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The production of binding materials in southern Florence area: stones and their properties (Greve in Chianti, Italy)

Andrea Aquino[1], Elena Pecchioni[2], Fabio Fratini[3], Emma Cantisani[3], Sonia La Felice[4], Tsegaye Abebe[5], Claudia Principe[4], Marco Lezzerini[1]

[1]Dipartimento di Scienze della Terra, Università di Pisa, Via Santa Maria 53 – 56126 Pisa, Italy, andrea.aquino@phd.unipi.it, marco.lezzerini@unipi.it

[2] Dipartimento di Scienze della Terra, Università di Firenze, Via G. La Pira, 4, Firenze, Italy, elena.pecchioni@unifi.it

[3] Istituto per la Conservazione e la Valorizzazione dei Beni Culturali, Consiglio Nazionale delle Ricerche, Via Madonna del Piano, 10 - 50019 Sesto Fiorentino (FI), Italy fabio.fratini@cnr.it, emma.cantisani@cnr.it

[4] Istituto di Geoscenze e Georisorse, Consiglio Nazionale delle Ricerche, Via Giuseppe Moruzzi 1 – 56124 Pisa, Italy, sonia.lafelice@igg.cnr.it, c.principe@igg.cnr.it

[5] Adhana Geological Consultancy Service, Via M.L. King 9 – 56021 Cascina (PI), Italy, tsegaye.abebe28@gmail.com

Abstract **– The carbonate rocks outcropping in the area south of Florence can be useful for the production of binding materials. The aim of this paper is to characterize the rocks to be used for the production of cement and limes in the area south of Florence by means of chemical, mineralogical and petrographic studies and by defining their main physical properties. In particular, this study analyses rock samples from different outcroppings around the south of the province of Florence in the Greve in Chianti - Passo dei Pecorai area. Based on the collected data the rock samples coming from the Greve in Chianti area can be used for producing mainly eminently hydraulic lime.**

I. INTRODUCTION

Since the Roman times, the exploitation of natural resources has been a catalyst for the expansion and developments of cities and population in general. As long as the seeking of far more precious natural materials, like gold and silver, even the exploitation of limestones and other lithotypes of stones for building purposes, as the production of quicklime, hydraulic lime and cements, has covered and still has a great importance in Tuscany [1-3].
The study of mortar and concrete binders has an important role in the knowledge of ancient and modern building, providing essential information about the used technologies [4-6], construction phases [7-9], characteristics and properties of building materials [10-11], provenance of raw materials [12-13], binder/aggregate ratios [14] and characteristics for restoration project [15-16]. The use of mortars in architecture dates back to ancient times and in Tuscany there are several examples of buildings in which quick lime and hydraulic binders were used to produce soft and strength mortars, respectively [17-19].
The scientific bibliography on the characterization of binders, mortars and concretes is very extensive and usually it is performed by combining chemical, mineralogical and petrographic data collected by macroscopic observations, minero-petrographic analysis, micro-chemical techniques and thermogravimetric analysis [20-22].
The limestone exploitation to produce binders for mortars and concretes in the territories of Florence and Prato has been active in the area since the Roman times [23]. In the southern area of Florence (Greve in Chianti, Passo dei Pecorai), the exploitation of limestones for the production of binders has been active in the past centuries and is still active nowadays. The most used limestone in this area is the so called “Pietra Alberese”, a marly limestone used even by the Romans [2].
For the purpose of this preliminary work, we collected several samples of limestone belonging to the Mt. Morello Formation. The Mt. Morello formation widely outcrops in the area between Mt. Calvana and Mt. Morello north of Florence and in Passo dei Pecorai, south

of Florence [24]. It is an alternation of marls and limestones. The bottom layers are mostly fine grained, and its colour varies from grey to whiteish. It then goes to marly calcilutite and light grey marls. It is a deep water turbiditic limestone-marl deposit aged between low and middle Eocene [24-26].

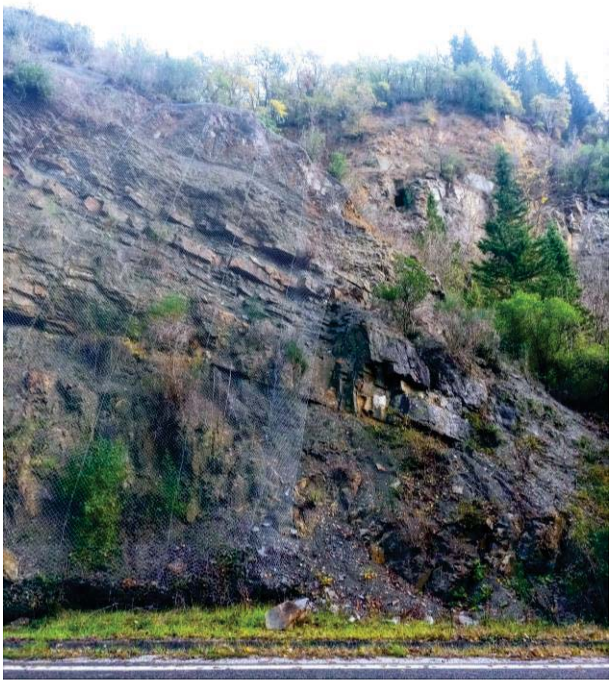

Figure 1: Outcropping of Mt. Morello F. (ex Alberese) limestone close to the former quarries. It is still visible on right top one of the old accesses to the underground galleries.

Lime was the ancient binding materials of masonry. Until the production and advent of Portland cement during the 19th century, this binding medium was used almost exclusively in architecture, then the use of lime mortar in new constructions gradually declined. Lime can be classified according to its ability to set in air and/or under water. The hydraulic character of the hydraulic limes is produced by 'impurities' of silica and clay in the carbonate stone from which they are burnt. In fact, when carbonate stones containing impurities of silica and clay are burned, the impurities decompose and combine at 950 to 1250°C with some of the lime forming silicates and aluminates, especially dicalcium silicate and dicalcium aluminate. Depending on the initial composition of the raw materials, the lime produced consists of a mixture in different proportion of quicklime (or 'freelime'), cementitious material and inert material such as uncombined silica or clay. These limes need to be slaked with enough water to convert only the quicklime to calcium hydroxide, otherwise a chemical set begins.

II. ANALYTICAL METHODS

For the purpose of this preliminary work, we collected twenty different samples of limestone belonging to the Mt. Morello Formation and selected four of them for the sake of comparison.
The analytical techniques as listed below:

- chemical analysis through X-ray fluorescence [27] for the determination of major and minor compounds (Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3). The measurement uncertainty results between 4-7% by weight for concentrations <1%, between 2-4% for concentrations between 1 and 10% and around 1% for concentrations > 10% [28-29].
- volatile compounds content (mainly H_2O^+ and CO_2) determined by thermal treatment (105-950°C) using a simultaneous TG-DSC thermo-microbalance Netzsch STA 449 C Jupiter according to the following operative conditions: ~25 mg fine grinded sample dust; thermal rate 10°C per minute; nitrogen flux 30 ml/min.
- CO_2 content was measured by calcimetry to estimate the amount of $CaCO_3$ in the tested sample [30]. The content of calcite was calculated with reference to a calibration curve constructed by linking the volume of CO_2 developed by acid attack of the powdered rock with the amount of pure $CaCO_3$.

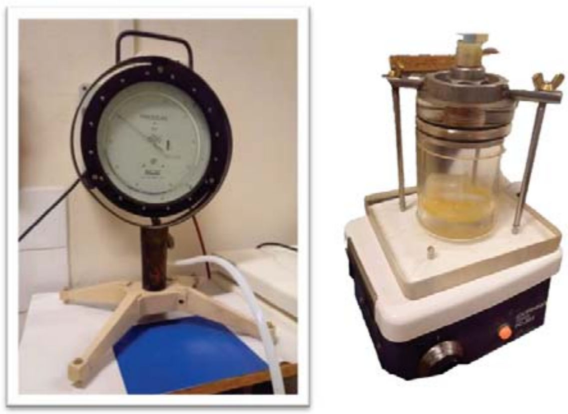

Figure 2. Calcimeter.

- mineralogical analysis through X-ray diffractometry (XRD) (D2 Phaser by Bruker with Cu anticathode and filter Ni Detector 1D Lynxeye; Diffrac.suite XRD software for acquisition and Diffrac.suite Eva software for interpretation of the data) $\lambda = 1.5406$ Å, angle range 4-66°2θ;
- petrographic analyses: transmitted light

microscopic observation (Zeiss Axioplan microscope); and scan electron microscopy using FEI Quanta 450 ESEM FEG at the Centro Interdipartimentale di Scienza e Ingegneria dei Materiale of University of Pisa;

- physical properties of the stones like real (ρ_r) and apparent (ρ_a) density, water absorption coefficient by capillarity, water absorption at atmospheric pressure, total and open porosity have been determined following EN standards [39-41];
- real density (ρ_r) has been determined using a gas pycnometer (ultrapycnometer 1000 by Quantachrome Corporation) [31]. The measurements were performed on approximately 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 minutes of continuous flow; maximum number of runs, 6; number of averaged runs, the last three;
- apparent density (ρ_a) has been determined by ratio between dry mass and volume of each sample. The specimens were placed in a stove at 60° C until the dry weight was reached, (i.e. when the difference between two successive weighing at an interval of 24 h is not greater than 0.1 % of the mass of the specimen). Then the specimens were immersed in distilled water following [31]. The volume of the specimens was measured by means of a hydrostatic balance on water-saturated samples [34];
- water absorption coefficient by capillarity has been determined on the same samples used for apparent density determination following [32]. Measurements taken after 1, 3, 5, 15, 30 minutes, 1 h;
- Determination of water absorption at atmospheric pressure has been carried out on the same specimens [33].
- The total porosity has been calculated according to (1)

$$P\ (\text{vol. }\%) = 100 \cdot (1 - \rho_a / \rho_r) \qquad (1)$$

III. RESULTS AND DISCUSSION

The analysed samples are marly limestones with a relatively high content of calcium carbonate; the grain size of the rock is fine, and its fracture is conchoidal.

The analysed rocks are grey in colour on fresh surface, whitish to yellowish brown for chromatic alteration due to the long exposures to light or because of weathering process. Ochre-coloured, bluish-green veins and impurities due to the amount of clay minerals are often present.

The main mineralogical phases identified by XRPD analysis are calcite, clay minerals and quartz as shown in Figure 3. According to the XRD data, the chemical analysis by means of XRF shows a high presence of calcium oxide, ranging from 41.8 to 44.3 wt.%. The amount of $CaCO_3$ for the analysed samples measured by calcimetry ranges from ~74 to 77 wt.%.

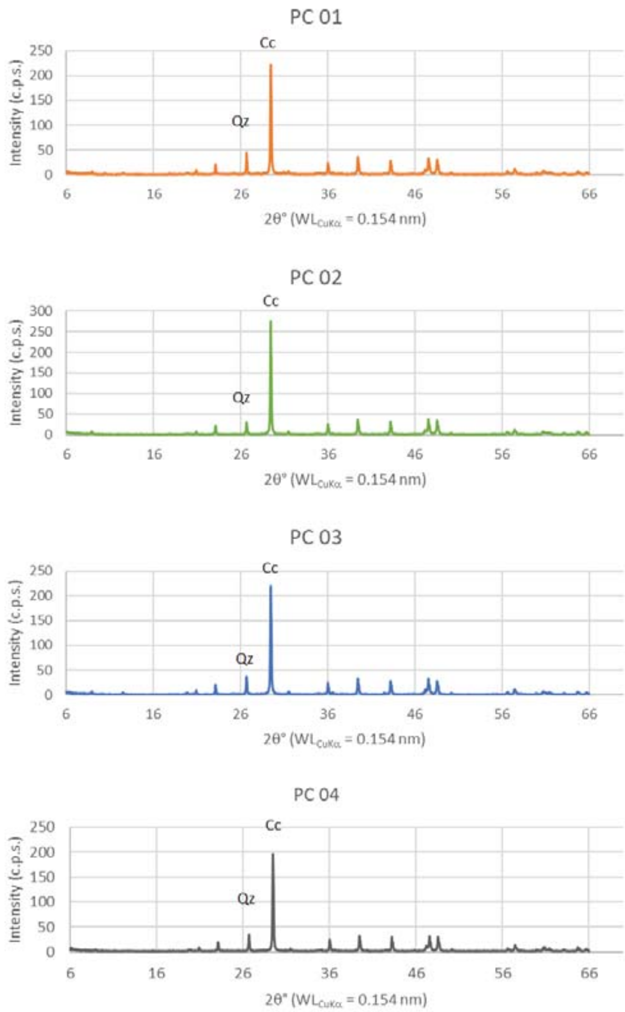

Figure 3: Diffractograms of the selected samples PC01, PC02, PC03 and PC04. Calcite, clay minerals and quartz are the identified mineralogical phases. Cc: calcite, Qz: quartz.

Table 1: Average chemical composition of four limestone samples coming from Passo dei Pecorai determined by XRF analysis: the major elements are expressed in oxides wt.%. L.O.I.: loss on ignition.

	L.O.I.	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	Other <1%
Mean	37,00	1,00	3,67	13,93	0,63	42,84	0,90	0,06
Dev. St.	0,29	0,16	0,36	0,99	0,05	0,98	0,16	0,02

Table 2: Average mineralogical composition of four limestone samples from Passo dei Pecorai calculated after chemical analysis, wt.%. Calcite values are from calcimetry analysis.

	Calcite	*Quartz*	*Feldspars*	*Clay minerals*
Mean	77	5	tr	18
Dev. St.	2	0	-	2

Table 3: Average values of the physical properties of four limestone samples from Passo dei Pecorai. ρ_r, real density; ρ_a, apparent density; w. atm., water absorption at atmospheric pressure.

	ρ_r (g/cm³)	*ρ_a (g/cm³)*	*w. atm. (wt.%)*	*total porosity (Vol.%)*
Mean	2,72	2,71	0,19	0.51
Dev. St.	0,01	0,01	0,01	0,02

IV. CONCLUSIONS

Hydraulic limes have a content of carbonates ranging between 70 and 95 wt.%, while a content above 95 wt.% results in aerial limes. In fact, natural hydraulic limes can be divided in three different classes based on their carbonate content: feebly hydraulic limes, <95-90 wt.%, moderately hydraulic lime, <90-80 wt.%, eminently hydraulic lime, <80-70 wt.% [35]. According to Louis-Joseph Vicat, the best hydraulic limes contain 0.2 part of clay for 1.00 of lime [35]. Based on the collected chemical data the analysed samples have proved useful for producing eminently hydraulic limes.

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