Original Paper

Chemical characterization of Cretan clays for the design of restoration mortars

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Abstract. Three clays and a marly-limestone from the West of Chania, Crete, fired at temperatures ranging from 200 to 1200 °C, were characterized by XRD, FTIR, EDXRF and wet chemical analyses. The aim of this study was to assess the pozzolanic and hydraulic properties of these materials for potential use as binders in the design of restoration mortars. The mineralogical composition of the clays is quartz, illite, calcite, plagioclase, kaolinite and hematite. The identification of larnite and gehlenite in the calcined marly-limestone established it as potential cementious binder. Among the clays, one with low amount of calcite and considerable kaolinite content exhibited the best pozzolanic activity upon heating at 600 °C. Therefore, it can be considered as an appropriate material for restoration purposes. It is deduced that the pozzolanic activity of fired clays is greatly dependent on the firing temperature and is enhanced in clays containing low calcite and high kaolinite amounts.

Keywords: Clays and marly-limestone; FTIR; EDXRF; calcination; pozzolanic activity

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Mortar is a material resulting from the intimate mixture of binder, aggregates and water. The properties and characteristics of mortars mainly depend on the nature of the binder component [1]. The binder of the lime mortars is calcium hydroxide (portlandite), which is transformed in calcium carbonate upon reaction with carbon dioxide. The binders can be classified as non-hydraulic and hydraulic; hydraulic binders are mainly composed of calcium silicates, calcium aluminates and calcium hydroxide [1, 2]. The aggregates used in lime mortars include sands, gravels and crushed materials, as well as pozzolanic materials introducing a degree of chemical set to the mortar [3].

Pozzolanic materials are natural substances or industrial by-products having partially crystalline structure formed by silica, siliceous aluminous compounds or a combination of both. Natural pozzolans include materials such as diatomaceous earths, opaline cherts and shales, tuffs and volcanic ashes. The artificial pozzolans are obtained by heat treatment of natural materials such as clays, shales and pulverized fuel ash [4]. Pozzolans do not harden when mixed with water; in the presence of water, when pozzolans are finely powdered, are able to react with lime at ambient temperature, to form hydrated calcium silicates and to develop suitable mechanical strengths for mortar. The term pozzolanic activity denotes the ability of a

material to react with portlandite in the presence of water. Natural pozzolans in the form of calcined earths blended with lime have been used to produce cementitious materials for thousands of years [5].

Clay is a generic term for an aggregate of hydrous siliceous particles less than $2\,\mu m$ in diameter. Clay consists of a variety of phyllosilicate minerals rich in silicon and aluminum oxides and hydroxides, which include variable amounts of structural water [6]. The most common mineral in clays of the kaolin group is kaolinite $[(OH)_8Si_4Al_4O_{10}]$, characterized by alumina octahedral sheets and silica tetrahedral sheets stacked alternately. In order to develop pozzolanic activity the kaolinite clay needs to be submitted to a heat treatment process [7]. The kaolinite loses water between 500 and $600\,°C$ transforming into meta-kaolinite; the most significant structural change in this endothermic reaction is the transformation of octahedrally coordinated aluminum in kaolinite to tetrahedrally and pentahedrally coordinated alumina in meta-kaolinite [8]. While kaolinite is crystalline, metakaolinite has a highly disordered structure, is much more reactive than kaolinite and offers good properties as pozzolanic additive [9]. The pozzolanic activity of the meta-kaolinite depends on a number of factors, among them the crystallinity, calcination temperature and mineralogy of the original kaolinite [10].

Historic mortars in Crete, especially those dated to Roman, Byzantine and Ottoman Empires historic periods contained crushed bricks as aggregates. New repair mortars and plasters with crushed bricks, designed for conservation purposes, fail to strengthen the construction, since they lack resistance to the environmental loading, especially salt decay. Research directed to the quality control of the raw materials indicated that crushed bricks used in conservation applications were not adequately manufactured [9]. The bricks burning temperature and their mineralogical composition did not enable them to react with lime in order to produce durable mortars. Therefore, it was deemed important to search out clays that can be used as restoration materials.

Into this context, clay samples collected from the west part of Crete were characterized to evaluate the best performing pozzolanic additives in the design of new restoration mortars. The clay characterization was performed in fired samples at temperatures ranging from 200 to $1200\,°C$, by using X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), energy dispersive X-ray fluorescence (EDXRF) and wet chemical analyses, as well as pozzolanic activity tests.

Experimental

In the present work four samples of clays were collected from different places of the west area of Chania, Crete, namely Alonia (AL), Church of Vouves (CB), Metohi (ME) and Giamlidika (GM). The sampling areas were selected on account of the traditional kilns utilized local clays for the production of domestic ceramic vessels; the sampling areas are characterized by homogeneous in colour clay formation. The clay samples were ground to size smaller than $63\,\mu m$. Samples were heated in a box kiln at temperatures of 400, 500, 600, 800, 1000, $1200\,°C$ with a heating rate of $10\,°C\,min^{-1}$.

The mineralogical composition of clay samples was determined by X-ray diffraction (XRD) analysis using a Philips PW 1710 automatic X-ray diffractometer. Cu-K_α radiation (monochromatized by high resolution graphite monochromator) was used with automatic grate, flashing counter and digital recorder. The accelerating voltage and electric current at the Cu anode were 40 kV and 30 mA, respectively. The scanning speed of goniometer ($2\theta° \sec^{-1}$) and scanning step ($\Delta 2\theta°$) were 0.005 and 0.025, respectively.

Fourier transformed infrared spectroscopic analysis (FTIR) was performed in a Perkin Elmer System 1000. FTIR indicated the minerals and their transformation after the heating of the clay samples. The clay samples were homogenized with KBr and pressed by a vacuum hydraulic press up to 10 t pressure to obtain a pellet. Different concentrations of samples and KBr were tested and the best spectrum performance was obtained by using 1 mg of sample with 100 mg of KBr. The spectra were recorded with a spectral resolution of $4\,cm^{-1}$ and 250 consecutive scans were added and averaged before Fourier transform in order to obtain a good signal-to-noise ratio. All spectra were collected in the absorbance mode. The infrared frequencies were assigned to clay minerals according to various bibliographic sources [11, 12]. In particular, the relevant second derivative was taken into consideration, which allows discrimination of overlapping bands even between minerals with similar absorptions [12].

The calcimetry (Dietrich-Fruhling gas volumetric method) was used for determining the CO_2 content of the clay samples. The amount of CO_2 was determined from the volume of the gas evolved upon acid attack. For the determination of SiO_2 and Al_2O_3 traditional wet chemical methods were employed after acid attack with perchloric acid ($HClO_4$) [13]. In this test method silicon dioxide was determined gravimetrically more rapidly than the standard method with hydrochloric acid attack. Aluminum and iron were precipitated from the filtrate by means of ammonium hydroxide. The precipitate, consisted of aluminium and iron oxides, was ignited and weighed. Aluminum oxide was considered to be the difference between the combined oxides and Fe_2O_3 determined by EDXRF.

An EDXRF unit was employed for the qualitative and quantitative analyses of the clays. This unit consisted of: [55]Fe and [109]Cd radioactive sources (Isotope Products Laboratories), a Si (Li) semiconductor detector (PGT, active area $30\,mm^2$, resolution 150 eV at 5.9 keV), a Tennelec TC-244 Spectroscopy Amplifier (including pile-up rejection and dead time correction) and a PCA-II Nucleus Multi-channel card. The spectra were analysed (spectrum fitting and concentration calculations) by the AXIL computer program analysis (supplied by the International Atomic Energy Agency). The main advantages of the EDXRF technique are the capability of direct analysis of solid samples, the simultaneous detection of almost all the elements with an atomic number higher than aluminium, and the short analytical time.

Determination of pozzolanic activity of clay samples ($<63\,\mu m$) was obtained according to the Luxan Method [14]. In this method,

the electrical conductivity of samples was measured before and after the reaction with saturated calcium hydroxide solution; the difference measured in electrical conductivity was used to express the pozzolanic activity. The samples exhibiting an electrical conductivity difference in excess of $1.2\,mS\,cm^{-1}$ showed good pozzolanicity.

The ionic character of the samples was determined by conductivity measurements, according to the UNI 11087 protocol [15].

Results and discussion

Unfired samples

Table 1 shows the mineralogical composition of the studied clays according to the results of the XRD

Table 1. Minerals identified by XRD at the unheated samples

Samples	Minerals
Alonia	calcite (+++), quartz (++), illite (++), muscovite (+), sanidine (+), montmorillonite (+)
Church of Vouves	quartz (+++), illite (++), kaolinite-montmorillonite (+), plagioclase (+), hematite (+), calcite (+)
Metohi	quartz (+++), illite (++), calcite (++), plagioclase (+), paragonite (+), chlorite (+), hematite (+)
Giamlidika	quartz (+++), illite (++), paragonite (+), calcite (+), kaolinite (+), muscovite (+), hematite (+)

+++ Dominantly present, ++ present, + traces.

Quartz (SiO_2), illite [$K(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$], calcite ($CaCO_3$), plagioclase [$Na_xCa_{1-x}Al_{2-x}Si_{2+x}O_8$], kaolinite [$Al_2Si_2O_5(OH)_4$], muscovite [$KAl_2(Si_3Al)O_{10}(OH,F)_2$], sanidine [$K(AlSi_3O_8)$], montmorillonite [$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{16}(OH)_2 \times H_2O$], hematite ($Fe_2O_3$), paragonite [$NaAl_2(Si_3Al)O_{10}(OH)_2$], chlorite [$(Mg,Fe)_5(Al,Si)_5O_{10}(OH)_8$].

analysis. From Table 1, it can be seen that the mineralogical composition of the studied samples consisted mainly of quartz, illite, calcite, plagioclase, while in the GM and CB clays kaolinite was also identified. Figure 1 illustrates the infrared spectra of the unfired studied samples. The CB, GM and ME samples contain kaolinite, whose main infrared absorptions are at 3699, 3620, 1112, 913, 694, 537 and $471\,cm^{-1}$, illite with main peaks at 3423, 1632 and $1031\,cm^{-1}$, quartz (798, 778 and $694\,cm^{-1}$) and calcite (1432 and $876\,cm^{-1}$) [11, 12]. Although FTIR indicated the presence of kaolinite, in the XRD analysis of the ME clay, kaolinite could not be identified, most probably due to its low quantity. The AL sample showed the highest quantity of calcite along with nitrates, whose absorption lies at $1392\,cm^{-1}$ [11]. The presence of nitrates can be reasonably attributed to soluble salts originating from cultivation and farming activities in the sampling area.

The results of the chemical analysis of samples are reported in Table 2. The amount of calcite varied in the clay samples. The AL sample with a ~70% quantity of calcite cannot be considered a clay, but rather a marly-limestone. Nevertheless, given its considerable silicon dioxide content (~20%), it will be submitted to a heat treatment, in order to assess if a lime-silica reaction, capable of providing samples with hydraulic properties, would occurred. Among the analyzed clays, the ME clay contained the highest quantity of calcite and the lowest quantity of silicon oxide.
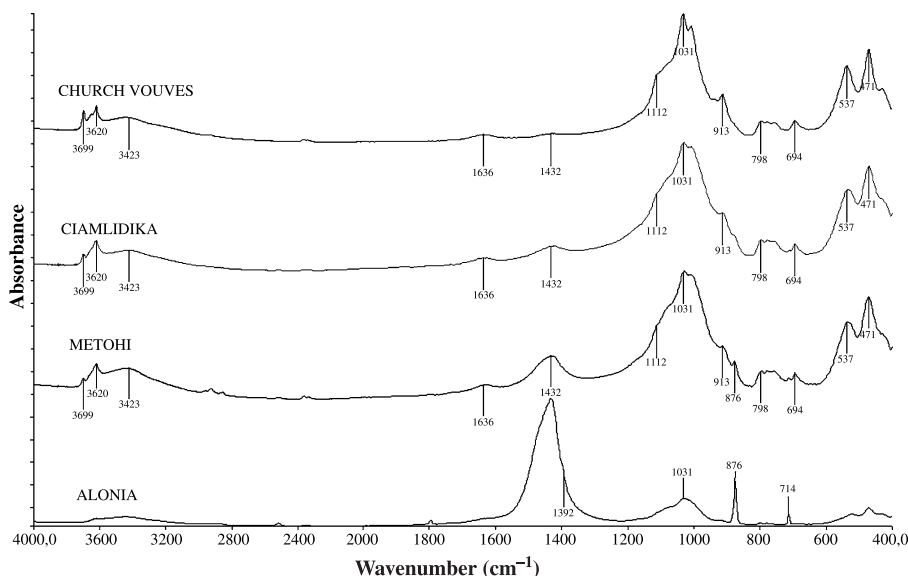

Fig. 1. FTIR absorbance spectra from the unfired studied samples

Table 2. Results of chemical analyses of the studied samples

	Alonia	Church of Vouves	Metohi	Giamlidika
%H_2O[a]	2.39	5.98	2.48	4.26
%CO_2[b]	29.4	0.21	3.85	1.58
%CaO[c]	44.5	0.48	6.09	2.18
%SiO_2[d]	19.6	82.1	76.4	78.8
%Al_2O_3[d]	1.59	5.16	5.04	6.25
%Fe_2O_3[c]	0.82	2.69	3.15	2.61
%K_2O[c]	1.75	2.09	3.08	2.45
Total	100	98.7	100	98.1
%$CaCO_3$[b]	66.8	0.48	8.75	3.59

[a] Calculated from weight loss between 0 and 500 °C.
[b] Dietrich-Fruhling gas volumetric method.
[c] EDXRF analysis.
[d] Attack by $HClO_4$.

Heat treatment

The structural changes of the heated samples fired at temperatures ranging from 400 to 1200 °C were assessed by XRD and FTIR analyses. Figures 2 and 3 depicted the XRD patterns of the AL and GM heat-treated samples, respectively, by firing at temperatures ranging from 500 to 1200 °C. Table 3 summarized the changes in minerals due to the heat treatment of all the studied samples.

For the heat-treated AL sample depicted in Fig. 2, it is important to emphasize that temperatures higher than 600 °C caused the formation of lime (CaO), gehlenite [$Ca_2Al(AlSi)O_7$] and larnite (Ca_2SiO_4). These calcium silicate phases indicated that after decomposition of calcite at temperatures higher than 600 °C, a reaction occurred between the produced lime and silicon oxide. In the X-ray pattern, it can be observed that after heating at 1000 °C, the amount of lime is rather
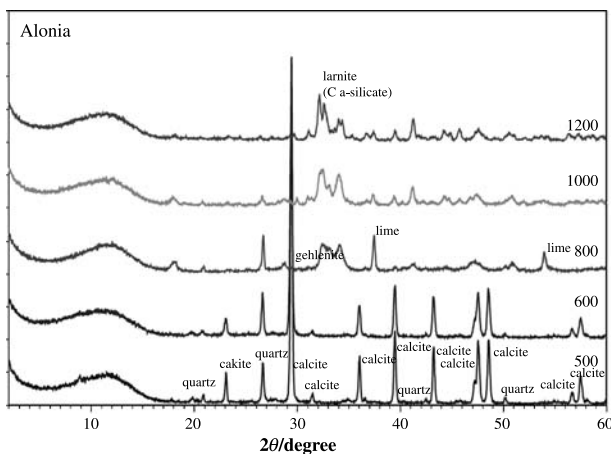

Fig. 2. XRD patterns of the Alonia sample (*marly-limestone*) heated at 500, 600, 800, 1000 and 1200 °C
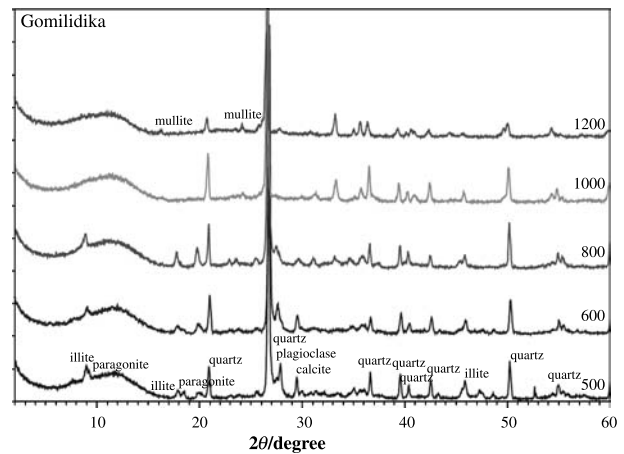

Fig. 3. XRD patterns of the Giamlidika sample (*clay*) heated at 500, 600, 800, 1000 and 1200 °C

low confirming that lime was mostly consumed in the reaction with silicon oxide. In natural hydraulic limes larnite and gehlenite constitute the basic components exhibiting hydraulic properties after hydration [16]. Therefore, the identification of larnite and gehlenite in considerable amounts during the calcination process, denotes that hydraulic properties can be achieved after slaking, rendering this marly-limestone potential cementious binder.

In all the clay samples, the XRD peaks of illite, calcite and paragonite disappeared in the range of 800–1000 °C, due to the heat treatment causing dehydration, dehydroxylation and decomposition (Fig. 3 and Table 3). The existence of mullite [$Al_{(4+2x)}Si_{(2-2x)}$-$O_{(10-x)}$, where x from 0.17 to 0.59] at temperatures higher than 1000 °C denoted the kaolinite presence in the GM and CB samples. Plagioclase, quartz and hematite are fire-resistant minerals and, therefore, remained unchanged during the heat treatment [17]. The presence of amorphous phases in the heated samples is clearly indicated by the background hump, which approximately appeared between 10 and 18° in the X-ray diffraction patterns. This amorphous phase is probably the result of sintering of the initial constituents of clays during the firing process [17].

FTIR also used for studying characteristic reactions such as dehydration, dehydroxylation, and decomposition associated with the heating process. Although XRD analysis is a powerful tool in the mineral determination, some limitations associated with small quantity, amorphous structure, changes in orientation and overlapping of peaks establish FTIR as a complementary tool in the identification of reaction products.

Table 3. Changes in minerals of samples due to the heat treatment between 0 and 1200 °C

| Minerals	0 °C	200 °C	400 °C	500 °C	600 °C	800 °C	1000 °C	1200 °C
Alonia								
Quartz	+	+	+	+	+	+	+	+
Calcite	+	+	+	+	+	−	−	−
Gehlenite	−	−	−	−	−	+	+	+
Larnite	−	−	−	−	−	+	+	+
Church of Vouves								
Quartz	+	+	+	+	+	+	+	+
Illite	+	+	+	+	+	−	−	−
Plagioclase	+	+	+	+	+	+	+	+
Calcite	+	+	+	+	+	−	−	−
Kaolinite	+	+	+	+	−	−	−	−
Metakaolin	−	−	−	−	+	+	−	−
Mullite	−	−	−	−	−	−	+	+
Hematite	+	+	+	+	+	+	+	+
Metohi								
Quartz	+	+	+	+	+	+	+	+
Illite	+	+	+	+	+	−	−	−
Calcite	+	+	+	+	+	+	−	−
Paragonite	+	+	+	+	+	−	−	−
Plagioclase	+	+	+	+	+	+	+	+
Hematite	+	+	+	+	+	+	+	+
Chlorite	+	+	−	−	−	−	−	−
Giamlidika								
Quartz	+	+	+	+	+	+	+	+
Illite	+	+	+	+	+	−	−	−
Calcite	+	+	+	+	+	−	−	−
Plagioclase	+	+	+	+	+	+	+	+
Hematite	+	+	+	+	+	+	+	+
Paragonite	+	+	+	+	+	−	−	−
Kaolinite	+	+	+	+	−	−	−	−
Metakaolin	−	−	−	−	+	+	−	−
Mullite	−	−	−	−	−	−	+	+

+ Existed, − not existed.
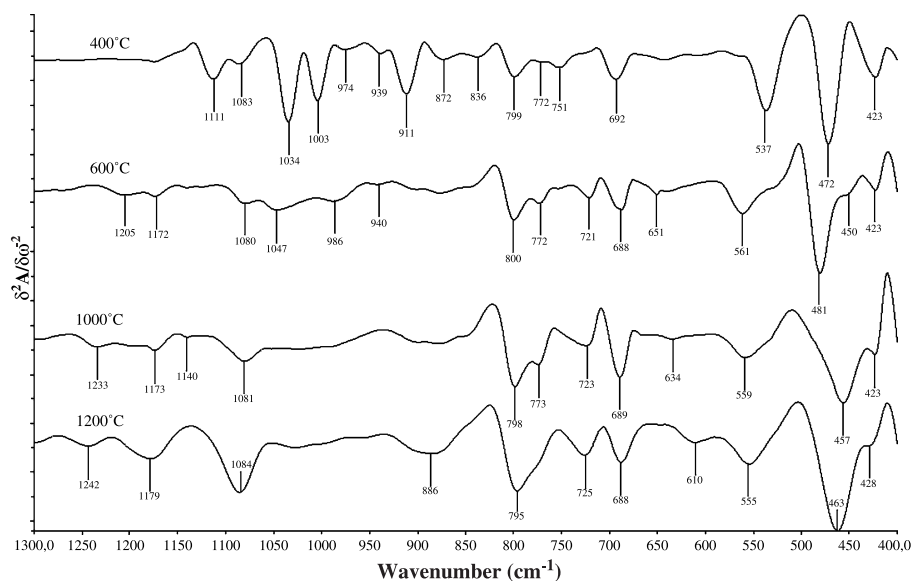
Fig. 4. Infrared second derivative of the Church of Vouves clay heated at 400, 600, 1000 and 1200 °C

For this reason the heat-treated clay samples were characterized by FTIR. As an example, the absorption frequencies of the infrared second derivatives in the range between 1300 and 400 cm^{-1}, of the CB clay heated at 400, 600, 1000 and 1200 °C are illustrated in Fig. 4. The calcite characteristic peak at 872 cm^{-1} disappeared upon heating at 600 °C, as a result of the calcite decomposition. Quartz existed during all the heating process and can be identified by its characteristic doublet at 800–772 cm^{-1}, as well as other absorptions at ∼1170, 1080 and ∼690 cm^{-1}.

Kaolinite dehydrates between 400 and 600 °C to form metakaolinite (Al$_2$Si$_2$O$_7$), an often X-ray amorphous intermediate phase. At about 970 °C, metakaolinite transforms into a cubic phase and upon further heating in mullite. The dehydration of kaolinite upon heating at 600 °C, introduces a number of important changes in the spectrum. In particular, modes involving vibrations of OH− groups disappeared, such as the in-plane bending vibration of inner hydroxyl at 911 cm^{-1} [11]. Absorption bands at 1003 and 1034 cm^{-1} assigned to Si-O-Al and Si-O-Si stretching modes, respectively, shifted to higher wavenumbers (e.g. at 1047 cm^{-1}) [11]. The same is valid for the Si-O-Al vibration at 537 cm^{-1} observed in the clay heated at 400 °C; upon heating, this band shifted to higher frequencies (∼560 cm^{-1}). Furthermore, the heating at 1000 and 1200 °C introduced a band at ∼460 cm^{-1}, which can be assigned to (Al-O)- and (Si-O)-bending modes in a random arrangement of [AlO$_4$]- and [SiO$_4$]-tetrahedral [11].

Metakaolinite, due to its amorphous structure, cannot be identified by XRD, while its infrared spectroscopic identification demonstrated that FTIR is a well established technique for the determination of the mineral composition. Another application concerned the wollastonite (CaSiO$_3$) identification by FTIR in the ME clay heated at 1000 °C. The ME clay contained ∼9% of calcite; therefore, in this case a reaction with silica after calcite decomposition yielding wollastonite was very likely.

Pozzolanic activity

Table 4 reports the results of pozzolanic activity of the heated samples at various temperatures, according to the Luxán method [14]. Taking into account that good pozzolanic properties are associated with conductivity values higher than 1.2 mS cm^{-1}, it can be deduced that the GM clay heated at 600 °C with conductivity

Table 4. Results of the pozzolanic activity [Conductivity values (mS cm^{-1})] of the heated samples

Temperature (°C)	Alonia	Church of Vouves	Metohi	Giamlidika
400	0.38	1.1	0.37	1.04
600	0.53	1	0.66	1.48
800	−0.14	0.66	−1.74	−0.22
1000	−5.98	0.1	−0.1	0.1

equal to 1.48 mS cm^{-1} exhibited appropriate pozzolanic properties. Generally all samples heated at 600 °C showed the highest values of pozzolanic activity.

From the results of Table 4 it is worth noticing that AL, ME and GM samples heated at 800 °C showed negative conductivity values. The same holds true for AL and ME samples heated at 1000 °C. This observation can be correlated with the calcite content determined in the above-mentioned samples. Calcite showed high concentration in the AL sample, modest in the ME sample, low concentration in the GM clay, while in the CB clay it is found in values lower than 0.5% (Table 2). Upon heating calcite transformed in calcium oxide; part of the latter reacted with silicon oxide to form calcium silicate and the remained calcium oxide subsequently hydrated to calcium hydroxide. The presence of calcium hydroxide enhances the ionic character of the samples. This can be also confirmed by the conductivity measurements performed in the water solutions of the samples heated at 800 °C. The AL sample showed a conductivity of 2140 μS cm^{-1}, while the CB, ME and GM showed conductivity values of 2.32, 304.95 and 58.59 μS cm^{-1}, respectively. Based on the above-mentioned conductivity values, the negative pozzolanic activity can be explained.

In an attempt to gain insight into the high pozzolanic activity of the GM clay, the chemical and mineralogical compositions were taken into consideration. Samples with the best pozzolanic properties, such as the GM and CB clays, contain kaolinite and low amount of calcite. Especially, the transformation of kaolinite to metakaolinite upon heating at 600 °C offers good pozzolanic properties. This can be considered as important information concerning the pozzolanic properties of fired clays used for restoration purposes. Firstly, the firing temperature of clays plays an important role and according to our results, should not exceed the 600 °C, and secondly, the mineralogical composition should include kaolinite and a low amount of calcite. Modern kilns surpass by far the temperatures reached by traditional wood kilns and,

therefore, yield fired clays overheated with lack of pozzolanic properties. This is one of the main reasons of failure of mortars and plasters prepared by mixing lime and commercial fired clays.

Conclusions

The studied clay samples (ME, CB and GM) consisted mainly of quartz, illite, calcite, plagioclase, kaolinite and hematite as indicated by XRD, FTIR, EDXRF and wet chemical analyses. The CB and GM clays contain the lowest quantity of calcite and considerable amounts of kaolinite, while the ME clay showed a modest amount of calcite. The AL sample, according to its chemical and mineralogical composition, can be considered a marly-limestone; the identification of larnite and gehlenite in considerable amounts during the calcination process, denote that hydraulic properties can be achieved after slaking, rendering AL potential cementious binder.

In the CB, GM and ME clays metakaolinite was formed upon heating between 400 and 600 °C, as proved by FTIR. Further heating up to 1200 °C leads to mullite formation in the CB and GM clays, while the ME clay, exhibiting modest calcite content, yields wollastonite as a reaction product between lime and silicon oxide.

The studied samples heated at 600 °C showed the highest values of conductivity, but only the GM clay heated at 600 °C exhibited appropriate pozzolanic properties. Negative conductivity measurements for samples heated at 800 and 1000 °C are related to the lime deriving from their calcite content.

The design of repair materials for cultural heritage conservation should be directed towards rediscovering and ameliorating the production technologies of historic ones. Bibliographic data indicated [18, 19] that mortars with hydraulic ingredients offer compatibility and good performance on the masonry. The hydraulicity of the mortar could also be obtained with the use of finely powdered bricks, provided that the bricks were pozzolanic [20]. Modern bricks may contain a low content of clays and are seldom pozzolanic as they were fired at high temperature. When they employed for conservation interventions failed to produce adhesion properties between the mortar constituents and demonstrated a limited duration on masonry. From this study it can be deduced that the best pozzolanic properties of clays suitable of being used as restoration materials can be achieved when their firing temperature does not exceed the 600 °C, their calcite content is low and their kaolinite content is high.

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