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Original article

# Laboratory and onsite study of barium hydroxide as a consolidant for high porosity limestones



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## ABSTRACT

The paper focuses on the study of barium hydroxide applied to two high porosity limestones from Portugal (Ançã stone, with 27% porosity) and Italy (Lecce stone, with 37% porosity), both in the laboratory and onsite. The results show that barium hydroxide acts both through carbonation with atmospheric CO<sub>2</sub> and by replacing calcium for barium in the calcite lattice followed by carbonation of the released calcium hydroxide. This double mechanism proved to be particularly efficient in the Ançã limestone, possibly due to a higher reactivity linked to its smaller grain size. The mechanism is far slower than simple carbonation and has a better outcome when the stone can be totally immersed in the solution. Onsite experiments on the Ançã stone were less striking than in the laboratory, possibly due to the insufficient amount of product made available for reaction, but a positive outcome was visible after six years of natural exposure.  
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## 1. Research aims

The research aims at testing barium hydroxide as a consolidant for very porous limestones. The working mechanisms were searched to validate the hypothesis raised by previous authors. The consolidation action, both in the laboratory and onsite was tested and implications for the conservation practice are drawn. Performance in natural exposure conditions is also evaluated.

## 2. Introduction

Very porous limestones, such as those with a porosity above 15%, rank among the most vulnerable lithotypes in terms of deterioration, and are often the most difficult to consolidate. Their high porosity has frequently two contradictory consequences: on the one hand it facilitates the absorption of the consolidation products, but on the other it frequently tends to favour a high concentration of products within a very thin superficial layer, thus creating significant differences in the physical properties between treated and untreated areas leading to subsequent severe harmful consequences in the medium and long-term time frames. The porous structure and the type of voids (mostly equidimensional pores and

absence of fissures) also influence the behaviour of consolidated stones.

Porous limestones tend to deteriorate through powdering and scaling, two severe deterioration forms that may lead to damage of the stone surfaces and eventually to heavy loss. Two examples of this type of limestone are Ançã (from Portugal) and Lecce (from Italy) and they are well known for their high vulnerability, especially in the presence of soluble salts. Therefore, they were the materials chosen for testing in the present study.

The present paper falls within the context of a research project evaluating inorganic consolidation products, namely barium hydroxide – Ba(OH)<sub>2</sub>. The experiments carried out bring together data from laboratory studies presented elsewhere as preliminary results [1] with new data obtained from onsite experiments.

Barium hydroxide (for simplification, here also designated as BaHy) has a long history as a potential consolidant for stone, with reported use since the 19th century [2–4] for consolidation of plasters and stones. It is based on the idea that the product once inside the stone it precipitates as barium hydroxide that converts to barium carbonate by the action of the atmospheric CO<sub>2</sub>, with a possible complementary mechanism in the case of calcite and dolomite substrates.

Absorption properties, depth of penetration and strength increase in laboratory and in field conditions are used to identify the working mechanisms and to explain the observed behaviours.

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**Table 1**  
Some physical properties of Ançã and Lecce stones.

Stone	Porosity (%)	Real density (kg.m <sup>-3</sup> )	Bulk density (kg.m <sup>-3</sup> )	Maximum water content (%)	Coefficient of water absorption by capillarity (10 <sup>-4</sup> g.cm <sup>-2</sup> .s <sup>-1/2</sup> )
A - Ançã stone	26.7 ± 0.4	2712 ± 1	1989 ± 10	13.4 ± 0.3	169.7 ± 7.0
L - Lecce stone	37.1 ± 0.4	2722 ± 0.5	1712 ± 6	21.7 ± 0.2	121.2 ± 2.7

The values correspond to the mean ± standard deviation of eight specimens.

### 3. Materials and methods

The research is integrated into a project focused on the application of barium hydroxide and ammonium oxalate to treat marbles, limestones and sandstones, in collaboration with Italian partners. The Portuguese team was responsible for testing the limestones and part of the laboratory research was carried out under the EU-Artech project framework. The preliminary results were published elsewhere [1,5]. The present paper discusses the results on the treatment with barium hydroxide, both in the laboratory and onsite.

#### 3.1. Stone materials

The laboratory study was carried out on two very porous limestones (Ançã stone from Portugal and Pietra di Lecce from Italy). The Ançã stone is a very homogeneous, whitish aphanitic limestone, with no macroscopic components identifiable by the naked eye. It is a very soft material with high porosity and low compressive and bending strengths. It is a very pure calcitic limestone quarried in Cretaceous outcrops near Coimbra.

Lecce stone is also a calcitic limestone, with some minor accessory minerals, quarried in Cretaceous outcrops near Lecce. It has very high porosity and low strength values and it is also very soft.

The main physical properties of both stones are presented in Table 1. Their very high porosity is striking, as well as their high water absorption rate.

Porosity, real and bulk densities were determined by hydrostatic weighings with saturation made under vacuum conditions. The values of real density are typical of calcite, while the apparent densities are in line with their high porosity values. Maximum water content corresponds to saturation under vacuum. Capillarity coefficient was determined in 5 × 5 × 10 cm specimens oven dried at 70 °C and cooled in a desiccator at room temperature. The test consists in measuring the amount of water absorbed at regular time intervals. For this purpose, the specimens are periodically weighed and the mass of water absorbed is calculated.

Mercury Intrusion Porosimetry was performed on at least two specimens of each stone using a QUANTACHROME mercury porosimeter, model AUTOSCAN60. Ançã stone has typical unimodal pore size distribution with a very narrow range of pores centred around 0.3 μm; Lecce stone has larger pores in a wider range of radius dimensions. Its mode is centred around 1–2 μm (Fig. 1).

Onsite tests were made on a balustrade located in the Hanging Garden of the Queluz National Palace carved from a highly porous limestone that is supposed to have been extracted in the Ançã region and similar to the typical Ançã stone tested in the lab. Some of the tested areas showed grooves left by the artificial removal of the decayed thickness in undocumented previous interventions, thus suggesting that deterioration has long been active.

A few small samples were collected from the balustrade and characterised in the laboratory. Their porosity and pore space evaluated by mercury intrusion porosimetry prove that they are nearly identical to the Ançã stone used in the laboratory study (Fig. 2).

Some measurements were made with the contact sponge method [6] to characterise the hydric properties. Fig. 3 presents

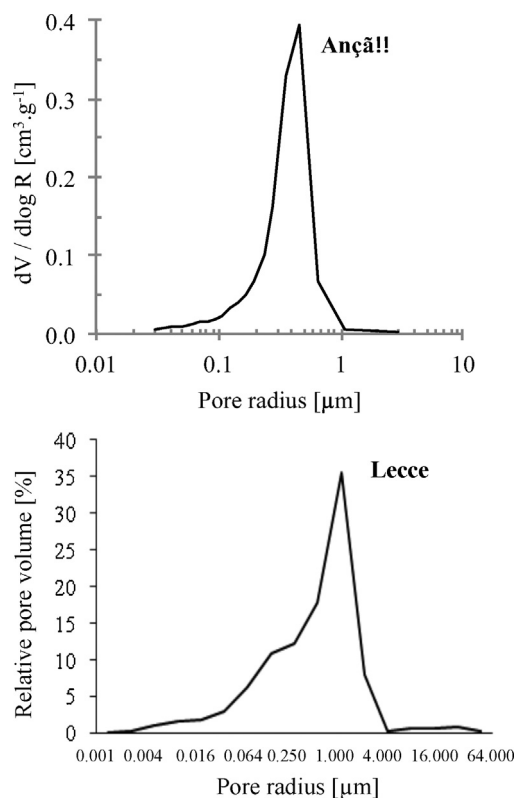


Fig. 1. Pore size distribution of the tested stones.

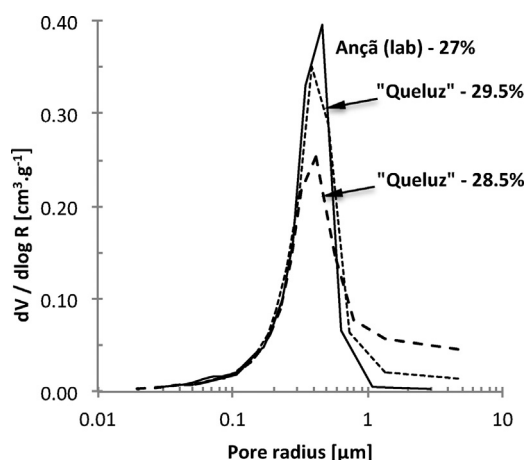


Fig. 2. Porosity and pore size distribution of Ançã stone (lab) and of two samples collected in the Queluz Garden (Queluz).

the average values and the standard deviation of the onsite water absorption values compared to the results for the Ançã stone used in laboratory testing. As it can be observed, the onsite water absorption values are lower and, although some differences were to be

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