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Composition of coal combustion by-products: The importance of combustion technology

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ABSTRACT

The combustion by-products (fly ash and bottom ash) from a pulverized fuel boiler and hybrid boiler (pulverized fuel burners and fluidized bed) were compared, where both boilers were fired with predominantly the same coal. The mineral (phase) composition was determined using an optical and scanning electron microscopy and X-ray diffraction; the chemical composition of particles by using energy dispersive spectrometry. The chemical composition of the bulk samples was also determined. The fly ash and bottom ash from the pulverized boiler were relatively enriched in glass and mullite, while the fly ash from the hybrid boiler also contained glass and mullite, but the bottom ash from the hybrid boiler was devoid of these high-temperature phases. The difference in ash chemical composition from both boilers was also noted. Differences between the combustion products from both boilers are related to the combustion technology (mostly temperature), and partly due to the addition of bed material.

1. Introduction

Coal combustion in energy-generating (electricity or electricity and heat) plants results in the production of a significant amount of by-products, e.g. fly ash and bottom ash (slag). Because of the relatively limited range of hard coal composition variations used in plants and similar technologies of combustion in use (pulverized fuel boilers), the composition of fly ash and bottom ash from different plants is similar. Utilization of coal combustion by-products, especially of fly ash, has increased significantly in recent decades. Fly ash is used mainly in the production of cements, building materials, road construction, mine backfill, and numerous other applications (e.g. [1,2]). Fly ash from coal combustion in pulverized fuel boilers is composed mainly of glassy spheres or partially vitrified forms. In mineral composition, glass, quartz, and mullite dominate with minor content of Fe-spinels and other compounds.

There has, however, been a shift in recent times, and the composition of combustion by-products is now more differentiated. This is related in part due to the co-combustion of coal and biomass, as well as to modifications in combustion technology. An increasing number of power plants are equipped with fluidized bed boilers globally (e.g. [3,4]), as well as in Poland (e.g. [5]), resulting in the production of meaningful amounts of fly ash and bottom ash which differ significantly in mineral composition and particle morphology from the by-products of coal combustion from conventional pulverized fuel boilers (e.g. [6,7]). Traditional methods of utilizing fly ash from conventional power plants cannot be applied in the case of fly ash from fluidized bed boilers. Fly ash from fluidized bed boilers does not correspond to fly ash characteristics that are acceptable as component of cements, or as additions to concrete, which should be composed mainly of spherical and glassy grains [8].

In this paper we present, data on the chemical and mineral composition of fly ash and slag obtained from two types of boilers: a pulverized fuel boiler and a hybrid boiler with fluidized bed and burners for pulverized fuel. The same fuel was used in the pulverized fuel burners of both boilers, but in the fluidized bed zone in the hybrid boiler the coal from the other suppliers was combusted. Taking into account that 70% of the fuel in hybrid boilers is fired in pulverized fuel burners, it is possible to consider the differences in the composition of fly and bottom ashes as being related primarily to the technology of combustion. Comparison of ash obtained in different installations from the same, or predominantly the same coal is interesting because coal type significantly influences the ash's characteristics (e.g. [9]).

2. Material

Samples were collected from a combined heat and power station in the Azoty Tarnów in Tarnów, Poland. The station is equipped with five

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Table 1
List of samples.

Sample symbol	Sample description	Boiler	Sampling site	Sampling date
TAR-3S	Bottom ash (slag)	K-3	Behind slag crusher	27 April, 2012
TAR-3A	Fly ash	K-3	Funnel of electrofilter	27 April, 2012
TAR-4S	Bottom ash (slag)	K-4	Behind slag crusher	30 April, 2012
TAR-4A	Fly ash	K-4	Funnel of electrofilter	30 April, 2012

boilers. We studied the fly ash and bottom ash (slag) from two boilers (K-3 and K-4), with the studied samples listed in Table 1.

Boiler K-3 operates as a conventional pulverized fuel installation (thermal power — 119 MWt; boiler capacity — 170 Mg/h) fired with pulverized hard coal in low-emission burners. In boiler K-4, a hybrid combustion system is applied. The stationary fluidized bed is situated in the lower part of the boiler; in the upper part the pulverized fuel is combusted. Fine gravel (<8 mm) is used as a bed in boiler K-4. During combustion, any unburned material from the pulverized fuel burners mixes with the bed after falling down. The uppermost layer of the bed is removed once every twenty-four hours. The size of the coal particles fired in the fluidized bed zone of boiler K-4 (<2 mm; usually from 0.2 to 1.0 mm) is significantly higher than the coal dust fired in pulverized fuel burners.

The temperature of combustion in boiler K-3 in the space near the burners is approximately 1300–1500 °C. In boiler K-4, the temperature near burners is approximately 1300 °C, and in the stationary bed, approximately 800 °C.

3. Analytical methods

Optical microscopy was employed both using a reflected and transmitted light. Scanning electron microscopy with energy dispersive spectrometry (SEM-EDS) was applied using a HITACHI S-4700 field emission microscope and NORAN spectrometer with Nordlys II detector. The latter samples were prepared as carbon-coated polished sections or natural surfaces of ash or slag particles. Quantitative determination of the chemical elements' content was based on the standardless method.

X-ray diffraction (XRD) analyses of the powdered samples were performed using a Philips X'Pert APD diffractometer (PW1830 generator and PW3020 vertical goniometer). A voltage of 40 kV and current 30 mA were applied. Samples were irradiated by CuKα radiation and the data were collected in the range of 2–64 °2Θ, with a step of 0.02 °2Θ and dwell time of 1 s.

The chemical composition was analyzed using ICP AES and ICP MS methods for major and trace elements in the Acme Laboratory (Vancouver, Canada). Loss of ignition (LOI) was determined by the mass difference after heating to 1000 °C, while the Leco method was used for determination of total carbon and sulphur content.

4. Results

4.1. Chemical and mineral composition of fly ash

Fly ash from pulverized fuel boiler (boiler K-3) — sample TAR-3A. The ash is brown-grey, and composed of particles up to 70 μm in diameter. Spherical glassy particles dominate (Fig. 1A, B and F), accompanied by subordinate quartz grains and irregular aluminosilicate grains (Fig. 1C). The irregular aluminosilicate grains, usually larger than the spherical particles, are often hollow and built of porous material (Fig. 1D). The spherical grains composed of metallic Fe or Fe oxide vary broadly in size (Fig. 1D and E). The spherical glassy particles are composed of Si and Al as dominant components, together with variable quantities of Fe, Ti, K, Na, Mg, Ca, and other elements (Table 2). The size of spherical particles varies from below 1 μm to 50 μm. Any differences in chemical composition between very small (<1.5 μm) and larger (>4 μm) spherical particles are not significant, except for the Ca content and much wider range of Si content variation (Table 2). The larger spherical particles (>30 μm) are often empty inside (but the thickness of their walls is higher than that found in typical cenospheres). Another group of spherical particles is represented by Ca, Mg and Fe oxides. Usually, Ca strongly dominates the composition and spheres of this composition are usually porous. Char grains are rare in the fly ash from boiler K-3 and their size is variable. The highly porous char grains often contain small aluminosilicate spherical particles (Fig. 1F).

The chemical composition of the ash from the pulverized fuel boiler is presented in Tables 3 and 4. SiO_2 and Al_2O_3 constitute about 80 wt.% of the sample. The value of LOI is 1.8 wt.% and ca. 1 wt.% of the total carbon, therein.

The mineral composition determined using XRD is simple: quartz dominates besides the mullite and glassy material (Fig. 2).

Fly ash from the hybrid (fluidized bed and pulverized coal) boiler (boiler K-4) — sample TAR-4A. The ash is dark grey because of the high content of unburned coaly matter. The char particles of different size (from >250 μm to several μm) and shape are abundant (Fig. 3A, B, C, D and E). The char particles formed shards (Fig. 3A), fragments with numerous voids (Fig. 3C), massive forms (Fig. 3D), or open-work forms (Fig. 3E). Inorganic material, usually aluminosilicate spherical particles, is often dispersed within the char material (Fig. 3C and D), but char material can also be enclosed inside irregular aluminosilicate fragments (Fig. 3C). Based on the EDS analysis the variable content of Si, Al, S, Fe, Ca, and K was determined in the char particles. The irregular aluminosilicate particles are relatively common in the ash (Fig. 3C), with Si and Al dominating in these particles, but other elements are also present in smaller amounts (e.g. Ca, Fe, Na, and K). Spherical particles are much less abundant in sample TAR-4A compared with sample TAR-3A. The spherical particles, both solid and hollow, are typically smaller than the irregular ones. The concentration of chemical elements in the spherical particles is presented in Table 2, where it can be seen that a much wider range of Si content variation is typical of the larger particles (>4 μm). Three different groups of spherical particles can be determined. Aluminosilicate particles (Fig. 3C, D, E, F), sometimes empty inside (Fig. 3C, F), form a group characterized by a relatively wide range of variation of chemical composition (Table 2). Spherical particles of mixed Ca, Mg, Fe, and Mn oxides belong to the second group. The oxide particles are porous (Fig. 3F), commonly non-homogenous in composition and less frequent than aluminosilicate. The iron oxide (or partly oxidized metallic Fe) particles are variable in size and internal structure (Fig. 3C). Beside Fe, small amount of Ti and V were noted. Irregular, highly porous, and strongly-differentiated-in-size particles are also present in sample TAR-4A (Fig. 3C, D, F). This group of particles represents rock fragments ("lithic grains") derived from the gravel added to the boiler as a bed or from fuel.

The chemical composition of the ash from the hybrid boiler is presented in Tables 3 and 4. The sum of SiO_2 and Al_2O_3 is slightly above 70 wt.%, and the value of LOI is above 11 wt.%, with the total carbon content above 10 wt.% contributing significantly to the high LOI value.

The mineral composition of sample TAR-4A determined using XRD is relatively simple (Fig. 4). Quartz strongly dominates and the content of mullite and glass is subordinate. In comparison with sample TAR-3A, the content of mullite and glass is lower (Figs. 2, 4), and the content of quartz in this sample is higher.

4.2. Chemical and mineral composition of bottom ash

Bottom ash from pulverized fuel boiler (boiler K-3) — sample TAR-3S. The irregular bottom ash particles are highly porous (Fig. 5A). Less porous and homogenous in composition particles rarely occur (Fig. 5B). Silica fragments (quartz grains) can be noted within the slag particles (Fig. 5B). Tangential cracks often occur around the quartz embedded in the slag. Irregular forms of slag are variable in chemical composition. Aluminosilicate glass that forms slag particles is composed, besides Si and Al, of other elements. Local accumulations of Ca,