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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 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 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

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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:

– 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 4000–450 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 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