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Concrete durability improvement in presence of sulphates using a silane based hydrophobic impregnating agents

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SUMMARY: Hydrophobic impregnation is a well-known and proven technique to prevent the ingress of water and soluble aggressive ions (e.g., chlorides, sulphates) into a structure. Although there are numerous papers about chlorides and hydrophobic impregnations, little has been published about the effect of sulphates. The aim of this study is to show the effect of a pure silane based hydrophobic impregnating agent when different concrete mixes are subjected to sulphate attack. Two test methods are compared. The results clearly show the beneficial effect brought by the use of a silane based hydrophobic impregnating agent in order to protect concrete structures from sulphate attack.

KEY-WORDS: hydrophobic impregnation, sulphates.

INTRODUCTION

Hydrophobic impregnation is a well-known and proven technique to prevent the ingress of water and soluble aggressive ions (e.g., chlorides, sulphates) into a structure. Although there are numerous papers about chlorides and hydrophobic impregnations, few papers have been published about the effect of sulphates[1-3].

Ibrahim[1,2] showed that the use of a silane/siloxane mix combined with an acrylic top coat was a very effective solution against sulphate attacks. However, Aguiar [3] showed that the highly diluted solvent-based siloxane compound tested was ineffective against sulphate attacks.

The aim of this study was to test different concrete mixes that follow the recommendations of EN 206-1 and were treated with pure silane using two methods (SIA 262/1 & ASTM C 1012:13) to determine their effectiveness against sulphate attack.

DEFINITIONS ACCORDING TO EN 206-1 STANDARD

EN 206-1[4] defines the different class of exposure according to the environment of the structure, as shown in Table 1.

Table 1: Exposures classes from EN 206-1:2000 for chemical attack.

Class designation	**Description of the environment**	**Informative examples where exposure classes may occur**
Where concrete is exposed to chemical attack from natural soils and ground water as given in Table 2, the exposure shall be classified as given below. The classification of sea water depends on the geographical location; therefore the classification valid in the place of use of the concrete applies. NOTE A special study may be needed to establish the relevant exposure condition where there is: ▪ limits outside of Table 2; ▪ other aggressive chemicals; ▪ chemically polluted ground or water; ▪ high water velocity in combination with the chemicals in Table 2.		
XA1	Slightly aggressive chemical environment according to Table 2	
XA2	Moderately aggressive chemical environment according to Table 2	
XA3	Highly aggressive chemical environment according to Table 2	

The exposure classes for chemical attack are listed in Table 2. The below classified aggressive chemical environments are based on natural soil and ground water at water/soil temperatures between 5°C and 25°C and a water velocity sufficiently slow to approximate to static conditions. The most onerous value for any single chemical characteristic determines the class.

Where two or more aggressive characteristics lead to the same class, the environment shall be classified into the next higher class; unless a special study for this specific case proves that it is not necessary.

Table 2. Limiting values for exposure classes for chemical attack from natural soil and ground water.

Chemical characteristic		**Reference test method**	**XA1**	**XA2**	**XA3**
Ground water	SO_4^{2-} mg/l	EN 196-2	≥ 200 and ≤ 600	> 600 and $\leq 3\,000$	$> 3\,000$ and $\leq 6\,000$
	pH	ISO 4316	≤ 6.5 and ≥ 5.5	< 5.5 and ≥ 4.5	< 4.5 and ≥ 4.0
	CO_2 mg/l aggressive	EN 13577:1999	≥ 15 and ≤ 40	> 40 and ≤ 100	> 100 up to saturation
	NH_4^+ mg/l	ISO 7150-1 or ISO 7150-2	≥ 15 and ≤ 30	> 30 and ≤ 60	> 60 and ≤ 100
	Mg^{2+} mg/l	ISO 7980	≥ 300 and $\leq 1\,000$	$> 1\,000$ and $\leq 3\,000$	$> 3\,000$ up to saturation

Soil	SO_4^{2-} mg/kg[a] total	EN 196-2[b]	≥ 2 000 and ≤ 3 000[c]	> 3 000[c] and ≤ 12 000	> 12 000 and ≤ 34 000
	Acidity ml/kg	DIN 4030-2	> 200 Baumann Gully	Not encountered in practice	

[a] Clay soils with a permeability below 10^{-5} m/s may be moved into a lower class.

[b] The test method prescribes the extraction of SO_4^{2-} by hydrochloric acid; alternatively, water extraction may be used, if experience is available in the place of use of the concrete.

[c] The 3 000 mg/kg limit shall be reduced to 2 000 mg/kg, where there is a risk of accumulation of sulphate ions in the concrete due to drying and wetting cycles or capillary suction.

EN 206-1 also defines the concrete mix design according to the different class of exposures, as shown in Table 3.

Table 3. Concrete mix design according the exposure class.

	Aggressive chemical environments		
	XA1	**XA2**	**XA3**
Maximum W/C	0.55	0.50	0.45
Minimum strength class	C30/37	C30/37	C35/45
Minimum cement content (kg/m^3)	300	320	360
Other requirements	Sulphate resisting cement (see Note below)		

NOTE: *When SO_4^{2-} leads to exposure classes XA2 and XA3, it is essential to use sulphate-resisting cement. Where cement is classified with respect to sulphate resistance, moderate or high sulphate-resisting cement should be used in exposure class XA2 (and in exposure class XA1 when applicable) and high sulphate-resisting cement should be used in exposure class XA3.*

CONCRETE MIX DESIGNS AND CHARACTERISATION

Table 4 lists the concrete mix designs and their characterisation parameters.

Table 4. Concrete mix designs and characterisation.

	Control	**XA1**	**XA2**	**XA2bis**	**XA3**
Cement type	CEM II/A-LL 42.5 N	CEM II/A-LL 42.5 N	CEM III/B 32.5 N HS	CEM I 42.5 R HS	CEM III/B 32.5 N HS
Cement Content	320	300	320	280	310
Fly-ash	—	—	—	40	50
Aggregates (mm)	0-32	0-32	0-8	0-8	0-8
Superplasticizer (carboxylate) (% w/w)	0.25	0.25	0.55	1.8	1.0
W/C	0.53	0.53	0.48	0.48	0.43
Density (kg/m^3)	2421	2430	2418	2442	2440
Air content (%)	1.2	1.4	1.2	1.6	1.3
Consistency test					
Flow table (mm)	400	420	440	390	430
Slump (mm)	70	100	170	160	190
Compactability	1.05	1.06	1.03	1.05	1.03
Compressive strength (28 days) (N/mm^2)	41.1	42.5	51.1	65.7	59.6
Dry density (kg/m^3)	2420	2420	2339	2388	2364
Water conductivity (g/m^2)	4.8	5.5	3.8	2.5	3.0
Air content (%)	1.2	1.5	0.7	1.2	0.50
Porosity (%)	14.1	13.6	11.8	10.1	9.5

NOTE: *2 different concrete mix designs were used for the exposure class XA2 (both XA2 and XA2bis). The former uses a CEM III cement while the latter uses a normal OPC with the addition of fly ash.*

SAMPLE PREPARATION AND HYDROPHOBIC TREATMENT

For all experiments, cubes of 150 mm side length were produced. The cubes were prepared according to EN 12390-2, and stored for 28 days after casting at 20°C / 95% relative humidity.

After humid storage, the cubes were stored at 20°C / 60 % RH until they are older than 90 days from their preparation. Then cores with the required dimensions for the various tests were taken and left to dry at 20°C / 60% RH.

Application of the hydrophobic agent (pure triethoxy(2,4,4-trimethylpentyl) silane with 99% active content) was carried out by total immersion for 60 seconds.

Preliminary tests were conducted to determine the number of necessary immersion per concrete mix design to reach an application of 180-200 g/m^2 of the hydrophobic impregnation agent. With two to three immersions per sample, this amount could be achieved in each case and the penetration depth obtained ranged from 2.5 to 4.5 mm.

After application, the core samples were stored again at 20°C / 60 % RH for at least three weeks. Subsequently, the tests were carried out on both untreated reference and the treated (hydrophobic) samples for comparison using the two different procedures described below.

TEST METHODS

SIA 262/1:2013

“The concrete specimens subjected to cycle of drying followed by immersion in sulphate solution absorb sulphates. These can react with the specimen constituents and cause a modification of its volume.”

Sulphate solution: 5% of Sodium sulphate (5 g of anhydrous sodium sulphate in 95 g of water)

Specimen sizes: concrete cores (Ø = 28 ±2 mm; length l = 150 ± 20 mm)

Age of specimen: 28 days

Cycle 1: drying at 50 ± 5°C during 120 ± 2 hours
Cooling down to 20°C during 1 hour in desiccator
Immersion during 48+1 hours in sulphate solution

Cycles 2 to 4: drying at 50 ± 5°C during 120 ± 2 hour
Cooling down to 20°C in desiccator
Immersion during 48+1 hours in sulphate solution

Further: Full immersion in the sulphate solution for 56 days

Authoritative sulphate expansion for the limit value for sulphate resistant concrete is the difference between the expansion of the first four cycles and the end of the further expansion after 56 days, that is: $\Delta Ls = L_{56} - L_{4;}$ ΔLs shall be $\leq 1.2‰$

ASTM C1012-13

“This test method covers the determination of length change of mortar bars immersed in a sulphate solution. Mortar bars made are cured until they attain a compressive strength of

20.0 ± 1.0 MPa [3000 ± 150 psi], as measured using cubes made of the same mortar, before the bars are immersed.”

Sulphate solution: 0.35 moles of sodium sulphate (50 g of anhydrous sodium sulphate per litre of water)

Specimen sizes*: Prisms: 25 x 25 x 285 mm and cores for expansion measurement.

Age of specimen: Until they achieved 20 MPa

Immersion: Continuous immersion in the sulphate solutions and measurement carried out at least after 1, 2, 3, 4, 8, 13 and 15 weeks

Subsequent measurements can be done at 4, 6, 9 and 12 months.

The used pH solution are replaced after 1, 2, 3, 4, 8 13, 15, 16 weeks, 6, 9, 12, 15 and 18 months

NOTE*: *To measure the induced sulphate expansion, cores of 30 mm and 50 mm diameter, both 150 mm long were used.*

RESULTS

SIA 262/1

The results obtained are summarized in Figure 1 and Table 5.

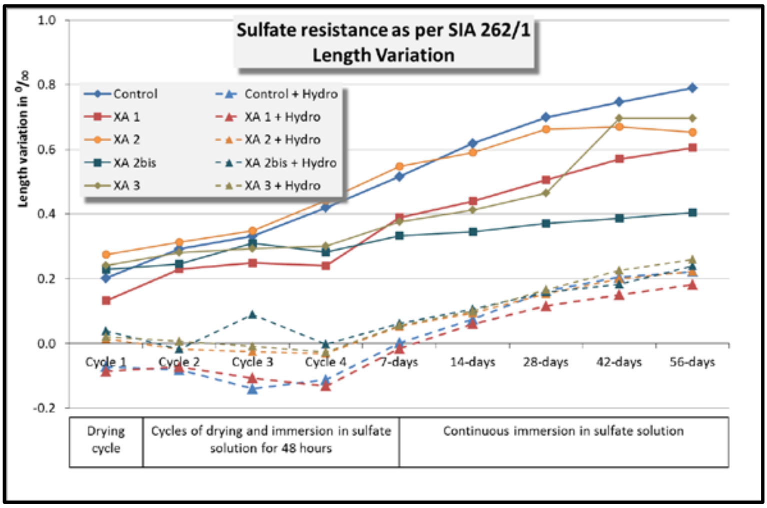

Figure 1. Length variation results obtained with the SIA 262/1 test

Table 5. Results of the SIA 262/1 tests

Sulphate resistance SIA 262-1 annex D (Limit sulphate expansion Δls ≤ 1.2‰)					
	Control	**XA1**	**XA2**	**XA2bis**	**XA3**
Cement type	CEM II/A-LL 42.5 N	CEM II/A-LL 42.5 N	CEM III/B 32.5 N HS	CEM I 42.5 R HS (+ 14% Fly Ash)	CEM III/B 32.5 N HS
Untreated – values in ‰					
after cycle 4; l_4	0.420	0.240	0.442	0.283	0.375
After 56d; l_{56}	0.790	0.605	0.653	0.406	0.470
$\Delta L_s = L_{56} - L_4$	0.370	0.365	0.211	0.123	0.169
Treated with Hydrophobic Impregnation – values in ‰					
after cycle 4; l_4	-0.112	-0.132	-0.031	-0.002	-0.027
After 56d; l_{56}	0.222	0.182	0.223	0.239	0.260
$\Delta Ls = L_{56} - L_4$	0.334	0.314	0.254	0.241	0.287
Reduction of the total expansion after the storage of 56 days in sulphate solution					
	72%	70%	66%	41%	45%

ASTM C1012-13

The sizes of the specimens were modified (refer to the note in the test description above) and the results obtained are summarized in Table 6 and Figures 2 and 3.

Table 6. Results from the ASTM C1012-13 test.

Sulphate resistance ASTM C1012-13 with modified sample size						
	Control	**XA1**	**XA1**	**XA2**	**XA2bis**	**XA3**
Core diameter	30 mm	30 mm	50 mm	50 mm	50 mm	50 mm
Untreated – values in ‰						
After 28 days	0.386	0.388	0.355	0.376	0.318	0.386
After 56 days	0.396	0.350	0.323	0.444	0.343	0.422
After 91 days	0.448	0.416	0.394	0.464	0.398	0.435
Treated – values in ‰						
After 28 days	0.206	0.248	0.198	0.191	0.246	0.198
After 56 days	0.246	0.290	0.244	0.257	0.331	0.256
After 91 days	0.301	0.346	0.285	0.298	0.369	0.299
Reduction of expansion (after 91 days)						
	%	**17%**	**28%**	**36 %**	**7%**	**31 %**

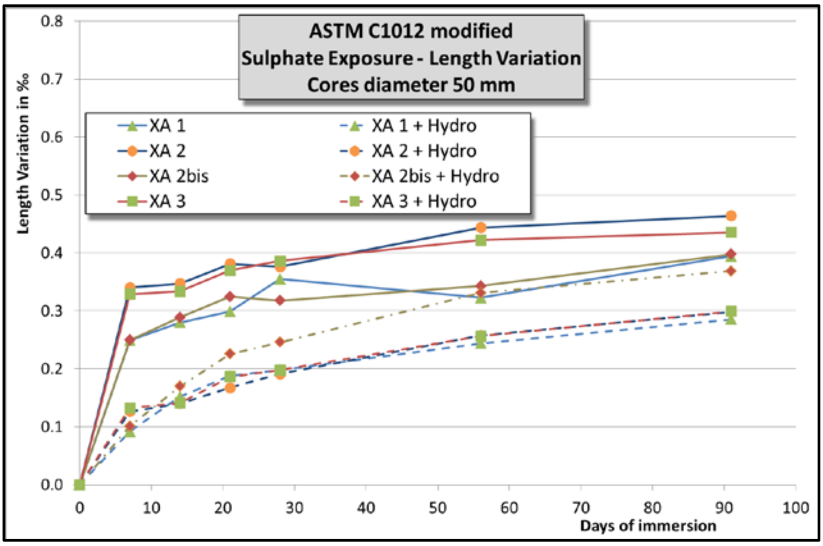

Figure 2: Length variation of XA-1, XA-2 and XA-3 exposure class mix design (treated and untreated)

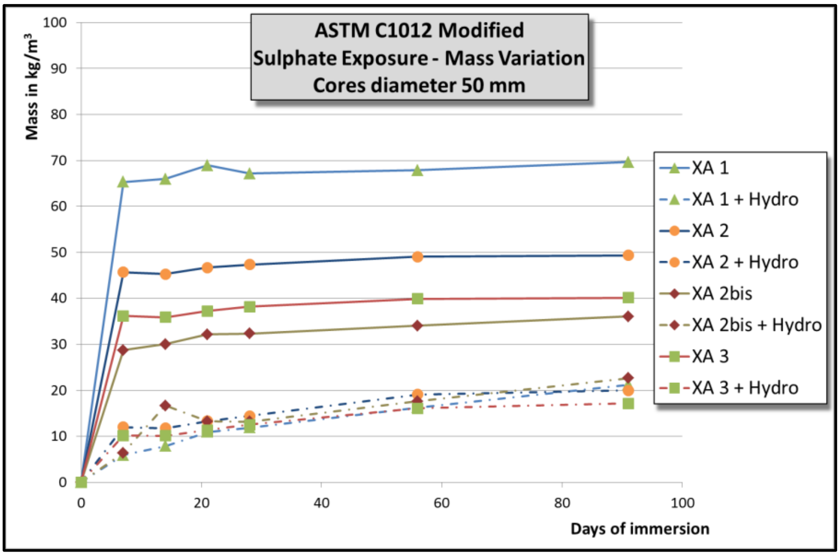

Figure 3 Mass variation of XA1, XA2 and XA3 exposure class mix design (treated and untreated)

DISCUSSION

SIA 262/1

The sulphate solution used in the Swiss standard has similar concentration than that for the ASTM method (5% of sodium sulphate). However during the first 4 cycles the specimens undergo a severe regime of drying and immersion that promote the migration of the sulphate into the concrete.

56 days after the last cycles of drying/immersion regime, the untreated specimens exhibit an expansion that ranges between 0.406 to 0.790 ‰. XA2bis concrete shows the lowest expansion. The results of XA2 bis shows the benefit brought by the use of fly ash in the mix containing normal OPC as this mix behaves somehow better than the XA2 mix containing CEM III cement.

Mix XA3 results appear to follow a normal path until 28 days. Thereafter, it shows a sudden unexpected increase of the expansion.

All the tested concrete mixes (including the control which is not designed to be sulphate resistant) comply with SIA 262/1 requirements (<1.2‰ between the measured at 56 days and the last cycles of drying/immersion).

The specimens treated with the hydrophobic agent absorb significantly less water compared to the untreated specimens during the first four cycles of drying/immersion. Thereafter, during the subsequent testing procedure (constant immersion from 7 to 56 days), the differences in expansion between treated and untreated remain more or less constant.

Due to the low expansion of the treated specimens during the first four cycles, the resulting final expansion of these specimens is much lower than the expansion of the control specimens (41 to 72% reduction).

ASTM C1012-13

The high concentration of sulphate in the testing solution induces most of the expansion to occur during the first 7 days of immersion. Thereafter, the evolution of expansion is slower. The mass evolution seems to differentiate better the effect of the sulphate than the expansion induced in the different mix designs.

From the results of the first 90 days, it would appear that all untreated specimens will exceed the accepted limit of 0.5‰ at 180 days.

With a hydrophobic treatment, all the different concrete mixes have a lower expansion and from extrapolation, it appears that all specimens will be within the accepted limit.

CONCLUSIONS

There are some differences between the two methods tested mainly due to the cycling regimes, SIA 262/1 and ASTM C1012-13 but each of them shows the importance of mix design with regards to sulphate attacks.

The obtained results show that the use of hydrophobic treatments, such as the tested silane, is an effective means of preventing ingress of water and soluble aggressive substances into concrete thus reducing the damaging effects of sulphates. This product also improves sulphate resistance of concrete mixes even e.g. not designed for such an aggressive environment, as the control mix in Table 4.

REFERENCES

[1] MOHAMMED, Ibrahim. 1996. *Performance evaluation of concrete surface treatment materials*. PhD Thesis Faculty of the college of graduate studies King Fahd University of petroleum and minerals Dhahran, Saudi Arabia.

[2] MOHAMMED, Ibrahim; A.S. Al-Gahtani; M. Maslehuddin; D. H. Dakhil. 1999. *Use of surface treatment materials to improve concrete durability*. Journal of materials in civil engineering, 11[1]:36-40.

[3] AGUIAR, Jose B.; A. Camões; P. M. Moreira. 2008. *Performance of Concrete in Aggressive Environment.* International Journal of Concrete Structures and Materials, 2[1]: 21-25.

[4] EN 206-1 December 2000; Concrete — Part 1: Specification, performance, production and conformity