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FLY ASH FROM TERMAL POWER PLANTS BURNING DOMESTIC LIGNITE COALS AS A SILICATE MATERIAL FOR ZEOLITE SYNTHESIS

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ABSTRACT

Fly ash (FA) from the electrostatic precipitators of Thermal Power Plant (TPP) "Maritza-East 2" has been subjected to morphological, compositional and crystallographic studies by sieve fractionation, quantitative chemical and X-ray diffraction analyses. FA is composed of particles with grain sizes up to 250 mm and containes ~ 43 % of amorphous components (a:SiO_2 and black C) and ~ 57 % of crystalline phases (α-SiO_2, mullite, brushite, α-Fe_2O_3). The investigation of the FA chemistry reveals that it contains 52.66 mass % SiO_2, 23.37 mass % Al_2O_3, 8.72 mass % Fe_2O_3, and smaller amounts of alkaline and alkaline-earth oxides. This chemical composition is appropriate for the synthesis of alumosilicates which can be converted easily into zeolites in alkali solutions.

Keywords: Fly ash, synthetic zeolites, silicate materials

INTRODUCTION

Enormous amounts of fly ash (FA) are produced from the combustion of coals in thermal power plants (TPP) and factories. FA is collected by electrostatic or mechanical precipitation from the flue gases at the end of the incineration installations, and its proportion reaches ~ 85 % of the total generated ash residues. It is a fine powder composed of spherical micro-particles, which mainly contains amorphous material (a:SiO_2) and a number of crystalline phases: α-quartz (α-SiO_2), mullite ($2SiO_2.3Al_2O_3$), hematite (α-Fe_2O_3), magnetite (γ-Fe_3O_4), etc. [1, 2]. According to the International Crystallographic Standard of the *American Society for Testing and Materials* ASTM C618, FA is specified in two types (F and C) depending on the amounts of CaO, Al_2O_3, SiO_2 and Fe, which determine its practical applicability. FA from different incineration systems has been thoroughly characterized with respect of its application relevant characteristics, such as compactness, electrical, thermal, mechanical properties [3 - 5], etc.

Commonly, FA is reused as a raw material for cement and concrete production, or disposed as a solid waste in landfills or surface impoundments. Attempts to recycle FA as a soil amendment agent are limited because of the small amounts of beneficial nutrients, undesirable pH value, salinity, and toxic trace elements, and its adequate disposal creates a severe problem [6, 7]. Therefore, the development of novel possibilities for FA recycling is of great importance [8].

Recently, synthetic and natural zeolites have been synthesized [9, 10] and successfully applied as adsorptive materials for effective removal of flue gases contaminants (SO_x, HCl, HI, HBr, HF, metal vapors (Hg, Cd, Pb) and dioxins) [11, 12].

The aims of the present paper are the compositional and crystallographic studies of FA collected in the electrostatic precipitators of the TPP "Maritza-East 2", burning lignite coals, with respect to its further utilization as a raw material for the preparation of low-cost nanoporous synthetic zeolites. Our previous studies confirm that this FA is characterized by comparatively low alkaline and sulfur dioxide storage capacities [13].

A promising new approach for the preparation of low-cost sorbents is the conversion of the byproducts from coal burning TPP into highly-adsorptive materials, which can replace successfully the natural zeolites [14,15]. The most used methodology for the preparation of zeolites from FA is a hydrothermal process based on the dissolution of Al-Si-bearing FA phases with alkaline (mainly NaOH and KOH) solutions and the subsequent precipitation of the zeolitic material. FA alkaline conversion employs combinations of different alkaline solution/FA ratios with variable molarity of the alkaline solution, temperature, reaction time and pressure for the preparation of different types of zeolites (up to 15 different zeolites from the same FA composition can be obtained) [16]. The zeolite content of the resulting material varies widely (20 - 50 %), depending on the reaction conditions.

EXPERIMENTAL

FA was collected in the electrostatic precipitator of steam-generator No. 9 at TPP "Maritza-East 2", burning local lignite coals, and was subjected to the present study. The investigated FA was an average sample from all electrical fields of the precipitator device. The chemical composition of FA was determined combining the possibilities of the clasical silicate analysis and the instrumental techniques of atomic absorption spectroscopy (AAS) [17 - 19]. Before the analyses, FA samples were subjected to preliminary thermal treatment in order to eliminate the humidity and some organic constituents which could drawback the chemical procedures. AAS analysis was performed by the Perkin-Elmer 5000 aparatus in the flame of acetylene and air mixture. The investigated samples were subjected to alkaline melting and, thereafter, they were converted in liquid state by acidic dilution. The silicon dioxide was determined by mass measurement, as it was separated as a solid residual after evaporation of the solution at 1000°C. The concentration of the basic and the accompanying components in the filtrate was measured by complexonometric volume analyses and AAS, respectively. Potassium and natrium were determined in a separate sample treated according to the AAS technique. The total content of the sulfur was measured applying the Eshca's procedure.

The granulometric composition of FA was determined by sieve fractionation.

FA density was measured by the hydrostatic method in toluene as an immersed liquid.

FA crystallography was studied by X-ray diffraction using Diffractometer Brucker D2 Phaser with CuKα radiation and Ni filter ($\lambda_{CuK_\alpha} = 1.54$ Å).

RESULTS AND DISCUSSION

The grain size distribution of the FA particles, determined by sieve separation, was found to be between 125 and 250 μm. The measured density of the FA is ~ 3.07 g/cm^3. The mass loss after heating of the investigated FA at 800°C for 15 min is of the order of 3.53 %. The obtained results from the chemical composition analyses are given in Table 1.

The X-ray diffractogram of the FA collected in the electrostatic dust collectors at TPP "Maritza East

Table 1. Chemical composition of the FA collected at TPP "Maritza-East 2".

Component	Composition, mass %
SiO_2	52.66
Al_2O_3	23.37
Fe_2O_3	8.72
CaO	5.75
MgO	2.75
SO_3	2.40
MnO	0.06
ZnO	0.04
Na_2O	0.01
K_2O	0.01

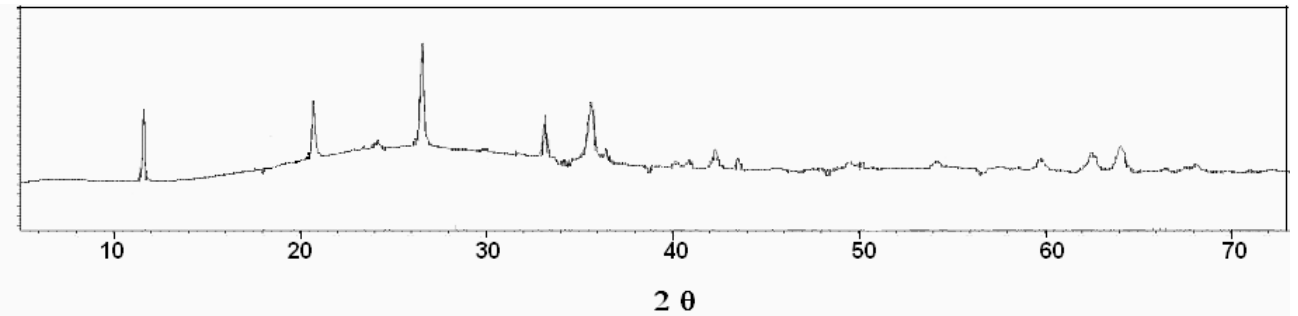

Fig. 1. X-ray diffractogram of the FA produced by TPP "Maritza-East 2".

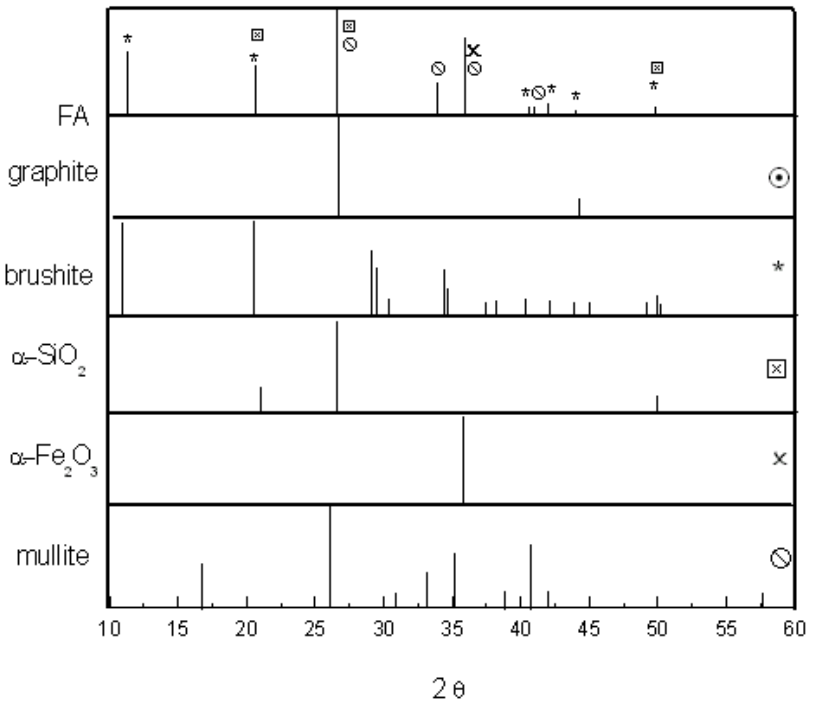

Fig. 2. Line-diagram for identification of the diffraction reflexes observed in the fly ash (FA) X-ray diffractogram. The characteristic lines of the phases are indicated as: graphite (⦿); brushite (*); α-SiO_2 (⊠); α-Fe_2O_3 (x); mullite (⦸).

2", burning domestic lignite coals, is plotted in Fig. 1. It reveals an amorphous-crystalline nature of the investigated FA. A well-expressed amorphous plateau, typical for amorphous state and intensive diffraction reflections of crystalline phases can be observed. It was established that the crystalline portion is dominant, as it was calculated that the crystalline / amorphous ratio is 56.61 versus 43.39.

The line-diagram of the X-ray diffraction patterns of FA, as well as of the expected constituents is plotted in Fig. 2. It was composed taking into account the characteristic reflexes with higher than 15 % of arbitrary intensity.

Taking into account the literature diffraction data, the characteristic peaks of the following crystalline phases could be identified:

- Hematite (α-Fe_2O_3), with main diffraction peak at 2θ=35.640° (d=2.517Å) is rhombohedral from R-3c spaces group with crystalline lattice parameters: α= 5.0342Å; b=5.0342Å; c=13.7483Å, and lattice angles: α=90°, β=90° and γ=120 [20]. The calculated density of α-Fe_2O_3 is 5.27 g/cm^3;

- Brushite (Calcium Phosphate Hydroxide Hydrate ($CaPO_3(OH)\ 2H_2O$)) can be identified by several intensive diffraction peaks situated at 2θ of 11.681° (d=7.570Å); 20.935° (d=4.240Å); 29.258° (d=3.050Å);

Table 2. Crystalline composition of the FA calculated from the X-ray diffraction data

Component	Crystalline composition, mass %
α-SiO_2	19
Brushite ($CaPO_3(OH).2H_2O$)	14
α-Fe_2O_3	9
Mullite ($Al_2O_3.2SiO_2$)	8
Others	7

30.506° (d=2.928 Å); 34.156° (d=2.628 Å) and 34.426° (d=2.603 Å). The observed brushite is monoclinic from Cc spaces group with crystalline lattice parameters: a=5.0342Å; b=5.0342Å; c=13.7483Å, and lattice angles: α=90°, β=90° and γ=120° [21]. The density of brushite is 2.31 g/cm^3;

- Quartz (α-SiO_2), with main diffraction peaks at 2θ=20.827° (d=4.262Å); 2Q=26.607° (3.348Å); 2θ=50.079° (d=1.820Å) is hexagonal from P3221 spaces group with crystalline lattice parameters: a= 4.9209Å; b=4.9209Å; c=5.4091Å, and lattice angles: α=90°, β=90° and γ=120° [22]. The calculated density of α-SiO_2 is 2.64 g/cm^3;

- Mullite ($Al_6Si_2O_{13}$) is characterized with a rich in reflex diffractogram, peaks with higher intensity being placed at 2θ of 16.43° (d=5.391Å), 25.97° (d=3.428Å), 26.27° (d=3.390Å), 33.23° (d=2.694Å), 35.28° (d=2.542 Å), 40.87° (d=2.206 Å), 60.71° (1.524 Å), etc. Mullite is orthorhombic with crystalline lattice parameters: a=7.5456Å; b=7.6898Å; c=2.8842Å [23]. The density of mullite is 2.8 g/cm^3

The most intensive peak on the FA diffractogram, observed at 2θ=26.6°, is attributed to α-SiO_2. The reflexes situated at 2θ above 55° could be addressed to mullite. As the characteristic reflexes of the different constituents are situated very closely, it is difficult to associate them undoubtedly to an exact compound. Moreover, the crystalline phases coexist as solid solutions, which causes displacement of the characteristic lines and renders dificulties in the recognition of the X-ray peaks. For these reasons, X-ray diffractogram has to be decoded taking into account the results obtained from the chemical analyses.

The results from the quantitative calculations performed for the crystalline constituents on the basis of the experimental X-ray diffractogram of FA and their crystallographic data are given in Table 2.

Comparing the results from the chemical (Table 1) and X-ray diffraction analyses (Table 2), it could be supposed that the amorphous part of FA is mainly composed of glassy allumosilicates from the type a:SiO_2xAl_2O_3.

As the main characteristic reflection of the graphite (see Fig. 2) corresponds to the region of the amorphous plateau on the FA diffractogram [24], it could be suggested that amorphous black C exists in the amorphous phase, which could not been detected by the chemical analysis since it is transformed to CO_2 and leaves the sample.

The mullite established in the FA composition is not present as a natural mineral in the coals. It could be expected that its formation during the burning process is a result of thermal decomposition of the allumosilcates composing the fuel mineral mass, such as kaolinite [25]:

$$A1_2O_3.\ 2SiO_2.2H_20 \xrightarrow{500\ ^oC} A1_2O_3.\ 2SiO_2 + 2H_2O \quad (1)$$

kaolinite $\longrightarrow$ metakaolin + steam

The mullite and silica formation occurs according to the reaction:

$$3(A1_2O_3.\ 2SiO_2) \xrightarrow{980\ ^oC} 3A1_2O_3.2SiO_2 + 4SiO_2 \quad (2)$$

metakaolin $\longrightarrow$ mullite + silica

The quantity of the resultant mullite in the FA is a function of the quenching rate for solidification of the melt obtained by the mineral mass fusion in the incineration system, as well as of the rate of its crystallization. The ratio between the quantity of the quartz (α-SiO_2) and the amorphous (glassy) SiO_2 in the FA residue, generated by the decomposition of the metakaolin (described by eq.2), depends also on the cooling rate.

In general aspect, the ratio between the amorphous and the crystalline fraction in the FA composition is not constant at one and the same initial fuel

composition and depends on the quenching rate of the mineral melt. The higher cooling rate is favorable for the melt solidification in an amorphous state.

On the X-ray diffractogram of FA can be clearly observed the characteristic lines of brushite. They could not be registered by the chemical analysis, as brushite is decomposes during the sample melting to its constituents, namely CaO, P_2O_5 and H_2O, undergoing several intermediate stages [26]. As a result, the liberated P_2O_5 is burned and could not be detected. Taking into account that 1 mol of brushite contains 32.59 % of CaO, it could be concluded that the main part of the measured content of CaO in the FA composition (about 4.6 mass %) is present as brushite and less than 1.5 mass % of it is lime.

The results from the chemical and X-ray diffraction analyses of FA reveal the presence of a significant quantity of silicates: α-SiO_2, a:SiO_2 and a:$SiO_2xAl_2O_3$. As the total content of $SiO_2+Al_2O_3+Fe_2O_3>70$ % and the content of CaO is rather low (5.75 mass %), according to the crystallographic standard ASTMC-168, the investigated FA, despite that it is obtained as a byproduct from the comparatively young lignite coals, refers to the class F. This classification means, that the utilization of the investigated FA as a raw material for the building industry requires additives of additional cementing components, such as portland cement, burnt or hydrated lime. Independently, the addition of appropriate catalysts to FA from class F leads to formation of geopolymers. For this reason, it can be expected that the FA collected in the electrostatic precipitator of "Maritza-East 2" is an appropriate material for zeolite synthesis.

CONCLUSIONS

As a result of the performed investigation it could be concluded that the fly ash collected in the electrostatic precipitators of TPP "Maritza-East 2" is characterized by a mixed amorphous-crystalline structure in a ratio 43/57. Four crystalline phases are identified to exist in significant quantities: α-SiO_2, brushite, α-Fe_2O_3 and mullite. The amorphous phase is mainly composed of a:SiO_2 and glassy allumosilicates. The investigated FA is predominantly silicate and alumosilicate material, which according to the crystallographic standard ASTMC-168 refers to class F. The chemical and crystallographic characteristics of the FA are appropriate for its further utilization for preparation of synthetic zeolites.

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