Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 420 (2004) 135–140

thermochimica acta

www.elsevier.com/locate/tca

Evaluation of pozzolanic activity of natural and artificial pozzolans by thermal analysis

Antonia Moropoulou*, Asterios Bakolas, Eleni Aggelakopoulou

Section of Materials Science and Engineering, Department of Chemical Engineering, National technical University of Athens, 9 Iroon Polytechniou St., 15773 Zografou, Athens, Greece

Received 29 July 2003; accepted 25 November 2003
Available online 13 July 2004

Abstract

In this research, the pozzolanic activity of natural and artificial pozzolan used for preparation of restoration mortars was evaluated. For this purpose, several pastes were prepared, by mixing two artificial pozzolans and a natural one with commercial hydrated lime, in different ratios. The pastes were cured in standard conditions (RH $= 98\%$, $T = 25\,^{\circ}\mathrm{C}$). The pozzolanic activity was evaluated by using simultaneous differential thermal and thermogravimetric analysis (DTA/TG) after curing for 3, 7, 14, 28 days. The obtained results revealed that the various lime/pozzolan pastes displayed different reaction kinetics and therefore the various pozzolans present different reactivity, in proportion to its mineralogical, physical and chemical characteristics.

Keywords: Pozzolans; Mortars; Lime; DTA/TG

1. Introduction

Lime mixed with pozzolanic additions (natural and artificial) has been used extensively in the past as mortars for the construction of historic and traditional buildings [1,2]. Therefore, nowadays in the restoration interventions that take place in historic buildings, in order to assure the compatibility of the restoration mortars to authentic ones, analogous materials should be used. One of the major problems of selecting the appropriate pozzolan used as a pozzolanic addition in restoration mortars is its reactivity since the use of high reactive pozzolans as an addition to lime mortars produce hydraulic, durable mortars with sufficient mechanical strength, similar to historic ones.

The pozzolanic reactivity has been studied thoroughly in the past [2–4]. Various physicochemical characteristics influence a pozzolan reactivity such as: the glassy compounds content, the total and active silica content, the grain size distribution, the specific surface area [5]. Furthermore, regarding the artificial pozzolans some other parameters play a significant role to its reactivity like the clay quality, the calcination temperature, the calcination and the freezing process [6]. However, these factors are only indicators of the pozzolanic reactivity and they could not assure that the lime/pozzolan mortar produced would present the best potential behavior. Therefore, in the literature, several studies state that the $Ca(OH)_2$ consumption that takes place in lime/pozzolan pastes could be a reliable factor for the evaluation of the pozzolan reactivity and the detection of the pozzolanic products [7–12].

The characterization of pozzolanic historic mortars revealed that two types of pozzolans have been used in the past: natural, usually of volcanic origin and artificial like ceramic powder [13–15]. Nowadays, the most natural pozzolans do not present the appropriate specifications for using them as pozzolanic additives (low reactivity, unstable quality, etc.) and therefore in order to produce restoration mortars, similar to historic ones, except the traditional artificial pozzolans several others are, also, used, such as: fly ash, silica fume, metakaolin, etc.

In this research several pastes were prepared, by mixing two artificial pozzolans (a traditional and a current one) and a natural one with commercial hydrated lime, in different ratios, in order to study their pozzolanic activity, by DTA/TG analysis.

---

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

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2003.11.059

Table 1
Chemical composition and physical properties of the materials used for the pastes preparation

MT	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	Na_2O (%)	SO_3 (%)	LOI (%)	$Ca(OH)_2$ (%)	$CaCO_3$ (%)	Density $(g/cm^3)^a$
L	0.17	0.18	0.07	70.06	2.35	–	–	0.77	25.60	88.75	5.13	2.34
MK	51.70	40.60	0.64	0.71	0.96	2.00	0.31	0.11	1.19	–	–	2.52
EM	69.66	12.21	2.34	2.01	0.70	3.28	0.62	–	7.35	–	–	2.36
CP	53.30	13.05	4.63	16.49	2.83	2.54	–	–	3.40	–	4.07	2.73

MT: material, *according to ASTM C-188-95.

2. Materials and methods

Several pastes were prepared by mixing a commercial lime with three types of pozzolans: earth of Milos (EM)—a natural pozzolan deriving from the island of Milos in Greece, a ceramic powder (CP)—an artificial pozzolan produced by grinding handmade bricks baked at low temperatures (<900 °C) and a metakaolin (MK)—Metastar 501 of IMERYS Minerals Ltd.—as an artificial high reactive pozzolan [6]. Table 1 reports the chemical composition and the physical properties of the materials used for the pastes preparation. Furthermore, Fig. 1 presents the grain size distribution of the pozzolans as they derived by laser CILAS 715 method. The metakaolin is the finest pozzolan with cumulative passing percentage at 64 μm of 100% and at 16 μm up to 95.6%. Regarding the earth of Milos and the ceramic powder, the first one seems to be finer than the second one. Earth of Milos presents a cumulative passing percentage from 64 μm up to 95.9% and the corresponding percentage for the ceramic powder is up to 88.1%.

Table 2 reports the weight ratios of the various components employed for manufacturing the pastes. The mixing procedure was the same for all pastes: first, the amount of lime was mixed with the total amount of water, it was stirred for 3 min in a mixer and afterwards the amount of pozzolan was added gradually in the paste and it was stirred for other 20 min. The pastes were casted in cubic moulds of 2 cm × 2 cm × 2 cm and stored in standard conditions (RH = 98%, $T = 25\,°C$).

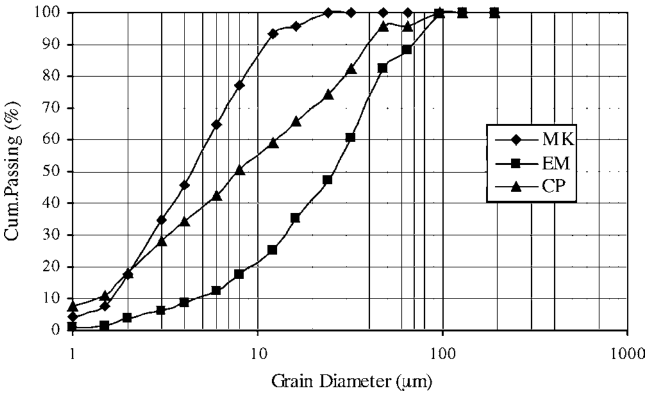

Fig. 1. Grain size distribution of pozzolans.

Table 2
Weight ratios of the various components used in pastes

Code	Material	Water/solid
MK05	Lime/metakaolin: 1/0.5	1.00
MK1	Lime/metakaolin: 1/1	1.00
MK2	Lime/metakaolin: 1/2	1.00
EM1	Lime/earth of Milos: 1/1	0.69
EM2	Lime/earth of Milos: 1/2	0.59
EM3	Lime/earth of Milos: 1/3	0.54
CP1	Lime/ceramic powder: 1/1	0.69
CP2	Lime/ceramic powder: 1/2	0.59
CP3	Lime/ceramic powder: 1/3	0.54

The pastes are investigated regarding their rate of reacted $Ca(OH)_2$ and the pozzolanic reaction products at time of 0, 3, 7, 14, 28 days of curing, using the simultaneous differential thermal and thermogravimetric analysis (DTA/TG—Netzsch 409EP), in a static air atmosphere with heating rate of 10 °C/min from 25 to 1000 °C in order to investigate the $Ca(OH)_2$ consumption in time and to determine the pozzolanic reaction products.

3. Results and discussion

3.1. MK pastes

Fig. 2 presents the DTA/TG thermograms for the MK1 paste for 0, 3, 7, 14 and 28 days of curing. At the first hours of reaction (up to 3 h), the thermogram presents an endothermic peak at about 450 °C that is attributed to the decomposition of $Ca(OH)_2$, a second one at 750 °C due to the CO_2 release by the $CaCO_3$ decomposition and an exothermic peak at about 980 °C with insignificant weight loss on the TG, that is attributed to formation of crystalline phases, like spinel and mullite ($Al_6Si_2O_{13}$) where silica is totally or partially segregated [16]. At 3 days of curing, an endothermic peak at about 120 °C is detected that indicates the presence of CSH. Furthermore, at the same time it is possible to detect the presence of C_2ASH_8 (stratlingite) and C_4AH_{13} at about 180 and 265 °C, respectively. For the other times of curing 7, 14, 28 days the amounts of these phases increase while the amount of $Ca(OH)_2$ decrease. Finally, at 14 days of curing the whole amount of $Ca(OH)_2$ was bounded and

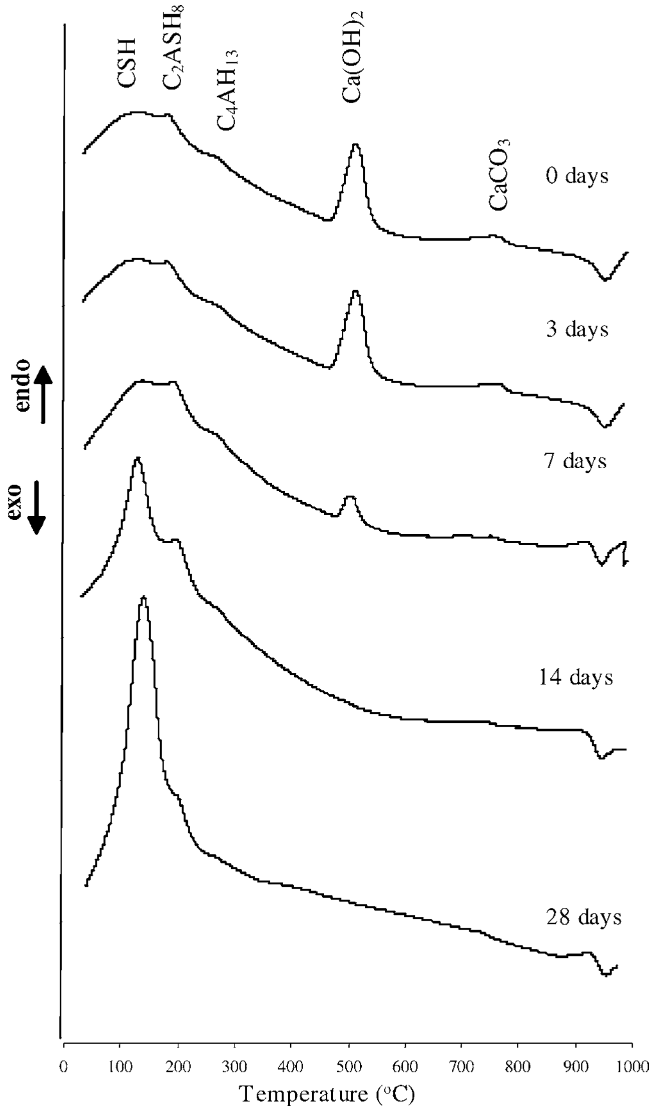

Fig. 2. DTA/TG thermograms for the MK1 paste for 0, 3, 7, 14 and 28 days of curing.

no peak is detected. Furthermore, the exothermic peak at about 980 °C was detected in all thermograms, at 0, 3, 7, 14, 28 days of curing times. In addition, no hydrogarnet is detected in these thermograms, as other authors have detected in previous research for pastes of lime/metakaolin [7]. Analogous thermograms present the MK05 and the MK2 pastes. The products of the pozzolanic reaction are detected at 3 days of curing and they present a significant increase at the times of 7, 14, 28 days while simultaneously the $Ca(OH)_2$ amount decreases.

Fig. 3 presents the percentage of reacted $Ca(OH)_2$ versus time for the MK05, MK1, MK2 pastes. One can notice that the highest rate of $Ca(OH)_2$ consumption is reported for the MK2 and the MK1 paste. For these two synthesis the 100% of the initial amount of $Ca(OH)_2$ is consumed after 14 days of curing, whereas at 7 days of curing the 80% of the initial amount of $Ca(OH)_2$ has reacted. On the other hand, the MK05 synthesis exhibit a slower rate of $Ca(OH)_2$ consumption, fact that is attributed to larger amount of lime that was added in the paste. Therefore, for this synthesis, at 28 days the 80% of the total $Ca(OH)_2$ has reacted while at 14 days the proportional percentage is about 60%.

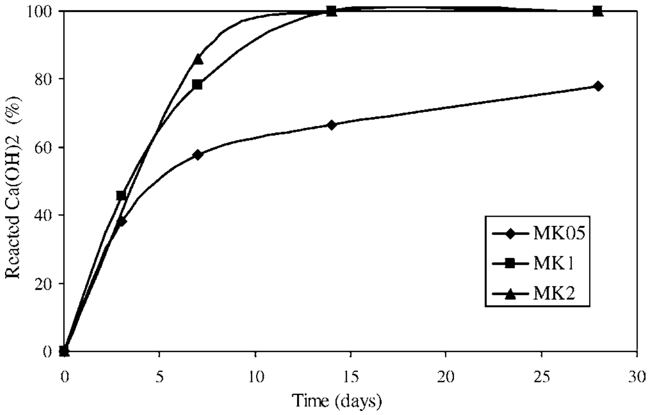

Fig. 3. Percentage of reacted $Ca(OH)_2$ vs. time for the MK05, MK1, MK2 pastes.

Fig. 4 shows the weight loss (%) of the chemical compounds detected in paste MK1 versus time of curing as it is determined by the TG analysis. It is clear that the C_2ASH_8, is formed after 3 days and the maximum percentage is formed after 7 days and it remains stable from 7 to 14 days, followed by a slight increase to 28 days. On the other hand, small quantities of C_4AH_{13} are formed that became stable after 7 days of curing while the CSH content is sharply increased after 7 days until 28 days. This fact is accompanied with a pronounced decrease in the $Ca(OH)_2$ content that after 14 days, it is all consumed.

3.2. CP pastes

Fig. 5 presents the DTA/TG thermograms for the CP2 paste, at 0, 3, 7, 14 and 28 days of curing. It could be noticed

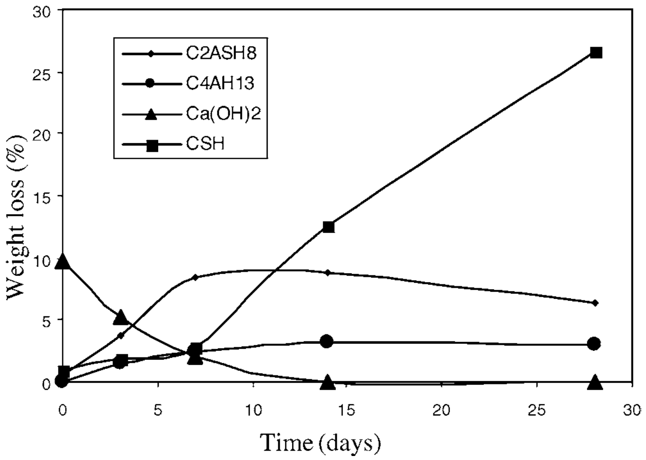

Fig. 4. Weight loss (%) of the compounds detected in paste MK1 vs. time of curing.

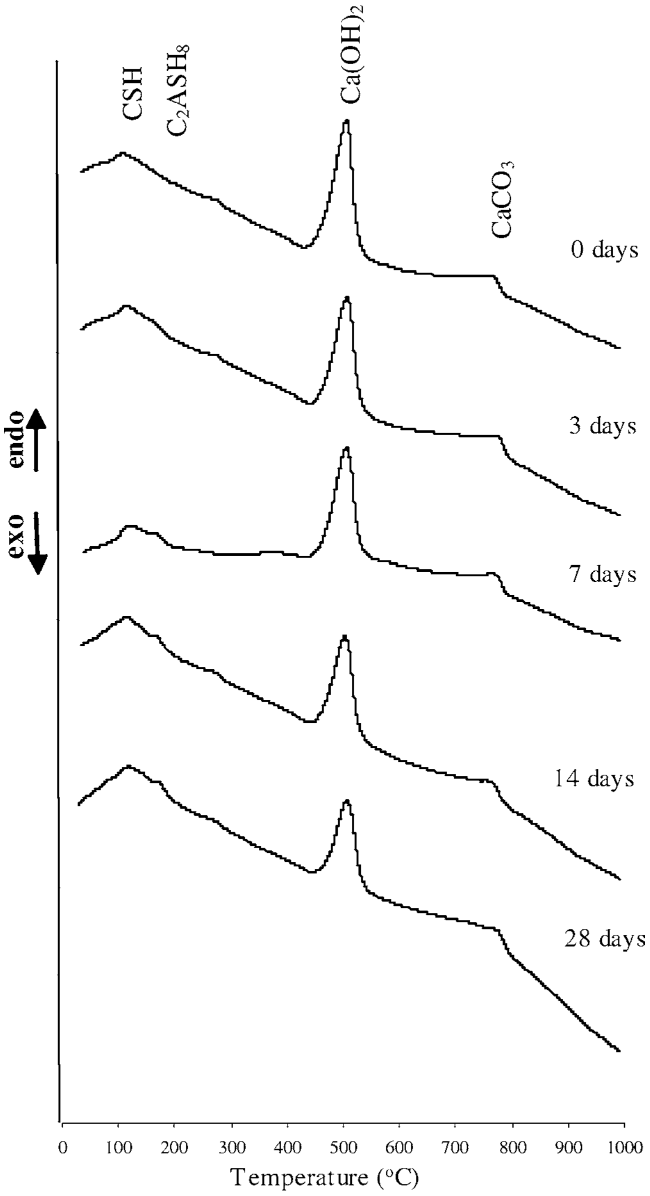

Fig. 5. DTA/TG thermograms for the CP2 paste for 0, 3, 7, 14 and 28 days of curing.

that at temperatures of 120 and 180 °C are detected slightly, the characteristic endothermic peaks of CSH and C_2ASH_8, respectively. These peaks detected with DTA are accompanied by a weight loss presented in TG that exhibits an anodic trend in evolution of time. At around 470 °C, a typical endothermic peak was detected, correlated to dehydration of calcium hydroxide that exhibits a decreasing trend with time of curing. Finally, at about 780 °C, the thermoanalytic curves show the endothermic phenomenon of decarbonation due to carbonates present in modest quantities both in hydrated lime and in the pozzolans. The corresponding weight loss of CO_2 that is determined by the TG remains stable from 0 to 28 days.

Fig. 6 presents the percentage of $Ca(OH)_2$ that was consumed versus time for the CP1, CP2, CP3 pastes. One can notice that the highest consumed percentage of $Ca(OH)_2$ is reported for the CP3 paste that shows an amount of reacted $Ca(OH)_2$ at 28 days of curing about 38%. The corresponding percentage for CP2 and CP1 paste is 28 and 22%, respectively. Therefore, it is observed that in the case of ceramic powder pastes the $Ca(OH)_2$ is consumed very slowly and therefore this type of pozzolan present a much lower reactivity regarding the metakaolin pastes.

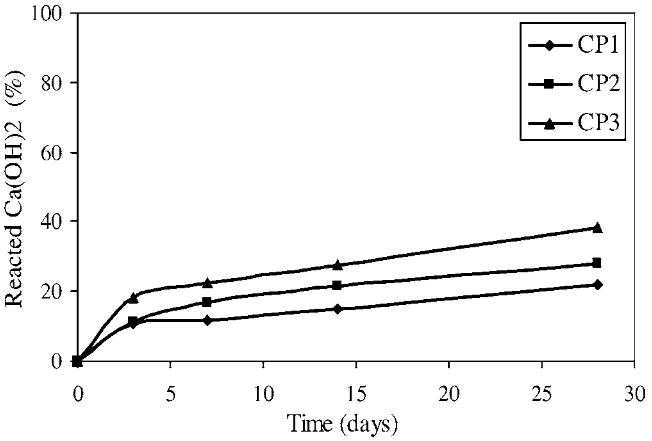

Fig. 6. Percentage of reacted $Ca(OH)_2$ vs. time for the CP1, CP2, CP3 pastes.

The weight loss regarding the pozzolanic reaction products and the $Ca(OH)_2$ that were determined for CP2 paste versus time of curing is presenting in Fig. 7, where the slow rate of $Ca(OH)_2$ consumption is observed along with the slow rate of CSH and C_2ASH_8 production.

3.3. EM pastes

The DTA/TG thermograms for the EM3 paste at 0, 3, 7, 14 and 28 days of curing are reported in Fig. 8. At 3 days of curing, an endothermic peak at ~120 °C is detected that indicates the presence of CSH that increase constantly as the curing time increase. For this kind of pastes no C_2ASH_8 and

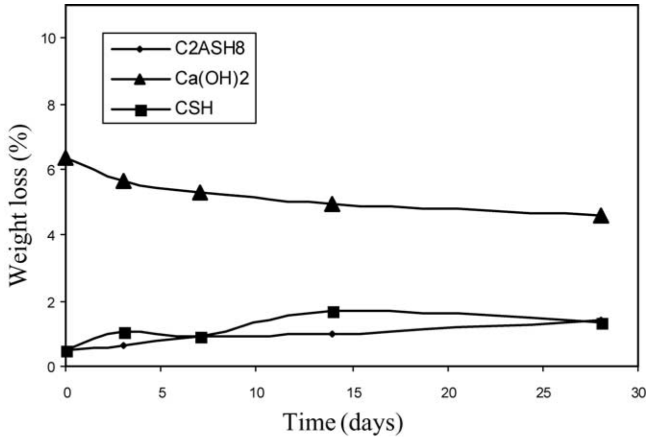

Fig. 7. Weight loss (%) of the compounds detected in paste CP2 vs. time of curing.

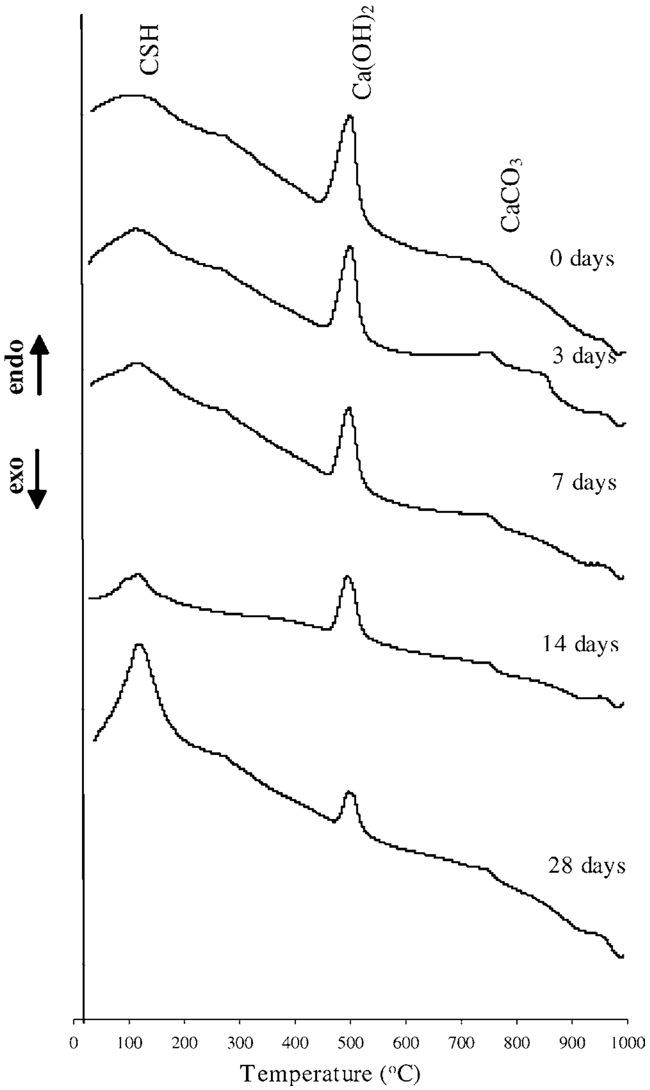

Fig. 8. DTA/TG thermograms for the EM3 paste for 0, 3, 7, 14 and 28 days of curing.

C_4AH_{13} was detected. Furthermore, the characteristic curve of $Ca(OH)_2$ is detected in the temperature about 480 °C and the relative weight loss amount measured by TG, decreases with time. At last, the decomposition of $CaCO_3$ is detected at about 730 °C. The corresponding weight loss of CO_2 that is determined by the TG remains almost stable from 0 to 28 days, fact that reveal that the $CaCO_3$ do not participate in the reactions that take place. This hypothesis is confirmed by DTA analysis since no monocarboaluminate was detected in the pastes, as other authors have revealed in previous work for pastes of lime/natural pozzolans [9]. The other pastes EM1, EM2 present analogous behavior under DTA/TG investigation. The main product that is formed as a result of the pozzolanic reaction that occurs is the CSH that exhibits an anodic trend with time of curing, with a simultaneous of $Ca(OH)_2$ percentage decrease.

Regarding the consumption rate of $Ca(OH)_2$ for the EM1, EM2, EM3 pastes, the EM3 present the highest values of $Ca(OH)_2$ consumption that is about 30% at the time of 7 days of curing and 60% at the time of 28 days (Fig. 9). Analogous behavior is observed in the case of EM2 paste with slight lower values. On the other hand EM1 present lower values of $Ca(OH)_2$ consumption, equal to 35% for 28 days of curing, that indicates that this ratio mixing is rather insufficient for restoration mortars preparation since the time needed for its chemical stabilization is large.

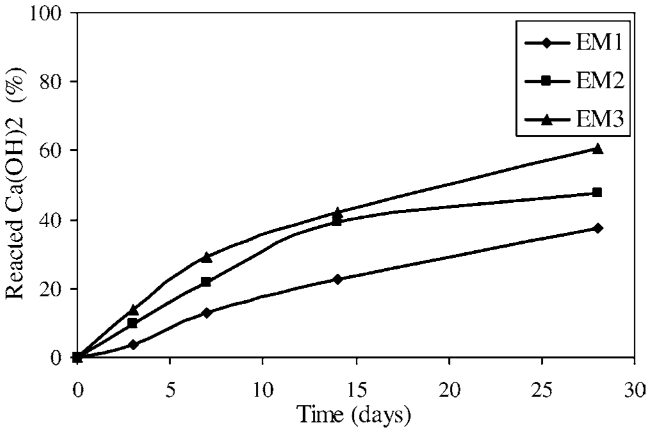

Fig. 9. Percentage of reacted $Ca(OH)_2$ vs. time for the EM1, EM2, EM3 pastes.

Fig. 10 presents the weight loss (%) of the compounds detected in paste EM3 versus time of curing, determined by TG curves. It is clear that as the $Ca(OH)_2$ percentage decreases the amount of CSH increases in the evolution of time. Finally, it could be pointed out that the earth of Milos pastes are still in chemical evolution after 28 days of curing and therefore they should, also, be investigated after 90 and 180 days of curing.

Fig. 11 reports the reacted percentage of $Ca(OH)_2$ for the synthesis that present the highest rate of $Ca(OH)_2$ consumption of each pozzolan group of pastes versus time of curing. It is clear that the metakaolin paste presents the highest reaction rate of $Ca(OH)_2$ with the pozzolan, fact that was expected since metakaolin is the most reactive pozzolan of

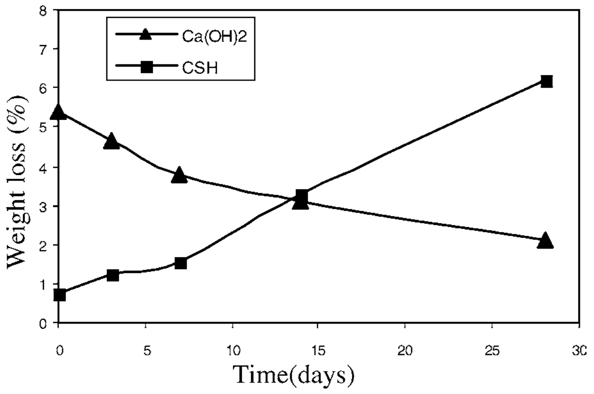

Fig. 10. Weight loss (%) of the compounds detected in paste EM3 vs. time of curing.

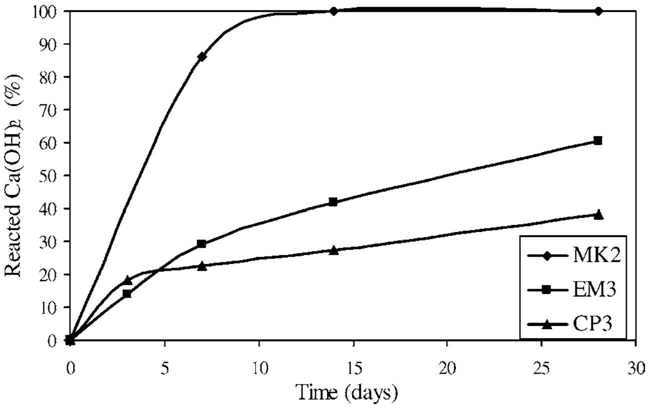

Fig. 11. Reacted percentage of $Ca(OH)_2$ for the MK2, EM3, CP3 pastes vs. time of curing.

the investigated ones. More specifically, metakaolin paste exhibits a percentage of reacted $Ca(OH)_2$ up to 88%, at 7 days of curing, while the corresponding percentage comes up to 28 and 22% for the earth of Milos and ceramic powder pastes, respectively. Furthermore, it could be observed that the lime/metakaolin paste is stabilized chemically at the time of 14 days of curing while the ceramic powder and earth of Milos pastes are still in evolution after 28 days of curing.

In addition, at 3 days of curing ceramic powder paste presents a higher rate of $Ca(OH)_2$ consumption than the earth of Milos paste, that decreases from 3 to 28 days. On the other hand, earth of Milos paste present a more stable rate of $Ca(OH)_2$ consumption that from 3 to 28 days is larger than the ceramic powder one.

4. Conclusions

From the obtained results the following conclusive remarks can be point out:

- The reacted $Ca(OH)_2$ determined by DTA/TG analysis, in pastes of lime/pozzolans systems could be an indicative factor for pozzolans reactivity evaluation.
- DTA/TG investigation has revealed different reaction kinetics for the various lime/pozzolan pastes. In particular, the lime/metakaolin paste present the highest reactivity of all the materials investigated. This fact could be ascribed to its physical and chemical characteristics. Furthermore, the lime/metakaolin paste is stabilized chemically at the time of 14 days of curing while the ceramic powder and earth of Milos pastes are still in evolution after 28 days of curing.
- The lime/natural pozzolan pastes present a higher rate of $Ca(OH)_2$ consumption than the ceramic powder pastes.
- Regarding the metakaolin pastes, the paste produced by mixing lime/metakaolin in ratio 1/2 exhibits the highest rate of $Ca(OH)_2$ consumption. In the case of natural pozzolan and ceramic powder pastes, the best reacted $Ca(OH)_2$ rate values were observed for a lime/pozzolan ratio up to 1/3.
- Several pastes are still in evolution regarding the chemical reactions at 28 days of curing and they should be investigated after 90 and 180 days.
- The DTA/TG results should be correlated with mechanical strength and X-ray diffraction data at time of 1, 3 and 6 months in order to investigate the correlation among rate of $Ca(OH)_2$ consumption, mechanical parameters, and the formation of pozzolanic reaction products.

References

[1] A. Bakolas, R. Bertoncello, G. Biscontin, A. Glisenti, A. Moropoulou, E. Tondello, E. Zendri, Chemico-physical interactions among the constituents of historical walls in Venice', in: J.R. Druzik, P.B. Vandiver (Eds.), Materials Issues in Art and Archaeology IV, Materials Research Society, Pittsburgh, 1995, pp. 771–777.

[2] M. Giua, Trattato di Chimica Industriale, vol. 3, UTET, Torino, 1958.

[3] G. Gallo, Studio Microscopico delle Malte a Pozzolana, Gazzetta Chim. Ital. 38 II (1908) 158.

[4] G. Gallo, Strutura delle Malte a Calce e Pozzolana Segni, Il Cemento, 1947, fasc. 9–10, p. 106.

[5] F.M. Lea, Lea's Chemistry of Cement and Concrete, 3rd ed., Arnold, London, 1988.

[6] B.B. Sabir, S. Wild, J. Bai, Metakaolin and Calcined Clays as Pozzolans for Concrete: A Review, Elsevier, New York, 2001.

[7] J. Cabrera, M.F. Rojas, Mechanism of hydration of the metakaolin–lime–water system, Cement Concrete Res. 31 (2001) 177–182.

[8] W. Roszczynialski, Determination of pozzolanic activity of materials by thermal analysis, J. Therm. Anal. Calorim. 70 (2002) 387–392.

[9] P. Ubbriaco, F. Tasselli, A study of the hydration of lime–pozzolan binders, J. Therm. Anal. Calorim. 52 (1998) 1047–1054.

[10] P. Ubbriaco, P. Bruno, A. Traini, D. Calabrese, Fly ash reactivity—formation of hydrate phases, J. Therm. Anal. Calorim. 66 (2001) 293–305.

[11] M.F. Rojas, J. Cabrera, The effect of temperature on the hydration rate and stability of the hydration phases of metakaolin–lime–water systems, Cement Concrete Res. 32 (2002) 133–138.

[12] A.A. Amer, Thermal analysis of hydrated fly ash-lime pastes, J. Therm. Anal. Calorim. 54 (1998) 837–843.

[13] L. Binda, G. Baronio, Indagine sull' aderenza tra legante e laterizio in malte ed intonachi di 'cocciopesto, Bolletino d' Arte 35–36 (1986) 109–115.

[14] A. Moropoulou, A. Bakolas, K. Bisbikou, Characterization of ancient, byzantine and later historic mortars by thermal analysis and X-ray diffraction techniques, Thermochim. Acta 269/270 (1995) 779–795.

[15] A. Moropoulou, G. Biscontin, K. Bisbikou, A. Bakolas, P. Theoulakis, A. Theodoraki, T.H. Tsiourva, Physico-chemical study of adhesion mechanisms among binding material and brick fragments in 'cocciopesto', Scienza e Beni Culturali IX (1993) 415–429.

[16] A. Shvarzman, K. Kovler, G.S. Grader, G.E. Shter, The effect of dehydroxylation/amorphization degree on pozzolanic activity of kaolinite, Cement Concrete Res. 33 (2003) 405–416.