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Correlation of physicochemical and mechanical properties of historical mortars and classification by multivariate statistics

A. Moropoulou*, K. Polikreti, A. Bakolas, P. Michailidis

Department of Chemical Engineering, National Technical University of Athens, Zografou Campus, 9 Iroon Polytechniou Street, Athens 157 73, Greece

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Abstract

This work uses multivariate statistics in an attempt to classify historical mortars in more or less distinct groups, depending on their physicochemical characteristics. Four types of mortars are studied: "typical lime," "cementitious," "crushed brick" and Portland cement. Fifty samples in total were analysed by thermal analyses (differential thermal analysis [DTA] and thermogravimetric analysis [TGA]), mercury intrusion porosimetry and mechanical strength tests. The results give us useful information on the understanding of the technology of historical mortars and planning syntheses for restoration ones. The inverse hydraulicity ratio (CO_2/structurally bound water, SBW) is correlated to CO_2 content (%) as measured by thermal analysis. The tensile strength increases with the amount of hydrated phases and the mechanical properties of the aggregate and the binder. Medians, ranges and extremely rare values were determined for each property showing compact groups. These groups were discriminated by principal component analysis (PCA) giving a tool for characterisation of historical mortars.

Keywords: Historical mortars; Principal component analysis; Classification; Mercury porosimetry; Thermal analysis

1. Introduction

The term *historical* is used for all types of mortars produced before the end of 19th century, when the Portland cement first appeared in building constructions. Historical mortars are composite materials formed by a binder (hydraulic or aerial lime), a variety of inert materials (silicate, carbonate, or dolomite sand) and some additives (finely ground bricks, volcanic pozzolans etc.) for improving adhesion, workability, strength or durability. In several cases, these mortars present high durability and remarkable resistance to weathering factors [1]. Well-documented examples are the mortars of the basilica of Agia Sophia, Istanbul, Turkey [2] or those from Byzantine monuments in the island of Crete, Greece [3].

The physicochemical and structural study of historical mortars gives invaluable information about their production technology, their expected behavior and possible replacement during restoration works [4]. The production of restoration mortars compatible with the original ones, in aesthetic and functional terms, is very difficult to be standardised. This is inevitable because of the great variety in a large umber of factors: the original mixture, the type of the building blocks, the acting environmental factors (rising humidity, pollution, sea spray etc.) and the aesthetic demands of the particular monument to be restored. Guidelines for constructing compatible mortars do not exist yet [5,6]. Recommendations are still in the form of limits of acceptance in physical and mechanical properties, drying behavior, resistance to salt crystallisation etc. [7,8].

All the discussed evidence, i.e., the high durability of the historical mortars, the difficulty in defining certain rules and guidelines in the preparation of restoration mortars and the need for compatibility lead us to deduce that the more we know about the original historical mortars, the more easily we can reach a decision on the mortar synthesis we need for a specific application. Towards this direction, this work uses multivariate statistics in an attempt to classify historical mortars in more or less distinct groups, depending on their physicochemical characteristics. This is a meticulous job because although the chemical composition and granulometry may be similar, the induced texture, microstructure and type of adhesion bonds are occasionally totally different [9].

* Corresponding author. Tel.: +30-2-10-722-1433.

E-mail address: amoropul@central.ntua.gr (A. Moropoulou).

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Principal component analysis (PCA) has been used by Giuffrida et al. [10] for discriminating mortars between bricks from mortars for covering plasters and mortars used for painted plasters. Continuing this first attempt, Musumarra et al. [11] distinguished mortars used in the Gothic painting from those used in the Flemish one, in Chiaravalle Abbey. Both works used the results from the determination of the percent acid-soluble component and of the aggregate granulometric distribution.

The present work uses PCA in order to classify historical mortars from Byzantine and Ottoman monuments in groups with respect of their thermal analysis results, microstructural characteristics and mechanical strength.

2. Materials and methods

The samples used in this work were chosen from a large number of mortar samples analysed during the last 10 years, so as to cover four mortar types: "typical lime," "crushed brick-lime," "cementitious" mortars and Portland cement. Gypsum and hot-lime technology mortars were not included in this study because they were only rarely found on Byzantine and post-Byzantine monuments. The definition of the previous groups has been given elsewhere [12] but will be summarised here for clarifying the type of the used samples. The group of "typical lime" mortars (TL) includes mixtures consisting mainly of calcite ($\sim$80%) and quartz. The binding material is finely crystallised calcite. The aggregates are mainly calcitic consisting of microfossils and coarse clastic quartz grains. The group of "crushed brick-lime" mortars (CBL) includes mixtures of an exclusively calcitic, binding material with finely ground bricks. This technology spans from early Byzantine to Venetian and late Ottoman periods and gives mortars with excellent pozzolanic properties due to the adhesion reactions at the ceramic–matrix interface. "Cementitious" mortars represent "opus caementicium" of Vitruvius, which was described as an artificial conglomerate of gravel with sand, lime and pozzolana (volcanic earth). The basic silicates are formed by burning and then hydrolysed by water, yielding lime and hydrated silicates. The last two groups belong to the so-called pozzolanic mortars. Two samples of Portland cement will also be presented for comparison. All samples used here were mortars between bricks, carefully collected for avoiding weathering of any type. In order for the correspondence between mortar type and physicochemical properties to be meaningful and reliable, the collected samples show similarities in grain size distribution. All samples show a more or less symmetric distribution around the range of 0.25 mm, a fact that, in terms of weight percentage, gives about 25% of the total weight to the fine fraction ($<$0.038 mm).

The mortars were analysed by thermogravimetric and differential thermal analyses, mercury porosimetry analysis and mechanical strength tests. The results are given in Table 1, together with their mineralogical composition (XRD data presented in Ref. [12] were obtained with a Siemens D-500 diffractometer and Diffract—EVA software). The thermal analysis was performed with a Mettler TG 50, thermobalance, thermal analyser system. In parallel to the thermogravimetric analysis (TGA), differential thermal analysis (DTA) was performed with a Perkin-Elmer thermoanalyser TG S-2 and DTA 1700. These recordings done together give the temperature of the phase transformations occurring in the mortar, the quantity of the transformed substance and the heat balance of each transformation.

Given the fact that the majority of pores in these mortars is expected to be in the macropore region, mercury intrusion porosimetry was considered a satisfactory technique for determining basic structural characteristics, such as pore size distribution, surface area and pore volume. A Carlo Erba 4000 mercury porosimeter was used for porosimetry measurements and the cylindrical mathematical model was employed to elaborate the results. From all the parameters obtained by mercury porosimetry, only total porosity (%) will be used in the statistical treatment followed in the following paragraphs.

In order to overcome the difficulty to take and test adequately large mortar samples from historical monuments, a special method named "fragment test" has been developed in the Laboratory of Reinforced Concrete (National Technical University of Athens) for the determination of the tensile strength [13]. Mortar fragments are arranged in a special mould within a strong matrix (an epoxy resin or a much stronger mortar). An easily applied direct-tension test is then carried out, giving tensile strength values ($F_{mt,fr}$) lower than those of the intact mortar specimens ($F_{mt,fr} < 0.70\ F_{mt,int}$). Double tests were done for each mortar to ensure the statistical significance of the results.

The results of analyses were treated by PCA. PCA is a technique used to reduce the number of parameters obtained by experimental data in a way that minimises the loss of information. It relies on the fact that most of the parameters are intercorrelated. From a set of N correlated parameters, we can derive a set of N uncorrelated parameters (the principal components, PCs). Each PC is a suitable linear combination of all the original parameters. The first PC accounts for the maximum variance (eigenvalue) in the original data set, the second is orthogonal (uncorrelated) to the first and accounts for most of the remaining variance and so on. Once the N PCs have been calculated using eigenvalue/eigenvector matrix operations, only PCs with variances above a critical level are retained. The M-dimensional principal component space has retained most of the information from the initial N-dimensional descriptor space, by projecting it onto orthogonal axes of high variance [14]. The complex tasks of prediction or classification are made easier in this compressed space. In our case, if PCA gives satisfactory results, discriminant analysis could be used in

Table 1
Thermal analysis and porosimetry results, strength values and mineralogical composition of the analysed samples

Sample	SBW (%)	CO_2/SBW	CO_2 (%)	Porosity (%)	Tensile strength (MPa)	Mineralogical composition[a]
Lime mortars						
Agarathos1	3.02	11.1	33.46	44.46	0.32	Cc, S
Arkadi1	3.13	11.6	36.31	32.70	0.32	–
Toplu5	2.86	13.3	38.01	46.20	0.14	Cc, S
Metochi4	2.90	11.1	32.16	38.55	0.30	Cc, S
Rhodes1	2.82	10.8	30.50	43.90	0.27	Cc, S, Do
Rhodes2	2.99	10.4	31.21	33.40	0.33	Cc, S, Pg, Msc, Chl
Rhodes3	2.93	11.2	32.82	45.75	0.37	Cc, S, Pg, Msc, Chl
Rhodes4	2.02	16.1	32.45	40.60	0.25	Cc, S, Do
Agarathos3	3.40	11.9	40.34	34.69	0.20	–
Agarathos4	2.76	15.9	43.78	42.10	0.27	Cc, S
Agarathos7	3.21	11.6	37.11	39.30	0.31	Cc, S
Portland						
Metochi6	14.05	2.72	17.14	27.53	0.67	Prt, Cc, S, K
Rhodes34	12.06	2.46	17.97	30.62	0.61	Prt, Cc, S, K
Cementitious						
Kerkyra1	6.51	3.1	20.21	42.84	0.45	Cc, S, CASH, Il
Kerkyra2	12.67	1.0	12.08	29.80	0.52	Cc, S, Pg, $C_{1.1}SH_{2.1}$
Kerkyra3	6.61	2.0	13.10	28.50	0.50	Cc, S, CASH
Arkadi2	8.83	1.7	14.92	41.56	0.45	Cc, S, Msc, Chl, Pg, CAH
Preveli1	5.40	2.3	12.67	33.16	0.55	Cc, S, Msc, Chl, Pg, CAH
Preveli2	5.87	5.2	30.40	33.27	0.44	S, Cc, Msc, Pg, Chl, CAH
Preveli3	8.04	2.1	17.23	41.54	0.37	–
Chrysopigi1	11.38	1.3	14.79	32.48	0.54	Cc, S, CASH, Il
Agarathos2	3.77	6.1	22.88	40.04	0.47	Cc, S, Msc, Chl, Pg, CAH
Toplu6	5.38	3.3	17.65	32.84	0.51	Cc, S, CASH
Rethymno1	5.56	2.7	15.24	23.79	0.52	–
Rethymno2	4.13	2.7	11.23	34.16	0.53	Cc, S, Msc, Chl, Pg, CAH
Rethymno3	6.37	4.0	25.66	25.46	0.54	S, Cc, Msc, Pg, Chl, CAH
A. Sophia1	7.56	1.5	11.67	35.49	0.53	Cc, S, Pg, $C_{1.1}SH_{2.1}$
Rhodes5	10.51	1.9	19.65	42.76	0.42	–
Rhodes6	15.59	0.8	12.32	38.18	0.51	S, Cc, Msc, Pg, Chl, CAH
Rhodes7	15.04	0.9	12.93	21.52	0.51	–
Agio Oros6	12.93	1.1	14.32	36.46	0.45	S, Cc, Msc, Pg, Chl, CAH
Agio Oros1	10.12	1.2	11.97	27.76	0.53	Cc, S, Pg, $C_{1.1}SH_{2.1}$
Agio Oros2	4.34	3.9	17.10	31.12	0.50	S, Cc, Msc, Chl, Pg, Tb
Agio Oros3	6.32	1.8	11.52	34.71	0.46	Cc, S, CASH
Crushed brick						
Toplu7	6.47	1.6	10.25	25.13	0.65	Cc, S, Pg, $C_{1.1}SH_{2.1}$
Metochi5	6.31	3.6	22.65	45.19	0.57	Cc, S, Pg
Rhodes10	3.74	9.1	33.85	38.79	0.57	Cc, S, Pg, $C_{1.1}SH_{2.1}$, CAH, CACH, Tb
Rhodes11	4.85	6.2	30.14	40.20	0.62	Cc, S, Do, Pg, Msc, Tc, CACH, Tb
Rhodes12	4.40	6.2	27.09	42.80	0.55	Cc, S, Pg, Tb, $C_{1.1}SH_{2.1}$
Rhodes14	5.20	6.0	31.12	43.52	0.57	Cc, S, Pg, $C_{1.1}SH_{2.1}$, Msc
Rhodes15	4.91	4.6	22.73	46.10	0.64	Cc, S, Pg
A. Sophia1.2	4.78	4.1	19.45	35.62	0.59	Cc, S, Pg, $C_{1.1}SH_{2.1}$, Mnt
A. Sophia2.2	4.75	2.3	11.01	41.67	0.52	Cc, S, Pg, $C_{1.1}SH_{2.1}$, Mnt
A. SophiaW2	3.52	4.0	13.99	37.90	0.59	Cc, S, Pg, $C_{1.1}SH_{2.1}$
A. Sophia3.1	5.18	2.4	12.67	35.39	0.63	Cc, S, Pg, CAH
A. Sophia3.2	4.31	2.6	11.18	32.71	0.57	Cc, S, Pg, CAH
A. Sophia4	3.79	3.3	12.35	42.12	0.57	Cc, S, Pg, $C_{1.1}SH_{2.1}$
Toplu8	5.21	3.3	17.00	26.94	0.58	–
Rhodes16	6.12	2.6	15.98	29.67	0.52	Cc, S, Pg, $C_{1.1}SH_{2.1}$, Msc
Rhodes17	5.10	3.0	15.20	32.16	0.64	Cc, S, Do, Pg, Msc, Tc, CACH, Tb
Rhodes20	4.76	5.5	26.23	38.60	0.52	Cc, S, Pg, $C_{1.1}SH_{2.1}$, Msc
Rhodes21	5.67	4.3	24.48	42.37	0.53	Cc, S, Pg, Tb, $C_{1.1}SH_{2.1}$

[a] Cc = calcite; S = silica; Dol = dolomite; Pg = plagioclase; Pt = portlandite; Chl = chlorite; Ms = muscovite; Tobe = tobermorite; Mm = montmorillonite; Tlc = talc; Ill = illite; Kao = kaolinite; CAH = calcium aluminate hydrate; $C_{1.1}SH_{2.1}$ = pozzolanic C-S-H; CACH = tetracalcium aluminate carbonate; CASH = calcium aluminum silicate hydrate.

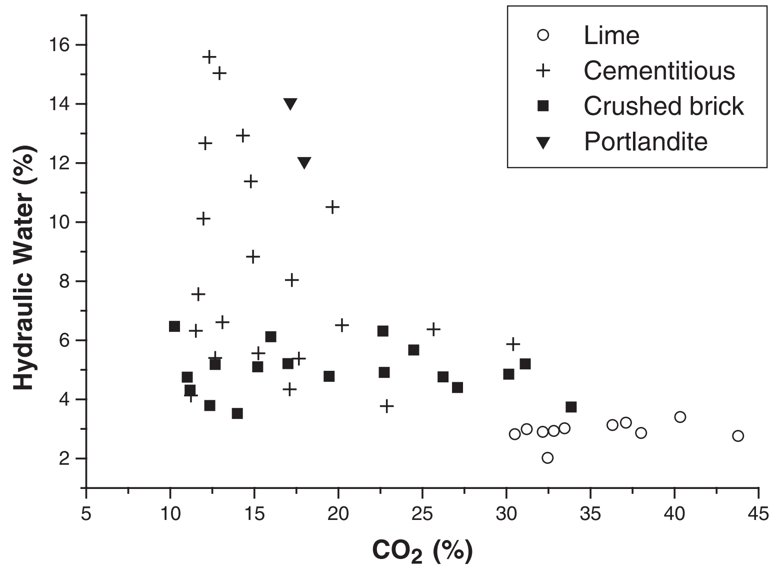

Fig. 1. SBW versus CO_2.

order to find one or more functions for predicting the mortar type, given its physicochemical properties.

3. Results and discussion

3.1. Correlation among microstructural, thermal and mechanical characteristics

The structurally bound water (SBW) values shown in Table 1 represent the percentage of the weight loss between 200 and 600 °C in thermal analysis. The so-called pozzolanic peaks in this region are attributed to water bound to the several calcium aluminum silicate hydrates (CSH, CAH, Tb, CACH). The CO_2 values indicate the percentage of weight loss at temperatures near 750 °C, corresponding not to pure $CaCO_3$ (which decomposes at higher temperatures) but to recarbonated lime, which includes some cementitious material in case the original limestone contains suitable clay minerals.

The water bound to hydrated components in relation to CO_2 as measured by thermal analysis is shown in Fig. 1. All typical lime mortars show a percentage of water bound to "hydraulic" components lower than 3% and are well separated from the pozzolanic mortars. The pozzolanic mortars (crushed brick and cementitious) can be distinguished in two groups: one with over 8% of SBW content, where the more condensed and higher strength mortars are identified and another subgroup with less than 6% of SBW. This latter subgroup consists of cementitious and

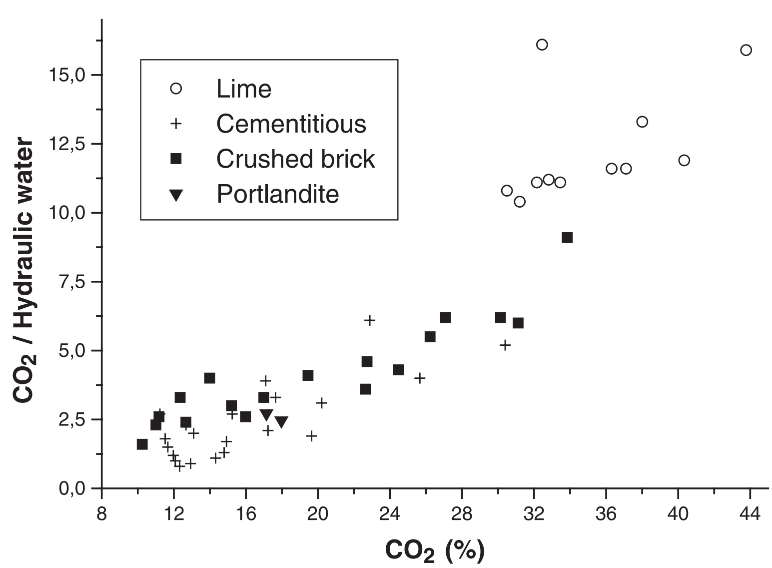

Fig. 2. Inverse hydraulicity ratio versus CO_2 percentage.

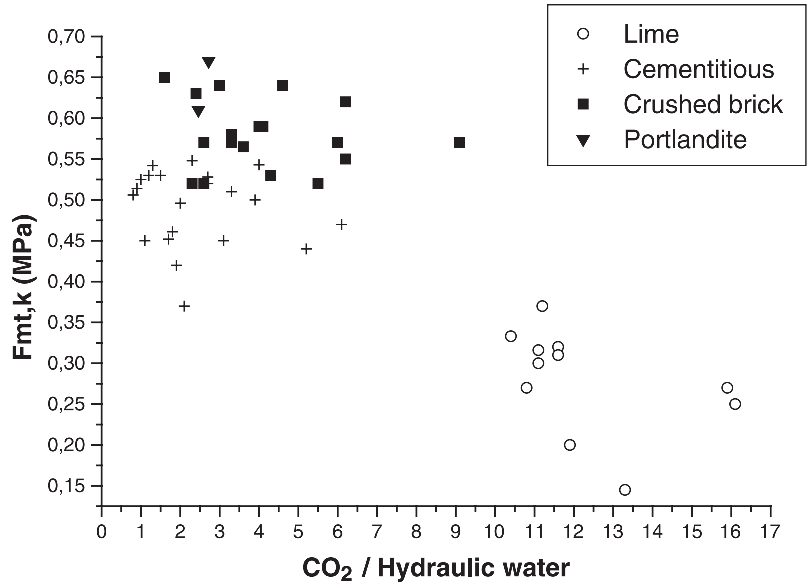

Fig. 3. Tensile strength versus inverse hydraulicity.

crushed brick mortars. The large variation in SBW contents exhibited by the cementitious mortars, reflects both different mixes (gravel/sand/lime ratios) and technology of production (different conditions during the burning–hydrolysis process). It seems that all samples with SBW values higher than 8% are cementitious, those with a content between 4% and 7% are crushed brick or cementitious and finally those with contents lower than 4% are crushed brick, cementitious or typical lime. The reasons of such classification are not obvious. The different amounts of bound water can be due to different percentages of the same hydrated phase or to prevailing of more or less water-rich hydrated phase. More experimental evidence is needed towards this direction. Besides, the typical lime mortars are discriminated from the pozzolanic ones by the weight loss due to CO_2 release, which is an expression of the weight percentage of $Ca(OH)_2$ in the initial mixture [15].

The same results are seen in Fig. 2, where the ratio of CO_2/SBW, which inversely expresses the hydraulic character of the mortar in relation to the CO_2 values. The inverse trend of hydraulicity seems to decrease exponentially with CO_2. The cementitious mortars are concentrated at the bottom, the crushed brick in the middle and the typical lime mortars at the upper right part of the figure, with CO_2/H_2O>10% and CO_2>30%.

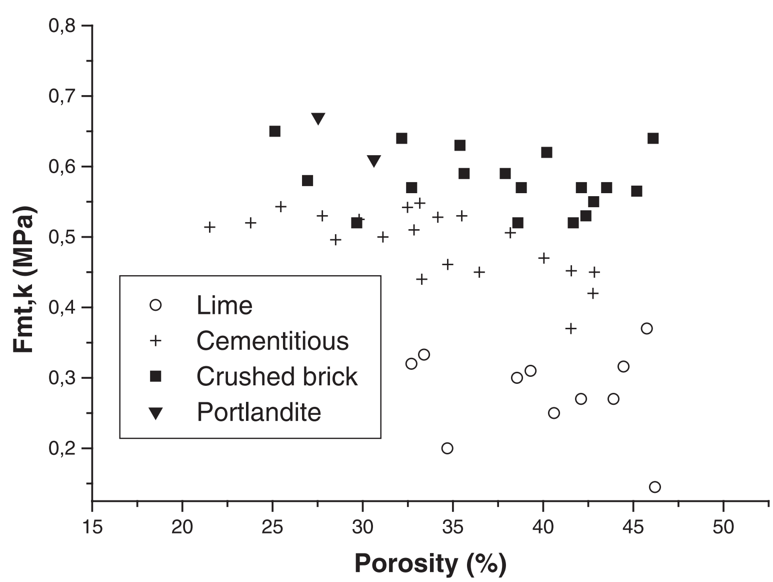

Fig. 4. Tensile strength versus porosity.

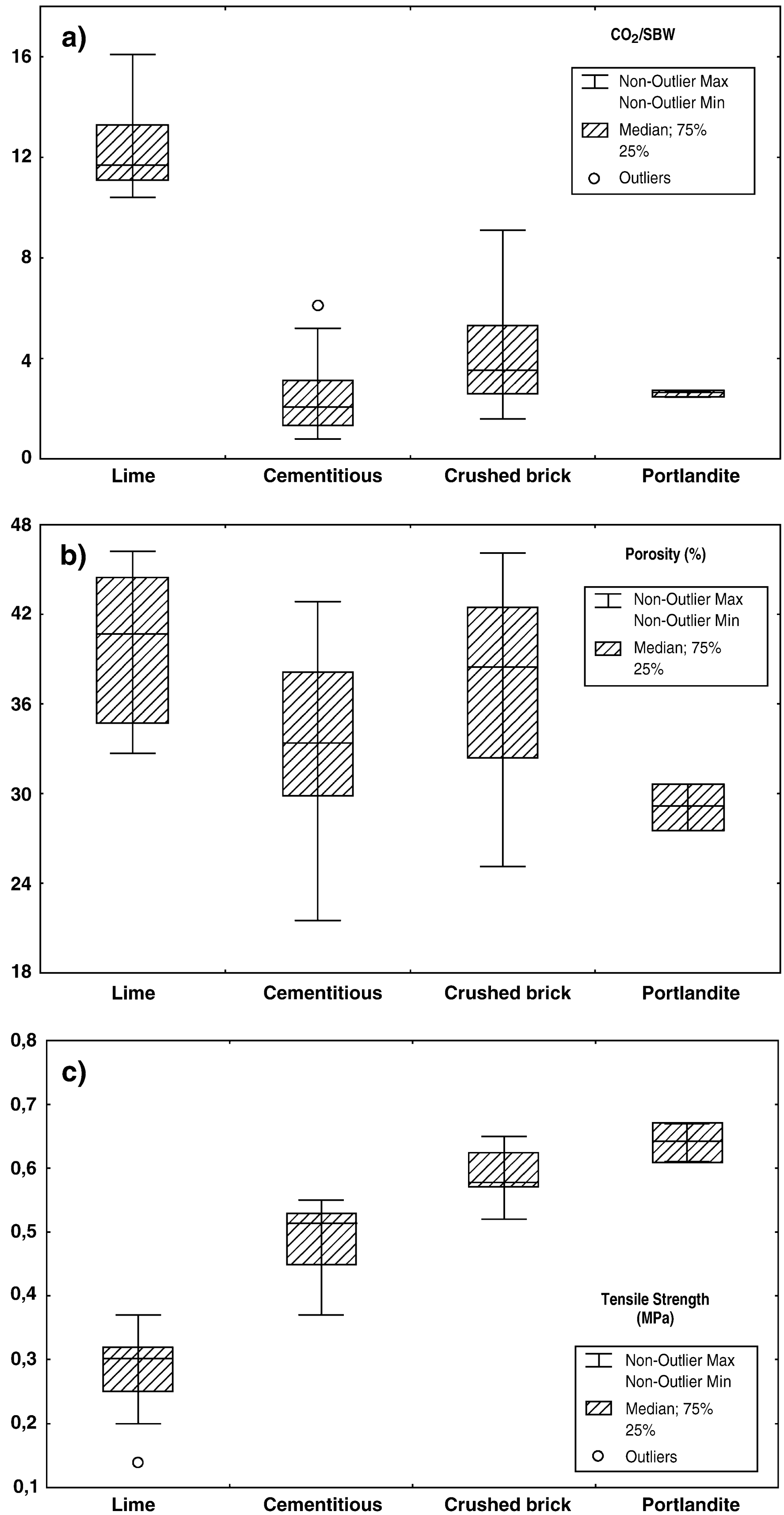

Fig. 5. Boxplots for (a) inverse hydraulicity ratio, (b) porosity and (c) tensile strength.

Fig. 3 shows the tensile strength versus the inverse hydraulicity ratio. Low values of inverse hydraulicity (i.e., for mortars presenting high hydraulicity) correspond to high values of tensile strength and vice versa. Following the classification deriving from thermal analysis, we observe a sequence of $f_{mt,k}$ values:

– for lime mortars, $f_{mt,k} < 0.40$ MPa
– for cementitious mortars, $0.35 < f_{mt,k} < 0.55$ MPa
– for crushed-brick mortars, $f_{mt,k} > 0.50$ MPa
– for Portland cement, $f_{mt,k} > 0.60$ MPa

As expected, there is a distinct increase in strength with an increase in the amount of hydrated phases in the binder. The observed variations mainly result from the differences in the binder/inert ratios for the examined mortars. Another assumption needed, in order to deduce that the measured tensile strength of the mortars is proportional to their level of hydraulicity, is that aggregates of calcitic nature are prevailing so as for the CO_2/H_2O ratio to reach maximum values. However, a correction should be assumed for mortars with different gradation, because in that case the CO_2/H_2O values for the binder (fragment < 63 μm) would be diversified.

Mortar is a two-phase material and in a first approximation, its strength is proportional to the strength of the weaker component, i.e., the binder matrix. The strength of the binder matrix depends on the type of the binder, its theoretical strength and on the porosity of the matrix. Consequently, for mortars made of the same components, the strength of the mortar is expected to decrease as the binder porosity increases. In Fig. 4, the porosity of the studied mortars is given versus their tensile strength. For each mortar type, the rate of decrease, i.e., the effect of porosity on the strength of the material, depends on the amount of the hydrated phases [16]. For the cementitious mortars of Fig. 4 for example, the decrease rate is higher than in the case of lime or crushed brick mortars of the same figure.

3.2. Classification by PCA

All parameters of Table 1 were used in PCA but the inverse hydraulicity ratio, porosity and strength together gave the best results and will be presented in here. Fig. 5 shows the boxplots with medians, minimums and maximums and outliers (extremely rare values) for these three parameters. The boxes are defined by percentiles of 25% and 75%. The discrimination potential of each parameter is obvious, as inverse hydraulicity or strength alone can distinguish lime mortars from all other types. Cementitious mortars are differentiated from crushed brick mortars by their lower strength, while low porosity characterises Portland cement.

Two factors were extracted by PCA, from which only Factor 1 was kept, because the eigenvalue of Factor 2 was lower than 1 (0.69). Factor 1 carries 68.8% of the total variance and presents the following loadings: .91 for CO_2/SBW, .68 for porosity and $-.88$ for tensile strength. Despite its low eigenvalue, Factor 2 was used in a biplot together with Factor 1, as well as all the other original parameters. However, the best discrimination between different groups was obtained with Factor 1 and tensile strength, as given in Fig. 6. The ellipses were drawn for each group with 90% confidence limits.

Obviously, the lime mortars form a well-defined and discriminated group. All three parameters, hydraulicity, porosity and strength contribute to this discrimination.

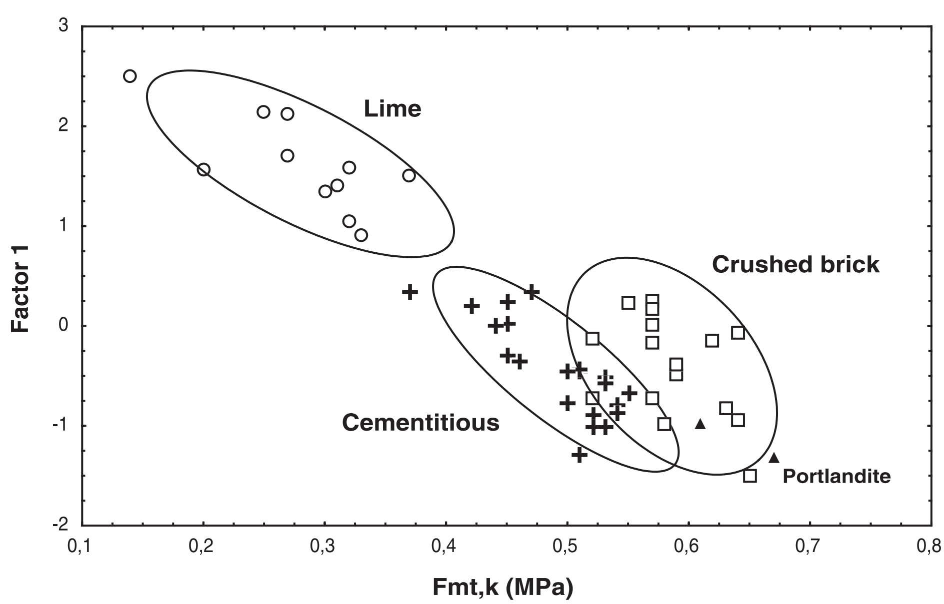

Fig. 6. Biplot of PCA Factor 1 versus tensile strength.

However, cementitious and crushed brick mortars show a certain overlap, with tensile strength being their main distinguishing factor. The two Portland cement samples fall in the field of the crushed brick mortars.

4. Conclusions

The compactness of the studied mortar groups confirms that there were in the past, traditional mortar technologies that remained unaltered for large historical periods. The properties of crushed brick mortars for example, do not show extended changes from early Byzantine to late Ottoman period. This most probably implies a powerful tradition not only in preparation of the original mixtures but also in the application procedures.

It seems that typical lime, cementitious and crushed brick mortars, for close values of binder/aggregate ratios, show microstructural and mechanical properties in certain predictable ranges. We have to note here again that this study includes only nonweathered samples, with fine fraction around 25% of the total weight, collected very carefully.

PCA can serve the role of a bridge between original mortars and restoration syntheses by making a correspondence between raw material types and ratios to physico-chemical and mechanical properties. This information can be extended to other types of mortars (gypsum mortars for example) and different binder to inert ratios, as an aid for decide on syntheses for restoration mortars.

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