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POZZOLANIC MATERIALS – EVOLUTION OF MECHANICAL PROPERTIES*

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Abstract

Natural pozzolans from different origins were characterised and used to make lime-pozzolan mortars. Mortars with these materials have been used since ancient times and the knowledge of their properties contributes toward understanding their performance as renders. A special emphasis was put on the evolution of their mechanical properties through a period of time up to 3 years, resulting in varied patterns depending on the proportion of materials and curing conditions. However, in a general sense, mechanical properties decreased with age, a finding that must be complemented by other analysis techniques, such as SEM, in order to evaluate the micro-structural changes in mortars that induce this phenomenon.

Keywords

Pozzolans, lime, mortar, mechanical properties.

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1 Introduction

The use of rendering mortars is an ancient practice that has suffered variations in mortar composition and application related to geographic and temporal factors. The use of pozzolans in mortars is said to have been initiated by the Greeks in 1500 B.C. Their employment during the Roman period can still be found in ruins widespread throughout the Roman Empire (Rua,1998). Later, during the Byzantine period, they were applied in both Turkey (Oguz Kiliç *et al*, 2004; Çizer *et al*, 2004) and Greece (Moropoulou *et al*, 2004). In volcanic regions, such as the Azores islands in Portugal, these materials were used in pointing and rendering mortars until recently, when they were replaced by portland cement. The specificity of lime-pozzolan mortars is their ability to harden under water. This capability enabled their application in Roman baths and tanks, and in maritime structures during the nineteenth century. Although knowledge of pozzolanic mortars is available and a few studies of their characterization have been conducted, their behaviour as renders deserves a further insight. With this intention, two different natural pozzolans were incorporated into lime-based mortars, and testing campaigns were developed to determine their performance when different proportions and curing conditions were used.

2 Pozzolanic Materials

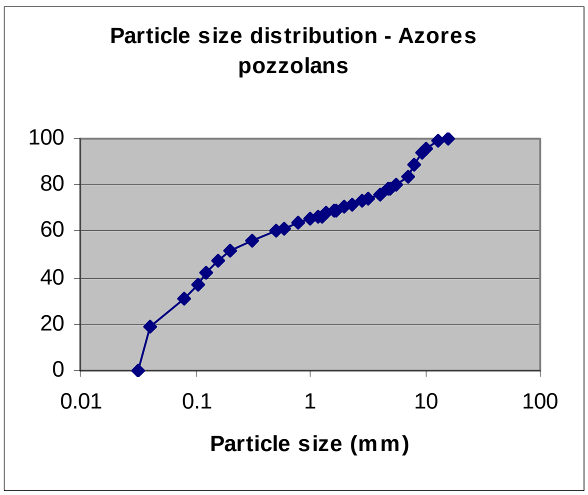
Natural pozzolans were chosen according to their availability in the Portuguese market; Cape Verde pozzolans had been commercialised and used by the construction industry and pozzolans from the Azores had been used to manufacture pozzolanic cement in the island of S. Miguel. Use of this last material in construction during the 19th Century is vastly documented, especially in the field of coastal defense works.

Both materials were characterised by Blaine's specific surface, following the procedures in NP EN 196-6 (Metodos de Ensaio de Cimentos; Determinacao da Finura), and by particle size distribution, determined by dry sieving in accordance with NP EN 1015-1 (Methods of Test for Mortar for Masonry; Part 1 – Determination of Particle Size distribution). A further study was conducted to characterise these materials both by chemical composition, using XRF, and by mineralogical composition, using XRD.

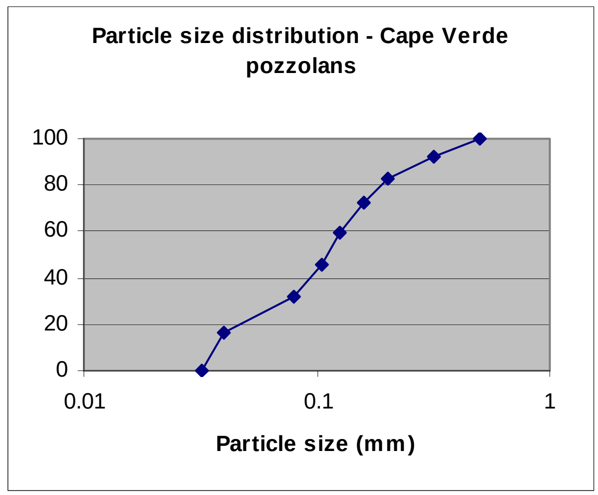
In terms of visual characterization, Azores pozzolans (Figure 1 and Graph 1) are of a yellow-brown color, whilst Cape Verde pozzolans are light grey (Figure 2 and Graph 2). Although Azores pozzolans have larger particles, both materials were passed through the 0.500 sieve and, for that fraction, national pozzolans present a higher specific surface (6870 cm^2/g versus 3250 cm^2/g for the other material). XRD analysis of both materials indicates the presence of amorphous material, classified as aluminosilicates.

Figure 1 Azores pozzolans

Figure 2 Cape Verde pozzolans



Graph 1 Particle size distribution of Azores pozzolans



Graph 2 Particle size distribution of Cape Verde pozzolans

Although both materials seem suitable for use as pozzolanic additions, based on this preliminary analysis, tests for pozzolanic reactivity were performed according to the Portuguese legislation (RBLH – Caderno de Encargos para Fornecimento e Recepção de Pozolanas). These tests, performed at the ages of 7 and 28 days and based on mechanical strength developed by reaction of the pozzolans with lime, classified Cape Verde pozzolans as highly-reactive and Azores pozzolans as low-reactivity. Neither of these materials complies with the compressive strength requirement of 4,1MPa at 7 days contained in ASTM C 593 Standard Specification for Fly Ash and Other Pozzolans for Use With Lime.

3 Testing Campaign

The results presented in this paper pertain to flexural and compressive strength tests that provide a basic characterization of the mortars' mechanical properties and give a first insight into the mortars' applicability. The testing campaign was developed in three different phases. In the first phase, mortars incorporating both pozzolans were made with a 1:1:4 volumetric ratio (lime:pozzolan:aggregate), which were compared with a lime mortar executed with a commonly-used 1:3 (lime:aggregate) volumetric ratio. Ratio 1:1:4 was chosen because both carbonation and pozzolanic reaction play important roles in the strength evolution of mortars, and pozzolanic material is composed of reactive and non-reactive phases. A commercial aerial hydrated lime was used and the sand was siliceous river sand. All mortars were cured under the same conditions (23ºC, 50%RH) and were designated as shown in the following table (Table 1).

Table1 Mortar Composition with Different Pozzolans

Designation	Lime	Azores Pozzolans	Cape Verde Pozzolans	River Sand
L	1	-	-	3
LAP	1	1	-	4
LCVP	1	-	1	4

Tests for flexural and compressive strengths were carried out at the ages of 28 days, 90 days, 1 year and 3 years, according to NP EN 1015-11 (Methods of Test for Mortar for Masonry; Part 11 – Determination of Flexural and Compressive Strength of Hardened Mortar). Test results (average and standard deviation) are shown in the following tables (Table 2 and Table 3):

Table 2 Evolution of Flexural Strength

Flexural	L		LAP		LCVP	
strength (MPa)	**A**	**S.D.**	**A**	**S.D.**	**A**	**S.D.**
F 28 d	0.27	0.037	0.20	0.012	0.37	0.054
F 90 d	0.26	0.060	0.11	0.041	0.30	0.042
F 1 yr	0.40	NE	0.20	NE	NE	NE
F 3 yrs	0.42	0.147	0.14	0.025	0.30	0.085

Table 3 Evolution of Compressive Strength

Compressive	L		LAP		LCVP	
strength (MPa)	**A**	**S.D.**	**A**	**S.D.**	**A**	**S.D.**
C 28 d	0.50	0.024	0.57	0.034	1.29	0.050
C 90 d	0.84	0.028	0.52	0.040	1.12	0.145
C 1 yr	0.80	NE	0.48	NE	NE	NE
C 3 yrs	0.84	0.077	0.42	0.030	1.01	0.059

Based on these results, mortars incorporating Cape Verde pozzolans have higher initial flexural and compressive strengths, whilst mortars with Azores pozzolans possess initial flexural and compressive strengths similar to that of lime mortar with no additives. An improvement in mechanical properties is visible in mortar L at 90 days, but mortars with pozzolanic additions seem to decrease in strength over time, in comparison to results obtained at 28 days. Despite this pattern, LCPV retains higher compressive strength than L, but lower flexural strength at the age of 3 years.

Considering these results, a second phase of tests were carried out with Cape Verde pozzolans, using different proportions in the mortar. In the first additional mortar, the pozzolanic component and the sand ratio were decreased by using a 1:0.5:2.5 volumetric ratio (LCVP2). Another alternative was to reproduce a mortar quoted by Vitruvius in ‘The Ten Books of Architecture’ (LCVP1), and mortars with a 1:1:1 volumetric ratio were also made (LCVP3). These ratios are shown in Table 4.

Table 4 Mortar Composition with Cape Verde Pozzolans with Different Volumetric Ratios

Designation	Lime	Cape Verde Pozzolans	River Sand
LCVP1	1	1	4
LCVP2	1	0.5	2.5
LCVP3	1	1	1

Results of flexural and compressive strength tests for the additional mortars made with Cape Verde pozzolans are shown below in Table 5 and Table 6.

Table 5 Evolution of Flexural Strength

Flexural	**LCVP1**		**LCVP2**		**LCVP3**	
strength (MPa)	**A**	**S.D.**	**A**	**S.D.**	**A**	**S.D.**
F 28 d	0.37	0.054	0.53	0.041	1.04	0.160
F 90 d	0.30	0.042	0.42	0.043	NE	NE
F 1 yr	NE	NE	NE	NE	0.90	0.197
F 3 yrs	0.30	0.085	0.36	0.073	NE	NE

Table 6 Evolution of Compressive Strength

Compressive	**LCVP1**		**LCVP2**		**LCVP3**	
strength (MPa)	**A**	**S.D.**	**A**	**S.D.**	**A**	**S.D.**
C 28 d	1.29	0.050	1.51	0.348	6.01	0.214
C 90 d	1.12	0.145	1.53	0.058	NE	NE
C 1 yr	NE	NE	NE	NE	5.48	0.284
C 3 yrs	1.01	0.059	0.89	0.207	NE	NE

The behaviour of LPCV2 is very similar to that of LPCV1, with an increase in flexural strength but similar compressive strength values. In this case, the change from a binder/aggregate ratio of 1:2 to 1.5:2.5 may be significant. LPCV3 presents much higher mechanical strength values, which are related to a 2:1 binder/aggregate ratio.

A clear tendency for decrease in both flexural and compressive strength over time is visible for all three mortars, but seems more accentuated in LPCV3. In that mortar, the lime/pozzolan reaction may have been responsible for the achievement of higher mechanical strength at an early age. However, the values obtained by testing this mortar are still significantly higher at 1 year of age than those obtained for the other mortars.

In the third phase, further tests were carried out by changing curing conditions and comparing mechanical test results at different ages. The additional mortars that were tested are listed in Table 7. Mortar LCVPb was kept in water for the first 28 days. External conditions were the autumn/winter environment in Lisbon, Portugal, with rainfall protection, temperature ranging from 3ºC to 26ºC, and relative humidity varying from 40% to 90%.

Compressive and flexural test results for all mortars with Cape Verde pozzolans are shown in the following tables (Table 8 and Table 9).

Table 7 Mortar Compostion Using Cape Verde Pozzolans with Different Volumetric Ratios and Curing Conditions

Designation	Lime	Cape Verde Pozzolans	River Sand	Conditioning
LCVP2a	1	0.5	2.5	20ºC; 65%RH
LCVP2b	1	0.5	2.5	In water
LCVP2c	1	0.5	2.5	External conditions
LCVP3a	1	1	1	20ºC; 65%RH

Table 8 Evolution of Flexural Strength

Flexural	LCVP2a		LCVP2b		LCVP2c		LCVP3a	
Strength (MPa)	A	S.D.	A	S.D.	A	S.D.	A	S.D.
F 28 d	0.35	0.025	0.75	0.030	0.18	0.015	0.69	0.057
F 90 d	0.31	0.035	NE	NE	0.14	0.010	NE	NE
F 1 yr	NE	NE	0.54	0.109	NE	NE	0.79	0.235
F 3 yrs	NE	NE	NE	NE	0.32	0.015	NE	NE

Table 9 Evolution of Compressive Strength

Compressive	LCVP2a		LCVP2b		LCVP2c		LCVP3a	
strength (MPa)	A	S.D.	A	S.D.	A	S.D.	A	S.D.
C 28 d	1.50	NE	1.90	0.346	1.10	0.094	6.01	0.214
C 90 d	1.03	0.021	NE	NE	0.89	0.037	NE	NE
C 1 yr	NE	NE	2.12	0.111	0.44	0.017	6.73	0.353
C 3 yrs	NE	NE	NE	NE	NE	NE	NE	NE

Upon a first analysis, the behaviour of these mortars is complex and does not follow a pattern based on different compositions and curing conditions. Generally, mortars with the addition of Cape Verde pozzolans suffer a decrease in mechanical strength with age. In terms of mortars with a 1:0.5:2.5 ratio, LCVP2b, which was kept in water for the first 28 days, continued to increase its mechanical strength until the age of 1 year, while accompanied by a decrease in flexural strength values. On the other hand, mortars cured in outside conditions increased in flexural strength at later ages. The most interesting result is provided by mortars with a 1:1:1 ratio, where we believe pozzolanic reaction (versus carbonation) is highly responsible for mechanical strength. In this case, mortars cured at higher relative humidity increased their compressive strength and maintained their flexural strength over time.

The use of SEM/EDS techniques provided additional data that may further elucidate the behaviour of lime/pozzolan mortars, by taking into account the possible relation between strength development and the development of CSH in lime/pozzolan mortars. SEM photographs of LCVP2 at an early age (prior to 28 days) and at 3 years of age show a predominance of CSH filaments shortly after mortar production (Figure 3) and very few of these structures after 3 years in laboratory conditions (Figure 4). This fact suggests that the hydraulic components resulting from pozzolanic reactions are unstable, changing quickly with time.

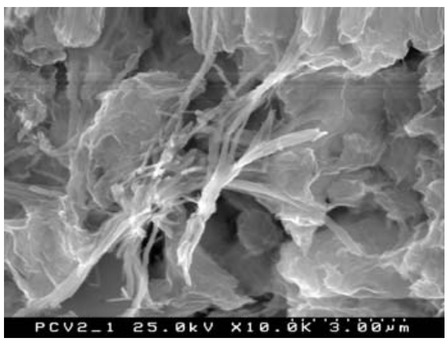


Figure 3 LCVP2 aged a few days showing CSH filaments

(x 10 000)

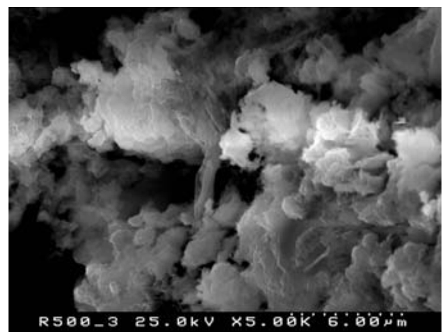


Figure 4 LCVP2 aged 3 years with hardly any CSH filaments

(x 5 000)

4 Conclusions

With these tests, the variation in mechanical strength in mortars with pozzolanic additives became evident. Preparation of mortars with very different characteristics for different ends is a possibility that must be supported by further tests of mechanical and physical characteristics. Decrease of mechanical strength seems to be gradual, but not very accentuated. This decrease does not jeopardize the use of mortars with adequate strength for application in conservation practice (Veiga, 2003).. Furthermore, these mortars seem to attain high durability and capability to endure salt decay, since mortars with pozzolanic additives that were applied in construction in Portugal seawater sustained in good condition.

The influence of humidity and initial conditions on the development of strength of mortars with pozzolanic additives seems very significant. Knowledge of the evolution of strength with time and the curing conditions that are possible to obtain in actual work must be taken into account when prescribing the application of these kinds of mortars as renders.

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