

Solidifying/stabilizing properties of pastes of a hydraulic binder based on thermally activated red earth

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Abstract DTA/TG/DTG thermoanalytical investigation and X-ray diffractometry were carried out on hydraulic lime pastes obtained by mixtures of thermally activated red earth with lime. Hydration reactions proceed properly mostly due to the high silica and alumina content. In a long period of curing the paste presents calcium silicates hydrate in high quantities while there are moderate quantities of calcium monocarboaluminate hydrate, ettringite and gehlenite hydrated. In presence of chloride, pastes lead, after few days, a sensible acceleration of the hydration with the formation of calcium silicate hydrate and calcium chloroaluminate hydrate. The total amount of neo-formed hydrate products in the hardened paste, indicate a development of the solidifying/stabilizing capacity of the hydraulic binder.

Keywords DTA/TG/DTG · XRD · Hydraulic lime · Red earth

Introduction

Various studies concerning fly ash mixtures of FDR (Fuel Derived from Residues) and hydraulic binders [1–4] have revealed a particular behaviour with hydration. The released quantity of some constituents, polluting elements, is a determining factor in the evaluation of the solidifying and stabilizing capacity of the hydraulic binder. The use of an artificial pozzolanic hydraulic lime produces an interesting hydration process of the binder matrix [4–7]. In the

case of the fly ashes characterized by a moderate concentration of heavy metals and by a high content of sulphate and chloride it is necessary to optimise the solidifying/stabilizing (S/S) properties of the binder by means of an enrichment in reactive aluminate and silicate phases. To this end an artificial hydraulic lime was produced utilizing thermally activated red earth as pozzolanic material. The choice of the red earth (clay deposits) deposits was dictated by their abundance in Apulia, as well as by their appropriate chemical and mineralogical composition. Chloride salts are typically present in great quantities in the residues from combustion and have a negative influence on the solidifying and stabilizing processes of the hydraulic binders, and so a different S/S of the mixture can be found. This work describes the behaviour of a hydraulic lime by means of DTA/TG/DTG thermoanalytical and XR diffractometry investigation.

Experimental

For the experiment red earth collected in Apulia was utilized (Cassano Murge—Bari/Italy). Its chemical composition is shown in Table 1. The different samples were submitted to X-ray diffractometric analysis (Philips PV-1710 using $\text{CuK}\alpha$ radiation) and to DTA/TG/DTG thermoanalytical investigations using a heating rate of 10 K min^{-1} in static air (Netzsch STA 409 apparatus). The main mineralogical constituents of the utilized red earth are kaolinite, quartz, hydrate oxides of aluminium, oxides and hydrate oxides of iron, an amorphous fraction and a small quantity feldspars (Fig. 1). The red earth was heated to a temperature of 1023 K, suitable for transformation of the clay minerals in metakaolinite [5]; the relative powders were mixed with hydrated lime ($\text{Ca(OH)}_2 >90\%$) and

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Table 1 Composition of red earth (mass%)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	Na ₂ O	K ₂ O	TiO ₂	CuO	ZnO	L.O.I.
%	49.00	19.71	9.81	1.92	0.71	0.08	0.47	1.15	0.07	0.01	0.02	14.50

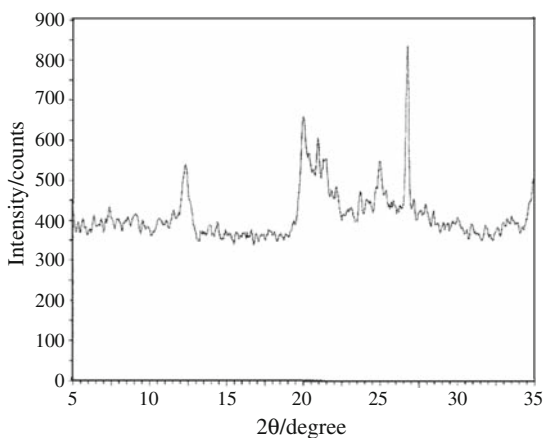


Fig. 1 XRD of red earth

gypsum (CaSO₄·2H₂O) in the ponderal ratio: 71/24/5. A second binding mixture richer in hydrated lime was also prepared (62/33/5). The first binder was artificially enriched with the addition of different quantities (0, 8, 10 and 12%) of sylvite (KCl) and mixed with water (water/solid = 0.7); pastes (paste: 0, 1, 2, 3) were thus obtained. With the second mixture, another paste was prepared with the addition of 12% of KCl (paste 4). All the pastes were cured in a controlled environment (*T* = 293 K; R.H. >90%). The quantity of chemically bound water in the hydrated pastes, drawn by dehydration, between 333 and 613 K, on the thermo-gravimetric curves is reported in Fig. 2.

Results and discussion

The thermoanalytical DTA/TG/DTG and XR diffractometry investigations indicate a characteristic hydration

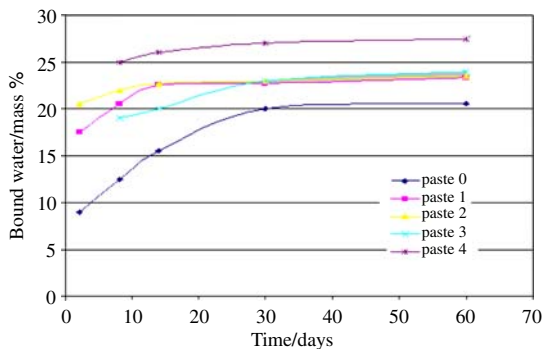


Fig. 2 The chemically bound water in the past in function of the curing time

process of the binder; particularly after the first day of hydration the sulphate has already reacted in a large quantity with the aluminate phase in order to form ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O) (2θ: 9.20, 15.90). This new hydrated phase is noticed on the DTA/TG/DTG curves by endothermic effect of decomposition at 368 K.

After the quick consumption of free sulphate, the formation of calcium silicate hydrate (CSH semi-crystalline) begins and so there is a good improvement of the hardening of the paste [1]. The endothermic effect at 398 K is correlated with dehydration of CSH which overlaps the effect of the ettringite (Figs. 3, 4). The thermoanalytical curves also show the peaks characteristic of the calcium

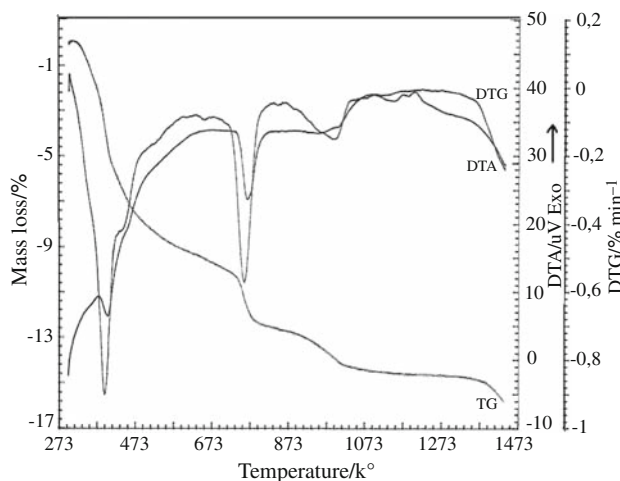


Fig. 3 DTA/DTG/TG curves of paste 0 cured for 2 days

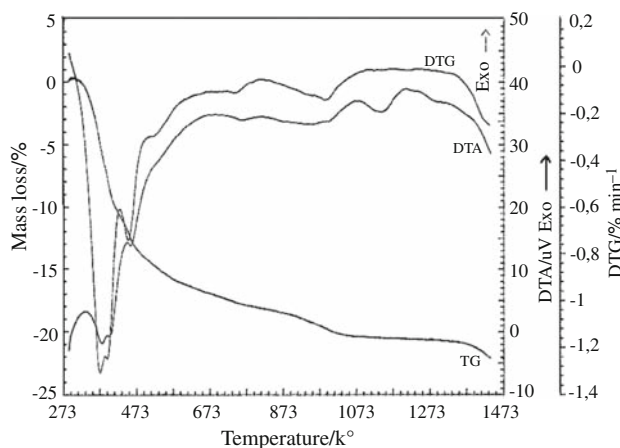


Fig. 4 DTA/DTG/TG curves of paste 0 cured for 14 days

monocarboaluminate hydrate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$), at 463 and 533 K, the more moderate development is due to the reaction of reactive alumina with the carbonate present as impurity in the hydrate lime utilized. Monocarboaluminate hydrate is also evident on XRD (2θ : 11.70, 23.60). The endothermic effect of decomposition at 753 K of the $\text{Ca}(\text{OH})_2$ in CaO and H_2O shows that after 20 days the free calcium hydroxide is consumed by the pozzolanic reactions of the reactive alumina and of the reactive silica that are main constituents of the thermally activated red earth. After 20 days, the XRD shows peaks attributable to $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ and to the relative solid solution $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 1/2\text{CO}_2\cdot 12\text{H}_2\text{O}-3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ (2θ : 11.00) [1, 8]; XRD shows also peaks attributable to gehlenite hydrate ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot 6\text{H}_2\text{O}$) (2θ : 31.00, 7.02) [5].

After the consumption of free $\text{Ca}(\text{OH})_2$ the degree of hydration reaction is lower. For paste cured for half year, DTA/TG/DTG curves and XR diffractogram show a reduction of the quantity of ettringite and calcium monocarboaluminate hydrate, while CSH increased. Whereas for paste cured for 1 year, DTA/TG/DTG curves and XR diffractogram show a moderate increase of CSH while there is a reduction of ettringite, that is in mixtures with calcium ferrite sulphate hydrate ($3\text{CaO}\cdot\text{Fe}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$) (2θ : 9.02); this mineral is similar to ettringite (Figs. 5, 6). Formation of calcium ferrite sulphate hydrate needs Fe^{3+} . This is confirmed by XRD examination that shows the decreasing of $\text{Fe}(\text{OH})_3$ peaks (2θ : 35.02) in later curing pastes. CSH amount increases also in paste with 2 years of curing, this formation could be correlated to the transformations of all the aluminate hydrate phases. As confirmed by the decreasing of XRD peaks attributable to all aluminate hydrate phases.

In a long period of curing the paste presents CSH phase in high quantities while there are moderate quantities of

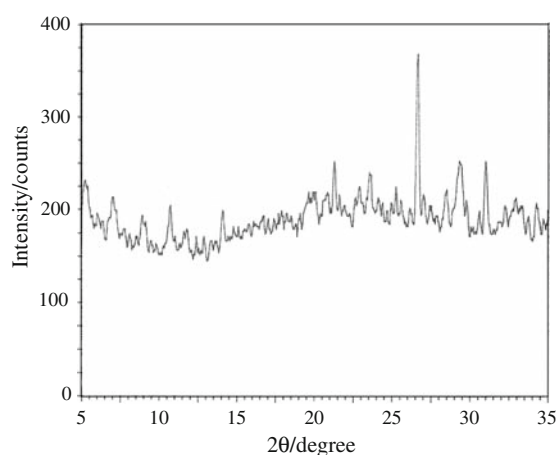


Fig. 6 XRD of paste 0 cured for 14 days

calcium monocarboaluminate hydrate, ettringite and gehlenite hydrate. This behaviour of the paste leads us to the hypothesis that small quantities of Ca^{++} , come from aluminate hydrate phases, in which Ca^{++} is substituted by other ions. Ca^{++} present in aqueous phase reacts with silica phase to produce CSH. The total amount of neo-formed hydrate products in the hardened paste indicate a development of the solidifying capacity of the matrix binder.

In the pastes containing chloride we observe a slow initial hydration, corresponding to the formation of ettringite, but with the beginning of the hardening, the hydration rapidly intensifies. For paste 1 with a lower chloride content, after the setting process, the process of hydration is accelerated. Infact, already after 8 days the thermoanalytical curves show a consumption of $\text{Ca}(\text{OH})_2$ in the pastes (Figs. 7, 8). XR diffractometry and DTA/TG/DTG investigation (Figs. 7, 8, 9, 10, 11) indicate the reduction of free chloride (KCl) (2θ : 28.34) that is

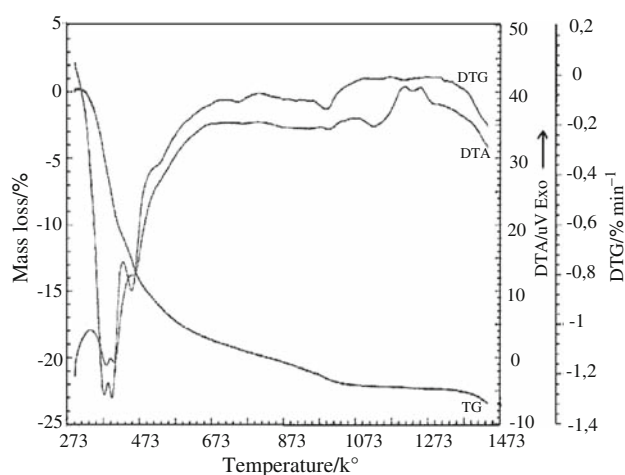


Fig. 5 DTA/DTG/TG curves of paste 0 cured for 120 days

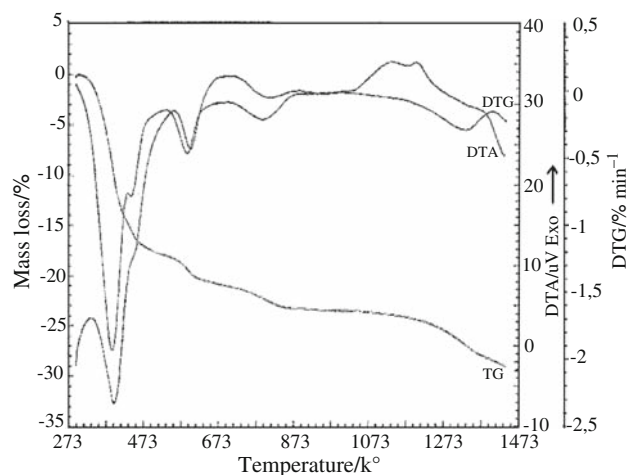


Fig. 7 DTA/DTG/TG curves of paste 1 cured for 8 days

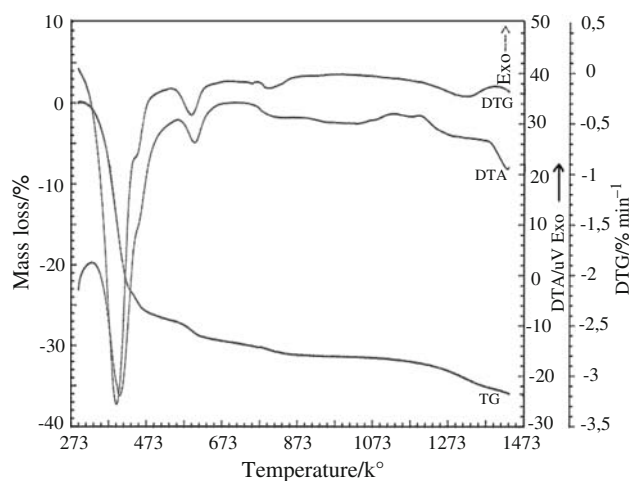


Fig. 8 DTA/DTG/TG curves of paste 1 cured for 120 days

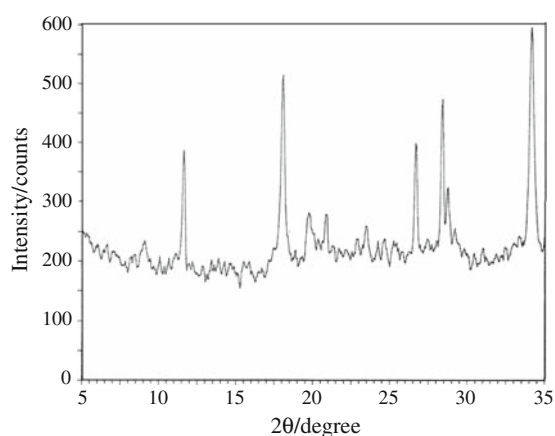


Fig. 9 XRD of paste 1 cured for 2 h

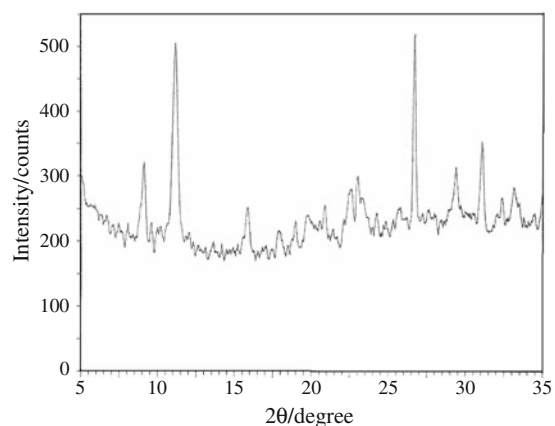


Fig. 10 XRD of paste 1 cured for 14 days

principally employed in the formation of calcium chloroaluminate hydrate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$) (2θ : 11.30). On the thermoanalytical curves, the chloroaluminate produce two endothermic effects of decomposition at

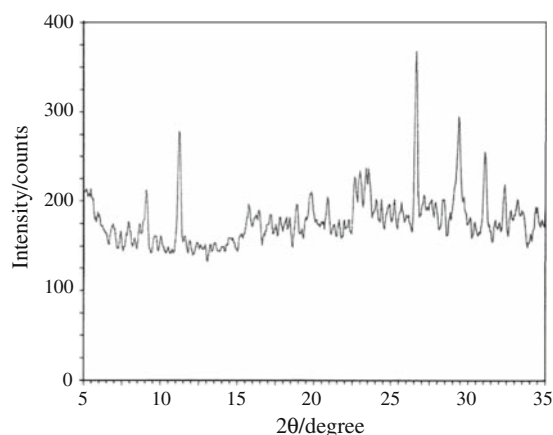


Fig. 11 XRD of paste 1 cured for 550 days

453 K and 593 K. The same curves show the production of CSH. After 14 days, the KCl peaks disappears on XRD. For paste 2, the period of reaction of free chloride is extended to 30 days of curing.

Different kinetics of hydration are observed for the paste with a higher chloride content where the absence of free $\text{Ca}(\text{OH})_2$, consumed after some days in the production of the abovementioned phases, represents a limiting factor of the process of interaction of KCl with the matrix (Fig. 2). The thermoanalytical curves indicate an ‘mobilization’ of calcium from carbonate phases [4] to the aqueous phase of the matrix in which there is a moderate formation of chloroaluminate hydrate in the long curing process. A high quantity of free chloride is fixed in the hydrate phases of the paste only after 60 days of curing. In view of this behaviour it may be that the process of hydration induces an interaction of CSH with the free chloride as it has been found also in our previous researches [2, 4, 9] and in the studies of other authors [10]. However the process of hydration is clearly accelerated in paste 4 that is richer in

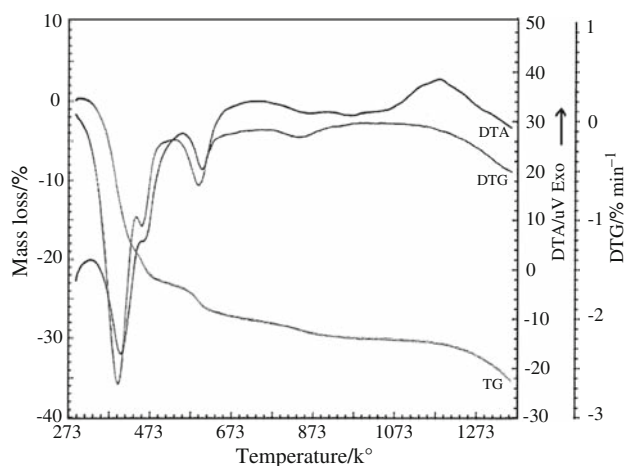


Fig. 12 DTA/DTG/TG curves of paste 4 cured for 28 days

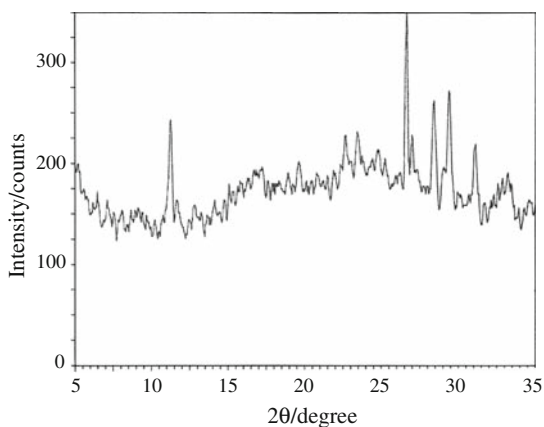


Fig. 13 XRD of paste 4 cured for 440 days

$\text{Ca}(\text{OH})_2$ and in which after around 30 days it is possible to note an intense formation of the neo-hydrate phase through which free chloride disappears (Figs. 12, 13).

In a long period of curing paste 1 presents CSH phase, calcium chloroaluminate hydrate and ettringite while pastes 2, 3, 4 CSH and chloroaluminate hydrate as a main hydrate phases.

Conclusions

The results obtained as a whole indicate a good behaviour of the thermally activated red earth that is particularly interesting in the production of artificial hydraulic lime characterized by an adequate development of the pozzolanic reactions that ensure high solidifying and stabilizing capacities in the hydrated matrix. DTA/TG/DTG and XRD investigations have shown the hydrate phases responsible of good hardening of pastes. For the paste lime-thermally activated red earth the main neo-formed hydrate phases are

calcium silicate hydrate, calcium monocarboaluminate hydrate, ettringite and gehelenite hydrate. For the pastes containing chloride the main neo-formed hydrate phases are calcium silicate hydrate, calcium chloroaluminate hydrate and ettringite. After having revealed a reactivity to lime superior to that normally presented by natural pozzolan, the thermally activated red earth also qualifies it self as a reactive material suitable for being added to lime-fly ash mixtures rich in chloride and sulphate to optimize the solidifying/stabilizing properties.

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