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Non-ionic silane emulsion as integral water repellent – impact on cement hydration process

Nenad Milenković
4MAT, Université Libre de Bruxelles, Bruxelles, Belgium, nemilenk@ulb.ac.be
Stéphanie Staquet
BATir, Université Libre de Bruxelles, Bruxelles, Belgium, sstaquet@ulb.ac.be
Jean-Paul Lecomte
Dow Corning, Rue Jules Bordet, B-7180, Seneffe, Belgium, j.lecomte@dowcorning.com
Christian Pierre
CRIC - OCCN, Av. Adolphe Buyllaan 87B, 1050, Bruxelles, Belgium, c.pierre@cric-occn.be
Marie-Paule Delplancke
4MAT, Université Libre de Bruxelles, Bruxelles, Belgium, mpdelpla@ulb.ac.be

SUMMARY: Silanes or siloxanes have been used as post-treatment water repellents for a long time. They are capable of chemically reacting with the pore surfaces thus protecting the cementitious matrix from water penetration. The study evaluates the combination of a non-ionic emulsion of a silane monomer with a silicone resin used as integral water repellent. Detailed analyses of cement hydration process were carried out by means of isothermal calorimetry, setting time measurements, and SEM investigation. It was possible to show that the hydrophobic agent introduced as integral water repellent influences the cement hydration process. Mercury porosimetry analysis showed that porosity and pore structure in cement matrix does not change due to the presence of silane emulsion. Reduction of water uptake by this emulsion was also assessed as well as its impact on the mechanical properties.

KEY-WORDS: silane emulsion, integral water repellent, cement hydration, mechanical properties

INTRODUCTION

The post-treatment of building materials by silane and siloxane water repellent is a proven protection method against water penetration [1-5], however, in many cases, this technique is not used due to the extra labor costs. Presently, bulk hydrophobization of cementitious materials appears to be more attractive than surface treatments, which in turn requires complicated in-situ preparation and, furthermore, it is influenced by climatic weathering [6]. Thus it would appear to be more efficient and convenient to treat the bulk of the construction material itself instead of applying a water repellent post-treatment.

This technology which consists in adding a silicone or silane-based water repellent into the cementitious matrix has gained the attention of the industry for several years. Hydrophobic agents have been directly added into the concrete mixture in the order to make both the surface and the bulk material hydrophobic [2, 7-9]. Silanes can be introduced to the cement or mortar in the form of powder, as an ad-mixture and neat (pure) emulsion. Integral water repellency via water based silane emulsions are useful as they can be easily blended into the cement matrix. For example, addition of a silane emulsion [10], hardly modifies the pore size distribution, it does not block the capillary pores but modifies the affinity of the walls of capillary pores for water (hydrophobic treatment), thus significantly reducing the water capillary suction [11]. Several studies have shown the influence that bulk waterproofing with silanes has on mechanical properties and concrete corrosion [8, 9, 12]. The study of Spaeth [13] showed that silane and siloxane can be incorporated into fresh cement as a powder supported via a zeolite. The incorporation of n-*octyl-ethoxysilane* and *dihydro-poly-dimethoxysiloxane,* modifies the setting time and water uptake. However, a limited reduction of the mechanical resistance was observed.

This study presents the evaluation of a non-ionic water based silane emulsion as “integral water repellent” added into the cement paste of mortars. The influence of the active silane agent on mechanical strength and water absorption was assessed. The aim was to examine the influence of a bulk waterproofing treatment on the early hydration steps of cementitious materials. In order to understand the way silane and cement particle interact, micro and macro structural characterization was carried out.

EXPERIMENTAL

A non-ionic water based silane emulsion (IE) was used as hydrophobization material. The active agent in the emulsion is a combination of a silane monomer (*n-octyl-triethoxysilane*) and a silicone resin. The hydrophobic agent is delivered in the form of small droplets dispersed in water, with the non-ionic surfactant to stabilize the emulsion after formation. Its influence on the hydration process of ordinary Portland cement (OPC) and Blast Furnace Slag (BFS) cement (CEM I 52.5 R LA and CEM III/A 42.5 N LA, respectively) were studied. The main characteristics of the two cements are given in Table 1. The slag content in CEM III/A was determined to be 45.7% by selective dissolution method according to the standard NBN EN.

Table 1. Physico-chemical characteristics of the OPC and BFS cements tested.

Analysis	OPC: CEM I 52.5 R LA	BFS: CEM III/A 42.5 N LA
Normal Vicat consistency [%]	31.5	29.0
Density [g/cm³]	3.13	3.00
Blaine fineness [m²/kg]	509	412
Sieve residue on 200 µm [%]	0.0	0.0
SO_3 content [%]	3.24	2.48

Specimen preparation and characterization

For cement paste and mortar preparation, de-ionized water was used instead of tap water, in order to eliminate the presence of ions which might have an influence on the cement hydration process. For cement pastes, the amount of silane emulsion added was 2% w/w of the cement, while for mortars two formulations were prepared, with 0.5 % and 2% w/w. The silane emulsion was added to the water (the listed amount of “water” includes the contribution of the emulsion) and stirred for 2 minutes with a magnetic stirrer and then it was added to the dry mix (cement+sand). The proportions used to prepare for cement pastes and mortars are provided in Tables 2 and 3, respectively. For mortars, normalized river sand was used (CEN Normsand EN 196-1).

Both the mechanical strength and water uptake characteristics were measured on the cured mortars. The standardized mortars with and without silane emulsion were prepared according to the admixture standard NBN EN 480-1. The mortars were moulded in 4x4x16 cm prisms. The comparative measurements were carried out after 2, 7 and 28 days curing. The hydrophobic effect was evaluated by capillary water absorption measurements according to the admixture standard NBN EN 480-5 on mortar prisms (4x4x16 cm). Mortar prisms were immersed vertically in tap water at 20°C. The prims masses were subsequently measured: before the test, at 1 day, at 7 days and at 28 days.

Table 2. Cement pastes abbreviation and composition (W/C – water to cement ratio).

Samples	Composition	W/C ratio	Emulsion (IE) (% w/w of cement)
CEM1	OPC	0.5	
CEM1IE	OPC, emulsion	0.5	2
CEM3	BFS	0.5	
CEM3IE	BFS, emulsion	0.5	2

Table 3. Mortar samples abbreviation and composition (C/S – cement to sand ratio).

Samples	Composition	W/C ratio	C/S ratio	Emulsion (IE) (% w/w of cement)
MOR1	OPC, sand	0.5	1/3	
MOR1IE0.5	OPC, sand, IE	0.5	1/3	0.5
MOR1IE2	OPC, sand, IE	0.5	1/3	2
MOR3	BFS, sand	0.5	1/3	
MOR3IE0.5	BFS, sand IE	0.5	1/3	0.5
MOR3IE2	BFS, sand, IE	0.5	1/3	2

SEM and XRD measurements were carried out on cement pastes to have insight on the crystalline phase development. The samples for SEM analysis were coated with a thin carbon layer to provide electric conductivity.

To determine open porosity and pore size distribution of the cement paste, mercury intrusion porosimetry (MIP) was performed using a Micromeritic Autopore IV apparatus. The principle of total porosity determination can be found in [14].

The heat released during the bulk hydrophobic treatment of cement paste was followed by isothermal calorimetry using a Tam Air Microcalorimeter. All samples were prepared according to the following procedure: 5 g of cement were weighed and mixed with de-ionized water (or water +IE) in a flask. Immediately after mixing, the flask was placed in the isothermal calorimeter in a climatic chamber with a fixed temperature of 20 °C. The thermal evolution was followed for 3 days.

RESULTS AND DISCUSSION

Physico-mechanical characterization

Figures 1 and 2 show the effect of the silane emulsion on compression and tensile bending strengths of mortars manufactured with the two reference cements. MOR3 has a lower mechanical strength at short term (2 days of curing) and a similar one at longer term (28 days of curing) to that of MOR1. This can be explained by the slower hydration of blast furnace slag in CEM3 cement. Indeed, in a slag based cement, the slag hydration requires the formation of cement hydration products (portlandite, $Ca(OH)_2$) for its activation. It was also noticed that the relative decrease of the compressive strength (due to the addition of 2% w/w of IE) is more significant (18% against 10%) for the MOR1 (18%) than for the MOR3 (10%) after 28 days curing. The mechanism by which the silane emulsion affects the mechanical properties decrease has as yet not been elucidated.

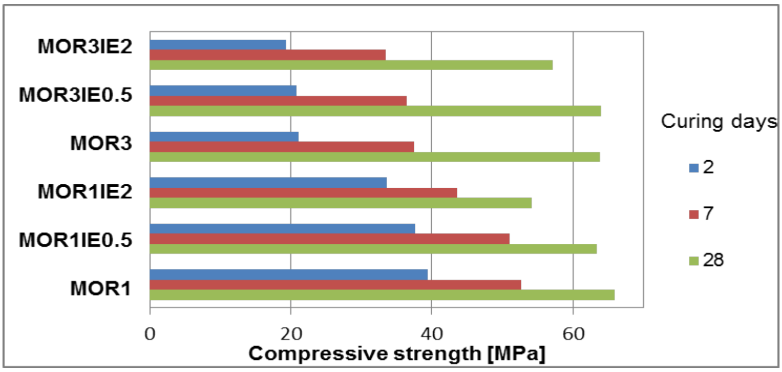

Figure 1. Compressive strengths values (average of three measurements) for mortar samples.

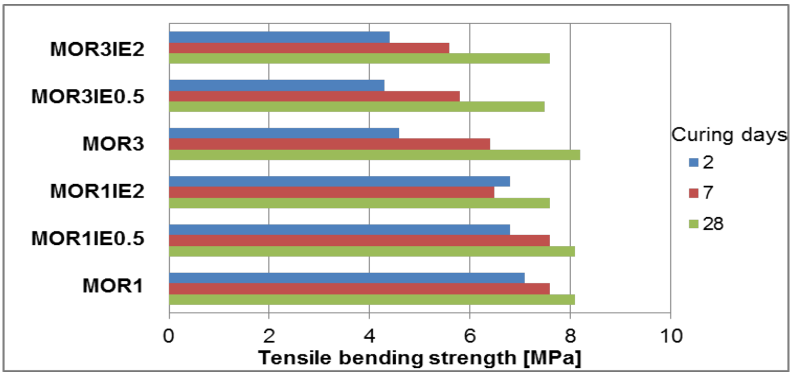

Figure 2. Tensile bending strengths values (average of three measurements) for mortar samples.

Water uptake reduction as a function of silane content

Figure 3 illustrates the reduction in water uptake for mortars with different IE contents. Absorbed water is expressed as difference between the dry and water saturated prisms masses at different curing times. It was noticed that sample MOR3 absorbs more water than MOR1 at all times. On the other hand, the relative effect of hydrophobic agent is more important for MOR3 than for MOR1 for equal silane amount. This effect can be attributed to the presence of blast furnace slag in the MOR3 samples. At 28 days, water uptake is about 3 and 6 times lower for MOR3IE0.5 and MOR3IE2 respectfully, and about 2 times (MOR1IE0.5) and 4 times (MOR1IE2) lower, as compared to that of the control samples.

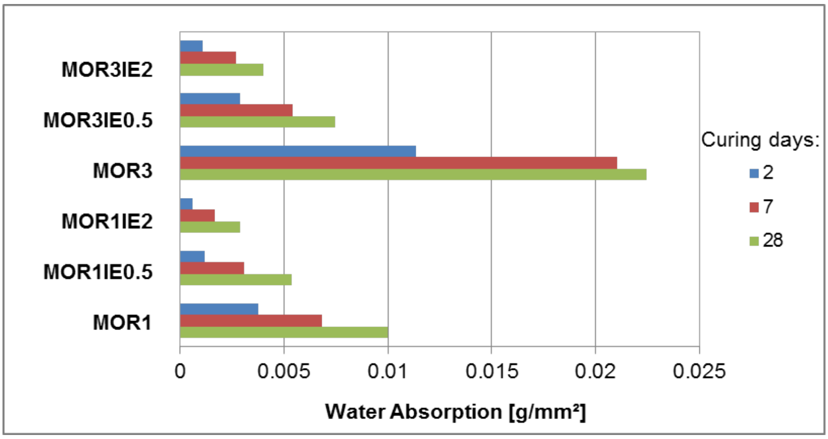

Figure 3. Capillary water absorption of mortars samples.

Porosity of cement paste

Table 4 presents the average total porosity % from 3 measurements for each cement paste samples, after 1 and 7 days of curing. No significant influence of IE on the porosity of the cement paste was noticed. The pore size distribution does not change. The mechanical strength decrease cannot be correlated to a porosity modification.

Table 4. Mercury intrusion porosimetry results for cement paste samples.

	Total porosity, %	
	After 1 day	After 7 days
CEM1	30	29
CEM1IE	31	30
CEM3	36	34
CEM3IE	37	36

SEM and XRD Rietveld analysis

The images of cement paste microstructure obtained by scanning electron microscopy (SEM) after one day curing are presented in Figure 4. Different crystalline formations were identified as hydration products. Hexagonal platelets of CH ($Ca(OH)_2$-portlandite) appear with different orientations and groupings when comparing a paste with or without admixture. The size of these crystals is larger when silane was incorporated (CEM1IE). Ettringite was also identified as needles surrounding non-hydrated cement particle.

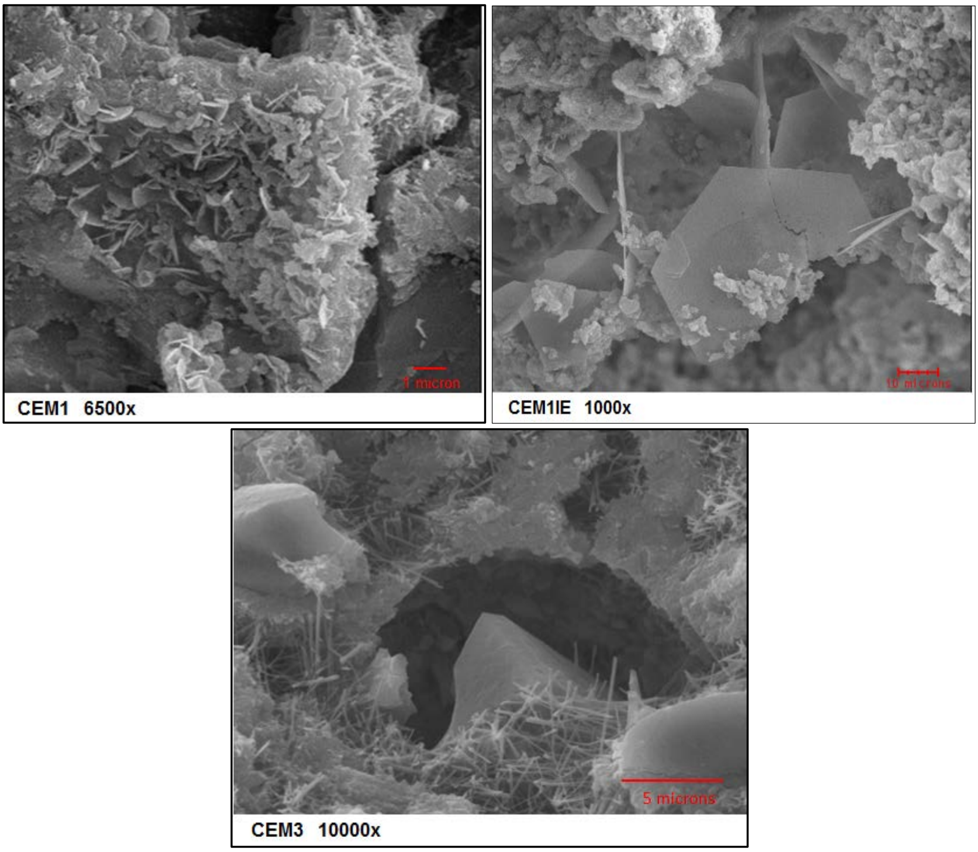

Figure 4. SEM images of cement paste after one day of curing: larger crystals of portlandite were found in CEM1IE (upper right) as compared to the reference (upper left). Ettringite formation on CEM3 cement with BFS particle was also observed (bottom).

Table 5 lists the main phases present in the cement paste after curing for 1 day. The proportions were obtained by applying a Rietveld analysis to the X-ray diffraction data [15]. The hydration of tricalcium silicate (C_3S) appears to be influenced by the silane. The amount of portlandite is higher in both CEM1 (OPC) and CEM3 (BFS), as more C_3S is consumed by water. When silane is present, its hydrophobic alkyl group prevents reaction between water and C_3S, thus retarding the formation of portlandite. In comparison to C_3S, the hydration reaction of the tricalcium aluminate (C_3A) phase is not significantly affected by the presence of the silane. The influence of silane on ettringite formation is not clear.

Table 5. Phase composition (by weight %) of cement pastes calculated with Rietveld analysis of the XRD diffractograms.

	CEM1	CEM1IE	CEM3	CEM3IE
C_3S	21.75	23.76	24.79	29.93
C_2S beta	15.66	15.84	5.36	5.11
Portlandite	18.27	16.72	12.06	9.49
C_3A	4.35	4.40	3.35	4.38
C_4AF	13.92	14.96	13.4	13.14
Ettringite	13.05	12.32	8.04	10.95
Amorphous phase	13	12	33	27

DSC-TG analysis and isothermal calorimetry on cement pastes

The results of thermal analysis on CEM3 and CEM3IE, after one day of curing, are shown in Figure 5. Absorbed and interstitial water in the samples firstly evaporates (endothermic peaks around 100 °C). An endothermic peak at 460 °C indicates the decomposition of $Ca(OH)_2$ present in cement paste. The decomposition of $CaCO_3$ is indicated by an exothermal effect around 700 °C.

In presence of silane after 1 day of curing, an additional exothermic peak at 300 °C is observed and corresponds to the decomposition of the alkyl chains attached to the silane. At higher temperatures, crystallization of the amorphous phase of BFS is taking place as shown by the exothermic effect around 900 °C for the CEM3. Mass change during thermic process is influenced by the presence of IE.

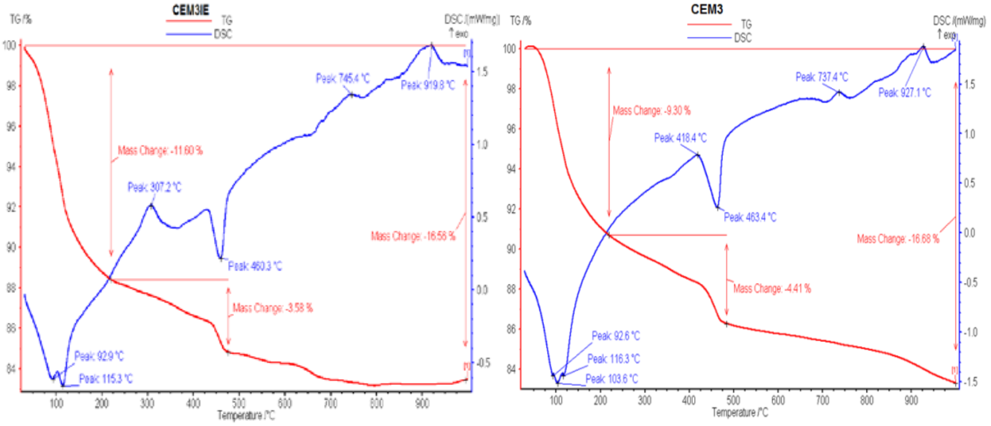

Figure 5. DSC of CEM3 paste with and without IE after one day of curing.

The isothermal calorimetry studies provide information on the exothermal reactions during cement hydration. The results of the isothermal calorimetry are given in Figure 6. After an initial hydration peak, the calorimetric curve related to the dormant period is shorter in CEM1 (OPC) compositions than in CEM3 (BFS) ones. Lower heat flow in the latter is due to the presence of the slag and the second peak is related to its hydration. With the addition of the emulsion, the maximum heat flow is about 10% lower in both cements.

The delayed hydration in CEM3 (BFS) is due to the required activation of the slag by the alkaline medium generated by the hydration of the C_3S phase and the formation of portlandite [16]. After a certain time, silane hydrolysis takes place providing the R-Si-O-H active species for the reaction with the cement particle. First, trialkoxy silane hydrolyzes to silanetriols and ethanol. The hydrolysis is driven by the protonation of the -OR group. Free R-Si-O-H species polymerize forming siloxanes which are chemically bonded to the CSH-gel. The rate of hydrolysis is affected by several factors: pH value and the structure of both the alkoxy groups and the alkyl groups. It has been shown that an elevation in pH increases the hydrolysis rate [17]. Long alkyl chains on the silane provide good steric isolation to the alkoxy groups, thus the combination of siloxane and a silicone resin remain stable in an alkaline interstitial pore solution. The hypothesis that needs to be further analyzed is that the silane monomer and resin interact with the cement phases and the CSH on the surface, preventing water molecules to reach the cement particles. This effect is especially strong in CEM3 (BFS). With the modification of the hydration reaction the mechanical characteristics of the mortars are reduced.

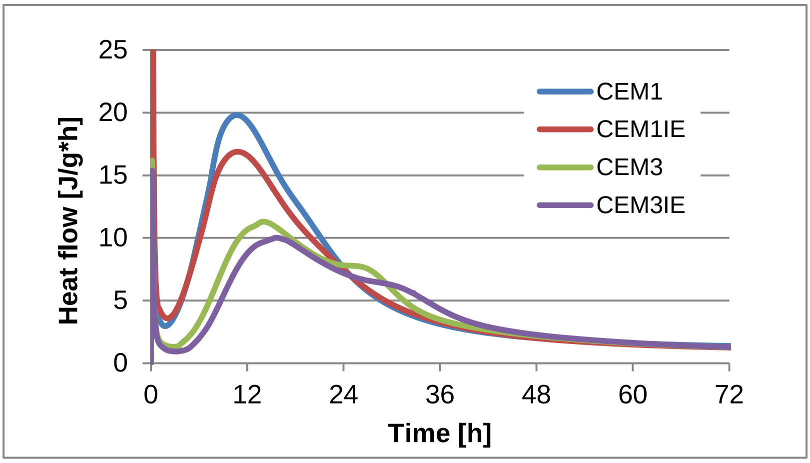

Figure 6. Heat evolution rate of cement paste in the presence of a silane emulsion.

CONCLUSIONS

The study focused on the effect of a non-ionic water based silane emulsion when used as an integral water repellent in cementitious materials. Its influence on the early cement hydration in ordinary Portland and blast furnace slag cement was investigated. Mortars with silane emulsion show a reduction of about 7% in mechanical strength while the capillary water absorption is significantly lowered and were even more significant for BFS cement. The mechanical strength decrease could not be correlated to a porosity modification. The hydration of C_3S appears to be influenced by the silane. The amount of portlandite is higher in both CEM1 and CEM3, as more C_3S is consumed by water. The presence of silane influences the reaction between water and C_3S, resulting in a retarded formation of portlandite. SEM investigation showed bigger crystals of portlandite in samples with silane.

The calorimetric measurements show that silane modifies the hydration process of cements, as the maximum of the heat production in CEM1 and CEM3 is lowered by around 10% when silane is present. Further investigations are in progress in order to better understand the reaction mechanisms of silane and the hydrating cement phases.

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