

A STUDY OF THE HYDRATION OF LIME-POZZOLAN BINDERS

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Abstract

DTA/TG and TG/DTG thermal studies and XRD investigations were carried out on pastes of lime-pozzolan binders to examine the relative hydration process. The binders were prepared with two natural pozzolans and hydrated lime, mixed together in different proportions. The main hydrated phases formed in the pastes are calcium silicate hydrate (CSH) and monocarboaluminate. The growth of CSH was greater for the paste of the pozzolan richer in reactive constituents. For pastes with a higher lime/pozzolan ratio, a slowing of the formation of CSH was observed, while the formation of monocarboaluminate was more intense. The calcium hydroxide contents of the pastes obtained by thermogravimetric analysis made it possible to determine the pozzolanic activities of the two pozzolans under examination. The mortars for the various lime-pozzolan binders displayed characteristic hardening.

Keywords: DTA/TG, lime, mortars, natural pozzolans, TG/DTG

Introduction

The present study examines the characteristics of some lime-pozzolan binders obtained by using natural pozzolan from the region of Basilicata (Italy) [1, 2]. A knowledge of the hydration process of the lime-pozzolan pastes, together with determination of the mechanical strength, is fundamental for improvement of the characteristics of these binding materials [3-5]. Two different pozzolans were used. After chemical and mineralogical characterization, these were suitably ground and then mixed with hydrated lime in different ratios.

The study of the binders involved determination of the hydrated products formed during the hydration reactions of the different pastes. To this end, DTA/TG and TG/DTG analysis and X-ray diffractometry investigations were carried out on lime-pozzolan pastes. The results obtained from the thermogravimetric analyses allowed determination of the calcium hydroxide contents of the hydrated samples and then the pozzolanic activities of the natural pozzolans. With the lime-pozzolan binders, standards mortars were prepared the hardening of which was evaluated in different curing periods by means of compressive strength tests.

Experimental

The pozzolans examined in the present study (pyroclasts of Vulture) are from two different localities in the territory of Rionero in Vulture. The pozzolans from the two localities will be denoted pozzolan 1 and pozzolan 2. Samples of the pozzolanic materials were subjected to chemical and mineralogical characterization. From the two pozzolans, powders were produced with the same degree of grinding (sieve size (μm): passing (%)=180:99.3; 90:97.9 and 63:95.8). A commercial hydrated lime ($\text{Ca}(\text{OH})_2$: 93%) was employed for the lime-pozzolan mixtures (mass ratios 33.3/100 (I) and 42.8/100 (II)). With the four hydraulic binders, pastes were prepared (water/binder: 0.38). After setting, they were cured in water saturated with calcium hydroxide; pastes hydrated for various periods (from 1 h to 365 days) were submitted to DTA/TG analysis (Netzsch STA 409) in static air, to TG/DTG analysis (Perkin-Elmer TGA 7) in a N_2 flow (40 ml min^{-1}) and to X-ray diffractometric (XRD) analysis (Philips PV-1710, using $\text{CuK}\alpha$ radiation).

With the different binders, standard mortars were prepared according to the procedure for hydraulic limes [6]: the sand used was the standard one of Torre del Lago and the water/binder ratio was 0.62; after curing for 3, 7, 28, 90, 180 and 365 days, the compressive strengths of these mortars were determined.

Results and discussion

The chemical compositions of the pozzolanic materials are indicated in Table 1; Figs 1 and 2 show X-ray diffractograms on the two pozzolans.

Table 1 Chemical compositions of natural pozzolans

	l.o.i.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	ZnO	P_2O_5	CO_2
P1	8.58	46.32	15.39	6.73	9.99	3.25	0.19	2.66	2.68	0.03	0.72	1.50
P2	7.60	46.06	14.73	10.58	10.59	3.79	0.22	1.72	2.34	0.02	0.85	1.40

l.o.i.: loss on ignition/% (1000°C)

The XRD examinations on the whole samples revealed the presence of the following main minerals: zeolitic minerals (principally analcime and lesser quantities of chabasite and phillipsite), feldspars, feldspathoids, plagioclases, micas, augitic-egirinic pyroxenes, magnetite and hematite, cristobalite, quartz and calcite. The XRD examinations on small fractions additionally demonstrated the presence of clay minerals of smectitic and halloysitic types, associated with significant quantities of material characterized by a low degree of crystallinity, which appears in the form of diffraction bands attributable to silica and alumina in a semi-amorphous state. A comparative examination of the minera-

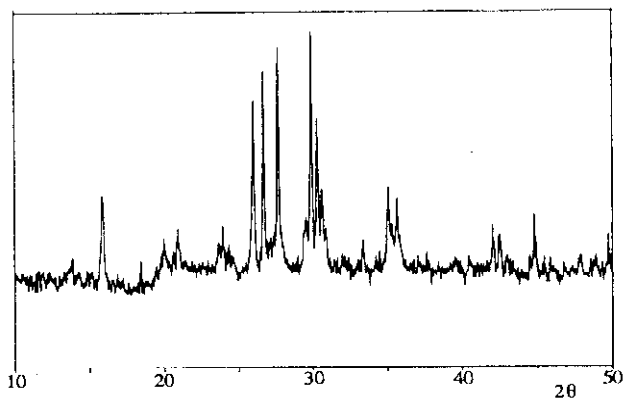


Fig. 1 XRD of pozzolan 1

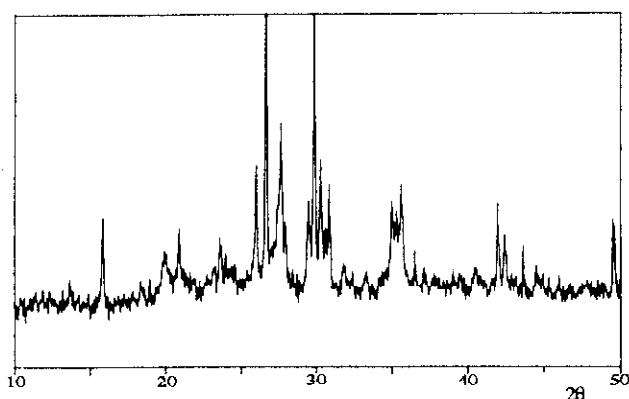


Fig. 2 XRD of pozzolan 2

logical compositions of the two pozzolans showed that pozzolan 1 contains more semi-amorphous and vitreous phases than those in pozzolan 2, and also a higher analcime content. Pozzolan 2 has a higher content of clay material of micaceous type relative to pozzolan 1.

The DTA/TG investigations on the pastes (I/1 and I/2) characterized by the lower lime/pozzolan ratio (33.3/100) demonstrated an endothermic effect at 90°C, due to the dehydration of calcium silicate hydrate (lime-rich CSH) (Fig. 3). This hydrated product is already observed in the pastes after 1 h of curing. The development of CSH with increase of the curing time of the samples is more intense in the paste of pozzolan 1. After a brief period of hydration of the binders, the DTA/TG curves and more particularly the TG/DTG curves (Fig. 4) show that the endothermic phenomenon of dehydration of CSH has a second effect at 125°C (less basic CSH-1), together with the effect at 90°C [7, 8]. An exothermic effect is correlated with the CSH at around 850°C, due to the recrystallization of wollastonite [9].

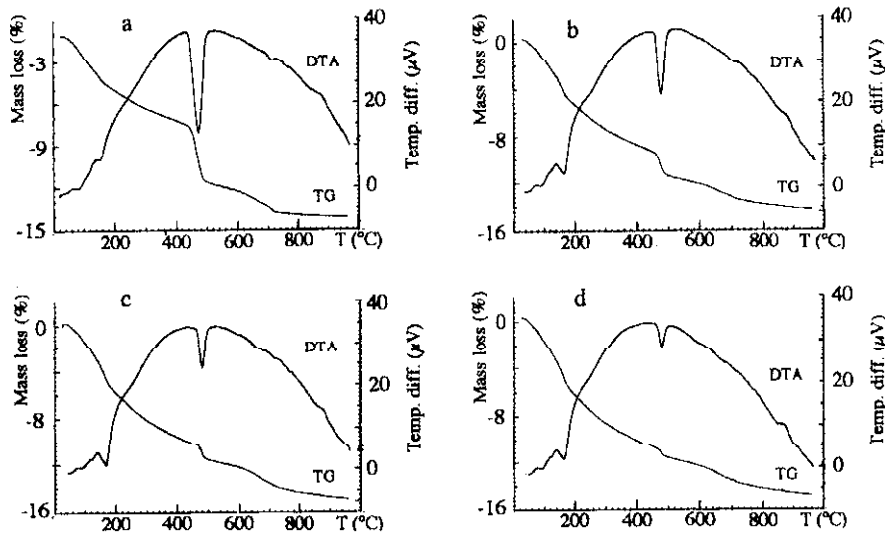


Fig. 3 DTA/TG curves of paste I/1 (a: 1 day, b: 28 days, c: 90 days, d: 180 days)

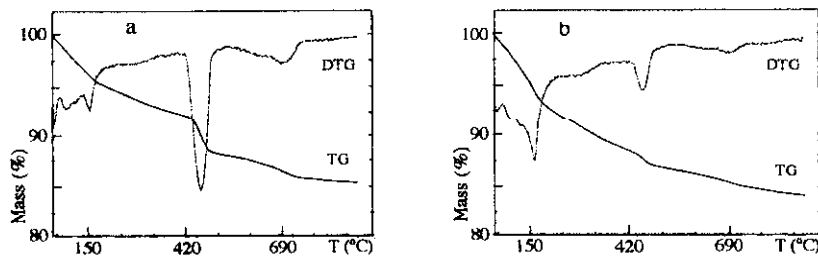


Fig. 4 TG/DTG curves of paste I/1 (a: 3 days, b: 365 days)

In the same thermoanalytical curves at 160°C, the development of an endothermic effect is observed, due to calcium monocarboaluminate hydrate ($C_3A \cdot CaCO_3 \cdot 11H_2O$; where $C=CaO$, $A=Al_2O_3$), whose presence in the pastes is confirmed by XRD examination ($d:7.55 \text{ \AA}$) (Figs 5 and 6). This hydrate phase appears in the thermal curves after 7 h and exhibit an especially intense increase after 3 days of curing. The amounts of $C_3A \cdot CaCO_3 \cdot 11H_2O$ after brief and intermediate curing times are greater for the paste of pozzolan 1 than for that of pozzolan 2; for the longest hydration period, the quantities of the product tend to equalize in the pastes of the two pozzolans.

The DTA/TG and TG/DTG curves display a weak endothermic effect at around 265°C, which increases slowly with increase of the curing times of the samples. This effect leads to the hypothesis that small quantities of the phase $4CaO \cdot Al_2O_3 \cdot 13H_2O$, and probably also the solid solution $C_4A \cdot 1/2CO_2 \cdot 12H_2O - C_3A \cdot CaCO_3 \cdot 11H_2O$, are present in the pastes; in fact, the XRD examination

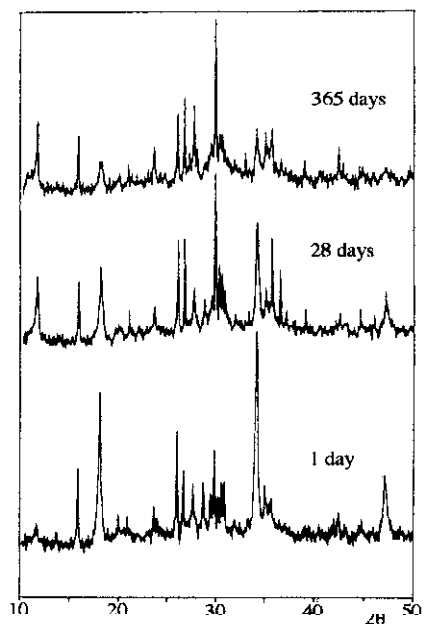


Fig. 5 XRD of paste I/1

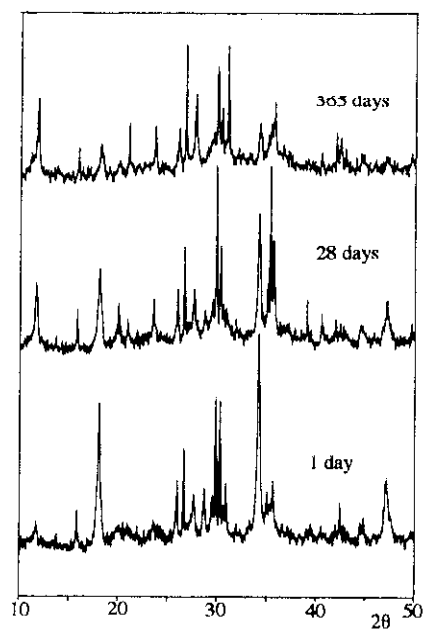


Fig. 6 XRD of paste I/2

shows peaks attributable to C_4AH_{13} ($d: 7.92 \text{ \AA}$) and to the relative solid solution ($d: 8.00 \text{ \AA}$) [10].

At around 470°C , a typical endothermic effect develops, correlated with the dehydration of 'free' calcium hydroxide. The mass ponderal variation which accompanies the loss of water is recorded by means of thermogravimetric analysis, which allows determination of the $\text{Ca}(\text{OH})_2$ still available for the pozzolanic reaction.

At around 700°C , the thermoanalytical curves show the endothermic phenomenon of decarbonation due to the carbonates present in modest quantities both in the hydrated lime and in the pozzolans. The formation of monocarboaluminate leads to a reduction of the 'free' carbonate content. The monocarboaluminate after 90 days shows only a modest quantity increase, while for the CSH there is also growth after 365 days.

From the TG/DTG analysis, the quantity of water bound in the hydrate products is determined: these phases are found to be mainly the CSH phase and the $C_3A \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$ phase (the quantity of the latter is about half that of CSH). The total amount of neoformed hydrate products in the hardened pastes (after curing for 365 days) can be estimated at around 40% in mass, while the free $\text{Ca}(\text{OH})_2$ content is about 4%.

The free lime content shows different trends for the two pozzolans in relation to the duration of curing of the pastes (Fig. 7). In particular, for the pastes of pozzolan 1, a reduction in free lime is noted from 1 h to 3 days and is even more marked from 3 to 90 days. For the mixtures of pozzolan 2, the reduction of free

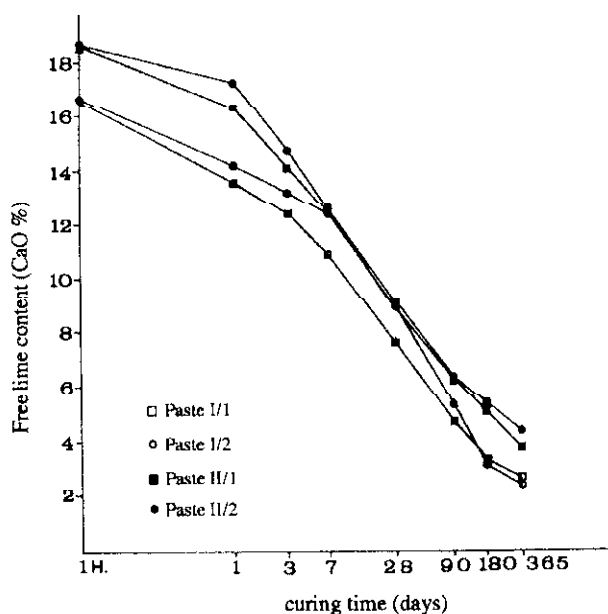


Fig. 7 Variation of free lime content with curing time

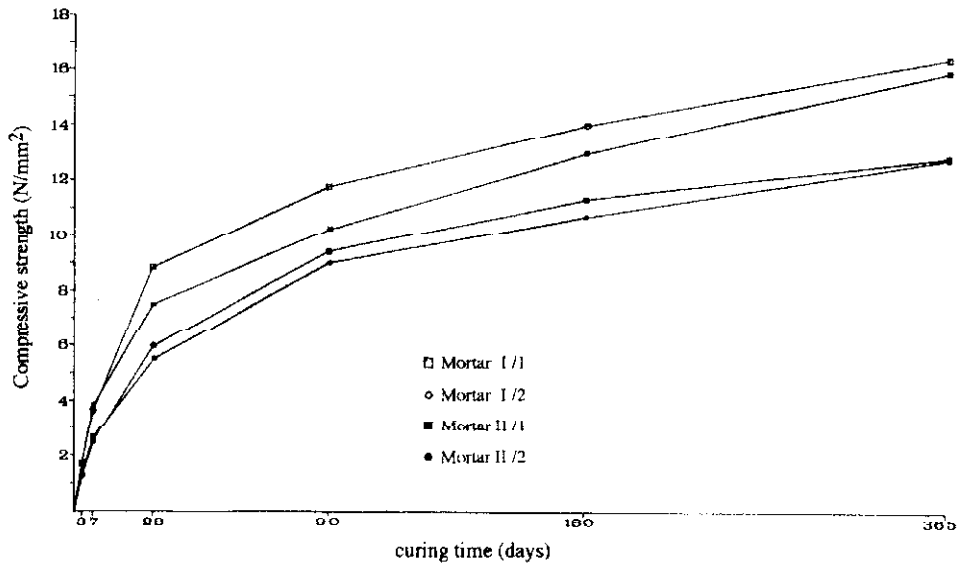


Fig. 8 Strength development of mortars

lime indicates an initially slower hydration process, which becomes rapid only after 7 days.

As regards the binders (II/1 and II/2) with the higher lime/pozzolan ratio (42.8/100), the thermoanalytical and XRD investigations indicate some differences in hydration behaviour with respect to the previous binders examined. Up to 1 day of curing, slower CSH and monocarboaluminate formation is observed, which is even slower in the paste of pozzolan 2. With increase of the curing time, for the pastes of the two pozzolans there is an acceleration of the process, due to a more intense formation of monocarboaluminate with respect to that of the preceding binders characterized by the lower lime/pozzolan ratio. The quantity of CSH is slightly lower, but after a longer period of curing (around 365 days) it gradually becomes comparable to that of the previous pastes with the lower lime/pozzolan ratio.

The free lime values (Fig. 7) for all binders exhibit a characteristic trend for both of the pozzolans, which indicates a greater reactivity towards calcium hydroxide on the part of pozzolan 1, characterized by a higher content of silica and alumina active phases. The compressive strengths of the mortars in relation to the curing time (Fig. 8), in the case of the binders with the lower lime/pozzolan ratio, indicate development of a higher strength for the binder of pozzolan 1 than that for the binder of pozzolan 2. In the case of the binders with the higher lime/pozzolan ratio, up to 7 days of curing, the compressive strengths observed are higher than those of the binders poorer in lime. In the subsequent curing period, in con-

trast, these strengths are lower. With a curing period of more than 180 days, the strengths of the materials richer in lime tend gradually to reach the values for the materials with the lower lime/pozzolan ratio.

Conclusions

This study of the hydration processes of the lime-pozzolan binders and determination of the compressive strengths of the relatively hardened mortars has provided particularly interesting results on the characteristics of the binders based on lime and natural pozzolans from the Vulture area.

As a whole, the thermal studies have revealed different hydration kinetics for the various lime-pozzolan binders. In particular, up to an intermediate time of curing, there is a greater reactivity to lime in the pozzolan characterized by a higher content of amorphous components and thus richer in active phases of silica and alumina. With increase of the lime/pozzolan ratio, there is a slowing of the formation of CSH in the pastes, while the formation of monocarboaluminate is more intense. This behaviour is confirmed by compressive strength tests on the materials.

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References

- 1 L. La Volpe and G. Piccarreta, *Ren. Soc. It. Min. Pet.*, 27 (1971) 167.
- 2 M. Di Pierro, M. Moresi and F. Vurro, *Miner. Petrogr. Acta*, 29 (1985) 205.
- 3 P. Ubbriaco, *J. Thermal Anal.*, 47 (1996) 7.
- 4 P. Ubbriaco, *Proc. of Int. Sem. on Material and Thermal Properties in Cultural Heritage*, Rome 1996.
- 5 P. Ubbriaco and F. Tasselli, XVIII, *Con. Naz. di Calorimetria e Anal. Termica*, Pavia 1996, p. 147.
- 6 Italian Law, D. M. 31-8-1982.
- 7 H. F. W. Taylor, *The Chemistry of Cements*, Academic Press, London 1964, p. 167.
- 8 F. Massazza and U. Costa, *Proc. of XII. Conf. on Silicate Industry and Silicate Science*, 1, Budapest 1977, p. 537.
- 9 A. M. Amin, B. A. Sabrah and H. El Didamony, *Silicates Industriels*, 5-6 (1992) 77.
- 10 H. H. Roberts, *Proc. V. Intern. Symp. on the Chem. of Cement*, 2, Tokio 1968, p. 104.