Journal of Thermal Analysis, Vol. 47 (1996) 7-16

HYDRATION BEHAVIOUR OF A LIME-POZZOLAN CEMENT CONTAINING MSW INCINERATOR FLY ASH

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Abstract

A lime-pozzolan cement was used to make pastes containing different quantities of MSW fly ash. After setting, the pastes were cured in water at room temperature from 1 h to 260 days. The hydration characteristics and the nature of the hydration products of the various pastes were studied by simultaneous TG/DSC thermal analysis and X-ray diffractometry. The MSW fly ash was found to induce a slowing of the hydration process in lime-pozzolan pastes, and after some days an evident acceleration of hydration reactions occurred. Sulphate and chloride in the MSW fly ash yield hydration products forming a cementitious matrix.

Keywords: lime, MSW fly ash, natural pozzolan, TG/DSC, XRD

Introduction

The fly ash produced by burning Municipal solid urban waste (MSW) and separated during depulverization from fumes is classified as a hazardous waste owing to its particular chemical composition, generally characterized by a high content of heavy metals [1]. The use of cement materials is one of the methods for the detoxification of residue wastes.

In this context, the present study reports on a series of investigations relating to the stabilization/solidification of MSW fly ash with a hydraulic binding material formed by hydrated lime and natural pozzolan. In particular, with the help of thermal analysis TG/DSC and X-ray diffractometry, the process of hydration of the lime-pozzolan pastes containing MSW fly ash is examined over the curing cycle. These investigations allow a better understanding of the influence of MSW fly ash on the hydration process in cementitious pastes.

Experimental

The cement binding material was produced from commercial hydrate lime (84% $Ca(OH)_2$, 14% $CaCO_3$) and natural pozzolan, both in powdered form. The latter material was taken from a quarry at Rionero (Basilicata) and corresponds to the 'pyroclast of vulture' [2]. The weight ratio of the two elements of

0368-4466/96/ $ 5.00

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Table 1 Composition of natural pozzolan %

l.o.i.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	TiO_2	ZnO	P_2O_5	CO_2
8.58	47.00	15.39	6.73	9.99	3.25	0.19	2.66	2.68	1.25	0.03	0.72	1.32

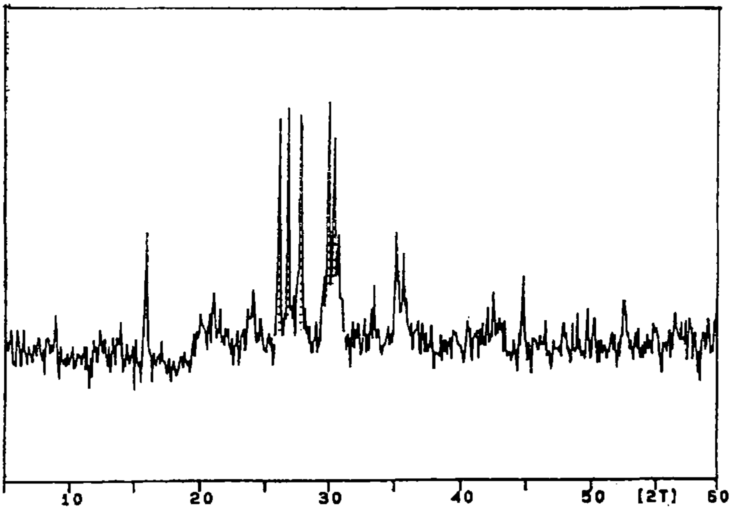

Fig. 1 XRD of pozzolan

the mixture was 40:100. From the chemical (Table 1) and mineralogical (Fig. 1) characterizations, the pozzolan was found to contain a vitreous fraction (partially crystallized) and a crystalline one.

The main components of the crystalline fraction were augitic pyroxene, feldspar, quartz, zeolites (principally analcime), phyllosilicates (mica), feldspathoids (hauyine) and calcite.

The chemical composition of the MSW fly ash used in the solidification process with the cement binding material is shown in Table 2. The main mineralogical constituents determined by XRD (Fig. 2) were KCl (sylvite), NaCl

Table 2 Composition of MSW fly ash

Element	Concn./ mg kg^{-1}	Element	Concn./ mg kg^{-1}	Element	Concn./ mg kg^{-1}	Element	Concn./ %
Al	36400	K	75500	Cr	485	CO_3^{2-}	4.2
Ca	233200	Na	34750	Zn	11250	P_2O_5	0.39
Si	95262	Mn	859	Pb	6120	Cl^-	14.05
Fe	12000	Cu	1040	Ni	76	SO_4^{2-}	4.94
Mg	13680	Cd	206	Hg	< 1	l.o.i.	4.93

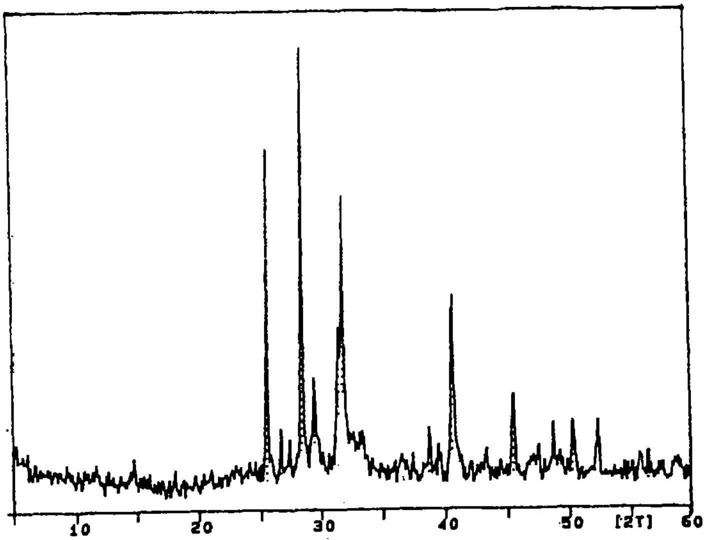

Fig. 2 XRD of fly ash

(halite), $CaSO_4$ (anhydrite), $CaCO_3$ (calcite) and α-SiO_2. Smaller quantities of other components, such as $Ca(OH)_2$ (portlandite), CaO (lime), α-Fe_2O_3, silicate and calcium aluminate, were also found.

The different fly ash-binding material – water mixtures representing the pastes studied correspond to the following ratios: 0:74.0:26.0 (Mix I), 18.5:55.5:26.0 (Mix II), and 29.6:44.4:26.0 (Mix III).

Results and discussion

The samples of hydrated pastes after different curing periods of from 1 h to 260 days in water at room temperature were subjected to TG/DSC thermoanalytical investigations in static air at a 10°C min^{-1} heating rate (Netzsch STA 409 equipment) and XRD analysis (Philips PV-1710 using CuK_α radiation).

From an examination of the DSC curves (Fig. 3) for the hydration of the pure binding material, a considerable endothermic effect is observed between 420 and 520°C, due to the decomposition of $Ca(OH)_2$; the loss in mass relating to water elimination was quantified from the TG curve. The total amount of unreacted $Ca(OH)_2$ after different curing periods was therefore found. Figure 8 shows a plot of the free lime content as a function of the hydration time.

After the first day of hydration (Fig. 3), it is possible to observe a slight endothermic effect at ca. 90°C, attributable to calcium silicate hydrate (CSH). The formation of this hydrosilicate is also connected with a slight exothermic effect between 850 and 900°C, which is not accompanied by a mass loss and corresponds to the recrystallization of wollastonite derived from CSH [3, 4].

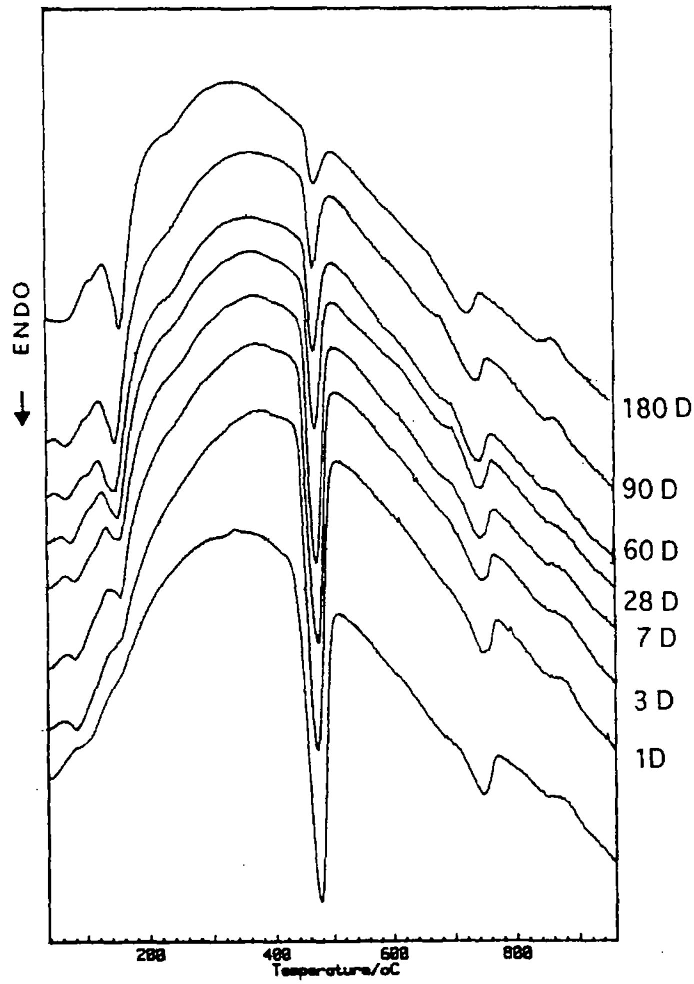

Fig. 3 DSC curves of Mix I

After curing for 3 days, an endothermic effect whose intensity increases with time is observed at around 160°C; this is attributable to $C_3A\cdot CaCO_3\cdot 11H_2O$ (hydrocarboaluminate) [5]; the presence of this constituent is confirmed by XRD investigation (d=7.57 Å) (Fig. 4).

In all the DSC curves, the endothermic effect due to the decomposition of $CaCO_3$ is present between 700 and 780°C.

As shown in Fig. 8, the free lime content indicates a variable decrease in relation to the hydration time. In particular, there is a major decrease after 1 day of hydration, and this becomes increasingly evidenut after 3 days. After 7 days of hydration, a gradual decrease of the free lime content occurs until 180 days; after this hydration time, the decrease of free lime is much slower.

The DSC curves for the hydrated pastes containing MSW fly ash are depicted in Fig. 5 (Mix II) and Fig. 6 (Mix III). After 1 h of hydration, these curves exhibit 2 endothermic effects, with peak temperatures of 95 and 140°C. For Mix II the two effects intensify up to 1 day of hydration, but for Mix III the resulting effect is a major one and develops further during 3 curing days. At the lowest temperature, the effect may be related to the decomposition of the neo-

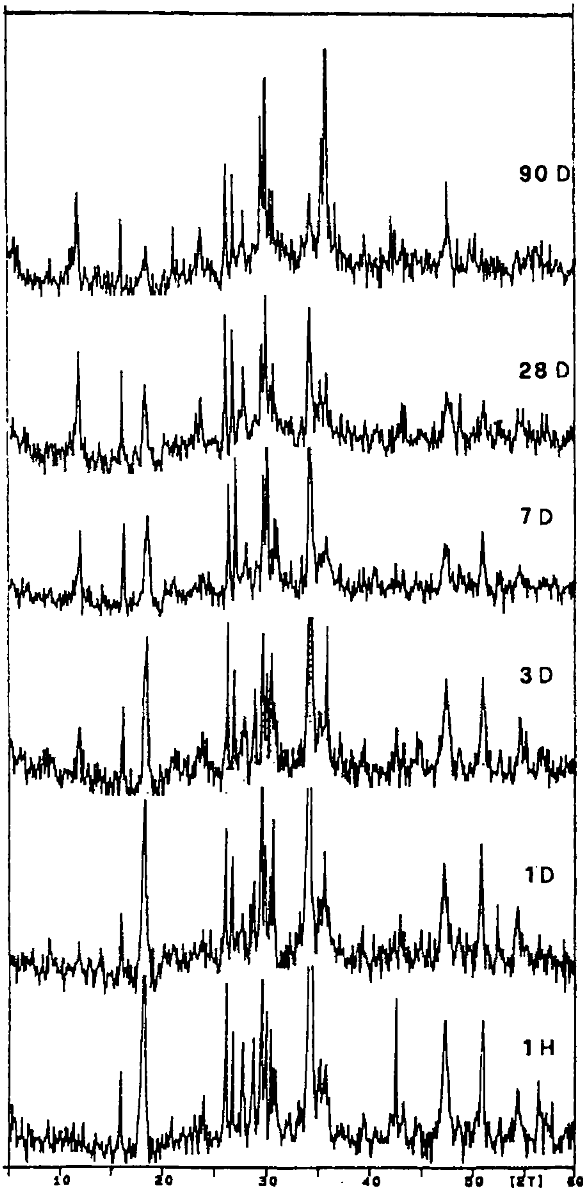

Fig. 4 XRD Mix I

formed hydration product ettringite; the second effect is connected with the dehydration of $CaSO_4 \cdot 2H_2O$ (gypsum), which originates in these early hydration stages from $CaSO_4$ contained in the MSW fly ash. Between the two considered temperatures, a single endothermic effect develops after 3 days of hydration for Mix II and 7 days for Mix III, with a peak temperature of 115°C; this is associated with ettringite dehydration.

XRD on the same samples (Fig. 7) shows the presence of ettringite as the main neo-formed hydration product. The sulphate necessary to form calcium

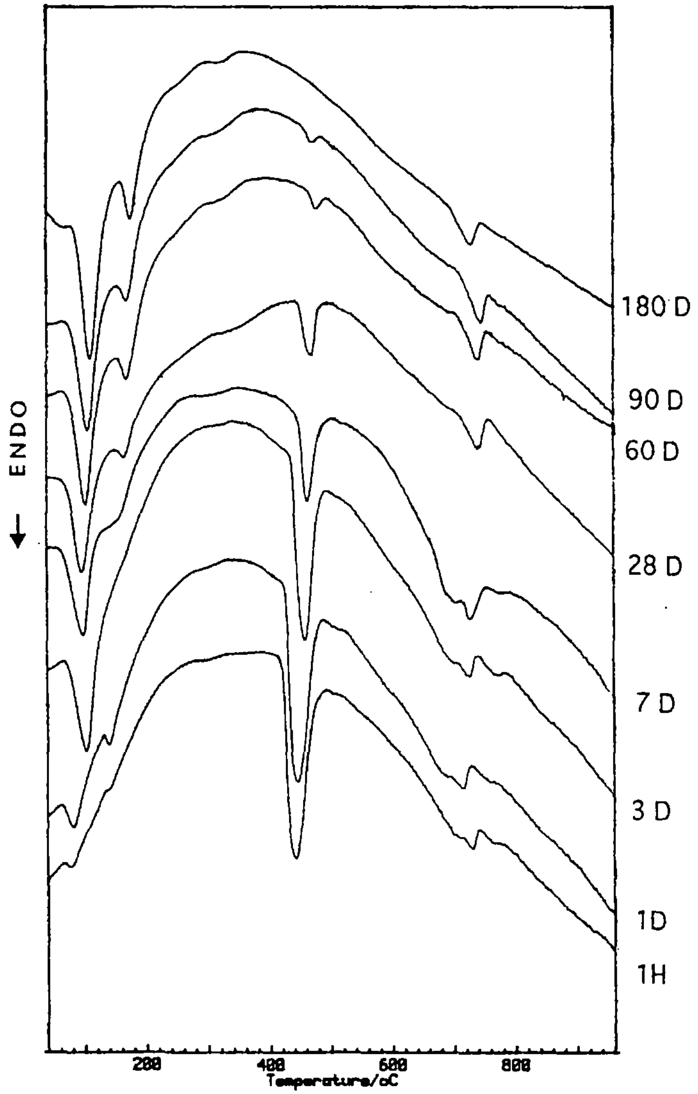

Fig. 5 DSC curves of Mix II

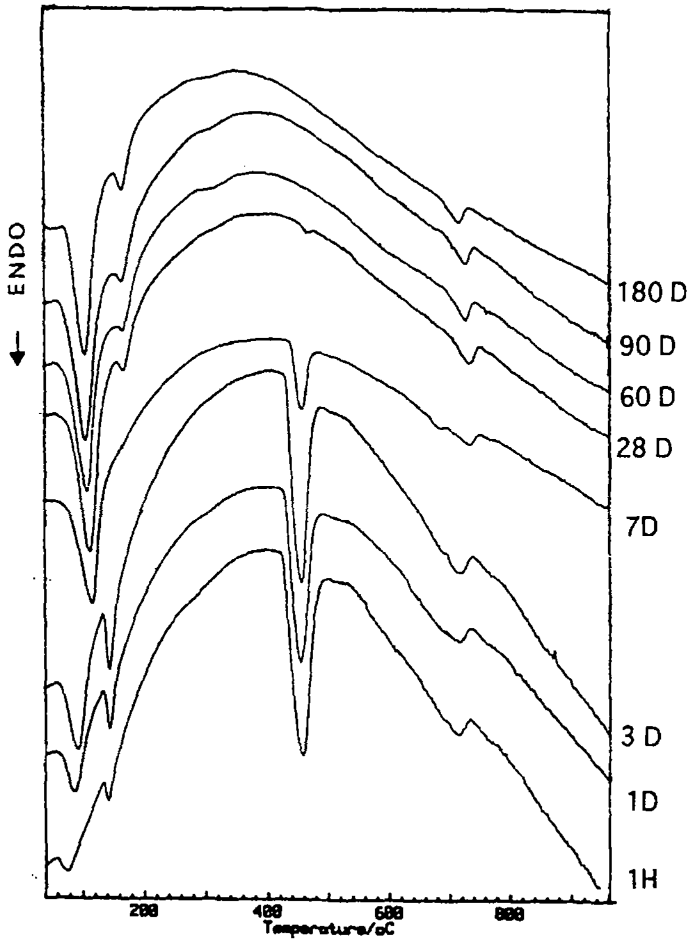

Fig. 6 DSC of Mix III

trisulphoaluminate hydrate is supplied by the MSW fly ash. Accordingly, as the amount of ash in the pastes is increased, a higher availability of sulphate ion results.

For both mixtures (Figs 5 and 6), the endothermic effect at 180°C, together with a weaker effect at 320°C which appears in the subsequent hydration period, can be attributed to hydrated monochloroaluminate, $C_3A\cdot CaCl_2\cdot 10H_2O$ [6], which is also demonstrated by XRD examination (Fig. 7). The formation of this hydrated product is determined by the high concentration of chloride in the MSW fly ash.

Partially overlapping peaks corresponding to a small amount of hydrated calcium silicate are observed in the XRD patterns.

The characteristic endothermic effect of calcium hydroxide in the pastes is notably reduced, and after 60 days it disappears from Mix III (Fig. 6); for

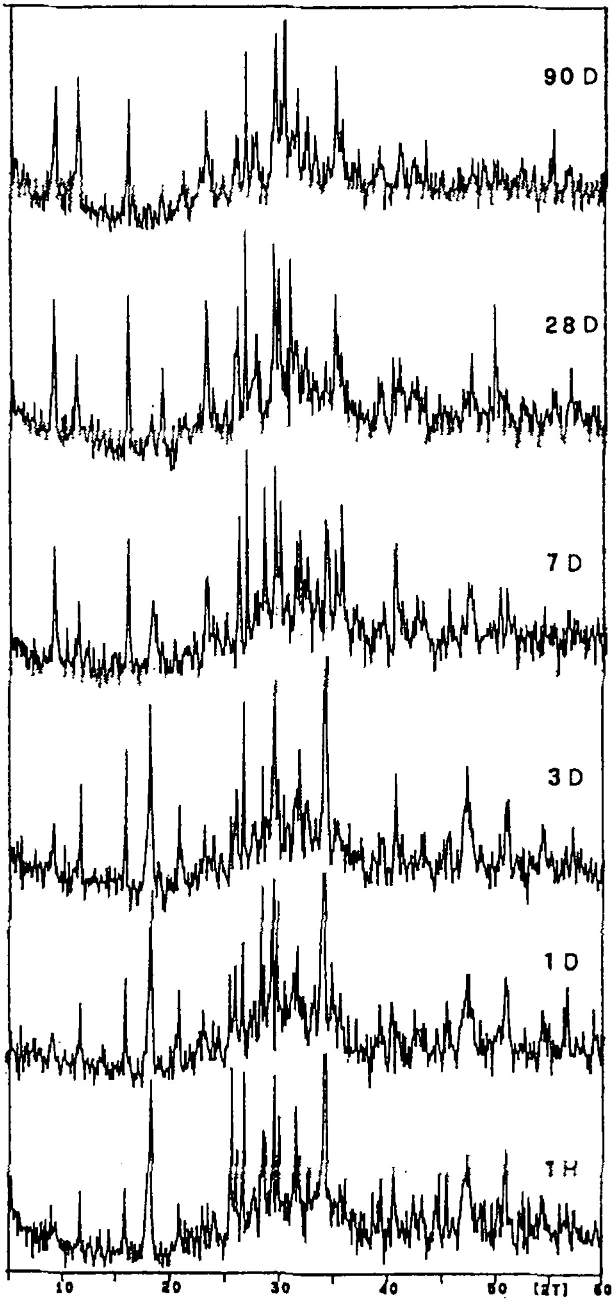

Fig. 7 XRD of Mix III

pastes containing smaller amounts of MSW fly ash, the effect of $Ca(OH)_2$ disappears after around 180 days of hydration (Fig. 5).

As seen in Fig. 8 for mixtures containing MSW fly ash, the free lime content undergoes a weaker decrease for Mix I (lime-pozzolan mixture); in particular, the reduction of free lime is much lower for Mix III in the early hydration stage. The MSW fly ash induced a slowing of the hydration process in the pastes up to 3 days, after which an acceleration of the process occurred. After 7 days, the hydration reactions proceeded at a lower rate than in the immediately previous stage and the free lime available for these reactions became negligible at around 60 and 180 days, respectively, for Mix III and Mix II.

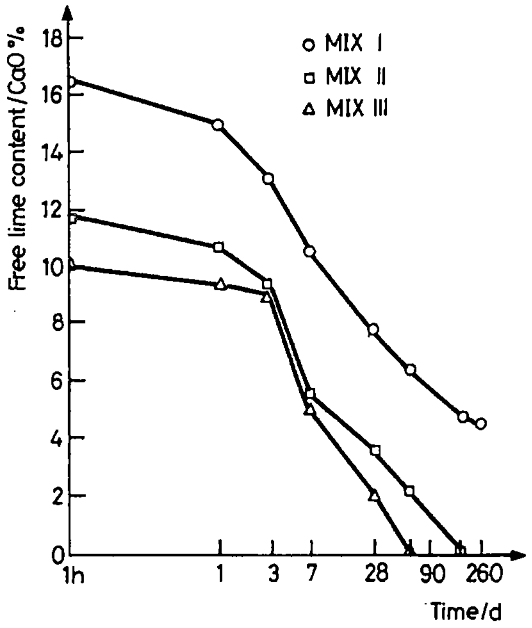

Fig. 8 Variation of free lime content with curing time

Conclusions

In lime-pozzolan pastes, calcium silicate hydrate and hydrocarboaluminate have been shown to be the main hydration products. The addition of MSW fly ash to lime-pozzolan pastes results in a slowing of the hydration process up to 3 days of curing, after which the process accelerates. The main hydration products of lime-pozzolan-MSW fly ash pastes are ettringite and chloroaluminate hydrate, the latter formed in a smaller quantity and at a more advanced hydration stage. The formation of these two products is induced, respectively, by the sulphate and chloride contained in the MSW fly ash; these react with the reactive constituents of the pozzolan and calcium hydroxide, creating a cementitious matrix from the solidified mixture.

The rate of the hydration process and the nature of the hydrated products in pastes made of lime and pozzolan indicate lime-pozzolan cement and the corresponding raw materials are capable of stabilizing/solidifying MSW fly ash. This is supported by results relating to the physical-mechanical characterization of hardened materials and the heavy metal leaching test, which will discussed in a future publication.

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The author is grateful to D. Calabrese for assistance with the thermal and XRD analyses.

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