Investigation of commercial ready-mixed mortars for architectural heritage

D. Gulotta¹, L. Toniolo¹, L. Binda², C. Tedeschi², R. P. J. van Hees³,⁴ & T. G. Nijland³
¹Dipartimento di Chimica, Materiali e Ingegneria Chimica “Giulio Natta”, Politecnico di Milano, Italy
²Dipartimento di Ingegneria Strutturale, Politecnico di Milano, Italy
³TNO Built Environment and Geosciences, The Netherlands
⁴Faculty of Architecture, Delft University of Technology, The Netherlands

Abstract

In conservation practice, operations aimed at restoring the structural functionality of historical buildings are of primary relevance. Partial rebuilding, substitution of damaged elements and integration of deteriorated joints are interventions which require the introduction of new materials in heterogeneous and aged masonry systems. An appropriate durability of these interventions can only be assured if a deep knowledge of the original materials, as well as of their state of conservation, is combined with a reliable understanding of the behaviour of the new ones. The present paper reports the preliminary results of the investigation of four commercial ready-mixed mortars based on NHL binders. The initial composition of the products was assessed by means of XRD and FTIR. The hardened mortars characteristics were evaluated and their mechanical behaviour was tested as well. Though supposedly comparable products, the mortars showed remarkable differences for what concerning compositional features, microstructures, presence of additives and mechanical strength. All these aspects are crucial in order to evaluate their compatibility with respect to the historic materials and should be properly considered for the selection of the most appropriate product for each single case. Moreover, as they are often neglected or, at least, only partially stated in the technical data sheet provided by the manufacturers, they need to be determined prior to the application.

Keywords: ready-mixed mortars, mortar characterization, NHL, XRD, FTIR.
1 Introduction

A number of commercial ready-mixed mortars designed for restoration purposes are currently available on the market and their use in the conservation field is increasing. The diffusion of such products is mainly related to their ease of use, which also determines a generally higher cost respect to a manually prepared traditional mortar mix. Ready-mixed mortars are available as packed powder material composed of binder, aggregates of different nature and granulometry and additives already mixed together in appropriate ratios. The technical data sheets state the precise amount of water to be added and often supply indications about the mixing procedure. In such way, mortar’s preparation is clearly a quicker operation compared to the traditional method and it can be easily performed also by unskilled labour.

Natural hydraulic lime is one of the most common binders used in commercial mixes for restoration. Technical standard UNI EN 459-1 [1] gives a definition for NHL (natural hydraulic lime) based on raw materials, production process, calcium hydroxide content and final mechanical behaviour. Natural hydraulic lime results from the burning of argillaceous or siliceous limestone, followed by reduction to powder by slaking, with or without grinding. NHL are able to set and harden even under water through hydration of the hydraulic compounds. Atmospheric carbon dioxide contributes to the hardening process, allowing the carbonation of calcium hydroxide. The burning temperature is kept below the clinkering point so that di-calcium silicate (C\textsubscript{2}S) is the dominant hydraulic phase together with some gehlenite (C\textsubscript{2}AS) and only low amount of highly reactive tri-calcium silicate (C\textsubscript{3}S) typical of Portland cement can form [2].

Despite the increasing diffusion of NHL based ready-mixed mortars, a thorough characterisation of commercial products is rarely available. Several studies have been conducted in the past in order to develop methodologies for the characterization of ancient mortars and to evaluate the overall compatibility of the new materials introduced during the restoration operations [3–5]. Recent studies have also been focused on the characterisation of some XIX and XX century mortars [6, 7]. Methodologies have been defined in order to identify the nature of binders and to distinguish between natural hydraulic mortars, natural cements and Portland cements. FTIR, XRD analysis and SEM observation have been employed to identify gehlenite and di-calcium silicates as characteristic hydraulic phases of natural hydraulic lime, whereas a large amount of C\textsubscript{3}S, is generally associated to the higher burning temperature occurring during cement’s production.

The restoration materials used in the conservation field must fulfil special requirements in order to be compatible with the original ones [8]. As a matter of fact, the current lack of information about commercial ready-mixed mortars’ composition and durability at work may complicate the selection of the most suitable restoration materials based upon the compatibility evaluation.

The present work proposes a methodology for the characterization of ready-mixed mortars for the conservation of the architectural heritage and reports on the results of its application on four widely diffused commercial products.
Compositional, morphological and mechanical features are discussed and compared.

2 Experimental

2.1 Products and supplier

Four commercial ready-mixed mortars designed for restoration purpose, all classified as cement-free, with a minimum content of soluble salts and based on NHL – natural hydraulic lime binder were selected. The sample materials were named MA, MB, MC and MD without any reference to the manufacturer.

2.2 Specimens preparation

Mortars were prepared according to the indication reported in the technical data sheets. Casting was performed following two different procedures: a) traditional casting in 4x4x16 cm demountable steel mould, b) porous substrate casting. The porous substrate for the latter type of specimen was provided by fire-clayed brick, type “San Marco”. Bricks underwent 12-hours water imbibition followed by the removal of the superficial liquid water layer before mortars’ application. Specimens were let to harden for 48 hours at 20°C – 90% RH. Specimens prepared following traditional casting were then removed from the mould, while specimens prepared on porous substrate were stored together with their brick substrates. The curing conditions were 20°C – 90% RH for 60 days for specimens on porous substrate and for 28 days and 60 days for traditional prismatic specimens.

2.3 Analytical techniques

The initial composition of the mortar mixture was analysed 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 ($\lambda = 1.54058 \text{ Å}$). FTIR spectroscopy was carried out on a Thermo Nicolet 6700 instrument. Fine grinded samples were analysed after dispersion in KBr pellets (KBr FTIR grade by Sigma-Aldrich).

The mechanical behaviour of hardened mortars was studied on traditional 4x4x16 cm specimens while the observation of the microstructural features was made on specimens prepared on porous substrate.

Compressive strength was evaluated after a curing time of 28 days and 60 days, according to standard protocol [9]. Five specimens of each mortar were tested and the reported results are average values of 5 different measurements.

Polarization-and-fluorescence microscopy was performed on thin sections. Mortars’ fragments were vacuum impregnated with a UV-fluorescent resin and observed with 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.

3 Results

3.1 XRD analysis

The diffractograms reported in fig. 1 highlight the abundance variability of the crystalline phases of the four analysed mixes.

![X-ray diffractograms of anhydrous powder samples of the four studied mortars](image)

Figure 1: X-ray diffractograms of anhydrous powder samples of the four studied mortars (A = albite; C = calcite; D = dolomite; K = kyanite; L = larnite; M = muscovite; P = portlandite; Q = quartz).

The XRD results show significant differences in the binder and aggregate composition of the four examined mortars. As far as the binder is concerned, mortar MA is the only one showing the characteristic peaks of portlandite, Ca(OH)$_2$. A certain amount of portlandite is expected to be found in NHL, as unreacted calcium oxide can derive from calcination of the binder and it is
transformed into hydroxide after slaking. In all other cases, results only show the presence of larnite (Ca$_2$SiO$_4$, i.e. an analogue of C$_2$S) in the binder composition, thus confirming the hydraulic behaviour of the mortar.

Calcite and quartz are present in all samples with different ratios and they belong to the aggregate fractions. The calcite content is particularly high in the case of mortar MB. MA and MB also contain micas and plagioclase. MC aggregate is partially composed of dolomite, which can be observed as the most abundant crystalline phase in MD. Therefore the aggregate phases of MA and MB can be defined as rather heterogeneous, made of quartz-siliceous and carbonatic compound, whereas those of MC and MD are mostly carbonatic.

3.2 FTIR analysis

The results of FTIR characterization of anhydrous commercial materials are reported in fig. 2.

![FTIR spectra of anhydrous mortars' samples in the spectral range 4000–400 cm$^{-1}$](image)

Figure 2: FTIR spectra of anhydrous mortars’ samples in the spectral range 4000–400 cm$^{-1}$.
MC and MD spectra are quite similar. In both cases the absorption peaks indicate that a large amount of carbonates are present as calcite (peaks at 1430, 875, 713 cm\(^{-1}\)) in MC sample, and as dolomite (1440, 880, 729 cm\(^{-1}\)) in MD sample. MC also contains a significant amount of free portlandite, with a sharp peak at 3643 cm\(^{-1}\). Si-O and Si-O-Si bonds vibrational modes are detectable in the range of frequencies between 1100–750 [7] and are associated to both the quartz-siliceous aggregates and to the hydraulic compounds of the binders: quartz around 1080 cm\(^{-1}\) with a characteristic doublet at 797 and 779 cm\(^{-1}\); calcium silicates at 1000–1010 cm\(^{-1}\) and 930 cm\(^{-1}\); pozzolan or other poorly crystalline siliceous phases giving a broad peak around 1035–1030 cm\(^{-1}\). Peaks related to the presence of quartz can be detected in both samples, while those related to the presence of calcium silicates are more evident in sample MC.

MB sample contains calcite and portlandite, similar to the samples discussed above. However, this mortar show a high absorption in the region of Si-O and Si-O-Si region, where quartz (1093 cm\(^{-1}\)), calcium silicates, amorphous compounds and pozzolan (1030 cm\(^{-1}\)) peaks are detected.

Finally, MA sample shows a quite different vibrational spectrum in the mid-IR region. In particular, the C-O/Si-O ratio is reversed in this case respect to the previous ones, with quartz/siliceous peaks prevailing over carbonates. This is due to the fact that the aggregate fraction is rich in quartz (1082, 797, 779 cm\(^{-1}\)) and siliceous phases as already pointed out by XRD, whilst calcite (1425, 876 cm\(^{-1}\)) is present in lower amount. Moreover, the broad overlapped absorption peak around 1040 cm\(^{-1}\) is also related to the presence of hydraulic compounds, namely calcium silicates. The sharp and very intense peak at 3643 cm\(^{-1}\) indicates the abundant presence of portlandite.

### 3.3 Petrography

Thin sections observations were carried out on specimens prepared on brick surfaces in order to properly evaluate the influence of a porous substrate on the microstructure of the hardened mortars. The results are presented according to the different commercial materials.

Mortar MA is composed of a hydraulic lime binder with irregular porosity. No cracks or fractures are present (fig. 3): the mortar’s matrix shows a quite compact microstructure with a fine grained binder.

Aggregates are poorly sorted and vary in size up to 2 mm. Quartz is confirmed to be the most common aggregate, with rounded shape. Limestone, calcite, feldspar, plagioclase and few amphibolites are also present. Limestone is generally present as coarse, rounded shape aggregate while angular calcite grains are smaller in size. The very high amount of fine grained calcite crystals indicates that calcite has been used as filler. A few small grains of pozzolan are also present.

The hydraulic phases of the binder are uniformly dispersed within the binder matrix. Few grains of not reacted C\(_2\)S are detected [10]. A carbonation front proceeds from the external borders into the bulk, with some isolated carbonated patches at deeper levels, along pores.
Mortar MA: carbonation front and irregular porosity (left, CPL); dark coloured not reacted C₂S particles dispersed in the carbonated binder matrix (right, PPL).

Mortar MB has a completely different binder structure respect to the others (fig. 4). Porosity is irregular and generally lower than observed in mortar MA. Pores and voids of different shape are connected by a network of micro-cracks. Cracks occur both in the binder matrix and along the binder-aggregate interface.

Aggregates are heterogeneous; quartz and calcite are the main constituents, together with phyllosilicates and few amphibolites. Calcite is present as rounded limestone particles and as crushed angular fragments. The mortar has a very dense microstructure. No traces of hydraulic compounds, such as C₂S grains, are detected. Few grains of not reacted pozzolan are observed. The coarse grained binder is very rich in slag fragments, which appear as transparent angular vitreous grains and are homogeneously dispersed in the mortar. Carbonation is limited to a thin region at the margin of the sample and along pores walls. Some fractures cross the binder’s matrix, as observed in mortar MA.

Mortar MC is composed of a lime binder with an apparently high porosity due to the presence of abundant air voids (fig. 5). This can most probably derive from the introduction of an air-entraining agent in the mortar mix. Some
de-bonding between mortar and aggregate occurred, but cracks are generally absent in the mortar’s matrix.

Aggregates are poorly sorted and vary in size up to 1.5 mm. Carbonatic aggregates are dominant. No quartz aggregate can be observed.

The binder is coarse grained, with not reacted C$_2$S particles heterogeneously distributed in the matrix. Very few C$_3$S grains surrounded by a clear hydration rim occur. Some pozzolan particles are present.

Figure 5: Mortar MC: calcite and limestone aggregate and abundant air voids (left, CPL); arrows indicate partially hydrated C3S particles in the binder matrix (right, PPL).

Mortar MD has a hydraulic lime based binder with irregular porosity (fig. 6). Small air voids occur together with large irregular ones. The mortar shows no micro-cracks.

Aggregates are poorly sorted and vary in size up to 2 mm. Limestone, crushed angular calcite and quartz, are the main aggregates; minor feldspar is also present. Limestone occurs as coarse rounded grains while the smaller aggregate fraction is composed of quartz and crushed calcite. No pozzolan grains are present.

Figure 6: Mortar MD: limestone and quartz aggregates and non-homogeneous distribution of C2S particles (left, PPL); carbonation front along the margin (right, CPL).
The distribution of hydraulic phases within the binder matrix is not homogeneous and several darker zones due to high C_{2}S concentration are present. A thin carbonation front proceeds from the external margins of the sample.

### 3.4 ESEM observation

ESEM observation of the hardened mortar samples allows the identification of the newly formed structure related to the hydration process of the binder. In all examined samples hydrated calcium silicate phases (CSH) are clearly visible, and they have a variable morphology (fig. 7).

Mortar MA shows a diffuse fibrous CSH network covering most of the aggregate grains, with occasional isolated clusters of needle shaped CSH [11]. Within the CSH network, some quartz grains can be observed together with few non reacted pozzolan particles, appearing as well defined globular grains with a smooth surface.

Mortar MB shows a denser CSH structure as a result of the hydration of the hydraulic compounds together with the slag fragments (fig. 7a). These latter can hardly be identified as they are almost completely covered by the hydrated phases. CSH develops globular cluster connected by numerous and particularly elongated crystals. No pozzolan can be observed.

Sample MC (fig. 7b) and sample MD have a similar microstructure. Globular CSH are crossed by a number of acicular, needle shaped crystals. Some isolated clusters of hydrated particles occur. A significant amount of portlandite crystals, occurring as typical hexagonal plates, are embedded within the binder’s matrix.

### 3.5 Mechanical test

As might be expected for NHL mortars, compressive strength results of the mortars (fig. 8) show a considerable increase as the curing time proceeds [12]. The average compressive strength values after 28 days curing vary considerably. MC and MD are based respectively on NHL 3.5 and NHL 5 binder [1], thus their strength value is in accordance with the class of resistance they belong to only in the case of MC. On the contrary, MD has a 28 days resistance significantly lower than the 5 MPa limit expected for its class. Similar consideration cannot be extended to MA and MB because of the lack of information about the classes of binder used in mixes. MD shows indeed the lowest compressive strength among all the tested mortars after 28 days curing, while both MA and MB have values higher than 9 MPa.

As the hydration of the hydraulic compounds takes place, the compressive strength resistance increases in all cases, except for MA which shows a slight decrease respect to the 28 days value. It can be observed that the significant initial differences between the mortars’ resistance tend to be reduced during curing. MA and MB have a rather similar mechanical behaviour between 9.5 and 10 MPa. The final compressive strength of MC is slightly lower, around 9 MPa, and MD is confirmed to be the less resistant mortar.
Figure 7: ESEM images of the microstructure of a) mortar MB, showing a dense CSH structure with elongated crystals; and b) mortar MC, showing hexagonal portlandite crystals (1) and CSH particles (2).
4 Conclusions

The investigation of four commercial ready-mixed mortars allows the discrimination of distinctive compositional and microstructural features of the tested products. MA has a portlandite-rich binder with some pozzolan and limestone filler. During hardening a diffused CSH network homogeneously covers the aggregates and may explain the high compressive strength after 60 days curing.

MB is, unexpectedly, a slag-lime mortar. The hydraulic behavior of the mortar is given by the hydration of the slag and by the presence of pozzolan. The hardened mortar has a compact structure and the 60 days compressive strength is comparable with that of MA.

At first glance, analyses show that MC and MD have a rather similar composition. They both have a high amount of calcareous aggregate (mainly calcite in MC and dolomite in MD). However, the microstructure of MC differs in one aspect, i.e. the air void content, which is probably due to the presence of an air-entraining agent in the mix. MC is also the only sample clearly showing some partially hydrated C$_3$S grains. C$_3$S is generally uncommon in NHL mortars and may derive from a higher burning temperature respect to the other products. As a consequence, MC and MD show different compressive strengths. The high strength of MC may be related to the presence of C$_3$S in the binder and it seems not be affected by the apparently high porosity of the mortar, while the lower one of MD can be influenced by the predominant dolomitic aggregate.
The analytical methodology adopted for the characterization of the ready-mixed mortar samples proved to be useful to discriminate the products. Though they are supposed to be comparable NHL mortars, they show different compositional features, microstructures, presence of additives and mechanical behaviour. These are essential to evaluate compatibility with historic materials and should be stated on the technical data sheets, or they have to be thoroughly determined prior to the application.

Additional measurements, such as pores structure, pores size distribution and hydraulic Si amount could be useful for a better understanding of these products and to evaluate their durability at work.

References