition of FA, but the reduction is limited if the addition of FA is not more than 25%.
- In consideration of both chloride resistance and potential effect of alkalinity on the chloride threshold value, the concrete with mineral additions have significantly better resistance to chloride ingress which outperforms any negative effect on the chloride threshold value.

Values of minimum cover specified in current standards need to be revised by consideration of the type of binder used. From the ClinConc model and the concrete mixes tested, some suggested values are given in Figure 2. To assure the designed service life, the resistance of concrete to chloride ingress should be tested using e.g. the rapid chloride migration test or similar standardized tests and a performance based approach should be used to determine required concrete covers.

Finally, it can be point out that the overall effect of mineral additions in concrete is significant in terms of resistance to chloride ingress with a marginal influence on the chloride threshold value. Therefore, the use of mineral additions in concrete should have a clear, great advantage from viewpoint of sustainability in terms of technical performance, cost-effectiveness and ecological benefit.

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