POSSIBILITIES OF RECYCLING BOTTOM ASH WITH HIGH CONTENT OF ORGANIC MATTER RESULTING FROM INCOMPLETE COAL COMBUSTION IN COAL-FIRED POWER PLANTS

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ABSTRACT: *Coal fired power plants contribute with a large share to the world electricity consumption. Alternative sources of energy do not offer the reliability required by the grid connected consumers, which makes coal and hydrocarbons the main fuel that ensures stability of the grid and consumption variations. However, coal combustion for producing electricity poses many challenges. Environment requirements become increasingly difficult to meet in the context of regulations turning more and more restrictive. One of the many problems resulting from coal combustion for electricity production is the large amount of ash. Recycling technologies were developed, mainly to reduce the amount of waste that would otherwise occupy significant areas turning them unusable for any other purpose. Such technologies aim mainly fly ash collected from flue gas for usage in cement industry. Bottom ash, collected at the bottom of the boiler contains variable amounts of organic matter due to incomplete combustion, which render such ash type not suitable for cement industry. The paper presents a number of recycling directions for such ash type in order to mitigate the amount of waste in the form of ash resulting from coal combustion for electricity generation.*

KEY WORDS: Unburned Organic Matter, Loss on Ignition, Recycle, Bottom Ash.

1. INTRODUCTION

Today's modern society relies heavily on energy with a steady increasing trend [1] for electricity and industrial consumption and a slow decrease for residential due to an increase of energy efficiency. A consumption breakdown on various primary sources shows that the main share will be that of the natural gas, a slow increase of renewables and a flat curve for coal until 2050. As most primary energy forms, coal is a resource not evenly distributed throughout the Earth surface. As a result, coal share in the national energy balance varies significantly from country to country. Approximately one third of the national electricity consumption is covered by coal in Romania. Coal used for electricity generation in Romania is mostly lignite, which has low calorific power and high ash and moisture content compared to other coal types such as anthracite. These properties make lignite unsuitable – economically speaking – to be transported on large distances. Consequently, large coal-fired power plants built in the vicinity of the coal mining areas have been built to exploit this abundant resource in Oltenia region.

The quality of the lignite combustion process is a main concern regarding the process flow for coal-fired power plants using low grade coal. Lignite mined in Oltenia region has an ash content varying from 35 to 45%. With an installed capacity of approximately 1700 MW it is clear that combustion of such coal results in large amounts of ash, continuously generated. A significant share from the total amount of ash generated is the fly ash. The main recycling direction for fly ash is construction material industry. Fly ash contains large amounts of silicon dioxide and calcium oxide [2], which confer it frictional and abrasive properties. Depending on the coal nature and combustion equipment, fly ash has a fine particle size distribution with most less than 100 microns. Given the fine particle size, frictional nature and high temperature, fly ash can be a difficult material to handle safely. Usually, the content of organic matter due to incomplete combustion is very low in this type of ash, which renders it chemically stable and guarantees long term conservation of physical properties.

In Romania, the interest for recycling fly ash is not new. Developing road concrete [3] has been reported based on Portland cement and fly ash. Road concrete must have a special set of properties in order to face the mechanical stress and weather factors. Fly ash from cogeneration power plant Govora (Romania) has been used in various experimental mixtures. Govora power plant has implemented a type-approval procedure for fly ash that can be used in mixture with cements according to SR EN 450-1 + A1:2007.

2. BOTTOM ASH PROPERTIES

Bottom ash differs significantly from fly ash in several aspects:

- Bottom ash amounts to 10-20% from the total amount of ash while the main share is that of the fly ash;
- Important amount of slag and sintered material are present in the bottom ash;
- Organic matter resulting from incomplete combustion is present in varying amounts, depending on the coal type and quality, combustion technology and momentary combustion conditions.

While for fly ash mature technologies for recycling in several directions exist the problem of bottom ash has been relatively little studied. The organic matter present in such ash type can indicate both qualitatively and quantitatively the inefficiencies in the combustion process. The content of unburned organic matter in the bottom ash is an indicator of Loss of Ignition parameter, which can offer guidance on measures to increase the efficiency of the combustion equipment.

There are in place several methods to determine the content of unburned organic matter in ash. The most widely used consists of measuring LOI to a high temperature (such as 950 °C, ASTM Standard D7348, 2013) [4]. The LOI measuring in order to determine the unburned matter content has been criticized though, since weight loss under high temperature (the LOI) is not only caused by destruction of the UC present, but also by breakdown of mineral phases (e.g., decomposition of carbonates, oxidation of sulfides, release of structure water from clay minerals, and dehydration of lime) and to water physically adsorbed on measured samples [4].

Determination method for unburned organic matter in bottom ash is also a debate subject. Bartonova et al [5] established that sampling protocol and pretreatment (e.g. grinding) can influcnce the results significantly. Bartonova et al [5] found that the content of unburned organic matter (Figure 1) in the bottom ash is influenced to a high degree by the coal type, with higher contents in bituminous coal (6% in the study

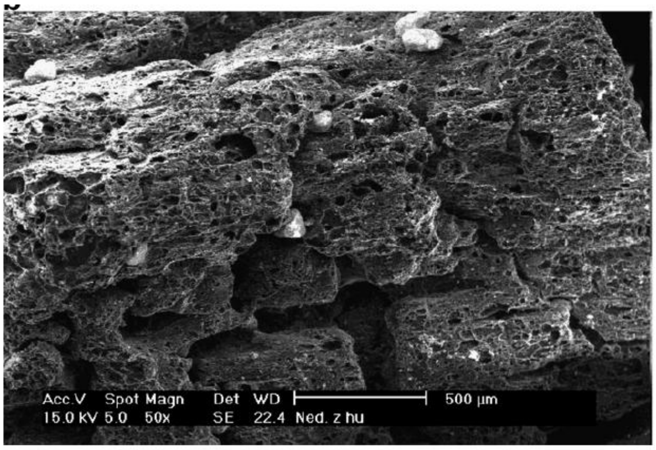

Figure 1. SEM photograph of unburned carbon from bottom ash obtained from lignite [5]

cited) and lower in lignite (0.7%). In addition to carbon, which is present in the bottom ash as a result of the unburned organic matter, other trace elements can be found such as HG, Se,Cu, As, Ni, V, S and Cl [5].

The unburned carbon particles found in bottom ash have high porosity [5] and large specific area (39 m^2/g for bituminous coal and 16 m^2/g for lignite). The large value of the specific area can be explained by the high volatile matter content. The complex system of macropores, cavities and ruptures of unburned organic matter from lignite combustion is also shown in Fig. 1 [5].

3. BOTTOM ASH USES

Wang et al [6] employed a physical sieving method followed by sink-float separation with water to prepare a higher concentrated unburned carbon sample with the purpose of developing a low-cost adsorbent for treatment of methylene blue-containing wastewater. It was found that unburned carbon derived from coal ash is a highly efficient adsorbent for dye adsorption in aqueous solutions. Its adsorption capacity depends on initial concentration and temperature. The dynamic adsorption of the unburned carbon follows the pseudo-second-order adsorption model and
adsorption is dominantly by a two-step intra-particle diffusion process.

Within the frame of the research project CHARPHITE an innovative use for the bottom ash containing various amounts of unburned organic matter was identified. Refractory insulation elements were manufactured by burning at approximately 950 °C. The high temperature determines complete combustion of the unburned organic matter present in the ash. The complete combustion leaves behind pores, which contribute to obtaining a high value of the thermal resistance. It was found that such a technology guarantees fabrication of insulating materials with high thermal resistance. The raw material used in the study consisted of mineral residue categorized in four classes depending on the coal separation process that generates that particular product. A significant percentage of unburned organic matter was identified in all four residue types.

Unburned organic matter present in the bottom ash is usually found in an extremely oxidized state [7] which confers a high reactivity to release a variety of organic impurities upon disposal. Șahbaz et al [7] studied separation of the unburned organic matter from the bottom ash of a power plant using the Jameson cell flotation technique. A bottom ash sample containing pieces of semi-sintered material was subjected to size reduction to enhance liberation of unburned organic matter by using a laboratory ball mill. A recovery of 67.5% corresponding to a reduction of ash content from about 90% to 44% has been obtained. Due to the highly reactive state in which the unburned carbon is present in the bottom ash it can be employed for adsorption of various compounds. Wang and Li [8] developed an experimental method for dye adsorption and decolorisation of textiles. Unburned carbon was separated from ash and subject to an enrichment treatment. Two dye samples were used in the experiments. The results show that the amount of dye adsorbed depends on the exposure time with a flat line occurring after 100 h for large carbon particles (diameter larger than 200 mm) and after 250 h for small particles (diameter no larger than 125 mm).

Graphitization of unburned coal contained in the bottom ash is another major recycling direction. Yeh et al [9] developed a graphitization technology for unburned coal to fabricate anode materials for high power Li-Ion batteries. It was found that anode elements fabricated from graphitized unburned carbon exhibit good electrical performance and stability.

High reactivity and large area to mass ratio make the unburned carbon found in bottom ash a efficient adsorbent for SO2 removal. Kisiela et al [10] investigated the possibility to use unburned carbon from lignite bottom ash to remove SO_2 from flue gas. Enriched unburned carbon samples were separated from lignite fly ash, by mechanical classification system, into three fractions. Measurements were carried out in a fixed-bed reactor, considering a flow rate of 2 l/min of gas containing: 5% (v/v) sulphur dioxide and 95% (v/v) nitrogen as balance, passing through a 0.028 dm^3 of bed at 100 °C. The results of the study show that the possibilities of application of carbonaceous materials for the gas purification processes, besides the parameters of the porous structure also depend significantly on the chemical nature of the surface. The research results presented in this article indicate that studied unburned carbons can be successfully used as adsorbents for flue gases desulphurization process. However, since temperature conditions in the boiler differ significantly from the conditions that can be reproduced in the laboratory the results must be regarded cautiously. Wang et al [11] investigated the possibilities to use unburned carbon from bottom ash resulting from coal combustion for removal of humic acid from water. Two carbon samples were obtained from coal ash using standard dry-sieving method followed by water floating. It was found that unburned carbons separated from coal ashes present varying properties depending on the source. The two unburned carbons analyzed exhibit different textural structure and chemical composition but have similar surface functional groups.

4. CONCLUSIONS

Bottom ash resulting from coal combustion (especially lignite) is present in varying amounts in bottom ash depending on the coal composition and combustion technology. The interest for mitigation of environmental impact caused by waste resulting from coal combustion stimulated research on identifying possible uses for unburned organic matter present in ash. A significant number of recycling directions exists, based on the chemical and physical characteristics of the unburned carbon:

- obtaining synthetic graphite
- production of adsorbents
- adsorbent for the retention of dyes (or other pollutants) from effluents
- retention of Hg and other toxic volatile compounds from flue gas
- high thermal insulation refractory construction elements

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