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Influence and effectiveness of water-repellent admixtures on pozzolana–lime mortars for restoration application

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HIGHLIGHTS

- We designed innovative water-repellent pozzolana–lime mortars suitable for restoration of historical buildings.
- We performed an accurate study of the influence of water-repellent admixtures on the hydration of the designed mortars.
- The results are extremely useful to evaluate the compatibility of the designed mortars with the historical structures.

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ABSTRACT

Pozzolana–lime mortars modified with water-repellent admixtures were designed and studied to obtain mortars for restoration application. Powdered silane and calcium stearates were mixed with pozzolana, lime and sand and the chemical–physical properties of the resulting mortars were evaluated by X-ray diffraction, electron microscopy (SEM-EDX), thermogravimetric analysis and FT-IR spectroscopy. The mechanical behavior, the pore structure and the hygric behavior were measured. The resistance of water-repellent mortars to the salt crystallization was evaluated. Both calcium stearates and powdered silane allowed good water-repellent protection even if the water-repellent agents and their dosage modified some physical properties and the hydration kinetic.

1. Introduction

Hydraulic lime mortars are defined as mortars capable of setting and hardening by chemical reaction with water in humid and wet environment. Although hydraulic lime and hydraulic lime mortars are described by EN 998-1 and EN 459-1, EN 459-2, EN 459-3 [1,2], the first use of volcanic sands in mortars seems to be dated back to the 10th century B.C. when Phoenicians mixed natural pozzolana in water engineering structures and ports [3]. Greeks used to add some volcanic pozzolanas from Santorini to their mortars, and then through Romans the use of pozzolanas in mortars became a well-regulated practice [4]. A similar hydraulic effect could be obtained also by substituting ordinary sand with finely ground bricks or tiles: this technique was commonly used in Venice since the 14th century A.D. for rendering mortars, plasters, mosaics, frescoes and floors in "Venetian style", thanks to the good resistance of these mixtures in the wet/salty climate of the lagoon [5,6]. But from the 19th century Portland cement gained more and more a position of predominance replacing natural cements [7]. In the last century cement-based materials have been often used also in restoration treatments for historical buildings. However, nowadays the conservation scientists agree that cement is not always the best solution for repairing and restoring ancient constructions [8] because the mechanical, microstructural and chemical properties of cement mortars often differ from the ones of the historical building materials [9].

In the field of conservation the requirements of adopting compatible, reliable, durable solutions (able to repair ancient and historic structures without causing any new damages), leads to rethink on the use of cement mortars and to prefer natural hydraulic lime mortars or pozzolana–lime mortars. These kinds of mortars demonstrate better chemical, mechanical and microstructural

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characteristics compatible with several traditional building materials and historical mortars [10–12]. In the last years scientific interest in lime-based mortars has increased and different studies have focused in particular on the use and the properties of pozzolanas in hydraulic lime mortars [13–15].

The above mentioned, compatible, pozzolana–lime mortars show a better durability in moist environments in comparison to aerial lime mortar [16], they are however wettable and usually present a higher capillary water absorption in comparison to cement mortars. This means that also pozzolana–lime mortars can be exposed to the most severe deterioration factors which could affect their durability due to the damaging action of water: wet and dry cycles, weathering/rain exposure, freezing and thawing cycles, exposure to salt solutions [17]. To enhance the capabilities of these mortars to protect the surfaces of historical architectures from the damaging action of water or of salt solutions, it is possible to use water-repellent admixtures, analogue to the use in cement mortars [18–21].

In the presented study water-repellent hydraulic lime mortars made with hydrated lime, Greek natural pozzolana, sand and water-repellent admixtures were prepared and studied. The purpose of investigation was: (i) the evaluation of the influence of hydrophobising additives on binder hydration reactions, (ii) the influence on the microstructure and porosity of the mortars, (iii) the resistance of the water-repellent mortar to moisture and salt crystallization.

In a series of preliminary tests different water-repellent admixtures, i.e. sodium oleates, zinc stearates, silane emulsions, calcium stearates (commonly used to obtain water-repellent cement mortars) and powdered silanes/siloxanes [22–24] were evaluated. Even if in some studies the better water repellence performance of calcium oleates compared to calcium stearates was reported [25], the preliminary tests showed that with oleate workability, setting, and mechanical properties of the mortars were negatively affected compared to calcium stearates and the powdered silanes/siloxanes. Therefore these products were studied in detail and the results are presented in this paper.

The use of instrumental techniques such as X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), Fourier-transform infrared spectroscopy (FT-IR), thermal analysis (DTA-TG), and different tests to evaluate mechanical and physical properties of the mortars allowed studying the different water-repellent systems and the influence of the additives on the systems' properties. Moreover, the effect of salt crystallization on the water-repellent mortars was studied [26,27], in order to evaluate their durability towards salt attack.

2. Materials and methods

2.1. Starting materials

A mixture of industrial lime hydrate and a pozzolana of volcanic origin from Greece was used as binder system. The lime was a pure calcium hydroxide ($Ca(OH)_2$) supplied by BASF®. The pozzolana was the S&Bμ-silica®, a buff colored volcanic ultrafine siliceous material with a high glass content supplied by S&B Industrial minerals. CEN standard sand defined by EN 196-1 [28] was chosen as aggregate (siliceous sand with a size fraction of 0/2). Two different kinds of water repellent products were chosen: 82% pure calcium Stearate purchased from Sigma Aldrich as a mixture of calcium stearates–palmitates and other fatty acid; Silres A® purchased from Wacker Chemie®, a silane/siloxane supported on silica powder (henceforth named simply 'silane').

Dry powder samples of the starting materials were characterized via X-ray diffraction (XRD) and X-ray fluorescence (XRF) analysis. The XRF analysis was carried out with an EDAX EAGLE III instrument, with a X-ray tube at 40 kV (Rh), 80 mm^2 nitrogen cooled lithium-drifted silicon crystal detector. EDAX Data Acquisition Module via PCI interface was used to acquire and process the data. The XRD measurements were done with a Rigaku Ultima IV X-ray diffractometer (40 kV and 40 mA Cu X-ray tube). The measurements ranged from 3° to 63° 2θ with a 0.02° 2θ step size.

2.2. Water-repellent pastes and water repellent mortars

Two different kinds of samples were prepared and studied:

- binder pastes mixed with water-repellent admixtures allowed to study the hydration reactions of the pure binder in presence of water-repellent agents;
- mortar mixes made of pozzolana–lime binder, sand and water-repellent admixtures allowed to evaluate the physical–chemical performances of water-repellent mortars and the resistance to salt crystallization.

2.3. Study of the hydration reactions of pozzolana–lime pastes

Binder pastes were prepared by mixing calcium hydroxide and pozzolana by a mass ratio of 1:1. The water-repellent admixtures were added at 1% by mass of the binder, while water was added in a water to binder (w/b) ratio of 0.8. The same w/b ratio was used for the mortars, as described below. The dosage of the water-repellent admixtures was chosen considering previous literature data and the necessity of having enough admixtures to observe possible effects [18,21]. One mix was prepared without admixture and was used as reference. The mixes were stored in closed PET vessels at 23 °C. Samples were collected at different hydration times (0, 2, 4 h; 1, 2, 7, 14, 21, 28, 42, 56, 84, and 140 days) and dried in a vacuum oven at 40 °C and 40 mbar for 7 h to stop the hydration processes. The samples were then stored under nitrogen atmosphere to avoid carbonation.

Different analyses were performed to observe the formation of hydration products to better understand the setting and hardening mechanisms involved when the selected pozzolana is mixed to calcium hydroxide, and how the presence of water-repellent admixtures can influence the hydration reactions of this system.

Qualitative XRD powder analysis was performed on dried and ground samples. The same measurement parameters were used as for raw-material characterization.

SEM-EDX observation was carried out on fractured surfaces using a Philips Quanta 200FEI instrument with a Tungsten cathode and a Si(Li) Brucker 133 eV EDS detector.

The TG-DTA analyses were performed on powdered samples at 0, 2, 7, and 28 days of hydration. The samples were ground and measured with a Netzsch STA 409/C instrument in alumina crucible, a heating program of 10 °C/min from 20 °C to 1000 °C in N_2 atmosphere was used.

A Perkin Elmer Spectrum One FT-IR ATR with diamond cell was used to measure the transmittance in the 500–1400 cm^{-1} range, with 1 cm^{-1} resolution and 32 scan/sample on ground samples collected at 0, 7, 28, and 84 days.

2.4. Physical–chemical characterization of water-repellent mortars

Water-repellent mortars were prepared by mixing pozzolana and calcium hydroxide in a ratio of 1:1 by mass and a mass ratio of 1:7 (1:3 by volume) binder/aggregate was used. The different admixtures were added at 0.5%, 1%, and 1.5% of the total dry mortar's weight. These three different percentages were chosen considering previously published data in order to evaluate the influence of different dosage on the mortars performances, beside the different nature of the water-repellent admixture [18,21]. Mortars prepared without water-repellent admixtures were used as reference mixes.

The materials were mixed with water in a planetary mixer for 10 min, to allow a homogeneous distribution of the different components. The amount of water was adjusted in order to achieve a mortar slump flow of (170 ± 10) mm with the flow table test according to EN 1015-3 [29]. The bulk density of the fresh pozzolana–lime mortars was measured following UNI EN 1015-6:2007 [30].

On two fresh samples of each mixture the setting time with the Vicat's needle method (UNI-EN 196-3) [31] was determined at 20 °C. The other fresh mixtures prepared were poured in oiled 4 × 4 × 16 cm moulds (a veil of oil was necessary to allow the de-moulding of the mortar samples), and then placed in a curing chamber at RH = 90% and T = (23 ± 2) °C for 28 days.

The physical–chemical characterization of water-repellent mortars after 28 days of curing included the evaluation of the density and microstructure, the evaluation of the mechanical strength and the evaluation of the behavior of water-repellent mortars in the presence of water. The test performed completely characterized the systems, obtained interconnected data, and allowed a full understanding of the effects of the added water-repellent admixtures on lime–pozzolana mortars. For all the tests, the average of the results of three specimens for each mixture was considered.

The bulk density of the hardened mortars was calculated on dried prismatic specimens considering the ratio between their masses and their apparent volumes, while the real density was measured with a helium pycnometer on ground samples (particle diameter <63 μm). With mercury intrusion porosimetry (MIP) the bulk density, the total open porosity and the pore size distribution were measured. MIP analysis was performed on samples collected from the bulk of 28 days-aged mortars as described in the Normal 4/80 [32] using a Pascal 140 and a Pascal 240 Thermo Quest/Finnigan instruments, able to measure minimum pore radii of 3.7 nm.

Mechanical tests were performed on 28 days aged mortars according to UNI EN 12390-3:2009 and UNI EN 12390-5:2009 [33,34]. A Zwick/Roell Z010 press was used with a pre-load of 10 N and a loading rate of 5 N/s for the flexural strength,