Panchina Calcarenite: A Building Material from Tuscany Coast

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Abstract. The “Panchina” calcarenite widely outcrops along the Tuscan coastline from Livorno to Baratti (western Tuscany). It is a stone, highly porous with medium sized grains rich in organogenic carbonate fragments, mainly consisting in shells of bivalves, gastropods, and echinoderms visible to the naked eye or by using a lens. In the framework of the ongoing research on the building stones and mortars used throughout the Middle Ages in and surrounding the Pisa’s city (western Tuscany), this study focuses on the determination of the main physical and mechanical properties of “Panchina” stone samples from Livorno coast (Tuscany, Italy). The “Panchina” stone is no longer quarried and data is collected from unweathered rocks sampled from currently accessible outcrops. The data collected on twenty-eight samples from six outcrops of the Tuscan coast showed that the analysed specimens are made up of abundant calcite, subordinate quartz and feldspars, and traces of phyllosilicates. The analysed samples are characterized by medium-high porosity, highly variable water absorption by both capillarity and total immersion at atmospheric pressure, low uniaxial compressive resistance. Thanks to the good physical and mechanical properties that characterize the stone, the “Panchina” calcarenite is easy to work and extensively used in the necropolis of the Gulf of Baratti since Etruscan times and, in medieval times, in various public and religious buildings in the city of Pisa.

1. Introduction

Studies and research on the lithotypes used in Tuscan monumental constructions have been in progress for several years at the Earth Sciences Department of the University of Pisa [1-6]. Among these, a calcarenitic rock, called "Panchina" stone, is still poorly studied. It has been used in Tuscany since the Etruscans and Romans time, as testified from the presence of large ashlars in the archaeological areas of Luni and Baratti, and of small ones among the Roman remains in Pisa, at the so-called Nerone Thermæ [7]. Even in Pisa the use of the “Panchina” stone was intense, particularly in ancient buildings, until the mid-twelfth century, and subsequently was sporadic. The most relevant buildings built with this stone are S. Zeno and the façades of San Frediano and San Nicola [8-9]. Thanks to the ease of quarrying and carving of the stone, it was used to realise several ashlars worked for small arches. The “Panchina” stone was also used in the northern portion of the defensive walls of the city [7]. The aim of this work is to investigate the physical-mechanical properties of the "Panchina" calcarenite outcropping along the Livorno coast. The collected samples were preliminarily characterized from a chemical, mineralogical and petrographic point of view and, subsequently, the main physical and mechanical properties were determined following the indications of the European standards.
2. Geological setting

The "Panchina" stone of the western coast of Tuscany outcrops mainly along the coast between Livorno and Rosignano Marittimo, and in the Gulf of Baratti [10]. The typical outcrop of this rock is located within the city of Livorno and belongs to a morpho-sedimentary element, known in the literature as "Terrazzo di Livorno" [11-12] that represents the substrate on which the city was built. The "Terrazzo di Livorno" was interpreted as a polycyclic marine terrace by Federici & Mazzanti [13]. It developed during stage 5 of marine isotopic stratigraphy (MIS 5) starting around 125,000 years ago [14-16]. From the bottom to the top it is possible to distinguish the following stratigraphic sequence: 1) Sandstones and conglomerates of coastal marine environment ("Panchina I" or "Calcareniti sabbiose di Castiglioncello" and "Conglomerati di Chioma"), sometimes containing typical hot faunas [11-13] and referable to MIS 5e [14-17]. 2) Silty clays, sometimes peaty, of a mainly continental environment, sometimes containing terrestrial malacoфаunas and the remains of large mammals. These faunas are indicative of a phase of climate deterioration [12-13, 18-19] related to MIS 5d [18]. 3) Conglomerates in silty sandy matrix of river environment (Conglomerati di Rio Maggiore) that follow upward and in probable heterotopia to "Panchina I". 4) Sandstones of variable environment, from coastal marine to aeolian ("Panchina II"; [11, 20]), of uncertain dating, but probably corresponding to MIS 5c [14, 18]. This sequence refers to the "Calcareniti di Castiglioncello", cartography 1: 25.000 (QCP = q8) [20]. 5) Continental sands and sandy silts, strongly reddened or brown or orange in colour ("Sabbie di Ardenza" by [20]); often inside them there are Moustarian industries [21-22]. It has recently been proposed that their deposition occurred during MIS 3 and 4 [18, 23]. The substratum of the rather varied Pleistocene deposits consists of Pliocene deposits of the "Blue Clays" replaced to the west by sands and clays of the Lower Pleistocene of the Morrona Formation [24-25].

3. Materials and methods

Twenty-eight samples have been collected from six different areas along the coast from Livorno to Baratti: Salt Beach (PAS) and Accademia Beach (PAA) at Livorno, Quercianella (PAQ), Fortullino Beach (PAF) at Rosignano M.mo, Gulf of Baratti (PAR), Bucà delle Fate at Populonia (PAB). The analytical procedures used for this work are as follows: a) chemical analysis through X-ray fluorescence [26-27] for the determination of major and minor compounds (Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, K₂O, CaO, TiO₂, MnO, Fe₂O₃); b) CO₂ content was measured by calcimetry to estimate the amount of CaCO₃ in the tested sample [28]. The content of calcite was calculated with reference to a calibration curve constructed by linking the volume of CO₂ developed by acid attack of the powdered rock with the amount of pure CaCO₃; c) mineralogical analysis through X-ray diffractometry (XRD) λ = 1.5406 Å, angle range 4-66°20; d) petrographic analyses: transmitted light microscopic observation of thin sections (Zeiss Axioplan microscope); e) physical properties of the stones like real (ρ₁) and apparent (ρ₂) density, water absorption coefficient by capillarity, water absorption at atmospheric pressure, total and open porosity and saturation index have been determined following EN standards [29-31]. Real density (ρ₁) has been determined using a gas pycnometer (Ultrapycnometer 1000 by Quantachrome Corporation) [29]. 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 (ρ₂) has been determined by ratio between dry mass and volume of each specimen. 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 [29]. The volume of the specimens was measured by means of a hydrostatic balance on water-saturated samples [32]. Water absorption coefficient by capillarity has been determined on the same samples used for apparent density determination following EN 1936:2007 [30]. Measurements were taken after 1, 3, 5, 15, 30, 60, 120, 180, 240, 300, 360, 420, 480, 1440, 2880 minutes. Determination of water absorption at atmospheric pressure has been carried out on the same specimens [31]. Measurements were taken after 1, 3, 5, 15,
30, 60, 120, 180, 240, 300, 360, 420, 480, 1440, 2880 minutes. Total porosity has been calculated according to the following formula: \( P \text{ (vol. %)} = 100 \cdot (1 - \frac{\rho_a}{\rho_r}) \).

4. Results and discussions

The description of the “Panchina” stone samples, their sampling locations and their properties observed with naked eye are reported in Table 1.

| Sample | Location | Colour | Grain size | Porosity | Decay       |
|--------|----------|--------|------------|----------|-------------|
| PAB01  | PAB      | G      | Medium Sand| Medium   | Medium - Low|
| PAB02  | PAB      | G      | Medium Sand| Medium   | Medium - Low|
| PAB03  | PAB      | G      | Medium Sand| Medium   | Medium - Low|
| PAB04  | PAB      | G      | Medium Sand| Medium   | Medium - Low|
| PAB05  | PAB      | G      | Medium Sand| Medium   | Medium - Low|
| PAB06  | PAB      | G      | Medium Sand| Medium   | Medium - Low|
| PAB07  | PAB      | G      | Medium Sand| Medium   | Medium - Low|
| PAB08  | PAB      | G      | Medium Sand| Medium   | Medium - Low|
| PAB09  | PAB      | G      | Medium Sand| Medium   | Medium - Low|
| PAB10  | PAB      | G      | Medium Sand| Medium   | Medium - Low|
| PAF01  | PAF      | M      | Medium Sand| High     | High         |
| PAF02  | PAF      | M      | Medium Sand| High     | High         |
| PAQ01  | PAQ      | GB     | Silt       | Very Low | Almost absent|
| PAQ02  | PAQ      | GB     | Silt       | Very Low | Almost absent|
| PAS01  | PAS      | GB     | Fine Sand grain| Low | Medium     |
| PAS02  | PAS      | GB     | Fine Sand grain| Low | Medium     |
| PAS03  | PAS      | GB     | Fine Sand grain| Low | Medium     |
| PAS04  | PAS      | GB     | Fine Sand grain| Low | Medium     |
| PAA1   | PAA      | G      | Medium Sand| Medium   | High         |
| PAA2   | PAA      | M      | Coarse Sand| High     | High         |
| PAB11  | PAB      | G      | Medium Sand| Medium   | Medium - Low|
| PAB12  | PAB      | G      | Medium Sand| Medium   | Medium - Low|
| PAR1   | PAR      | G      | Fine Sand grain| Low | Low         |
| PAR2   | PAR      | M      | Fine Sand grain| Low | Low         |
| PAR3   | PAR      | G      | Medium Sand| Medium   | Medium - Low|
| PAR4   | PAR      | GR     | Medium Sand| Medium   | Medium - Low|
| PAR5   | PAR      | G      | Fine Sand grain| Low | Low         |
| PAR6   | PAR      | M      | Medium Sand| Medium   | Medium - Low|

PAA = Livorno, Accademia Beach; PAS = Livorno, Salt Beach; PAQ = Quercianella; PAF = Rosignano M.mo, Fortullino Beach; PAR = Gulf of Baratti; PAB = Buca delle Fate at Populonia; G = yellow; B = white; M = brown; R = red.

The colour of the analysed samples varies from white to brownish red. “Panchina” stone is a calcarenite with variable grain size between silt and coarse sand. The porosity is quite variable from high to very high, and the samples present an external alteration from almost absent to high.
In Table 2, we report the chemical composition of the analysed samples of “Panchina” stone. The main components, excluding the Loss On Ignition (LOI) values that is essentially due to the CO₂ contents, are represented by CaO, with values ranging from 35.01 wt. % to 49.91 wt. % and SiO₂ even though the latter one highly varies from 8.31 wt. % to 32.92 wt. %.

Table 2. Chemical compositions (wt. %) of the analysed samples of “Panchina” stone.

| Sample  | LOI   | Na₂O | MgO | Al₂O₃ | SiO₂ | P₂O₅ | K₂O | CaO | TiO₂ | MnO | Fe₂O₃ |
|---------|-------|------|-----|-------|------|------|-----|-----|------|-----|-------|
| PAB01   | 28.60 | 0.15 | 0.30| 1.59  | 32.92| 0.06 | 0.42| 35.01| 0.16 | 0.28 | 0.51  |
| PAB02   | 34.65 | 0.14 | 0.39| 1.38  | 17.88| 0.05 | 0.39| 43.94| 0.32 | 0.31 | 0.55  |
| PAB03   | 33.30 | 0.16 | 0.32| 1.56  | 21.26| 0.05 | 0.39| 41.87| 0.20 | 0.35 | 0.54  |
| PAB04   | 32.22 | 0.08 | 0.26| 1.01  | 24.62| 0.04 | 0.35| 40.48| 0.21 | 0.23 | 0.50  |
| PAB05   | 32.45 | 0.11 | 0.27| 1.24  | 24.18| 0.06 | 0.41| 40.29| 0.26 | 0.30 | 0.43  |
| PAB06   | 31.34 | 0.15 | 0.32| 1.46  | 25.84| 0.05 | 0.37| 39.56| 0.20 | 0.33 | 0.38  |
| PAB07   | 32.82 | 0.13 | 0.29| 1.03  | 23.66| 0.05 | 0.34| 40.82| 0.23 | 0.26 | 0.37  |
| PAB08   | 29.48 | 0.12 | 0.28| 1.26  | 30.40| 0.05 | 0.35| 37.12| 0.19 | 0.29 | 0.46  |
| PAB09   | 28.16 | 0.21 | 0.32| 1.61  | 32.77| 0.05 | 0.37| 35.39| 0.21 | 0.45 | 0.46  |
| PAB10   | 30.01 | 0.11 | 0.29| 1.25  | 29.09| 0.08 | 0.37| 37.70| 0.37 | 0.27 | 0.46  |
| PAF01   | 35.23 | 0.15 | 0.25| 1.20  | 17.49| 0.06 | 0.35| 44.33| 0.28 | 0.22 | 0.44  |
| PAF02   | 35.41 | 0.14 | 0.29| 1.09  | 17.95| 0.05 | 0.29| 43.88| 0.30 | 0.18 | 0.42  |
| PAQ01   | 36.11 | 0.36 | 0.25| 1.72  | 15.36| 0.05 | 0.32| 45.01| 0.25 | 0.22 | 0.35  |
| PAQ02   | 31.98 | 0.23 | 0.28| 1.81  | 24.44| 0.09 | 0.38| 39.61| 0.29 | 0.33 | 0.56  |
| PAS01   | 38.49 | 0.07 | 0.27| 0.99  | 10.93| 0.07 | 0.36| 47.92| 0.18 | 0.31 | 0.41  |
| PAS02   | 37.77 | 0.07 | 0.17| 0.87  | 11.95| 0.15 | 0.24| 47.83| 0.20 | 0.37 | 0.38  |
| PAS03   | 39.96 | 0.04 | 0.22| 0.66  | 8.31 | 0.03 | 0.25| 49.91| 0.19 | 0.14 | 0.29  |
| PAS04   | 38.45 | 0.18 | 0.34| 1.46  | 9.86 | 0.15 | 0.39| 47.96| 0.24 | 0.46 | 0.51  |

| Mean    | 33.69 | 0.14 | 0.28| 1.29  | 21.05| 0.07 | 0.35| 42.15| 0.24 | 0.29 | 0.45  |
| St.Dev. | 3.45  | 0.07 | 0.05| 0.30  | 7.57 | 0.03 | 0.05| 4.36 | 0.05 | 0.08 | 0.07  |

PAA = Livorno, Accademia Beach; PAS = Livorno, Salt Beach; PAQ = Quercianella; PAF = Rosignano M.mo, Fortullino Beach; PAR = Gulf of Baratti; PAB = Buca delle Fate at Populonia; LOI = Loss on Ignition at 950 °C; Fe₂O₃ = total iron expressed as Fe₂O₃.

The results of the analyses of the physical and mechanical properties are reported in Tables 3 and 4. The apparent density, ρₐ, varies from 1.73 to 2.13 g/cm³ in agreement with the total porosity values, ranging from 21.6 to 36.3 vol.%. The water absorption varies from 9.0 to 19.6 wt.%, and from 19.0 to 28.6 vol.%, with a saturation index that varies from 73 to 87.

The uniaxial compressive resistance of the "Panchina" stone samples is relatively low, but highly variable due to the heterogeneity of its composition. The analysed samples have uniaxial compressive strength values ranging from 2.2 to 8.1 MPa, rebound index values from 64 to 66, and ultrasound pulse velocity values from 3748 to 4018 m/s.
Table 3. Main physical properties of the analysed samples of “Panchina” stone.

| Campione | $\rho_r$ (g/cm$^3$) | $\rho_a$ (g/cm$^3$) | $C_1$ (g/m$^2$s$^{0.5}$) | w. Abs. (wt. %) | w. Abs. (vol. %) | Total porosity (% in vol) | Saturation Index |
|----------|----------------------|----------------------|---------------------------|----------------|----------------|--------------------------|----------------|
| PAB mean | 2.71                 | 1.97                 | 131.08                    | 11.3           | 21.8           | 27.2                     | 79             |
| St. Dev. | 0.01                 | 0.14                 |                           |                |                |                          |                |
| PAF mean | 2.71                 | 1.92                 | 143.33                    | 11.2           | 21.4           | 29.2                     | 73             |
| St. Dev. | 0.01                 | 0.02                 | 63.52                     | 1.0            | 1.7            | 0.7                      | 4              |
| PAQ mean | 2.71                 | 2.13                 | 391.50                    | 9.0            | 19.0           | 21.6                     | 87             |
| St. Dev. | 0.01                 | 0.08                 | 173.24                    | 3.4            | 6.5            | 2.9                      | 19             |
| PAS mean | 2.71                 | 1.73                 | 340.33                    | 19.6           | 28.6           | 36.3                     | 79             |
| St. Dev. | 0.01                 | 0.03                 | 88.34                     | 1.3            | 1.8            | 1.1                      | 3              |

$\rho_r$ = real density; $\rho_a$ = apparent density; $C_1$ = water absorption coefficient by capillarity; w. Abs. = water absorption at atmospheric pressure. PAA = Livorno, Accademia Beach; PAS = Livorno, Salt Beach; PAQ = Quercianella; PAF = Rosignano M.mo, Fortullino Beach; PAR = Gulf of Baratti; PAB = Buca delle Fate at Populonia.

Table 4. Main mechanical properties of the analysed samples of “Panchina” stone.

| Campione | Compressive Strength (MPa) | Rebound Index | Ultrasound velocity (m/s) |
|----------|-----------------------------|---------------|--------------------------|
| PAB mean | 7.6                         | 64            | 3865                     |
| St. Dev. | 6.7                         | 4             | 244                      |
| PAF mean | 5.6                         | 64            | 3993                     |
| St. Dev. | 5.6                         | 5             | 193                      |
| PAQ Mean | 8.1                         | 66            | 4018                     |
| St. Dev. | 8.1                         | 3             | 277                      |
| PAS mean | 2.2                         | 64            | 3748                     |
| St. Dev. | 2.2                         | 6             | 247                      |

PAS = Livorno, Salt Beach; PAQ = Quercianella; PAF = Rosignano M.mo, Fortullino Beach; PAB = Buca delle Fate at Populonia.

5. Conclusions
The “Panchina” calcarenite, outcropping on the coast from Livorno to Baratti, is mainly composed of calcite (63-90% wt) and quartz (8-34% wt) with some feldspars and phyllosilicates in traces. The rock is characterized by medium-high porosity (12-37% by volume) and shows variable water absorption by capillarity (at 5 minutes, 10-514 g/m$^2$s$^{0.5}$) and by total immersion at atmospheric pressure (3-19% by weight). The compressive resistances are medium-low (1-31 MPa). We notice an inverse proportionality between porosity and mechanical compressive strength in the material. The stones have evident variations of physical-mechanical properties related both to different outcrop places and from the same area of origin (e.g. PAS). The low apparent density and easy workability favoured the use of this stone since the ancient times for the construction of the Etruscan necropolis of Baratti and, in medieval times, in various public and religious buildings in the city of Pisa.

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