

CALCINED CLAYS AND LIMESTONE AS HYDRAULIC BINDERS

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ABSTRACT

Clay samples from the west area of Chania, Crete, Greece (3 clays) heated at 600 °C were selected to react with saturated lime, due to their high lime reactivity. When the clay is mixed with lime, the silica and alumina minerals of clay samples react with lime yielding calcium silicate hydrate (CSH), which is the main cause of hardening of mortar. The formation of CSH depends on various conditions; in this part of the work the effect of time and chemical characteristics of clay samples on the lime-clay reaction has been investigated. In order to assess, if the initial rapid absorption of lime observed for clays calcined at 600 °C, is followed by rapid reaction, the clays were left to react with saturated lime for a period of time up to 60 days. The products of this reaction over time have been characterized with the aid of FTIR, XRD and TGA-DTA. In the FTIR spectra, the pozzolanic reaction evolution can be observed through the progressive reduction of portlandite peaks (3647 cm^{-1}) and the appearance of peaks at $\sim 1620 \text{ cm}^{-1}$, attributed to the presence of combined water, while the absorptions in the spectral range of 1020-901 cm^{-1} can be assigned to the Si-O stretching of CSH products. DTA curves and XRD patterns showed similar trends for the studied systems. The lime consumption over time in the CB clay is more rapid than that of the GM clay, contrary to the results obtained for the lime reactivity determined in a short time scale. This may be related to the lower calcite content of the CB clay. Therefore, only considering the lime reactivity over a short time scale, does not reflect the overall response of the material. A marly limestone heated at 800 °C was mixed with water and the hydration products have been investigated with the above mentioned techniques after a period of 1 day, 1 week and 1 month. The marly limestone, after one month of hydrolysis, showed CSH products; therefore, it can be considered as a potential hydraulic binder.

INTRODUCTION,

Pozzolans are materials which, when combined with calcium hydroxide, exhibit cementitious properties. These are commonly used as an addition to Portland cement concrete mixtures to increase the long-term strength and other material properties of Portland cement concrete and in some cases reduce the material cost of concrete. Pozzolanic materials are natural substances or industrial by-products having partially crystalline structure formed by silica, siliceous aluminous compounds or combination of both. Natural pozzolans include materials such as diatomaceous earths, opaline cherts and shales, tuffs and volcanic ashes. The artificial pozzolans are mainly the products obtained by heat treatment of natural materials such as clays, shales and pulverized fuel ash [1]. Pozzolans do not harden when mixed with water, but when they are finely powdered, in the presence of water, they are able to react with lime at ambient temperature, to form hydrated calcium silicates developing suitable mechanical strengths for mortar.

The term pozzolanic activity denotes the ability of a material to react with portlandite in the presence of water. It depends on the quality and quantity of active phases present in pozzolana,

the type of treatment, the Si/Al molar ratio, the lime/pozzolana ratio of the mix, water to binder ratio, curing conditions and specific surface area. Natural pozzolans in the form of calcined earths blended with lime have been used to produce cementitious materials for thousands of years.

Mortar is a material resulting of the intimate mixture of binder, aggregates and water. The properties and characteristics of mortars mainly depend on the nature of the binder component [2]. 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 limes. Hydraulic limes mainly composed of calcium silicates, calcium aluminates and calcium hydroxide [3]. 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].

Clay is a generic term for an aggregate of hydrous siliceous particles less than 2 μm 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. The most common mineral in clays of kaolin group is kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$, 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. The kaolinite losses water between 500-600 $^\circ\text{C}$ 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. While kaolinite is crystalline, metakaolinite has highly disordered structure, is much more reactive than kaolinite and offers good properties as pozzolanic additive [4, 5]. The pozzolanic activity of the metakaolinite depends on a number of factors, among them the calcination temperature, crystallinity and mineralogy of the original kaolinite.

When the calcined clay is mixed with lime, the silica and alumina minerals of clay samples react with lime and form the calcium silicate hydrate, which is the main cause of hardening of mortars. The formation of this product depends on various conditions. In this part of the work the effect of time and chemical characteristics of clay samples on the lime-clay reaction have been investigated. Calcined clay samples and marly limestone collected from the west part of Crete Island were mixed with lime and subsequently evaluated, in order to ascertain the best performing pozzolanic additives, as well as suitable hydraulic binder for the production of new restoration mortars.

EXPERIMENTAL

Clay samples heated at 600 $^\circ\text{C}$, and a marly limestone heated at 800 and 1000 $^\circ\text{C}$ were selected on the grounds of the highest values of pozzolanic activity, as it was indicated on a previous work [6]. The calcined clays at 600 $^\circ\text{C}$ were chosen for the reaction with lime due to their high pozzolanic activity. All the studied materials exhibited grain size lower than 63 μm .

The lime clay reaction is a complex physico-chemical interaction still not well-studied [7]. In order to assess, if the initial rapid absorption of lime observed for clays calcined at 600 $^\circ\text{C}$ is followed by rapid reaction, the clays were left to react with lime for a period of time up to two months. The mixing clay and lime has been applied according to the methodology described in Ninov et al [7], at a temperature of 23 $^\circ\text{C}$. The products of this reaction have been characterized after a period of 1, 2, 3, 4, 5, 6, 7, 23, 30 and 60 days, with the aid of FTIR, XRD and TGA-DTA.

In particular, the kinetics of calcined clays-lime reaction has been determined by dissolving 0,495 g of $\text{Ca}(\text{OH})_2$ with solubility 1,65g/L in 300 mL water at ambient temperature (≈ 20 $^\circ\text{C}$). Afterwards, a

0,5 g of clay sample was added, a quantity that is almost equal to the content of $\text{Ca}(\text{OH})_2$ in the solution. The mixture was then placed on a magnetic stirrer for two months with a speed of 180 rpm. The contact with the atmosphere was limited and the temperature was constant at 20 °C. Analyses were performed on samples reacted with lime after 1, 2, 3, 4, 5, 6, 7, 23, 30 and 60 days. The mixtures of clays and lime, before conducting the analyses, were dried in an oven at 90 °C for 10 hours and then were placed in desiccators for 1 hour.

It is known from previous studies, that at a low relative humidity (RH=30%), carbonation of calcium hydroxide powders is either very low or non-existent [8]. This information can be used in the study of the evolution of the pozzolanic reaction. Given the low or non-existent carbonation rate of $\text{Ca}(\text{OH})_2$ in ambient conditions of low relative humidity, it is reasonable to assume that the drying of the analyzed samples did not modify the rate of the pozzolanic reaction. Furthermore, even in a case of low carbonation, the exactly similar procedure followed during the sample analysis, allowed for comparisons.

Fourier transformed infrared spectroscopic analysis (FTIR) was performed in a Perkin Elmer System 1000. FTIR indicated the minerals and their transformation after reaction of the clay samples with lime. The clay-lime samples were homogenized with KBr (1 mg of samples with 100 mg of KBr) and pressed by a vacuum hydraulic press up to 10-15 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 75 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 [9, 10].

Differential thermal and thermogravimetric analysis was performed on the apparatus type Setaram LabSys Evo, TG-DTA-DSC 1600 °C, in a static air atmosphere with a heating rate 10 °C min^{-1} from 30 °C up to 1000 °C in order to determine the $\text{Ca}(\text{OH})_2$ consumption and the products of the pozzolanic reaction over time.

The marly limestone heated at 800 °C dissolved in water and the hydration products have been investigated by the above mentioned techniques after a period of 1, 4, 5, 7 and 30 days.

RESULTS & DISCUSSION

The mineralogical composition of the studied clays consisted mainly of quartz, illite, calcite, plagioclase, while in two clays kaolinite was also identified. The chemical analysis showed major CaO content 6% (in mass), SiO_2 content 70% and aluminum and iron oxides 15%. The AL sample with a ~70% quantity of calcite and a ~20% silicon dioxide content can be considered a marly-limestone.

The mineralogical composition of samples fired at 600, 800 and 1000 °C was identified with XRD and is reported in table 1. The chemical composition of the unfired samples is reported in table 2.

Larnite and gehlenite identified in the heated marly limestone at 800 and 1000 °C (table 1), can be considered as potential indicators for the production of hydraulic silicates and aluminates upon hydrolysis. Metakaolinite is a compound resulted at firing temperatures from 600 up to 800 °C for clays contained kaolinite. The metakaolinite is considered by numerous bibliographic data as the amorphous compound capable of reacting with lime for the production of hydraulic components. Clays present a sharp lime reactivity when heated at temperatures in the range of 600–900 °C and ground in sufficient fineness. During the thermal treatment, silica and alumina loses the combined

water, leading to a demolition of the crystalline network and the formation of unstable amorphous phases that could react with hydrated lime and water, producing pozzolanic products [5]. Each clay showed an amorphous phase content at an optimum firing temperature. A high content of clay and a high specific surface area favours the pozzolanic activity of a ceramic powder [4]. In our case the optimum firing temperature resulted the 600 °C, therefore, clays heated at this temperature were selected for the reaction with lime. According to the results of pozzolanic activity of clay samples determined with a procedure described by Luxan [11], the clay samples GM and CB heated at 600 °C, exhibited the best pozzolanic properties, because of the presence of metakaolinite and low amount of calcite [6].

Table 1: Properties of the specimens

Samples ----- Minerals	ALONIA 600 °C	ALONIA 800 °C	ALONIA 1000 °C	BOUVES CHURCH 600 °C	METOHI 600 °C	GIAMLIDIKA 600 °C
Quartz	+	+	+	+	+	+
Calcite	+			+	+	+
Gehlenite		+	+			
Larnite		+	+			
Illite				+	+	+
Plagioclase				+	+	+
Metakaolinite				+		+
Hematite	+			+	+	+
Paragonite					+	+

Quartz (SiO_2), Illite $[\text{K,H}_3\text{O})(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$, Calcite (CaCO_3), Plagioclase $[(\text{Na,Ca})(\text{Si,Al})_4\text{O}_8]$, Kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$, Hematite (Fe_2O_3), Paragonite $[\text{NaAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2]$, Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), Larnite (Ca_2SiO_4), Metakaolinite ($\text{Al}_2\text{O}_3, 2\text{SiO}_2$)

Table 2. Results of chemical analysis of the unfired samples

	AL	CB	ME	GM
%H ₂ O	2.39	5.98	2.48	4.26
%CO ₂	29.41	0.21	3.85	1.58
%CaO	44.47	0.48	6.09	2.18
%SiO ₂	19.55	82.14	76.38	78.81
%Al ₂ O ₃	1.59	5.16	5.04	6.25
%Fe ₂ O ₃	0.82	2.69	3.15	2.61
%K ₂ O	1.75	2.09	3.08	2.45
%CaCO ₃	66.84	0.48	8.75	3.59

The kinetics of pozzolanic activity were measured by taking into account the hydroxyl groups of the unreacted calcium hydroxide released during the TA analysis at around 470 °C, as well as the combined water contents determined in the temperature range from 200 up to 450 °C [12]. The results obtained by thermal analysis were also corroborated with the FTIR analysis of the same mixtures.

On the studied clays, the results revealed that the free lime sharply decreased for up to 30 days,

but in different amounts and times. The GM calcined clay reacted completely with lime after 1 week, the ME clay after one month, while the CB sample completed its reaction with lime just in 2 days. These results are in full accordance with the increase of the combined water determined in the temperature range from 200 up to 450 °C. The calcined clays lost their combined water content upon heating, therefore, the mass loss determined during the thermal analysis expresses the water of the hydration products formed upon the reaction clay-lime.

Figure 1 depicted the products of the reaction of GM clay and lime after 30 days of curing. The evolution of the pozzolanic reaction can be observed through the progressive reduction of the portlandite peak (3647 cm⁻¹) and the formation of calcium silicate hydrate (CSH) gels. The latter, exhibit absorptions at 1621 cm⁻¹ attributed to the presence of combined water, while the absorptions in the spectral range 1020-901 cm⁻¹ can be assigned to the Si-O stretching vibrations of the CSH products [10, 13]. After a curing period of 23 days, the peak of combined water appeared simultaneously with the Si-O stretching at ~970 cm⁻¹ can be mostly attributed to the CSH gel formation, and to a lesser extent to the hydration of phylloid clays. The quantity of quartz (double peak at 778-796 cm⁻¹) remained unchanged during the curing period indicating that quartz did not react with lime [9].

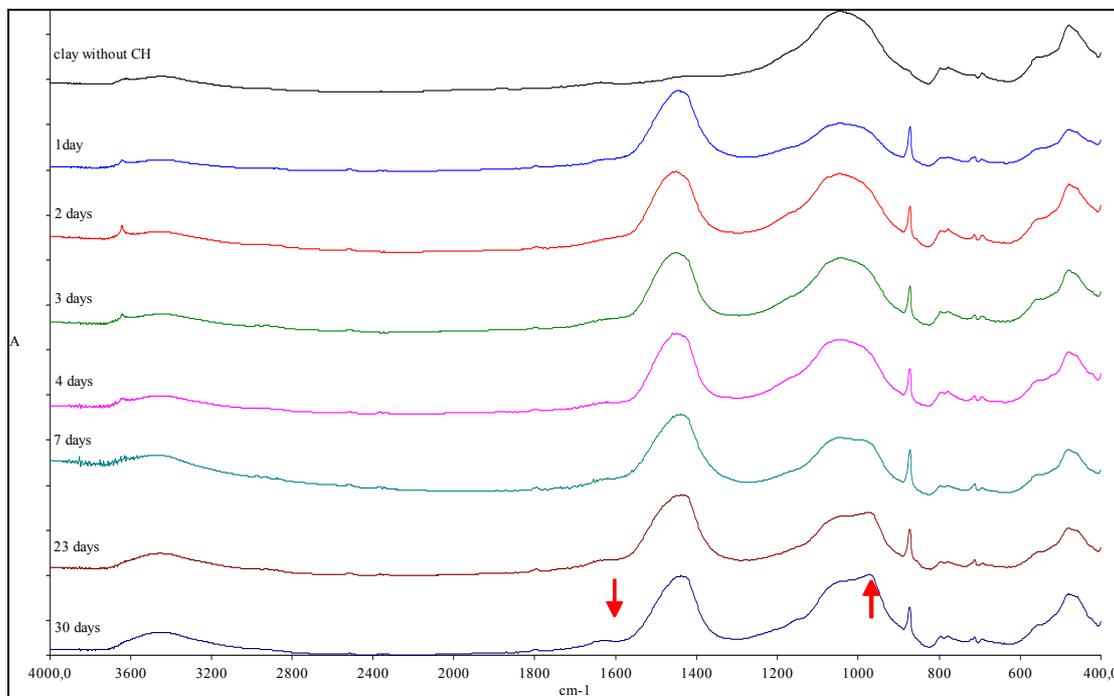


Figure 1: FTIR results of GM clay after reaction with CH at 1, 2, 3, 4, 7, 23 and 30 days

DTA curves of GM clay after reaction with CH at 1, 3, 6, and 23 days in the temperature range from 100 up to 700 °C are shown in fig. 2. An endothermic peak at ~120 °C denotes the dehydration of CSH, an endothermic peak at ~370 °C can be correlated with the release of structural bonded water of the CSH, while the endothermic peak at ~470 °C expresses the dehydration of the unreacted Ca(OH)₂. The latter, diminishes progressively upon time and disappears after a curing time of 7 days.

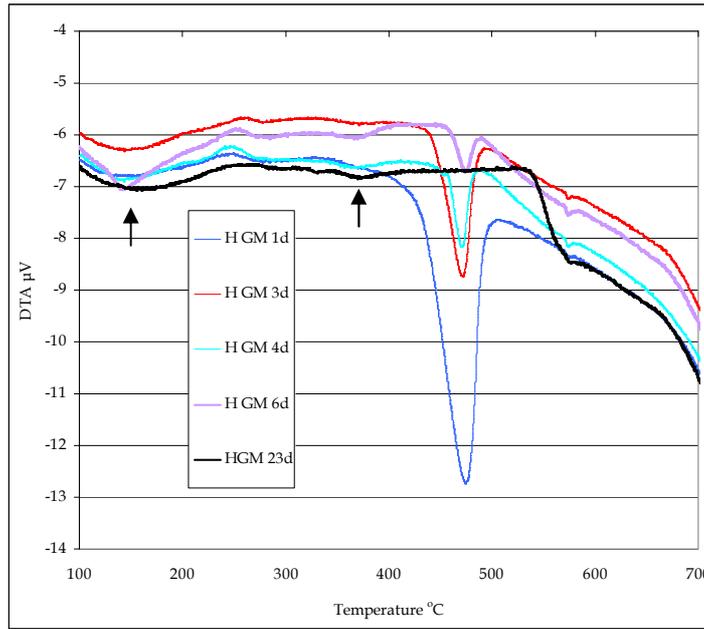


Figure 2: DTA curves for the lime consumption in the reaction with GM clay at 1, 3, 6, and 23 days

Figs 3 and 4 illustrate the FTIR patterns for the CB and ME clays reacted with lime in different time intervals. Portlandite (3647 cm^{-1}) disappeared in the CB clay after 2 days, while in the Me clay portlandite still exists up to 23 days. The peaks at 1621 cm^{-1} and in the spectral range of $1020\text{-}901\text{ cm}^{-1}$ can be attributed to the combined water and the Si-O stretching of the formed CSH products, respectively, which are progressively increased with the consumption of lime.

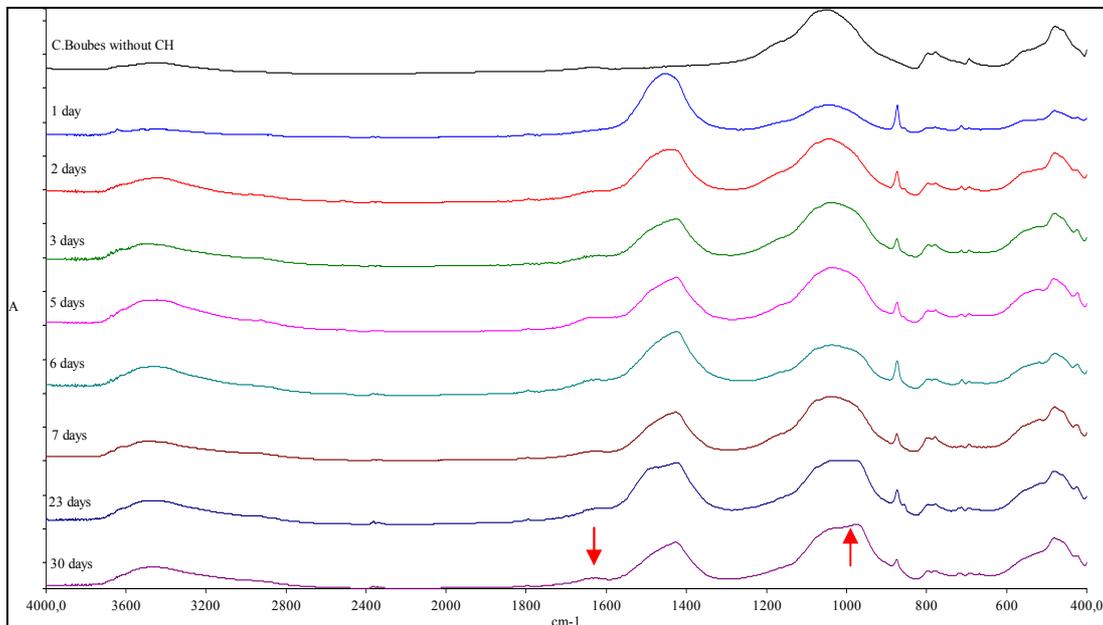


Figure 3: FTIR results of Church of Boubes after reaction with CH at 1, 2, 3, 5, 6, 7, 23 and 30 days

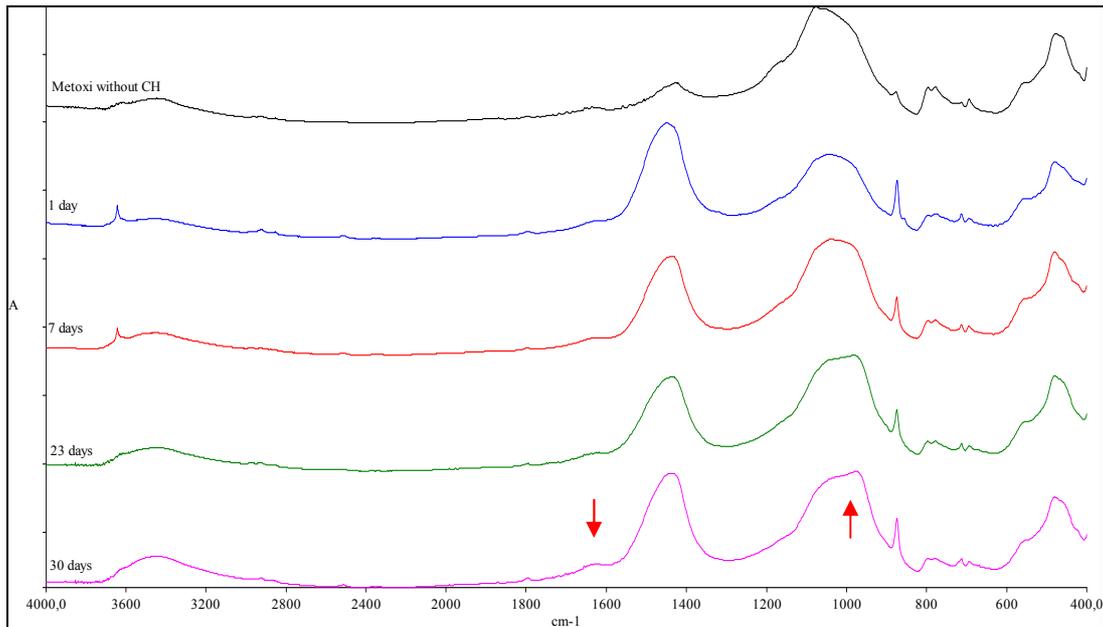


Figure 4: FTIR results of Metoxi after reaction with CH at 1, 7, 23 and 30 days

The data describing the dependence of the pozzolanic activity of clays as a function of time are presented in fig. 5. These plots express the percentage of the unreacted lime (CH) with clay, as it was determined by the thermogravimetric analysis, starting with a saturated CH solution. The lime consumption is more rapid in the CB clay than the GM clay, contrary to the results obtained for the pozzolanic activity determined by the Luxan method. The presented plots show a very good correlation concerning the reaction of clays with lime. It could be inferred that this drop in lime consumption could, itself, be taken as an indicator of the pozzolanic activity - the greater the reduction, the better the pozzolanicity of the material. However, only considering the data over a short time scale (2 minutes) according to the Luxan method, does not reflect the overall response of the material. It should be followed by a period extending up to approximately 100 h, where the rate of change of lime consumption remains relatively constant and attains a low value. This is denoted in the plots presented in fig. 5.

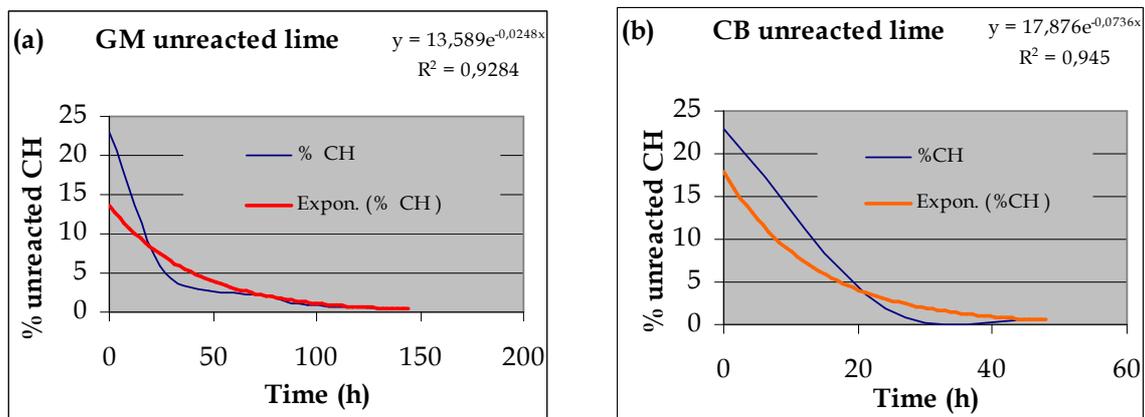


Figure 5: Experimental data and exponential curves for the percentage of the unreacted lime (CH) with the GM (a) and CB (b) clays versus time

Figure 6 depicted the marly limestone heated at 800 °C and the hydration products obtained after 30 days of curing with water. The calcined marly limestone contained lime and gehlenite, which are transformed into calcite and CSH after slaking. The peaks at 1620 and 962 cm⁻¹, which are progressively increased over time, denote the formation of hydraulic hydration products. Therefore, the studied marly limestone heated at 800 °C can be used as a hydraulic binder.

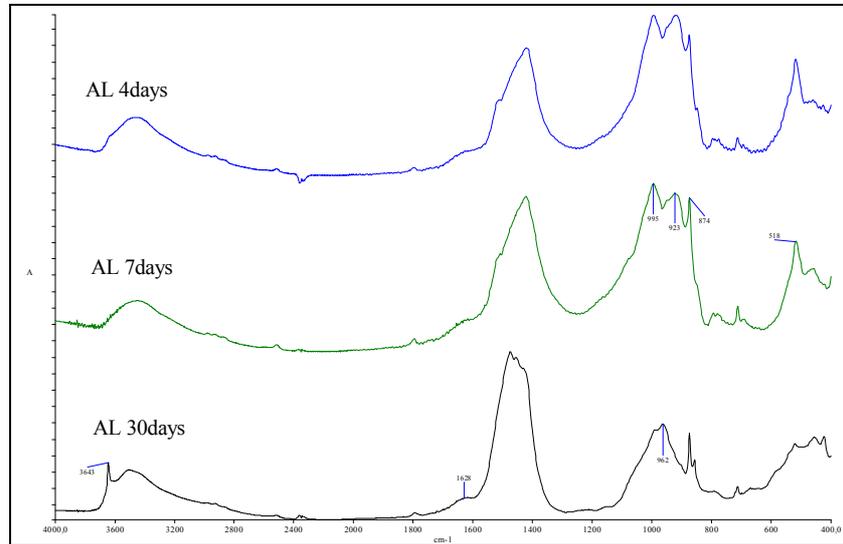


Figure 6: FTIR results of the hydrolysis of marly limestone at 4, 7 and 30 days

CONCLUSIONS

FTIR and DTA-DTG analyses have been applied to calcined clay/saturated CH mixtures in order to ascertain and follow the lime reactivity within the mixture over time. On the studied clays, the results revealed that the lime was consumed in up to 30 days, but in different amounts and times. The GM calcined clay reacted completely with lime after 1 week, the ME clay after one month, while the CB sample completed its reaction with lime just in 2 days. Comparisons were drawn between the results obtained for similar mixtures measured over a short time scale. Considering only the data over a short time scale does not reflect the overall response of the material. A period extending up to approximately 100 h should follow, where the rate of change of lime consumption remains relatively constant and attains a low value. The chemical composition of the clay and especially the low calcite content and the presence of kaolinite play an important role in the overall lime reactivity. This is one of the reasons of the greatest lime reactivity exhibited by the CB clay. As far as the hydraulicity of the calcined marly limestone is concerned, it acquired hydraulic properties after one month curing of water. This study demonstrated that, by combining FTIR and DTA-DTG analyses over a time scale of up to two months, it is possible to index/rank the lime reactivity and hydraulicity of the materials tested.

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