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IMPROVING THE ENVIRONMENTAL SAFETY OF COAL-FIRED THERMAL POWER PLANTS BY USING FLY ASH IN RECYCLING TECHNOLOGY

Abstract: *The paper presents the results of hydrothermal zeolitization of fly ash from hard coal combustion in one of the Polish power plants and possible further applications of zeolites. The synthesis was carried out using various NaOH fly ash mass ratio and the effect of NaOH concentration in the activating solution on composition of synthesized sample was tested. The present work proves the benefits from development of fly ash utilization and further opportunities in the use of zeolites. There exist the need for research to expand options to reduce harmful impact derived from energy production.*

Keywords *coal fly ash, utilization, thermal power plants, fusion-hydrothermal treatment process, removal, zeolite*

Introduction

Coal is one of the most widely use type of energy carrier. Despite efforts it is impossible to completely eliminate the demand of using coal in power plants. Great example on this field can be Poland where there is no other opportunity caused by insufficiently diversified sources of energy. In this case, it is necessary to take into account the need to eliminate harmful factors arising in the processes of coal combustion.

Fly ash is a combustion by-product constituting about 60-88% of total combustion residues from coal-fired power plants. To meet increasingly stringent limits for air pollution, the power industry has progressively improved its coal firing technology. Circulating fluidized-bed combustion, as an advanced and clean coal technology, allows solid fuels with wide range of qualities and sizes to be burnt at lower temperature (800-950°C) with high combustion efficiency, which results in considerably reduction in NOx emission compared to pulverized coal combustion [1]. Around 90-95% SO_2 reduction can also be achieved by injecting limestone in the furnace to capture the sulphur in the coal. Given all these environmental and economic benefits, circulating fluidized-bed combustion has been growing steadily all over the world since its commercialization in the late 1970s [1], resulting in large amount of waste fly ash discharge. Although a portion of the generated fly ash is used as fillers in brick manufacturing and road or dam construction, a significant amount is still disposed in land-fills or ash ponds with serious environmental consequences.

Thus, there exist the need for research and development to expand options for fly ash utilization as this will result in higher utilization rates and ameliorate the harmful environmental impacts of its disposal.

Brief analysis of recent publications

The emission of coal fly ash increases annually. The main factors of the technogenic impact of thermal power facilities on the level of atmospheric air pollution include the type of fuel, technologies for cleaning emissions, the height of chimneys, climatic conditions of atmospheric dispersion, and the nature of the terrain (Fig. 1). Thermal power plants operating on fossil fuels are most "responsible" for the greenhouse effect and acid precipitation, since the technology of electricity production is associated with the conversion of almost all of the spent material resources and the vast majority of fuel energy into waste released into the environment. One of the reasons for the increased indicators of environmental pollution is the use of low-quality coal at TPPs with high ash content.

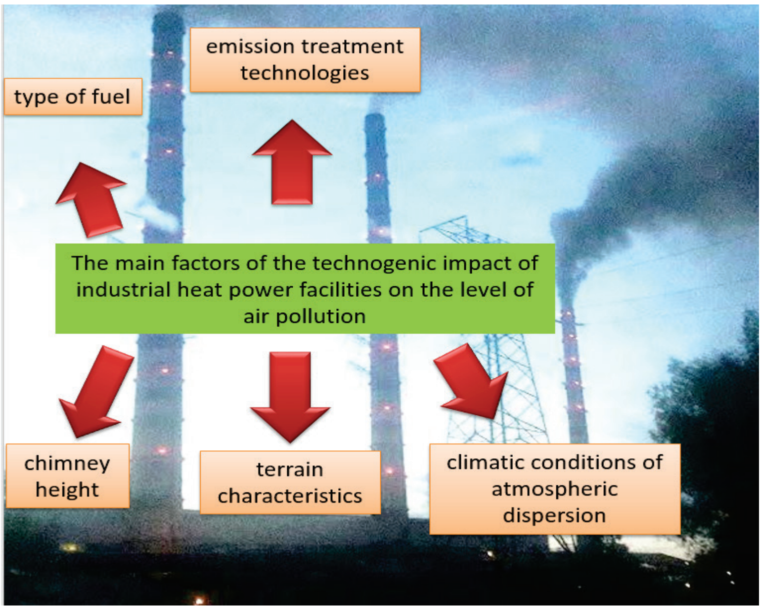

FIGURE 1. *The main factors of technogenic impact of industrial heat power facilities on the level of atmospheric air pollution*

As a result of coal combustion, the main share of technogenic carbon is emitted into the atmosphere in the form of CO_2, about 50% SO_2, 35% NOx and fly ash. An equally significant factor in the impact of coal-fired thermal power plants on the environment are emissions from fuel storage systems, its transportation, dust preparation and ash removal [2]. Pollution of the soil around coal-fired thermal power plants occurs due to the spread of pulverized ash by the wind, as well as due to the infiltration of its components through the soil into groundwater. Ash, due to its physical and chemical characteristics, is the cause of the formation of increased dust content in the air. Atmospheric aerosol is one of the main pollutants that affect the urban environment and human health, and it directly or indirectly causes haze, photochemical smog, acid rain, and other climate changes. If not properly disposed of, it can cause water and soil pollution, disrupt ecological cycles and pose environmental hazards (Fig. 2).

According to the European standard EN 450–1, coal fly ash is a fine grained, loose material, which is predominantly composed of spherical aluminosilicate glass particles, formed as a result of coal burning. Coal fly ash contains heavy metals, polycyclic aromatic hydrocarbons, silica, and other toxic substances [3].

Fly ashes essentially consists of SiO_2 and Al_2O_3 (in both amorphous and crystalline form) [4], which have great similarity with the composition of zeolites, a valuable material widely applied in many fields related to radioactive waste management, petroleum refining, purification of gases, agriculture etc. Table 1 presents the typical chemical compositions of fly ash.

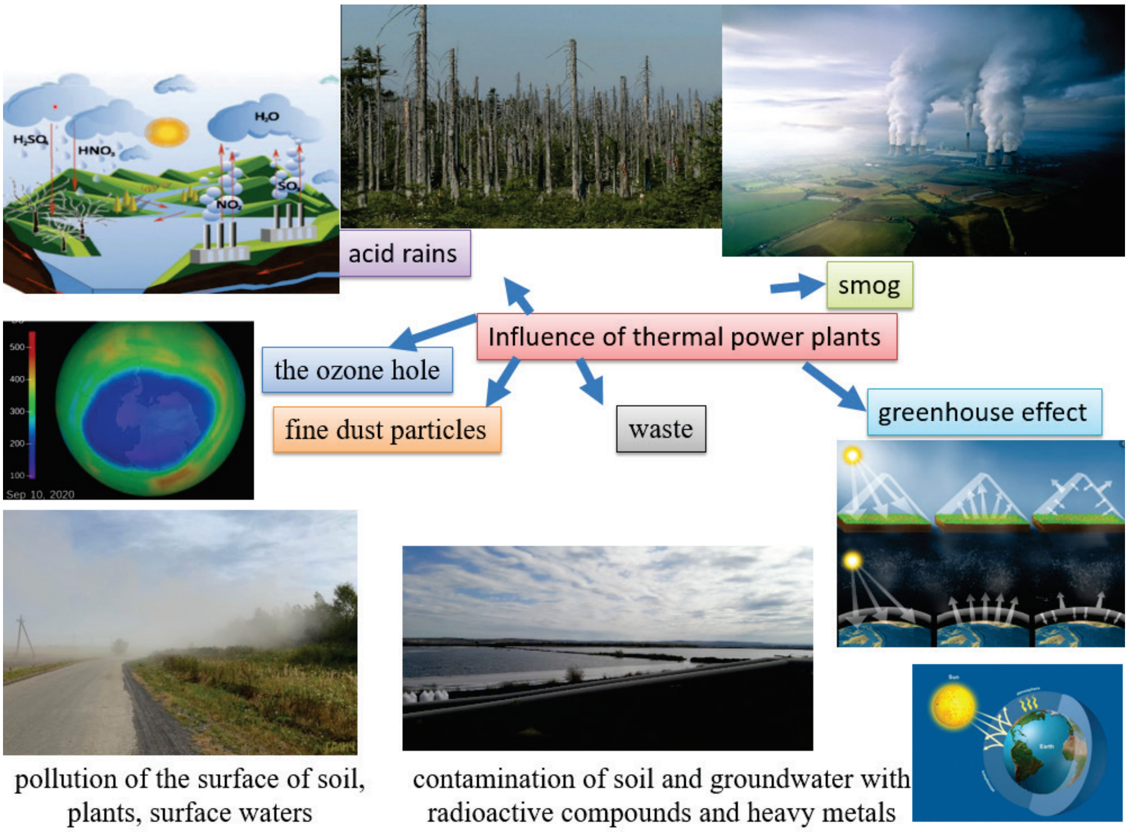

FIGURE 2. *The effects of thermal power plants on the environment*

TABLE 1. *Typical composition of fly ash from different coals*

Component	Bituminous, %	Sub-bituminous, %	Lignite, %
SiO_2	20-60	40-60	15-45
Al_2O_3	5-35	20-30	10-25
Fe_2O_3	10-40	4-10	4-15
CaO	1-12	5-30	15-40
MgO	0- 5	1-6	3-10
SO_3	0-4	0-2	0-10
Na_2O	0-4	0-2	0-6
K_2O	0-3	0-4	0-4
LOI	0-15	0-3	0-5

The elements found in fly ash exhibit a wide range of toxic effects on humans, terrestrial and aquatic organisms, and plants. A number of these elements are bioaccumulative, including arsenic, chromium, lead, mercury, nickel and zinc. Elderly people, children and patients with chronic respiratory or ardiovascular diseases are most at risk from air pollution because they are more susceptible to the damage caused by pollutants. Prolonged exposure to air pollution can cause ischemic stroke and other cerebrovascular diseases (Fig. 3).

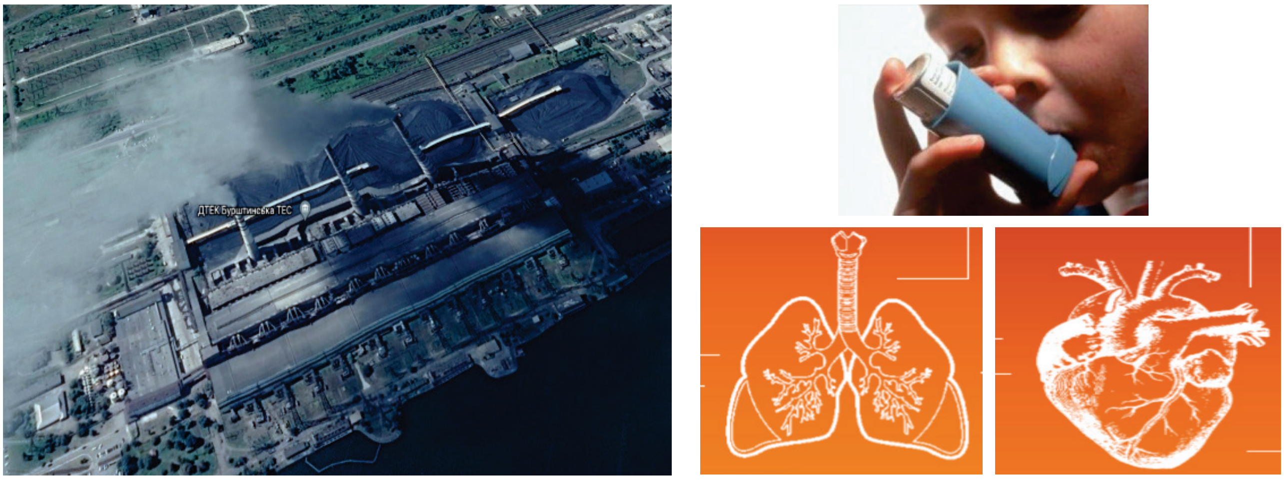

FIGURE 3. Health effects of coal ash

Understanding the physical, chemical and mineralogical properties of coal fly ash is important, as these properties influence its subsequent use and disposal. The specific properties depend on the type of coal used, the combustion conditions, and the collector setup, among other factors. Fly ash normally occurs as fine, powdery particles with an average size of less than 20 µm, bulk density ranging from 0.54 g/cm³ to 0.86 g/cm³, surface area varying from 170 m²/kg to 1000 m²/kg band light texture. The color of fly ash is dependent on the content of unburned carbon left in ash, varying from yellow to grey to black [5]. The particle shape of fly ash also varies with the different combustion conditions applied.

Carbon capture, utilization and storage is one of the proposed technologies for reducing global CO_2 emissions, and it presents many opportunities for fly ash utilization. The use of cheaply available fly ash in various parts value chain could help reduce these costs while decreasing the environmental risks associated with fly ash disposal. In some cases, it might be possible to use the carbonated fly ash as a construction material or additive. All of which improve the economics of the capture process while benefiting the overall environmental impact of these processes. A schematic of the pathways for utilization and application of fly ash in is provided in Figure 4 [6-8].

FIGURE 4. Pathways for fly ash application

Recently, intensive efforts were made to promote the recycling of fly ash through zeolitization. Synthesis of zeolites, as one of the effective uses for coal fly ash, is gaining more attention, due to the compositional similarity between fly ash and zeolites. Zeolites are microporous crystalline aluminosilicates with three-dimensional framework structures. Due to the high thermal and good dimensional stability, they have attracted a particular attention as catalysts in acid-mediated reactions [9]. Zeolite has broad application prospects due to its potential molecular sieving, high specific surface area, and good thermal and chemical stability. Zeolite is a kind of aluminosilicate molecular sieve crystal with uniform pores, and its skeleton contains Al, Si, and O. These structural features provides a various characteristics for zeolites, of absorption selectivity, high specific surface and high ion exchange capacity [10]. Zeolites have been widely used for air pollution control due to their excellent performance.

Ever since the first study conducted by Holler and Wirsching [11], many methods and process have been proposed for zeolite synthesis using fly ash and all those aim at the digestion of Si – Al containing insoluble glass phase and crystalline phases such as mullite and quartz and subsequent crystallization of zeolite [12]. Simple hydrothermal process was most commonly used for direct synthesis of zeolites, where fly ash mixed with in alkaline solutions such as sodium hydroxide with different concentration at temperature from 80°C to 200°C for up to 96 hours. However, this method usually leads to a low conversion (<75%) leaving a significant amount of fly ash residual in the products. In comparison, a two-step synthesis method proposed by Shigemoto et al. [13], where an alkali fusion stage is introduced prior to the hydrothermal treatment, demonstrated significant improvement on zeolitization process and high crystalline zeolite products were produce.

One of the effective methods for the synthesis of zeolites is the use of microwave radiation. The microwave method uses microwaves in a hydrothermal process. Microwaves promote zeolite synthesis at an earlier stage by stimulating the dissolution of SiO_2 and Al_2O_3 from fly ash and shortening its reaction time. However, this will delay the formation of zeolite in the middle and late stages. Therefore, the use of microwaves in the earlier hydrothermal process can effectively shorten the reaction time for the synthesis of zeolite from fly ash [14].

Object, subject, and methods of research

The object of research: The object of research is fly ash from hard coal combustion in one of the Polish power plants.

The subject of research is the methods of the synthesis was carried out using various NaOH fly ash mass ratio and the effect of NaOH concentration in the activating solution on composition of synthesized sample was tested.

Methods of research: The morphology and chemical composition in the micro-area of the main mineral components of the tested materials was determined using a scanning microscope (SEM). The FEI Quanta 250 FEG scanning microscope was used, equipped with a chemical composition analysis system based on radiation energy dispersion X-ray – EDS by EDAX.

Study results and their discussion

The studied fly ash is dominated by oxides of SiO_2 and Al_2O_3, and the main phase components are mullite, quartz and hematite and a significant proportion of amorphous matter (glass and unburned organic matter) – Table 2.

TABLE 2. Elemental analysis of coal fly ash in wt%

Component	Bituminous, %
SiO_2	49.73
Al_2O_3	29.57
Fe_2O_3	7.15
CaO	4.65
MgO	3.19
Na_2O	1.39
K_2O	2.86
LOI*	7

*Loss on ignition

Fly ash is a material that is heterogeneous in terms of its phase and chemical composition. The presence of oxide minerals – Al_2O_3, Fe_2O_3, MgO, CaO was established in the mineral composition of bottom ash; silicates and aluminosilicates – with island, ring, chain, layered and spatial structure. In terms of phase composition, the ashes are also agglomerates of various nature. Fly ash was examined using scanning electron microscopy (SEM). Micromorphology observation reveals that the fly ash particles are predominantly spherical in shape and consist of solid spheres, cenospheres, irregular-shaped debris and porous unburnt carbon (see Fig. 5).

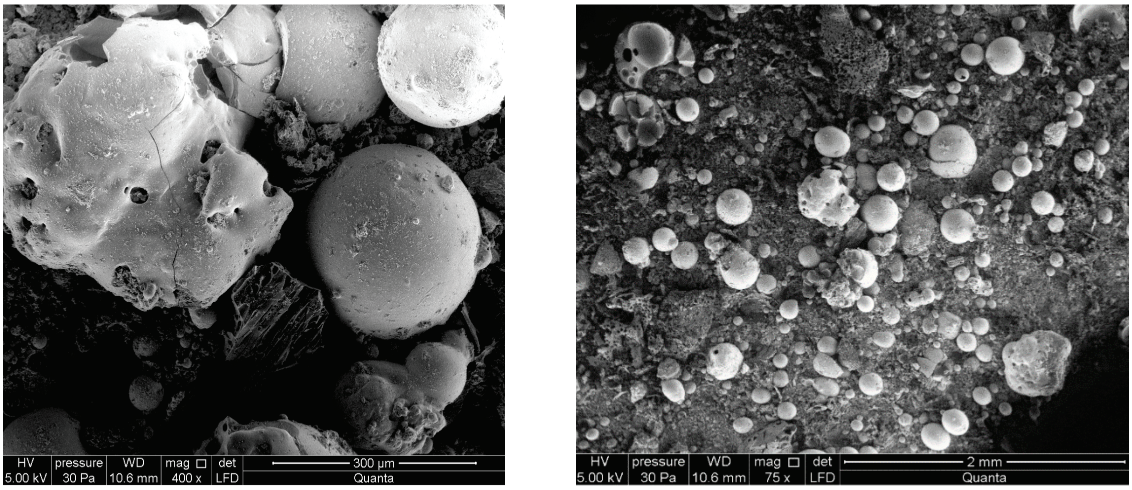

FIGURE 5. Micromorphology fly ash

The process was carried out at a NaOH/fly ash ratio (g) of 1.4:1.0; 1.8:1.0. Fly ash activation was carried out by the melting method using NaOH as an activator. The mixed sample was separately calcined at high temperatures (550-850°C) in air for 1 h. After cooling to room temperature, the resulting solid product was crushed, mixed separately with 50-120 mL of H_2O, and kept for 12 h under stirring. The solid-liquid mixture was kept without stirring at a temperature of 60-95°C for 6-24 hours. The resulting solid was cooled to room temperature, collected, and washed until a pH of 8-9 was reached. Finally, the resulting solid was dried overnight at 105°C. The morphology of the crystalline products was studied using a Phillips XL 30 scanning electron microscope (SEM) – Figure 6.

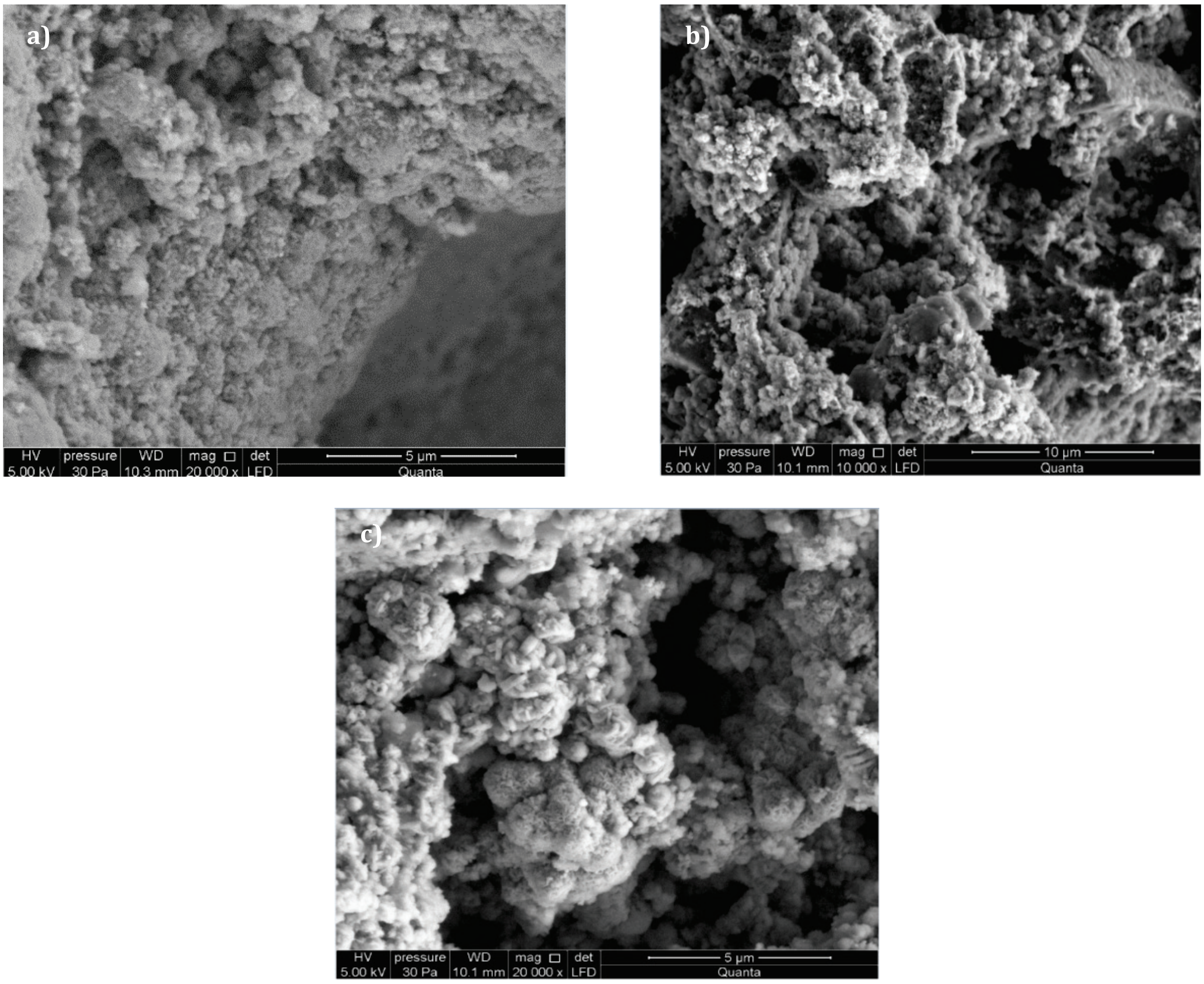

FIGURE 6. *Zeolite material*

Grain morphology of the products after synthesis, revealed in the electron microscope observations, confirms the new phases.

Conclusions

In the studied fly ash, originating from the hard coal combustion, the dominant chemical components were SiO_2 and Al_2O_3, while the main phase components were mullite, quartz and hematite, and the significant share of an amorphous substance (glass and unburnt organic substance). The products of hydrothermal synthesis with the highest content of zeolite phases (NaOH/fly ash ratio (g) of 1.4:1.0) were examined with SEM (Fig. 5). The spherical particles from input sample of fly ash were totally or partially dissolved and transformed into zeolite phases. Some of them were formed on the residuum surface. The results obtained in this study encourage the author to scale up the synthesis in order to obtain more zeolite material. This material will be used in research to produce an adsorbent, as well as an additive to degraded soils to retain water and as a nutrient carrier for plants.

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