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FLY ASH REACTIVITY
Formation of hydrate phases

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Abstract

In this study the process of hydration of fly ash, produced by a municipal solid waste (MSW) incinerator, is examined in water and in a solution enriched with $Ca(OH)_2$. The examined fly ash samples are characterized by a high content of alkaline chlorides and anhydrite and by remarkable amounts of heavy metals. Investigations using differential thermal analysis/thermogravimetry (DTA/TG) and X-ray diffractometry (XRD) show particular kinetics of the formation of the ettringite phase. The development of such a hydrated phase is much more intense in the presence of an excess of $Ca(OH)_2$ so as to consume the 'free' sulphate in the case of the more reactive fly ash. Experimental results from thermal analysis and X-ray diffractometry show the presence of different hydrated phases during the interaction between fly ash and aqueous solution. The analytical determinations, related to the aqueous solution, point out an interesting decrease in concentration of metals Pb, Zn and Cr(VI), relating to the middle period of the interaction.

Keywords: DTA/TG analysis, ettringite, fly ash from MSW, heavy metals, XRD analysis

Introduction

Previous studies concerning the leaching of fly ash produced by a municipal solid waste (MSW) incineration plant have shown the presence of the ettringite phase in the solid residue, after 24 h of leaching with water [1].

Such behaviour together with other interesting results obtained in various studies concerning the solidification/stabilization processes by means of hydraulic binders [1–4], ascertain that ettringite and calcium silicate hydrate (CSH) are the main neo-formed phases giving a good degree of stabilization of the hardened material. This has led to the development of research in order to specify the kinetics of the formation of ettringite and other hydrated phases during the treatment with water of different fly ash samples. A deeper knowledge of the hydration process regarding the fly ash alone is of fundamental importance owing to the high content of sulphate and

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chloride, as well as that of a relevant concentration of heavy metals, that modifies remarkably the normal processes of setting and hardening of cement mixtures.

Treatments to render fly ash, which is classified as a hazardous residue, innocuous involve remarkable costs to prevent the release of polluting elements and, therefore, to assure the protection of the environment. In such a perspective, therefore, further studies are very useful on the characterization of residues and particularly on their behaviour in aqueous systems as only a few works are reported in the scientific literature on this interesting argument [5–8].

For the aforesaid purpose, the interaction with both water and a saturated solution of $Ca(OH)_2$ of two different fly ashes, particularly rich in sulphate and chloride (fly ash1: SO_4^{2-}=9.9% and Cl^-=14.0%; fly ash2: SO_4^{2-}=14.5% and Cl^-=21.0%), has been studied in order to underline the processes of hydration of the reactive phases enclosed in the same fly ashes.

The investigations of the residues, after treatment with an aqueous solution for different periods, were performed using a DTA/TG thermoanalytical technique and X-ray diffractometry, the combined results of which are essential to understand the kinetics of hydration of the constituents.

Experimental

The two fly ashes examined were separated in different periods by the electrostatic precipitator (ESP) of an incineration plant for municipal solid waste. The chemical composition of each fly ash is shown in Table 1; a comparison of the values indicates that fly ash2 is characterised by a higher concentration of sulphate and chloride, together with a more appreciable amount of heavy metals, such as Pb, Zn, Cu, and Cd. The experimental results of XRD analysis on the two fly ashes, as shown in Figs 1 and 2, indicate that the main mineralogical constituents are anhydrite ($CaSO_4$),

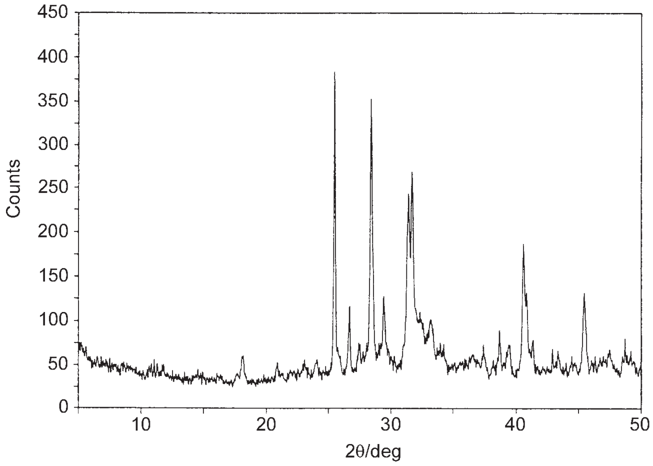

Fig. 1 XRD of fly ash1

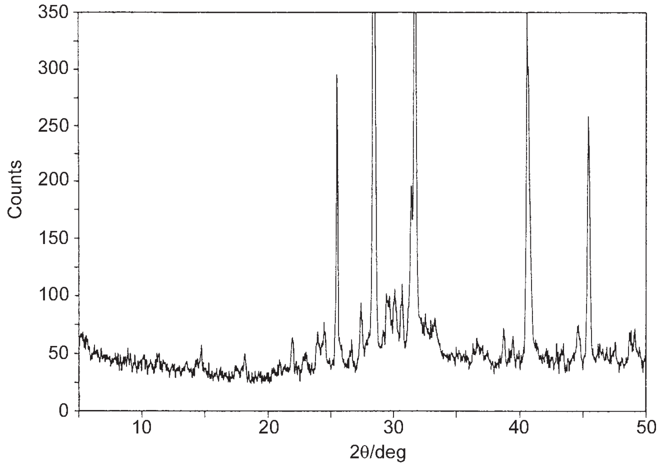

Fig. 2 XRD of fly ash2

sylvite (KCl) and halite (NaCl), together with a lesser quantity of many other minerals, such as quartz (α-SiO_2), calcite ($CaCO_3$), calcium silicate ($2CaO{\cdot}SiO_2$), alumino-silicates (Gehlenite, Feldspar), and various oxides, such as CaO, MgO, Fe_2O_3, ZnO, TiO_2 and $CaTiO_3$. As well as a few metallic phases in small quantities, an amorphous fraction is also present in both fly ashes. It is noteworthy that fly ash2 shows a smaller fraction of the minor minerals and a lower content of CaO.

Table 1 Composition of fly ashes

Element	Fly ash1/%	Fly ash2/ %	Element	Fly ash1/ppm	Fly ash2/ppm
Ca	23.320	13.800	Cu	1040	1790
Si	9.526	5.395	Mn	859	645
Al	3.640	2.188	Cr	485	475
Fe	1.200	0.993	Cr(VI)	280	91
Mg	1.368	1.250	Cd	206	325
K	7.550	10.375	Sn	–	390
Na	3.475	5.675	Ba	1500	930
Zn	1.125	1.410	Ni	76	115
Pb	0.612	0.773	Hg	<1	<1
Ti	0.600	0.560			
Cl^-	14.050	21.050			
SO_4^{2-}	9.880	14.499			
CO_3^{2-}	4.200	1.500			
P_2O_5	0.390	–			

The examined fly ashes present mainly a thin granulometry (>250 μm: 7%; >150 μm: 52%; >75 μm: 80%; >45 μm: 96%).

The mass ratio of fly ash/water performed during the preparation of the various systems was 1:20; for systems enriched with $Ca(OH)_2$, 10% of solid is lime (lime with 98% $Ca(OH)_2$).

During every treatment the solid-liquid system was agitated at a constant rate. Each suspension was filtered through a glass micro-fibre membrane.

At the end of the allotted time periods each hydrated residue was dried in two steps using the following procedure: – dried for 4 h in a vacuum over calcium chloride; – ground (<100 μm) and dried for further 6 h in a vacuum over calcium chloride.

The different samples (around 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, calibrated by using standard metals, such as In, Sn, Bi, Zn, Al, Ag and Au) and to X-ray diffractometry analysis (Philips PV-1710, using CuK_α radiation).

The filtered solutions were analysed to determine the content of heavy metals, chloride and sulphate ions, by using atomic absorption flame spectrometry (Pye Unicam SP9) and ion chromatography (Dionex DX-300, Ion Pac AS4A HPIC column) respectively. Cr(VI) was evaluated by spectrophotometric ortho-phenanthroline method [9].

Results and discussion

Thermoanalytical investigations (Fig. 3) performed on the solid residue of the fly ash1–water system underline the rapid formation of ettringite ($3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$) after a few min of treatment with water: such a hydrated phase introduced an endothermic effect of dehydration at 90°C (peak maximum temperature). XRD examination confirmed the presence of ettringite (2θ: 9.14; 15.83; 22.98; 18.96°), as shown in Fig. 4; there was a considerable quantity of anhydrite, while the alkaline chlorides (NaCl, KCl) were completely dissolved. Some peaks can also be seen that more clearly correspond to a moderate quantity of larnite ($2CaO\cdot SiO_2$), an original component of the fly ash, (2θ: 32.56; 32.97; 32.02°) and to the presence of CaO with the relatively small quantity of $Ca(OH)_2$, coming from hydrolysis. The alkaline hydrolysis of different constituents of the fly ash gave the solution an elevated pH (pH 12.5), which favoured a rapid reaction of the aluminate phase, in the presence of the ‘free’ lime by hydrolysis, with the sulphate to produce ettringite. After one hour of interaction, there were peaks at 2θ= 28.60; 14.20; 31.05° in the XRD spectrum of the solid residue attributable to calcium hydroxyzincate ($Ca(Zn(OH)_3)_2\cdot 2H_2O$), confirmed by the thermoanalytical curves that underline a small endothermic effect of dehydration at 180°C. The production of hydrated hydroxyzincate is due to the presence of $Zn(OH)_2$ that reacted with $Ca(OH)_2$ [10]. By increasing the interaction time between fly ash and water, the thermoanalytical behaviour (Fig. 3) showed an intense growth in the quantity of ettringite, with the shift of the correlated peak from 90 to 140°C. In the XRD spectrum related to the residue, after treatment for around 30 days, the disappearance of the anhydrite was observed, which was consumed in forming ettringite in a good part while the remaining part was completely hydrated to gypsum ($CaSO_4 \cdot 2H_2O$) (Fig. 4). Later, after around 50 days the investigations also showed a high consumption of gypsum in the residue and subsequently a more modest development of ettringite. At the same time the quantity of calcium hydroxyzincate was reduced. The behaviour of the quantity of chemically bound water in the hydrated phase (ettringite), which is drawn by the effect of its dehydration on the thermo-gravimetrical curve, is reported in Fig. 5.

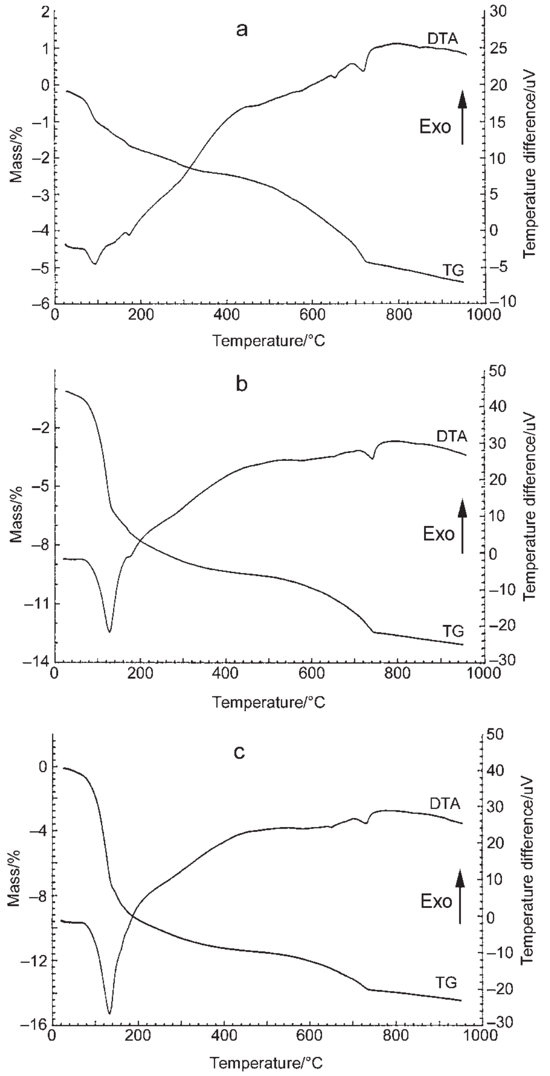

Fig. 3 DTA/TG curves of the hydrated fly ash1 (a – 1 h, b – 7 days, c – 28 days)

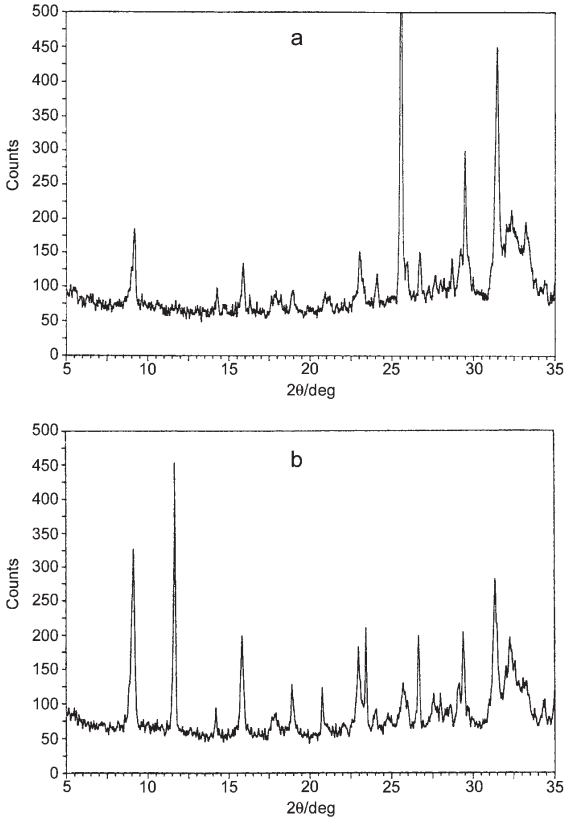

Fig. 4 XRD of hydrated fly ash1 (a – 1 day, b – 28 days)

For the same fly ash1, treated with a saturated solution of $Ca(OH)_2$, a light deceleration of the production of ettringite was noted, in the short term (Fig. 5), but later after 7 days a clear acceleration could be seen in the formation of the hydrate phase, as shown in Fig. 5. After about 45 days, the thermoanalytical and XRD (Fig. 7) results indicated a consumption of sulphate and the water solution became unsaturated in $Ca(OH)_2$. Moreover, the disappearance of the calcium hydroxyzincate was noted. After this period of interaction, the formation of the calcium silicate hydrate (CSH) phase became evident. XRD measurements on the solid residue point out small reflexes (2θ: 29.24; 32.05°), that are attributable to such a hydrated product. The modest quantity of CSH introduced an endothermic effect of dehydration that was superimposed on that due to ettringite. Therefore, the amount of bonded water, drawn by the main effect and reported in Fig. 5, corresponded, in this more advanced period, both to ettringite and to the CSH phase. The disappearance of the peaks related to $2CaO{\cdot}SiO_2$ in the XRD spectra emphasizes the contribution of this silicate, a constituent of the fly ash, to the production of calcium silicate hydrate. Later, after 90 days, a continuous deceleration of the processes of hydration of the fly ash was observed (Fig. 5).

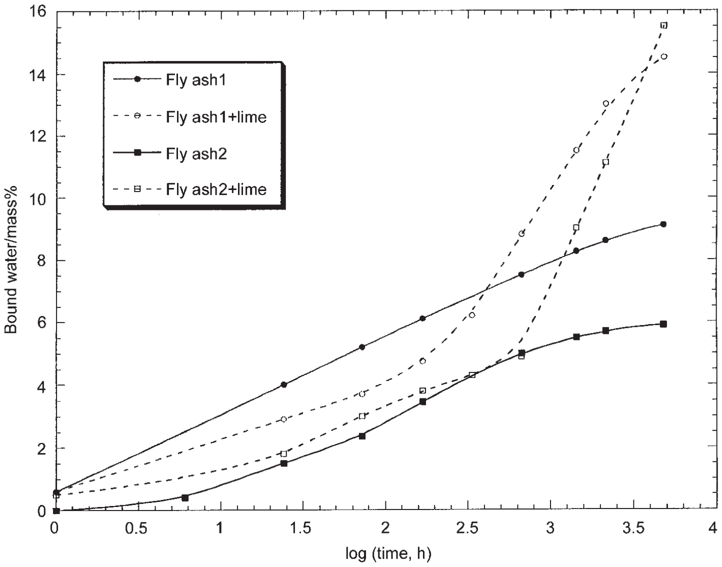

Fig. 5 The chemically bound water in the hydrated phase in function of the interaction time

The whole investigation led us to hypothesize, for this fly ash1–lime–water system, that the presence of an excess of $Ca(OH)_2$ favours the attack of the glassy particles of the fly ash and then greater availability of the aluminate phase to react with the whole sulphate. Such an activation process of the glassy fraction subsequently allowed the fixation of the free sulphate, to dispose of the silicate phase and produce calcium silicate hydrate.

As regards fly ash2, characterized by an elevated content of sulphate and chloride, the formation of ettringite during the treatment with water began after some hours and with a slower development (Fig. 8). Such behaviour can be justified by the low alkalinity of fly ash2, pH 9.0 after 5 min, because of a lesser supply of alkaline oxides and $2CaO{\cdot}SiO_2$. In fact, after only a few hours the pH of the solution became sufficiently alkaline (pH: 11.0) to allow the formation of ettringite [11]. The examination of the diffractograms showed leaching of NaCl and KCl (Fig. 9), with a small quantity of such chlorides remaining in the residue, and the rapid formation of laurionite (Pb(OH)Cl) (2θ: 27.00; 22.15; 35.16°), which is not found 24 h later. A very small quantity of syngenite ($K_2SO_4{\cdot}Ca\ SO_4{\cdot}H_2O$) was also noticed in the residue.

As hydration proceeds, anhydrite is slowly hydrated to gypsum (2θ: 31.14; 11.64°), a process which is completed after around 30 days. During the first period of hydration the relative XRD spectrum also shows the shift lower of 020 reflection towards 2θ (11.38°), which is attributable to the substitution of Ca, of $CaSO_4{\cdot}2H_2O$ with cations of a wider ionic radius. After a longer period of interaction the production of ettringite only showed a limited increase due to the insufficient availability of phases aluminate in fly ash2 and also because of the low amount of lime coming from hydrolysis. Consequently, a large quantity of 'free' sulphate remained in the residue. The lack of 'free' lime is confirmed by the non-appearance of hydroxyzincate hydrate.

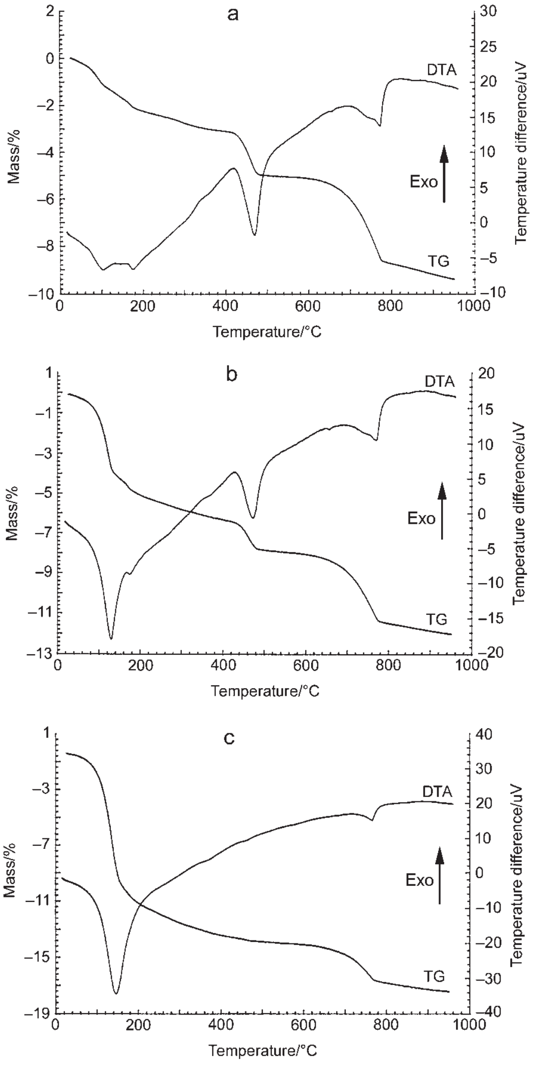

Fig. 6 DTA/TG curves of the hydrated fly ash1 – system with lime (a – 1 h, b – 4 days, c – 45 days)

The analysis of the DTA and TG curves and diffractograms (Fig. 10), regarding fly ash2–$Ca(OH)_2$–water system, showed the rapid formation of $Ca(Zn(OH)_3)_2 \cdot 2H_2O$, and of hemihydrate ($CaSO_4 \cdot 1/2H_2O$) in modest amounts, and an anticipated production of ettringite. The solution had a high alkalinity, pH: 12.8. Furthermore, after around 30 days a particular acceleration in the development of the ettringite phase was observed.

The latter behaviour can be ascribed to the availability of reactive phases supplied by the glassy fraction that, even though limited in this residue, contributed remarkably to the reaction. In this middle period of interaction, gypsum was also formed. After about 45 days, owing to the consumption of lime, the interactive solution became unsaturated in $Ca(OH)_2$. After a long period of hydration, approximately 200 days, a significant consume of gypsum was noticed in the residue, however a small amount of ‘free’ sulphate

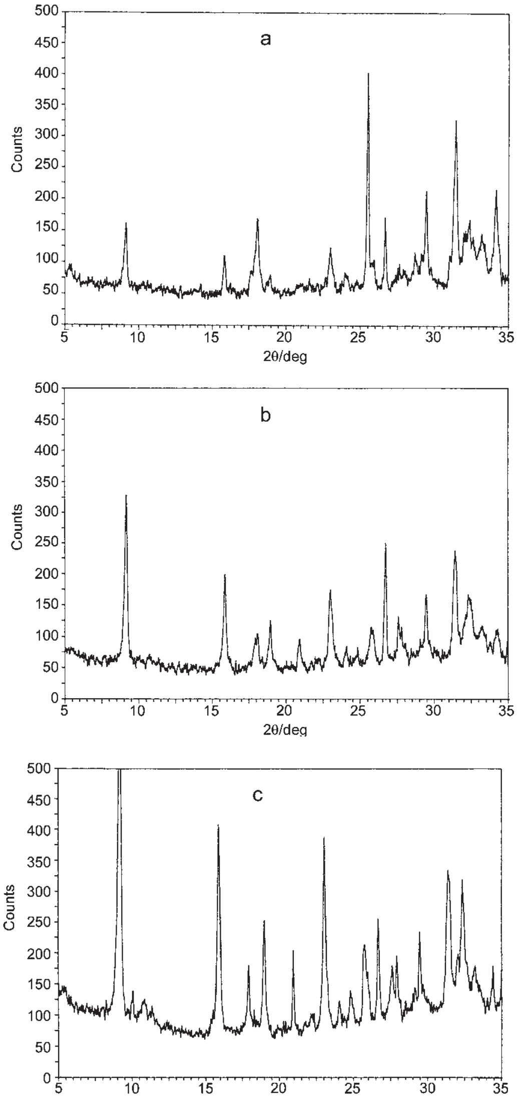

Fig. 7 XRD of the hydrated fly ash1 – system with lime (a – 4 days, b – 45 days, c – 90 days)

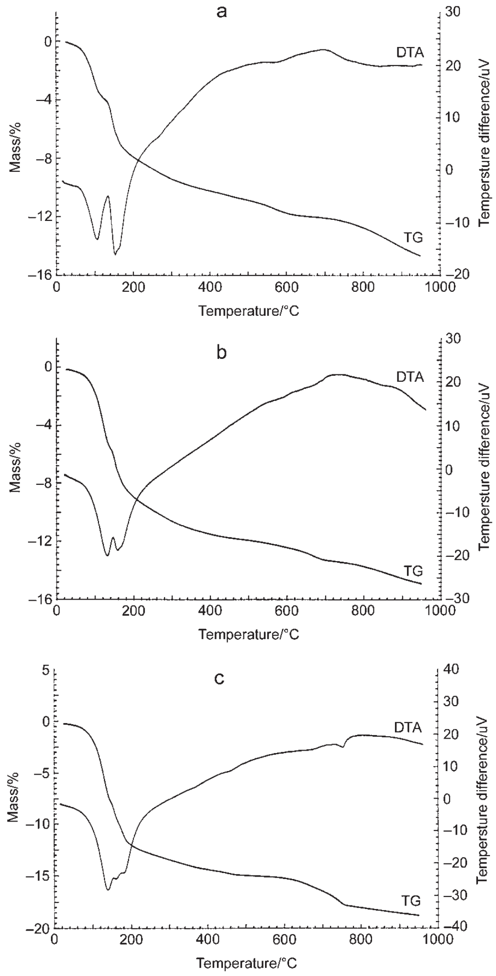

Fig. 8 DTA/TG curves of the hydrated fly ash2 (a – 7 days, b – 28 days, c – 45 days – system with lime)

was still available because of the insufficient content of the aluminate phases in fly ash2. A modest quantity of hydroxyzincate was also noticed.

The remarkable amount of ettringite formed despite the low stoichiometric content of Al_2O_3 allows the hypothesis, also considering the results of other researchers [12], that various elements, in particular Pb, Zn, Si and Fe, have been engulfed in ettringite and, therefore, have contributed to the production of the hydrated phase.

Regarding the heavy metal concentration in the solution, a particular behaviour was noticed for Pb, Zn and Cr(VI) ions dissolved in the examined systems in large quantities. In fact, in reference to fly ash1, Pb ion, that reaches the highest concentration in the aqueous solution during the first 15 min of interaction (equal to 100 ppm), both without and with the addition of $Ca(OH)_2$, remarkably decreased in concentration during the interaction, reaching a few ppm after 30 days and 0.3 ppm after 50 days. Similarly, Zn ion concentration presented values close to 3 ppm in the first period of interaction (15 min), but decreased to 0.2 ppm later after 30 days.

In reference to fly ash2, the Zn concentration in the solution had initial values of 2 ppm with a reduction to 0.2 ppm 60 days later. Pb concentration, without addition of lime, is about 1 ppm during the first 15 min and decreased to 0.3 ppm 14 days later. Because of the amphoteric behaviour of this element [1, 2], strong leaching was noticed

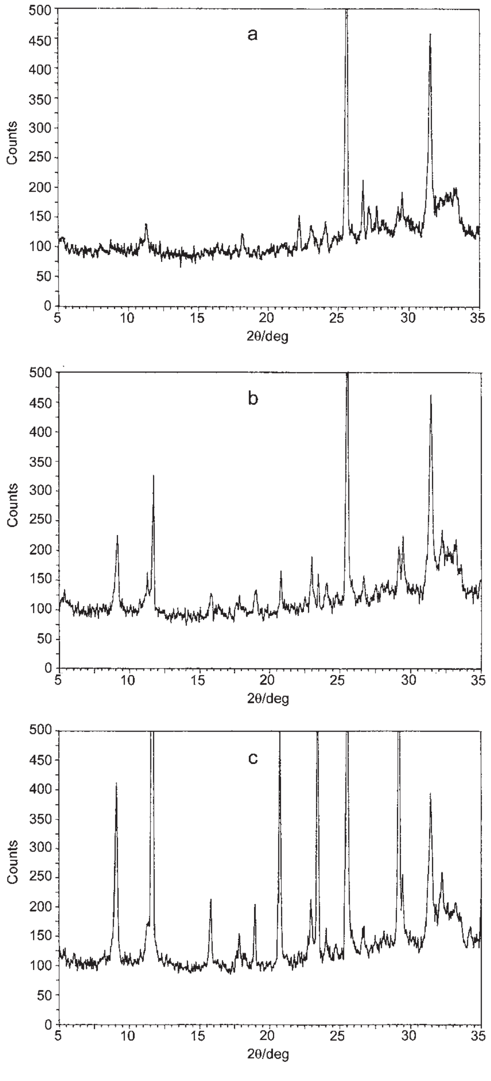

Fig. 9 XRD of hydrated fly ash2 (a – 6 h, b – 1 day, c – 7 days)

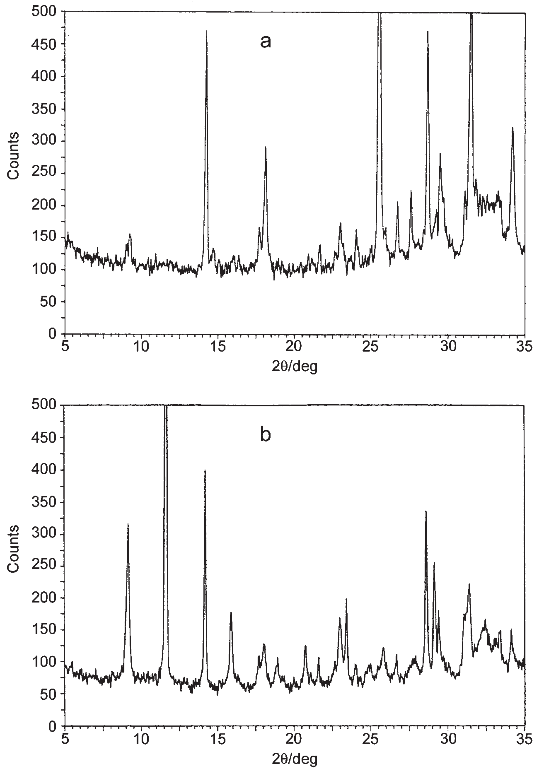

Fig. 10 XRD of the hydrated fly ash2 – system with lime (a – 1 day, b – 45 days)

with addition of $Ca(OH)_2$, reaching concentrations of around 300 ppm during the first min of interaction and then decreasing to values of around 20 ppm 30 days later.

The behaviour of Cr(VI) in the systems enriched in $Ca(OH)_2$ was interesting. The initial concentration in the solution was equal to 3 ppm for fly ash1 and 1 ppm for fly ash2, but it decreased to 0.3 ppm after 50 days for both residues. Considering the chemical analytical investigations as a whole, it is evident that fly ash1 shows better behaviour on treatment with aqueous solution, further contributing to confirm the hypothesis that a few heavy metals can be incorporated into the ettringite phase. Certainly, further research is needed in order to investigate this interesting aspect.

Conclusions

DTA/TG thermoanalytical and XRD results as a whole underline the characteristic behaviour of fly ash on contact with aqueous solutions. In particular, the high content of anhydrite can be considered an important source of sulphate interacting with the aluminate phases to produce ettringite. Though, the fly ash samples examined were characterised by a remarkable content of soluble salts and other compounds, and a moderate stoichiometric amount of Al_2O_3, they are able to produce a notable quantity of ettringite. In addition, the kinetics of the formation of this hydrated phase is favoured by an appropriate quantity of $Ca(OH)_2$ and obviously by a more relevant amount of aluminate reactive phases. The study on the interaction of the fly ash with aqueous solutions shows that the hydration process of residues can be improved with appropriate additives to enhance 'self-stabilizing' properties. The chemical results, showing a decrease in the concentration of some heavy metals in the solution with the development of hydration, are in good agreement with the hypothesis of fixation of some heavy metals in the hydrated phase.

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