Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 1, 301–305

CHARACTERIZATION OF FDR FLY ASH AND BRICK/LIME MIXTURES

P. Ubbrìaco[1*], *Angela Traini*[2] *and D. Manigrassi*[2]

[1]Dipartimento di Ingegneria Civile ed Ambientale, Politecnico di Bari, via Orabona 4, 70125 Bari, Italy
[2]Dipartimento di Chimica, Università di Bari, via Orabona 4, Bari, Italy

The present research is concerning the characterization of FDR (fuel derived from residues) fly ash and mixtures with lime/brick hydraulic binder by DTA/TG/DTG thermo-analysis, X-ray diffractometry and chemical analysis. The use of hydraulic binder obtained from building brick rejects, which is less expensive than the usual solidifiers such as cementitious binder and silicates, allows us to reutilize, in the meantime, this wreckage material, to the advantage of environmental sustainability. Fly ash samples investigated in the present study were separated in a thermo-incineration plant. Mineralogical DTA/TG/DTG and XRD investigations reveal the presence of different phases as well as chemical analysis shows a moderate concentration of heavy metals and high content of chloride and sulphate. Results obtained from leaching tests with water carried out on hardened pastes containing fly ash lead to interesting results, which highlight behaviour to the release of contaminants. The whole of the results obtained in the present study make it possible to regard the objective of disposing such hardened materials in inert waste landfill sites as achievable.

Keywords: *DTA/TG/DTG thermo-analysis, FDR fly ash, lime/brick binder, XRD*

Introduction

Previous studies regarding hydrated mixtures of fly ash from the combustion of municipal solid waste (MSW) and hydraulic binders showed a characteristic leaching behaviour with aqueous solution [1, 2]. Due to the high chloride and sulphate content and to the significant concentration of heavy metals, MSW fly ash requires an optimization of the hydraulic binder in order to ensure a good detoxifying quality of the matrix.

Due to the low concentration in contaminants, fly ash produced from fuel derived from residues (FDR) gives more appropriate results for the preparation of mixtures with solidifying/stabilizing qualities [3, 4] to be sent to non-hazardous waste landfills and, in particular, to inert waste landfills, which appear to be the most economical and the most environment-compatible. It is from this perspective that the present study has been carried out on the characterization of mixtures of FDR fly ash and lime/brick hydraulic binder. The use of hydraulic binder obtained from building brick rejects, which is much less expensive than the usual solidifiers such as cementitious binder and silicates, allows us to reutilize, in the meantime, this wreckage material, to the advantage of the environmental sustainability.

The present research concerns the characterization of FDR fly ash and hardened pastes with lime/brick hydraulic binder by DTA/TG/DTG thermo-analysis, XRD and chemical analysis by atomic absorption spectrometry (AAS) and high performance ionic chromatography (HPIC).

Experimental

The fly ash samples are separated in a FDR incineration plant (Appia Energy S.p.a./Massafra – TA). The FDR bio-mass is burnt by suspension combustion. Dusts are sampled before undergoing smokes neutralization process.

Chemical analysis is carried out by means of atomic absorption spectrometry by flame and electro-thermic atomisation and HPIC for quantifying of anions and alkaline metals. The chemical composition of the fly ash is reported in Table 1. Chemical results show a tent, features that make it necessary for this 'hazardous waste' to be detoxified before disposal in landfill.

X-ray diffractometric analysis is carried out by using Philips PV-1710 diffractometer (with CuK$_\alpha$ radiation) and DTA/TG/DTG thermoanalysis using a heating rate of 10°C min^{-1} in static air (Netzsch STA 409 apparatus). The fly ash is made up of calcite ($CaCO_3$), quartz (αSiO_2), halite (NaCl), portlandite ($Ca(OH)_2$), calcium oxide (CaO), sylvite (KCl), anhydrite ($CaSO_4$), hematite (Fe_2O_3), amorphous material, residual carbon and smaller amounts of calcium silicate, calcium aluminosilicate and various

---

[*] Author for correspondence: p.ubbriaco@poliba.it

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Composition of FDR fly ash

Element	%	Element	mg kg^{-1}	Element	%
Si	11.15	Mn	741	Cl	8.80
Ca	23.18	Co	898	SO_4	3.00
Al	3.44	Ni	233	L.O.I.	10.65
Fe	1.42	Cr total	34	(1000°C)	
Na	4.53	CrVI	1.6		
K	1.50	Pb	170		
Mg	0.71	Cd	20		
Cu	0.61	PO_4	300		
Zn	0.63	Br	538		
		F	45		

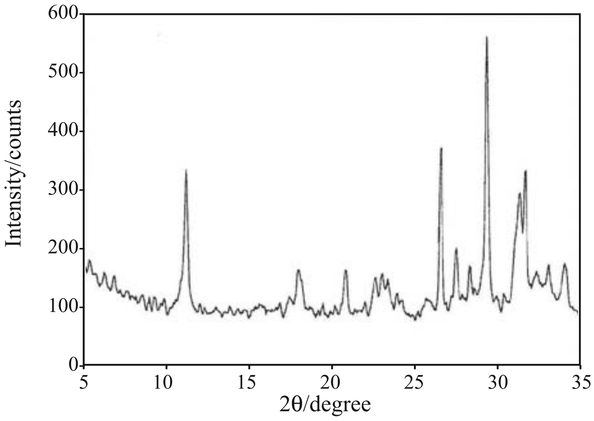

Fig. 1 XRD of fly ash

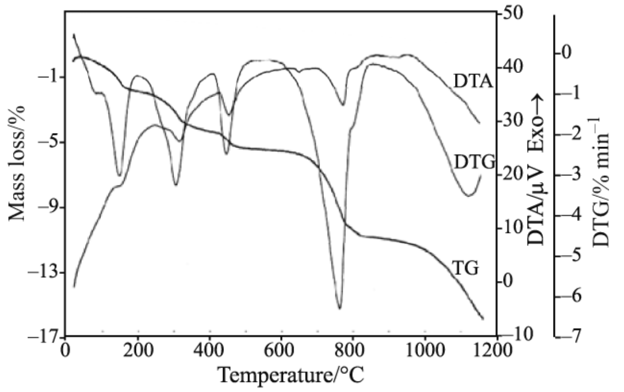

Fig. 2 DTA/TG/DTG curves of fly ash

oxides (Figs 1 and 2). This FDR fly ash shows a chemical composition, except of presence of heavy metals and high chloride content, similar to fly ash from combustion of coal in fluidized furnace [5, 6].

The XR diffractometry indicates peaks (2θ=11.33; 22.63; 31.14) of calcium chloroaluminate hydrate ($3CaO·Al_2O_3·CaCl_2·10H_2O$). The presence of chloroaluminate is confirmed by DTA/TG/DTG curves that show two endothermic effects of decomposition at 160 and 320°C. The formation of this hydrate phase reveals the presence of reactive aluminate phases in fly ash that react with chloride and $Ca(OH)_2$ as a consequence of cooling in the plant. The presence of reactive aluminate phases is confirmed by the simultaneous formation of ettringite ($3CaO·Al_2O_3·3CaSO_4·32H_2O$) in fly ash, relieved by moderate endothermic effect at around 90°C on DTA/TG/DTG curves.

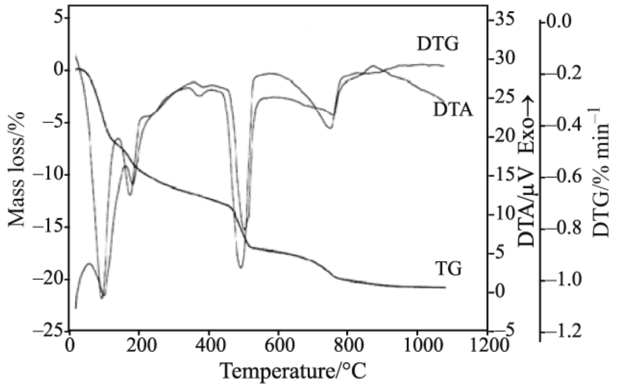

Fig. 3 DTA/TG/DTG curves of paste 0 cured for 28 days

A hydraulic lime is prepared with a mixture of ground brick, from hollow clay tile, and hydrated lime ($Ca(OH)_2$>90%) (Italian Law, D.M. 31-8-1982). Fly ash is mixed with lime/brick binder (ash/binder mass ratio=0:100 (0); 25:75 (1); 45:55 (2)), from which pastes (paste 0, paste 1, paste 2) are prepared (water/solid=0.50) that are cured in a controlled environment (*T*=25°C; R.H.=95%). Hardened pastes are leached with deionized water (solid/liquid ratio: 1/13) in a dynamic test with two subsequent renewals [7]. Results are reported in Tables 2–4.

Results and discussion

For the lime-brick binder (paste 0) the main neoformed hydrated phases are calcium silicate hydrate

Table 2 Elution test of paste 1 cured at 30 days

	Concentration/μg L^{-1}		
	Elution time 2 h	Elution time 18 h	Elution time
Cu	68.8	81.5	62.3
Ni	<5.0	<5.0	<5.0
Zn	<4.0	16.8	5.6
Co	<7.0	<7.0	<7.0
Cd	<1	<1	<1
Pb	<2	<2	<2
CrVI	<10	<10	13.2
Cl	27460	44323	34393
SO_4	1280	2110	2690

Table 3 Elution test of paste 2 cured at 30 days

	Concentration/μg L^{-1}		
	Elution time 2 h	Elution time 18 h	Elution time 48 h
Cu	51.5	63.8	57.0
Ni	<5.0	<5.0	<5.0
Zn	6.7	17.0	6.0
Co	<7.0	<7.0	<7.0
Cd	<1	<1	<1
Pb	<2	<2	<2
CrVI	10.0	14.5	10.7
Cl	955450	124680	55720
SO_4	1143	1317	850

Table 4 Elution test of paste 2 cured at 60 days

	Concentration/μg L^{-1}		
	Elution time 2 h	Elution time 18 h	Elution time 48 h
Cu	2.0	0.6	1.1
Ni	<5.0	<5.0	<5.0
Zn	<0.5	<0.5	<0.5
Co	<7.0	<7.0	<7.0
Cd	<1	<1	<1
Pb	<2	<2	<2
CrVI	10.0	10.0	13.2
Cl	489980	108800	53000
SO_4	1167	911	785

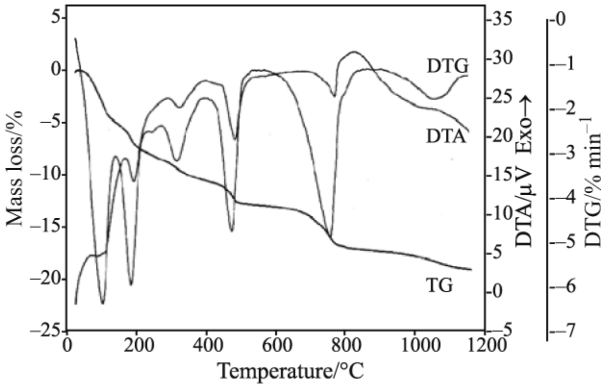

Fig. 4 DTA/TG/DTG curves of paste 1 cured for 7 days

(CSH) and calcium monocarboaluminate hydrate ($3CaO\cdot Al_2O_3\cdot CaCO_3\cdot 11H_2O$). Carboaluminate hydrate on the DTA/TG/DTG curve (Fig. 3) reveals two endothermic effects of dehydration at 180 and 260°C. After 28 days curing $Ca(OH)_2$ is present in the paste which does not contain fly ash.

The DTA/TG/DTG curves of paste 1 (Fig. 4), with 1 week hydration, reveal an endothermic effect at around 100°C due to the dehydration of ettringite ($3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$) which overlaps with that of calcium silicate hydrate (CSH). XRD analysis confirms the presence of ettringite (2θ: 9.20, 15.90, 22.96). The formation of ettringite involves a consumption of 'free' sulphate in the first 2 days. A weak initial solidification of the paste, due to ettringite, evolves into a progressive hardening with development of the CSH phase. The CSH product results from the pozzolanic reaction of the reactive silica phase with $Ca(OH)_2$.

Calcium chloroaluminate hydrate ($3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$) also forms during the progress of hydration. This hydrate phase is also noted in XRD analysis (2θ: 11.30) (Fig. 5). Two endothermic effects of dehydration at 180 and 320°C are associated with the calcium chloroaluminate hydrate phase (Figs 4 and 6). This results from the reaction of 'free chloride' with the reactive aluminate of the pozzolanic material.

For paste 2, which contains a greater quantity of fly ash, the process of hydration develops intensely over a 1 week curing period. After this, for want of 'free' $Ca(OH)_2$ the overall process of hydration is

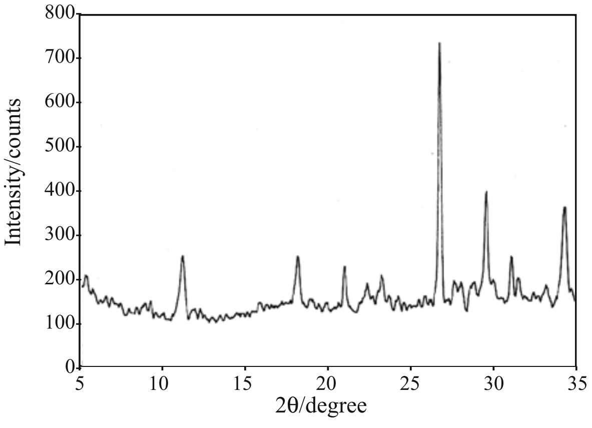

Fig. 5 XRD of paste 1 cured for 7 days

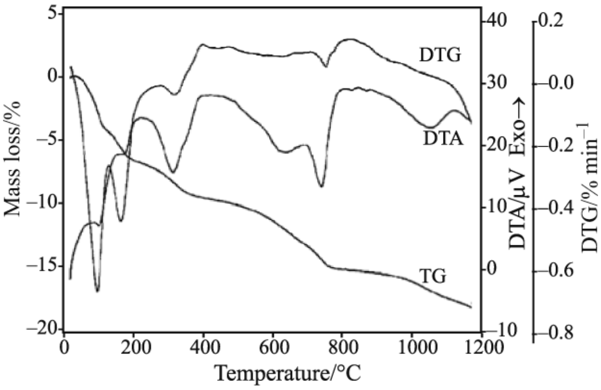

Fig. 6 DTA/TG/DTG curves of paste 2 cured for 7 days

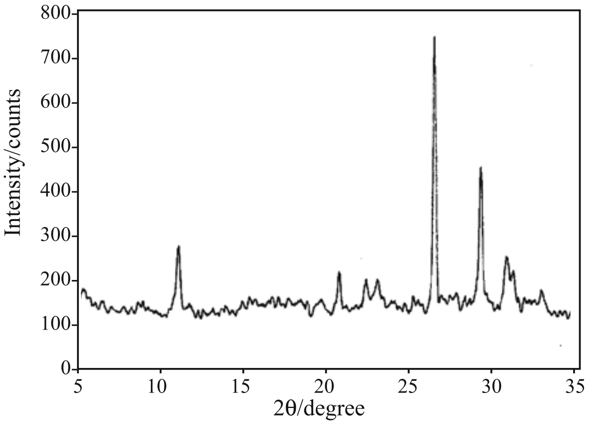

Fig. 7 XRD of paste 2 cured for 7 days

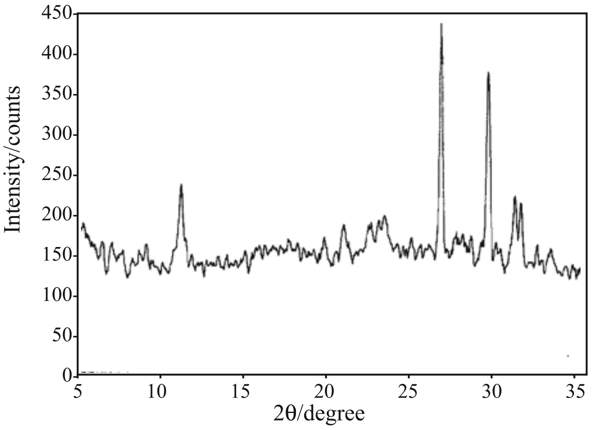

Fig. 9 XRD of paste 2 cured for 120 days

greatly slowed [8]. In this more advanced curing period the formation of the calcium chloroaluminate hydrate phase marks a shift of the main peak to lower values of 2θ (11.18) (Fig. 7). It is possible to assert the hydrate phase corresponds to the solid solution in the series $3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$–$3CaO\cdot Al_2O_3\cdot CaCO_3\cdot 11H_2O$–$4CaO\cdot Al_2O_3\cdot 13H_2O$ richer in chloride [9, 10]. Another shift involves the decomposition effect of the carbonate on the thermoanalytical curves, towards lower temperature of the characteristic effect at about 750°C (Fig. 8). This shift indicates a 'mobilization' of calcium from the carbonate phases to the aqueous phases of the matrix at the expense of other ions that replace it in $CaCO_3$. A high quantity of 'free' chloride (NaCl, KCl) is fixed in the hydrate phases of the paste (Fig. 9). In view of this behaviour it may be that the process of hydration induces an interaction of the CSH with the free chloride as has been found also in our previous researches [11] and in the studies of other authors [12].

Chemical analysis mainly has been focused on the more hazardous elements in fly ash as well as on the parameters, indicators of the good degree of stabilization in the matrix, as has already highlighted in our previous research [2].

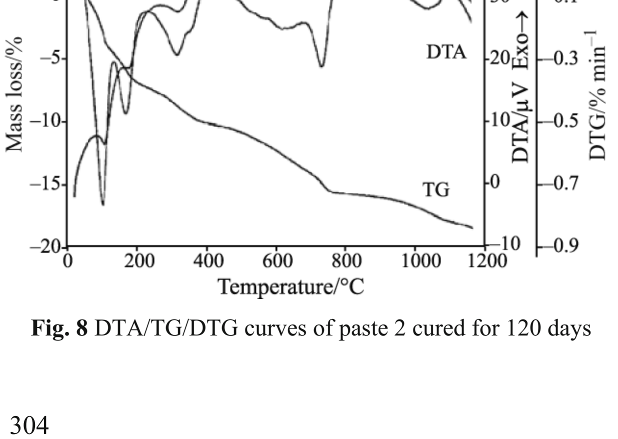

Fig. 8 DTA/TG/DTG curves of paste 2 cured for 120 days

As far as Cd and Pb are concerned, where contamination tolerability limit is lower, a negligible release can be detected at different leaching times (Tables 2–4). This indicates good behaviour for the hydraulic constituents of the lime/brick binder to incorporate elements.

As far as Cr is concerned, a minimum release can be observed for fly ash rich paste 2, which suggests the binding matrix is suitable for incorporating an element, whose behaviour is connected to the pH of the water phase of the paste as well as to the stability of the aluminate hydrate phases. It is possible to improve the stabilizing capacity of the binder by adding reactive ceramic powder characterized by good pozzolanic behaviour, as shown in our previous studies [11].

As far as the release of Cl^- and SO_4^- anions is concerned, analysis shows a very low release for sulphate, while a value lower than the limit (80 mg L^{-1}) can be observed for chloride. Only paste 2, which is richer in fly ash, shows a perceptible release of chloride which decreases in the eluates of the pastes over a longer curing period.

Conclusions

DTA/TG/DTG and XRD investigations have shown the peculiar hydrate phases responsible of good hardening of FDR fly ash and lime/brick mixtures.

Leaching tests with water carried out on the hardened pastes containing fly ash lead to very interesting results from which a tendency to release of contaminants can be inferred. The results show the good behaviour of the hydrated matrix to stabilise the various contaminants of the residue. The hydraulic binder created thus represent a good and economical FDR fly ash solidification/stabilization system involving the recycling of brick rejects and building residue. Results from the present study on hydration and leaching of solidified and stabilized mixtures containing FDR fly ash make it possible to regard the objective of disposing such hardened pastes in inert waste landfill sites as achievable. This would represent the most economical and environment-compatible waste disposal system.

References

1 P. Ubbrìaco, P. Bruno, A. Traini and D. Calabrese, J. Therm. Anal. Cal., 66 (2001) 293.
2 P. Ubbrìaco, P. Bruno and A. Traini, J. Anal. Environ. Chem., 92 (2002) 903.
3 P. Ubbrìaco, P. Bruno, A. Traini, S. Misceo, D. Calabrese and D. Manigrassi. 8th Con. Naz. AIMAT, 27 Giugno–1 Luglio, Università di Palermo, Palermo 2006, p. 129.
4 J. Havlica, I. Odler, J. Brandstetr, R. Mikulikova and D. Walther, Adv. Cem. Res., 16 (2004) 61.
5 B. Pacewska, G. Blonkowski and I. Wilinska, J. Therm. Anal. Cal., 86 (2006) 179.
6 K. Rajczyk, E. Giergiczny and M. A. Gliniki, J. Therm. Anal. Cal., 77 (2004) 165.
7 UNI 10802.
8 Z. Giergiczny, J. Therm. Anal. Cal., 76 (2004) 747.
9 P. Ubbrìaco and D. Calabrese, J. Therm. Anal. Cal., 61 (2000) 615.
10 M. H. Roberts, Proc. Vth Int. Symp. on the Chem. Cement, Tokyo 1968, p. 21.
11 P. Ubbrìaco, M. Di Pierro and D. Calabrese, XXVIIIth AICAT–GICAT Conference Milan, 11–15 December, 2006.
12 J. J. Beaudoin, V. S. Ramachandran and R. F. Feldman, Cem. Concr. Res., 20 (1990) 875.

DOI: 10.1007/s10973-007-8853-6