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Kinetic and thermodynamic studies on the thermal behaviour of fly ash from lignite coals

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HIGHLIGHTS

- The thermal behaviour of fly ash is studied by differential-thermal analysis.
- The thermodynamic characteristics of the thermal effects are obtained.
- The kinetic equations for magnetite–hematite oxidation are derived.
- The relationship of fly ash chemistry and its thermal behaviour are discussed.

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ABSTRACT

The kinetic and the thermodynamic characteristics of the physical and the physicochemical processes, taking place under thermal treatment of fly ash (FA) from lignite coals, were investigated. The obtained results are important for the thermal stability of this material, as well as for the determination of appropriate regimes for its zeolitization, vitrification and thermal activation. The thermal treatment is essential for the development of advanced technologies for utilization of ash residues. FA was subjected to differential thermal analysis (DTA) as the heating was performed at different rates: 2.5, 5.5, 11.0, 15.0, 25.0 and 35.0 °C min^{-1}. The obtained experimental thermograms were divided conditionally in three thermal zones: up to 200 °C, 200–675 °C and 675–950 °C, where the following thermal effects were registered: first zone – an endothermic effect, attributed to the water desorption and the liberation of adsorbed gases; second zone – two exothermic effects, related to the chemical oxidation of the magnetite in the FA composition; third zone – a small endothermic effect in the interval 760–861 °C related to the glass transition of the amorphous constituents of the FA. The activation energy E_a of the surface and the bulk oxidation of magnetite to hematite, corresponding to the exothermic peaks in the second zone, was calculated by the derived kinetic equations. The process thermodynamic parameters, such as enthalpy ΔH and entropy ΔS, were computed comparing the areas of the characteristic thermal effects of the investigated FA and an appropriate etalon. The values of E_a, ΔH and ΔS of the low- and the high-temperature oxidation were found to be $\overline{E}_a^L = 29.3$ kJ mol^{-1}, $\Delta H^L = 1.01$ kJ mol^{-1}, $\Delta S^L = 1.67$ J mol^{-1} K^{-1}, and $\overline{E}_a^H = 51.7$ kJ mol^{-1}, $\Delta H^H = 3.97$ kJ mol^{-1} and, $\Delta S^H = 5.05$ J mol^{-1} K^{-1}, correspondingly.

1. Introduction

Fly ash (FA) is a by-product from the incineration of coals in Thermal Power Plants (TPPs). It is a mineral mixture with macrocomposition that can be expressed by the SiO_2–Al_2O_3–MeO systems, where MeO are alkaline (Na_2O, K_2O), alkaline-earth (CaO, MgO) and/or transition metal oxides (MnO, ZnO, etc.) [1]. Furthermore, a broad variety of micro-components and trace elements is contained in the ash mixture [1,2]. The disposal of FA creates ecological risks because of the acidification and the infiltration of heavy metals and radioactive components into the soil [3]. Different approaches have been developed to solve these problems. One of them is the reduction of the volume of the ash residues by their sintering or vitrification under thermal treatment. Moreover that the leaching of harmful components into the soil can be reduced to a big extent [4,5]. A variety of technological approaches has been developed for the utilization of FA taking into account its predominant aluminosilicate composition. The application of FA in the silicate and the ceramic industries, in the building of road surfaces, and as an additive in cement, concrete, bricks, etc., is mostly spread in the practice [6,7].

Recently, FA is considered as a raw material for the processing of many valuable components with practical importance. Therefore, different advanced technologies are under development for

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its effective utilization [6,8]. The practices of preliminary magnetic treatment of ash residues for the magnetite separation followed by the synthesis of glass-ceramics are well established [9]. A perspective technological approach is the conversion of FA by alkaline reagents in zeolites with a dirigible structure and morphology. They are applicable for highly effective adsorbents, molecular sieves, ion-exchangers, catalyst carriers, etc. [10–12].

The melting of FA generally occurs at temperatures above 1300 °C [13]. Much attention has been paid on the investigation of the ash behaviour in the interval 1000–1500 °C related to the risk of slug formation into the boilers [14]. The knowledge about the thermal behaviour of FA at temperatures below 1000 °C is quite superficially interpreted, despite that the low-temperature processes are more interesting from the point of view of the FA utilization. The fusion process at high temperatures (above 1000 °C) is energetically inefficient. For this reason, the effect of different additives on the reduction of the FA melting temperatures has been studied [4,15].

The success of FA in many applications is predicted by its chemical composition, morphology and crystallography. The thermal behaviour is a key stone for the development of effective advanced technologies for utilisation by its conversion into valuable materials. Therefore, the knowledge about the physical and the physicochemical processes, taking place during the FA thermal treatment, is of substantial importance related to its thermal stability and the determination of appropriate regimes for zeolitization, vitrification and activation. The realization of each one of these technological aspects is governed by the energetic barrier of the separate processes, their thermodynamic potential and probability, which are all part from the environmental effect of FA utilization related to the energy demands.

The present study is focused on the clarification of the thermal behaviour of FA form lignite coals at temperatures below 1000 °C, and the calculation of the main kinetic and thermodynamic parameters of the transformations observed in this thermal region.

2. Materials and methods

2.1. Materials

FA was collected from the electrostatic filters of the biggest thermal power plant in Bulgaria TPP "Maritza-East 2" supplied by domestic lignite coals. The chemical composition of FA was determined by the combination of the classical silicate analysis and the instrumental techniques of the atomic absorption spectroscopy (AAS). The investigated samples were subjected to alkaline melting at 800 °C and thereafter, they were converted in liquid state by acidic dilution. The silicon dioxide was determined by weighting, as it was separated as a solid residue after evaporation of the solution at 1000 °C.

The AAS analysis was performed by a Perkin–Elmer 5000 apparatus in the flame of a mixture of acetylene and air. The FA crystallography was studied by X-ray diffraction (XRD) using a diffractometer Brucker D2 Phaser with Cu Kα-radiation and a Ni filter ($\lambda_{Cu\ K\alpha}$ = 1.5418 Å). The granulometric composition of FA was determined by sieve fractionation.

The performed compositional and crystallographic studies on this material showed a predominant content of silicon and aluminium oxides in a mixed amorphous–crystalline structure. The experimental X-ray diffractogram and its deconvolution are presented in Fig. 1. The quantitative determination of the amorphous/crystalline ratio was performed as the areas of the amorphous plateau and the summarized area of the all crystalline peaks computed form the deconvoluted experimental diffractogram (Fig. 1b) were divided to the total area of the X-ray diffraction pattern. The mathematical approach for this quantitative determination is described in Ref. [16]. The proportion between the amorphous and the crystalline constituents in the investigated FA was found to be of 43/57. Four crystalline phases were identified by XRD that exist in significant quantities: quartz (α-SiO_2), mullite ($3Al_2O_3{\cdot}2SiO_2$), magnetite (Fe_3O_4) and brushite ($CaPO_3(OH){\cdot}2H_2O$). Comparing the results from XRD and the chemical analysis, it was indicated that the amorphous phase is mainly composed of amorphous silicon dioxide (a:SiO_2) and glassy aluminosilicates [17]. The total iron concentration obtained by the silicate analysis is expressed as Fe_2O_3 due to the specifics of the chemical determination. The XRD determination revealed that the iron is presented in FA predominantly as magnetite but due to the complicated nature of the investigated material and the limits in the accuracy of the quantitative X-ray analysis up to about 2% could be included in the amorphous matrix. The results for FA composition are summarized in Table 1. The weigh loss of 3.53% was measured after FA heating at 800 °C for 15 min due to the incineration of unburned carbon, decomposition of brushite and sulfates. Besides the components listed in Table 1, FA normally contains a big variety of trace elements, which present in such residues [1].

Some diffraction peaks could not be associated for certain with exact crystalline phases and their summarized area was calculated to be of the order of 7% of the total one.

The grain size distribution of the FA particles, determined by sieve separation, was found to be between 125 and 250 μm.

2.2. Methods

The thermal investigations were performed by differential thermal analysis (DTA) using an apparatus F. Paulik–J. Paulik–L. Erday, MOM–Hungary under six different heating rates: 2.5, 5.5, 11.0, 15.0, 25.0 and 35.0 °C min^{-1}. The studied thermal interval was from room temperature to 950 °C. Annealed α-Al_2O_3 was used as a reference material for DTA. The investigated FA and the etalon were heated in air-opened quartz containers to avoid their distortion because of the liberation of significant quantity of adsorbed water and gases. FA was preliminary dried at 105 °C for 2 h to reduce the endothermic effects from the water desorption. The requirements for similarity of dispersion of the sample and the etalon, as well as the equality in the shape, size and the congestion rate of the vessels were observed for each experiment.

3. Theory and calculations

DTA is successfully applied for quantitative evaluation of the heat energy of the processes of phase transitions, oxidation, decomposition, and adsorption and desorption. Heat energy together with the temperatures of the beginning and the end of the corresponding effects are the basic parameters, characterizing the thermal stability of each investigated system. The area of the peak on the experimental thermogram, corresponding to some physical or physicochemical process depends on internal and external factors. The internal one are the nature of the investigated material, the quantity of the sample and the etalon, their thermal capacity, thermal conductivity, granulometric size, etc. The external conditions include the heating velocity, the shape and the material of the containers and the extent of their congestion, the position of the thermocouples, the surrounding atmosphere, etc.

The area F of the registered effect on the differential curve is proportional to the value of the process heat Q in a case that the experimental thermograms are measured at equal external conditions and the investigated sample and the etalon possess similar thermophysical characteristics: