The influence of water-repellent admixtures on the behaviour and the effectiveness of Portland limestone cement mortars

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Abstract

Water-repellent mortars were prepared using different hydrophobic compounds as admixtures. Calcium and zinc stearates, silane/siloxane products (as liquid solution and powder) were mixed into limestone cement mortars for obtaining in-bulk water-repellent mortars suitable for building protection and resistant to the degrading action of water. The influences of the admixtures on the hydration and structure of the designed mortars were

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investigated by SEM, TG-DSC, FT-IR, XRD, and isothermal calorimetry. The effectiveness

of these agents against water action was evaluated by using techniques and methods such as

mercury intrusion porosimetry, water absorption tests and contact angle measurements.

Siloxane products conveyed good water-repellent effectiveness, without strongly influencing

the setting and hydration of the binder, while the zinc stearates slowed down the hydration

reactions.

1. Introduction

Portland limestone cement, according to EN 197-1 [1] denominated as CEM II/B-L(LL), is

one of the most commonly used blended cements in Europe [2]. The formulation of rendering

mortars is one of the major application of Portland limestone cement. In Italy alone, 6.8

million tons of Portland limestone cement CEM II/B-L, which is 20.5 % of the whole Italian

cement production, was produced in 2011 [3]. This type of cement helps (together with other

blended cements) to considerably reduce CO_2 emissions by the cement industry. Replacing

cement clinker by limestone (up to 35 %) allows the reduction not only of CO_2 emissions

from the calcination of limestone but also from burning fuel and by saving grinding energy in

the clinker grinder [3-6]. Therefore, the use of Portland limestone cement can be considered

as more sustainable in comparison to Portland cement (CEM I).

The presence of limestone in the system influences the hydration mechanism, kinetics and the

structure of the hardened cement paste [8-12]. Compared to Portland cements, Portland

limestone cements usually have lower compressive strengths, if the limestone content is

higher than 10 % [7], a reduced water demand, and improved workability due to the presence

of fine limestone powder, which acts as a filler between the cement clinker and aggregate

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grains [4, 7-8]. Especially for rendering materials, lower strength and stiffness of the binder matrix is preferred, since it increases the compatibility of the materials with a variety of different substrates. Likewise, the porosity of Portland limestone cement pastes is usually 10% higher compared to Portland cement pastes [11]. Furthermore, with increasing limestone content, the AFm phase monocarboaluminate is earlier and preferably formed, instead of monosulfoaluminate as in pure Portland cement binders [8,9].

In order to obtain sustainable construction materials, it is not only important to reduce the greenhouse gas emissions involved in their production, but also to obtain materials with enhanced durability in order to assure a longer service life and to reduce maintenance costs. Water represents one of the main degradation factors for rendering mortars, which can seriously affect the material properties, reducing its durability. Portland limestone cement mortars, like most inorganic materials, are completely wettable and can degrade over time when exposed to water and to salt crystallization [12- 14]. Many research studies have dealt with the development of strategies to enhance the durability of cement mortars and plasters towards the resistance to the action of water, salt attack and frost attack, by reducing the water uptake through the use of water-repellent systems. Different water–repellent solutions have been investigated: i) aqueous or solvent-based water repellent systems used for impregnation treatments [15- 17], and ii) water-repellent admixtures added directly to the mortars' formulation [18- 24]. In the latter case, different hydrophobic compounds (as dry powder or liquid) can be selected and mixed into fresh mortar mixtures. One of the major advantages of these systems is that the protection should be maintained also in the presence of cracks and erosions of the surface layer [19]. For in-bulk water repellence of mortars, metal soaps and liquid silane emulsions are the most commonly used water-repellent admixtures, but in recent years, the availability of powder silane/siloxanes, obtained by coupling functionalized siloxanes on powder substrates, has allowed the use of silanes also in dry-mix mortars [20]. However, water-repellent admixtures not only reduce the water uptake of the mortar system,

but they affect also the fresh and hardened mortar properties, as well as the hydration of the binder [22- 24].

The interactions between water-repellent admixtures and Portland limestone cement mortars are not well known yet. Therefore, a study is presented that focused on CEMII/B-LL mortars admixed with water-repellents. The goal was to understand the interaction between Portland limestone cement binders and the water repellents during the hydration in context of the effectiveness of the resulting water repellent mortars. In order to better understand the chemical interaction between water-repellent admixtures and Portland limestone cement and to study the hydration mechanisms, electron microscopy (SEM-EDX), infrared spectroscopy (FT-IR), X-ray diffraction (XRD), isothermal calorimetry and thermogravimetric analysis with differential calorimetry (TG-DSC) were employed. The influence of water-repellent admixtures on the physical and structural characteristics of the hardened mortars was evaluated by strength testing and pore structure analysis with mercury intrusion porosimetry (MIP). The water repellency of the mortars was assessed by capillary water absorption and surface wettability with contact angle measurements.

2. Materials and methods

2.1 Starting materials

A Portland limestone cement CEM II/B-LL 32.5 R supplied by CementiRossi® (Pederobba, Italy), with a clinker content around 70 % by mass and a limestone content around 23 % by mass was used as binder. A local sand commonly used in the Venetian area for mortar preparation -consisting of siliceous and carbonate grains (size fraction of 0/1.3)- was used as aggregates for the production of mortar specimens. The sand was chosen in order to obtain less stiff mortars, compatible with the existing substrates.

Four different types of water-repellent admixtures were considered in this study:

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- Calcium Stearate 82 % (Sigma Aldrich®), mixture of calcium stearates-palmitates and other fatty acids;

- Zinc Stearate Pure (Sigma Aldrich®), mixture of zinc stearates-palmitates and other fatty acids;

- Sitren P750 from Evonik®, modified silane/siloxanes in powder form;

- Tegosivin HE 328 from Evonik®, a water-based silane micro emulsion with 50 % content of silane.

The starting materials were characterized by X-ray fluorescence analysis (XRF), Fourier transform infrared spectroscopy (FT-IR) and thermo gravimetry-differential scanning calorimetry (TG-DSC) obtaining information that allowed the interpretation of the analytical results on cement pastes and mortar samples. The XRF analyses were carried out with an EDAX EAGLE III instrument, with a X-ray tube at 40 W (Rh) and an 80 mm^2 nitrogen cooled lithium-drifted silicon crystal detector. An EDAX Data Acquisition Module via a PCI interface was used for data elaboration. A Nicolet Magna FT-IR 750 spectrometer was used to collect FT-IR spectra in the 4000 cm^{-1}-450 cm^{-1} range with a resolution of 4 cm^{-1} on KBr pellets obtained with compression at 10 tons. Thermo gravimetric and calorimetric analysis (TG-DSC) were done with a Netzsch STA 409/C instrument by heating from 40 °C to 950 °C with a heating rate of 10 °C/min, while purging with a 40 ml/min nitrogen flux and using Al_2O_3 as an inert material.

2.2 Preparation of cement pastes for investigation of their hydration

To study the interactions between water repellents and binders during the hydration reactions, Portland limestone cement pastes with and without water-repellent admixtures were prepared and sampled at different curing times of hydration for XRD and SEM analysis. The hydration of a part of the cement pastes was also analysed by isothermal calorimetry over 7 days. The

use of cement pastes instead of mortars was preferred in order to avoid interference of the aggregate on the analytical results.

The pastes were prepared with a water/cement ratio by mass (*w/c*) of 0.8 (correspondent to the w/c used to obtain workable cement mortar mixtures –see also Section 2.3) and with a water-repellent content of 1 % of the cement mass. The dosage of admixtures was chosen considering previous literature [23,24]. A reference paste series contained no water repellent. No other admixtures (such as air entraining agents, plasticizers, accelerators) were added in order to avoid an influence on workability or on the hydration of the pastes. The pastes were poured into plastic vessels, which were closed and stored at 23 °C (the temperature was chosen in order to condition the systems in a similar way to what is prescribed by EN1062-11:2003 for mortars with coatings/hydrophobization treatments [25]). Samples were collected immediately after mixing with water, after 2 h, 7 h and after 1, 2, 3, 7, 14, 21, 28, 42, and 56 d of hydration. The samples were dried in a vacuum oven at 40 °C and 40 mbar for 7 h to stop the hydration and stored under nitrogen to avoid carbonation.

A Rigaku Ultima IV X-ray diffractometer (40 kV and 40 mA Cu X-ray tube) was used for XRD analysis. The measurements ranged from 3° to 63° 2θ with a 0.02° 2θ step size. Fractured surfaces of the samples were analysed with a Jeol-JSM -5600LV scanning electron microscope to investigate their morphology and microstructure.

A Tam Air isothermal calorimeter was employed to measure the heat release of sealed cement pastes for 7 d of hydration in order to evaluate the reactivity in presence of admixtures. The measurements were performed on two different samples of each batch at 23°C.

2.3 Preparation of cement mortars with and without admixtures for investigation of water repellent effectiveness

Portland limestone cement mortars with or without water-repellent admixtures were prepared by mixing the Portland limestone cement with the aggregates in a volume ratio 1:3 (mass ratio

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1:4.1). The water-repellent admixtures were added by 1 % of the total dry mass (cement and sand). One reference mixture was prepared without water-repellent admixtures. First, cement and sand were well mixed with the dry water-repellent admixtures. Then, water was added and mixed for another 3 min. In the case of the water-based silane microemulsion Tegosivin HE 328® ,the admixture was added to the dry cement/sand mixture together with the water. A *w/c* of 0.8 was necessary in order to reach a slump flow around 16 cm -corresponding to a good workability of the mortar mixtures- due to the fineness of the aggregates and the complete absence of plasticizers or other water-reducing admixtures. Workability and density of the fresh mortars were measured with the flow table test according to EN 7044 [26] and EN 1015-6 [27], respectively. Prismatic specimens were prepared using disposable polystyrene moulds, demoulded after 2 d, and stored at (20 ± 2) °C and (90 ± 5) % RH for 28 d and then at (65 ± 5) % RH [1].

The evaluation of the hardening process was performed by analysing mortars samples (collected at 2, 7, 14, 21, 28, 42, 56 d and dried in a vacuum oven at 40 °C) via FT-IR and TG-DSC in the same way described for the starting materials in section 2.1. In the case of TG-DSC analysis, the content of calcium hydroxide was estimated by considering the mass losses in the range from 400 °C to 450 °C [28].

Furthermore, the effectiveness of the water repellents on the admixed mortars was evaluated by determining the structural properties, the mechanical strength and the behaviour in presence of liquid water on mortar prisms (40 mm x 40 mm x 160 mm) hardened 28 d. For all the tests, the average of three specimens for each mixture was considered.

The bulk density of the mortars was determined on the specimens considering the ratio between their mass and their geometric volumes. The total open porosity, the pore size distribution and the bulk density were analysed with mercury intrusion porosimetry (MIP) using a Pascal 140, 240 Thermo Quest instruments, able to measure minimum pore radii of 3.7 nm, following the standard NorMaL 4/80 [29] on samples collected from the inner core

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(1.5 cm depth, in order to avoid external carbonated parts) of the mortar specimens at 2, 7, 28, and 56 d. The pore structure was investigated at different hydration times to observe possible differences due to the influence of the water-repellent admixtures.

The mechanical properties were determined according to EN 12390-3 [30] and EN 12390-5 [31] using a Zwick/Roell Z010 press to test the flexural strength (pre-load of 10 N and a loading rate of 5 N/s) and the compressive strength (pre-load of 20 N and a loading rate of 50 N/s).

The water-repellent admixtures effectiveness was evaluated by measuring:

i) the capillary water absorption on cubic specimens (40 mm x 40 mm x 40 mm) according to EN 1015-18 [32], both the capillary water absorption of the outer layer (i.e. the surfaces originally in contact with the mould walls) and of the inner core (i.e. new surfaces obtained by cutting off a layer 20 mm from the surface) were measured;

ii) the wettability of mortar surfaces by contact angle measurements with the sessile water drop method according to the standard NorMaL 33/89 (using a Data Physics ETT/XL instrument and extrapolating the water drop profile by the ellipse fitting method, 20 measurements for each sample) [33].

3. Results and discussion

3.1 Starting materials

Table 1 summarizes the density and average particle size of the water-repellent admixtures indicating that calcium and zinc stearates had lower density and smaller particles in comparison to Sitren P750. This might produce a different distribution of the water repellents inside the pastes and the mortars. The stearates, having smaller size, might be better distributed inside the matrix with a higher surface in contact with the binder that can influence

the interactions. On the other hand, the silane microemulsion, as a water- based liquid , can be more easily dispersed in the matrix during the mixing process.

Table 2, Fig. 1 and Fig. 2 summarize the data obtained from XRF, TG-DSC and FT-IR analyses of the Portland limestone cement and of the sand used as aggregate. XRF analysis of the Portland limestone cement indicated the presence of high percentages of Ca and Si and the FT-IR analysis showed the peaks relative to anhydrous silicates centred at 1097cm^{-1} (Si-O-Si stretching in the 1090-1100 cm^{-1} range). The presence of gypsum, added to regulate the set of the cement, is indicated by the peak at 671 cm^{-1} and confirmed by the TG-DSC analysis (around 3.2 % as calculated by the mass loss between 100 °C and 200 °C); a slight presence of calcium hydroxide (around 0.6 % as calculated by the mass loss between 400 °C and 450 °C) was observed too. The presence of a high percentage of calcium carbonate in the Portland limestone cement was indicated by the XRF analysis, by the typical FT-IR absorptions at 1795 cm^{-1}, 1428 cm^{-1}, and 875 cm^{-1} and by the mass loss between 650 °C and 800 °C in the TG curve (that allowed calculating a content of 22.8 % of calcium carbonate in the sample). In the FT-IR spectra of the aggregates, strong peaks due to different silicates (1090-1100 cm^{-1} range) were observed together with calcium carbonate and dolomite (peaks at 875 cm^{-1}, 713 cm^{-1} and 729 cm^{-1}, respectively) confirmed by TG-DSC (mass loss and endothermic peak at 650-800 °C).

3.2 Study of the hydration of Portland limestone cement pastes with water repellent admixtures via XRD, SEM-EDX, and isothermal calorimetry analysis

Qualitative XRD analysis of cement pastes without and with water-repellent admixtures at different curing times allowed recognition of the phases and the hydration products [34-37]. The XRD patterns registered for the cement paste without water-repellent admixtures are shown in Fig. 3. The XRD pattern of the anhydrous binder (Fig. 3 - 0h) allowed identification of the clinker phases (C_3S, C_2S, C_3A, C_4AF), gypsum and calcite. After 7 h, it was possible to

identify the formation of portlandite, and after 7 d a strong decrease of C_3S and C_2S occurred. Gypsum reacted completely with C_3A forming ettringite (9.1° 2θ) within 24 h. Interesting is the reaction of C_4AF, which is consumed almost completely after 21 d, indicated by the disappearance of the peak at 12.1 ° 2θ.

Calcium hemicarboalmuminate hydrate (hemicarbonate) was formed after 7 d (Fig. 4). After 21 d, calcium monocarboaluminate hydrate (monocarbonate) appeared and became until a curing age of 56 d the major AFm phase. Calcium monosulfoaluminate hydrate (monosulfate) appeared at 7 d, but the amounts were very low. Ettringite as the major AFt phase was stable throughout the hydration (Fig. 3 and 4). The hydration reaction was very similar to an ordinary Portland cement (OPC) paste up to a curing age of 7 d. After that, the formation of monocarbonate was much higher compared to an OPC paste [9].

The effects caused by the presence of water-repellent admixtures were evaluated analysing and comparing the XRD patterns of water repellent pastes at different times (Fig. 4). The main differences relative to the reference paste were as followed:

– The series containing calcium and zinc stearates showed the formation of monocarbonate after 7 d instead of 14 d as in the reference series. The coexistence of hemicarbonate and monocarbonate peaks was observed, which was probably due to a faster transformation of hemicarbonates into monocarbonates. The presence of the two distinct peaks of C_3S and C_2S at 32° 2θ and 33° 2θ indicated a slightly slower hydration of these phases.

- Silane/siloxane admixtures yielded a lower amount of ettringite after 4 and 7 h, respectively. However, after 7 d, no differences relative to the other series were observed. The AFm phases developed in the same way as in the reference series.

SEM images highlight the presence of needle-like crystals of hydrate phases and a more cross-linked matrix in the reference series CP (Fig. 5), indicating faster hydration reactions and higher hydration rates in comparison to the admixed pastes. When zinc stearate was added, the matrix appeared less compact. When the siloxane powder (Sitren P750) was used

the admixture grains were visible and orthorhombic-shaped grains of hydration products were observed near the admixture grains.

Isothermal calorimetry measurements of the total heat and rate of heat development reflect the hydration processes occurring in the system and therefore provide information on the kinetics and mechanism of hydration [38]. Table 3 reports on the evolved heat values, while Fig. 6 shows the heat evolution curves dQ/dt (expressed as thermal power) and the total heat evolved Q(t) up to 7 d.

In the reference series CP, the initial reaction and the induction period lasted around 2 h and 40 min. Afterwards, the main peak of heat evolution reached its maximum at 17 h followed by a period of deceleration. This is in average a delay of approx. 7 to 9 h compared to an OPC paste and is due to the high limestone content in this cement. The initial reaction was due to the release of Ca^{2+} and OH^- ions as soon as the clinker came into contact with water, then the acceleratory period was controlled by the rate of C-S-H and $Ca(OH)_2$ formation. After 25-30 h (after the main hydration peak), a weak and broad shoulder appeared before the end of the deceleration period. Ylmén et al. (2010) observed a similar, but less distinct, behaviour in some Portland cements and attributed it to the dissolution of aluminate phases, e.g. C_3A and subsequent formation of ettringite [39]. However, in the present study XRD analyses showed the formation of ettringite within 24 h and then formation of hemicarbonate. Therefore, the observed shoulder in the heat of hydration curve can be attributed to the formation of hemicarbonate.

According to the data in Table 3 and in Fig. 6, the use of calcium stearates (CPCaSt) accelerated the heat evolution process and produced a higher total heat both at 24 h and after 7 d. This effect might be due to a higher release of calcium ions and subsequent oversaturation of the pore solution, which could have increased portlandite precipitation.

The retardation of heat evolution, i.e. hydration, was significant in the case of CPZnSt, where the maximum dQ/dt is reached only after 19 h. In spite of this delay, the total heat evolved

after 7 d was higher than in the reference series CP. The strong delay caused by the zinc stearates is presumably due to the presence of zinc ions, and to the formation of insoluble zinc hydroxides, which cover the surface of the cement grains preventing their hydration in the first days [40].

The siloxanes did not cause important variation: the heat evolution processes of CPSi750 and CPSiliq were similar to the reference CP. Even if the dormant period was slightly longer, the maximum of dQ/dt was reached slighty faster. The presence of silanolic acid groups on the admixtures could have promoted the formation of the C-S-H phases, accelerating the hydration. Furthermore the carrier material in case of Sitren, which consists of silica, might have contributed to the filler effect, thus enhancing the nucleation and formation of C-S-H phases.

To discuss the results obtained from the study of the hydration of pastes, some observation are emphasized in the following. The hydration mechanism of Portland limestone cement differed from the hydration mechanism of an ordinary Portland cement because of the presence of limestone, which promoted the formation of hemicarbonate and monocarbonate instead of monosulphate. Furthermore, it stabilized the presence of a larger quantity of ettringite together with monocarbonate after a longer time period [7, 9, 36-37].

The use of stearates seemed to accelerate the formation of monocarbonate. However, calcium stearate increased the hydration reaction in the first 24 to 48 h, while zinc stearate decreased significantly the hydration rate in the same time period (low heat release). The principal explanation to this behaviour might be related to ion exchanges between the metal soaps and the calcium present in the limestone grains or in the clinker. The consequent adsorption of the long aliphatic chain of the stearates might cause the formation of a hydrophobic layer on the clinker surfaces, which could constitute a barrier for the normal hydration (see Fig. 7) [18, 41]. The minor production of monocarbonates observed by XRD analyses in CPCaSt and CPZnSt suggest that the stearates probably covered preferentially the limestone particles

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instead of the clinker grains, therefore the delay effect should be limited. The different influence on the hydration due to calcium stearates in comparison to zinc stearates could be explained considering that in the case of calcium stearates, the ion exchange caused the release of calcium ions in the pore solution. This could have promoted the precipitation of portlandite in the early stage and, therefore, counteracting the adsorption of stearates on clinker grains. In the case of zinc stearate, the presence of free zinc ions might have caused the formation of calcium hydroxyl-zincate consuming calcium and hydroxide ions from the solution, delaying the supersaturation of Ca^{2+} in the pore solution and thus delaying the precipitation of calcium hydroxide and the formation of an inferior (weaker) C-S-H. (Fig. 7) [40].

The presence of silane/siloxanes water repellent admixtures caused a slight delay of the formation of ettringite and a longer dormant period. This delay could be due to the hydrophobic nature of the admixtures, which dispose themselves near the clinker grains creating a hydrophobic barrier. However, in this case there is not a direct ion exchange with adsorption on the clinker surfaces, which could explain why the hydration is only slightly delayed in comparison to the effect of the metal soaps. On the other hand, the presence of fine amorphous silica grains in one of the silane/siloxane products (CPSi750) promoted a filler effect, which helped the nucleation of C-S-H and increased the hydration during the first 24 to 48 h (see also Fig. 7).

3.3 Evaluation of the hardening of Portland limestone cement mortars via TG-DSC and FT-IR analysis

The hardening of Portland limestone cement mortars was monitored by TG-DSC measurements on samples drilled from the inner core of the mortar specimens, not affected by the carbonation processes. The analysis revealed the mass losses and the DSC peaks relative to the hydrated compounds to 300 °C, calcium hydroxide between 400 °C and 450 °C,

calcium carbonate at 650-800°C. The percentage of calcium hydroxide present in samples collected at different curing times, calculated from the relative mass loss, was chosen as an indicator for the progression of the hydration reactions since it is formed by the hydration of C_3S and C_2S [10, 42]. Fig. 8 shows its progression over the hardening time. At early ages until 7 d, a strong increase of the production rate of calcium hydroxide was observed for the mortar without water-repellent admixture (CM), and at 7 d the maximum rate was reached. Afterwards, the formation of calcium silicate hydrates (C-S-H) went further on, together with the formation of the other hydrate phases. Therefore, the calcium hydroxide content of the samples after 7 d decreased in relation to the increase of C-S-H and AFm phases. A slight formation of calcium carbonate was observed after 56 days (around 1 %). In the presence of water-repellent admixtures, the samples showed in general a lower formation of calcium hydroxide in the first 7 d, while higher amounts were observed at later ages (15, 28 and 56 d) (Fig.8). This was assumed to be due to the delaying effect on the cement hydration caused by the water-repellent admixtures. This was in particular the case when zinc stearates were added, with an increase of the calcium hydroxide production rate until 56 days.

The FT-IR spectra of the different mixtures were compared at different times (Fig. 9). The presence of calcium carbonate was confirmed in all samples by the strong bands at 1480 cm^{-1}, 875 cm^{-1} and 712 cm^{-1}, together with silicates (1100-900 cm^{-1}) and in particular quartz from the aggregates at 1090 cm^{-1}. In the presence of calcium or zinc stearates, also strong peaks of -CH$_2$ stretching were visible at 2920 cm^{-1} and 2850 cm^{-1}[43], which did not change during the hydration process. In the spectra, no peaks associated with gypsum in the anhydrous cement or with ettringite in the hydrated cements were visible, as probably covered by other stronger peaks related to the aggregates or to the binder. In the spectra collected at early ages (day 0 in Fig. 8), it is possible to recognize the broad peaks in the 3500-3000 cm^{-1} range due to the symmetric and asymmetric stretching of the O-H vibration of the water molecules. During the hydration, the intensity of these peaks increased with the formation of hydrate compounds (7

and 28 d). In the spectra collected after 7 d, the typical sharp peak of calcium hydroxide –OH stretching was also visible at 3645 cm^{-1}. Another main characteristic of the hydrated samples was the displacement of the stretching mode Si-O-Si from 915 cm^{-1} in the dry cement to 1009 cm^{-1} in the samples after 24 h of hydration. This second peak was due to the formation of C-S-H, as already reported from previous research [44; 45]. Both the –OH stretching peaks of the calcium hydroxide and the 1000 cm^{-1} peak of the C-S-H appeared and developed in different ways in the presence of different water-repellent admixtures. In fact, the absorbance of these two peaks was higher for the reference mixture CM at 7 d in comparison to the other mixtures, but lower at 28 d as shown in Fig. 9.

The increasing of the peak at 1009 cm^{-1} over time (related to the formation of C-S-H) might be considered as an indicator of the reaction progress, but the FT-IR analyses were mostly qualitative. Therefore it was chosen to consider the ratio between the absorbance intensity of the C-S-H peaks at 1009 cm^{-1} divided by the absorbance intensity of quartz peaks at 1089 cm^{-1} because the presence of quartz and the relative peaks should not change with time. The C-S-H/quartz absorbance ratio ($A_{(1009)}/A_{(1089)}$) is plotted versus the hydration time in Fig. 10 for observing possible differences between the mixtures. The absorbance ratio $A_{(1009)}/A_{(1089)}$ increased rapidly in the first 7 d for each mortar mixture, due to the increase of the C-S-H peak showing a fast hydration rate, and stabilized afterwards. A higher reactivity was observed in the mortar without admixtures (CM) or with the siloxane powder (CMSi750) after 56 d, while for the other mortar mixtures the ratio remains relatively stable after 7 d (see Fig. 10). These observations are consistent with the data obtained from the hydration of the pastes (XRD and isocalorimetry) and TG analysis, which showed a slower formation of calcium hydroxide and C-S-H when admixtures were present, indicating a general delay of the hydration reactions.

3.4 Pore structure and mechanical properties of mortars with water-repellent admixtures

The effects of the water-repellents on the mortars were determined by also measuring the workability and density of fresh mortar, the pore structure and the mechanical properties of hardened mortars. The data obtained on the fresh mixtures and on the mortars cured for 28 d are listed in Table 4.

The fresh mortars were characterized by similar workability with a slump flow around 16.5 cm for the mixtures CM, CMZnst, CMSi750, and around 15.0 cm for CMCast and CMSiliq. The densities of the fresh mortars were similar (approx. 2.1 g/cm^3); the densities of the hardened mortars were approx. 1.75 g/cm^3. Slightly lower densities were observed for mixtures with siloxanes.

Pore structure information of hardened mortars was obtained from mercury intrusion porosimetry (MIP) analyses (Table 4 and Fig.11, 12). For the reference mortar without admixture (CM) after 28 d of hardening, a total cumulative volume of 147 mm^3/g of open porosity and a total open porosity of 28 % was measured, with a wide distribution of the pore radii over the range 0.006 μm – 2.00 μm with peaks at 0.02 μm, 0. 2 μm and 0.09 μm [46]. Over time the pore size distribution of CM remained similar with an overall decrease of the total open porosity (Fig. 12).

Compared to the reference series, the porosity development of the admixed mortars showed a strong decrease in the total open porosity between the 2nd day and the 7th day (Fig. 12). Afterwards, the total porosity decreased slowly for CM, CMCaSt, CMZnSt until 365d and faster in the case of CMSi750 and CMSiliq.

The silane/siloxane series showed lower bulk densities and higher total open pore volumes after 28; 56 and 365 d (Fig. 12), with a bimodal distribution of pore radii in CMSiliq (peaks: 3 μm; 0.2 μm) and trimodal in CMSi750 (0.006 μm; 0.2 μm; 0.9 μm) visible in Fig.11. In particular for the series CMSiliq, the pore sizes between 1 and 100 μm were much higher at the different curing times than for the other series, due probably to an air entraining effect of the liquid siloxane. The pore distribution of CMsiliq shift slightly to lower pore radius in the

first 7 days (see 1-10 μm and 10-100 μm ranges), at 7, 28, 56 d the cumulative volume of pores between 1-10 μm remain proportionally similar to the corresponding total cumulative volumes. Only after one year the production of hydrated compounds resulted in a pore size distribution more similar to CM. The changes in the pore size distribution of CMSi750 over time indicated that the final pore structure was formed after one month and that the pore distribution became similar to CM after one year.

For the series containing stearates, the total open pore volumes were a little lower than those of the reference series. However, the pore size distributions of CMCaSt and CMZnSt were almost mono-modal and wide in the 0.02 μm-1 μm range (with shoulders in 0.5 and 0.2, respectively) (fig.11), the content of pores with radii between 1 and 100 μm was significantly lower compared to the reference series and the series containing silane/siloxane.

The compressive strength values of the mortars with water-repellent admixtures were always lower in comparison to the reference mortar CM, while the flexural strength was not altered much. The results of compressive strength tests correspond well to the respective porosity data at 28 d, except for the series containing Zn-stearate (Table 4). Here, compressive strength is much lower than that of the reference series, but the porosity of the reference is much higher. It might be that Zn-stearate as an admixture slightly increased the dispersion of the binder paste and aggregate, but it could contaminate the cement surfaces leading to a slight hydration delay and precipitation of a weaker C-S-H . This might explain a denser packing and, at the same time, a lower compressive and flexural strength.

3.5 Study of the behaviour of mortars with admixtures in presence of water

The capillary water absorption curves of the mortars measured on the external surfaces are shown in Fig. 13, while Table 4 summarizes the calculated capillary water absorption coefficients CI of the outer surfaces and inner core and the contact angles of water drops on the mortar surfaces.

The mortar without water-repellent admixtures (CM) easily absorbed a high quantity of water and reached saturation after 8 h, while the mortars admixed with water-repellents did not have high water uptakes [47]. The capillary water absorption was significantly reduced due to the addition of silanes/siloxanes (CMSi750; CMSiliq), despite their higher total open porosity in comparison to CM. The silane/siloxanes series showed also higher contact angles in comparison to the stearates series and the reference mortars. The stearates, in particular zinc stearate, were less effective in reducing the absorption in comparison to the siloxanes and contact angles lower than 90° were measured (Table 4).

The capillary water absorption of admixed mortars might depend not only on the admixture composition, but also on its distribution inside the mortar matrix. Wittmann et al. (2011) [48] observed that the siloxane and stearates concentration on concrete was highest close to the surface. This was attributed to a transportation of the siloxane or stearate during the drying process with the water into the surface near zone. The comparison between the capillary absorption coefficients measured on the outer surface CI_{out} or inner core CI_{in} highlights that the capillary suction increases in the inner part of CM, CMSi750 and CM Siliq, while it remained almost unchanged for CMCasSt and CMZnSt (Table 4). For the reference series CM, this was probably due to a lower open porosity of the external area, resulting from a higher compaction of the fresh mortars on the mould wall during the mortars preparation and from the mortar carbonation that proceeded from the outside to the inside.

For the admixed mortars, the different capillary absorption coefficients could be related not only to the different porosity, (due to carbonation and compaction of the external layer), but also to a different distribution or interaction of the water repellent admixtures inside the specimens as indicated by the different percentage variations $\Delta CI = (CI_{in} - CI_{out})/ CI_{out}$ of the mortars in comparison to CM (Table 4). In particular the ΔCI of the mortars with siloxanes, being higher than CM, could indicate the presence of a higher amount of siloxanes on the surfaces than in the inner core. On the other hand, the stearates seem to be less present on the

surfaces, as indicated also by the lower contact angles. Given that the admixtures represent only 1% of the system and that the differences are quite small, the lower effectiveness of the stearates could be linked also to their distribution, influenced, in turn, by a partial subtraction from the surfaces due to the ion exchange (see paragraph 3.2).

4. Conclusions

The results showed that the hydration of the pastes studied proceed in a different way in comparison to an Ordinary Portland Cement paste and that the water-repellent admixtures influenced in different ways the chemical-physical behaviour of limestone cement mortars depending on their nature.

To summarize the results regarding the hydration the following conclusions can be drawn:

- The presence of limestone in Limestone Portland cement promoted the formation of hemicarbonate and monocarbonate and stabilized the presence of ettringite in comparison to Ordinary Portland Cement.

  - All the water-repellent admixtures investigated were responsible for delaying the hydration process,. Early hydration within 48 h was partially enhanced by the filler effect, providing nuclei for the formation of C-S-H, except in the case of the series containing Zn-stearate.

  - The adsorption of the long aliphatic chain of the stearates and the ion exchanges with limestone grains might cause the formation of a hydrophobic layer on the clinker surfaces, which could constitute a barrier for the normal hydration.

  - In the case of zinc stearate, the presence of free zinc ions might have caused the formation of calcium hydroxyl-zincate and of an inferior (weaker) C-S-H hydrate.

  - The silane/siloxanes delay slightly the hydration by disposing themselves near the clinker grains and by creating a hydrophobic layer.

Beside studying the hydration processes in-depth, the experiments and the analysis of the results, allowed gaining information about the chemical-physical characteristics of different water-repellent limestone cement mortars:

- The products based on silanes/siloxanes modified the pore structure (increased the volume of capillary pores). They demonstrated high effectiveness as water-repellent admixtures, since a low capillary water absorption of the admixed mortars was measured.

- Mortars with calcium stearates showed low water repellent effectiveness in comparison to the other admixed mortars, but maintained mechanical properties similar to the reference mortar.

- Within the different water-repellent admixtures, zinc stearates showed the strongest influence on the hydration of the binder and the mechanical properties, and a reduced water repellent effectiveness in comparison to mortars with addition of silanes/siloxanes. Despite zinc stearate being one of the most frequently used water-repellent admixtures, based on the obtained results, the amount of zinc stearate should be maintained below 1% to avoid excessive delay of hydration and setting of limestone cement mortars. Lower percentage of zinc stearate might be recommended in order to enhance the mechanical properties, when a reduced water repellent effect is acceptable.

The results also allowed evaluation of the performance of rendering mortars made of CEMII/B-LL with the addition of water-repellent admixtures. A lower mechanical strength of Portland limestone cement mortars with w/c of 0.8 and the local silicate-carbonate sand as aggregates in comparison to standard Portland cement mortars was observed, that decreased further in presence of the admixtures. However, high mechanical strength is not a property strictly required to a rendering mortar: a render should not have structural functions. Instead, one of the major features requested is the compatibility with the existing wall structures and a

certain durability, which includes different aspects such as the stiffness, thickness, the materials, the appearance, and the resistance to external environment. Plasters, which are too stiff for the brickwork substrate tend to detach [49]. Several examples of this detachment can be seen in Venice, where the traditional venetian bricks, with compressive strengths around 18 MPa, and the adverse environmental conditions, require the use of less stiff renders with high permeability, that can be assured by a higher open porosity and the right choice of starting materials.

The higher porosity caused by the addition of silane/siloxanes and the modified pore size distribution help to obtain a frost and salt resistant material, while its water repellency prevents the water (rain, salt solution) penetration into the render and the underlying wall.

Acknowledgments

References

1. EN 197-1:2011. Cement- Part 1. Composition, specification and conformity criteria for common cements. European Committee for Standardization.
2. European construction in service of Society. In: Henrichsen A, editor. Proceedings of Eco-serve Seminar Challenges for Sustainable Construction: the "concrete" approach. Warsaw, 2006. http://www.eco-serve.net/seminar/Proceedings.pdf
3. AITEC Associazione Italiana Tecnico Economica Cemento (Italian Economical-Technical Cement Association) . Relazione annuale 2011. Roma, 2011.
4. Hawkins P, Tennis P, Detwiler R. The use of limestone in Portland cement: a state-of-art review. EB227. Portland Cement Association. Skokie. 2003.
5. Hooton RD, Nokken M, Thomas MDA. Portland-Limestone Cement: State-of-the-Art, Report and Gap Analysis for CSA A 3000. Ontario, University of Toronto, 2007.
6. World Business Council for Sustainable Development (WBCSD) and International Energy Agency (IEA). Cement Technology Roadmap 2009, carbon emissions reductions up to 2050. Switzerland, 2009 [online] http://www.wbcsdcement.org/.
7. Tsivilis S, Chaniotakis E, Kakali G, Batis G. An analysis of the properties of Portland limestone cements and concrete. Cem Concr Comp 2002; 24:371-378.
8. Voglis N, Kakali G, Chaniotakis E, Tsivilis S. Portland-limestone cements. Their properties and hydration compared to those of other composite cements. Cem Concr Comp 2005;27:191-196.
9. Lothenbach B, Le Saout G, Gallucci E, Scrivener K. Influence of limestone on the hydration of Portland cement. Cem Concr Res 2008;38:848-860.
10. Tsivilis S, Kakali G, Chaniotakis A, Souvaridou A. Study on the hydration of Portland limestone cement by means of TG. J Therm Anal 1998; 52:863-870.

11. Ramezanianpour AM, Hooton RD. A study on hydration, compressive strength, and porosity of Portland-limestone cement mixes containing SCMs. Cem Concr Compos 2014;51:1–13. doi:10.1016/j.cemconcomp.2014.03.006.
12. Tsivilis S, Tsantilas J, Kakali G, Chaniotakis E, Sakellariou A. The permeability of Portland limestone cement concrete. Cem Concr Res 2003;33:1465-1471.
13. Collepardi M. Thaumasite formation and deterioration in historic buildings. Cem Concr Comp 1999; 21:147-154.
14. Stambolov T, Van Aspered de Boer JRJ. The deterioration and conservation of porous building materials in monuments: a litterature review. Rome: International Centre for Conservation, 1972.
15. Maravelaki-Kalaitzaki P. Hydraulic lime mortars with siloxane for waterproofing historic masonry. Cem Concr Res 2007;37: 283-290.
16. Schueremans L, Van Gemert D, Friedel M, Giessler-Blank S. Durability of hydrophobic agents applied in a marine environment. In De Clerque H, Charola AE, editors. Proceedings of Hydrophobe V. Brussels: Aedificatio Publishers 2007, p. 1- 11.
17. Carmona-Quiroga PM, Martínez-Ramírez S, Sánchez de Rojas MI, Blanco-Varela MT. Surface water repellent-mediated change in lime mortar colour and gloss. Constr Build Mater 2010;24:188-2193.
18. Lanzon M, Garcia-Ruiz PA. Evaluation of capillary water absorption in rendering mortars, made with powdered waterproofing additives. Constr Build Mater 2009; 23:3287-3291.
19. Zhang P, Wittmann FH, Zhao TJ, Lehmann EH, Tian L, Vontobel P. Observation and quantification of water penetration into Strain Hardening Cement-based Composites (SHCC) with multiple cracks by means of neutron radiography. Nucl Instrum Meth A 2010; 620:11–21.
20. Roos M, König F, Stadtmüller S, Weyershausen B. Invited Lecture: Evolution of Silicone Based Water Repellents for Modern Building Protection. In De Clerque H, Charola AE, editors. Proceedings of Hydrophobe V. Brussels: Aedificatio Publishers 2007.
21. Izaguirre A, Lanas J, Álvarez JI. Ageing of lime mortars with admixtures: Durability and strength assessment. Cem Concr Res 2010;40:1081-1095.
22. Maranhao FL, John VM. The influence of silicone based Water Repellents as Admixtures on the Rheological properties of Cement Slurry. In De Clerque H, Charola AE, editors. Proceedings of Hydrophobe V. Brussels: Aedificatio Publishers 2007, p. 255-257.
23. Klisińska-Kopacz A, Tišlova R. Effect of hydrophobization treatment on the hydration of repair Roman cement mortars. Constr Build Mater, 2012;35:735-740.
24. Falchi L, Müller U, Fontana P, Izzo FC, Zendri E. Influence and effectiveness of water-repellent admixtures on pozzolana–lime mortars for restoration application. Constr Build Mater 2013;49:272-280.
25. EN1062-11:2003 Coating materials and coating systems for exterior masonry and concrete. Methods of conditioning before testing. European Committee for Standardization.
26. EN 7044:1972 Determination Of Consistency Of Cement Mortars Using A Flow Table. European Committee for Standardization.
27. EN 1015-6 2007-05; Methods of test for mortar for masonry - Part 6: Determination of bulk density of fresh mortar. European Committee for Standardization.
28. Ramachandran VS, Paroli RM, Beaudoin JJ, Delgado AH. Handbook of thermal analysis of construction materials. Norwich, New York, 2002.
29. CNR-ICR NorMaL 4/80 Distribuzione del Volume dei Pori in Funzione del loro Diametro (Italian normative on stone material-Distribution of pores volume vs. their diameter). Commissione Beni Culturali UNI NorMaL
30. EN 12390-3:2009 Testing hardened concrete. Compressive strength of test specimens. European Committee for Standardization.
31. EN 12390-5:2009 Testing hardened concrete. Flexural strength of test specimens. European Committee for Standardization.
32. EN 1015-18:1999 Methods of Test for Mortar for Masonry - Part 18: Determination of Water Absorption Coefficient due to Capillary Action of hardened Rendering Mortar. European Committee for Standardization.
33. CNR-ICR NorMaL 33/89 Misura dell'angolo di contatto (Italian normative on stone material-Contact angle measurement). Commissione Beni Culturali UNI NorMaL
34. Lea M. Chemistry of Cement and Concrete, 4th ed. London: Peter C Hewlett, 1997.
35. Taylor HF. Cement Chemistry. 2nd ed. London: London Academic press, 1997.
36. De Weerdt K, Ben Haha M, Le Saout G, Kjellsen KO, Justnes H, Lothenbach B. Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash. Cem Concr Res 2011;41:279-291.
37. Matschei T, Lothenbach B, Glasser FP. The AFm phase in Portland cement. Cem Concr Res 2007;37:118-130.
38. Nocuń-Wczelik W, Czapik P, Use of calorimetry and other methods in the studies of water reducers and set retarders interaction with hydrating cement paste. Constr Build Mater 2013;38:980-986.

39. Ylmén R, Wadsö L, Panas I. Insights into early hydration of Portland limestone cement from infrared spectroscopy and isothermal calorimetry. Cem Concr Res 2010;40(10):1541-1546.

40. Weeks C, Hand RJ, Sharp JH. Retardation of cement hydration caused by heavy metals present in ISF slag used as aggregate. Cem Con Composites, 2008;30:970-978

41. Song MG, Kim JY, Kim JD. Effect of sodium stearate and calcium ion on dispersion properties of precipitated calcium carbonate suspensions. Colloid and Surfaces A: Physicochemical and Engineering Aspects. 2003;229(1):75-83

42. Ramachandran VS. Thermal analyses of cement components hydrated in the presence of calcium carbonate. Thermochimica Acta 1988;127:385-394.

43. Robinet L, Corbail M C. The characterization of metal soaps. Stud Conserv 2003;48:23-40.

44. Trezza MA, Lavat AE. Analysis of the system $3CaO \cdot Al_2O_3$–$CaSO_4 \cdot 2H_2O$–$CaCO_3$–H_2O by FT-IR spectroscopy. Cem Concr Res 2001;31:869-872.

45. Maravelaki-Kalaitzaki P, Agioutantis Z, Lionakis E, Stavroulaki M, Perdikatsis V. Physico-chemical and mechanical characterization of hydraulic mortars containing nano-titania for restoration applications. Cem Concr Comp 2013;36:33-41.

46. Pipilikaki P, Beazi-Katsioti M. The assessment of porosity and pore size distribution of limestone Portland cement pastes. Constr Build Mater 2009;23:1966-1970.

47. Ramli M, Tabassi AA, Hoe KW. Porosity, pore structure and water absorption of polymer-modified mortars: An experimental study under different curing conditions. Composites Part B: Engineering 2013;55:221-233.

48. Li W, Wittmann FH, Jiang R, Zhao T, Wolfseher R. Metal soaps for the Production of Integral Water Repellent Concrete. In Borelli E, FassinaV, editors. Proceedings of Hydrophobe VI. Rome: Aedificatio Publisher, 2011. p.145-154.

49. Bidwell TG. Some aspects of the restoration of historic brickwork in London. In Proceedings of Il Mattone di Venezia- Bricks of Venice, stato delle conoscenze tecnico-scientifiche. Venice, 1979. p.395-404.