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Chloride Ion Diffusion Resistance of Bulk Hydrophobic Concrete: Comparison of w/c and Dosages

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ABSTRACT

Post-cast application of hydrophobic agents onto hardened concrete is successful at reducing external ion diffusion into cement paste, this work examines pre-cast application of hydrophobic admixtures in fresh concrete. Concretes, with water to cement ratios (w/c) 0.45 and 0.50 (CEM I; low C_3A), were mixed. Adding alkyltrialkoxysilane or triacylglycerol admixtures ranging from 1 to 3 $wt\%_{cem}$ in these concretes were evaluated. Increasing the dosage of hydrophobic admixtures decreased the compressive strength. The usage of these admixtures did not hinder the further development of the microstructure as all concretes gained strength after one year, but not in the same percentage increase as the reference concrete.

Chloride ion diffusion, after exposure to 3 wt% NaCl solution at 20 °C for 91 days, in concretes with 1 $wt\%_{cem}$ admixture showed slight reductions in diffusion rate (8-17%) compared to the reference. At 3 $wt\%_{cem}$, triacylglycerol admixtures showed better hindering effects of inward chloride diffusion, this was especially evident in w/c = 0.45. Equivalent addition of alkyltrialkoxysilane-based admixtures increased the diffusion of chloride ions transferred into the cement matrix.

Key words: Admixtures, alkyl trialkoxysilanes, chloride diffusion, concrete, hydrophobic, silane, triacylglycerol, vegetable oil.

1. INTRODUCTION

The main constituents of concrete are aggregates, cement and water. Aggregates suitable for concrete are generally non-porous. The main structural products from the reaction of cement clinker minerals (e.g. alite and belite) and water, which aids mass transfer, are gel and capillary pores. These differ in size and in volume depending on several factors; a higher water to cement ratio (w/c) will increase the number of capillary pores compared to a lower one, a young cement paste will not have hydrated as much as a mature one, etc. It is generally established that gel pores do not contribute to mass transfer at the same rate as within the capillary pore system [1]. Most of the water flow in [2] and [3] relate to the pores with a size greater than 100 nm.

It should also be noted that a thin region of approximately 15-25 µm between the aggregate and cement paste also provides for a region of increased porosity [4]. These dimensions are far greater than those found in capillary or gel pores. According to [5], the average gel pore diameter is approximately 1.3 nm, in [6] a distinction between macro and micropores lies either side of 0.5 nm. One can though find capillary pores spanning from 5 nm up to 5 µm depending on w/c, mixing, compaction and admixtures used [7]. A well hydrated low w/c cement paste will have pores (gel or capillary) in the sub 100 nm range.

The flux of water and that of ions or gases of interest into concrete differs somewhat, as in all cases the solute concentration is relatively low, except in the case of saturated sodium chloride salt solutions. The rate of diffusion of oxygen in the gaseous form is dependent on the internal RH of the cement paste and its pores' structural dimensions as described in [8] & [9].

The mass flow of chloride ions (diffusion and or capillary action) in cement pastes is an important subject of research for durability aspects and predictions of technical life spans of reinforced concrete infrastructure. The chloride ion does not affect the integrity of the cement matrix directly. The secondary reaction (rust formation) of the steel rebar due to the depassivation of its oxide layer, by said ion, does affect the concrete due to increased tensile stresses, resulting in spalling. The monetary aspect of these mechanisms to society is substantial [10]. The repair costs and maintenance of infrastructure are significant, especially in regions where deicing salts, marine or land-based salts are present.

In Sweden, there has been a reluctance up until recently to use alternatives to ordinary Portland cement (OPC) in infrastructural projects. This cement type and that used in the experiments have both a low C_3A and sodium oxide equivalent content. Other countries have been adding ground granulated blast furnace slag or pulverized fly ash for some time in their concrete mixes, with the added benefit of having a greater capability to reduce mass transfer and or bind chloride ions. The presence of C_3A, a typical cement clinker mineral, has a beneficial effect in terms of reacting with a small portion of the incoming chloride ions [11]. It does though increase the water demand of the fresh cement paste and has a higher exothermic capacity.

By changing the cement paste's hydrophilic nature to hydrophobic, one could reasonably assume that by preventing the solvent (water) into the microstructure, the solute (with a detrimental ion e.g. Cl^-) would also be hindered from access. This could be achieved by positioning hydrophobic chemicals in the capillary pores or possibly within the network of C-S-H. The solubility of water molecules with hydrocarbon chains numbering 12 in length or above is miniscule and can be considered hydrophobic [12].

The external application of alkyltrialkoxysilanes on existing concrete structures is an existing technology to prevent the ingress of moisture and hence chloride ions into the cement paste and its benefits are described in [13], but the treatment process is not without its difficulties as described in [14]. The "silane" condensation process is generally believed to occur on the pore wall structure, hence leaving the internal pore volume open for mass transfer of fluids.

In [15], [16] and [17], the potential to alter external water uptake in cement paste, by using triacylglycerols and alkyltrialkoxysilanes as an admixture, has been demonstrated. These though were oven dried (40 °C) mortar specimens and so the pore structure was not saturated, i.e. the area for mass transfer was limited to the outer circumferences of the available pores.

In this paper, concretes with $w/c = 0.45$ & 0.50 (CEM I) and $d_{max} = 16$ mm (natural aggregates) were altered to contain varying amounts of bulk hydrophobic admixtures based on cement weight (1 to 3%). Their effects on fresh properties, compressive strength, and chloride ion transport by immersion in a 3% NaCl solution are presented in this paper.

2. MATERIALS

2.1 Cement

The cement used in these experiments is a bagged CEM I 42,5 N LA/SR3/MH commonly used in civil engineering structures in Sweden. This particular clinker production facility (Degerhamn, Öland, Sweden) is no longer in operation. According to the manufacturer, the specific surface area is 330 m^2/kg, the clinker mineral C_3A lies in the range 1.3 to 2.7% and the Na_2O_{eq} ranges from 0.40 to 0.58%.

All aggregates, 0 to 8 mm and 8 to 16 mm, are natural glaciofluvial aggregates from a local supplier in the Stockholm region. The bulk density is 2670 kg/m^3.

2.2 Hydrophobic chemicals

Table 1 – Hydrophobic agents used as admixtures

Component	CAS	Abbreviation	Notes
Food grade extra virgin olive oil (Olea europea)		O.O.	
Food grade rapeseed oil (Brassica napus) RBD, also known as Canola oil in some regions.		R.S.O.	
Commercial hydrophobic agent 1 (octyltriethoxysilane based)	35435-21-3	C.H.A.	Only w/c = 0.45
n-octyltriethoxysilane; Alfa Aesar (97.8%)	2943-75-1	NOTES	Only w/c = 0.50
n-octyltrimethoxysilane; Alfa Aesar (97.7%)	3069-40-7	NOTMS	Only w/c = 0.50 & 1%
Iso-butyltriethoxysilane; Hüls (98%)	17980-47-1	IBTES	Only w/c = 0.50 & 1%

CAS = Chemical Abstracts Service
RBD = Refined, bleached and deodorized

2.3 Concrete mixes

Table 2 – Concrete mix w/c = 0.45 & 0.50. Including 1-3% hydrophobic admixture

Component	**REF**	**1 %**	**2 %**	**3 %**
w/c = 0.45	[kg/m^3]	[kg/m^3]	[kg/m^3]	[kg/m^3]
Cement (CEM I) 42,5 N LA/SR3/MH	431.6	431.6	431.6	431.6
Water (potable)	194.2	194.2	194.2	194.2
0-8mm (nat. aggregates)	868.3	868.3	868.3	868.3
8-16mm (nat. aggregates)	869.3	856.9	844.5	832.1
Hydrophobic admixture	0.0	4.3	8.6	12.9
w/c = 0.50	[kg/m^3]	[kg/m^3]	[kg/m^3]	[kg/m^3]
Cement (CEM I) 42,5 N LA/SR3/MH	429.0	429.0	429.0	429.0
Water (potable)	214.5	214.5	214.5	214.5
0-8 mm (nat. aggregates)	863.0	863.0	863.0	863.0
8-16 mm (nat. aggregates)	823.1	810.5	798.0	785.6
Hydrophobic admixture	0	4.3	8.6	12.9

2.4 Salt bath

The container was filled with 30 litres per salt bath using deionized water (ultrapure water; < 18.2 MΩ·cm) and NaCl (sodium chloride AnalaR NORMAPUR® ACS, Reag.Ph. Eur. CAS: 7647-14-5) to obtain a 3 wt% sodium chloride solution.

3. EXPERIMENTAL PROGRAM

The concretes were produced on different days and in sequential order from the lowest addition of hydrophobic agent to the highest, no demoulding oils were used on the moulds as these have similar chemical make up as some of the hydrophobic admixtures used.

All raw materials, except the hydrophobic admixture and a quantity of water, were mixed in a UEZ ZM 50 mixer (4-armed) for two minutes, the first 30 seconds being dry mixed. The delivery of the hydrophobic admixture was as an emulsion to increase the surface area between hydrophobic agent and cement paste. A household blender (350 W) on its lowest setting was sufficient to produce a homogenous emulsion. 0.5 kg water and the varying amount of hydrophobic admixture were mixed simultaneously and added rapidly after two minutes post water adding time (WAT). The concrete was mixed for an additional three minutes and cast into moulds as described in [18] except point 5.1.1. The slump was measured according to [19] 10 minutes after WAT.

20 litre batches were produced for each mix. Three Ø 100 mm x 200 mm cylinders and twelve 100 mm sided cubes were cast for each batch. These were demoulded and placed in a climate room until required for the different tests (20 ± 2 °C RH 98 ± 2%).

After 28 days and subsequently one year, three 100 mm sided cubes were tested for compressive strength according to [20]. The top and bottom ca 15 mm from the three concrete cylinders were sawn off, also 28 days post casting, with a water-cooled diamond saw. The remaining 170 mm were sawn into 80 mm, 60-70 mm and 20 mm sections. The 80 and 20 mm sections were then weighed and placed in a forced air convection oven at 40 °C and used for water absorption tests [21]. The remaining 60-70 mm sections were placed back in the climate chamber for a total of ca five months and subsequently used for the chloride diffusion testing.

The unidirectional chloride diffusion testing was conducted according to [22] except point 6.2.1, the specimens were not vacuum saturated as the effects on the hydrophobic admixtures were unknown. To ensure unilateral mass transfer of chloride ions into the cement matrix, a 5 mm neoprene self-adhesive tape was applied to the bottom and the mantle surfaces of the 60-70 mm thick specimens. The joints between the bottom and side coverings were sealed with building grade “silicon”, the circular inner edge between the exposed sawn surface and the sides was also sealed in the same manner. The specimens were placed in lab conditions for 24 hours to facilitate the “silicon” sealing process (Figure 1). The specimens were then placed in deionized water for 3 days prior to submersion in the sodium chloride solution baths. Two specimens from each mix were prepared in the manner laid out above.

The sodium chloride solution baths (59 cm x 26 cm x 35 cm) were placed in a temperature-controlled room (20 ± 1 °C) and subsequently sealed after the specimens were positioned. The specimens were placed in two rows facing each other on opposite sides of the bath and rows

stacked upon one another equating to ca 5200 mm^2/l NaCl solution. Concretes of the same w/c were placed in the same salt solution bath.
The salt solutions were tested regularly for any changes in density.

Figure 1 – Above: Reference concrete after 24 hours, "silicon" sealant drying period and prior to immersion in deionized water. Below: The same concrete samples after immersion in the 3 wt% NaCl bath.

After 91 days of submersion, at which point the specimens were ca eight months old, the salt solutions were emptied from the container and the exposed sawn surfaces were not cleaned. All specimens (and container) were transferred to a cold storage room where 5 ± 1 °C & 60-70% RH prevailed. This was to allow sufficient time to grind the specimens without affecting the possible further diffusion of the chloride ions during this lag time. The total time for complete grinding was 4 months. One specimen from each batch was used in the dry grinding process. The specimen was placed in a lathe and a diamond tipped core bit was used to grind the concrete in millimeter steps. The outer 10 mm was not exposed to the grinding process. After each grinding step, the depth was measured and used as the concrete powder's depth reference. The collected samples were then analyzed for Ca^{2+} content and Cl^-/cement weight content using potentiometry and titration as prescribed in [23]. The results were then loaded into a curve fitting Excel macro by [24] to produce values for apparent chloride diffusion D_a [m^2/s] and initial chloride surface concentration C_s [mass %].

4. RESULTS

4.1 Fresh properties

The figures below (Figures 2 & 3) show the slump measurements of the concretes 10 minutes after the addition of water. The figures are divided into two groups representing the two different w/c.

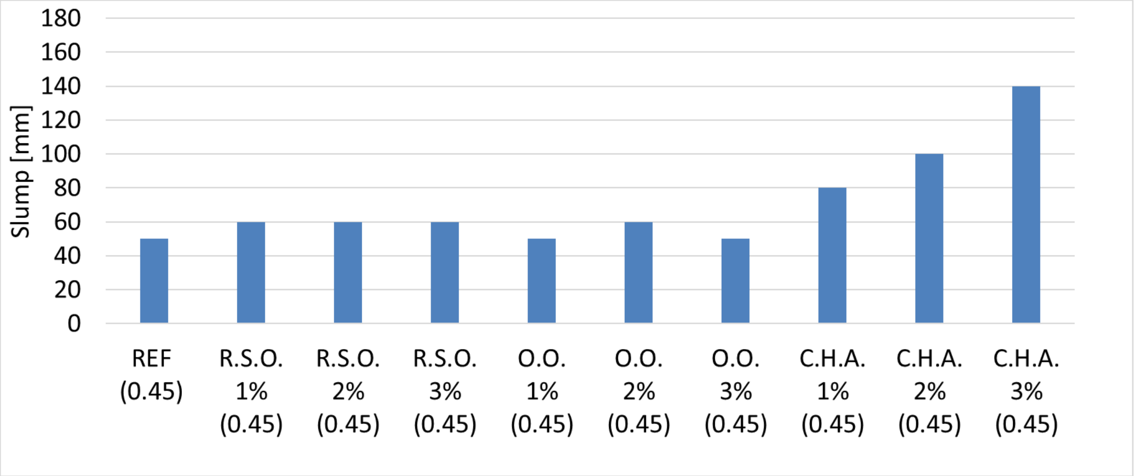

Figure 2 – Slump values w/c = 0.45 @ WAT = 10 min. REF (0.45) = reference mix without hydrophobic admixture

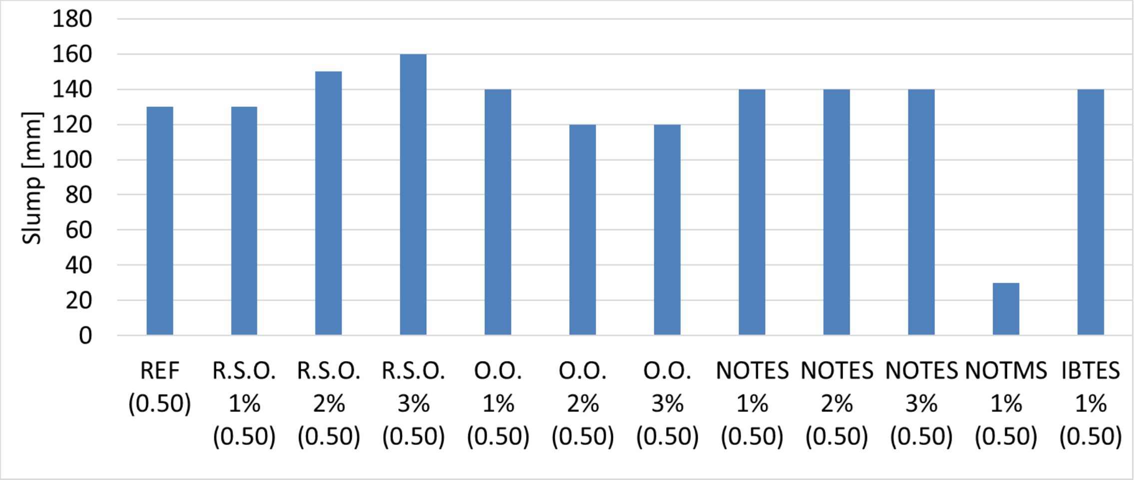

Figure 3 – Slump values w/c = 0.50 @ WAT = 10 min. REF (0.50) = reference mix without hydrophobic admixture.

Two observations of note are the increasing slump results in C.H.A. series, see Figure 2 and the low value in NOTMS 1% (0.50), see Figure 3.

4.2 Compressive strength

The compressive strength results of the 100 mm sided cubes are shown below, see Figures 4 & 5.

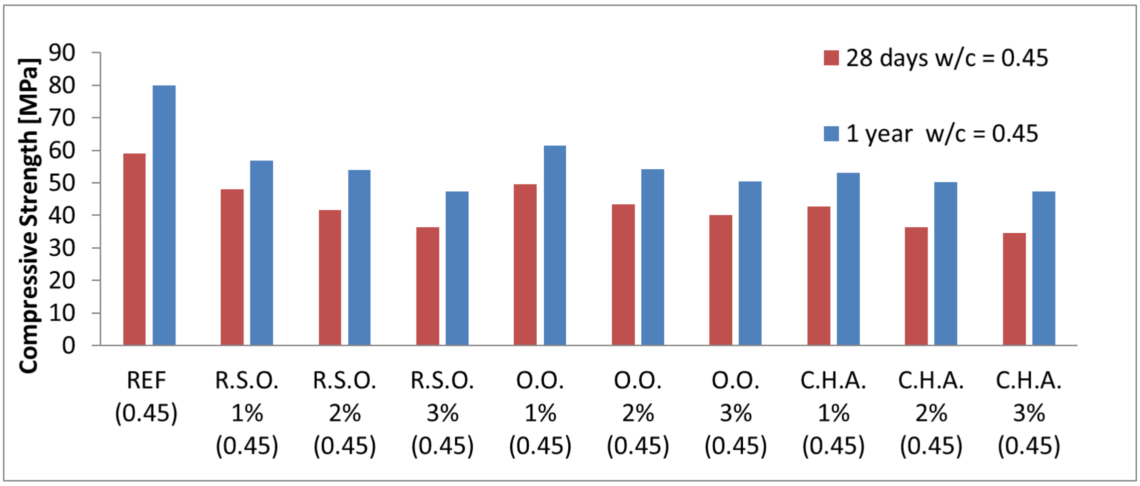

Figure 4 – Average compressive strength of 100 mm sided cube (n=3) after 28 days (left column) and 1 year (right column). REF (0.45) = reference mix; w/c = 0.45.

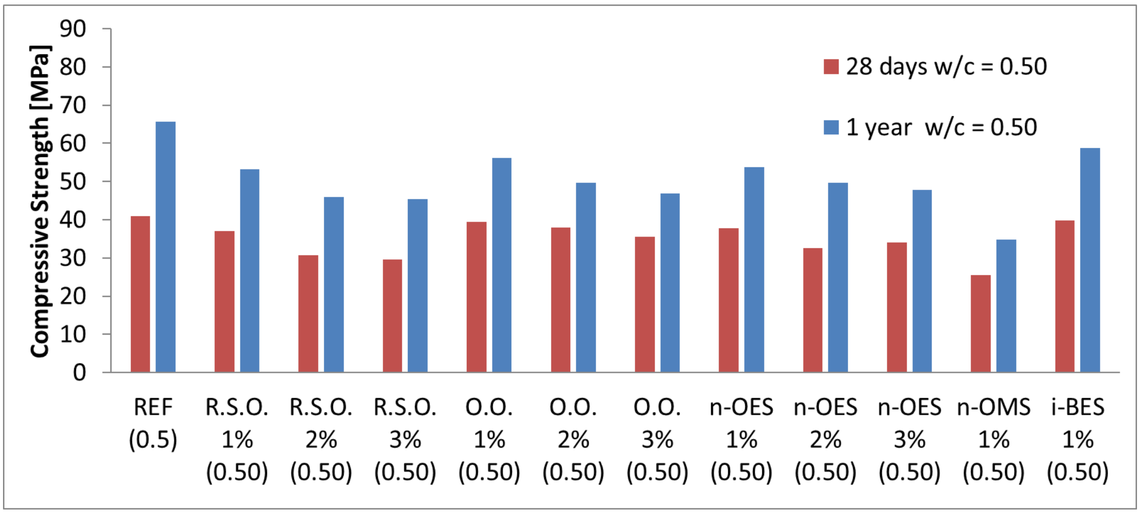

Figure 5 – Average compressive strength of 100 mm sided cube (n=3) after 28 days (left column) and 1 year (right column). REF (0.50) = reference mix; w/c = 0.50.

A downward general trend in compressive strength in both w/c concretes can be observed as the percentage of admixture increases.

4.3 Chloride diffusion profile

The graphic representation of the raw data from the chemical analysis of the dry grinding profiling of concretes with w/c = 0.45 are shown below in (Figures 6-10). Summaries of each admixture are illustrated in (Figures 8-10). In (Figure 11), the results from w/c = 0.50 (3%) are presented.

Concrete w/c = 0.45
Initially, the REF (0.45) and the concretes containing 3% admixtures were profiled and analyzed followed by the series containing 1%. The results from those determined if the concretes with 2% admixtures should be analyzed.

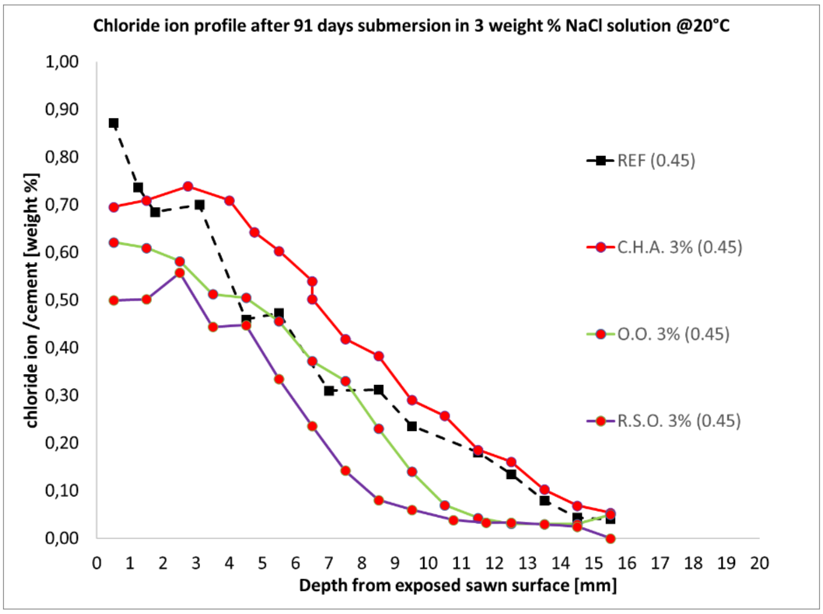

Figure 6 – Chloride ion analysis results from dry grinding of sawn concretes (3% hydrophobic admixture) immersed in 3% (weight) NaCl solution. Concretes' age ca 5 months at start of immersion.

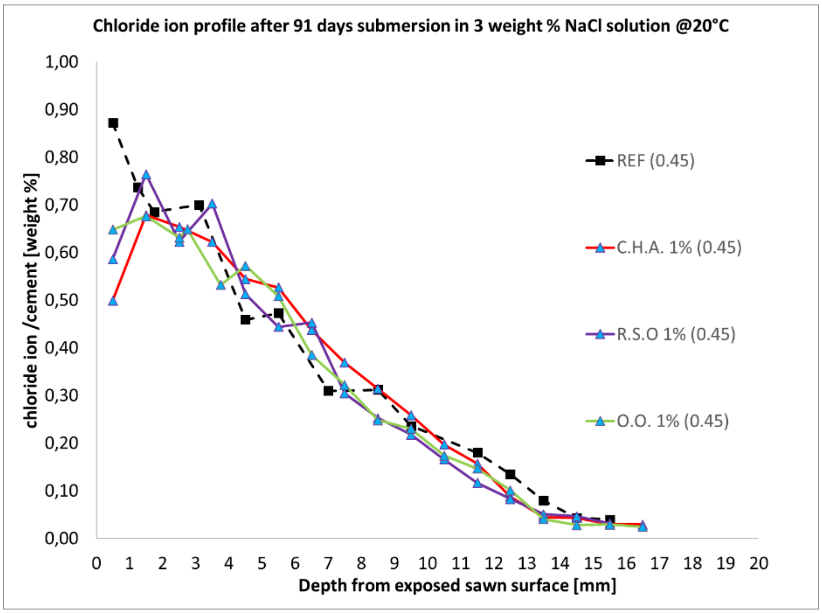

Figure 7 – Chloride ion analysis results from dry grinding of sawn concretes (1% hydrophobic admixture) immersed in 3% (weight) NaCl solution. Concretes' age ca 5 months at start of immersion.

It was decided to only analyze R.S.O. 2% (0.45) following the results from (Figures 6 & 7).

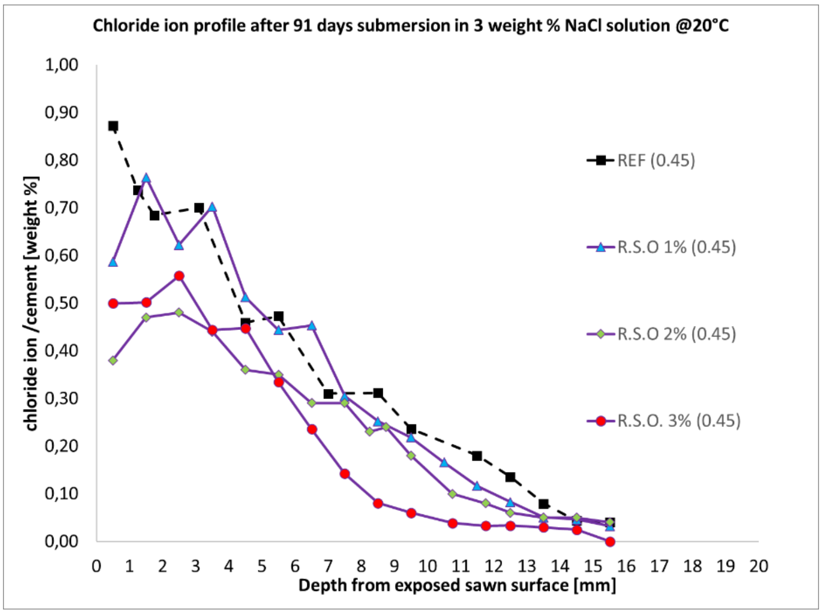

Figure 8 – Chloride ion profile in concrete w/c= 0.45, hydrophobic admixture R.S.O. (1,2 & 3%)

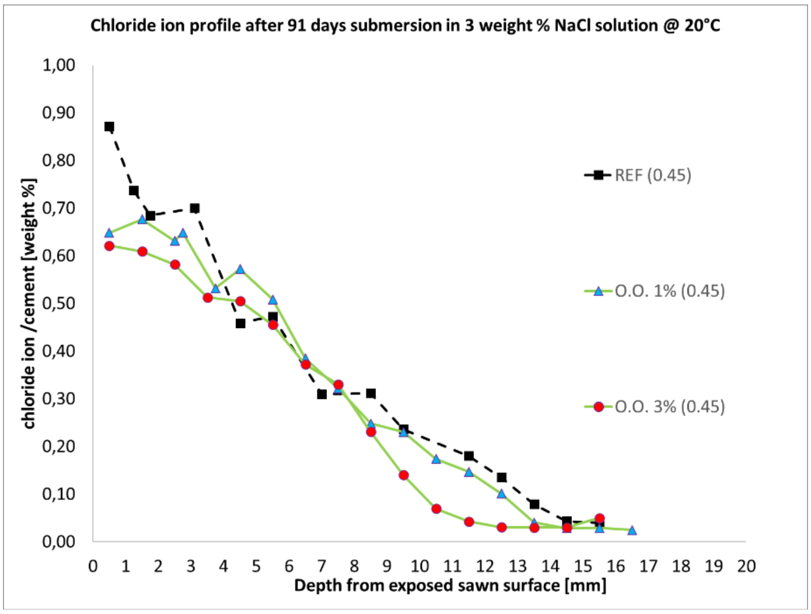

Figure 9 – Chloride ion profile in concrete w/c= 0.45, hydrophobic admixture O.O. (1 & 3%)

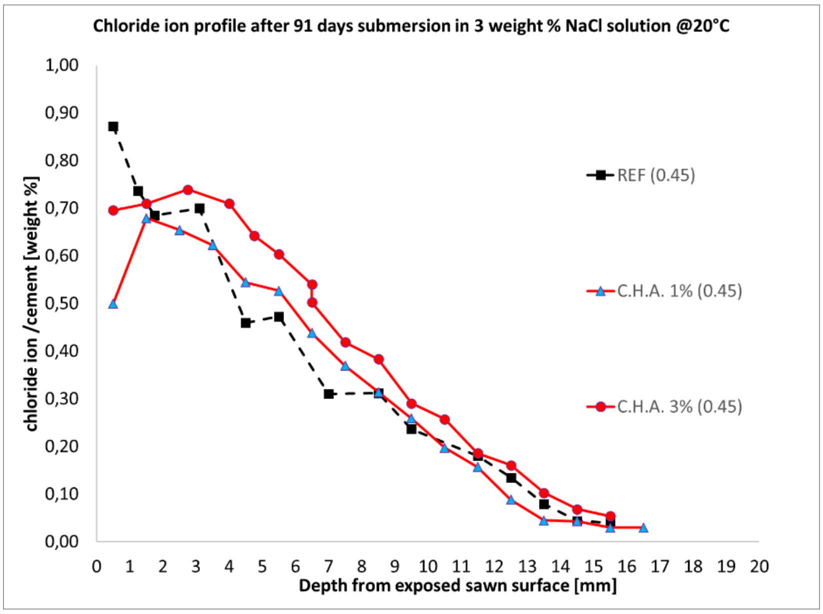

Figure 10 – Chloride ion profile in concrete w/c= 0.45, hydrophobic admixture C.H.A. 1 (1 & 3 %)

Concrete w/c = 0.50

With insight into the effects of increasing the dosage percentage when w/c = 0.45, the same profiling method was used, i.e., results determined whether to proceed to next dosage percentage level. Only concretes w/c = 0.50 with 3% admixture were analyzed, see (Figure 10) below.

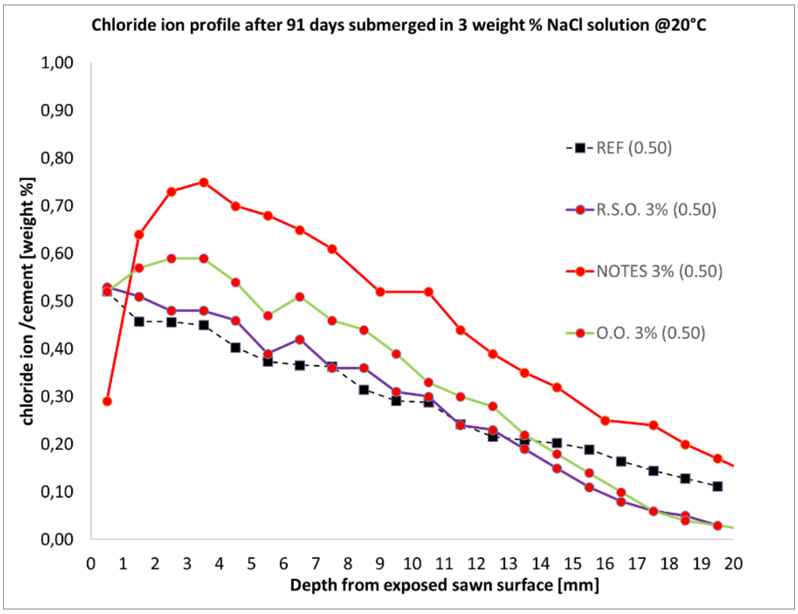

Figure 11 – Chloride ion profile of all concretes at w/c = 0.50 and 3% hydrophobic admixture addition.

4.4 Chloride diffusion coefficients based on least error method.

The raw data results from the chloride profiling were converted from chloride ion/cement weight % to chloride ion/concrete weight % and entered into a macro enabled numerical application [24]. The region 0-4 mm was disregarded as these could have noise issues due the effects of the hydrophobic admixtures, see example in (Figure 12 and Figure 13) or differences in chloride binding due to leaching [35] these can be seen with the $_{0\text{-}4mm}$ suffix, see (Table 3 & 4). Another aspect was used whereby the raw data were shifted from x = 5 mm to x = 0 mm and calculated in the macro, see the blue dots in (Figure 12).

Below, (in Figures 14-17), the results of the software calculations are presented.

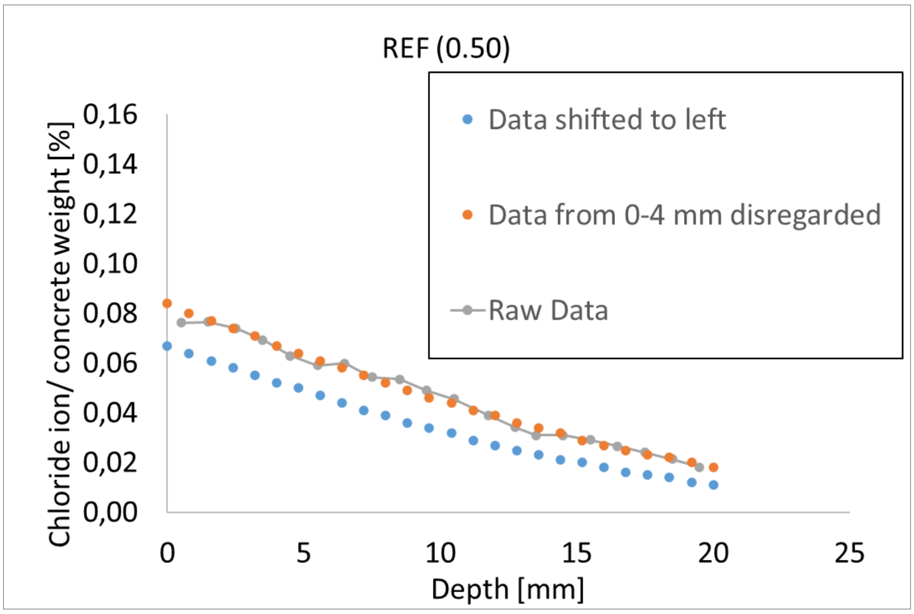

Figure 12 – Converted results from REF at w/c =0.50 after data analysis using [24]. Results raw data (converted); calculated results 0-4 mm disregarded and results shifted to the left i.e. 4 mm → 0 mm.

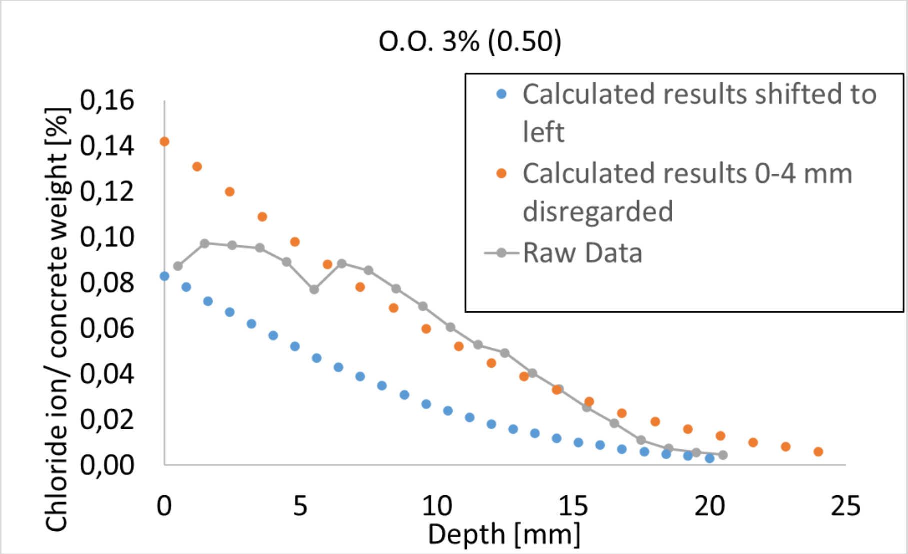

Figure 13 – Converted results from O.O. 3% at w/c =0.50 after data analysis using [24]. Results raw data (converted); calculated results 0-4 mm disregarded and results shifted to the left i.e. 4 mm → 0 mm.

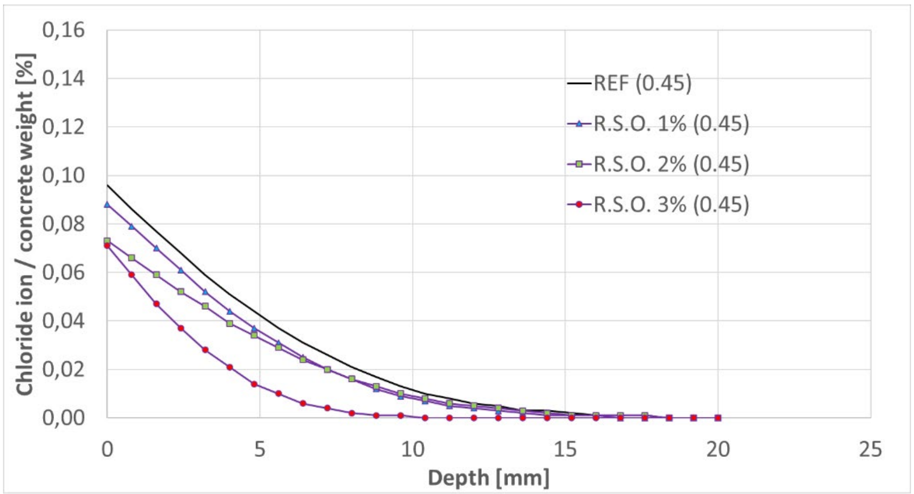

Figure 14 – Converted results from R.S.O 1-3% at w/c =0.45 and REF after data analysis using [24]. Results raw data; 0-4 mm disregarded

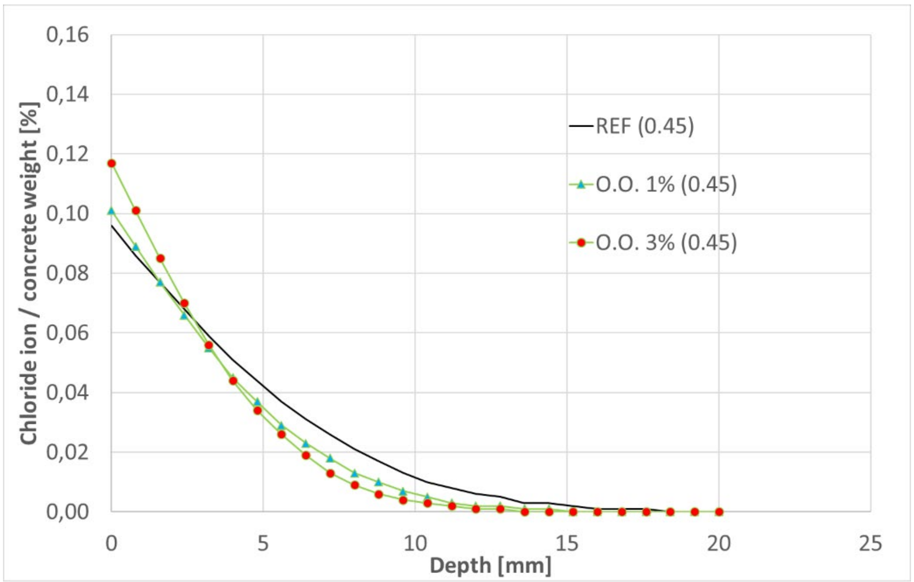

Figure 15 – Converted results from O.O.; 1 & 3 % at w/c =0.45 and REF after data analysis using [24]. Results from raw data; 0-4 mm disregarded

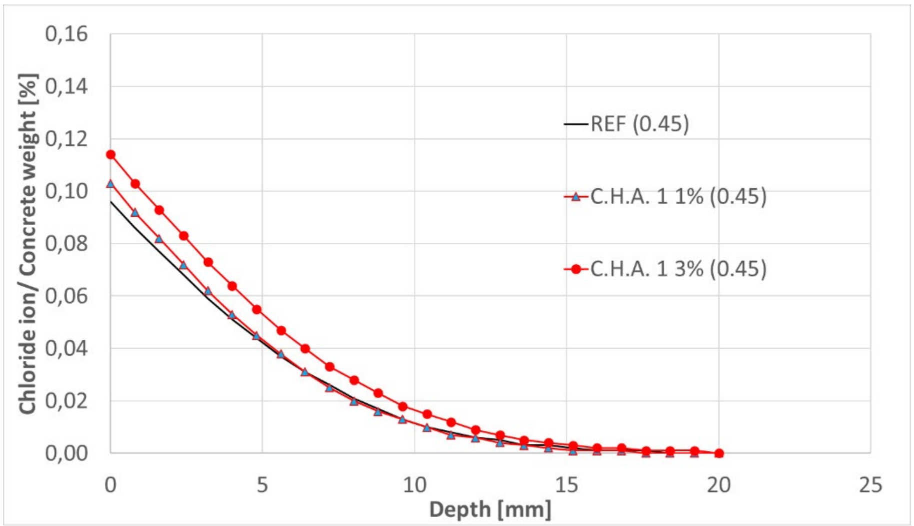

Figure 16 – Converted results from C.H.A 1; 1 & 3 % at w/c =0.45 and REF after data analysis using [24]. Results from raw data; 0-4 mm disregarded

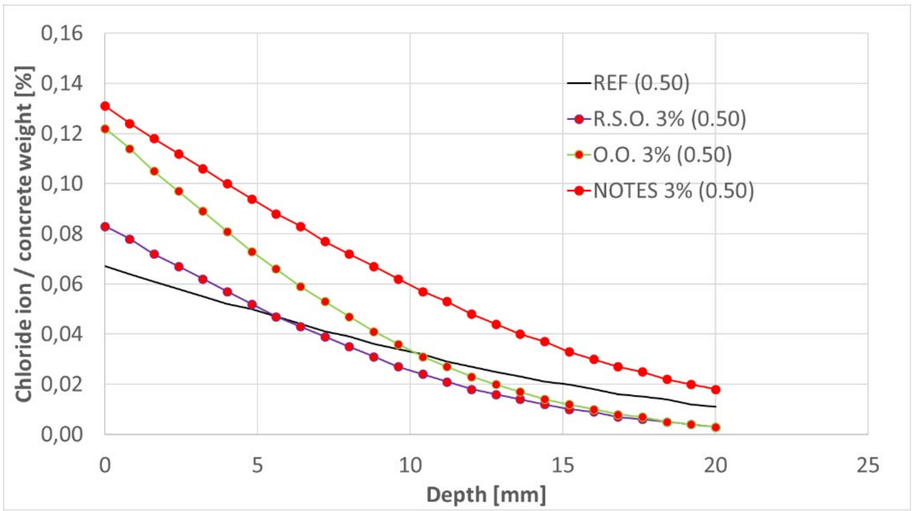

Figure 17 – Converted results from R.S.O., O.O. and NOTES(n-octyl) 3 % at w/c =0.50 and REF after data analysis using [24]. Results from raw data; 0-4 mm disregarded.

Table 3 – Chloride diffusion results based on erfc method based on [24] results from 0-4 mm disregarded = suffix $_{0\text{-}4mm}$ data shifted to left = suffix $_{adj\ 5mm}$. Concrete w/c = 0.45.

		$Da_{0\text{-}4mm}$	$Cs_{0\text{-}4mm}$	$Da_{adj\ 5mm}$	$Cs_{adj\ 5mm}$	$\Delta\ Da_{0\text{-}4mm}$	$\Delta\ Da_{adj\ 5mm}$
	w/c	$[m^2/s]$	[%]	$[m^2/s]$	[%]	[%]	[%]
REF (0.45)	0.45	4,12E-12	0,157	2.68E-12	0.096	100	100
R.S.O. 3%	0.45	1,71E-12	0,166	9.11E-13	0.083	42	34
R.S.O. 2%	0.45	4,17E-12	0,120	2.71E-12	0.073	101	101
R.S.O. 1%	0.45	3,53E-12	0,153	2.26E-12	0.088	86	84
O.O. 3%	0.45	2,27E-12	0,242	1.31E-12	0.117	55	49
O.O. 1%	0.45	3,41E-12	0,159	1.78E-12	0.101	83	66
C.H.A. 3%	0.45	4,81E-12	0,190	2.99E-12	0.114	117	111
C.H.A. 1%	0.45	3,78E-12	0,174	2.46E-12	0.103	92	92

Table 4 – Chloride diffusion results based on erfc method, results from 0-4 mm disregarded = suffix $_{0\text{-}4mm}$ data shifted to left = suffix $_{adj\ 5mm}$. Concrete w/c = 0.50.

		$Da_{0\text{-}4mm}$	$Cs_{0\text{-}4mm}$	$Da_{adj\ 5mm}$	$Cs_{adj\ 5mm}$	$\Delta\ Da_{0\text{-}4mm}$	$\Delta\ Da_{adj\ 5mm}$
	w/c	$[m^2/s]$	[%]	$[m^2/s]$	[%]	[%]	[%]
REF (0.50)	0.50	1,69E-11	0,084	1.33E-11	0.067	100	100
R.S.O. 3%	0.50	8,43E-12	0,115	6.14E-12	0.083	50	46
O.O. 3%	0.50	9,14E-12	0,142	5.29E-12	0.122	54	40
NOTES 3%	0.50	1,46E-11	0,167	1.14E-11	0.131	86	86

5. DISCUSSION

5.1 Fresh properties

The addition of triacylglycerol-based hydrophobic agents did not affect the fresh properties of the concrete with w/c = 0.45, even though the fluid volume increased for each additional percentage unit of admixture. This slump flow equates to S2 according to [25]. The commercial agent (C.H.A) did though increase the fluidity of the system as can be seen in the gradual increase in slump flow, see Figure 2. The complete contents of the commercial agent are proprietary, and as such, may contain chemical species with surface active agents, hence decreasing the yield stress in the system.

In the series w/c = 0.50, the volume of cement paste has of course increased, hence the increase in slump flow. Here, the increase in R.S.O. (triacylglycerol) also increased the slump flow but would keep the concrete classified within a S3 consistency class. The addition of O.O. (triacylglycerol) had no effect, and the NOTES (n-octyltriethoxysilane) series showed very stable results, which increased the theory of other agents in C.H.A. acting on the fresh properties of the cement paste.

5.2 Compressive strength

It is clear from the 28 day and one-year compressive strength results, see Figures 4 & 5, that the addition of triacylglycerols and alkyltrialkoxysilanes at all levels (1-3%) influenced the compressive strength. This can be seen as either a weakening or a decrease in the rate of the cement gel development or the formation of weaker cement clinker hydrates. The pattern of these results from the addition of triacylglycerols reflected those observed in [16], whereby the compressive strength of the cement pastes with olive oil (O.O.) was higher than those with rapeseed oil (R.S.O.), the range within that work though was limited to 0.5-1.5 % addition based on cement weight. No "silane" based admixtures were included in that work.

In the concrete series w/c = 0.45, the drop in strength ranged from 16% (O.O. 1%) to 42% (C.H.A. 3%) after 28 days. This gap increased when the results are compared after one year from 29% (R.S.O. 1%) to 43% (C.H.A. 3%). On average though, the compressive strength of all modified concretes increased by ca 27% after one year compared to the 28-day results.

At the age of one year, and at a slightly higher w/c of 0.50, the effects of the stepwise increase of the hydrophobic additions on compressive strengths generally followed a downward trend too. The reduction though was 3% (IBTES 1%) to 28% (R.S.O. 3%), the outlier being the NOTMS series (38%), mainly due to the poor casting properties. The drop in strength between series with 2% and 3% was also reduced. After one year the gap between the reference concrete and the altered ones was 11% (IBTES 1%) to 31% (R.S.O. 2%). The average increase for all modified concretes from 28 days to one year at w/c = 0.50 was 43%.

The volume occupied by a triacylglycerol molecule varies due to the numerous possible fatty acid combinations available, their associated lengths and/or the presence of double carbon bonds along the chain. The molecular weight (MW in g/mol) of 9c-octadecenoic acid (oleic acid), the main fatty acid component of olive and rapeseed oil, is 282.47. The MW of propane-1,2,3 triol (glycerol), the backbone of triacylglycerol, is 92.11 [26]. The existence of *cis* double carbon bonds (unsaturated) changes the geometry of these branched fatty acid structures. A complete triacylglycerol molecule length at approx. 1.5 nm [27] and molecular area ranging from ca 1.27-1.40 nm^2 [28] is larger than a water molecule (H_2O) at 0.25-0.27 nm according to [29]. It is possible that the triacylglycerol molecule could block some of the capillary and gel pores in the cement paste, hindering or blocking mass flow of water and hence further hydration of cement clinker minerals.

It is well known [30] that the pore system of cement pastes with higher w/c have larger diameter pores and a corresponding increase in the number of pores present in the system. The physical blocking effects of the different hydrophobic concretes may therefore be reduced, i.e. hydration can proceed at a faster rate when the w/c = 0.50 compared to 0.45. The cement clinker used in these experiments has a higher β-C_2S (belite) content than "normal" CEM I cements, which is a slower acting hydraulic mineral compared to C_3S (alite) [31]. Any hinder in belite mineral development will affect the outcome of the strength development. This would also explain the higher strength gains from 28 days to 365 days compared to the lower w/c concretes.

An outlier was the concrete mixed with NOTMS 1%, as the methyl-based alkyl component undergoes a more rapid hydrolysis than the ethyl based alkyltrialkoxysilanes (NOTES). See the slump flow measurements in (Figure 3), this rapid increase in yield stress resulted in less than ideally compacted specimens and affected its compressive strengths negatively.

5.3 Chloride diffusion

The raw data for w/c = 0.45, see Figures 6 & 7, show the concretes' resistances to the inward mass flow of chloride ions in a highly saturated environment. At 1% hydrophobic bulk addition (w/c = 0.45), there is a difference in chloride ion diffusion compared to the reference mix ranging from 8% to 17%. At 3%, the data show a reduction in the amount of chloride ions transported in the concrete with the triacylglycerols (olive and rapeseed oil). The opposite can be seen with the use of alkyltrialkoxysilanes with the same addition rate, whereby the Cl^- mass accumulated more from approx. 3 to 12 mm in the cement paste, see Figure 10.

The results from the R.S.O. (w/c = 0.45) series, the most resistant to chloride diffusion, were complimented with analyses of R.S.O. 2% (w/c =0.45) series, see Figure 8, but analytically shows no improvement to the calculated diffusion coefficient $D_{\mathrm{a0\text{-}4mm}}$.

The results in Table 3 show the converted results as $D_{a0\text{-}4mm}$, D_{aadj5mm} , $C_{\mathrm{s0\text{-}4mm}}$ and C_{sadj5mm}. Series R.S.O. 3% showed the highest reduction in chloride ion diffusion, D_{aadj5mm}, (9.11×10^{-13} m^2/s) followed by O.O. 3% (1.31×10^{-12} m^2/s). The diffusion rates are higher when $D_{a0\text{-}4mm}$ is used. Chemically, these two triacylglycerides, O.O. and R.S.O. differ in the array of fatty acids attached to the glycerol backbone. There is also a mixture of the percentage of C_{16} and C_{18} based fatty acids; olive oil having a higher percentage of oleic acid. Industrially, these are produced in a different manner, whereby Free Fatty Acids (FFAs) are removed in the rapeseed oil (R.S.O) compared to extra virgin olive oil, which is processed exclusively by mechanical extraction. A certain level of FFAs is acceptable in extra virgin olive oil, below 0.8g /100g [32], which is absent in R.S.O. The cold saponification of some of the triacylglycerols in the O.O. series is a possibility due to the presence of FFA in solution which acts as an accelerant [33]. The product of such a process would likely attach to a OH^- site on the pore wall, in a similar fashion as the silane/siloxane condensation reactions. The interaction between the pore wall and the pore solution would be curtailed due to the hydrophobic "tail" protruding out from the pore wall into the capillary pore. No interconnected network would be formed though. The extent of the saponification reaction is unknown, but in yet unpublished work by the author [21], water absorption rates of the concretes with O.O. are lower than with R.S.O. at similar dosages indicating a possible hydrophobic effect on the pore walls in dry specimens.

The use of C.H.A. (w/c = 0.45), which of course undergoes hydrolysis and condensation reactions in a basic environment, influences the mechanics of the diffusion rate of the chloride ion. This has been observed in [34], where the addition, based on cement weight, of 2% of a silane/siloxane (alkyl group unknown) in shotcrete (w/c = 0.35), increased the chloride migration by 40% from $D_{\mathrm{NTB\ 492}}$ 6.9 to 9.8 $\times 10^{-12}$ m^2/s.

A possibility for the higher diffusion of chloride ions in the alkyltrialkoxysilane series (C.H.A. & NOTES) is the condensation products forming a hydrophobic network along the pore walls (capillary and gel), which, following the same assumption, reduced whatever small binding capability the C_3A/aluminate phase had by hindering contact with the pore walls. The increased content from 1 to 3% increased the potential coverage of the pore walls, decreasing the adsorption of Cl^- onto the aluminate phases and possibly even reducing the friction at the pore walls, hence increasing the depth of penetration and amount of chloride ions. How the admixtures are incorporated into the cement mineral hydrates may even have a bearing on the diffusion properties.

Increasing w/c from 0.45 to 0.50, but maintaining the same admixture levels, did not have the same “hindering effect”, but statistically reduced the diffusion rates by the same percentage (approx. 50%). Graphically, it is only after ca 10 mm and 13 mm from the surface that the chloride amounts drop below those of REF (0.50), see Figure 11.

In more recent works e.g. [35], very similar experimental conditions found that the effect of leaching, more specifically portlandite [36], had a large impact on the amount and depth at which chloride ions were detected, due to the reduced pH in the pore solution. The larger and more extensive pore networks in w/c = 0.50 series should have increased the leaching rate into the salt bath solution, hence increasing the possibility of higher chloride ion adsorption and greater penetration depths. In the afore mnentioned work the solution was changed very frequently and therefore increased the rate and extent of leaching.

The concretes with TAGs performed better than the one with n-octylethyloxysilane . Note, the comparison between C.H.A. and NOTES are not strictly comparable. It was decided not to analyze any of the other series (1% or 2%) as these most likely would have performed at the same level as the reference mix as was the case in w/c = 0.45, see Figure 8.

6. CONCLUDING REMARKS

The addition of hydrophobic admixtures ranging from 1 to 3 % based on cement weight and some consequential effects have been presented.

The fresh properties of the concretes were very similar except in two instances, in the case of commercial hydrophobic agent (C.H.A.) and n-octyl methoxysilane (NOTMS). Other additions to the propriety mix (C.H.A.) have affected the yield stress of the concrete positively (higher slump). The rate of hydrolysis of NOTMS, even at low dosages, had a negative effect on the yield stress by consuming excess water in the cement paste (lower slump).
The compressive strength was lower after 28 days and one year compared to the reference in the respective w/c series. The higher the admixture dosage, the lower the resulting compressive strength result. The effect is not as acute at higher w/c, based on the percentage in strength reduction. Olive oil (O.O.) effected the results less than the refined rapeseed oil (R.S.O).

As two different alkyltrialkoxysilanes species were used in the two w/c series, it is impossible to compare directly, but similarities exist; increasing the dosage reduced the compressive strength on average. Compressive strength results at the lower w/c series were affected more by the hydrophobic admixtures than at the higher w/c.

The addition of 1% hydrophobic admixture at w/c = 0.45 exposed to 3% NaCl solution (ca 0.55 M) after 91 days resulted in minor differences in chloride ion diffusion, regardless of chemical structure, based on the raw data. However, using data analyses, differences can be detected, and O.O. (olive oil) showed a 34% reduction in the diffusion rate compared to the reference. The other two, R.S.O. & C.H.A., reduced the diffusion by 16 % and 8 %, respectively. At higher dosages (3%), the triacylglycerols show a higher reduction in chloride ion diffusion > 50% compared to the reference, the opposite was observed with the octyltriethoxysilane based agent (C.H.A.), where the rate increased by 11% compared to the reference.

At equivalent dosages, but with differing w/c, dissimilar chloride diffusion resistances were observed. Higher porosity due to larger and more numerous capillary pores, i.e. due to the higher w/c, and most likely more leaching, requires a higher dosage of the hydrophobic agent to obtain similar results (as lower w/c concretes), but this is not true of the alkyltrialkoxysilanes admixture.

The use of alkyltrialkoxysilanes as a hydrophobic agent increased the rate of chloride diffusion compared to the triacylglycerol-based agents. These most likely reduced the interaction between the Cl^- and C_3A component in the cement grain/hydrate. Another factor could be the reduction in effective pore area due to the presence of a network of condensed silanol. At higher w/c and similar dosages, the accumulation of Cl^- ion in the cement paste increased.
The effect of leaching on the cement paste's ability to bind more chloride ions (whilst not dropping below pH 12) is also a possibility.

7. FURTHER RESEARCH

More knowledge is required in terms of the difference the industrial processing of the "vegetable oils" has on the outcomes in concrete/cement paste contra the purely mechanical oil extraction process (extra virgin olive oil). Adjusting the free fatty acid content on a refined, bleached and deodorized (RBD) oil would complement the study and even open opportunities to use oils of lower quality, which would make the admixtures cheaper and less resource intensive to produce.

Another aspect is the decrease in compressive strengths due to reduced water mass flow in the capillary pores and a hydration issue, will these concretes eventually reach the strength of a "pure" cement paste system and when? Where do these molecules reside in the pore structure, do these accumulate in a particular interface and how stable are they over time?

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