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Cement and Concrete Research 37 (2007) 283 – 290
Cement and Concrete Research

Hydraulic lime mortars with siloxane for waterproofing historic masonry

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Received 13 April 2005; accepted 8 November 2006

Abstract

Mortars with different content of hydraulic lime and aggregates of a siliceous and carbonaceous nature differing in grain size, were designed for waterproofing historic masonry. The repair mortars design was taken into consideration the physico-chemical properties of the original ones. The water repellency of the designed mortars was enhanced through impregnation with an oligomeric organo-siloxane provided optimum water vapour permeability; this is due to the siloxane coating the capillaries without blocking the pores, as indicated from the slightly modified pore size distribution. The grain size of aggregates and the binder content influence the performance of mortars. Mortars with coarse aggregates develop high mechanical strength; nevertheless, micropores interconnected with macropores are responsible for the low salt-decay resistance. Increase of the binding content enhances the mechanical resistance but decreases the resistance to sulphate solutions, as a consequence of the small capillaries not allowing for salt crystallization. The mortar with the best performance consists of medium aggregates and a binder to aggregate ratio equal to 0.33; pores around 0.2 μm of radius enable salts to crystallize without provoking damage from crystallization pressure. The selected mortar, after fourteen months of application to the masonry, shows neither microcracks nor efflorescence formation.
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Keywords: Hydraulic lime mortars (E); Siloxane (E); Water repellency (C); Water vapour permeability (C); Sulphate Attack (C); Pore size distribution (B)

1. Introduction

This study deals with the conservation of the castle of Firkas, one of the bastions of the Venetian fortifications of the city of Chania (Canea), on the north-western side of Crete, Greece. The castle of Firkas comprises the walls, a neoclassic building in which the Naval Museum is located, a central building on two levels with a tower, six large embrasures and two squares. The construction of the complex of Firkas started in 1204 and was completed in 1538, as a part of the fortified "cinta muraria" of the city [1]. In 1965 the Venetian fortifications and the historical center of Chania were declared a historical, artistic and monumental patrimony of the Greek State. Since the '70s restoration and consolidation works have been carried out in various parts of the castle. In 1998 the 28th Ephorate of Byzantine Antiquities presented a plan for the restoration of the castle. The most critical conservation problems were the protection of the structure against moisture, salts and rain action. No particular structural problems have been observed in the castle.

The main objective of the restoration project is the conservation and rehabilitation of the central building of the castle. It was deemed important that the roof of the building be waterproofed by replacing the old mortar which was in an advanced state of decay. Conventional waterproofing systems based on asphalt, bitumen, polyurethane, polystyrene, fiberglass, mineral and wood fiberboards were deliberately avoided due to the lack of the water vapour permeability provided by these systems. Old buildings are characterised by the extensive flow of moisture through their walls. The transfer of water vapour through the walls is an essential requirement when dealing with the conservation of historic buildings. Water is considered the active medium for the transfer of soluble salts and any corresponding effects. Impeding this flow by any type of barrier is most likely to result in water vapour being retained, thus condensing and possibly generating serious damage.

Additionally, guidelines for the design of repair mortars suggest that strengthened mortars with properties and chemical composition similar to the corresponding original ones are required [2]. Previous work has highlighted the fact that repair mortars based on natural hydraulic lime attain chemical, physical and structural compatibility with the original mortars [3].

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0008-8846/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2006.11.007

Therefore, the use of natural hydraulic lime as a binding material in the design of the new waterproofing mortar was adopted.

This study presents the design and comparative evaluation of waterproofing mortars based on the results obtained from the physico-chemical analyses of the original mortars. The purpose of this study was to design a compatible waterproofing mortar, which would allow the water to evaporate but at the same time would prevent rain from penetrating the structure. These requirements can be achieved firstly by designing mortars simulating the grain size distribution of the analysed original mortars and secondly by adding a water repellent. The designed waterproofing mortars mainly consisted of hydraulic lime, siliceous sand, calcareous aggregates and a siloxane water repellent, which was added after curing to improve the impermeability characteristics. Four waterproofing mortars differing in grain size distribution and binder to aggregate ratio were selected and thoroughly evaluated in the laboratory with the aid of various physico-chemical and mechanical analyses. From the analytical results of the performance of the studied repair materials, the optimum mortar was selected and the required conservation intervention carried out.

2. Experimental procedure

2.1. Study of the original mortars

Mortar sampling was performed on four separate parts of the roof, the aim being to assess any differences in the construction mortar. The analyses were performed in a quantity of mortars guaranteeing that errors caused by heterogeneity would be avoided. The analyses of the four original mortars were carried out following a methodology established and presented in detail in previous work [3,4]. The mortars were examined by mineralogical and physico-chemical analyses, such as X-Ray diffraction analysis (XRD, Siemens D-500), infrared spectroscopy (FT-IR, Biorad FTS 40), calcimetry (Dietrich–Frühling gas volumetric method) and grain size distribution (ISO 565 series of sieves). For the determination of Ca, Mg, Fe_2O_3 and Al_2O_3 traditional chemical methods were employed after attack with a sodium carbonate-borax alkaline flux. The presence of hydraulic compounds was assessed by attacking crushed mortar with HCl (1:5) 2 M at room temperature for 3 h [4]. The amounts of SiO_2 in the acid soluble fraction of mortars were determined using atomic emission spectrometry (AES, Perkin Elmer 3030), while the amount of salts present was evaluated by means of conductivity measurements.

2.2. Design and evaluation of the repair mortars

In order to assess the suitable proportions for the waterproofing mortars, various mixtures of binder and aggregates were designed. Finally, four waterproofing mortars (A, B, C and D) were selected, differing either in the grain size of aggregates or in the ratio of binder to aggregate (B/Ag) (see also section 3.2). Hydraulic lime with pozzolanic additions (Lafarge NHL-z 3.5) was employed as a binding material. The aggregates comprised siliceous sand, calcareous angle-shaped gravels and crushed limestone. For the preparation of mortars, the aggregates were previously wetted for 5 h in order to eliminate both eventual powder and ensure a better workability of the mixture. After the aggregates were dried, water was added to the mixture and thoroughly stirred. The mixtures were prepared using a water/hydraulic lime ratio enabling the mortar to achieve a constant flow of 150 mm ± 10%. The proportion of binder to aggregates is equal to 0.33 per weight for A and B mortars and 0.50 for C and D mortars. The mixing of the mortars was mechanical and always uniform. The specimens were covered with wet burlap for 3 days and then kept in the open air at 20 °C and 60% relative humidity until testing. Fifteen specimens of each type of mortar were prepared. In three cubic samples of mortars and after 3 months of curing an oligomeric organo-siloxane water repellent (2.61 kg/m^2, Hydrophase ®-Plus, Phase Srl, Italy) was applied by brushing, as reccomended by the producers. The impregnated samples remained in the same conditions as the previously-mentioned samples and were tested 2 months after the application of the water repellent.

The repair materials were assessed by measuring resistance under the influence of saline solutions, water absorption by capillarity, water vapour permeability, porosity and their mechanical properties. In the evaluation of the most important characteristics of the repair materials the following tests were conducted:

Water absorption by capillarity (Norma UNI 10859) [5]: This test was carried out on six cubic samples (5 × 5 × 5 cm) of each waterproofing mortar and three samples of each impregnated mortar. By way of comparison, mortars of cement and aerial lime as binding materials (5 × 5 × 5 cm) were also prepared and underwent water absorption by capillarity. The cement and aerial lime based mortars comply with a ratio equal to 0.33 per weight as far as binder to aggregate ratio is concerned; these mortars comprise aggregates of similar grain size and quantity as the corresponding ones of the waterproofing mortar B.

Water vapour permeability measurements have been carried out in home made sample cells according to the wet cup DIN 52615 method [6]. Containers, closed by a sample of 3 cm in thickness were used containing a saturated solution of ammonium dihydrogen phosphate, producing an atmosphere of 93% relative humidity. The containers were placed at a controlled temperature of 23 ± 2 °C and in an environment of 50 ± 5% relative humidity, maintained by a saturated solution of sodium dichromate. The containers are weighed at suitable intervals of time and the water vapour transmission rate is determined by the change in mass at the steady state of the system. This test was run for 10 days when the required stability in the sample weight was obtained. The results are expressed both as $g\,m^{-2}\,24\,h^{-1}$ and $kg\,m^{-1}\,s^{-1}\,Pa^{-1}$ referring to water vapour transmission rate and permeability, respectively. For this measurement the waterproofing mortars were studied separately before and after the application of the organo-siloxane. The samples of cement and aerial lime mortars underwent the same measurement. Each determination of water vapour permeability was conducted in three samples of each category.

Determination of porosity and pore size distribution by means of mercury intrusion porosimetry (MIP, Micromeritics 9320) were carried out on three samples of each waterproofing mortar before and after the application of the resin.

Characterization of the mechanical properties of the restoration mortars was performed through determination of the compressive strength (fmc,k) and modulus of elasticity of cubic specimens (5×5×5 cm) after a six-month setting period. Compression tests were carried out on six samples from each category. Testing was performed with a Universal Mechanical Tester–INSTRON 1026–at a loading rate of 109 μm/min. In order to compare the mechanical properties of the repair mortars with the units of the old masonry, a bioclastic micritic limestone was also used for the mechanical tests. On the other hand, the sampled quantities of the original mortars did not allow further experiments for the determination of mechanical characteristics.

The resistance to chlorides was measured by immersing three samples of each mortar used in the water absorption by capillarity in a 10% (w/v) sodium chloride solution for 24 h and 21 h drying at 65 °C and 9 h for cooling and weighing until reaching constant mass [7]. This procedure comprises one cycle. In order to assess the performance of mortars under the sulphate attack an accelerated test was conducted using a solution of 16% (w/v) sodium sulphate (thenardite: Na_2SO_4) [7]. Three other samples of each mortar were immersed for 2 h in the solution and for the subsequent 22 h were dried in an oven at 105 °C. After each cycle, consisting of the 24 h previously described procedure, and until constant mass was reached, the mass loss was evaluated.

3. Results and discussion

3.1. Original mortars

The results of the chemical analyses of the original mortars are displayed in Table 1. The high values of the conductivity measurements indicate that mortars are liable to disintegrate due to the presence of soluble salts and, therefore, there is a need for their replacement. The analyzed mortars show noticeable amounts of soluble SiO_2. The quantity of the total SiO_2 is due to the aggregates of quartz and the clay minerals contained in the crushed brick. The amount of H_2O corresponds with the chemically bound water in some minerals such as clay minerals and calcium silicate hydrate. The amount of soluble SiO_2 combined with the detected chemically bound water indicates that hydraulic compounds were formed from the well-established interaction between the calcite of binder and alumino-silicates of crushed brick [8].

The presence of hydraulic compounds was also confirmed in the infrared spectra of the binders. As an example, the FTIR spectrum of the binder of sample F2 is illustrated in Fig. 1. Characteristic absorptions attributed to hydraulic compounds, such as the broad band at 1095 cm^{-1} arose from C-S-H vibrations [3].

Grain size distribution is an important factor in obtaining information about individual components of mortars and their mixture ratio during the mortar preparation. The grain size distribution of the aggregates in the original mortars is shown in Fig. 2a. In all mortars, almost 60% of the aggregates show grain size with diameters ranging from 1 to 4 mm, while the rest of the aggregates were distributed in sieves with diameters from 0.5 up to 0.125 mm. F3 and F2 aggregates exhibit diameters greater than 4 mm, while F1 and F4 aggregates exhibit a grain size distribution with fragments of diameter up to 4 mm. The analyzed mortars consist of an average of 30% of binding material in the <63 μm range. This grain size distribution permits an estimation of the binder/aggregate ratio per weight of mortars of about 1/3.

3.2. Repair materials

The analyses of the original mortars showed that raw materials and carbonate lime from the local area were used. Taking into consideration the performance of hydraulic lime based mortars used for restoring other Cretan monuments [3], as well as the presence of hydraulic compounds in the original mortars, the design of repair mortars should reasonably include hydraulic lime with natural pozzolanic additions as binding material. Table 2 shows the characteristics of the raw materials employed for the design of the waterproofing mortars. The coarse and medium gravels are of a carbonate nature (94–96% of calcite), while the prevalent composition of sand is quartz (~78%) with a quantity of ~13% of calcite.

The contribution of the binding content to the performance of the studied materials was assessed by designing mortars with different B/Ag ratio. In order to assess the contribution of the different grain size of aggregates in terms of water absorption, as well as salt and mechanical resistance and to select the best-performing mortar, coarser aggregates were chosen for mortars A and C in comparison with mortars B and D. This differentiation in grain distribution was also dictated by the differing sizes of aggregates in the original mortars. Fig. 2b depicts the grain size distributions of the aggregates used for the design of the waterproofing mortars.

Table 1
Results of mineralogical composition and chemical analysis of the original mortars

Samples	Composition	%CaO [a]	$\%Al_2O_3$ [a]	$\%Fe_2O_3$ [a]	%total SiO_2 [a]	%sol. SiO_2 [b]	$\%H_2O$ [c]	$\%CO_2$ (DF) [d]	Con. (μS/cm)
F1	Cc, Qz, K, Ill, Ha, CSH	22.56	1.45	0.23	35.74	2.01	1.45	24.02	185.23
F2	Cc, Qz, Mu, K, Ill, Ha, CSH	21.74	0.89	0.16	35.25	1.95	2.83	24.74	212.69
F3	Cc, Qz, Ha, K, Ill, CSH	26.14	1.42	0.41	30.78	1.89	2.93	24.89	186.55
F4	Cc, Qz, K, Ill, Ha, CSH	23.29	0.98	0.13	31.25	2.06	3.32	24.45	212.88

Percentages related to original dry mortar.
Cc: calcite; Qz: quartz; Mu: muscovite; Ha: halite; K: kaolinite; Ill: illite; CSH:calcium silicate hydrate.
[a] Sodium carbonate–borax alkaline flux.
[b] Attack by HCl (1:5) 2 M at room temperature for 3 h.
[c] Calculated from weight loss between 120 and 400 °C.
[d] Dietrich–Frühling gas volumetric method.

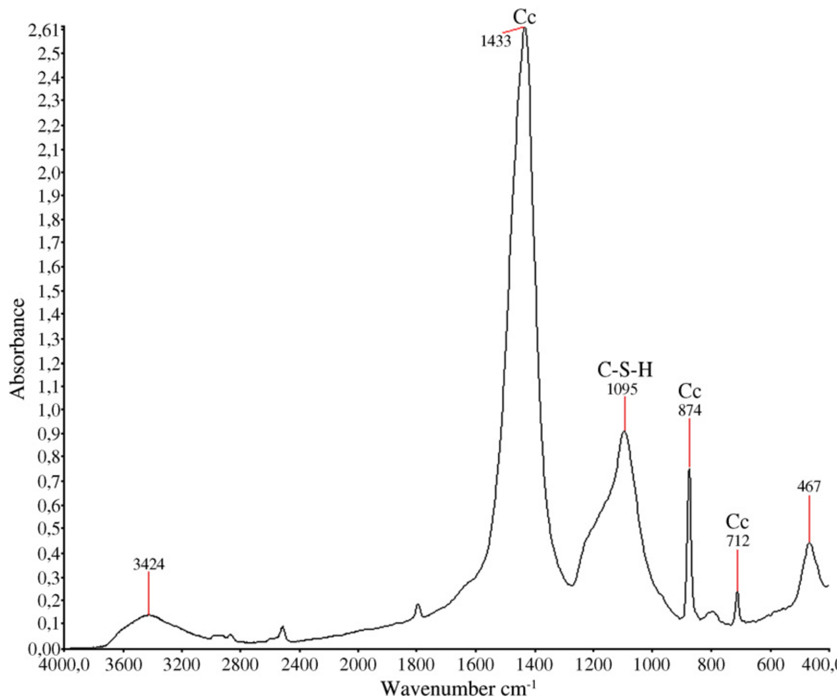

Fig. 1. Infrared spectrum of the binder of sample F2 with calcite (Cc) and characteristic absorption at 1095 cm^{-1} due to hydraulic compounds (C-S-H).

3.3. Evaluation of the repair materials

3.3.1. Water absorption and water vapour transmission

The weathering processes greatly depend on water circulation inside porous materials. Therefore, tests concerning water absorption and water vapour transmission are very important in determining the durability of repair materials. Table 3 shows the results of the determination of the water absorption coefficient, the asymptotic absorption value, the water vapour transmission resistance, the porosity and the average pore radius for the waterproofing mortars, with and without the water repellent. These results are also compared with the corresponding ones for aerial lime and cement-based mortars.

The waterproofing mortars without the resin have a very low capacity to transport water, but the same mortars with the resin show a high water repellency. The hydrophobic properties of the designed mortars were enhanced, since the organo-siloxane changes the hydrophilic surfaces of the capillaries into hydrophobic surfaces due to the large amount of hydrocarbon in its structure. The capillarity coefficient and the value of asymptotic absorption reflect the initial and total water absorption of a system, respectively, and are directly dependent on the microstructural characteristics, especially porosity and pore size.

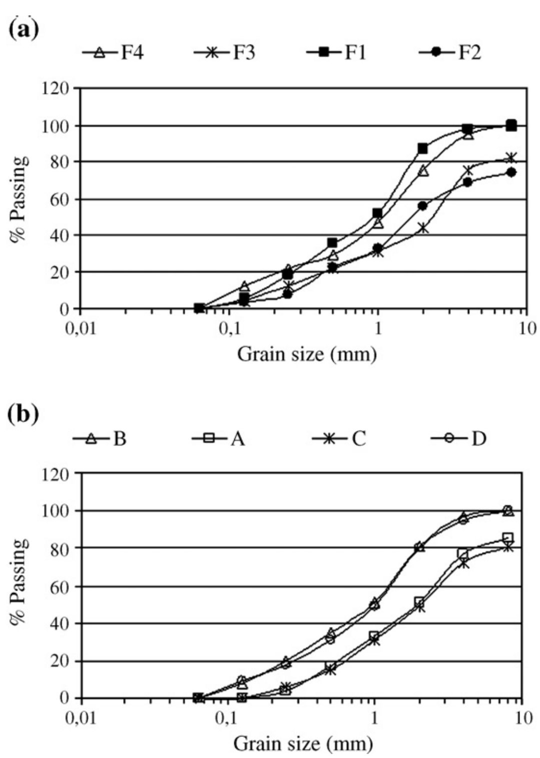

Fig. 2. Grain size distribution of the aggregates of the original (a) and repair mortars (b).

Table 2
Characteristics of the raw materials of the waterproofing mortars

Raw materials	Characteristics
Natural hydraulic lime (NHL)	65% CaO, 11% SiO_2, 12% CO_2, 9% H_2O, 0.8% Al_2O_3+Fe_2O_3, 0.5% MgO, 0.2% K_2O+Na_2O NHL-Z 3.5 according to CEN prEN 459–1
Sand	Siliceous sand 7.1% CaO, 78.2% SiO_2, 4.9% Al_2O_3, 0.5% Fe_2O_3, 1.5% MgO, 0.7% K_2O, 0.9% Na_2O, 4.2% CO_2
Very coarse gravel	Crushed calcareous stones 53.2% CaO, 0.3% SiO_2, 0.1% Al_2O_3, 0.2% Fe_2O_3, 0.5% MgO, 0.1% K_2O, 0.1% Na_2O, 42.1% CO_2
Medium gravel	Crushed calcareous stones 52.1% CaO, 0.2% SiO_2, 0.1% Al_2O_3, 0.2% Fe_2O_3, 0.6% MgO, 0.1% K_2O, 0.1% Na_2O, 41.2% CO_2

Table 3
Physico-chemical characterization of the repair mortars before and after application of the water repellent

Mortars	Capillary water absorption coefficient (CA: kg/m^2 s$^{1/2}$)	Asymptotic values (kg/m^2)	Water vapor transmission rate (g m^{-2} 24 h^{-1})	Permeability (kg m^{-1}s^{-1}Pa^{-1})	Porosity (%)	Average pore radius (μm)
Mortar A (1:3)	0.18 (±0.04)	3.52 (±0.72)	63.58 (±3.67)	1.83 10^{-11} (±1.06 10^{-12})	20.83 (±0.35)	1.41 (±0.16)
Mortar B (1:3)	0.15 (±0.04)	3.04 (±0.45)	62.14 (±1.74)	1.79 10^{-11} (±4.99 10^{-13})	29.88 (±1.35)	0.21 (±0.03)
Mortar C (1:2)	0.11 (±0.03)	2.57 (±0.37)	53.19 (±0.90)	1.53 10^{-11} (±2.59 10^{-13})	23.29 (±0.88)	1.38 (±0.08)
Mortar D (1:2)	0.12 (±0.06)	1.89 (±0.48)	51.23 (±2.12)	1.47 10^{-11} (±6.17 10^{-13})	33.76 (±0.61)	0.04 (±0.01)
A with WR	0.002 (±0.0005)	0.32 (±0.07)	57.25 (±1.46)	1.64 10^{-11} (±4.19 10^{-13})	19.34 (±1.38)	1.35 (±0.36)
B with WR	0.002 (±0.0005)	0.49 (±0.05)	52.39 (±0.90)	1.51 10^{-11} (±2.59 10^{-13})	25.99 (±0.23)	0.10 (±0.02)
C with WR	0.002 (±0.0004)	0.28 (±0.04)	45.78 (±1.54)	1.32 10^{-11} (±4.41 10^{-13})	21.89 (±0.47)	0.97 (±0.15)
D with WR	0.002 (±0.0007)	0.21 (±0.05)	44.23 (±1.75)	1.27 10^{-11} (±5.02 10^{-13})	32.16 (±2.94)	0.03 (±0.01)
Cement–sand (1:3)	0.02 (±0.01)	1.19 (±0.15)	3.24 (±0.29)	0.09 10^{-11} (±8.47 10^{-14})	nd	nd
Lime–sand (1:3)	0.18 (±0.03)	5.14 (±0.24)	82.24 (±1.01)	2.37 10^{-11} (±2.89 10^{-13})	40.15 (±1.29)	2.53 (±0.68)

WR: water repellent; nd: not determined.

The hydraulic lime mortars exhibit lower water absorption coefficients than the lime mortars. Lime mortars exhibit higher pore-diameter and porosity than hydraulic lime based mortars (see Table 3). Therefore, in the hydraulic lime based mortars it seems reasonable to attribute the low values of the asymptotic absorption to the larger amount of small pores present, a result of the hydration reactions of the hydraulic components. The same comment can be also applied to the comparison of the asymptotic values of hydraulic lime mortars with similar grain size but different binder content. The C and D mortars, e.g., show lower asymptotic absorption values than the A and B ones, due to the larger amount of finer pores, attributed to their increased binding content.

By comparison with the cement mortars which obstruct water vapour transmission, the lime mortar proved to be the most permeable material. The impregnated mortars show less water vapour permeability; nevertheless, the transpiration of water vapour through the surface has not been impeded by the application of the resin and the corresponding results are satisfactory. All the tested mortars have a much greater ability to transmit water vapour than the cement mortars.

3.3.2. Porosity and pore size distribution

Porosity and pore size distribution are important parameters which should be evaluated when studying the physico-chemical behaviour and durability of repair materials. Fig. 3 illustrates the percent relative volume as a function of the pore radius for the waterproofing mortars before and after impregnation with the resin. Both the quantity of binder and grain size distribution of aggregates influence the microstructure of mortars as indicated by the different pore size distributions. Mortars with coarse aggregates, such as A and C, exhibit an increment in pore radii between 80 and 200 μm, due most probably to coarse aggregates, which adhere badly to the binder. Mortars with a high binder content, such as C and D, have shown a sharper distribution of pores compared to the corresponding distribution of A and B mortars. Large binder amounts induce porosity and small radius pore ($<$0.05 μm) increment [9].

After impregnation with the water repellent a reduction in porosity and pore range were observed, as illustrated in Fig. 3. These changes are not, however, reflected in any significant reduction of the water vapour permeability. This result can be interpreted on the basis that siloxane has the ability to repel water molecules, to coat capillary walls and to bond to substrates without fully blocking capillaries.

3.3.3. Mechanical characteristics

The evaluation of the mechanical characteristics of the repair mortars should be carried out bearing in mind that compatibility with old masonry can be assured. Low mechanical resistance and moduli of elasticity characterize stone and mortars of old masonry. In our case, as shown in Table 4, the repair materials exhibit lower strength than the original stone. Therefore, they are compatible with the units of the building and can be used for repointing and re-rendering. The cement mortars, however, with approximately three times the compressive strength and modulus of elasticity than the original stone, proved to be inadequate for conservation interventions. The mechanical resistance is influenced by the presence of coarse aggregates and binder content, as is evident from the different values of the waterproofing mortars. Coarser aggregates and a higher binder content result in high mortar strength [10]. Mortars with more binder content show the highest compressive strength, as large amounts of binder give more CSH phases, thus increasing strength.

3.3.4. Salt crystallization test

The performance of repair mortars in the salt crystallization test was evaluated by identifying loss of mass and surface scaling. All mortars, except lime ones, resist chlorides effectively, and increase their mass after 30 cycles of ageing (see Table 5). After the end of the experiment efflorescence appeared in the studied mortars. As far as resistance to sulphates is concerned, the loss of mass in relation to the initial mass of the waterproofing mortars, during 15 cycles of artificial ageing, is plotted in Fig. 4. The studied mortars show a slight increase in mass up to the end of the first five cycles, except for the mortars A and C with coarse aggregates, which started to lose mass during the 4th cycle and completely deteriorated during the 8th cycle. On the other hand, the mortar (D) with medium aggregates and high binding content resisted up to the 6th cycle and then collapsed. The impregnated mortars of hydraulic lime and the untreated mortar (B) of medium aggregates and a B/Ag = 0.33 resisted sulphates better than the cement mortars, which started to deteriorate after the 6th cycle.

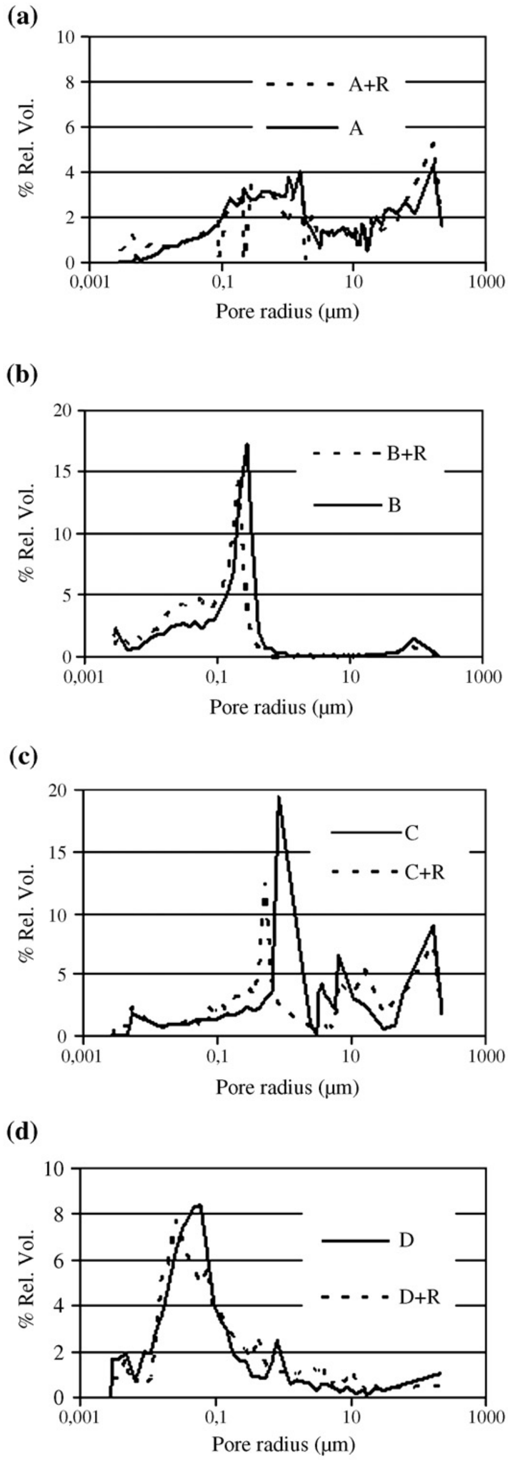

Fig. 3. Percent relative volume as a function of the pore radius for the waterproofing mortars A (a), B (b), C (c) and D (d) before and after impregnation with the water repellent (R).

3.3.5. Overall consideration

In order to gain an insight into the resistance of mortars to salt-decay phenomena the following parameters, which control the uptake and transport of liquid within a mortar, should be taken into consideration: water absorption, porosity, pore size distribution and strength. Previous studies had demonstrated that chlorides were preferentially crystallized into small pores ranging from 0.1 up to 1 μm [11]; during evaporation, sodium chloride, because of its high solubility, crystallizes either on the surface of the sample as efflorescence, or at a depth of a few micrometers. This produces a granular disintegration and powdering leading to mass loss [12]. This grain-by-grain loss is mainly dependent on the mechanical characteristics and is more intensive in less mechanically resistant mortars, such as lime mortars. On the other hand, the hydraulic lime mortars studied exhibit a modest mechanical resistance and this property is associated with a similar resistance to NaCl solutions. Therefore, the lower the mortar strength is, the higher the susceptibility to chloride destruction.

Although halite tended to grow as efflorescence, the crystallization pattern of sodium sulphate is more damaging since it tends to form subflorescence [13]. Two main mechanisms were proposed to explain the extensive damage caused by sodium sulphate: hydration pressure and crystallization pressure [14,15]. According to the experiments of Tsui et al. [16], ageing cycles, involving impregnation and drying result in extensive damage. This is due to mirabilite ($Na_2SO_4.10H_2O$) precipitation occurring during the wetting process and when the crystals no longer have the possibility of growing in unrestrained directions.

On the other hand, the experiments of Rodriguez-Navarro and Dohne [11] conducted under situations of constant capillary rise, demonstrate that precipitation of thenardite rather than mirabilite may be the culprit for damage from sodium sulphate. Additionally, these authors state that as evaporation progresses and once a critical supersaturation is reached, crystallization will take place in the smaller pores, which have been supplied in solution by the larger ones. The larger surface area of micropores facilitates both evaporation and slower solution transport, thus increasing the chances that high supersaturation ratios will be reached deep beneath the sample surface. On the other hand, in samples with larger pores the solutions reach the surface resulting in efflorescence. In general, samples with a high proportion of micropores connected to large pores are very susceptible to salt weathering.

In the studied samples it is important to emphasize the low resistance to sulphates of mortars with coarse aggregates such as A and C. Given that these mortars showed the highest mechanical resistance, their inadequate performance in the sulphate solution can be reasonably attributed to the presence of macropores interconnected with micropores. As previously discussed, this is evident in the pore size distribution of these

Table 4
Mechanical properties of the repair mortars calculated after curing of 6 months

Samples	Compressive strength (N/mm^2)	Modulus of elasticity (N/mm^2)
Waterproofing mortar A (1:3)	5.23 (±0.36)	7114 (±370)
Waterproofing mortar B (1:3)	4.12 (±0.40)	7052 (±250)
Waterproofing mortar C (1:2)	5.95 (±0.25)	7852 (±240)
Waterproofing mortar D (1:2)	5.05 (±0.62)	7178 (±355)
Cement–sand (1:3)	29.14 (±1.38)	12478 (±197)
Lime–sand (1:3)	1.95 (±0.50)	2430 (±73)
Stone (bioclastic limestone)	9.87 (±0.94)	9147 (±127)

mortars (Fig. 3). On the other hand, in the absence of macropores, as in the case of B and D, a critical parameter that determines the resistance to sulphates is the pore size of the fine pores. The extremely fine pores of mortar D did not allow space for salt crystallization. Since the crystallization pressure is inversely related to the radius of the pores, mortars with a high volume of small pores will be submitted to very intense crystallization pressures capable of destroying the material.

The mortars showed improvement in performance after siloxane treatment as is evident from their salt-decay resistance. The experiments under the influence of the saline solutions have shown that the water repellent applied to the surface of mortars allows efflorescence to form on that surface. Therefore, the evaporation of the water carrying the salts has taken place on the surface and not inside the mortar beneath the surface with the salts deposited in the pores.

3.4. Selection and application of the waterproofing mortar

The laboratory evaluation of the four waterproofing mortars led to interesting conclusions, as far as both the influence of binder content and grain size of aggregates in the performance of mortars are concerned. All mortars showed a low capacity to absorb water and sufficient mechanical resistance. Given the proximity of the castle to the sea, the criterion for the selection of the best-performing mortar was the resistance to saline solutions. Mortar B, with aggregates of diameter up to 4 mm and a B/Ag ratio equal to 0.33, resists sulphates better and can be fully recommended for restoring the roof of the castle. This mortar has a pore size distribution with pores around 0.2 μm, enabling salts to crystallize without exerting stress. By comparison with the other mortars, mortar B is the least mechanically resistant; nevertheless, it demonstrated the best performance in saline solutions. Therefore, in the evaluation of repair mortars a key role can be ascribed to the pore size.

Special attention was devoted to the application of the waterproofing mortar B. The deteriorated part of the old mortar of the roof was first removed. In order to achieve a maximum adhesion between the repair and original mortar, a rough surface was prepared capable of receiving the applied waterproofing mortar. The total thickness of the waterproofing layer ranged from 10 up to 20 cm depending on the desirable inclination of the roof. The water repellent was applied after curing the waterproofing mortar for three months. Macroscopic observations after fourteen months of application indicate the absence of either microcracks or efflorescence. Even though this constitutes a very short period of time in order to reach final conclusions on the effectiveness of the repair materials, nevertheless, changes in humidity levels inside the castle have become acceptable. More explicitly, the humidity levels measured in the castle permit its use as a museum, which was the objective of this intervention.

Table 5
Mass loss (%) of the repair mortars after accelerated aging in chlorides

Samples	Mass loss (%)	
	15 cycles	30 cycles
Waterproofing mortar A (1:3)	+1.78 (±0.30)	+4.11 (±0.14)
Waterproofing mortar B (1:3)	+2.08 (±0.09)	+3.23 (±0.26)
Waterproofing mortar C (1:2)	+3.12 (±0.34)	+4.72 (±0.19)
Waterproofing mortar D (1:2)	+2.76 (±0.53)	+4.32 (±0.52)
A with water-repellent	+1.21 (±0.21)	+3.21 (±0.21)
B with water-repellent	+1.89 (±0.12)	+2.98 (±0.18)
C with water-repellent	+2.09 (±0.17)	+3.65 (±0.27)
D with water-repellent	+1.67 (±0.16)	+3.78 (±0.28)
Cement–sand (1:3)	+2.21 (±0.21)	+5.85 (±0.21)
Lime–sand (1:3)	−2.89 (±0.23)	−6.05 (±0.17)

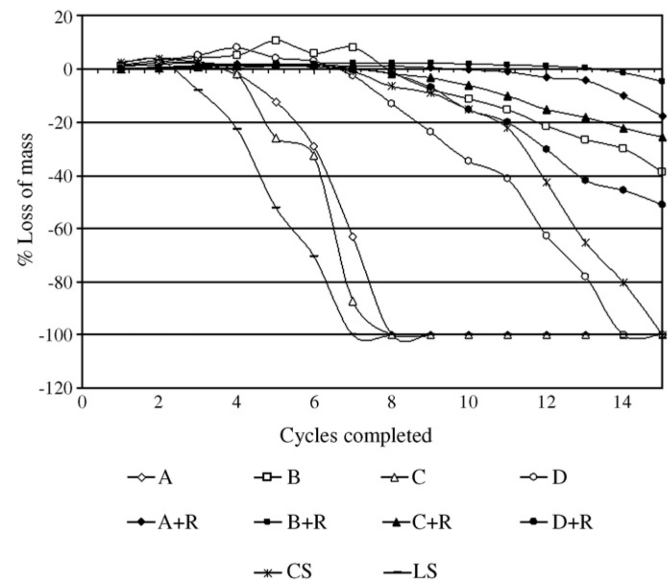

Fig. 4. Loss of mass (%) in relation to the initial mass of the waterproofing mortars, during 15 cycles of artificial ageing in saturated sulphate solution (A, B, C and D: waterproofing mortars; R: water repellent; CS: cement-sand mortar; LS: lime-sand mortar).

4. Conclusions

This study concerns the evaluation of hydraulic lime based mortars with aggregates of siliceous and calcareous nature impregnated with an oligomeric organo-siloxane as a water repellent for waterproofing the roof of a historic building. This waterproofing system was selected on the basis that in historic masonry the required water vapour permeability cannot be achieved through conventional waterproofing systems. After the siloxane treatment, the water vapour permeability of the mortars was not significantly affected. This is due to the siloxane coating the capillaries without blocking the pores, as indicated by the pore size distribution. The water absorption of the waterproofing mortars evaluated in this research can be significantly reduced through impregnation with the water repellent. Therefore, a twofold goal has been achieved: the mortars show adequate water repellency and allow for water evaporation.

This study clearly showed the influence of aggregates of different grain size and different binder content on the performance of mortars. Coarser aggregates lead to increment of mechanical strength and mean pore radius, as well as to the appearance of pores with radii between 80 and 200 μm. However, in those mortars with coarse aggregates, micropores interconnected with macropores are responsible for the low salt-decay resistance. Furthermore, an increase in the binding content develops high mechanical resistance but insufficient resistance to sulphate solutions, a result of the presence of small capillaries not allowing for salt crystallization.

Among the evaluated mortars, that which performs best consists of medium aggregates and a B/Ag ratio equal to 0.33. The presence of pores around 0.2 μm radius and the absence of macropores enable salts to crystallize without provoking damage by crystallization pressure. After fourteen months of application of the impregnated waterproofing mortar, visual inspection revealed neither microcracks nor salt efflorescence formation. Therefore, the use of hydraulic lime mortars of medium aggregates impregnated with siloxane can be considered as a compatible system for waterproofing historic masonry.

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