Durability testing of low clinker binders, chloride ingress in similar strength mortars exposed to seawater

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ABSTRACT
Resistance to chloride ingress of ten different binders was investigated. Most of the binders were prepared with 35% substitution of a new clinker by limestone filler, calcined clay, burnt shale and/or siliceous fly ash. Mortar samples with similar design compressive strength after 90 days were exposed to artificial sea-water for 270 days. The results indicate that the use of alternative binders may lead to up to around 15% reduction in CO_2 emission without compromising 90 days compressive strength and resistance to chloride ingress in marine exposure.

Key words: Cement, Chlorides, Supplementary Cementitious Materials (SCM)

1. INTRODUCTION

It is well known that cement production is responsible for around 5% of the total anthropogenic CO_2 emissions. Reduced clinker content is generally associated with lower CO_2 emission. The purpose of this paper is to investigate the resistance to chloride ingress of low clinker binders in similar strength mortars. Well hydrated mortars were exposed to seawater for 270 days and chloride profiles were determined by profile grinding and titration.

2. EXPERIMENTAL

Total chloride profiles were measured on mortar samples which were cast, cured and analysed according to procedures reported recently [2]. The chemical compositions of the binder constituents determined by XRF are given in Table 1. The binder compositions are given in Table 2. These binder compositions include hemihydrate, which is excluded when calculating clinker replacement according to EN 197-1 [1]. A binder composition typical for a Danish ready-mixed concrete for aggressive environments and strength class C35 was used as reference. The mortar compositions are given in Table 3. The mortars were designed to have similar compressive strength at 90 days; this led to variation in w/b. The mix design was based on 90 days compressive strength data according to EN 196-1 [3] (Table 2) and Bolomey's equation [4]. The paste volume was kept constant, and the SP content was adjusted to obtain fresh mortar flow comparable to the reference (R1). The CO_2 emissions per ton of binder (Table 3) were estimated considering hemihydrate, fly ash and burnt shale as CO_2 neutral, and assuming 0.85 t CO_2/t of clinker, 0.1 t CO_2/t of limestone filler, and 0.27 t CO_2/t of calcined clay. The CO_2 reductions were calculated considering the CO_2 emissions from each constituent and the w/b variations. Mixing was undertaken according to EN 196-1 [3], except that the mixing procedure was adjusted to include the delayed addition of a polycarboxylate ether based superplasticizer (SP). The mortar was cast in 125 ml plastic bottles (ø 50.5 mm). A small amount of water was added on top of the mortar to ensure saturated conditions. After 90 days curing, approximately 5 mm was cut from the bottom surface and the remaining surfaces were sealed by epoxy. The samples were re-saturated and finally exposed to artificial seawater with a composition according to ASTM D1141-3 [5]. Twelve samples were submerged in 2.5 L. The exposure solution was exchanged after 14 and 28 days and thereafter every 30 days. After 270 days of exposure, chloride ingress was determined by profile grinding and titration.

Table 1 - Chemical composition of binder constituents (main oxides) in [%] by mass.

	RAPID	Clinker in RAPID	New clinker	Calcined clay	Limestone filler	Burnt Shale	Fly ash
SiO_2	19.4	20.2	19.5	62.5	12.7	34.2	55.0
Al_2O_3	5.4	5.5	6.1	16.6	3.6	8.2	19.9
Fe_2O_3	3.8	4.0	3.3	9.4	1.8	4.8	5.5
CaO	63.2	65.4	66.0	0.8	44.0	30.1	4.5
MgO	0.94	0.80	0.92	2.95	0.60	5.59	1.81
K_2O	0.34	0.54	0.52	2.82	0.58	4.38	2.16
Na_2O	0.26	0.21	0.25	1.95	0.23	0.11	1.12
SO_3	3.4	1.5	1.6	0.4	0.4	5.6	0.4
LOI	2.6	0.24	0.47	2.39	35	4.55	3.2

Table 2 - Binder compositions in [%] by mass and mean and standard deviation of compressive strength at 90 days [MPa] determined in mortar according to EN 196-1 (w/b=0.5), but normalized to 2% air content.

id	Fly ash	New clinker	Hemi-hydrate	RAPID	Burnt shale	Calcined clay	Limestone filler	90 days strength
R1	16.7			83.3				67.9 ± 0.9
B1	16.7	76.5	2.8				4.0	67.2 ± 2.3
B2	18.2	63.7	2.3				15.8	62.1 ± 1.5
B3	18.2	63.7	2.3				15.8	64.5 ± 1.1
B4	19.0	63.7	1.5		7.9		7.9	67.2 ± 0.7
B5	19.4	63.7	1.1		11.9		4.0	66.3 ± 2.0
B6		63.7	2.3				34.0	58.2 ± 1.4
B7		63.7	2.3			25.5	8.5	79.3 ± 2.8
B8		63.7	2.3			34.0		71.6 ± 0.9
B9	7.5	58.9	2.2			15.7	15.7	72.0 ± 1.5

Table 3 – Mortar compositions (adjusted to same compressive strength) and CO_2 emission. The calculated CO_2 reductions combine the impact of binder composition and w/b.

id	Binder [g]	SP [g]	Demineralized water [g]	Sand [g]	w/b [-]	CO_2 [t/t binder]	CO_2 reduction [%]
R1	450.0		225.0	1350	0.50	0.65	0
B1	452.6		224.5	1350	0.50	0.65	0
B2	464.2	1.02	216.3	1350	0.47	0.56	13
B3	456.8	0.59	219.2	1350	0.48	0.56	14
B4	448.8	0.83	222.0	1350	0.50	0.55	17
B5	451.7	1.35	220.7	1350	0.49	0.55	17
B6	482.9	1.79	213.3	1350	0.44	0.58	6.2
B7	416.7	0.45	233.1	1350	0.56	0.62	13
B8	434.2	2.37	224.2	1350	0.52	0.63	7.2
B9	433.6	0.38	226.2	1350	0.52	0.56	18

3. RESULTS AND DISCUSSION

Chloride ingress profiles after 270 days exposure to seawater of mortars with comparable design compressive strength at 90 days are shown in Figure 1. The maximum total chloride concentration is found at a depth of approximately 2-3 mm for all mortar samples, while a decreased total chloride concentration is observed at the surface. The effect is explained by leaching and other phase changes causing a reduced binding capacity, see e.g. [6,7]. The ingress depths are comparable for all binders, expect for the binder with 34% limestone filler (B6), which exhibited a very low ingress resistance. The alternative binders appear to exhibit a higher total chloride content, indicating an increased binding capacity compared to the reference blend (R1). Furthermore, the beneficial impact of calcined clay (B7-B9) is illustrated in Figure 1 (right). The binding capacity for these blends is increased while the ingress depth is decreased, compared to the binder with only limestone filler (B6). The observations are in agreement with earlier findings, see e.g. [8].

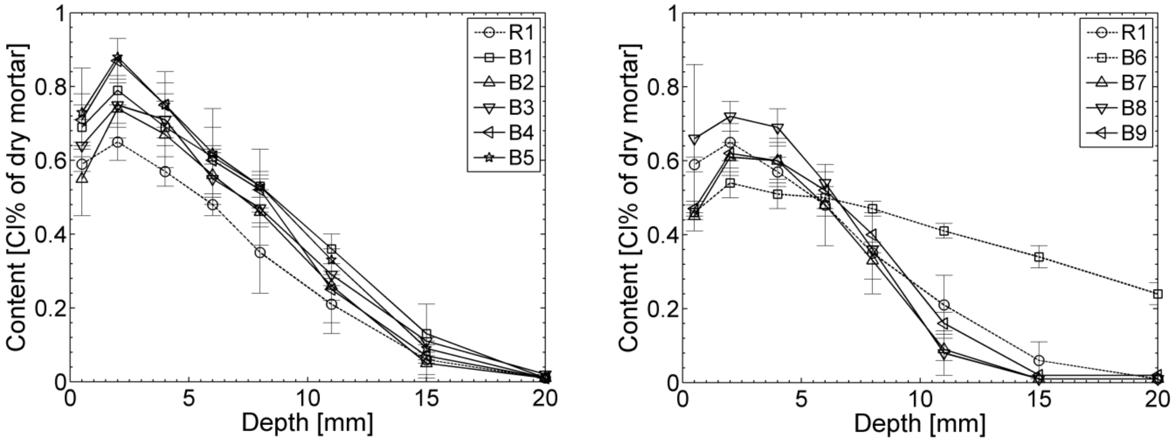

Figure 1 – Chloride profiles after 270 days exposure to artificial sea water at 20°C.

4. CONCLUSIONS

Based on the present investigation and assumptions, up to around 15% reduction in CO_2 emission from binder production might be obtained for selected binders without compromising the 90 days compressive strength and resistance to chloride ingress in marine exposure by using alternative binders instead of a binder composition typical for a Danish ready-mixed concrete for aggressive environments and strength class C35. Due to varying degree of reaction at testing the long-term chloride resistance needs to be documented. Other issues to be considered are e.g. carbonation resistance and conditions for reinforcement corrosion.

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