Thermochimica Acta 498 (2010) 1–6

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Review

The effect of the content of unburned carbon in bottom ash on its applicability for road construction

Prvoslav D. Trifunovic[a], Slobodanka R. Marinkovic[a,*], Rade D. Tokalic[a], Srdjan D. Matijasevic[b]

[a] *Faculty of Mining and Geology, University of Belgrade, Djusina 7, 11000 Belgrade, Serbia*
[b] *Institute for the Technology of Nuclear and Other Raw Materials, Franse d Eperea 86, 11000 Belgrade, Serbia*

ARTICLE INFO

Article history:
Received 10 June 2009
Received in revised form 26 October 2009
Accepted 31 October 2009
Available online 12 November 2009

Keywords:
Unburned carbon
Recycling of bottom ash
Road construction
Differential thermal analysis
Thermogravimetric analysis

ABSTRACT

The content of unburned carbon is an important characteristic of bottom ash which could make it unsuitable for incorporation as aggregate for road construction. In this work, the effect of the content of unburned carbon in the bottom ash from the Serbian power plant “Nicola Tesla” on its applicability for road construction was examined. Four samples with different contents of unburned carbon, *i.e.*, raw bottom ash, two size fractions obtained from it (2–5 and <2 mm) and bottom ash treated by the “float–sink” method, were investigated. When these materials were used as a component in the mixture: fly ash–Portland cement–bottom ash–water for road construction, it was found that only mixtures containing bottom ash with a lower carbon content (size fraction <2 mm and treated) were employable. The content of unburned carbon in the mentioned materials was determined by simultaneous DTA/TGA. This method was also used to investigate the composition of the hardened mixtures.

Contents

1. Introduction

Significant amounts of waste coal ashes are produced during combustion of coal in thermal power plants. For ecological and economical reasons, there is intensive research to find ways of increasing the use of these waste materials, especially if they can be utilized in bulk, such as for sub-base and base materials for road construction.

Two kinds of coal ashes are distinguished: fly ash (FA) and bottom ash (BA). There are three principal differences between them:

1. The contents of the oxides: SiO_2, Al_2O_3 and Fe_2O_3 are greater in FA, which consequently may exhibit pozzolanic properties, but BA is a more or less inert material, *e.g.*, bottom ash usually does not exhibit pozzolanic properties;
2. FA has a lower unburned carbon (coal) content;
3. FA consists of finer (powdery) particles than BA, the particles of which are coarse (sized between sand and gravel), fused and with a glassy texture [1,2].

According to the mentioned characteristics, FA could be applied as a partial substitute for Portland cement (PC) and BA as the entire source of aggregate, or blended with natural aggregates (sand and gravel) [2] in road construction.

The content of unburned carbon in the ashes is an important factor for their applicability in road construction.

It was reported in the literature [3] that a high percentage of carbon decreases the pozzolanic activity of fly ash.

Bottom ash, with a higher content of unburned carbon, has a more porous and vesicular texture and consequently is crushed more easily under compacting and loading. There are literature data [4] that show that bottom ash is not a suitable aggregate for most highway construction applications.

It is well known [5–7] that the carbon content is closely related to the particle size distribution in ash. The amount of unburned

---

* Corresponding author. Tel.: +381 11 3219108; fax: +381 11 3235539.
E-mail address: slobodankamarinkovic@gmail.com (S.R. Marinkovic).

0040-6031/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2009.10.022

Table 1
Chemical compositions of the fly ash and bottom ash.

	Fly ash (%)	Fly ash specifications (ASTM 618) (%)	Bottom ash (%)
SiO_2	52.27	–	42.09
Al_2O_3	22.34	–	14.72
Fe_2O_3	6.05	–	5.56
$SiO_2 + Al_2O_3 + Fe_2O_3$	80.66	50.0 minimum, Class C70.0 minimum, Class F	62.37
CaO	6.64	less than 10%, Class F more than 10%, Class C	2.64
MgO	4.41	–	2.69
SO_3	2.74	5.0 maximum	1.98
P_2O_5	0.08	–	0.08
TiO_2	1.07	–	0.70
Na_2O	0.41	1.5 maximum	0.33
K_2O	1.36	–	0.90
CaO free	–	–	–
Loss on ignition (L.O.I.)	2.04	6.0 maximum	6.23

carbon decreases with increasing fineness of the ash particles. Due to this, raw bottom ash and various size fractions obtained from it by sieving contain different contents of unburned carbon. Also, it is known that unburned carbon particles are characterized by a lower density than the bottom ash particles and, consequently, the float–sink method may be applied to reduce the carbon content in bottom ash [7,8].

In this work, a sample of raw bottom ash from the Serbian power plant "Nicola Tesla" and samples obtained from it by sieving and treatment by the float–sink method, which thus contained different contents of unburned carbon, were mixed with fly ash, Portland cement and water. After 7 days, the compressive strength and composition of the hardened mixtures were determined.

The aim of the work was to establish the effect of the content of unburned carbon in bottom ash on its applicability as the entire source of aggregate for road construction in the mixture (fly ash–Portland cement–bottom ash–water).

2. Experimental

Fly ash and bottom ash, both by-products or waste materials, from the "Nicola Tesla" thermal power plant, the biggest in Serbia, were used in this work.

The chemical composition of these materials (presented as oxide equivalents) was determined by classic chemical analysis.

The mineralogical composition of the fly ash and bottom ash was investigated by X-ray diffraction analysis, using a Philips PW 1729 X-ray generator and a Philips PW 1710 diffractometer.

The grain size distribution of the bottom ash was determined by sieving through sieves of mesh size 5, 4, 3, 2.5 and 2 mm.

Four samples of bottom ash: S_1, S_2, S_3 and S_4 were used. The S_1 sample was untreated-raw bottom ash. Samples S_2 (2–5 mm size fraction) and S_3 (less than 2 mm size fraction) were obtained by sieving the bottom ash sample. Sample S_4 (treated bottom ash) was prepared from the raw bottom ash by the float sink method.

The float–sink method consisted of immersion of the bottom ash in tap water and separation of the floating material (unburned carbon) by filtration. These operations were performed five times.

The four samples of bottom ash were examined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in order to determine their content of unburned carbon. The DTA and TGA examinations were performed using a Netsch STA 409 simultaneous differential thermal and thermogravimetric analyzer. All experiments were performed in an air atmosphere by heating the samples at a constant rate of 10 °C/min in the temperature interval 0–1000 °C.

Mixtures of the four bottom ash samples (S_1, S_2, S_3 and S_4) with fly ash, Portland cement and water (W) were investigated in the manner described below with view of determining their suitability for road construction.

Cylindrical specimens of the mentioned mixtures (with a diameter of 10.2 cm and a height 11.7 cm) were made by means of compression (so-called Proctor specimens). The mass ratios of fly ash:Portland cement and of fly ash + Portland cement:bottom ash were 3:1 and 1:1, respectively, in all mixtures. The required amount of water in the mixtures, *i.e.*, the optimum moisture content, was determined in preliminary research, according to the procedure for the standard Proctor test (SRPS U.B1.012 and SRPS U.B1.038), valid in Serbia. These values were: 47.22, 49.05, 45.80 and 45.99% of the mass of the solid phase in the mixtures with the four bottom ash samples: S_1, S_2, S_3 and S_4, respectively.

After preparation, the specimens were kept under wet condition (about 100% moisture content) at temperature 20 ± 2 °C for 7 days.

The specimens were made in triplicate and designated as:

$$S'_1:\quad \text{FA–PC–BA}(S_1)\text{–W};\qquad S'_2:\quad \text{FA–PC–BA}(S_2)\text{–W};$$
$$S'_3:\quad \text{FA–PC–BA}(S_3)\text{–W};\qquad S'_4:\quad \text{FA–PC–BA}(S_4)\text{–W}.$$

The compressive strength of the Proctor-sized specimens (S'_1, S'_2, S'_3 and S'_4) were measured after 7 days.

The specimens crushed during determination of their compressive strength were then pulverized and studied by DTA/TGA analysis in order to determine their composition. The DTA/TGA examinations were performed under the same conditions as those employed for the bottom ash.

3. Results and discussion

The chemical compositions of the fly ash and bottom ash are given in Table 1. The requirements (according to ASTM 618) for the potential use of fly ash as a pozzolan in the construction industry are also shown in Table 1.

Based on the results presented in Table 1, it is evident that the fly ash from the "Nicola Tesla" Power Plant can be classified as a class F fly ash and that it satisfies the chemical requirements for use as a pozzolon in the construction industry, because the content of pozzolan oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$) in this fly ash was greater (80.66%) than the minimum content of these oxides (70%) required by ASTM 618. Also, the contents of SO_3 and Na_2O, as well as the L.O.I. are in accordance with ASTM 618 (Table 1).

The bottom ash from the "Nicola Tesla" Power Plant can be classified as a class F ash according to its content of the oxide CaO, but the sum of the oxides: $SiO_2 + Al_2O_3 + Fe_2O_3$ was lower (62.37%) and the L.O.I. higher than regulated by ASTM 618 (Table 1) for a pozzolan. Consequently, it is a relatively chemically inert material.

Based on the X-ray diffraction study, it could be stated that the major crystalline phase in the fly ash was quartz-SiO_2. The other crystalline phases present in small amounts in the fly ash, were mulite-$Al_6Si_2O_{13}$, anhydite-$CaSO_4$, feldspar-$NaAlSi_3O_8$,

Table 2
Particle size distribution of the bottom ash.

Particle size	%
4–5 mm	0.93
3–4 mm	14.04
2.5–3 mm	1.02
2–2.5 mm	3.96
<2 mm	80.05

diopside-$CaMg(SiO_3)_2$ and hematite-Fe_2O_3. In the bottom ash, the major crystalline phase was quartz, then calcite-$CaCO_3$ and small amounts of anhydrite, feldspar, diopside and hematite.

In addition to the mentioned crystalline phases, a significant amount of amorphous aluminosilicates (glass) was inconcluded in the XRD pattern of the fly ash. The amount of amorphous aluminosilicates in the bottom ash was smaller than in the fly ash.

The SiO_2 present as quartz and in the crystalline aluminosilicates phase is inert. Similarly, the part of the alumina in the crystalline phase is inactive. Both the silica and alumina in the amorphous aluminosilicates (glass) are reactive.

Based on the results of the X-ray analysis, it is evident that the fly ash was more reactive than the bottom ash, which is in accordance with the chemical composition of the oxides of these materials (Table 1).

The particle size distribution of the bottom ash (raw, untreated) from the "Nicola Tesla" Power Plant is given in Table 2.

Based on the results presented in Table 2, the bottom ash was fractioned into two size fractions: (1) sample S_2, which consisted of particles of larger size (2–5 mm) but was present in a smaller amount in the bottom ash (19.95%) and (2) sample S_3 which had particles of smaller size (<2 mm) but was present in a larger amount in the bottom ash (80.05%).

The DTA/TG curves of the raw bottom ash (sample S_1), the fraction of bottom ash composed of 2–5 mm sized particles (sample S_2), the fraction of bottom ash composed of less than 2 mm sized particles(sample S_3) and the bottom ash treated by the float–sink method (sample S_4) are presented in Fig. 1.

The DTA curves in Fig. 1a–c exhibit one strong exothermic peak (at 469, 452 and 485 °C, respectively), while the DTA curve in Fig. 1d exhibits two exothermic peaks (at 462 and 531 °C). These exothermic peaks correspond to the combustion of unburned carbon [5,9]. The lower temperature exothermic peak in Fig. 1d represents the combustion of amorphous carbon and the higher temperature one is due to the combustion of a crystalline variety of carbon in the treated bottom ash [10].

The exothermic peaks present in the DTA curves in Fig. 1a–c are not split into two peaks, very probably because of the low content of the crystalline variety of carbon in the untreated bottom ash (raw bottom ash and its two fractions). However, during the treatment of the bottom ash by the "float–sink" method, amorphous carbon, which has a lower density [11], was partially separated from the bottom ash. In this way, the relative content of the crystalline variety of carbon was increased and the exothermic peak at 531 °C appeared in Fig. 1d.

The very small endothermic peaks in Fig. 1a–d (at 628, 685 and 680 °C, respectively), as well as two shoulders at 605 and 761 °C in Fig. 1b are attributed to the decomposition of carbonates [5]. This agrees with the results of X-ray diffraction analysis concerning the presence of carbonates in the bottom ash (mentioned above).

The mass loss in the 300–580 °C range, due to the combustion of carbon [12], and the mass loss in the 580–800 °C interval, due to decomposition of carbonate [12], which were read from the TG curves (Fig. 1), are presented in Table 3. Note that the mass loss in the 580–800 °C interval appeared only in Fig. 1b, which presents the TG curve of S_2, the sample of bottom ash with particles sized

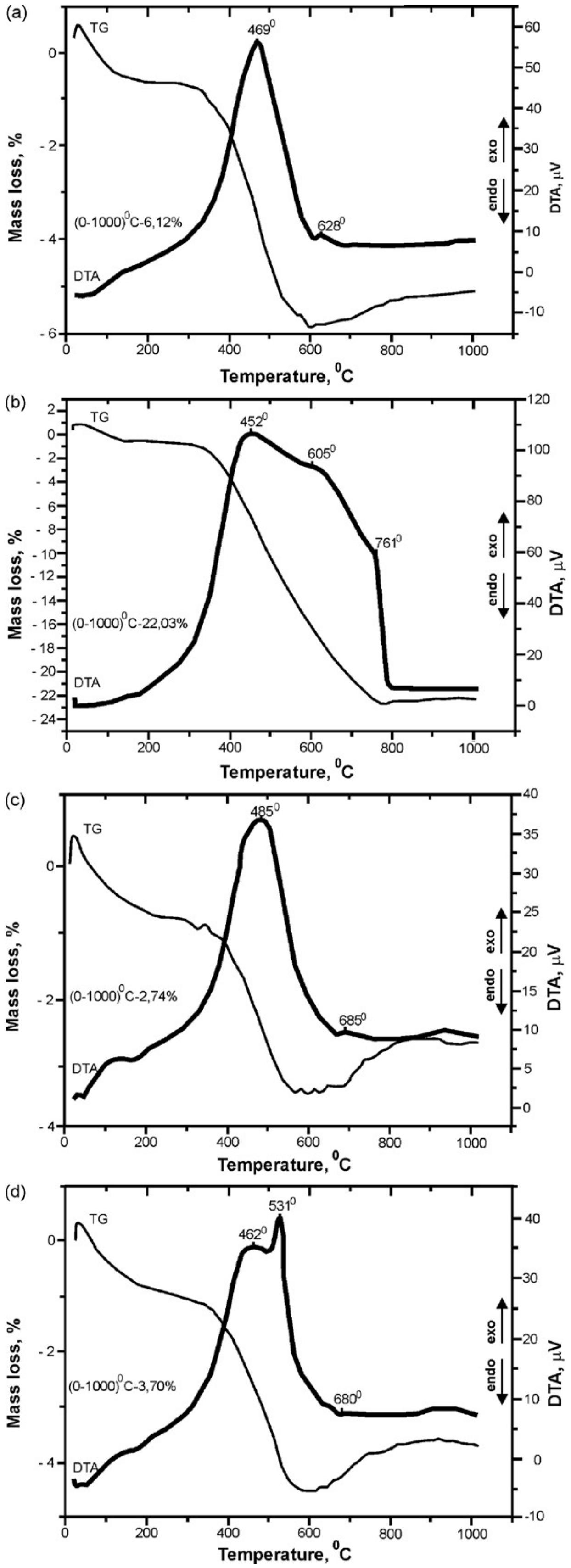

Fig. 1. DTA/TG curves of the samples of the bottom ash: a, S_1; b, S_2; c, S_3; and d, S_4.

Table 3
Mass loss of bottom ash.

Sample of bottom ash	Mass loss (%)	
	300–580 °C	580–800 °C
S_1	4.8	–
S_2	14.8	6.6
S_3	2.5	–
S_4	3.4	–

between 2 and 5 mm. In the other TG curves, there was no mass loss in this interval because of the low carbonate content in the bottom ash samples S_1, S_3, and S_4 (very small intensity of the endothermic peak for carbonate in the DTA curves of these samples). Some augmentation of the mass in this interval (Fig. 1a, c and d) can be attributed to the oxidation of sulfides, sulfur and some iron minerals present in bottom ash [5].

Based on the results presented in Table 3, it could be concluded that the unburned carbon and carbonates in bottom ash were concentrated in the fraction of bottom ash with particle sizes between 2 and 5 mm. Also, it is evident that the main fraction of the bottom ash (80.05%) consisting of particles of size less than 2 mm had a considerably lower content of carbon (6.02 times) than the other fraction in the bottom ash (19.95%), consisting of particles of size between 2 and 5 mm.

The contribution of each fraction of the raw bottom ash to the total carbon content was calculated according to the equation [7]:

$$\frac{\text{mass\% of the fraction} \times \text{mass\% of unburned carbon content in the fraction}}{\text{mass\% of unburned carbon content in the raw bottom ash}}$$

Calculated in this way, the contributions of each fraction to the total carbon content (4.85%) were: 60.88% for the 2–5 mm fraction and 40.60% for the fraction <2 mm.

The results of the determination of the compressive strength of the four specimens: S'_1, fly ash–Portland cement–bottom ash (S_1)–water; S'_2, fly ash–Portland cement–bottom ash (S_2)–water; S'_3, fly ash–Portland cement–bottom ash (S_3)–water; and S'_4, fly ash–Portland cement–bottom ash (S_4)–water, are given in Table 4.

Based on the results presented in Table 4, it is evident that the samples S'_3 and S'_4, which were prepared with bottom ash containing lower contents of unburned carbon (the fraction of untreated bottom ash of small particles – less than 2 mm and the bottom ash treated by the “float–sink” method) had greater compressive strengths (1.52 and 1.5 MPa, respectively) than the other two samples. The compressive strengths of the specimens S'_3 and S'_4 were greater, respectively, by 38.82% and 38.08% than the compressive strength of the specimen S'_2, and by 36.97% and 36.19% than the compressive strength of the specimen S'_1.

Consequently, it follows that the compressive strength value (Table 4) of the specimens augments in the order $S'_2 \rightarrow S'_1 \rightarrow S'_4 \rightarrow S'_3$, *i.e.*, in the same order as the content of unburned carbon in the bottom ash present in them decreases (see Table 3).

By comparing the compressive strength values in Table 5 with those for base and sub-base mixtures, proposed by the valid Standard in Serbia (Table 5), it could be concluded that only the mixtures S'_3 and S'_4 satisfied the requirement of SRPS U. E9.024 for sub-base mixtures for road construction.

Table 4
Compressive strength of the mixtures fly ash–Portland cement–bottom ash–water.

Specimen	Compressive strength after 7 days (MPa)
S'_1	0.96
S'_2	0.93
S'_3	1.52
S'_4	1.50

Table 5
Compressive strengths according to SRPS U. E9.024.

Compressive strength after 7 days (MPa)	
Base mixtures	2–5.5
Sub-base mixtures	1.5–4.5

The DTA/TG curves of powdered specimens of the examined mixtures: S'_1, fly ash–Portland cement–bottom ash (S_1)–water; specimen S'_2, fly ash–Portland cement–bottom ash (S_2)–water; specimen S'_3, fly ash–Portland cement–bottom ash (S_3)–water and specimen S'_4, fly ash–Portland cement–bottom ash (S_4)–water, are presented in Fig. 2.

On the DTA curves of the samples (Fig. 2), the following peaks are present:

- the endothermic peaks at: 52 °C (Fig. 2a), 59 °C (Fig. 2b), 40 °C (Fig. 2c) and 53 °C (Fig. 2d), corresponding to calcium silicate hydrates (C–S–H) [13,14];
- the endothermic peaks at: 106 °C (Fig. 2a), 110 °C (Fig. 2b), 106 °C (Fig. 2c) and 107 °C (Fig. 2d), corresponding to ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) [14];
- small endothermic peaks at 173 °C (Fig. 2a), 178 °C (Fig. 2b), 171 °C (Fig. 2c) and 179 °C (Fig. 2d), which could be attributed to monosulfate aluminate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$) [15];
- the endothermic peak at: 445 °C (Fig. 2a) and the shoulders at: about 500 °C (Fig. 2b) and at 480 °C (Fig. 2c) are due to the dehydration of calcium hydroxide [13,15];
- the endothermic peaks at: 745 °C (Fig. 2a), 755 °C (Fig. 2b), 746 °C (Fig. 2c) and 743 °C (Fig. 2d), corresponding to carbonates [13];
- the exothermic peaks at: 423 and 462 °C (Fig. 2a), 456 °C (Fig. 2b), 436 °C (Fig. 2c) and 452 °C (Fig. 2d), which arise from the presence of unburned carbon in the bottom ash and
- the exothermic peaks at 925 °C (Fig. 2a), 940 °C (Fig. 2c) and 940 °C (Fig. 2d), which are characteristics for C–S–H [16].

The presence of C–S–H, ettringite, monosulfate aluminate and calcium hydroxide in the hardened mixtures confirmed that hydration reactions of Portland cement and fly ash (amorphous SiO_2 and Al_2O_3 from the fly ash) had occurred. The carbonates in the hardened samples are due to carbonation of the specimens during their standing in air.

The mass losses in the temperature intervals:

1. 0–350 °C, due to dehydration of the products of the hydration reactions of PC and FA (C–S–H, ettringite and monosulfate aluminate);
2. 350–550 °C, due to the combustion of the unburned carbon and dehydration of calcium hydroxide, and
3. 550–800 °C, due the decomposition of carbonates, which were read from the TG curves (Fig. 2), are presented in Table 6.

Based on the results presented in Table 6, it is evident that the mass losses in the temperature interval 0–350 °C were the highest

Table 6
The mass loss of the specimens (the mixtures FA–PC–BA–W).

Specimen	Temperature interval		
	0–350 °C	350–550 °C	550–800 °C
S'_1	2.44%	3.76%	2.44%
S'_2	3.91%	9.3%	4.30%
S'_3	4.99%	1.72%	2.14%
S'_4	2.8%	2.07%	2.31%

(4.99%) for specimen S_3' (in which the unburned carbon content from the bottom ash was the smallest) and then for specimen S_2' (3.91%) (in which the unburned carbon content from the bottom ash was the highest). Consequently, it could be concluded that the content of unburned carbon from the bottom ash does not effect the hydration reaction of PC and FA in the mixtures: FA–PC–BA–W.

The mass losses in the temperature interval 350–550 °C for the hardened mixtures (S_1', S_2', S_3' and S_4') were in accordance with the content of unburned carbon in the bottom ash samples (S_1, S_2, S_3 and S_4, Table 3), which were components of the mixtures.

The results of the mass losses in the temperature interval 550–800 °C showed that carbonation of specimen S_2' was the greatest, which may be because it contained the highest content of unburned carbon from the bottom ash (unburned carbon is porous and can easy absorb CO_2 from the air).

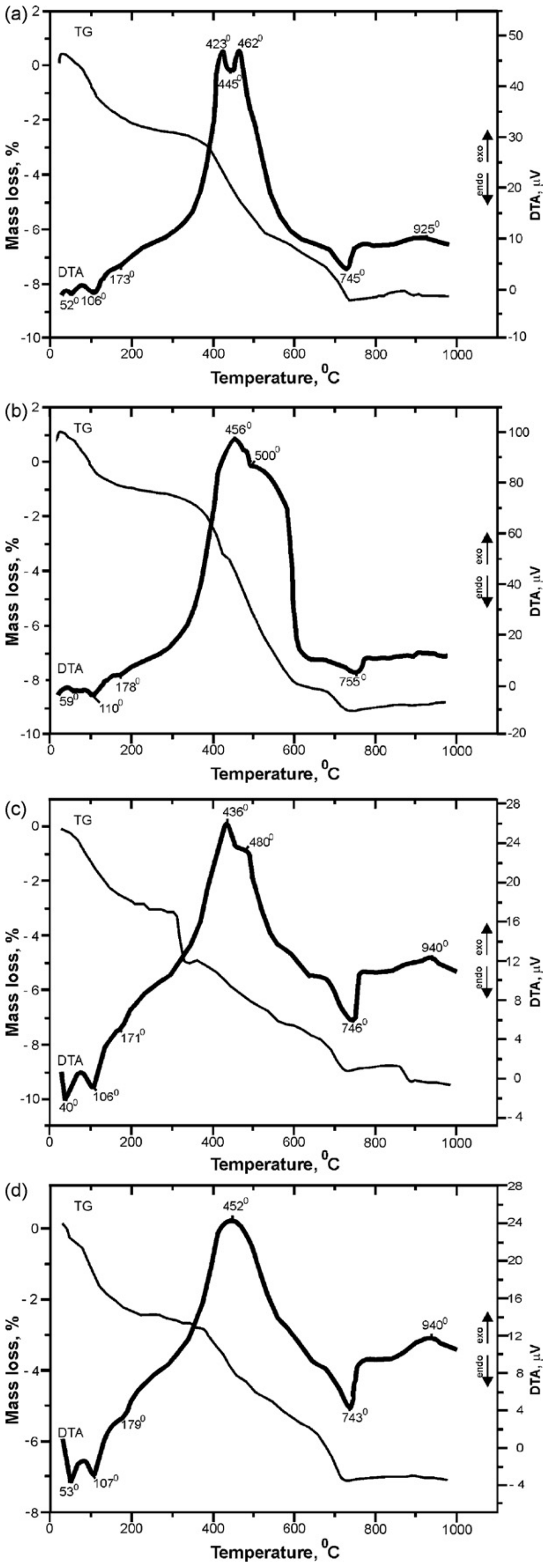

Fig. 2. DTA/TG curves of specimens of the mixtures: a, S_1'; b, S_4'; c, S_3'; and d, S_4'.

4. Conclusions

The results obtained in this study showed:

- The main fraction of the raw bottom ash (80.05%), consisting of particles of size less than 2 mm, had a lower content of unburned carbon than the other fraction, consisting of particles of size between 2 and 5 mm, and than the raw bottom ash, consisting of particles of size less than 5 mm: 6.02 times and 1.97 times, respectively.
- The compressive strength of the FA–PC–BA–W specimen prepared with the main fraction of bottom ash was greater than the compressive strength of the specimens prepared with the other fraction of bottom ash and with the raw bottom ash, by 1.63 times and 1.59 times, respectively.
- The bottom ash treated by the "float–sink" method had 1.43 times lower content of unburned carbon than the untreated bottom ash (raw bottom ash).
- The compressive strength of the specimen FA–PC–BA–W which was prepared with the treated bottom ash was 1.57 times greater than that of the specimen prepared with untreated bottom ash.
- The content of unburned carbon (coal) in the bottom ash affects the compressive strength of the FA–PC–BA–W mixtures for road construction, with the compressive strength increasing with decreasing content of carbon in the bottom ash.
- It is advantageous to perform some pre-treatment of the bottom ash to reduce its carbon content (sieving, treatment by the "float–sink" method, *etc.*).
- The content of unburned carbon of bottom ash as a component in the mixture: FA–PC–BA–W affects the applicability of the mentioned mixture for road construction. Only the specimens of FA–PC–BA–W containing bottom ash with a lower carbon content (size fraction <2 mm and "float–sink" treated) were employable for road construction, because they had compressive strength values (1.52 and 1.5 MPa, respectively) exceeding the lowest value (1.5 MPa) proposed for sub-base layer in road construction (SRPS U. E9.024).
- Based on the obtained DTA/TGA results, it is evident that unburned carbon in the bottom ash did not hinder the reaction of PC and FA with water in FA–PC–BA–W mixtures for road construction.

References

[1] E. Benavidez, C. Grasselly, N. Quaranta, Ceram. Int. 29 (2003) 61.
[2] M. Cheria, J. Cavalcante Rocha, J. Pera, Cem. Concr. Res. 29 (1999) 1387.
[3] N. Andian, J. Indian Inst. Sci. 84 (2004) 189.
[4] N. Kantiranis, A. Georgakopoulos, A. Filippidis, A. Drakoulis, Bull. Geol. Soc. Greece 36 (2004) 320.
[5] J. Paya, J. Monzo, M. Borrachero, E. Perris, F. Amahjour, Thermochim. Acta 346 (2000) 105.

[6] H. Foner, T. Robl, J. Hower, U. Graham, Fuel 78 (1999) 215.
[7] I. Kulaotos, R. Hurt, E. Suuberg, Fuel 83 (2004) 223.
[8] H. Kurama, M. Kaya, Constr. Build. Mater. 22 (2008) 1922.
[9] K. Umamaheswaran, V. Batra, Fuel 87 (2008) 628.
[10] R. Hill, S. Sarkar, R. Rathbone, J. Hower, Cem. Concr. Res. 27 (1997) 193.
[11] M. Maroto-Valer, D. Taulbee, J. Hower, Fuel 80 (2001) 795.
[12] T. Bojanac, S. Vlahović, S. Martinović, V. Vidojković, Interceramic 56 (2007) 436.
[13] J. Dweck, P. Buchler, A. Coelho, F. Cartledge, Thermochim. Acta 346 (2000) 105.
[14] L. Santoro, S. Vaccaro, A. Aldi, R. Cioffi, Thermochim. Acta 296 (1997) 67.
[15] W. Prince, M. Espagne, P.-C. Aitcin, Cem. Concr. Res. 33 (2003) 635.
[16] D. Klimesch, A. Ray, Thermochim. Acta 334 (1999) 115.