Commercial Ready-Mixed Mortars for the Conservation of Cultural Heritage: Characterization and Preliminary Durability Test

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Abstract Historic masonries of the cultural heritage are aged and heterogeneous systems which are subjected to long-term exposition to the external environment. In such conditions, they can easily come in to contact with a consistent range of damaging agents, including water and salts sources. The related salt-induced damage is widely considered as one of the most dangerous decay process for their preservation. Conservative operations become therefore necessary and are performed with new materials that must fulfil specific requirements regarding their compatibility with the original ones and their resistance to damaging agents, especially in term of salt-resistance. The use of ready-mixed mortars in the restoration field has become a common practice and the number of commercial products currently available in the market is increasing. The present work reports the investigation on four types of ready-mixed mortars based on NHL binders and on two commercial NHL binders, together with the preliminary laboratory tests to assess the durability of mortar specimens to salt decay. The investigation provided useful information on the relationship between compositional and microstructural features and damage.

Keywords: NHL, ready-mixed mortar, crystallization test, salt decay, historic masonry conservation

Introduction

Water and soluble salts act together in external environment as two of the most dangerous damaging agents for the conservation of historic masonries (Charola 2000, AA.V V 2007 and AA.V V 2008). The related salt-induced decay can reach such an extent so that even the structural integrity of some load-bearing elements (walls, columns, etc.) can be altered. In these conditions, conservative operations become necessary, including substitution of damaged bricks or stones and, more often, integration or replacement of deteriorated joints with repair mortars. These new materials are introduced in a complex masonry system and must fulfil specific requirements regarding their compatibility with the original ones (Binda, Saisi and Tedeschi 2006) and their resistance to damaging agents, especially in term of salt-resistance behaviour. The overall durability of the intervention can then be assured. Natural hydraulic lime (NHL) has become the most diffused type of binder to be employed for preservation purposes. A large number of commercial product based on NHL binders are distributed in the market for several uses and their application is increasing. The technical standard UNI EN 459-1 (2002) gives a definition for NHL based on raw materials, production process and final behaviour. Commercial NHL are supplied both as anhydrous binder and also as component of ready-mixed mortars, available as packed powder material composed of the binder itself, aggregates and additives already mixed together in appropriate ratios. The diffusion of ready-mixed mortars is mainly related to their ease of use which just requires simple mixing operations with the correct amount of water, as indicated in the technical data sheets. Unfortunately, notwithstanding the well-established studies devoted to the characterization of ancient mortars (Groot, Ashall and Hughes 2004) and of repair mortars based on traditional materials (Groot, 2009), diffusion of commercial ready-mixed products is not always associated to an adequate knowledge of their

compositional features and to a reliable understanding of their final behaviour. The present study provide a contribute in bridging this gap. Some characterization results were preliminary presented in a previous work (Gulotta, Toniolo and Binda et al2009) and are here summarized. Compositional, morphological and mechanical features of the raw materials and of the hardened mortars are discussed and compared to the results of mono-directional sodium sulfate crystallization test on mortar specimens, performed according to a modified version of RILEM MS-A2 protocol (1998). The adopted test is based on the results of long-term experimental experiences developed by G. Baronio and L. Binda (Binda and Baronio 1984, Binda and Baronio 1987) and internationally accepted.

Experimental

Products description Four ready-mixed commercial mortars and two commercial binders specifically designed for restoration purpose were selected. All products are classified as cement-free, with a minimum content of soluble salts and based on NHL binder. Samples materials belonging to the ready-mixed mortars were named MA, MB, MC, MD, while those coming from the commercial binders were named LA and LB. In all cases no relationship exists between the samples name and the supplier.

    Specimens preparation Commercial NHL binders were mixed with clean standard aggregate with a 1:3 B/A ratio (w/w) and then added with pure water. Anhydrous ready-mixed products were just added with the correct amount of pure water according to the indication of technical data sheets. All mixing operations were conducted under controlled conditions with the aid of a mortar mixer. Casting was performed in 4x4x16 cm demountable steel mould. Specimens were let to harden for 48 hours at 20°C - 90% RH and then removed from the mould. The curing conditions were 20°C - 90% RH for 60 days. Prismatic specimens were finally cut into 4x4x4 cm cubes by means of a diamond wheel cutter.

    Analytical techniques The initial composition of the mortar mixtures was analyzed by X-ray diffraction and IR spectroscopy on anhydrous powder samples. X-ray diffraction was carried out by means of a Philips PW1830 instrument using Cu Kα radiation (λ = 1,54058 Å). FTIR spectroscopy was carried out on a Thermo Nicolet 6700 equipped with a DTGS detector. Fine grinded samples were analysed as KBr pellets (KBr FTIR grade by Sigma-Aldrich) in the spectral range 4000-400 cm^{-1}. FTIR spectroscopy was also employed for the characterization of saline efflorescences at the end of the crystallization tests.

    The mechanical behaviour of hardened mortars was evaluated on 4x4x16 cm specimens after a curing time of 28 days and 60 days with a Controls press equipped with 250kN load cell. Five specimens were tested for each mortar and the reported results are average values from 5 different measurements.

    The mineralogical-petrographical characterization of hardened samples was made by means of polarization-and-fluorescence microscopy on thin sections, vacuum impregnated with a UV-fluorescent resin, using a Zeiss Axioplan microscope. Further microstructural characterization was performed by scanning electron microscopy on freshly fractured samples. An Environmental Scanning Electron Microscope (ESEM) Zeiss EVO 50 EP equipped with an Oxford INCA 200 - Pentafet LZ4 spectrometer was used in secondary electrons mode.

    The initial soluble salts content was evaluated by ionic chromatography using an anion column Ion Pac AS14A Dionex with 8 mM Na_2CO_3/ 1 mM $NaHCO_3$ and 1ml/min flux, equipped with a ASRS-ULTRA Dionex suppressor. The analyses was carried out on powdered sample in water solution (100 mg sample/100 ml distilled water). The salt uptake during the crystallization test was measured by electrical conductivity measurements using a AMEL 160 multi-range laboratory conductivimeter equipped with a conductivity probe, on powdered samples in water solution (100 mg sample/100 ml distilled water) according to UNI 11087 standard (2003).

Documentation of the superficial damage of mortar samples and observation of the crystallization patterns was made with a Leica M205C stereomicroscope, equipped with a Leica DFC290 digital camera.

Crystallization test The four lateral faces of each cubic specimen were sealed with a thin layer of epoxy resin in order to concentrate the evaporation only through the upper surfaces. Specimens were then dried in oven at T = 60°C until constant weight. The initial weight was recorded and the specimens were disposed in a plastic tank, placed over a grid to enhance imbibition. A saturated Na_2SO_4 solution (anhydrous Na_2SO_4 reagent grade, Fluka) was added until an imbibitions depth of 1 cm from the bottom of the specimens was reached. The tank was covered with a PET film to reduce evaporation of the solution and imbibitions went on for 2 hours at 20°C. At the end of the imbibition period specimens were placed in a dessicator for 20 hours at t = 20°C and RH 80% to promote mirabilite crystallization (Flat 2002). The daily cycles (2 hours imbibitions + 22 hours crystallization) were repeated four times a week (weekly cycle) and then samples were dried at 60°C and weighed again to assess the amount of salt introduced into the porous matrix. Once weight was recorded a new weekly cycle begun. The test was carried out until damage appeared on most of the evaporation surfaces.

Results

Characterization of raw materials Binder phases and aggregates belonging to ready-mixed products were manually sieved (0,75 μm sieve) and analyzed separately. Results of the XRD characterization are summarized in tab. 1. Larnite is the main binder phase in most of the analyzed samples. It is a dicalcium silicate (Ca_2SiO_4) typically occurring in the composition of NHL together with gehlenite and its presence confirms the hydraulic behavior of the binder. Larnite is the only hydraulic compound detected in samples MB, MC, MD and LB while in the case of binder LA it is associated to portlandite ($Ca(OH)_2$). MA is the only sample showing just the characteristic peaks of portlandite. Aggregates of the ready-mixed products are mainly composed of quartz and calcite, which are predominant in MC and present in all other cases together with plagioclase, mica and dolomite. FTIR analysis confirms the previous results and provides further information about some binder phases not detected by XRD. Portlandite with a characteristic IR sharp peak at 3643 cm^{-1} is confirmed also in the composition of MB, MC and LB. MD is the only exception and does not show any portlandite. Hydraulic compounds are identified in IR in a region roughly located at 1080 cm^{-1} either with single (MA) or multiple peaks. In all cases the peaks in this region appear particularly broad and scarcely defined.

Table 1: Summary of XRD results of anhydrous samples

	P	L	A	C	D	K	M	Q
MA	✓	-	✓	✓	-	✓	✓	✓
MB	-	✓	✓	✓	-	-	✓	✓
MC	-	✓	-	✓	✓	-	-	✓
MD	-	✓	-	✓	✓	-	-	✓
LA	✓	✓	-	✓	-	-	-	✓
LB	-	✓	-	✓	✓	-	-	✓

P = portlandite; L = larnite; A = albite; C = calcite; D = dolomite; K = kyanite; M = muscovite; Q = quartz

Characterization of hardened mortars Mortar MA is made of a hydraulic binder with C_2S grains uniformly dispersed within the matrix. Aggregates include quartz, limestone, calcite, feldspar, plagioclase and amphibole. A high amount of fine grained calcite is present as carbonatic filler. Mortar MB, on the contrary, is not NHL-based. The hardened matrix is very compact and particularly rich in slag fragments which contribute to the hydraulic behavior. Quartz is the main aggregate, together with calcite, phyllosilicates, and rare amphiboles. C_2S is the main hydraulic phase traceable in the binder matrix of mortar MC, but few C_3S grains are present as well. This mortar has a peculiar

microstructure with small and regular round shaped pores. This particular feature depends on the presence of an air-entraining additive in the commercial mix. Carbonatic aggregate, as calcite and limestone, is predominant. MD has a compact binder with only few C_2S grains dispersed in the matrix. Aggregates include quartz, calcite, limestone and rare feldspar. Mortars LA and LB are prepared with commercial binder and standard quartz-siliceous aggregate. Both binders show predominant C_2S and few partially reacted C_3S grains in the hardened mortars. Moreover, LB specimen has a carbonatic filler deriving from the original binder composition.

Samples microstructure and superficial morphology were observed in electronic microscopy. All mortars show the typical hydrated structures of calcium silicate phases (CSH). These compounds have several hydration patterns, varying from a diffused network covering most of the aggregates (MA), to denser structure with elongated crystals (MB) or grouped in globular formation crossed by acicular needles (MD). In all cases the typical hexagonal crystals of portlandite are traceable, with different sizes.

The mechanical properties of mortars after a curing time of 28 days and 60 days are reported in Fig. 1 (left). MB has the highest compressive strength after 60 day curing among the tested specimens, almost comparable to the one of MA. MD, on the other hand, demonstrates poor mechanical properties and a final compressive strength lower than that required for the NHL class it belongs to. A predictable general increase of mechanical properties is observed as the curing time proceeds, expect for MA.
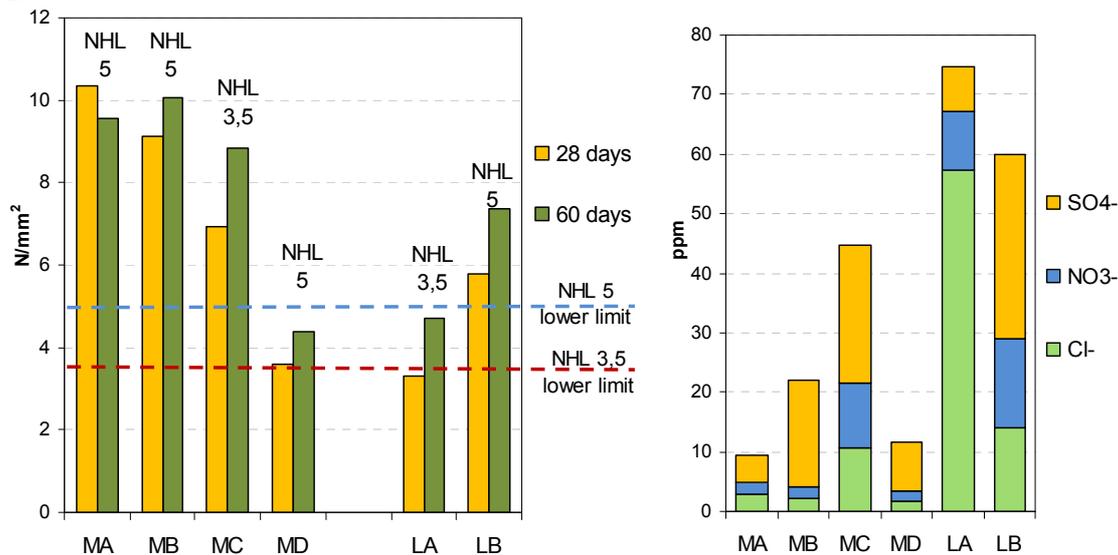

Figure 1: average compressive strength values with respect to the NHL class limits (left) and total amount of anions in hardened samples (right)

The assessment of the initial salt content (Fig.1, right) reports minimum values for MA and MB, which tend to increase respectively for MB, MC and LB to finally reach the maximum for LA. Sulfates are the most diffused ionic species in five examined mortars out of six, but sample LA shows a predominance of chloride.

Crystallization test Two weekly cycles (4 daily cycles/week) were sufficient to induce severe damage in most of the mortars. The evaluation of the mass variation (percentage variation between initial and final dry mass of specimens) confirms that most of the sodium sulfate accumulation occurs during the first imbibition cycles and that in several cases (MB, LA, LB) any further salt penetration is prevented after the first weekly cycle. On the contrary, accumulation in MA samples keeps going on since the very last cycle and determines the highest final mass increase for this mortar, while MB has the smallest one. Crystallization initially occurs on the evaporation surfaces either with formation of elongated and powdered crystals (MA) or with a non homogeneous white veil, which indicates a localized salt accumulation just beneath the mortars surface (MD). In the first case, as the imbibition/crystallization cycles proceed, the damage occurs with material disaggregation and

powdering, while in the latter one delamination and cracking are observed. FTIR analysis of samples from efflorescences and from the superficial white veil confirm their sodium sulfate composition, no other ionic species coming from the mortars are traced. At the end of the test, the damage level was evaluated by visual observation of the decay extent and depth.
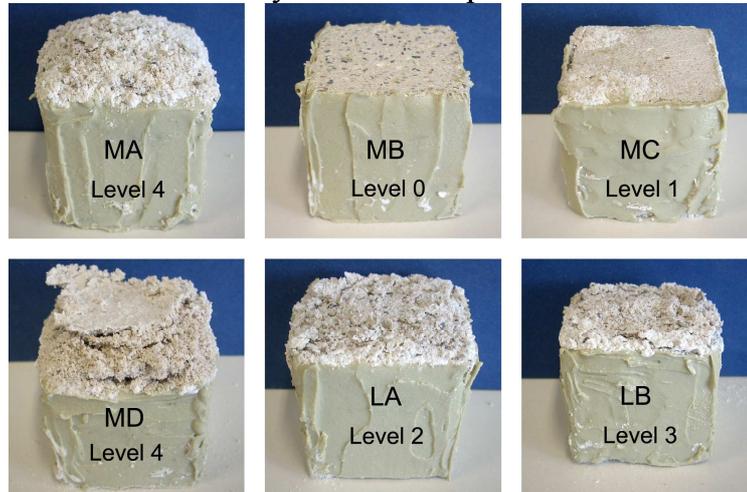

Figure 2: photographic documentation of the specimens at the end of the test

According to these criteria, five damage levels were defined and reported in Fig. 2: *level 0* - no damage; *level 1* - rare superficial efflorescences, no damage; *level 2* - limited damage, superficial efflorescences on a partially cracked evaporation surface and small disaggregation; *level 3*- medium damage, diffused efflorescences on a cracked evaporation surface, medium scaling and disaggregation, loss of material; *level 4* - serious damage, diffused and elongated efflorescences on a very cracked evaporation surface, deep disaggregation with consistent scaling, powdering and loss of material. In Fig. 3 are reported the binary plots for the mass variation (left) and for the average compressive strength (right) as functions of the damage level.
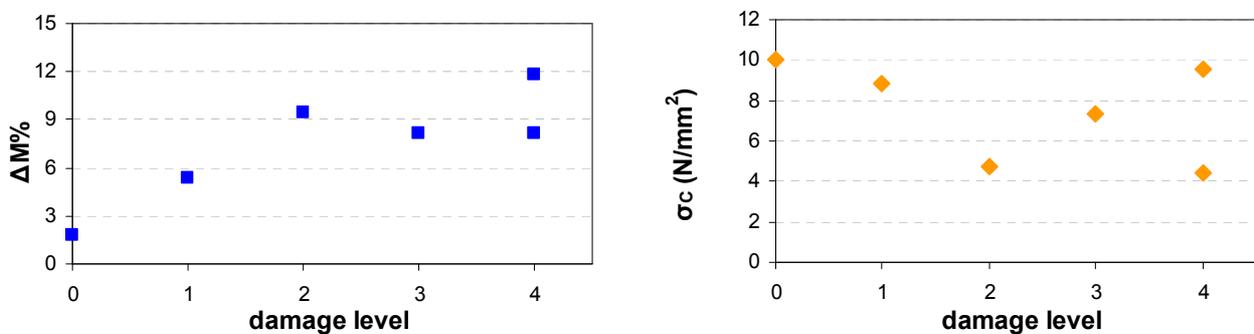

Figure 3: mass variation (left) and compressive strength (right) as function of the damage level

Conclusions

As expected, the amount of soluble salts that penetrates into the porous matrix of the mortars influences the damage, but even if in some cases the higher the mass variation is, the greater mortars decay is observed a linear correlation cannot be found. Therefore this parameter alone is not able to provide reliable indications on the salt resistance. The tested mortars show very different compositional characteristics and microstructural features once hardened. Compressive strength is undoubtedly another parameter of primary importance but, also in this case, it is not directly correlated to the final performance to salt decay. As a matter of fact, MA, which has the highest compressive strength value, is the most damaged by sodium sulfate crystallization. On the other hand, MB is totally undamaged at the end of the test despite its low mechanical strength. The outstanding resistance of MB is most probably due to its very compact microstructure, deriving from the slag lime-binder that does not allow massive imbibition as in the case of MA. The rather good

performance of MC can be influenced both by its good mechanical strength and by the presence of an air-entrain agent in its composition. The enhanced porosity in this case can provide further empty spaces where crystallization occurs without damaging effects to the mortar matrix. The two commercial binders, LA and LB, show a rather comparable behavior to salt decay, with a limited to medium damage level. The presence of a carbonatic filler in LB composition seems not to affect significantly its salt resistance, compared to the one of LA. In conclusion, the durability of the different mortars to salt decay is a function of a number of parameters acting simultaneously, especially when mortars with so different characteristics are considered. Crystallization test are valuable procedures to preliminary assess the final behavior of hardened materials, but a large number of specimens are required in order to obtain significant results. Moreover, an affordable way to quantitatively measure the damage evolution and final extent has to be applied.

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