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HYDRATION BEHAVIOUR OF MIXTURES OF CEMENT AND FLY ASH WITH HIGH SULPHATE AND CHLORIDE CONTENT

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Abstract

DTA/TG thermoanalytical investigations and X-ray diffractometry were carried out which demonstrate the effect of MSW fly ash on the hydration reactions of pozzolanic cement. The MSW fly ash has high content of calcium sulphate, alkali chlorides and heavy metals. During the first curing period the calcium aluminate reacts with the sulphate to form ettringite. In that period also the presence of syngenite is noted in the pastes. With the growth of the fly ash content of the mixture there is a lengthening of the period in which the hydration reactions of the calcium silicates are inhibited. Subsequently with the progress of hydration in the pastes the CSH phase develops and the formation of calcium chloroaluminate phase is observed.

Keywords: cement pastes, DTA/TG, fly ash from MSW, XRD

Introduction

As the fly ash from a municipal solid waste (MSW) incinerator is a hazardous residue, its disposal requires a preventive detoxification treatment in order to protect the environment from the eventual release of polluting elements. Cement-based solidification is one of the preferred chemical treatment techniques for inorganic hazardous wastes [1, 2]. Studies carried out on fly ash from an MSW incinerator have shown that mixtures of fly ash and pozzolanic cement develop good mechanical strength and chemical stability [3]. In those previous studies fly ash was utilized which contained heavy metals, sulphate (SO_4^{2-}: 10.00%) and chloride (Cl^-: 14.05%); the mixtures of this fly ash with cement and water began to harden a few days after preparation. Of particular interest is the application of the solidification and stabilization treatment to fly ash characterized by a very high content of soluble salts and a considerable concentration of heavy metals [4]. To this end pozzolanic cement-fly ash mixtures rich in sulphate (SO_4^{2-}: 14.05%) and chloride (Cl^-: 21.05%) were studied in order to examine the numerous forms of interference on the hydration process of the cement matrix and to characterize the hydrate phases formed in the pastes. DTA/TG thermoanalytical and X-ray diffractometry investigations were carried out on cement-fly ash pastes with different curing periods.

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Experimental

The fly ash employed in this study was separated by an electrostatic precipitator (ESP) of an incineration plant for municipal solid waste (C.I.A.: Cooperative, Rimini). The chemical composition of the fly ash is shown in Table 1. The fly ash, as reported in a previous work [4], is principally formed by the minerals halite (NaCl), sylvite (KCl), anhydrite ($CaSO_4$), quartz (αSiO_2), calcite ($CaCO_3$), aluminates, aluminosilicates and various oxides (Fe_2O_3, MgO, TiO_2); an amorphous fraction is also found in the fly ash. Chloride and sulphate salts are a predominant part of the fly ash. In fact, the concentrations of Cl^- and SO_4^{2-} amount respectively to 21.05 and 14.05%.

The hydraulic binder is pozzolanic cement IV/A 42.5 UNI ENV 197/1, formed by a mixture of ordinary portland cement and an Italian natural pozzolan. The characteristics of this binder have been described in a previous work [3]. The pastes were prepared with pozzolanic cement and fly ash with fly ash/cement/deionized water ratios of 18.5:55.5:26.0 (paste 1), 29.6:44.4:26.0 (paste 2) and 40.7:33.3:26.0 (paste 3). A paste was also prepared with only pozzolan cement. The solidification and curing of these mixtures took place in a controlled environment (*T*: 20°C, R.H.>90%).

At the end of the allotted time periods, each hydrated paste was dried in two steps: 1) ground (<1000 μm) and dried for 4 h in vacuo over calcium chloride; 2) ground (<100 μm) and dried for 6 h in vacuo over calcium chloride.

The different samples (100 mg) were submitted immediately to DTA/TG thermoanalytical investigations using a heating rate of 10°C min^{-1} in static air (Netzsch STA 409 apparatus) and to X-ray diffractometry analysis (Philips PV – 1710 using CuK_α radiation).

Table 1 Composition of MSW fly ash[4]

Element	mg/kg	Element	mg/kg	Element	mg/kg	Element	mg/kg
Al	21880	K	103750	Ti	5596	Hg	0.90
Ca	138000	Na	56750	Zn	14100	CO_3^{2-}	15000
Si	53950	Mn	645	Pb	7730	Cl^-	210500
Fe	9930	Cu	1790	Ni	115	SO_4^{2-}	144990
Sn	390	Ba	930	As	11.7		
Mg	12500	Cd	325	Cr	475		

Results and discussion

The paste with the lower fly ash content (paste 1) hardens after 10 days; in fact, in the preceding period the formation of ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) is observed from the DTA/TG thermoanalytical curves (Fig. 1), and its endothermic dehydration effect develops at around 80°C (peak maximum temperature). With the increased quantity of ettringite in the paste, the shift of the correlated peak from 80 to 120°C is also observed. The DTA/TG curves reveal an endothermic effect at 280°C attributable to the dehydration of modest quantities of syngenite ($K_2SO_4·CaSO_4·H_2O$); this salt originates from precipitation of sulphate present in the solution of the paste. The XRD examination confirms the presence of ettringite (2θ: 9.20, 15.90, 22.96) and syngenite (2θ: 9.35, 15.58, 19.16, 31.36) (Fig. 3). The formation of ettringite involves a consumption of 'free' sulphate in the first 10 days, then in the subsequent period the hydration of the calcium silicates ($3CaO·SiO_2$, $2CaO·SiO_2$) of the cement begins and these produce calcium silicate hydrate (CSH) and $Ca(OH)_2$.

A weak initial solidification of the paste, due to ettringite, evolves into a progressive and intense hardening with the development of the CSH phase. On the TG curve the CSH shows a dehydration peak at around 120°C which overlaps that of ettringite [3]; the endothermic peak at 470°C is linked to the dehydration of $Ca(OH)_2$ (Fig. 2). In this more advanced curing period the formation of the calcium chloroaluminate hydrate phase is noted ($3CaO·Al_2O_3·CaCl_2·10H_2O$) to which the two endothermic effects of dehydration at 180 and 320°C are correlated [5], growing progressively with the curing period; the product results from the reaction of chloride with the calcium aluminate of the cement and with the reactive aluminate phase of the pozzolanic material [3, 6]. This hydrate phase is also noted in the XRD examination (2θ: 11.30) (Fig. 3), and, with the development of hydration, it also shows a shift of the main peak to lower values of 2θ (11.22). It is possible to hydrate phase corresponds to the solid solution of the series $3CaO·Al_2O_3·CaCl_2·10H_2O$ – $3CaO·Al_2O_3·$

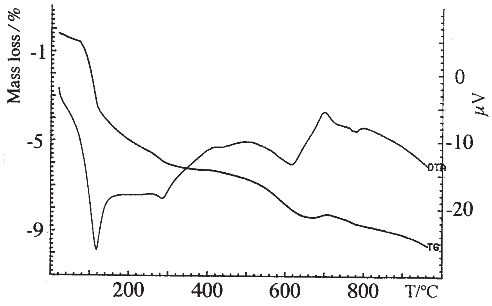

Fig. 1 DTA/TG curves of paste 1 cured for 7 days

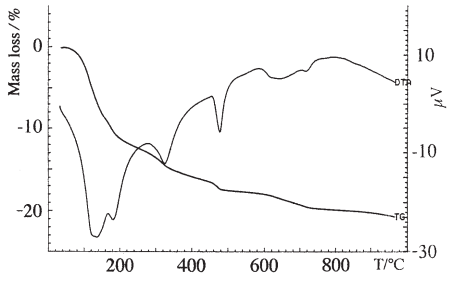

Fig. 2 DTA/TG curves of paste 1 cured for 90 days

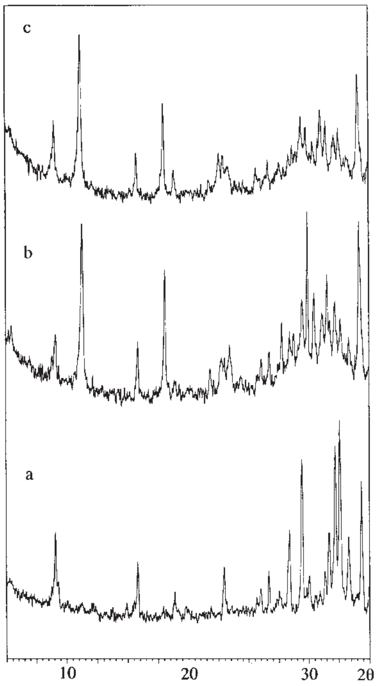

Fig. 3 XRD of paste 1 cured for a – 7 days, b – 28 days, c – 200 days

$CaCO_3 \cdot 11H_2O$ – $4CaO \cdot Al_2O_3 \cdot 13H_2O$ richer in chloride [7]. Monocarboaluminate ($3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$) is one of the principal hydrate phases which forms in the paste of the simple binder, which does not contain fly ash, as already been described in a previous study [3]. Figure 4 shows the DTA/TG curves for that pastes with 90 days curing: the endothermic effect at 130°C is due to CSH which overlaps the effect of small quantities of ettringite, the endothermic effect at 190°C corresponds with the dehydration of the monocarboaluminate, the weak effect around 270°C is attributable to a small quantity of the $4CaO \cdot Al_2O_3 \cdot 13H_2O$ phase and the relative solid solution containing CO_3^{2-} [8]. The XRD examination of the paste containing fly ash shows a reduction in the quantity of the 'free' salts halite and sylvite with the

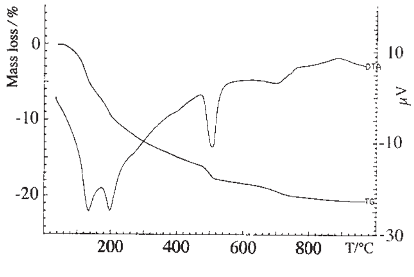

Fig. 4 DTA/TG curves of paste of the pozzolanic cement cured for 90 days

advancement of the hydration process of the mixture; after 90 days the NaCl peak disappears and a moderate quantity of KCl is found which is no longer found after 200 days (Fig. 3). The X-ray diffractogram also shows a considerable reduction of the peaks for the constituents of the portland cement ($3CaO{\cdot}SiO_2$, $2CaO{\cdot}SiO_2$, $3CaO{\cdot}Al_2O_3$, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$).

For paste 2, which contains a greater quantity of fly ash, the presence of a moderate quantity of syngenite is observed after 1 h of hydration, small quantities of ettringite and gypsum ($CaSO_4{\cdot}2H_2O$) are also present; the latter is found in pozzolanic cement as an additive which regulates setting. The syngenite is the salt that originates rapidly in the alkaline environment of the paste. The formation of ettringite develops particularly in the first 14 days of curing and the relative quantity is greater than that formed in paste 1 owing to the greater availability of $CaSO_4$. After 28 days the anydrite disappears, but syngenite is still present as can be observed on the XRD in Fig. 5.

The overall process of hydration is greatly slowed. The formation of ettringite is unfavored under lowly basic conditions [9, 10]. In fact, the considered fly ash was characterised by a low alkalinity [4]. Besides, the presence of heavy metals (Pb, Zn), from fly ash, in solution, interfering with the normal equilibrium of calcium [1]. So a long period of the inhibition of the hydration reactions of the binder is noted. In fact a good hardening of the paste begins only after around 50 days. This is confirmed by

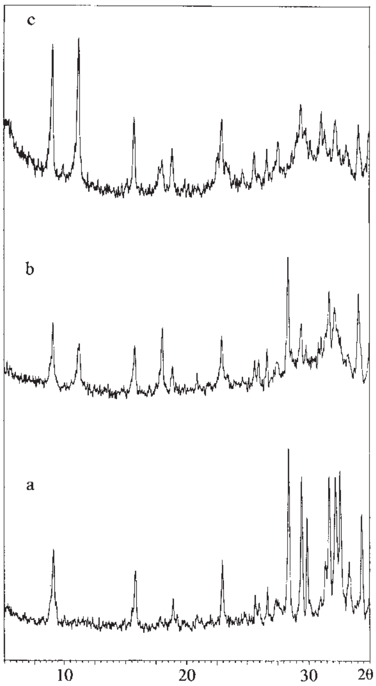

Fig. 5 XRD of paste 2 cured for (a) 28 days, (b) 70 days, (c) 200 days

the hydration of calcium silicates, which produces CSH and $Ca(OH)_2$, and by the development of solid solution of chloroaluminate (Figs 6, 7). The investigations show that after 70 days only a small quantity of syngenite is present which disappears rapidly in the successive period. With the advancement of hydration there is sharp reduction in the content of ‘free’ alkaline chlorides and after 200 days the XRD shows limited quantities of KCl and NaCl. The $3CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$ peaks are considerably reduced, in a more rapid way respect to paste 1, and the consumption of ‘free’ lime after 365 days indicates a sharp advance of the pozzolanic reactions of the pozzolanic material in the paste. Therefore, the process of hydration, which was slowed in the first period by the presence of ash, subsequently experienced a sharp acceleration. The formation of the chloroaluminate phase together with the initial formation of ettringite requires the availability of considerable quantities of aluminate phases in the cementitious matrix. The marked reduction of KCl and NaCl ‘free’ salts

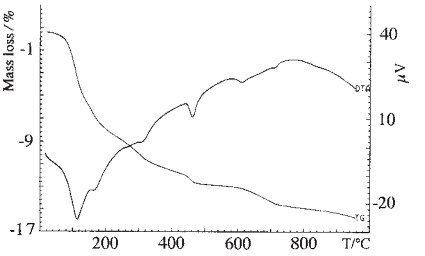

Fig. 6 DTA/TG curves of paste 2 cured for 70 days

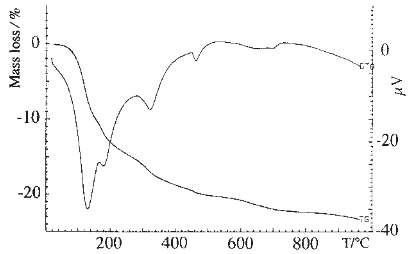

Fig. 7 DTA/TG curves of paste 2 cured for 200 days

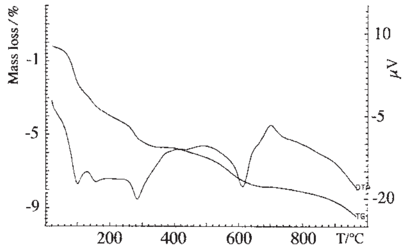

Fig. 8 DTA/TG curves of paste 3 cured for 7 days

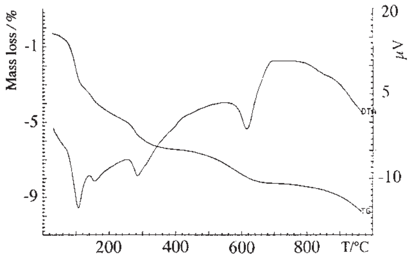

Fig. 9 DTA/TG curves of paste 3 cured for 28 days

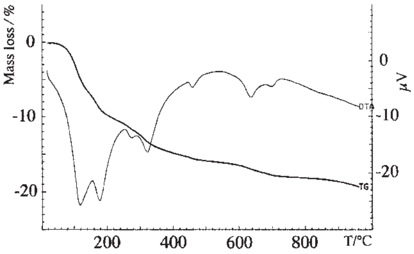

Fig. 10 DTA/TG curves of paste 3 cured for 200 days

in the paste suggests that, in view of the high content of chlorides in the fly ash, as well as the formation of chloroaluminate, a significant part of the chloride salts interacts with the CSH phase [3, 11].

The DTA and TG curves for samples of the different pastes under examination show an endothermic effect at around 600°C, which grows with the fly ash content. This effect is linked to the decomposition of complex carbonates, which precedes a smaller effect at 700°C due to calcium carbonate. Overall, the thermal range of decomposition of carbonates, mainly contained in the fly ash, and to a lesser extent in the pozzolanic material, is shifted to lower temperatures. With the development of free lime in the pastes, there is an increase of calcium carbonates (mixed carbonates) at the expense of complex carbonates. Therefore, the effect at 600°C is reduced and also the thermal range of decomposition tends to move to the range 650–700°C .

As regards paste 3, which is characterised by a higher fly ash content, the DTA/TG (Figs 8–10) and XRD (Fig. 11) investigations indicate a rapid initial formation of moderate quantities of syngenite and small quantities of ettringite; the latter continues to increase above all in the first 30 days. After some days from mixing, the endothermic effect at 150°C reveals the presence in the paste of a moderate quantity of gypsum. The presence of gypsum is confirmed by the XRD examination (2θ: 31.14, 11.64) which also indicates the shift of the 020 reflection towards lower 2θ (11.38). This is attributable to the substitution of Ca, of $CaSO_4 \cdot 2H_2O$, with cations of a wider ionic radius. With the advancement of the period of curing the overall hydration process is slowed down: the hardening of the paste is observed only after around 150 days. In fact, subsequent to that period the DTA/TG curves (Fig. 10) show an increase of $Ca(OH)_2$ and of CSH. With the development of hydration,

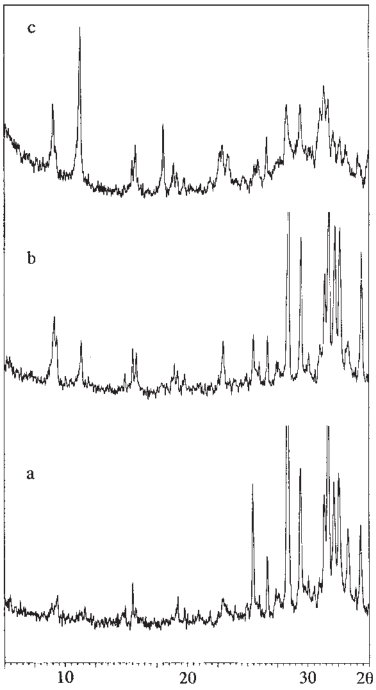

Fig. 11 XRD of paste 3 cured for a – 1 h, b – 7 days, c – 200 days

chloroaluminate phase also forms in the paste in amount that increases in time. With the formation of CSH, gypsum is no longer noted in the pastes while small quantities of syngenite are still found.

Under XRD examination the responses of 'free' KCl and NaCl chlorides show a slower reduction: this can be explained by the high ash content in paste 3. After 365 days these salts are still found. The constituents of the portland cement ($3CaO{\cdot}SiO_2$, $2CaO{\cdot}SiO_2$, $3CaO{\cdot}Al_2O_3$, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$) have been consumed. The fly ash/cement ratio of paste 3 corresponds to a maximum value for the development of suitable solidification and stabilisation characteristic of the cementitious matrix.

The morphological examination of the different samples examined indicates an excellent aspect of the pastes both for plastic state and hardened, in fact no expansion was observed during hydration. Previous studies have also established the good mechanical strength of the hardened pastes obtained by the same fly ash-cement mixtures under examination.

Conclusions

The DTA/TG thermoanalytical and X-ray diffractometric investigations carried out on the pastes of the mixtures of pozzolanic cement and fly ash with a high content of sulphate and chloride reveal the formation of ettringite in the first hydration period. In that period the presence of syngenite is also noted.

With the growth of the fly ash content there is a considerable slowing down of the hydration reactions.

The ettringite phase enables the paste to acquire sufficient consistency and it subsequently develops a good hardening with the formation of calcium silicate hydrate. With the progress of hydration in the paste, there is reaction of chloride with aluminate phase; thermoanalytical and X-ray diffractometric investigations lead us to suppose the formation of solid solution: $3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$ – $3CaO\cdot Al_2O_3\cdot CaCO_3\cdot 11H_2O$ – $4CaO\cdot Al_2O_3\cdot 13H_2O$.

Actually, both the consumption of 'free' lime, due to the pozzolanic reaction and to the formation of the chloroaluminate phase, and the interaction of Cl^- with the CSH phase, stimulate the silicates, $3CaO\cdot SiO_2$ and $2CaO\cdot SiO_2$, to hydrate themselves faster, then the overall hydration process of mixture is accelerated.

The promising results obtained both in this work and in other studies, which concern the release of heavy metals in leaching solutions, suggest to develop research in order to improve the hydration process by means of accelerating additives and, consequently to further exploit the potentiality of pozzolanic cement.

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