D-2-4 Bulk hydrophobic structural concrete for use in Nordic conditions - initial study

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ABSTRACT: Reinforced concrete is a universal composite product available globally. The ability to shape and cast concrete to fit the needs of the end user at a relatively low cost is its main advantage. The service life of a reinforced concrete structure can be over 100 years. Concrete and the embedded steel though can degrade over time due to frost damage, chloride induced corrosion, alkali silica reaction etc. Costly repairs and social inconvenience are often the consequence. External mass flow of water through defects in the concrete or in the concrete's pore structure is a leading cause of material breakdown of the cement paste or reinforcement bars. The reduction of this flow would be beneficial as this has the potential to hinder the transport of undesired ions such as chlorides or sulphates into the cement paste. In Justnes [1] various chemicals were summarized and demonstrated as having hydrophobic or damp proofing properties in concrete, in particular vegetable oils at an application 1.5% of cement weight with a water to cement ratio of 0.5. This paper will also extend beyond that limit for bulk hydrophobic agents in concrete in reducing water permeability and diffusion of external chlorides within this composite material. The resulting fresh and hardened properties will also be evaluated. Finally, the most effective concretes will then be exposed to real life external environments, such as a Nordic tunnel, over several years. The study is in its infancy and so preliminary results will be presented.

KEY-WORDS: Concrete, bulk hydrophobic agents, long term exposure, Nordic conditions.

INTRODUCTION

Concrete is a composite material usually containing just aggregates, cement and water. The amount of water added into the concrete is selected to take into account of the environment and the physical requirement where it will be placed. An excess of water is nearly always used compared to the amount that can chemically react with the cement. According to Powers [2], the amount of water required to react with all the cement minerals is approx. 19% of the cement weight. In reality most concretes contain an excess of water above this level and probably lie at 45 -50% of the cement weight. This excess of water has a number of consequences for the concrete. The extra water increases the cement paste volume (cement and water) and allows the concrete to flow. In time the water though forms capillary pores [3] which can act as a transport medium for which external ions, including water, can migrate into the cement paste.

Over time this mass transfer is usually disadvantageous for the cement paste or the embedded reinforced steel. Excess water can influence the effects of freezing conditions in the cement paste, chloride ions can lead to corrosion on the rebar etc. In order to increase the time for these external agents to have a significant effect on the concrete, a low water to cement ratio is used. Capillary pores still exist none the less. The aim of this study is to introduce bulk hydrophobic agents in to a concrete of reasonable performance and expose it to an external environment typical for Sweden. This study presents the initial bulk agents screening for the long term performance test. Addition of 3% cement weight was used in order to amplify any effects these agents may have on the cement paste matrix. The prime indicators are the water repellent effect and the compressive strengths after 28 days. Commercially available hydrophobic agents and fillers were also included.

EXPERIMENTAL

Experimental matrix

The base recipe for the screening process was based on mortar with a maximum aggregate size of 4mm. A high cement paste was desired, separation though was encountered with mortars with w/c = 0.6 and 0.7, these but were tested for compressive strengths. A water to cement (w/c) ratio of 0.5 was chosen in order to highlight potential differences between the bulk hydrophobic agents. This w/c was also used in Justnes et al. [4] but limestone filler was also included in these recipes. No additional binder, except the cement, or filler was used in the base recipe. No other chemicals were used to neither prevent air entrainment nor disperse the cement particles.

Base recipe

The vegetable bulk hydrophobic agents were added at 3 % weight of cement weight. The volume equivalent ca. 20 l/m^3 was used for the other agents. In order to keep the cement and water volume constant, the equivalent volume of 0/4 mm was reduced. Some recipes were adjusted to reflect that the agent was water based.

Table 1. Base Recipe

Raw Material	[kg/m^3]
Cement (CEM I 42.5N LA SR 3 MH)	642
Aggregates 0/4 mm	1284
Water	321

Table 2. Mortar containing hydrophobic agent

Raw Material	[kg/m^3]
Cement (CEM I 42,5N LA SR 3 MH)	642
Aggregates 0/4 mm	1228
Water	321
Vegetable oil	19

Table 3. List of hydrophobic agents and their properties

Potential Hydrophobic agent	**Dry content [%]**
Olive Oil (O.O.)	n/a
Corn / Maize Oil (C.O.)	n/a
Linseed Oil (L.S.O.)	n/a
Sesame Oil (S.S.O.)	n/a
Rape Seed Oil (R.S.O.)	n/a
Commercial **C**leaning **A**gent (fatty acid potassium soap) [C.C.A]	26.0
Commercial **W**ashing up **L**iquid [C.W.L]	20.0
Commercial hydrophobic agent and corrosion inhibitor (powder and liquid form) proprietary agent based on an alkali salt of dioic acid with branched hydrocarbons. [H.X.L (liquid)]; [H.M.P (powder)]	16.3 **(liquid)
Commercial water repellent/ hydrophobic agent (60 % alkoyl silane based) [W.BS]	60.0*
Commercial corrosion inhibitor based on octyl triethoxy silane and isotridecanol (ethoxylated) [C.M.E4]	Proprietary 50-100 %

*According to the manufacturer
** applicable to liquid form

Table 4. List of fillers

Filler Material
Commercial Filler MetaKaolin [C.F.MK]
Commercial Filler Ultrafine Limestone [C.F.UFL]

Method
The cement (CEM I 42.5 N SR3/LA/MH) was placed in the 4.7 l / 5 quarts Hobart mixer with the flat beater type B accessory at speed "1" (136 rpm). Approx. 60% of the water was added and after 60 seconds the speed setting was changed to "2" (284 rpm) for an additional 60 seconds.

Thereafter the setting changed to "1" followed by the addition of the remaining water and the bulk hydrophobic agent (if applicable). The fine aggregates were added and the composite was further mixed for 60 seconds. Total mixing time of 300 seconds per mix was the standard operating procedure. The mix was cast into 3 standard steel prisms (40 mm x 40mm x 160mm) and the rest was cast into a cylinder mould Ø 100mm.

These specimens were placed in a climate room (20 ± 2 °C and 98 ± 2 % RH) until the time of testing. Three prisms from each series were tested for compressive strength according to SS EN 196-1:2016 [5].The cylindrical cast mortar was cut into 20mm slices and placed into a drying oven at 40°C.

The hydrophobic (if any) effect of the bulk agents were determined with the application of deionised water droplets onto the multiple prism surfaces produced after the compressive strength testing. The angle created by the water droplets was not determined as the surface of the prism was not plane as seen in.

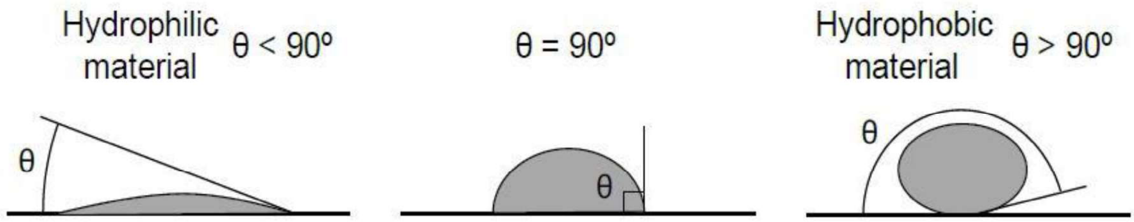

Fig.1. Schematic diagram of the definition of a hydrophobic surface. Taken from Selander et al. [6]

Water absorption coefficient (not complete at the time of writing)
In order to gain another factor of the hydrophobic efficiency, the water absorption will be measured. The cast cylinders were sawn in to ca. 20 mm thick discs and the procedure will follow EN ISO 15418 [7]. The exception being the total surface area of the three specimens will be below 300 cm2 and the thickness of the specimens will not reflect the actual construction dimensions as the drying times for these dimensions (100 mm and upwards) would be far too long. The testing time should be at least 24 hours including some set time intervals.

RESULTS

Compressive strengths
The prisms cast were tested for compressive strengths after 28 days a total of three prisms per series were tested (i.e. 6 individual results). The commercial washing liquid (C.W.L) specimens didn't hardened and were taken out of the screening process. Fig shows the results obtained from the testing.

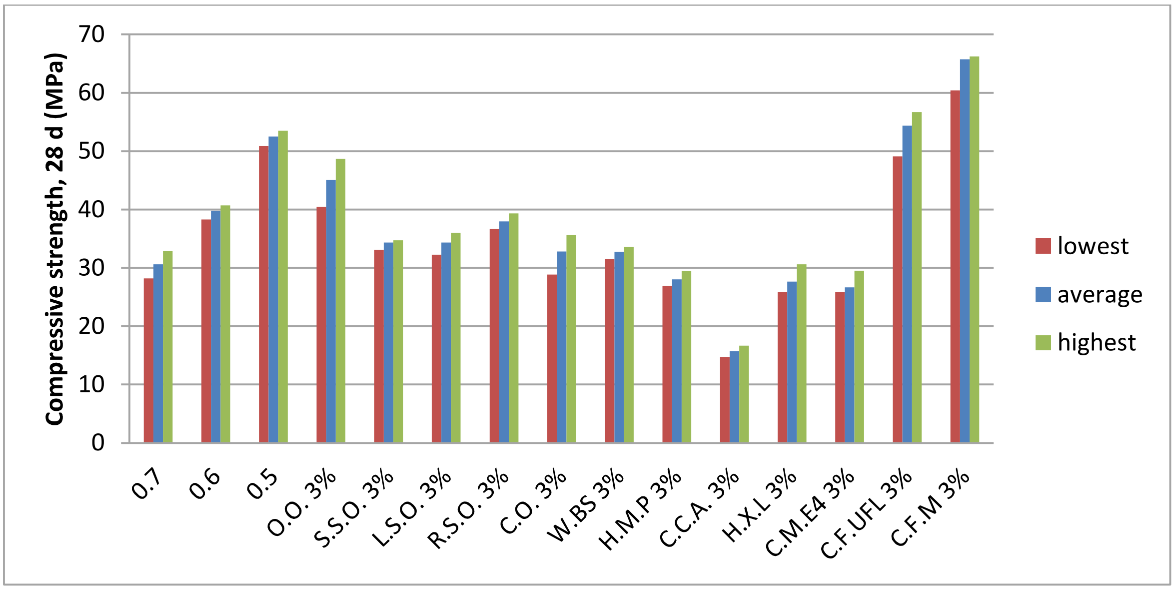

Fig.2. 28 day compressive strength of standard prisms

Below shows the raw data from the testing and some statistics. The specimens “0.7”, “0.6” and “0.5” represent the base recipe at different water to cement ratios, i.e. “0.5” = w/c 0.5. The “3%” refers to the amount used in terms of cement weights, the abbreviations are identified in table 3 and table 4.

Table 5. 28 day Compressive strengths including additional data

Series Name	Density	Compressive strengths				
	[kg/m3]	Average [MPa]	Lowest [MPa]	Highest [MPa]	Std. dev. [MPa]	Compressive Strength Reduction compared to “0.5”
w/c =0.7	2138	30.6	28.2	32.9	2.4	-42%
w/c =0.6	2212	39.8	38.3	40.7	1.3	-24%
w/c =0.5	2296	52.5	50.9	53.5	1.5	0%
O.O. 3%	2233	45.0	40.4	48.7	4.3	-14%
S.S.O. 3%	2195	34.3	33.1	34.8	0.9	-35%
L.S.O. 3%	2230	34.3	32.3	36.0	2.2	-35%
R.S.O. 3%	2199	37.9	36.6	39.3	1.4	-28%
C.O. 3%	2212	32.8	28.9	35.6	3.4	-37%
W.BS 3%	2236	32.8	31.5	33.6	1.0	-38%
H.M.P 3%	2128	28.0	26.9	29.4	1.3	-47%
C.C.A. 3%	2122	15.7	14.8	16.7	1.3	-70%
H.X.L 3%	2197	27.6	25.8	30.6	3.4	-47%
C.M.E4 3%	2216	26.6	25.8	29.5	1.2	-49%
C.F.UFL. 3%	2307	54.4	49.1	56.7	3.2	+4%
C. F.M 3%	2260	65.8	60.4	60.4	0.7	+25%

Density change

The addition of the hydrophobic agents had an effect on the density of the mortars. The replacement of 0/4mm aggregates with these agents would have a ca 30-40 kg/m^3 reduction in the overall density. The rest must be due to air entrainment, see table 6 below demonstrating the effect these had compared to the reference ("0.5"). The fillers "C.F.M" and "C.F.UFL" did not have a significant impact on density and this was also evident in the compressive strengths, see table 5. The different densities of the other agents would have a small bearing on the density change.

Table 6. Theoretical increased air content due to bulk agent

Series Name	Density	Increase in air content based on overall density difference / density of ref "0.5"
	[kg/m^3]	[%]
0.5	2296	
O.O. 3%	2233	1.4%
S.S.O. 3%	2195	3.1%
L.S.O. 3%	2230	1.6%
R.S.O. 3%	2199	3.0%
C.O. 3%	2212	2.4%
W.BS 3%	2236	1.3%
H.M.P 3%	2128	6.1%
C.C.A. 3%	2122	6.7%
H.X.L 3%	2197	3.2%
C.M.E4 3%	2216	2.2%
C.F.M. 3%	2307	-1.8%
C.F.UFL 3%	2260	-0.2%

Hydrophobic effect

In order to increase the speed of the screening process, a simple test involving the application of water droplets onto the bulk surface of the mortar cement paste was conducted. The vast majority of hydrophobic agents had a water repellent / hydrophobic effect. In Fig & Fig photos taken after the water application can be seen. Note "0.7" was not tested.

Table 7. Water droplet hydrophobic effect.

Series Name	Hydrophobe or water repellent?	Series Name	Hydrophobe or water repellent?
0.6	No	W.BS 3%	Yes
0.5	No	H.M.P 3%	Yes
O.O. 3%	Yes	C.C.A. 3%	Yes
S.S.O. 3%	Yes	H.X.L 3%	No
L.S.O. 3%	Yes	C.M.E4 3%	Yes
R.S.O. 3%	Yes	C.F.M 3%	No
C.O. 3%	Yes	C.F.UFL 3%	No

Fig.3. Bulk cement paste simple water droplet testing 1 (G.S = C.C.A)

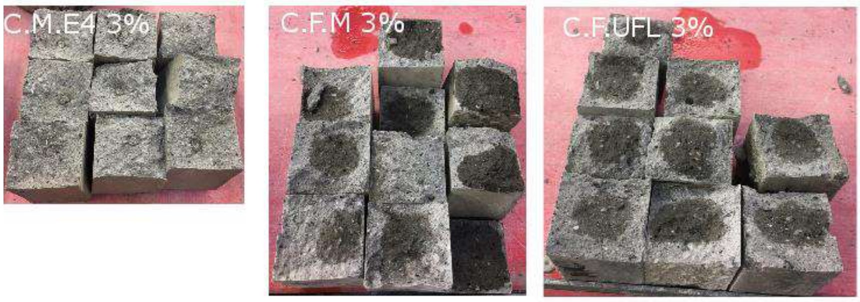

Fig.4. Bulk cement paste simple water droplet testing 2

Water absorption coefficient

The specimens were still being conditioned in the oven at the time of writing and no results were as yet present.

DISCUSSION

The initial aim was to screen various known hydrophobic agents and to demonstrate their effect without the addition of other chemicals such as anti-entrainment chemicals. The compressive strengths were reduced with the use of vegetable oils, see table 7 with an application of 3% cement weight. This ranged from 14-35% less than the reference "0.5" (52.5 MPa). Use of olive oil had the least negative effect on compressive strengths of the vegetable oils (-14 %) whereas linseed and sesame oil had the most impact (-35% each). In Justnes et al. [4] a similar effect was noticed especially with linseed oil, but the bulk agents were applied at 1.5% of cement weight. An investigation of mortars with w/c = 0.45 and 3 % addition of bulk hydrophobic agents (based on cement weight) also noticed a significant drop (24-32%) in compressive strengths at 28 days [8].

The effect of air intrusion on the compressive strengths though has to be considered. There are density differences between the reference and the vegetable oils ranging between 60-100 kg/m3 (or 2-4 %) which can also be seen in the commercial hydrophobic agents. It is known [9] that each additional percent of entrained air has an approx. 5% reduction in compressive strengths, see table 6 and table 7.

This would explain a portion of the loss in compressive strengths except in the case of linseed oil. Air content of the hardened mortars and the microstructure can be examined with thin section to determine the size and presence of air bubbles. The commercial hydrophobic bulk agents had a similar effect as the vegetable oils in terms of density change and a reduction in compressive strengths. The most profound effect was the "C.C.A. 3%" series whereby the compressive strengths were reduced by 70 %. It is believed that the presence of other chemicals caused it to entrain significantly more air than the other agents.

The commercial filler materials had no negative on the compressive strengths; the metakaolin even had a positive effect due to its pozzolanic effect. As expected the reference mortar, including the ones with commercial fillers had the largest wetted area and had little water repellence. All vegetable oils produced a bulk water repellent effect see Fig. The angle between the droplet and the surface has not been determined. Their efficiencies will be determined at a later date with the water absorption testing.

INITIAL CONCLUSIONS

1. The addition of vegetable oils produced a water repellent / hydrophobic bulk cement paste matrix at 28 days. These bulk agents decreased the density of the mortar specimens most probably due to the increased inclusion of air. This reduced the 28 day compressive strengths considerably. A drop of between 14 – 35 % was measured depending on the variety of vegetable oil used.

2. The entrained air may have a beneficial effect for freeze thaw testing but this requires the analysis of the air pore sizes and distribution. The long term testing specimens will have to be compliant to XD3 exposure classes see Table F.1 of SS-EN 206:2013 [10] and so the cement matrix will need to contain a minimum macro air volume of approx. 4.0-5.0 % (depending on aggregate size, D_{max})

3. The commercial hydrophobic agents did provide a water repellent cement paste except (H.X.L 3%) but had a more negative effect on the compressive strengths than the oils. The addition of the ultrafine fillers proves that it is the use of hydrophobic agents that caused the drop in density and thus compressive strengths.

4. In terms of comparing the various hydrophobic agents with each other, further testing is required and will be conducted in the interim. Thereafter, a select few agents will be used to produce concrete of suitable exposure class for further real life testing conditions in a Nordic road tunnel and other suitable environments.

FURTHER RESEARCH

The results on the density changes require more testing and analysis, especially the effect of air entrainment. Thin section analysis of select samples could be used to explain the amount and the size of the entrained air. In parallel, freeze thaw testing should be used to verify the specimens' actual ability to within stand these conditions. It was interesting to note the apparent less water repellent of one of the commercial products (H.X.L 3%). Do these have a limited shelf life and how would this effect the long term performance of the concretes?

REFERENCES

[1] H. JUSTNES, *Low water permeability through hydrophobicity*, COIN Project Report 1, (2008). Sintef, Norway.

[2] T.C. POWERS, *Structure and Physical Properties of hardened Portland Cement Paste*. J. Am. Ceram. Soc. 41(1958):1-6.

[3] P.C. HEWLETT, *LEA's Chemistry of Cement and Concrete.4th edition*. (1998). Arnold, London.

[4] H. JUSTNES, T. ØSTNOR, V. BARNILS, *Vegetable Oils as Water Repellents for Mortars. Proceedings of the 1st Int. Conf. of Asian Concrete Federation.* Chiang Mai Thailand. 2 (2004):689-698

[5] SIS, SS-EN 196-1Cement-Provning- Del1: *Bestämmning av hållfathet. (Methods of testing cement.* Determination of strength). Stockholm, (2016), SIS Förlag AB.

[6] A. SELANDER, N. DAVANT, K. MALAGA, *Hydrophobic shotcrete-a method to waterproof tunnels. Hydrophobe VII 7th Int. Conf. on water repellent treatment and protective surface technology for building material*, (2014), pp. 67-75, Elena Charola, A., Delagado Rodrigues, J. Laboratorio national de engenhavria civil, I.P. Lisboa.

[7] European Committee for Standardization. EN ISO 15148:2002 *Hygrothermal performance of building materials and products-Determination of water absorption coefficient by partial immersion.* (2002). CEN, Brussels.

[8] L. PARG, *Investigation of the hydration behaviour of concrete mixtures with water repellent agents.* Master thesis. Borås CBI Betonginstitutet AB, (2016). Sweden.

[9] A. M. NEVILLE, J.J. Brooks, Concrete Technology. 2nd Edition. Pearson Harlow, 2010. England.

[10] SIS, 2016. SS-EN 206:2013+A1 Concrete- Specification, performance, production and conformity. Stockholm, (2016), SIS Förlag AB.