Journal of Thermal Analysis and Calorimetry, Vol. 96 (2009) 2, 363–368

FLY ASH AS THE POTENTIAL RAW MIXTURE COMPONENT FOR PORTLAND CEMENT CLINKER SYNTHESIS

M. Komljenović[1], *Lj. Petrašinović-Stojkanović*[1], *Z. Baščarević*[1], *N. Jovanović*[1] *and A. Rosić*[2*]

[1]Institute for Multidisciplinary Research, Kneza Višeslava 1, 11000 Belgrade, Serbia
[2]Faculty of Mining and Geology, University of Belgrade, Đušina 7, 11000 Belgrade, Serbia

This paper presents the results of investigation of properties of fly ash from four major thermal power plants in Serbia. Chemical, mineralogical and thermal characterization of fly ash has been performed in order to determine the possibility of its use as the raw material for the construction material industry, primarily the cement industry. Thermal properties of the raw mixtures for Portland cement clinker production based on fly ash were also investigated. The conclusion was reached that the use of fly ash as a component of the raw mixture components for the production of cement clinker not only enables substitution of natural raw materials, but could also have a positive influence on reduction of the sintering temperature of Portland cement clinker.

Keywords: *characterization, fly ash, thermal properties*

Introduction

Solid waste material and solid waste sites are present all over the world, thus creating a need for wastes to be used. One of such waste materials is fly ash (FA) from coal fired thermal power plants (PP). Fly ash is obtained by electrostatic or mechanical precipitation of dust-like particles from the flue gases of furnaces fired with coal or lignite at 1100 to 1400°C. Fly ash is a fine powder, mainly composed of spherical glassy particles. Depending upon the type of boiler and the type of coal, siliceous, silico-calcareous and calcareous fly ashes with pozzolanic and/or latent hydraulic properties are produced [1].

The major portion of the Serbian coal production involves lignite of the low calorific value and high moisture and ash content [2]. Main power plants of the Serbian power supply system are located in the regions of Kolubara (Obrenovac and Lazarevac) and Kostolac with fly ash production of some 5 Mt year^{-1} of fly ash produced there [2]. Fly ash waste dumps are located close to the thermal power plants covering about 1800 hectares of the arable land. In Serbia, fly ash is mostly used as a pozzolanic additive in the cement and concrete industry.

However, fly ash may be used for other purposes such as traditional ceramics [3], glass ceramics [4], as the material for land consolidation in road construction [5], land stabilization in mining areas [6], sorbents for flue gas desulphurization [7], filler material in making various products [8], and synthesis of zeolites [9, 10]. Many authors investigated fly ash to determine its suitability for application in the cement and concrete industry [11–14], as lightweight aggregate [15, 16], as a replacement for cement [17, 18] and in mortar and concrete [19–21].

Each of these applications requires complete characterization of the fly ash involved. The European standard EN 197-1 (2000) related to cement (part 1: composition, specification and harmonization criteria for ordinary cement), specifies possible utilization of fly ash in the cement industry, but only as a pozzolanic additive to cement, not as a raw mixture component for the production of Portland cement clinker.

This research work aims to determine whether fly ash may be utilized as the raw mixture component for Portland cement clinker production. Although application of fly ash as the cement raw material has been reported [1, 22], only few articles refer to it as the cement raw feed component [23, 24]. In terms of such application, various properties of fly ash as the potential raw mixture component are of great interest. This paper presents research results obtained by testing properties of fly ash samples taken from four major thermal power plants in Serbia. Chemical, mineralogical and thermal characterization of fly ash has been performed to determine possibilities of its application as the raw material in the construction material industry, primarily in production of Portland cement clinker, i.e. cement.

* Author for correspondence: zvezdana@ibiss.bg.ac.yu

1388–6150/$20.00

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

Experimental

The tests have been carried out on fly ash samples taken from four major thermal power plants in Serbia: PP 'Morava' – Svilajnac, PP 'Kolubara' – Veliki Crljani, PP 'Kostolac' – Kostolac and PP 'Nikola Tesla' – Obrenovac. The tests include the total of six different samples of fly ash:

I PP 'Morava' – Svilajnac
II PP 'Kolubara' – Veliki Crljani
III PP 'Kostolac' B1 – Kostolac
IV PP 'Kostolac' B2 – Kostolac
V PP 'Nikola Tesla', TENT A – Obrenovac
VI PP 'Nikola Tesla', TENT B – Obrenovac

The chemical composition was determined using classical chemical analysis – alkali melting, according to the Serbian standards SRPS B.H8.359-369 (1973).

The phase mineral composition of fly ash samples was investigated on a Phillips PW 1710 powder diffractometer under the following conditions: anticathode copper radiation with the wavelength of CuK_{α}=1.54178 Å and a graphite monochromator. The tube working voltage was 40 kV and current strength was 30 mA. All samples were investigated in the same experimental conditions in the range 5–50° 2θ with a step of 0.02° and retention time of 0.5 s for each step.

Investigation of phase transformations during heating of fly ash samples, differential-thermal analysis (DTA) was carried out on a Q-600 SDT, TA Instruments device in the temperature interval from 20 to 1200°C. The samples were heated in air flow during heating of 100 mL min^{-1}. The heating rate was 20°C min^{-1}.

Changes of dimensions of fly ash samples during heating were investigated using E. Leitz Wetzlar, Germany, heating microscope with a platinum–rhodium/platinum thermocouple (T_{max}=1600°C). Investigations were performed in the temperature range of 20–1400°C, i.e. until the melting point.

In order to investigate the influence of fly ash on thermal properties of raw mixtures for Portland cement clinker production, six different raw mixtures based on fly ash were prepared, denoted as RM I, RM II, RM III, RM IV, RM V and RM VI (Table 1). A raw mixture from the industrial production of the 'Holcim-Serbia a.d.' cement factory was used as the reference material (denoted as RM 0). The reference mixture contained marl, limestone and quartz sand. In the fly ash raw mixtures, marl was completely replaced with fly ash. The thermal properties of the raw mixtures (DTA, heating microscope) were investigated in the same way as fly ash thermal properties.

Results and discussion

Chemical characterization

The chemical composition of fly ash samples is given in Table 2.

Basic oxides in chemical composition of all investigated fly ash samples are SiO_2, Al_2O_3, Fe_2O_3 and CaO, followed by a smaller amount of MgO and SO_3. According to ASTM C618-05 standard, based on the sum of SiO_2, Al_2O_3 and Fe_2O_3, they can be classified as the class F. The sum of SiO_2, Al_2O_3 and Fe_2O_3 in these fly ash samples is between 80.12% (FA 'TENT A') and 85.66% (FA 'TENT B').

Oxides of Si, Al, Fe and Ca are important chemical constituents of the raw mixture for Portland cement clinker production. In the process of the raw mixture sintering from these oxides clinker minerals are formed: calcium silicates, calcium aluminates and calcium alumoferrites. Ca oxide in the mixture is usually introduced through calcareous compound, such as limestone, while the oxides of Si, Al and Fe are introduced through clayey compound, most commonly – marl. By its chemical composition, fly ash is very similar to clayey compound, so it could be successfully utilized as the raw mixture component in Portland cement manufacturing. The significant amount of SiO_2 in fly ash samples can lead to decreased use of other SiO_2 carriers (for example, quartz sand).

Table 1 Raw mixtures composition and denotation

Raw material	Raw mixture denotation and composition					
	RM I	RM II	RM III	RM IV	RM V	RM VI
Limestone	79.78	79.64	79.87	79.86	79.48	80.28
Quartz sand	4.74	0.75	7.68	8.10	6.53	5.66
FA 'Morava'	15.48					
FA 'Kolubara'		19.61				
FA 'Kostolac B1'			12.45			
FA 'Kostolac B2'				12.04		
FA 'TENT A'					13.99	
FA 'TENT B'						14.06

Table 2 Chemical composition of fly ash samples

Investigated composition	Fly ash sample					
	'Morava'	'Kolubara'	'Kostolac B1'	'Kostolac B2'	'TENT A'	'TENT B'
SiO_2	55.23	62.13	46.85	45.56	48.71	54.26
Al_2O_3	21.43	17.20	23.20	22.90	24.60	24.90
Fe_2O_3	7.42	5.95	12.14	13.66	6.81	6.50
CaO	7.94	5.67	8.26	8.93	8.92	6.34
MgO	2.61	2.00	2.77	2.68	2.83	1.89
SO_3	0.81	0.67	1.48	1.79	1.00	2.51
LOI at 1000°C	1.66	2.88	4.44	3.34	4.38	2.06
Total	97.10	96.50	99.10	98.87	97.21	98.49

The chemical composition of the investigated samples indicates the presence of all important oxides usually present in the basic raw mixture components, i.e. mixtures for production of Portland cement clinker, significant for the formation of basic clinker minerals (calcium silicate and calcium aluminate) during the sintering process.

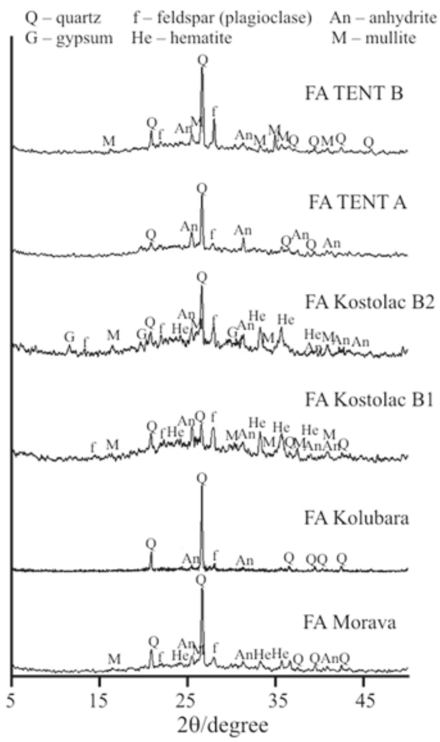

Fig. 1 XRD patterns of fly ash samples

Mineralogical characterization

The diffraction patterns of six investigated fly ash samples are presented together (Fig. 1). In this way it is possible to observe crystalline phases present as well as the differences between the amorphous phases amounts in these samples. The present crystalline phases were identified according to JCPDS standards.

Due to the significant presence of amorphous matter in the investigated samples of fly ash, the quantitative content of individual mineral phases cannot be identified with satisfactory precision. In general, all fly ash samples contain significant amount of amorphous matter and of crystalline phases, quartz and feldspar and in most cases hematite, anhydrite and mullite. From a thermodynamic viewpoint, the amorphous phase is more reactive compared to the present crystalline phases. This justifies the utilization of fly ash as a substitute for natural raw mixture components used for the synthesis of Portland cement clinker.

Thermal analyses (DTA) of fly ash

The results of differential thermal analysis (DTA) are given in Fig. 2.

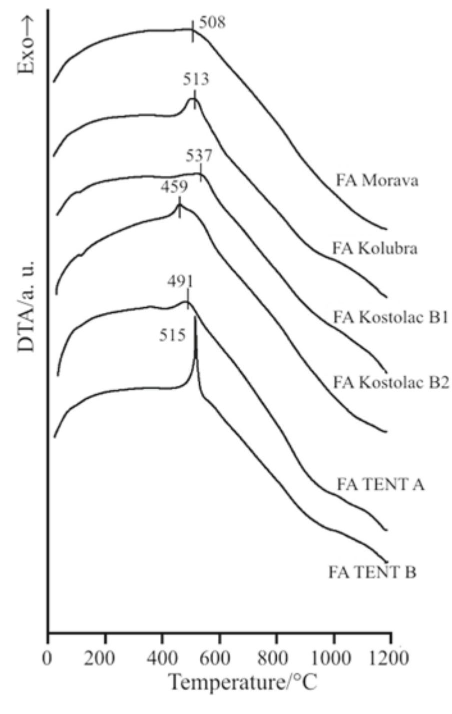

Fig. 2 DTA of fly ash samples

DTA indicates that exothermal peak occurred for all investigated fly ash samples at about 500°C, indicating the presence of unburned carbon. This exothermal peak at about 500°C is the most evident in the case of the FA 'TENT B'.

The presence of unburned carbon in fly ash represents an additional favorable occurrence, as the use of fly ash in the raw mixture would require smaller amounts of fuel thus leading to certain reduction of the energy needed for the sintering process [23].

DTA curves of the investigated samples of fly ash in the interval up to 1200°C did not show any other exothermal peaks that could eventually correspond to the formation of new mineral phases during heating and sintering.

Heating microscope analysis of fly ash

The results of heating microscope measurements of samples of fly ash are given in Table 3. Based on the data presented, intensive shrinkage of the investigated fly ash samples started in the temperature interval between 1080°C (FA 'TENT B') and 1160°C (FA 'Kolubara'). At the same time, the softening point of all investigated samples was in a very small range between 1200 and 1210°C. The melting point was also in a very small range from 1260 to 1280°C, except in the case of fly ash from the 'TENT B' which was 1340°C.

In spite of somewhat different chemical and mineralogical characteristics of the investigated fly ash samples, their thermal characteristics are very similar. The reason for this is not entirely clear and further research is required. This similarity of the fly ash thermal properties is very important in evaluation of possible application of fly ash as the raw mixture component in production of Portland cement clinker. Namely, the standard mixture in production of Portland cement clinker is sintered at the temperature of 1450–1500°C in the presence of a liquid phase, when a part of the raw mixture has melted. Liquid phase sintering certainly enhances the reaction and achieves more homogenous mineral composition of the product as well as more uniform characteristics. As the investigated fly ash samples start melting at lower temperatures, its use as a component in the raw mixture might positively influence earlier occurrence of a liquid phase and reduction of the sintering temperature [24]. Therefore, for the investigated fly ash samples, the liquid phase sintering interval starts from the softening point, i.e. with the first occurrence of a liquid phase. A more intensive reaction, i.e. higher sintering rates, can be expected between the softening point (1200–1210°C) and the melting point (1260–1340°C), i.e. in the temperature interval where more intensive liquid phase formation occurs.

The results of thermal characterization of fly ash samples demonstrate that all the investigated fly ash samples may not only substitute standard, natural components in the raw mixture, but also their application would lead to reduction of the sintering temperature of Portland cement clinker, i.e. saving energy.

DTA of the raw mixtures based on fly ash

The principal reactions taking place in the manufacture of Portland cement clinker are divided into three groups [25]:

- Reactions below about 1300°C, of which the most important are (a) the decomposition of calcite, (b) decomposition of clay minerals, and (c) reaction of calcite or lime formed from it with quartz and clay minerals to give belite (dicalcium silicate – $2CaO{\cdot}SiO_2$), calcium aluminate and calcium alumoferrite. Liquid is formed only to a minor extent at this stage, but may have an important effect in promoting the reactions.
- Reactions at 1300–1450°C (clinkering). A melt is formed, mainly from the aluminate and ferrite, and by 1450°C some 20–30% of the mix is liquid. Much of the belite and nearly all the lime react in the presence of the melt to give alite (tricalcium silicate – $3CaO{\cdot}SiO_2$).
- Reactions during cooling. The liquid crystallizes, giving mainly aluminate and ferrite. Polymorphic transitions of the alite and belite occur.

Table 3 Thermal characteristics of fly ash samples

Fly ash sample	Temperature/°C				
	significant expansion	initial shrinkage	intensive shrinkage	softening point	melting point
'Morava'	600–900	1080–1140	1140–1200	1200	1260
'Kolubara'	900–1100	1100–1160	1160–1210	1210	1280
'Kostolac B1'	500–1000	1000–1120	1120–1210	1210	1270
'Kostolac B2'	300–960	960–1150	1150–1210	1210	1280
'TENT A'	400–800	1000–1140	1140–1210	1210	1280
'TENT B'	200–600	1000–1080	1080–1200	1200	1340

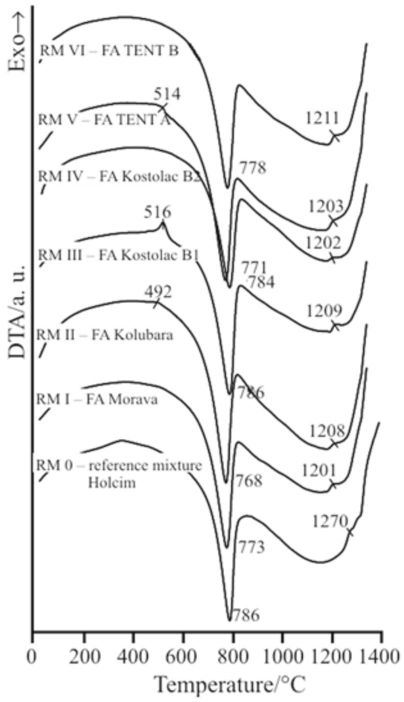

Fig. 3 DTA of the reference raw mixture from 'Holcim-Serbia a.d.' cement factory and raw mixtures based on fly ash

In this study, only reactions in the first group were observed, i.e. in the temperature range 20–1300°C. The results of DTA analysis of the reference raw mixture from 'Holcim-Serbia a.d.' cement factory and the raw mixtures based on fly ash are given in Fig. 3.

From the data given in Fig. 3 two exothermic and one endothermic peak can be noticed. The first exothermic peak, noticed at about 500°C indicates that combustion of unburned carbon occurred. This peak is of low intensity and cannot be noticed in all cases. Endothermic peak is very intensive and placed in the temperature range from 770 to 790°C. That peak is the consequence of the decomposition (thermal dissociation) of calcium carbonate (calcite) from limestone. The second exothermic peak is also of low intensity, but can be found in all cases. In the cases of the raw mixtures based on fly ash it can be noticed at temperatures from 1201 to 1211°C, but in the case of the reference raw mixture from the cement factory 'Holcim-Serbia a.d.', the position of this peak is at the temperature of 1270°C. This peak is corresponding to the formation of belite (dicalcium silicate – $2CaO{\cdot}SiO_2$), which is one of the main Portland cement clinker minerals. From these data it can be clearly seen that presence of fly ash has influence on decreasing of the sintering temperature because one of the clinker minerals appears at the lower temperature.

Heating microscope analysis of the raw mixtures based on fly ash

The results of heating microscope measurements of the reference raw mixture from 'Holcim-Serbia a.d.' cement factory and the raw mixtures based on fly ash are given in Table 4.

Intensive shrinkage of the raw mixtures based on fly ash begins in the temperature interval from 1100°C (in the cases of the raw mixture with FA Kostolac B1 – RM III and FA Nikola Tesla B – RM VI) to 1150°C (other raw mixtures). Intensive shrinkage of the reference raw mixture from cement factory 'Holcim-Serbia a.d.' starts at approximately 1200°C. Besides, the softening points for all investigated raw mixtures based on fly ash are in very small interval from 1280°C (raw mixture with FA Kolubara – RM II) to 1360°C (raw mixture with FA Morava – RM I), whereas the softening point of the reference raw mixture from cement factory

Table 4 Thermal characteristics of the reference raw mixture from 'Holcim-Serbia a.d.' cement factory and the raw mixtures based on fly ash

Raw mixture denotation	Temperature/°C			
	significant expansion	initial shrinkage	intensive shrinkage	softening point
RM 0 Reference raw mixture from 'Holcim'	400–1050	1050–1200	1200–1480	1480
RM I FA Morava	500–1000	1000–1150	1150–1360	1360
RM II FA Kolubara	100–500	600–1000	1150–1280	1280
RM III FA Kostolac B1	400–800	800–1050	1100–1300	1300
RM IV FA Kostolac B2	400–700	700–1100	1150–1340	1340
RM V FA TENT A	300–900	900–1150	1150–1320	1320
RM VI FA TENT B	500–800	800–1100	1100–1300	1300

'Holcim-Serbia a.d.' is only at 1480°C. Melting points for all investigated raw mixtures based on fly ash are above the investigated range of 20–1400°C.

These results are very important, because they prove that fly ash, as a component of raw mixture for Portland cement clinker synthesis, has a positive influence on decreasing of the softening temperature of the raw mixture, that is on the earlier appearance of liquid phase. As it was said before, by sintering in the presence of liquid phase, the rate of reaction is increasing and more homogeneous mineral composition and other characteristics of the clinker can be achieved.

Conclusions

The paper presents results obtained by testing properties of fly ash samples taken from four major thermal power plants in Serbia. The chemical, mineralogical and thermal characterization of fly ash was performed to determine its possible application as the raw material in the construction material industry, primarily Portland cement clinker.

It can be concluded that the properties of fly ash samples from several thermal power plants in Serbia justify possible application of fly ash as the raw mixture component in Portland cement clinker synthesis. Its use may not only lead to natural resources saving, but to significant energy savings as well. The exploitation of fly ash as the secondary raw material can also significantly contribute to sustainable development in the construction material industry and improvement of the ecological situation not only in Serbia, but in other countries as well.

Acknowledgements

The research presented in this paper is a part of the research results achieved in the project TR 19001, which was financed by the Ministry of Science and Technological Development, Republic of Serbia within the technological development program.

References

1 ECOBA – European Coal Combustion Products Association, www.ecoba.com.
2 Public Enterprise 'Electric power industry of Serbia', www.eps.co.yu.
3 A. Olgun, Y. Erdogan, Y. Ayhan and B. Zeybek, Ceram. Int.l, 31 (2005) 153.
4 L. Barbieri, I. Lancellotti, T. Manfredini, C. G. Pellacani, J. Ma Rincon and M. Romero, J. Am. Ceram. Soc., 84 (2001) 1851.
5 S. Kumar and C. B. Patil, Resources, Conserv. Recycling, 48 (2006) 125.
6 S. T. Jarvis and T. G. Brooks, Waste Manag., 16 (1996) 135.
7 A. Garea, J. R. Viguri and A. Irabien, Chem. Eng. Sci., 52 (1997) 715.
8 R. A. Kruger, Fuel, 76 (1997) 777.
9 I. Majchrzak-Kuceba and W. Nowak, J. Therm. Anal. Cal., 77 (2004) 125.
10 N. Moreno, X. Querol, J. M. Andrés, K. Stanton, M. Towler, H. Nugteren, M. Janssen-Jurkovicová and R. Jones, Fuel, 84 (2005) 1351.
11 B. Pacewska, G. Blonkowski and I. Wilinska, J. Therm. Anal. Cal., 86 (2006) 179.
12 H. A. Foner, T. L. Robl, J. C. Hower and U. M. Graham, Fuel, 78 (1999) 215.
13 S. H. Lee, E. Sakai, M. Daimon and W. K. Bang, Cem. Concr. Res., 29 (1999) 1791.
14 N. K. Koukouzas, R. Zeng, V. Perdikatsis, W. Xu and E. K. Kakaras, Fuel, 85 (2006) 2301.
15 M. Aineto, A. Acosta, J. Ma. Rincon and M. Romero, Production of Lightweight Aggregates from Coal Gasification Fly Ash and Slag, 2005 International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, http://www.flyash.info.
16 K. Ramamurthy and K. I. Harikrishnan, Cem. Concr. Compos., 28 (2006) 33.
17 F. Canpolat, K. Yilmaz, M. M. Kose, M. Sumer and M. A. Yurdusev, Cem. Concr. Res., 34 (2004) 731.
18 B. Li, W. Liang and Z. He, Cem. Concr. Res., 32 (2002) 1341.
19 J. Tangpagasit, R. Cheerarot, C. Jaturapitakkul and K. Kiattikomol, Cement Concrete Res., 35 (2005) 1145.
20 F. Blanco, M. P. Garcia, J. Ayala, G. Mayoral and M. A. Garcia, Fuel, 85 (2006) 2018.
21 K. Hwang, T. Noguchi and F. Tomosawa, Cem. Concr. Res., 34 (2004) 2269.
22 O. E. Manz, Fuel, 76 (1997) 691.
23 J. I. Bhatty, J. Gajda and F. M. Miller, Commercial Demonstration of High-Carbon Fly Ash Technology in Cement Manufacturing, 2003 International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, http://www.flyash.info.
24 M. K. Mukherjee, S. B. Hegde and R. A. Somani, Zement Kalk Gips, 55 (2002) 76.
25 H. F. W. Taylor, Cement Chemistry, Academic Press Ltd., London 1992, pp. 60–94.

Received: January 2, 2008
Accepted: October 6, 2008
Online First: February 4, 2009

DOI: 10.1007/s10973-008-8951-0