

Solidification and stabilization of cement paste containing fly ash from municipal solid waste

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Abstract

DTA/TG analysis and XRD investigations were carried out on pastes of pozzolanic cement and a mixture of pozzolanic cement and fly ash from municipal solid waste in order to examine their relative hydration processes. The presence of fly ash, from a municipal solid waste incinerator, provoked in the first curing period the slowing of hydration reactions of calcium silicates of cement and formation of gypsum and ettringite. With the progress of hydration in the pastes the calcium silicate hydrate phase developed and formation of calcium chloroaluminate was observed. The compressive strength of the hardened pastes confirmed good solidification attained by the materials. The leaching test allowed the degree of stabilization of the fly ash in the hardened pastes to be determined. © 1998 Elsevier Science B.V.

Keywords: DTA/TG; Cement pastes; Fly ash from municipal solid waste; Leaching test

1. Introduction

Cement-based binders are frequently used for the solidification and stabilization processes of hazardous wastes. The negative influence of waste on the hydration reactions of cement-based binders require further study in order to optimize the characteristics of these binders [1–3].

The present study was carried out as part of a research on the detoxification of fly ash produced by municipal solid waste (MSW) incineration plants; MSW fly ash is considered hazardous, largely due to the high content of heavy metals [4–6]. Particular examination is made of the solidification and stabiliza-

tion treatment of fly ash, separated by the electrostatic precipitator of an MSW incineration plant, based on the employment of pozzolanic cement.

For this purpose some DTA/TG analysis, as well as X-ray diffractometry investigations were carried out to demonstrate the effect of fly ash on the hydration reactions of cementitious binder.

Suitable solidification of the mixtures was verified by determining the compressive strengths of the hardened pastes in various curing periods. Stabilization of fly ash in cementitious pastes was evaluated through application of the leaching test, carried out at pH 5.0 with 0.5 M acetic acid [7], and subsequent determination of the concentration of the heavy metals Pb, Cd, Zn, Cu, Ni, Hg in the leaching solution. A low concentration of heavy metals in the solution [8] makes it possible to establish the suitability of cement binder in fixing these polluting elements.

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It was decided to employ pozzolanic cement formed by a mixture of portland cement and natural pozzolan; the choice of these materials was also based on previous studies on the utilization of a lime–pozzolan binder [5].

2. Experimental

2.1. Materials

The fly ash examined in this work was separated by an electrostatic precipitator (ESP) of an incineration plant for municipal solid waste (CIA Cooperative, Rimini). The chemical composition and mineralogical characteristics of these fine fractions were discussed previously [5].

The fly ash examined in this study is principally formed by the minerals halite (NaCl), sylvite (KCl), anhydrite (CaSO₄), quartz (SiO₂), calcite (CaCO₃), aluminates, aluminosilicates and various oxides (CaO, Fe₂O₃, MgO, TiO₂); an amorphous fraction is also found in the fly ash. Chloride and sulphate salts are predominant part of the ash. In fact concentrations of Cl⁻ and SO₄⁻, are respectively, 14.05% and 10.00%. The heavy metal content of the fly ash is shown in Table 3.

The hydraulic binder is pozzolanic cement IV/A 42.5 UNI ENV 197/1, formed by a mixture of ordinary portland cement (OPC) and an Italian natural pozzolan (pyroclast of Vulture) [5], in proportions of 72:28 (by mass). The chemical composition of portland cement and pozzolanic material is shown in Table 1.

2.2. Characterization

The pastes were prepared with the fly ash and pozzolanic cement with fly ash/cement/water ratios of: 0.0:74.0:26.0 (paste I), 18.0:55.5:26.0 (paste II) and 29.6:44.4:26.0 (paste III). After the mixing operation, different materials in the plastic state were

poured into 4×4×16 cm³ moulds with a similar procedure to that for mortars [9], subsequently the pastes were cured in a controlled environment (*T*: 20±1°C, RH: >90%) and protected from the action of CO₂ in the air. After different curing periods of 7, 28, or 90 days, the materials were submitted to compressive strength tests [9].

From the same materials, different samples were taken of pastes hydrated from 1 h to 180 days and after grinding and drying they were submitted to DTA/TG analysis, using a heating rate of 10°C/min in static air (Netzsch STA 409 apparatus), and to X-ray diffractometry analysis (Philips PV-1710 using CuKα radiation).

The leaching test was carried out on paste III, characterized by a higher fly ash/cement ratio and with 90 days curing. The leaching solution was deionized water maintained at pH 5.0 by means of the addition of 0.5 M acetic acid. The leaching, with solid/liquid ratio of 1/16 [7], lasted for 24 h. For comparison, the leaching tests was also carried out on this ash.

Metals were analyzed by using Atomic Absorption Flame Spectrometry (Pye Unicam SP9), while Hg was determined by cold vapour technique after acid reduction by NaBH₄. As regards chromium determination, the Cr(VI) fraction was evaluated by the spectrophotometric orthophenantroline method [10].

3. Results and discussion

Table 2 shows the compressive strengths of the different hardened cementitious pastes (pastes I, II,

Table 2
Compressive strengths of the pastes containing fly ash

| Days | 7 | 28 | 90 |
|---------------|-------------------|------|------|
| | N/mm ² | | |
| Paste I | 53.4 | 68.3 | 78.0 |
| Paste II | 25.6 | 31.1 | 35.2 |
| Paste III | 10.0 | 24.0 | 32.5 |
| Control paste | 29.8 | 43.3 | 48.0 |

Table 1
Composition of ordinary portland cement and natural pozzolan (wt.%)

| Oxide | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | Na ₂ O | K ₂ O | LOI |
|------------------|------------------|--------------------------------|--------------------------------|-------|------|-----------------|-------------------|------------------|------|
| Portland cement | 20.13 | 4.90 | 2.59 | 63.89 | 1.64 | 3.00 | 0.54 | 0.61 | 0.97 |
| Natural pozzolan | 47.00 | 15.39 | 6.73 | 9.99 | 3.25 | – | 2.66 | 2.68 | 8.58 |

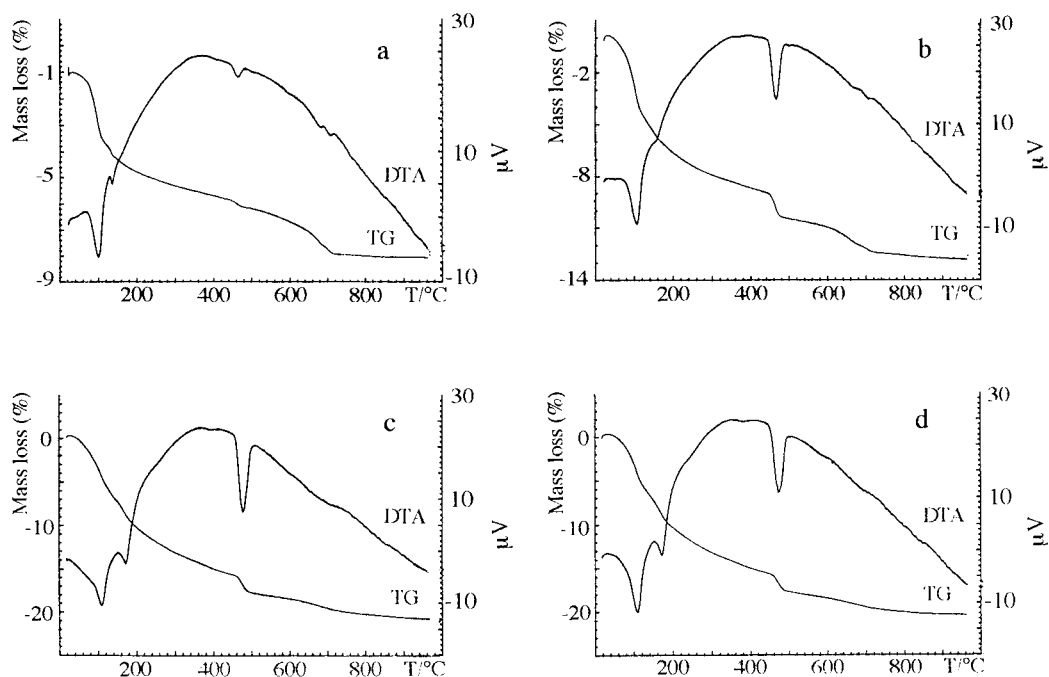


Fig. 1. DTA/TG curves of paste I cured for (a) 6 h, (b) 1 day, (c) 28 days, (d) 90 days.

III). The table also shows the compressive strength values of a control paste containing silicic inert powder substituting the fraction of fly ash and in the same ratio as paste III. The hardened pastes have lower strength with increase of fly ash content. It is interesting to note, however, that after 7 days curing paste III shows a percentage increase of strengths higher than the other pastes. On the whole the strength of the materials indicate that fly ash-cement mixtures attained a good solidification.

From the DTA/TG analysis and X-ray diffractometry investigations the characteristics of the hydration process of different cementitious pastes can be defined. The paste of the pozzolan cement (paste I), hydrated for 6 h (Fig. 1), shows on the DTA/TG curve, an endothermic effect at 100°C due to the dehydration of ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$) which overlaps the endothermic effect of small quantities of calcium silicate hydrate (CSH). This overlapping explains the slight movement of the endothermic effect of the ettringite from 100°C to higher temperatures (110°C).

The ettringite is formed by the reaction of tetracalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$), a constituent of

portland cement, with gypsum added as a setting regulator. The slight endothermic effect at 140°C is due to the small quantity of gypsum available for the reaction. There is limited formation of $\text{Ca}(\text{OH})_2$ shown by the effect at 460°C . At around 700°C there is an endothermic phenomenon of decarbonation due to the carbonate present in the natural pozzolan employed in the production of pozzolanic cement.

On prolonging the curing period, there is the predomination of hydration of calcium silicates ($3\text{CaO}\cdot\text{SiO}_2$, $2\text{CaO}\cdot\text{SiO}_2$) in the cement which produces calcium silicate hydrate and $\text{Ca}(\text{OH})_2$. The DTA curves show (Fig. 1) the development of the relative endothermic effects at 110°C and 470°C . The TG curve shows weight losses correlated to dehydration of the two products. A smaller contribution to the formation of calcium silicate hydrate is made by pozzolanic reaction between natural pozzolan and lime freed from the portland cement [5].

After the first day, a small endothermic effect, due to hydrocarboaluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$), appears on the DTA curve (Fig. 1) at 165°C gradually growing with the process of hydration. The presence of this hydrate product is also confirmed by the X-ray

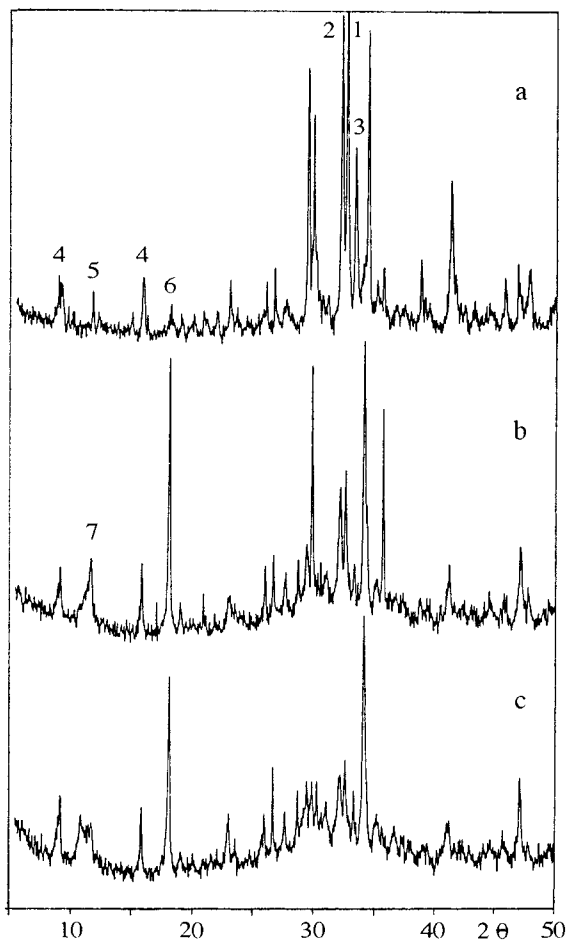


Fig. 2. XRD of paste I cured for (a) 6 h, (b) 7 days, (c) 90 days. (Legend: 1= $3\text{CaO}\cdot\text{SiO}_2$, 2= $2\text{CaO}\cdot\text{SiO}_2$, 3= $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, 4=Ettringite, 5=Gypsum, 6= $\text{Ca}(\text{OH})_2$, 7= $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$).

diffractogram examination (d: 7.58 \AA) shown in Fig. 2. DTA/TG curves of paste I cured for 28–90 days show that the decarbonation effect at around 700°C is reduced owing to the lesser availability of free carbonate to react with aluminat phases. After 28 days, the hydration process of the pozzolanic cement is slower.

As regards the fly ash–cement paste, DTA/TG analysis shows the appearance of small quantities of ettringite after 1 h of hydration for paste II (Fig. 3) while for paste III, which is characterized by a higher ash content, this hydrate product appears after 1 day

(Fig. 4). On the thermoanalytical curves, the endothermic effect appeared at 140°C due to gypsum formation which is linked to hydration of anhydrite contained in the fly ash. The small amount of gypsum in the cement also contributes to the effect. With the progress of hydration of the paste there is a growth of the quantity of ettringite greater for paste III, due to the larger CaSO_4 content.

Thermoanalytical studies on the pastes containing ash reveal slowing of hydration of the calcium silicates of cement. In fact, on the DTA curves in the first period of hydration, CSH and $\text{Ca}(\text{OH})_2$ are not formed and their formation is observed after the consumption of gypsum in the pastes. On the thermoanalytical curve for 2 days for paste II, and 4 days for paste III, an endothermic effect is observed at 450°C due to free lime. The calcium silicate hydrate phase shows an endothermic peak at around 110°C which overlaps the endothermic peak of ettringite. Therefore, with the growth of the quantity of CSH during hydration progress there is a movement of the overall endothermic effect from 90°C to 110°C (Figs. 3 and 4).

For both the pastes based on fly ash the thermal curves show, from 1 h until the disappearance of gypsum, a slight endothermic effect at 270°C attributable to small quantities of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$.

The same thermal curves corresponding to 1 h of hydration show an endothermic effect at around 600°C that is greater for paste III. This is linked to the decomposition of complex carbonates which precedes a lower effect at 670°C due to calcium carbonate. Overall the thermal range of carbonates' decomposition, mainly contained in ash and to a lesser extent in pozzolanic material, is shifted to lower temperatures. With the development of free lime, there is an increase of calcium carbonates (mixed carbonates) at the expense of complex carbonates [11,12]. Therefore, the first effect at 600°C is clearly reduced and also the thermal range of decomposition tends to move to about 700°C .

In a more advanced period of hydration in the paste, corresponding to 4 days for paste II and 7 days for paste III, there is the formation of calcium chloroaluminate hydrate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$) [13] the appearance of which on the thermal curves is observed from two endothermic effects at 160°C and 310°C . The amount of hydrated product grows with the progress of hydration. As seen in the thermal

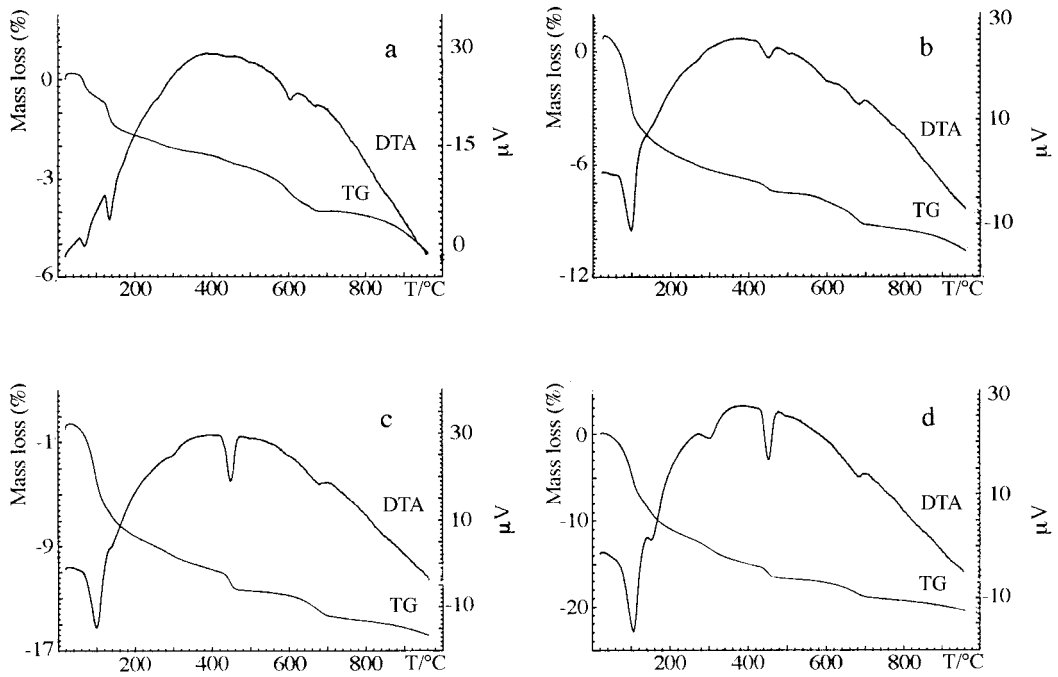


Fig. 3. DTA/TG curves of paste II cured for (a) 1 h, (b) 2 days, (c) 4 days, (d) 90 days.

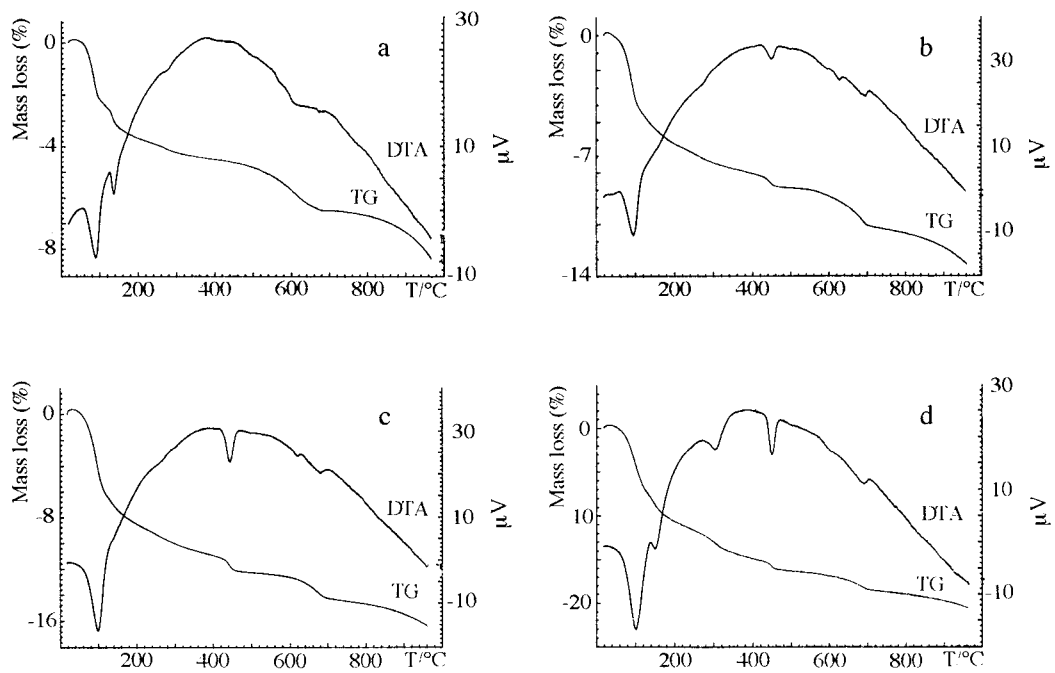


Fig. 4. DTA/TG curves of paste III cured for (a) 1 days, (b) 4 days, (c) 7 days (d) 90 days.

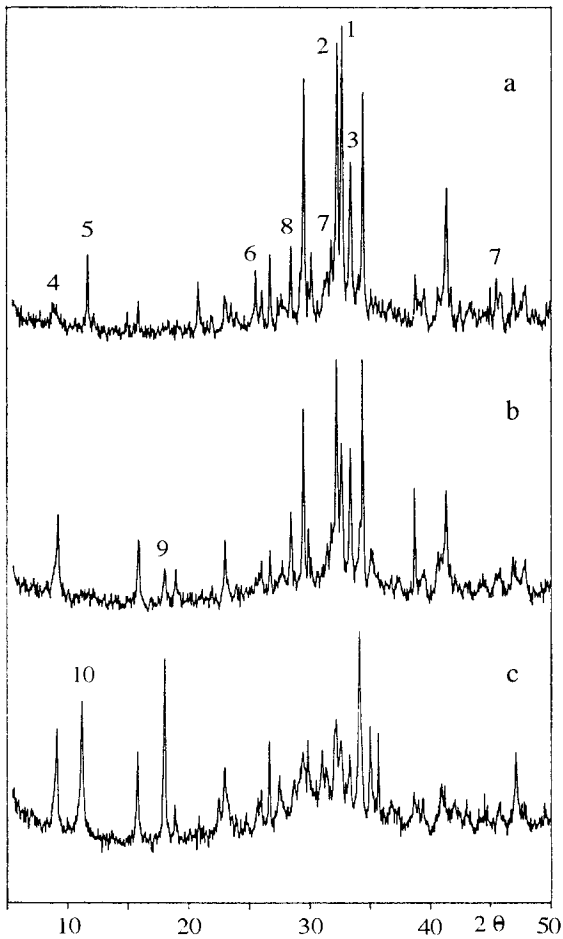


Fig. 5. XRD of paste II cured for (a) 1 h, (b) 2 days, (c) 90 days. (Legend: 1= $3\text{CaO}\cdot\text{SiO}_2$, 2= $2\text{CaO}\cdot\text{SiO}_2$, 3= $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, 4=Ettringite, 5=Gypsum, 6=Anhydrite, 7=Halite, 8=Sylvite, 9= $\text{Ca}(\text{OH})_2$, 10= $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$).

curves, after 90 days hydration there is a greater quantity of calcium chloroaluminate in paste III due to more intense reaction of chloride with calcium aluminate. XRD examination confirmed the formation of calcium chloroaluminate. Its peaks (d : 7.84 \AA) increases with the advancement of hydration, as observed in Figs. 5 and 6.

The development of hydration, also observed on diffractograms, leads to a reduction in peaks for halite and sylvite and this reduction is more rapid for halite. The formation of chloroaluminate provokes a consumption of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, as can be seen from the reduction

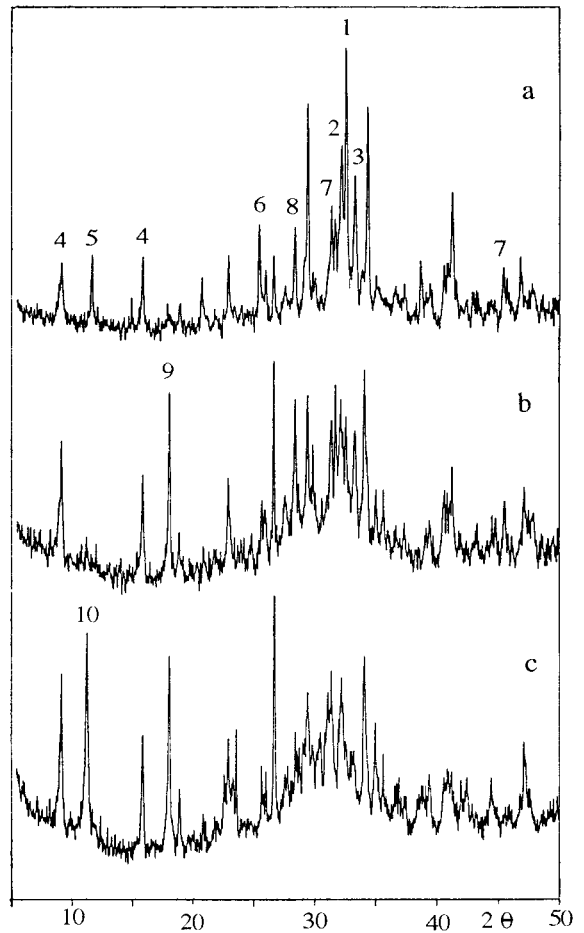


Fig. 6. XRD of paste III cured for (a) 1 day, (b) 7 days, (c) 90 days. (Legend: 1= $3\text{CaO}\cdot\text{SiO}_2$, 2= $2\text{CaO}\cdot\text{SiO}_2$, 3= $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, 4=Ettringite, 5=Gypsum, 6=Anhydrite, 7=Halite, 8=Sylvite, 9= $\text{Ca}(\text{OH})_2$, 10= $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$).

of the relative peak (d : 2.69 \AA). This consumption added to the quantity previously required for the formation of ettringite requires a high availability of aluminate phases.

In the light of previous studies [5], it can be assumed that the reactive alumina of pozzolanic material contributes to the formation of both ettringite and calcium chloroaluminate. Further, studies [6] have also shown that low quantity of reactive alumina contained in the same ash can interact with calcium sulphate to give ettringite. The clear reduction of free salts NaCl and KCl in the paste leads us to suppose, in view of high

Table 3
Concentration of heavy metals in the fly ash and leaching test

| | Pb | Cd | Cr | Cr(VI) | Zn | Cu | Ni | Hg |
|--|------|-------|------|--------|-------|-------|-------|--------|
| Fly ash (mg kg ⁻¹) | 6120 | 206 | 485 | 280 | 11250 | 1040 | 76 | <1 |
| Leaching fly ash (mg l ⁻¹) | 8.02 | 5.460 | 0.75 | 0.020 | 232 | 13.24 | 0.37 | <0.001 |
| Leaching paste (mg l ⁻¹) | 0.09 | 0.013 | 0.14 | 0.025 | 0.23 | 0.02 | <0.01 | <0.001 |

quantity of chlorides in fly ash, that apart from the formation of calcium chloroaluminate hydrate, a significant part of chloride salt interacts with calcium silicate hydrate phase [14].

The diffractograms show that for the paste with a high ash content there is a greater reduction of peaks of calcium silicates of the cement, as can be observed in the correspondence with 90 days curing. This behaviour indicates that in a more advanced curing stage, there is an acceleration of the hydration reactions of the calcium silicates in the paste.

On the TG curves, for the pastes containing ash, at a temperature greater than 800°C a marked weight loss is observed. This can be attributed to the process of sublimation of NaCl and KCl [15] constituents of the ash. With the reduction of the content of free chlorides, a clear reduction of weight loss is noted on the TG curves above 800°C.

The results of leaching tests, at pH 5.0, applied to solidified material containing fly ash (paste III) and to the same fly ash are shown in Table 3. Concentrations of heavy metals in the leaching solution are low and below the limits allowed by Italian law on water pollution [8]. Therefore, it is seen that the heavy metals are effectively fixed during the development of the hydration processes so as to ensure that a good degree of stabilization of fly ash in hardened cementitious pastes is obtained.

4. Conclusions

By coupling DTA/TG analysis with XRD investigations, it was possible to examine the hydration reactions of a pozzolanic cement and of pozzolanic cement–fly ash mixtures. The presence of fly ash in cementitious pastes explains the slowing of hydration reaction of calcium silicates of the cement in the first hydration period, in which formation of gypsum and

ettringite takes place. With the disappearance of gypsum, hydration leads to the development of CSH and free lime in the pastes. With the advancement of the hydration process there is formation of calcium chloroaluminate hydrate. The XRD investigations show a marked reduction of free chlorides (NaCl and KCl).

Development of hydration reactions in fly ash–cement pastes provokes an acceptable hardening of the materials as is also confirmed by compression strength tests carried out.

Application of the leaching test to hardened fly ash–cement paste and to the same fly ash made it possible to verify a good degree of fixation of heavy metals to cementitious matrix. In view of the overall results obtained with the above investigations the solidification/stabilization treatment of MSW fly ash with pozzolanic cement may be considered satisfactory.

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