POSSIBILITIES TO RECYCLE THE BOTTOM ASH FROM COAL FIRED BOILERS. PART I. METHODOLOGY

MIHAI CRUCERU, *University Constantin Brâncuși of Tg-Jiu, ROMANIA*
BOGDAN DIACONU, *University Constantin Brâncuși of Tg-Jiu, ROMANIA*
LUCICA ANGHELESCU, *University Constantin Brâncuși of Tg-Jiu, ROMANIA*

Abstract: *Ash dump sites – landfills – contain an aqueous mixture of bottom (BA) ash and fly ash (FA) accumulated over time in artificial pond-like structures. The content of the ash landfills has complex and non-homogenous properties, which limit drastically the applicability of complete recycling procedures aiming to landfill reclamation. The authors propose a technology to separate various components of the mixture depending on desired recyclability characteristic. A special characteristic of the BA component is the content of unburned carbon, due to incomplete combustion in the boiler furnace. A special, multi-objective procedure for separation of ash particles containing unburned carbon was developed with the purpose of obtaining synthetic graphite. The first part of the paper presents the methodology used to concentrate the unburned carbon, the results being analised in the second part of the paper*.

Keywords: Bottom Ash, Unburned carbon, Recycle, Synthetic graphite, Particle Size Distribution

1. INTRODUCTION

1.1. BA – properties, mechanisms of formation and issues

A significant percentage of the electricity demand is covered presently from coal-fired power plants. Variations exist in this percentage depending on local availability, presence of other primary energy resources and national policies in the respect of energy.

Coal processing technologies did not change significantly from the emergence of coal as a dominant energy resource. However, higher standards regarding utilization efficiency and environmental impact have been put in place recently, forcing the industry to comply.

Coal utilization technologies cause a multi-faceted environmental impact:

(1) extraction and primary processing;

(2) combustion and releasing flue gas and solid residues – ash and slag;

(3) transportation, processing and deposit of the ash and slag.

Solid waste material is perhaps the most problematic and it has carefully been considered. Flue gas cleaning technologies (retention of sulfur and nitrogen oxides) reached performances that comply even with the most restrictive environment regulations. Technologies to retain carbon dioxide are under research with promising results. Ash resulting from coal combustion, on the other side, is still a problem only partially solved.

Two types of ash, significantly different from both physical and chemical properties viewpoint, are generated, both in the coiler furnace. Fly ash (FA) consists of the fine grain fraction, with aerodynamic properties that make it easy to be entrained by the flue gas leaving the boiler. The vast majority of the FA is collected in the electrostatic precipitators. BA is the coarse grain fraction, with aerodynamic properties not adequate to be entrained by the flue gas. BA particles are a few orders of magnitude larger than FA particles.

A differential analysis of the two ash types is presented in Table 1.

Table 1. Differential analysis FA vs. BA

FA	BA
Approx. 80% of the total ash resulted*	Approx. 20% of the total ash resulted
Fine grain size	Coarse grain size
Narrow particle size distribution variation interval	Large particle size distribution variation interval
Negligible unburned carbon content	Significant content of unburned carbon
Relatively constant, and predictable physical and chemical properties, independent on the momentary coal quality	Chemical and physical properties, varying unpredictably with the momentary coal quality
Multiple recycling directions, significant percentage being currently recycled	Little recycling directions, a low percentage being currently recycled
Currently, integrally recyclable	Currently, recyclable to a low to medium degree
Highly homogenous physical and chemical properties	Highly heterogeneous physical and chemical properties

*Depends on the combustion system, coal type and quality

American Coal Ash Association (ACAA) claims that recycling rate of FA in concrete and concrete products is approximately 47%, while for BA this as low as 5.28% of the total recycling amount [1]. This significant difference is explained by significant grain size variations, variable amounts of organic matter, presence of slag particles. While fly ash has physical and chemical properties that make it suitable to be used as raw material or additive in construction material industry, BA does not comply with such standards due to the reasons presented above.

A number of complex recycling technologies have been developed for BA involving chemical pre-treatment with dangerous compounds, based on its properties (exactly those that render it unsuitable for construction material industry).

Ideally, all ash produced should be in FA form. Combustion kinetics and mechanisms resulting in generation of BA particles are complex and not fully understood [2], [3]. Unburned carbon occurring in BA particles is caused by the time interval too short spent in the boiler furnace for complete combustion to occur. Unburned carbon in BA can be reduced by various methods including adequate milling (with regard to the combustion technology employed) and in general, optimization of the combustion process [4].

Inagaki [5], Dong [6] showed the adjustment of the burners and the furnace (air preheat, excess air, mixing, residence time, combustion temperature, etc.) can improve burnout [5], reducing any air/coal distribution imbalance among the burners and matching of operating conditions and the coal characteristics are especially important.

1.2. Graphite

Graphite is a crystalline allotrope of carbon with applicability in many hi-tech industries [7]. Graphite is not a renewable resource. The increasing demand for graphite resulted in development of synthetic graphite fabrication technologies.

Graphite is a high-value material with application in many industries. Currently, oil coke is used as the main precursor material in the obtaining synthetic graphite [8]. Cameán and Garcia [9] investigated experimentally the possibility of using carbon concentrates from coal ash in order to obtain high grade graphite used in lithium ion batteries anodes. Several concentration techniques were tested resulting in samples with unburned carbon concentration ranging from 54% to 78%. The graphite was obtained through a of high temperature treatment in an electrical furnace under argon flow. The Li-Ion batteries fabricated using graphite as anode material showed good cycling behavior with no significant modifications after 50 cycles and low irreversible charge.

Synthesis of graphite from BA containing unburned carbon is a relatively new and little investigated recycling direction for BA.

The key process to achieve synthesis of graphite is separation of the carbon present in the BA which can be then used as raw material for graphitization technologies.

BA with very high content of unburned organic matter has more complex and highly efficient recycling options. Bartoňová et al [2] investigated the technical possibilities of unburned carbon co-combustion resulting from lignite combustion in conventional boilers. Three unburned carbon fractions were obtained by means of dimensional sorting (sieving), B08, B10 and B15. The experiments demonstrated that it was feasible to recycle the smallest fraction of unburned carbon (B08) and co-combust it with the main fuel (lignite). Larger fractions (B10 and B15) have the potential to be used as raw material for fabrication of briquettes or pellets, or, alternatively, activated carbon for flue gas purification.

Co-combustion has been presented as an interesting option considered in the study cited above, having the potential to turn BA into FA. The extent to which unburned carbon co-combustion influences the combustion process (ignition, flame stability, fuel burnout) emissions (SO_2 and NO_x), slagging and fouling potential has been investigated. It was reported that up to 40% unburned carbon do not influence significantly the overall performance of the boiler.

BA is definitely not suitable for construction materials (especially if meant to be subject to significant mechanical stress). BA has though the potential to improve some characteristics of concretes used in special applications. Agriz et al [10] investigated natural chloride diffusion and chloride migration, as well as electrical resistivity in concrete obtained by adding various percentages of BA to Portand cement. It was reported that concrete types prepared with 25% of coal BA result in lower migration and diffusion coefficients (Steady-State Chloride Diffusion Coefficient 0.98E-12 and Effective Chloride Diffusion Coefficient 0.42E-12) compared to concretes with 10% BA (4.12x-12 and 1.33E-12 respectively). Rybaka et al [11] found that that BA as additive for concrete used for road construction is not recommended unless the unburned carbon content is lower than a given limit.

Unburned carbon in the composition of the BA limits its applicability as additive for concrete. Various techniques to eliminate or reduce the organic matter in the BA to make it suitable as additive for cement in preparation of concretes were investigated. Kurama and Kaya [1] investigated three methods to reduce the amount of unburned carbon from BA: particle size classification, heavy medium separation and electrostatic separation. A non-uniform particle size distribution was found with 31.49% (wt) particles larger than 2.36 mm, 26.96% particles from 0.600 to 2.000 mm and 26.98% particles from 0.212 mm to 0.600. Other particle dimensions percentage did not exceed 4%. Crushing-screening pre-treatment method was used. It was found to provide a more advanced reduction of the unburned carbon compared to heavy medium separation and electrostatic separation. The treated BA was used as replacement for 10% Portland cement. It was found that the concrete obtained has improved its compressive strength from 42.65 N/mm^2 to 45.1 N/mm^2.

Separation of the unburned carbon from the BA must be achieved through techniques that meet several requirements in addition to the separation degree. Advanced chemical treatments with adequate reagents and equipment can result in virtually complete separation. However, such methods are not always industrially-feasible due to large consumption of reagents and expensive equipment. Flotation is a simple and cost-effective technique which can be applied for unburned coal separation with satisfactory results. Zhang and Honaker [12] studied flotation in order to separate unburned organic matter from FA. It was found that the flotation behavior is an effective method to separate unburned carbon due to the fact that porous structures in coarse carbon results in different flotation behavior.

The chemical composition of BA is by far more complex than that of FA. The factors that contribute to such complexity are:

- Presence of unburned carbon
- Formation process
- Exposure to different combustion processes

The degree to which BA can be recycled depends largely on separation techniques that can isolate the fractions with the desired properties. BA contains iron bound in different forms (oxides mainly) in the BA. The presence of ferromagnetic material allows magnetic separation, a method that can be applied in conjunction with other separation methods in order to screen out various fractions. Han et al [13] investigated magnetic separation as a method to recover ferromagnetic material from BA. Several BA samples from a ash dump site were used. The samples were subject to drying due to the high water content (57.78%) followed by grain size separation (standard sieving, 1.18 mm, 0.6 mm, 0.3 mm, 0.15 mm and 0.075 mm). With a magnetic force adjusted at 200 Gauss, it was found that the highest magnetic retention rate is reached in the case of the fraction 0.075 – 0.15 mm. The mechanism of ferrous materials formation is complex and not completely understood. It is known that in case of large particle size BA, ferrous materials binds to unburned carbon during combustion. Thus, separation of such ferromagnetic material from unburned carbon by magnetic separator becomes difficult. It has to be considered as well that ferrous material in small particle size exists independently, separated from other materials, rendering magnetic separation an efficient method for such particles.

The presence of unburned coal in the BA is related to the presence of coarse coal particles, although such particles have small mass fraction. Particles larger than 140 μm have a contribution of 70% on total UBC although fractional mass ratio of these particles is about 20% [11].

The particle size distribution (PSD) of unburned carbon present in the BA is a critical factor in further BA processing technologies.

The main organic component of BA is unburned carbon. The mechanisms of occurrence and chemical and physical properties have been reviewed by Bartoňová [4]. The main factors that influence the particle size and PSD were pointed out. Demir et al [14] performed a comprehensive analysis of BA from Tuncbilek power plant (Turkey). Low grade coal is being used at this power plant with fractions of lignitic coal with ash content 48.6%. PSD, weight distribution and unburned carbon content distribution on particle size ranges were the parameters investigated. It was found that the largest particle (32.15%) mass falls in the size interval <75 μm followed by 31.34% in the interval (75-106) μm. The most part of the unburned carbon is found also in the size interval <75 μm.

2. METHODOLOGY

BA key properties for defining a recycling strategy are the following:

- Quantitative PSD;
- PSD standard deviation;
- PSD skewness (left or right);
- PSD kurtosis;
- Unburned carbon content ;
- Presence of ferromagnetic material;
- Contamination over time in open ash-dumps exposed to environmental factors.

Given the number of factors that influence the characteristics of BA make the recycling of BA a complex challenge. A thorough literature review showed research in the direction of partial BA recycling exists but no complete recycling has been reported.

An attempt to achieve full recycling of BA is reported in [15], where the focus was a recycling direction for which scarce results have been reported in the literature: obtaining synthetic graphite by means of processing the BA.

Feasibility studies [16] were conducted on the ash evacuation process flow at a coal-fired power plant from Romania in order to estimate the potential of the technology to achieve the required economic indicators. It was shown that the relatively high content of unburned carbon present in the BA make it a suitable raw material for recovery of unburned carbon for synthetic graphite manufacturing. Full recycling of BA requires though processing of by-products resulted from primary graphite extraction process. Reports show that a relatively small percentage (approximately 16%) of BA (the fraction with high unburned carbon content) that can be directed to the graphitization process. The overall efficiency of the graphitization process flow is approximately 10% of the total BA. Integration of the graphitization process into a more complex and comprehensive technology can lead to complete recycling of BA. Specialized process flows must be defined for each type of by-product.

The main objective of the study is to concentrate the char from the BA to over 50% under low-environmental impact conditions. Environmental impact constraint, limits to three the number of procedures for char concentration:

- Dimensional sorting (sieving),
- Magnetic separation,
- Gravimetric separation (flotation in water).

Laboratory-scale tests demonstrated that each of these concentration procedures has its own efficiency limits in terms of maximum concentration that can be achieved.

Obtaining a higher purity of residual carbon required several combinations of the concentration methods allowed.

Eight coal concentration procedures were studied, as follows:

1. Grinding followed by sieving;
2. Gravimetric separation;
3. Magnetic separation;
4. Magnetic separation followed by grinding, followed by sieving;
5. Magnetic separation stage I, followed by grinding and sieving followed by magnetic separation stage II;
6. Grinding and sieving followed by magnetic separation;
7. Gravimetric separation followed by magnetic separation;
8. Gravimetric separation, followed by magnetic separation followed by grinding and sieving.

The main product for each procedure is the concentrated carbon graphitization precursor (CCGP), which is further used in the actual graphite obtaining technology. The fixed carbon content (FCC) in the CCGP exceeded 60% in two cases - procedures 7 and 8, and it ranged between 29.42% and 43.16% in the other procedures – Figure. 1.

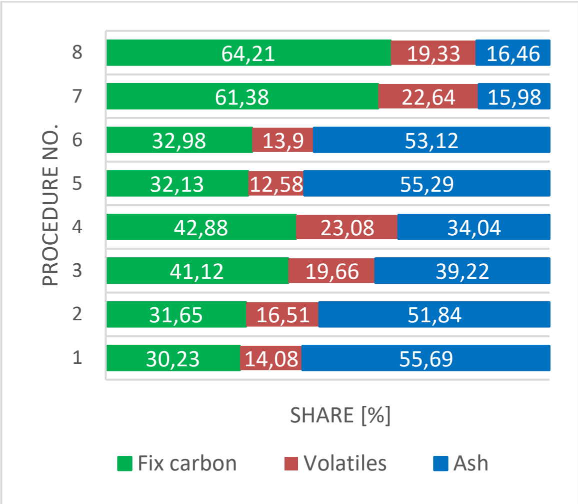

Figure 1. FCC percentage in CCGP

The next approach in order to achieve a higher efficiency in terms of CCGP content was carbonization at high temperature after volatile matter removal from the samples. The FCC percentage showed a significant increase, 78%, for procedures 7 and 8 as presented in Figure 2.

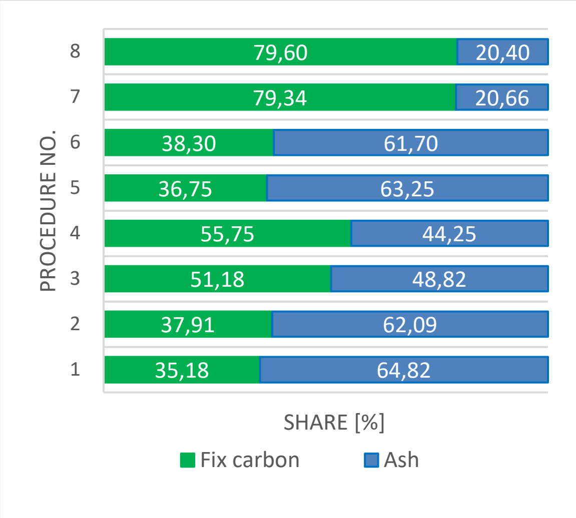

Figure 2. FCC value in CCGP following high temperature carbonization

With approximately equal values of the efficiency, procedures 7 and 8 both qualify for further integration. Procedure 7 was selected due to its simplicity compared to procedure 8. Procedure 8 assumes the use of the resulting 7 CCGP which should be grinded and passed through sieve. Other disadvantages of procedure 8 are: extra energy consumption for grinding and sieving, and reducing the amount of final product, the mass breakdown weight (MBW) being 46.07% .

Laboratory tests were carried out according to the specific standards

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