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Three-way ANOVA interaction analysis and ultrasonic testing to evaluate air lime mortars used in cultural heritage conservation projects

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Abstract

Lime mortar has been used throughout history despite current substitution by hydraulic mortars (cements). The chemical composition of the lime used in its manufacture, however, is determined by local geology. In addition, the type of slaking, which depends on the amount of water used, gives rise to different types of lime. The result is that the behavior of lime mortar can vary depending on the composition and type of lime used. A three-way ANOVA analysis was carried out to determine the composition, type, and temporal evolution and the interactions of these three variables for evaluation of the characteristics of air lime mortars for their use in cultural heritage conservation projects.

Keywords: Air lime mortars; Cultural heritage; Ultrasound test; ANOVA; Portlandite/calcite

1. Introduction

When carrying out a cultural heritage conservation project on highly degradable materials, the ideal course of action is to replace the damaged material by another of the same or similar characteristics. In practice, however, this can be quite complicated when traditional materials such as lime mortars are involved, because knowledge of them and their preparation have fallen into disuse. Currently, these mortars are substituted by hydraulic binders (cement), which have very different properties.

Lime mortars are commonly examined using analytical techniques such as X-ray fluorescence (XRF), inductively coupled plasma-mass spectrometry (ICP-MS), X-ray diffraction (XRD), optical microscopy [1], and mechanical tests [2]. The technique employed in this study, ultrasonic waves, has also been used in such analyses [3]; it counts among its advantages the fact that it is a nondestructive technique, easily managed and interpreted; it also enables the capture of a large number of measurements without great effort in a short period of time, which allows a better evaluation of the results obtained. This technique was used here to study the behavior of lime mortars over time in relation to their carbonation and subsequent use in the conservation of cultural heritage edifications.

The carbonation process in lime mortars is characterized by an increase in the velocity of the longitudinal ultrasonic waves in positive correlation to the degree of compactness. Therefore, the greater the longitudinal velocity, the greater the decrease in the total anisotropy of the samples (ΔM). There is thus an equivalence between the carbonation process and the anisotropy variation. Therefore, in the present case carbonation gives rise to a decrease in the anisotropy, attributable to the total anisotropy of the sample (ΔM) as a consequence of the transformation of lime (Portlandite, $Ca(OH)_2$, to calcite, $CaCO_3$) by the diffusion of CO_2 through the pore system. Four different types of traditional mortars were examined. The aim of this study was to determine what mortar (taking into account its composition and type) is suitable (greater rate of carbonation, i.e., $<\Delta M$) to use in cultural heritage conservation projects. Right after unmolding, the mortars were analyzed to determine the similarities and differences between them. The use of ANOVA techniques [4] in this context, when used on an exhaustive data set, can provide valuable information on the behavior of mortars.

2. Methods

The four types of mortars have been designated as CPS, CNS, DPS, and DNS, in accordance with the composition of the lime (C, calcitic; D, dolomitic), the type of lime (P,

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powder; N, putty), and the aggregate used (in this case, S refers to a siliceous aggregate).

The mortars were mixed by hand in the traditional manner [5] and standardized test samples were formed (4 × 4 × 16 cm). Siliceous aggregate was used in all the mortars. Binder-to-aggregate proportions were 1:3 and tapwater-to-mix portions were 1:1. Prior to preparation, the lime was kept at 18 ± 5°C and 60 ± 5% relative humidity.

Randomly oriented crystalline powder was used to identify the mineral phases in the materials employed in production of the mortar. The samples were ground in an agate mortar and sifted to obtain the fraction under 50 μm. The powder obtained was mounted on an aluminum support. The zone recorded was between 3 and 60° (2θ), using a Phillips PW 1710 diffractometer equipped with an automatic slit (Holland). The control and analysis of the XRD was carried out with a PLV software (J.D. Martín Ramos, Granada, Spain) [6].

The characteristics of the individual components were as follows:

Aggregate: This component is a filler, stabilizing the volume and reducing shrinkage during drying. In this case, we have used a natural siliceous aggregate that does not react with lime; it has rounded grains with a quartz content of at least 98%, and normalized grain size and sand UNE 80-101-88/CEN EN 196-1.

Lime: The binder occurs as $Ca(OH)_2$, or Portlandite, characterized by hardening in air upon contact with atmospheric CO_2, being transformed to $CaCO_3$, which hardens to the mortar over time. Four types of lime were employed. (1) powdered calcitic lime (Málaga, Spain): This is an industrial lime with a limited amount of water used in the manufacturing process. Its mineralogical composition is essentially Portlandite $Ca(OH)_2$ with traces of calcite $CaCO_3$ (Fig. 1a). (2) Calcitic lime putty (Málaga, Spain): This is an industrial lime hydrated with free water, a high content of Portlandite $Ca(OH)_2$, and traces of calcite $CaCO_3$ (Fig. 1b). (3) Powdered dolomitic lime (Sefrou, Morocco): This is an industrial quicklime with more than 5% magnesium. It contains Portlandite, $Ca(OH)_2$, brucite, $Mg(OH)_2$, periclase, MgO, and calcite, $CaCO_3$. The presence of the last three compounds indicates poor sintering and incorrect industrial slacking (Fig. 1c). (4) Dolomitic lime putty (Granada, Spain): Lime sold in lumps as quicklime and slaked in the laboratory with free water. Magnesium content is over 5%. It is comprised of Portlandite [$Ca(OH)_2$], calcium (CaO), and magnesium (MgO) oxides, and calcite ($CaCO_3$) (Fig. 1d).

The velocity of the propagation of ultrasound pulses was measured by direct transmission using a Steinkamp BP-5 ultrasound device (Germany) (wave frequency 100 kHz). This data was used to obtain information on the degree of compactness of the mortars as their carbonation advances as

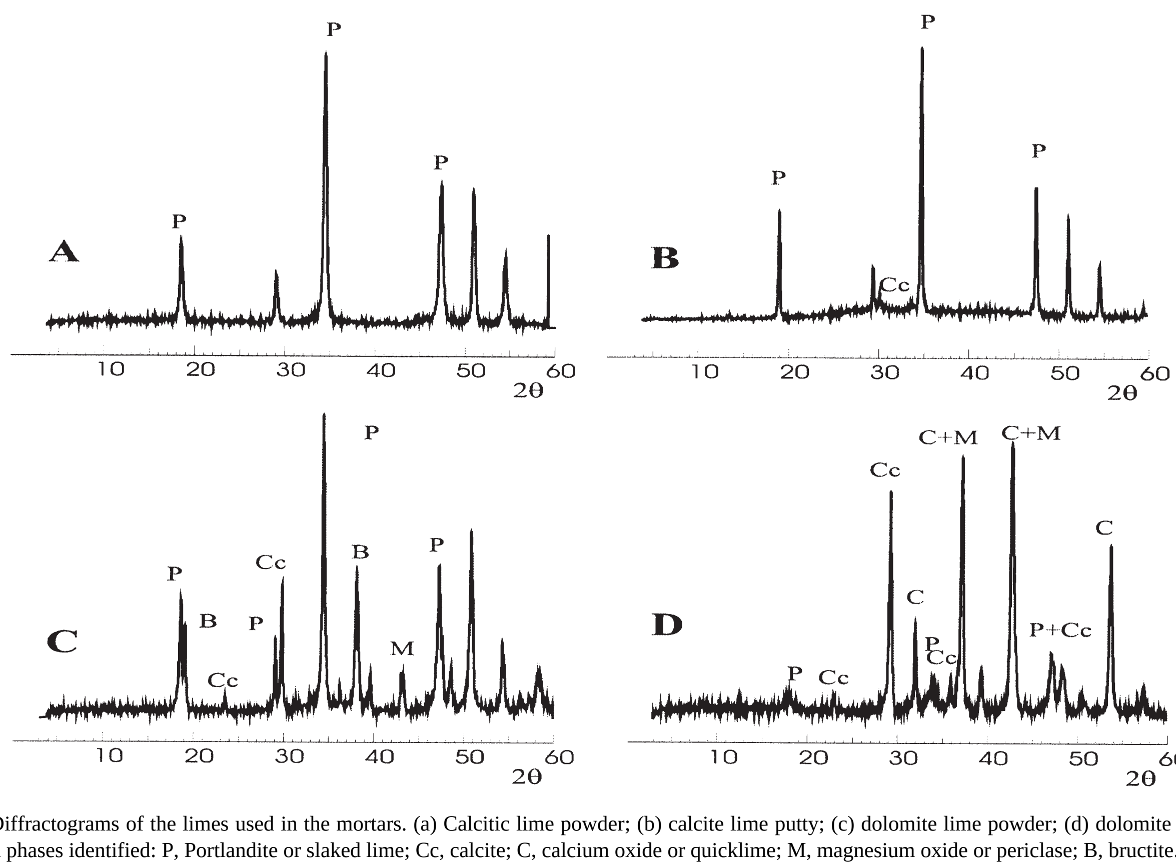

Fig. 1. Diffractograms of the limes used in the mortars. (a) Calcitic lime powder; (b) calcite lime putty; (c) dolomite lime powder; (d) dolomite lime putty. (Mineral phases identified: P, Portlandite or slaked lime; Cc, calcite; C, calcium oxide or quicklime; M, magnesium oxide or periclase; B, bructite.)

a function of time. Measurements were carried out on three test samples for each series of mortars, corresponding to different mixtures. The values calculated, summarized in Table 1, were V_1 (velocity of longitudinal waves perpendicular to the direction of compaction, 4 cm), V_2 (velocity parallel to the direction of compaction across the length of the test sample, 4 cm), and V_3 (velocity parallel to the direction of compaction along the length of the test sample, 16 cm), expressed as $m \cdot s^{-1}$. ΔM (total anisotropy in %) [3] was calculated from 60 measurements for each of the above set of velocities, using Eq. (1):

$$\Delta M = 100\left[1 - \frac{2V_1}{(V_2 + V_3)}\right] \quad (1)$$

The values obtained depend on the mineralogical composition (different densities of aggregate and lime), intercrystalline relations, water content, and volume of pores and fissures in the mortars.

In addition, the use of analysis of variance (ANOVA) models provides the user with a statistically based technique capable of producing meaningful models on the importance of the factors studied in the experiment [7]. Apart from this, ANOVA allows possible factor interactions within the data set that may have a bearing on the temporal evolution of the lime-mortar composition to be studied. The use of modelling in this context has proved to be highly relevant due mainly to the opportunity of finding the most suitable mortar for use in cultural heritage interventions.

A three-way ANOVA analysis using Statgraphics 6.0 (Statistical Graphics Corporation, Rockville, MD, USA) was selected to investigate factor effects (composition, type, and time) and interactions among them. The statistical data obtained correspond to the total anisotropy of each mortar type. The measurements were made at intervals of 10, 28, 49, 63, and 180 days. Taking into account the composition (C, D) and the type of lime (P, N), the aim was to determine which mortar provides the least total anisotropy (i.e., the fastest carbonation rate) and to observe the differences and similarities between these mortars over time.

3. Results and discussion

A three-way ANOVA analysis was selected to investigate the effects of different factors (composition, type, and time) and their interactions on total anisotropy (ΔM). Table 2 summarizes the ANOVA results. Note that the main effects due to the composition and type are statistically significant ($p < 5\%$). Nonetheless, the principal effect due to time is not significant ($p = 6\%$) although the average for $t = 63$ days is higher than the averages for other time intervals.

In the second-order interactions, the composition and type of interaction is significant ($p < 5\%$). This is reflected in the very different behavior of the mortars prepared with either powdered lime or lime putty (the latter always performing better due to less structural anisotropy, regardless of composition) (Fig. 2a). The interaction between composition and time is also significant ($p < 5\%$). A greater progression in the slaking process of the dolomitic lime can be

Table 1
Linear velocities of the propagation of the ultrasound pulses (V_1, V_2, and V_3; m/s), standard deviations (s), and total anisotropy (ΔM; %) values used in ANOVA analysis

	10 days	28 days	49 days	63 days	180 days
CPS					
V_1	796.25	1,337.28	1,503.27	1,517.37	1,682.36
s	70.34	85.94	85.54	85.01	100.39
V_2	1,058.68	1,646.57	1,750.66	1,774.45	1,880.85
s	70.14	73.97	80.88	88.08	106.50
V_3	953.10	1,513.97	1,495.73	1,701.60	1,870.47
s	78.19	79.68	155.82	107.78	54.38
ΔM	21.00	16.00	8.00	13.00	10.04
CNS					
V_1	1,446.67	1,554.41	1,613.41	1,823.86	2,093.81
s	37.22	22.38	88.08	261.75	6.93
V_2	1,500.71	1,677.87	1,722.34	1,828.25	2,024.41
s	31.63	64.12	93.27	0.37	19.62
V_3	1,475.98	1,584.47	1,511.62	1,703.85	2,167.21
s	73.39	158.91	118.55	416.88	120.87
ΔM	2.00	5.00	1.00	3.29	0.10
DPS					
V_1	1,037.92	1,321.88	1,413.41	1,446.13	1,881.59
s	36.55	55.22	33.68	25.46	149.85
V_2	1,110.58	1,379.26	1,460.10	1,419.76	1,944.64
s	21.82	67.89	40.71	30.48	93.73
V_3	938.67	1,178.26	1,108.38	1,098.96	1,821.07
s	20.10	88.05	59.06	84.48	100.84
ΔM	1.29	3.52	10.05	14.85	0.10
DNS					
V_1	1,202.46	1,707.09	1,677.89	1,772.88	2,160.23
s	139.91	114.08	24.97	64.95	65.31
V_2	1,304.92	1,798.81	1,775.76	1,882.58	2,275.26
s	112.44	55.17	31.39	10.02	64.09
V_3	1,234.06	1,710.23	1,606.45	1,594.86	2,311.97
s	145.49	154.66	238.01	33.22	86.73
ΔM	5.30	3.00	0.80	1.96	5.90

Table 2
Multiple analysis (least significant difference method, 95%)

Factor	Level	Count	LS mean	p value (%)	Homogeneous groups[a] Source		Type		Time	
Source[b]	C	30	6.075	0.20	X					
	D	30	8.554			X				
Type[c]	P	30	10.445	0.00			X			
	N	30	4.184					X		
Time	180	12	5.968	6.05					X	
	49	12	6.572						X	
	28	12	6.792						X	
	10	12	7.955						X	X
	63	12	9.288							X

[a]Off-set columns denote a statistically significant difference.
[b]C, calcitic; D, dolomitic.
[c]P, powder; N, putty.

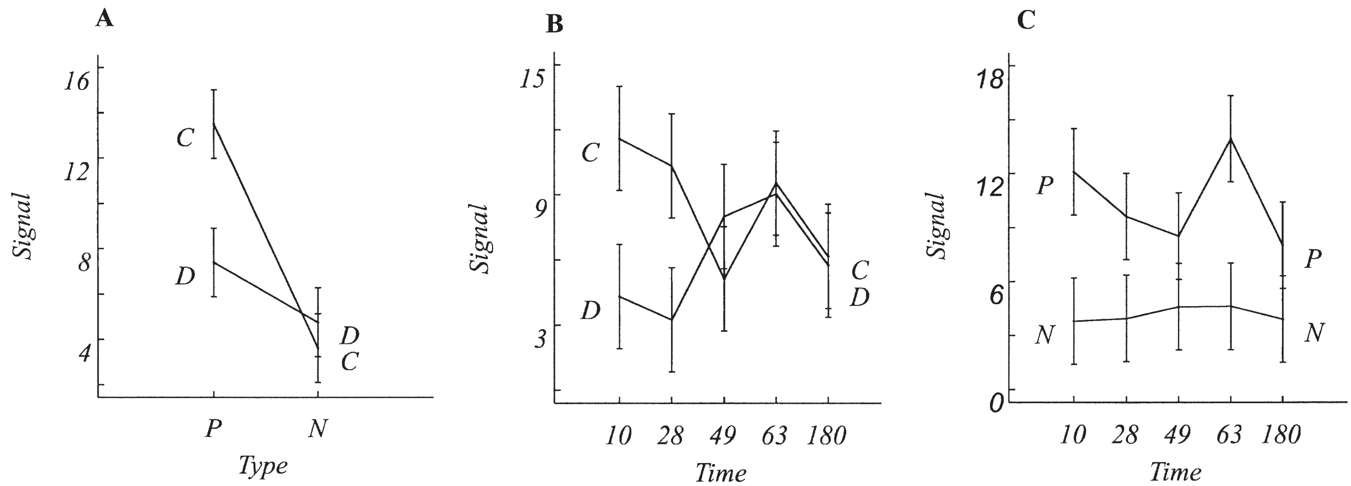

Fig. 2. Two-factor interactions of the variables studied. (a) Source-type interaction; (b) source-time interaction; (c) type-time interaction.

deduced in this case for the intervals studied (Fig. 2b). This result is surprising since dolomitic lime, according to most researchers [8], is characterized by slower slaking than calcitic lime. The type-time interaction is not significant ($p >$ 5%), with lime putty showing better behavior (Fig. 2c).

In all, the carbonation process of the lime mortars studied during the 6 months subsequent to their preparation is determined both by the composition and the type of lime used. The best results were obtained with lime putty, which was almost always the dolomitic type. Therefore, the hardening rate of the mortars prepared is (in descending order): DNS, CNS, DPS, and CPS. These results are corroborated by the findings of researchers using other analytical techniques (XRD, optical microscopy, phenolphthalein test, hydric test, mechanical test, etc.) [9].

4. Conclusions

The combination of the two techniques of nondestructive ultrasound analysis and ANOVA offers an interesting alternative in the study of the temporal evolution of the diverse materials used in the preservation of cultural heritage and, by extension, in modern construction. This combination allows the technical quality of the materials employed to be contrasted quickly and inexpensively. In our opinion the techniques and method presented could be used to research analogous properties in other construction materials such as bricks and wood, among others.

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References

[1] S.Z. Lewin, Symposium International Centre for the Study of the Preservation and the Restoration of Cultural Property, Rome, 1981, p. 101.
[2] Asociación Española de Normalización (AENOR), Normas UNE 83821, 1992.
[3] U. Zezza, Physical-mechanical properties of quarry and building stones, in: Advanced Workshop: Analytical Methodologies for the Investigation of Damaged Stone, F. Veniale, U. Zezza (Eds.), Pavia University, Pavia, Italy, 1990.
[4] D.L. Massart, B.G.M. Vandeginste, S.N. Deming, Y. Michotte, F. Kaufman, Chemometric: A Textbook, Elsevier, Amsterdam, 1988.
[5] E. Sebastián Pardo, O. Cazalla Vázquez, M.J. de la Torre López, C. Rodriguez Navarro, I. Valverde Espinosa, U. Zezza, IV Congreso Internacional de Rehabilitación del Patrimonio Arquitectónico y Edificación, La Habana, Cuba, 1998, p. 491.
[6] P.L.V. 2.01, Programa de control y análisis del difractómetro de rayos X, J.D. Martín Ramos Dep. Leg. M-11719, 1995.
[7] J.C. Miller, J.N. Miller, Estadística para Q. Analítica, 2d ed. (Spanish translation), Eddison-Wesley Iberoamericana, S.A. Wilmington, Delaware, 1993, p. 51.
[8] O. Cazalla Vázquez, E. Sebastián Pardo, M.J. de la Torre López, C. Rodriguez Navarro, I. Valverde Espinosa, U. Zezza, IV Congreso Internacional de Rehabilitación del Patrimonio Arquitectónico y Edificación, La Habana, Cuba, 1998, p. 227.
[9] F. Arredondo, F. Soria, Estudio de materiales, in: Tomo I, S.P. Mopu (Ed.), Revista de O. Públicas, Madrid, 1983, p. 589.