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THERMAL BEHAVIOUR OF RAW FLY ASHES

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Abstract

Thermal behaviour of raw fly ashes-wasted products from various Polish power plants has been investigated using X-ray diffractions (XRD), Fourier transform infrared spectroscopic (FT-IR), differential thermal analysis (DTA) and thermogravimetry (TG). On the basis of the DTA and TG analysis differentiation between examined ashes has been made, which could not be achieved by XRD and FT-IR methods.

Keywords: DTA, fly ashes, FT-IR, TG, XRD

Introduction

Fly ashes are the main combustion by-products of coal-fired power plants. Every year the energy utilities in Poland dispose several million tons of fly ashes in landfills, causing a major environmental problems. From a chemical point of view, fly ashes are oxide-based materials of different composition depending on the type of coal subjected to combustion. Chemical analysis can provide hardly any information on the mineral composition of ashes. X-ray analysis could not provide accurate results because of the overlapping of the interference lines, especially if a minor component is to be detected. Hence, differential thermal analysis and thermogravimetry may be applied for identification and determination of fly ashes constituents and their transformations. The present work illustrates thermal behaviour of fly ashes being by-products of coal combustion in various Polish power plants.

Experimental

Fly ashes studied by thermal analysis and their chemical analysis for the major elements and textural characteristics are given in Tables 1 and 2. Examined fly ashes were delivered from the following power plants: ZS-23 – Siekierki, ZS-24 – Kozienice, ZS-25 – Jaworzno, ZS-26 – Bełchatów and ZS-27 – Skawina. Chemical analysis of samples was made using X-ray fluorescence apparatus. X-ray patterns of powdered samples were taken on a TUR M-62 diffractometer using CuK_{α} radiation and Ni filter (λ=1.5418 Å). KBr pellet technique was applied for monitoring changes in the FTIR spectra which were recorded in the range 4000–400 cm^{-1} on a spectrometer. Thermal behaviour of fly ashes samples was studied on an OD-102 derivato-

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graph. The 400 mg of samples were heated in a ceramic crucible in air atmosphere under the following conditions: temperature 20–1000°C, heating rate 10°C min^{-1}.

Results and discussion

The fly ashes came from power plants using bituminous coal, except for the sample denoted as ZS-26, obtained as a result of combustion of brown coal. The molar ratio values R=SiO_2+Al_2O_3/CaO+MgO+Fe_2O_3 (Table 1) suggest that the ashes can be classified as silica type. X-ray diffraction studies revealed for all samples the crystallographic reflection corresponding to the interplanar distance of d=3.35 Å (Fig. 1). The reflection is the most intense in the patterns of all samples, and is assigned to quartz (hexagonal structure) [1]. The other crystallographic reflections for the samples obtained by-products of bituminous coal combustion (ZS-23 to 25 and ZS-27) are broad and of low intensity. They correspond to the following interplanar distances: 1.8, 2.2, 2.5, 2.7, 4.3 and 5.4 Å, in the pattern of ZS-26 sample (brown coal combustion) these distances are different d=1.8, 2.4, 2.7, 4.2 Å. These results indicate that the phase composition of the ashes studied is similar. It is reasonable to suppose that the ashes contain trydymite, characterised by the reflection at d=4.3 Å [1] and mullit $Al_2O_3 \cdot 2SiO_2$ – characterised by the reflection at d=4.2 Å. Formation of mullite from Al_2O_3 and SiO_2 in the coal combustion conditions is highly probable. Taking the presence of small amounts of other admixtures (Ti, Fe, Mg, Ca) into account, it can be assumed that at higher temperatures admixtures of different chemical composition and different chemical and phase composition will be formed.

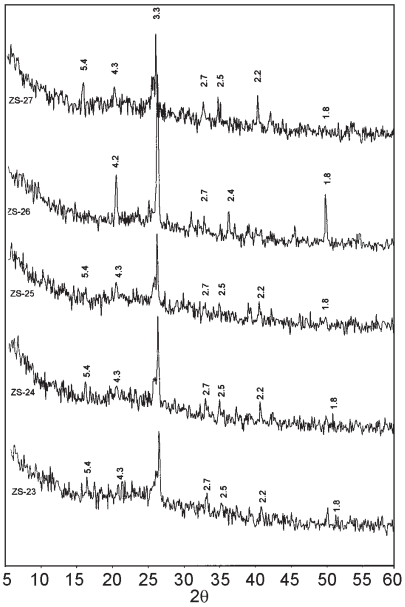

Fig. 1 X-ray diffraction pattern of fly ashes

Table 1 Chemical analysis of fly ashes

	Concentration of component in fly ashes/mass%								
Fly ash	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	R
ZS-23	50.73	26.77	1.10	5.63	2.66	3.50	1.14	2.81	5.13
ZS-24	51.66	25.81	1.08	6.65	2.93	3.63	1.03	2.94	4.14
ZS-25	49.99	25.77	1.10	6.55	2.59	3.27	0.91	2.73	4.17
ZS-26	63.62	17.12	0.84	3.47	0.93	9.78	0.08	0.20	4.88
ZS-27	48.67	29.65	1.22	6.71	2.92	4.04	2.10	2.66	4.19

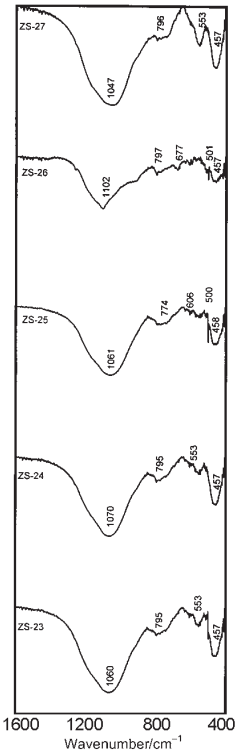

Fig. 2 FT-IR spectra of fly ashes

Table 2 Surface area, mean pore radius and pore volume of fly ashes

Fly ash	BET surface area/m^2 g^{-1}	Mean pore radius/Å	Pore volume·10^3/cm^3 g^{-1}
ZS-23	4.4	17	3.8
ZS-24	2.2	20	2.5
ZS-25	4.7	20	5.1
ZS-26	17.0	18	13.8
ZS-27	2.1	20	2.8

IR spectra of the ashes studied in the range 1750–400 cm^{-1} are shown in Fig. 2. These spectra reveal intense and broad band at about 1050–1070 cm^{-1} for samples ZS-23 to 25 and ZS-27, whereas for sample ZS-26 the most intense band was found at 1102 cm^{-1}. These bands are usually assigned to asymmetric stretching vibrations of Si(Al)–O. Another band at 797–774 cm^{-1} characterises symmetric stretching vibrations of Si(Al)–O. The band at 550 cm^{-1} is attributed to asymmetric valency vibrations of Si(Al)–O. These three spectral regions are particularly sensitive to structural changes in silica–alumina tetrahedra [2, 3], whereas other infrared bands (457–469 and 677 cm^{-1}) characterise internal vibrations in structural units. On the basis of the

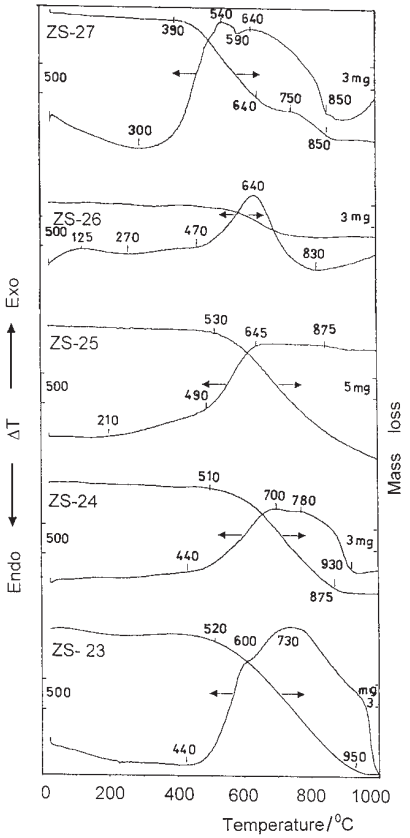

Fig. 3 DTA, TG curves of fly ashes

data we can conclude that the ashes studied are relatively highly organised structures containing $[Si(Al)O_4]$ tetrahedra. This is confirmed in particular by the occurrence of the band at 1100 cm^{-1} [4]. The presence of the band at about 795 cm^{-1}, after Fripiat *et al*. [5] testifies to a ring-arrangement of the tetrahedra. The ordering of these tetrahedra decreases with decreasing wave number e.g. to 774 cm^{-1}, which is observed for the sample ZS-25.

Heating of the fly ashes up to 1000°C induces different thermal effects (Fig. 3). In the sample ZS-23 at 440°C a wide exothermic effect is observed, which is composed of three components: the first effect characterised by the inflection point at 600, the other with a maximum at 730 and the third with the inflection point at 950°C. These effects are associated with mass loss of 3.6 mass% in the temperature range 500–950°C. Similar changes have been observed for the sample ZS-24. The exothermic effect starts also at 440°C and is composed of two effects characterised by the maxima at 700 and 780°C. The effect ends at 930°C and is accompanied by mass loss of 2.9 mass%. In the temperature range 500–900°C. For the sample ZS-25 the DTA curve has a different character. The exothermic effect starts at 210 and the heating of

the sample up to about 500 does not result in mass loss, however, further heating up to 1000°C causes mass loss of 6.4 mass% and a tendency of a greater mass loss is observed with further heating. The exothermic effect is very wide and is visible all the time on heating. The thermal conversions of fly ashes (ZS-26) formed as by-product of brown coal combustion are illustrated in Fig. 3. DTA curve reveals a low-temperature broad and small exothermic effect with a maximum at 125 and in the range 470–830 an exothermic effect with a maximum at 640°C, which is accompanied by small mass loss of 0.9 mass%. For the sample ZS-27 DTA reveals two clearly visible exothermic effects on heating. The first begins at 300, then an inflection point appears at 525 and a maximum at 540, the second effect begins at 590 and has a maximum at 640°C. The mass loss curve shows that the latter effect is composed of three components: the first in the range 590–640, the second in 640–750 and the third in 750–850°C. The mass loss in the range 400–1000°C is 3.3 mass%.

The structural and thermal properties of fly ashes obtained from coal combusted in Hungary have been described by Mészáros Szécsényi and co-workers [6]. The results of XRD, DTA and TG studies their report are significantly different from those reported in our work and the differences are chiefly a consequence of different kinds of coal combusted in our countries. The fly ashes they studied contained large amounts of Ca and C, while those studied in our work contained more silica. That is why a direct comparison of the results of [6] with our data is impossible.

Conclusions

The above-discussed results imply that the fly ashes studied do not show endothermic effects related to the loss of adsorbed water or water coming from dehydroxylation. This implication is confirmed by FT-IR spectra, which do not show clearly visible bands in the range 4000–3500 cm^{-1} (not presented in this work) and at 1640 cm^{-1}, assigned to water from hydroxyl groups. The ashes show exothermic effects and the related mass loss.

The differences in the courses of DTA and TG curves allow a reliable differentiation between the ashes coming from different power plants and being by-products of coal combustion in different conditions, which could not be achieved by the methods XRD and FT-IR.

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