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Hydration Process and Microstructure Development of Integral Water Repellent Cement Based Materials

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Abstract

Protection of cement based materials means above all, moisture protection because water is primarily responsible for inducing damaging physical and chemical processes in building materials.
New and existing building surfaces need to be protected against liquid water penetration. In all cases, water repellents are applied either directly during the construction or insulation process; or as a post-treatment of the exposed surfaces in order to protect the buildings from further decay. A new way is to develop a bulk treatment for cement based materials which should provide a long term protection without modifying the mechanical properties of the materials.
A fundamental study was initiated to investigate the influence of the incorporation of two active silicon-based agents (already used as post-building treatments) on the hydration processes of Portland cements and to understand the mechanisms involved. Three incorporation modes (pure liquids, oil in water emulsions and powders) are compared. The aim was to determine the best conditions for an efficient and sustainable treatment preserving the mechanical properties of the materials. The first results on capillary water absorption and mechanical tests on admixed mortars before ageing were obtained and are presented here.

Keywords: microstructure, reactivity, water repellent, bulk treatment, cement materials, silicon-based agents

1 Introduction

Polydimethylsiloxanes (or PDMS) and alkoxysilanes have become a very important class of materials used for water repellent treatment of masonry, where durability is critical. They will be referred here as silicon-based agents.

PMDS are available as fluids, in the form of linear or cyclic polymers, as viscous liquids and even resins depending on their degree of polymerization and cross-linking. Terminated by a silanol group, they are reactive and can be anchored on appropriate substrates.

Alkyltrialkoxy silanes ($RSi(OR')_3$) show a good reactivity towards construction materials. They can be viewed as materials bearing latent silanol groups, to be released by hydrolyzis, which can bond covalently to masonry materials through condensation reactions with metal hydroxyl functions. Silanol self-condensation also leads to cross-linking and the formation of oligomeric compounds, resulting in a good durability of water repellency. The R groups (most often, isobutyl or octyl) confer the hydrophobic character to the substrate to which the silane is anchored. Active silicon-based agents can be used as such (in the “pure” liquid form), or emulsified (oil in water emulsion) or formulated as powdery additive.

The study presented here reports on the bulk water repellent treatment of cement based materials. The advantages of a bulk treatment are obvious, i.e., only a small part of the hydrophobic agent is exposed. Therefore the integrity of the treatment is not affected by UV radiation degradation and/or surface abrasion.

Preliminary results on water absorption and mechanical resistance of mortars are summarized to show the relevance of these treatments. The first results dealing with the reaction modifications and microstructure development of the hydrates in presence of hydrophobic agents incorporated by three different modes are presented. The cement pastes were characterized, at different times, to evaluate the hydration progress and to characterize the type of products that were developed.

2 Experimental

2.1 Silicon-based agents and preparation of additives

Two silicon-based agents α, ω dihydroxypolydimethylsiloxane (PDMS) (Mw = 3000 $g.mol^{-1}$) and n-octyltriethoxysilane were chosen. Three incorporation modes (“pure” liquid, oil in water emulsion and powdery additive) were considered in the present study. Table 1 summarizes the ten different compositions that were prepared.

The first introduction mode consists of adding the unmixed neat or "pure" liquid additives directly to the water mixed with the cement (n° 4 and 5). To achieve even dispersion of active material but as well as to ease its incorporation, two others introduction modes were chosen: oil in water emulsion (n°6 and 7) and a powder additive (n°8, 9 and 10) containing the silicon-based agent [1].

The emulsions are composed of the active material based on silane or PDMS and stabilized with polyvinyl alcohol (PVA) used as surface active agent.

The powders were prepared by spraying an emulsion of the active materials (silane or PDMS) on zeolite (an aluminosilicate with a 1:1 Si/Al ratio), a fine powder used as carrier. After evaporation of the water, the resultant dry powder is ready to be used in dry cement compositions.

Table 1: The ten compositions studied. SH: silicon agent; A: silane; B: PDMS and C: Silane and PDMS and the different specimens of admixed cement pastes or mortars (cement + sand) studied.

Names of batches	Compositions prepared
1:Reference	Nothing
2:PVA control	PVA solution
3:Zeolite control	Zeolite
4:Pure Silane	"Pure" silane
5:Pure PDMS	"Pure" PDMS
6:Silane emulsion	Silane + water + PVA
7:PDMS emulsion	PDMS + water + PVA
8:SHA powder	Silane + zeolite + PVA
9:SHB powder	PDMS + zeolite + PVA
10:SHC powder	Silane+PDMS+zeolite+PVA

Studied admixed cement pastes/mortars
Water + cement/sand
Water + cement /sand+ n°2
Water + cement/sand + n°3
Water + cement/sand + n°4
Water + cement/sand + n°5
Water + cement/sand + n°6
Water + cement/sand + n°7
Water + cement/sand + n°8
Water + cement/sand + n°9
Water + cement/sand + n°10

2.2 Preparation of specimens and characterization methods

Two CEM I 42,5N Portland cements (Ordinary and White Portland Cements) were used for the admixed cement pastes/mortars given in Table 1.

Mortars were prepared according to EN 196-1 with a water to cement (w/c) ratio of 0.5, addition of 0.5% of silicon-based agents per cement mass and a sand to cement ratio of 3. For mortars, three prismatic (160x40x40 mm^3) and three round slab (100 mm diameter and 20 mm height) specimens per formulation were prepared for mechanical and water uptake tests, respectively. After demolding, the mortar specimens were stored at 20°C and >90% RH for 1 day and 20°C and 90% RH for 27 days.

Cement pastes were prepared according to EN 196-1 with a water to cement (w/c) ratio of 0.5 and addition of 0.5% of silicon-based agents per cement mass. For cement pastes, cylindrical specimens (30 mm diameter and 70 mm height) were prepared for analytical purposes. The specimens were cures at 20°C and 90% relative humidity (RH) for 28 days.

The performances of the admixed mortars were assessed by their water uptake reduction according to DIN 52 617. Measurements of slumps on fresh mortars were also taken. Measurements of compressive and flexural strengths on mortar specimens were carried out according to DIN EN 196 after curing. The results presented are an average of three identical tests. Capillary water absorption and mechanical tests were performed in order to determine the effect of the additives addition on water affinity and mechanical strength.

The hydration of cement–admixture pastes was followed qualitatively by Vicat needle, conduction calorimetry, differential scanning calorimetry (DSC) and thermo-gravimetry. Information concerning the progression of the hydration reactions of the reaction products is obtained by combining these different analytical methods.

3 Results

3.1 Effectiveness of hydrophobic treatments

Water uptake of admixed **cement pastes and mortars** was assessed by partial immersion of the specimens in water for 24 hours according to DIN 52 617 (see Table 2).

Table 2: Water absorption coefficient after 24 hours of immersion (Average over 3 mortar specimens and cement pastes). The lowest values are marked in bold.

Sample names	Water absorption coefficient at 24h (Kg/m^{2}h^{0,5})		
	Mortars		**Cement pastes**
	OPC* CEM I 42.5N	WPC* CEM I 42.5N	
1:Reference	0,490± 0,004	0,319± 0,004	0,076±0,006
2:PVA control	0,492± 0,003	0,410± 0,007	-
3:Zeolite control	0,467± 0,003	0,371± 0,011	0,069±0,006
6:Silane emulsion	0,083± 0,004	0,058± 0.008	0,028±0,009
7:PDMS emulsion	0,142± 0,004	0,115± 0.014	0,047±0,007
8:SHA powder	0,033± 0,005	0,033± 0,012	0,022±0,004
9:SHB powder	0,041± 0,001	0,038± 0,001	0,020±0,003
10:SHC powder	**0,028**± 0,001	**0,021**± 0,002	**0,004**±0,0003

*WPC: White Portland cement; OPC: Ordinary Portland cement

As reference, three specimens were not admixed or admixed with either zeolite or PVA. As expected, the addition of only PVA (n°2) or zeolite (n°3) does not reduce the water absorption of mortars. Both hydrophobic additives are efficient in reducing water uptake when introduced as oil in water emulsions (n°6 and 7) or as powders (n°8, 9 and 10). The latter method appears to be the most effective. These first results suggest that powders containing a mixture of silicon-based agents (SHC powder) lead to a significant reduction in water uptake in comparison to those containing the individual active material (SHA and SHB powder). The addition of “pure” silane or PDMS, to the water, results in an inhomogeneous paste or mortar. It was impossible to obtain reproducible data with this addition mode and therefore they are not reported. The trends are similar for the two types of Portland cements investigated here. Nevertheless, differences in absolute values can be observed.

3.2 Mechanical tests

Table 3 summarizes the mechanical results obtained from admixed **mortars** specimens. The addition of PVA only (n°2) decreases the mechanical strength by almost a factor of two. Addition of pure zeolite (n°3) does not affect significantly the compressive strength. A slight decrease of compression strength is observed for the samples containing emulsions (n°6 and 7). The incorporation of powdery additive (n°8, 9 and 10) does not affect significantly the mechanical properties of mortar cured for 28 days. Results for compositions nº4 and nº5 are not reported because the samples were highly inhomogeneous, as mentioned above.

Table 3: Slump of fresh **mortars**, Compressive (average of 6 specimens) and flexural (average of 3 specimens) strengths of mortar specimens after 28 days of curing. The outlying values are marked in bold.

Sample names	OPC*	WPC*	OPC*	WPC*	OPC*	WPC*
	Slump		Compressive		Flexural	
	Cm		N/mm²			
1:Reference	17,65±0,12	17,60±0,11	37,7±1,5	44,3±1,1	6,3±0,3	6,5±0,2
2:PVA control	**22,15±**0,21	**22,05±**0,18	**15,4**±0,3	**9,6**±1,3	**4,0**±0,2	**2,9**±0,3
3:Zeolite control	17,05±0,25	17,15±0,15	43,6±1.5	39,7±2,3	6,7±0,5	5,9±0,1
6:Silane emulsion	19,65±0,14	19,20±0,22	30,9±0,7	34,1±0,7	6,9±0,2	6,9±0,3
7:PDMS emulsion	19,70±0,17	19,60±0,19	32,0±0,6	29,3±1,1	6,9±0,2	6,5±0,5
8:SHA powder	18,55±0,13	18,30±0,15	40,6±1,6	40,7±0,7	7,4±0,4	5,5±0,1
9:SHB powder	18,65±0,18	18,00±0,23	35,9±0,7	35,9±1,3	6,5±0,3	6,6±0,8
10:SHC powder	18,75±0,22	17,70±0,12	39,1±1.5	38,8±0,6	7,7±0,2	5,9±0,2

*WPC: White Portland cement; OPC: Ordinary Portland cement

3.3 Influence of admixtures on setting period

The effect of admixtures on cement hydration of **cement pastes** at very early age, i.e., before 2 days, was examined through setting time using the Vicat needle and heat flow evolution. Table 4 presents the beginning and the end of the cement setting for each studied composition assessed by the Vicat needle, and heat flow evolution obtained by isothermic calorimeter conduction (ICC).

Table 4: Average (3 measurements) setting times of **cement pastes** (WPC), obtained by means of a Vicat needle and heat flow evolution assessed by Isotherm calorimeter conduction (ICC). The lowest values are marked in bold.

Sample names	Setting or so-called acceleration period			
	Setting times		Heat flow evolution	
	Beginning	End	Maximum peak of Acceleration hydration	Maximum peak of Transformation TSA* to MSA*
	Times (h)			
1:Reference	5,5 ± 0,4	7,6 ± 0,4	12,1± 0,2	22,1± 0,3
2:PVA control	5,7 ± 0,3	7,8 ± 0,4	14,1± 0,2	26,5± 0,3
3:Zeolite control	**3,2** ± 0,4	**5,2** ± 0,4	**11,2± 0,3**	**13,5± 0,3**
4: Pure Silane	5,2 ± 0,4	7,4 ± 0,3	12,8± 0,3	24,0± 0,3
5: Pure PDMS	5,3 ± 0,2	7,4 ± 0,4	11,8± 0,2	23,0± 0,3
6:Silane emulsion	5,3 ± 0,3	7,4 ± 0,4	14,0± 0,3	24,0± 0,3
7:PDMS emulsion	5,2 ± 0,4	7,2 ± 0,2	13,9± 0,3	21,0± 0,3
8:SHA powder	4,5 ± 0,3	6,6 ± 0,4	12,4± 0,3	20,6± 0,2
9:SHB powder	4,1 ± 0,3	6,1 ± 0,3	12,5± 0,3	16,0± 0,3
10:SHC powder	4,4 ± 0,4	6,5 ± 0,3	12,5± 0,2	16,1± 0,3

*TSA: Calciumtrisulfoaluminate (or so-called Ettringite);
*MSA: Calciummonosulfoaluminate

4 Discussion

Setting results from the transformation of a dense suspension of more or less dispersed particles into a mechanically irreversible network of connected particles. Coagulation and rigidification, the two fundamental steps leading to setting, are highly dependent on the calcium ion and silicate contents of the interstitial solution [2]. Both steps could be influenced by the presence of the additives and, if the interpenetration of the hydrates is modified, it could lead to a loss of mechanical strength.

Impact of the addition of silane and PDMS

The structure of the alkyl group attached to the silicon atom (methyl in PDMS, octyl in octyltriethoxysilane) induces the hydrophobicity of the admixture.

The reactivity of alkoxysilanes can be divided into two key successive steps: hydrolyzis of alkoxysilane into silanol and ethanol is followed by the condensation of silanol into an oligomeric material or attachment to the substrate. According to the studies of Arkles and al. and Osteiholz [3, 4], the rate determining step of the silane is the hydrolyzis. The rate of hydrolyzis depends on several factors such as the pH value and the R group.

The oligomerization of silane into higher molecular weight species in the interstitial solution and their anchorage on the cement components is responsible for their efficiency as a water repellent. After silane hydrolyzis, the reactive silanol groups can anchor to the cement phase or to the sand. The same anchoring reaction is expected to occur with silanol terminated PDMS. These silicon-based agents (either hydrolyzed silanes or PDMS) interact or react with the cement phases or calcium silicate hydrate (CSH) making their surfaces hydrophobic. The integral treatment of the cementitious specimens leads to a large decrease of the interaction with water, and hence a reduced water absorption. The impact of silane and PDMS on water absorption is observed independently of the used incorporation mode (“pure”, emulsion or powder). Although the cement phases or CSH surfaces are modified, the setting period and mechanical strengths of cement paste or mortar are not affected significantly.

Impact of PVA addition (no water repellent agent) [5-7]

Addition of PVA solution (n°2) does not affect the setting times although it does delay significantly the maxima of heat flow associated to hydration and the transformation of ettringite to calcium monosulfoaluminate during the acceleration period. This period is around four hours longer than for the reference material (n°1). It is hypothesized that this arises from the adsorption of PVA molecules on the hydrated and non hydrated cement particle surfaces, sterically stabilizing the particles against coagulation. A water layer (containing dissolved polymer) is maintained between the particles preventing coagulation. By reducing the flocculation tendency of the particles, the interparticle water effectively lowers the viscosity. Water is also held around the particles, preventing bleeding and particle settling. The PVA layer also hinders the diffusion of water molecules towards the unhydrated cement particles resulting in a global retardation of the hydration. This effect is especially marked at longer setting times, during the hardening period. DSC diagrams indicate a modification of the CSH gel surrounding the grains in presence of PVA.

The observations on **mortars** showed an influence of PVA addition as well. The slump was found to be increased by addition of composition n°2 (table 3). Physical properties (resistance to compression and flexion) of mortars were found to decrease significantly. Reduction of density of cured mortar upon addition of PVA (density of specimen including composition n°2: 1700 kg/m^3 versus reference mortar: 2150 kg/m^3) could partially explain this impact.

Impact of the addition of emulsions of silane or PDMS

The behaviour of the **cement pastes** admixed with oil in water emulsions of silane or PDMS (nº6 and nº7) is very similar at early age (up to 10 hours) to the reference. Their setting times were equivalent (as seen in Table 4). The emulsion additions only slightly delay the maxima of heat flow and the transformation of ettringite but not to the same extend as PVA addition does (Table 4). For longer curing times (28 days), mechanical properties of mortar are slightly affected by the addition of the two emulsions (Table 3). It appears that the availability of “free” PVA is much lower once added as component in an emulsion.

Impact of zeolite addition with and without water repellent agents

Addition of zeolite either as such (n°3) or as component of hydrophobic powder (n°8, 9, and 10) mostly impact setting properties as seen in table 4. Little impact of zeolite addition on mechanical properties was observed.

According to previous studies [8-10], the addition of inert mineral compounds has two antagonistic physical effects: a dilution effect reducing the amount of hydrated cement (a decrease of the total amount of hydrates without significantly changing the degree of hydration) and a surface effect related to heterogeneous nucleation. This last effect is very sensitive to the fineness of mineral admixture particles, the added amount and the affinity of the mineral compounds for hydrates. In addition, the particle size effect (or filler effect) implies a modification of the initial porosity of the mix, which can be related to variations in density and air content of fresh mortar mixtures. No impact of zeolite addition was seen on cured mortar density in this study.

In case of a pozzolanic material such as a zeolite, a chemical effect can also be observed. The silicate and aluminate groups of the zeolite can react with $Ca(OH)_2$ and produce hydraulic materials that result in CSH gels thus densifying the hydrated cement matrix. This could also explain the shorter induction period observed in our pastes: the coagulation and rigidification steps take place two hours earlier than in the reference material (see Table 4). Zeolite reactivity is partly related to its large external specific surface and metastability which favours its dissolution in the saturated lime solution and the successive precipitation of CSH (hydrated calcium silicates) and CAH (hydrated calcium aluminates) phases. Globally, zeolite consumption by portlandite, implies a modification of Ca^{2+} concentration and alkalinity [11] of the interstitial solution. When a $Ca(OH)_2$ –zeolite blend is mixed with water, $Ca(OH)_2$ in the blend dissolves leading to a fast increase of the pH value of the suspension. Under the OH^- attack the silicate or aluminosilicate network of pozzolanic materials is broken and depolymerized species enter the solution [12]. Ca^{2+} ions can then react with the dissolved monosilicates and aluminate species leading to the formation of a CSH gel.

For cement pastes and mortars containing powdery additives (n°8, 9 and 10), a slight reduction of the induction period and of the setting time was observed relatively to the reference material with no additive. This effect is smaller than when a zeolite only is used at the same overall concentration due to antagonistic effects. The mechanism of interaction of the zeolite, PVA, silane and PDMS with cementitious materials is still unclear.

5 Conclusions

The use of α, ω dihydroxypolydimethylsiloxane and n-octyltriethoxysilane as bulk water repellent agents for cement based materials was investigated.

Three incorporation modes were studied: addition of “pure” liquid agents, addition as oil in water emulsions, and addition of powdery agents.

The addition of the “pure” silicon-based agents was difficult to study since no homogeneous mixture was obtained.

The impact of the additives was investigated. PVA tends to retard setting significantly while the oil in water emulsions (which contains the same content of PVA) barely modify these properties. Availability of PVA for interaction with cement particles is reduced when incorporated in emulsions or powders. Zeolite tends to make the setting period shorter, which is attributed to a possible additional pozzolanic reaction.

Additions of oil in water emulsions and powdery agents appear to be an effective method for the introduction of the silicon-based agents and little changes of setting time or physical properties were observed.

Water uptake of mortars containing powdery agents is reduced by a factor of 8.

As a conclusion, it can be said that powder supported hydrophobic agents are efficient additives for integral treatments of cementitious materials.

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