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# Characterization of historical mortars from the bell tower of St. Nicholas church (Pisa, Italy)

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## HIGHLIGHTS

- Sixteen mortars from the bell tower of St. Nicholas church at Pisa were studied.
- Chemical compositions of binder and aggregate fractions were determined.
- High-quality hydraulic mortars were used for building the bell tower's masonry.
- Local raw materials employed in the mortar preparation were identified.

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## ABSTRACT

The aim of this research is to characterize the binder and aggregate fractions of sixteen mortar samples from the bell tower of the St. Nicholas church at Pisa, using X-ray fluorescence (XRF), X-ray powder diffraction (XRPD), simultaneous thermogravimetric/differential scanning calorimetry analysis (TG/DSC), optical microscopy (OM) and electron microscopy equipped with a microanalysis system (SEM/EDS).

The analytical procedure used for studying the mortars is based on TG/DSC analyses performed on the binder fractions, obtained by disaggregation of the mortar samples, and on micro-analytical data directly collected on the mortar binders combined with chemical, mineralogical (qualitative composition) and petrographic (modal composition) data measured on the bulk mortar samples.

The collected data indicate that the examined samples are hydraulic lime mortars with natural river sands (average binder/aggregate ratio 1:1), except for two of them which are artificial pozzolanic mortars with *cocciopesto*. The most probable raw materials used to produce the mortars are the binding materials obtained by firing carbonate rocks locally available, cherty limestone and subordinately *Mt. Pisano* marble, and the *Arno* River sands or, more likely, natural admixtures of *Arno* and *Serchio* River sandy sediments.

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## 1. Introduction

Mortar characterization plays an important role in the study of the historical buildings and associated structures. Recent papers deal with mortars as an excellent source for identifying the provenance of the building materials used in historical monuments and for acquiring detailed information on their construction phases [1–5].

Ancient mortars are complex systems, often characterized by an inhomogeneous structure. Their study for restoration purposes requires a multidisciplinary approach; various types of analysis can be made to provide useful data for a full characterization of the binder and aggregate fractions and for the identification of their raw materials including special additives. Optical microscope observations and calcimetry, XRF, XRPD, TG/DSC, SEM/EDS analyses are the methodologies usually performed in the research activities on mortars from historical buildings [6–22], although there are works in which statistical analysis [23], Fourier transform infrared spectroscopy [24,25], mercury porosimeter [26,27], gas adsorption analysis [26], digital image processing [28], atomic absorption spectroscopy [29], inductively coupled plasma-mass spectrometry [29], physical and mechanical testing [30–33] are also used.

Within the framework of multidisciplinary studies in the field of art history and restoration works of the St. Nicholas church at

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Pisa, a comprehensive characterization of the building materials used for the construction of the church has been carried out [34].

This paper deals with the mortars of the bell tower of the St. Nicholas church at Pisa (Fig. 1), the second most famous in the city after the *Leaning Tower* well known worldwide for its unintended tilt to one side. The bell tower is a medieval four-storey structure (total height: 34 m), which most likely dates to 1170 [35]. The lower part has the form of a hollow cylinder (external diameter: 5 m; internal diameter: 3 m; height: 12 m) followed by an octagonal hollow prism (height: 12 m), embellished at the top of each side with blind arches, including circles and lozenges. The belfry starts with an octagonal structure (height: 3.5 m), surrounded by a gallery with sixteen small arches supported by columns followed by another hexagonal structure (height: 4 m) with a single mullioned window on each side. The bell tower ends up with a pyramid-shape cusp.

In particular, this paper refers to the results obtained with the aim of assessing the chemical, mineralogical, petrographic and physical characteristics of the mortars useful for identifying the raw materials employed in their preparation and for determining the source from which these materials were drawn.

## 2. Materials and methods

### 2.1. Sampling

Sixteen mortar samples from the bell tower of the St. Nicholas church at Pisa were studied. Fourteen bedding mortar samples come from internal putlog holes at height ranging from 4 up to 19 m from the top of the foundation and a depth from 10 cm to 70 cm, and two samples of mortar for plaster were removed from the internal hollow cylinder at an approximately height of 50 and 100 cm from the top of the foundation. The function, the age and the sampling points of the mortars are reported in Table 1.

### 2.2. Methods

Macroscopic features of the mortar samples were observed with the naked eye and with a stereomicroscope up to 200 magnifications.

For the binder characterization, some fragments of each sample were disaggregated using a porcelain pestle, and the fraction passing through a sieve with 63 μm openings (ISO R 565 Series) was considered as a binder-enriched specimen.

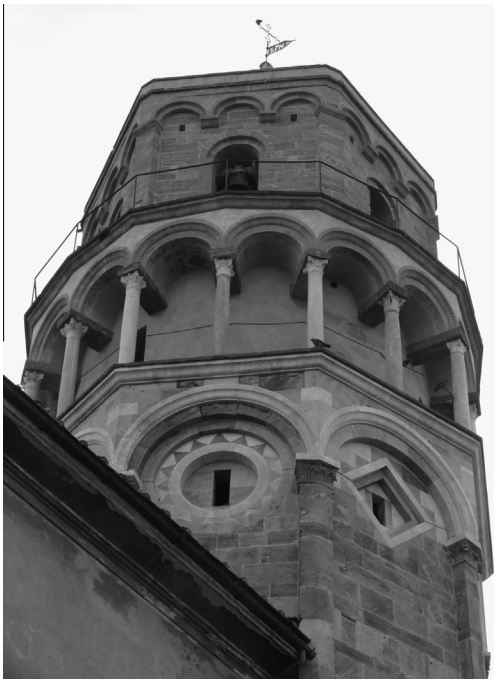

**Fig. 1.** The bell tower of the St. Nicholas church at Pisa.

After treatment with dilute HCl, the retained was used for estimating the grain size distribution of the aggregate fraction, which in the analyzed samples is essentially made up of non-carbonate grains.

Chemical analyses of bulk mortar samples were performed by X-ray fluorescence (XRF), according to the procedure suggested by Franzini et al. [36]. Within the range of the measured concentrations, the analytical accuracy determined on 54 international standards ranges from 20% (MgO) to 1% (CaO), with a mean value of 5% for the other major elements; with regard to trace elements the mean value of the accuracy is 10 ppm, ranging from 20 ppm for Ce to 1 ppm for Rb.

The amount of the total volatile components (LOI) was determined by a simultaneous thermal analyzer, which combines a sensitive balance for use in thermo-gravimetric analysis, with a heat-flux differential scanning calorimetry and a quadrupole mass spectrometry for simultaneous TGA, DSC and EGA experiments. Open alumina crucibles and heating rate of 10 °C/min, under 30 ml/min nitrogen gas flow, were used. $CO_2$ was also determined by calcimetry [37]. Thermogravimetric analyses (TGA) were obtained on ~25 mg of sample, dried (silica gel as drying agent) at room temperature for at least a week. Powders of both bulk mortar samples, lumps hand-selected under the stereomicroscope and fraction passing through a sieve with 63 μm openings were analyzed. TG analysis was also used for classifying the studied samples as non-hydraulic mortars or hydraulic ones as suggested by most authors [6–8,11,30]. The difference between LOI and $CO_2$ contents was entirely ascribed to $H_2O^+$.

$SO_3$ contents were derived by weighing the $BaSO_4$ precipitated from the filtered solution obtained during preparation of the HCl-insoluble residue [38].

Mineralogical and petrographic investigations of the mortar samples were performed by optical microscopy (OM) on polished thin sections using a polarising microscope. The grain sizes of the aggregate particles are reported according to the scheme proposed by the British Geological Survey based on the Wentworth scale [39].

Aggregate particle-size distribution was determined by sieving the sandy HCl-insoluble residue through sieves with 2, 1, 0.5, 0.250, 0.125 and 0.063 mm square openings; the collected results were expressed as fineness modulus ($M_f$) [40].

The quantitative mineralogical composition (volume percentages) of the mortar samples has been determined by modal analysis (no less than 200 points) performed on polished thin sections.

Qualitative mineralogical compositions of the mortars, enriched binders, aggregate fractions and lumps were performed by X-ray powder-diffraction (XRPD) by means of a diffractometer using the following experimental conditions: Bragg–Brentano geometry, Ni-filtered Cu Kα radiation obtained at 40 kV and 20 mA, 5–60 °2$\theta$ investigated range, 0.02° step, 2 s counting time per step.

Scanning electron microscope observations and micro-chemical compositions of intergranular binder and lumps were performed using a SEM–EDS with 20 kV acceleration voltage, 0.1 nA beam current, and 100 s live time.

Real density ($\rho_r$) was measured by means of an automatic He-pycnometer on ~10 g of very-fine-grained powders, dried at 105 ± 5 °C for 24 h, under the following experimental conditions: ultrahigh purity compressed Helium with outlet pressure of 140 kPa; target pressure: 100 kPa; equilibrium time: automatic; purge mode: 3 min of continuous flow; maximum runs: 6; number of averaged runs: the last three.

Apparent density ($\rho_a$) and open porosity (to water), which has been measured as water absorption at atmospheric pressure in respect to weight ($Ab_w$) or volume ($Ab_v$) of the sample, were performed on parallelepiped-shaped specimens (~30 $cm^3$ by volume), according to UNI 11060:2003 [41]. In particular, apparent density was calculated as the ratio between the mass of the dry sample and its volume, measured by means of a hydrostatic balance on water-saturated samples [42]. Total porosity ($P$) and saturation index ($SI$) were calculated as follows: $P\ (\%) = 100 \cdot (1 - \rho_a/\rho_r)$ and $SI\ (\%) = 100 \cdot Ab_v/P$.

## 3. Results and discussion

### 3.1. Mortars

#### 3.1.1. Main macroscopic features of the mortars

Based on hand specimen examination, i.e. color of the mortars, particle-size and distribution of aggregate grains, size and distribution of lumps and fractures, condition of the external surface and other interfaces [43], the mortars of the bell tower of St. Nicholas church (Table 1) were classified into 4 groups as follows:

**Group 1** (samples SNM 1–2): these are artificial pozzolanic mortars for plaster containing some amount of *cocciopesto* and a low content of river sandy aggregate (Fig. 2a). The binder is characterized by inhomogeneous structure due to the presence of some whitish portions devoid of aggregate (lumps), while the intergranular binder assumes the typical reddish color of the added ceramic material. The special additive consists of angular fragments of ceramic material, coarsely ground, and the aggregate is a poor fine sand