An Integrative Process and Technology for Reclamation of Ash Landfill with Complete Recycling of Ash

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Abstract: Ash dump sites – landfills – contain an aqueous mixture of bottom ash and fly ash 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. A process and technology is proposed 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 has been developed with the purpose of obtaining synthetic graphite. In order to achieve full recycling of the ash landfill content, various secondary waste materials resulting from separation and concentration phases of the process flow must be further processed and sorted in order to ensure properties that guarantee recyclability. The process flow presented incorporates the graphitization process flow in such way that all secondary waste fractions can be recycled in various directions.

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

1 Introduction

1.1 BA – Properties, Mechanisms of Formation and Issues

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 (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

A number of complex recycling technologies have been developed for BA involving chemical pretreatment 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 [1], [2]. 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 [3].

1.2 Graphite

Graphite is a crystalline allotrope of carbon with applicability in many hi-tech industries [4]. 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 [5]. Cameán and Garcia [6] investigated experimentally the possibility of using carbon concentrates from coal ash in order to obtain high grade graphite used in lithium ion batteries anodes. 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.

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 [7] 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.

The main organic component of BA is unburned carbon. The mechanisms of occurrence and chemical and physical properties have been reviewed by Bartoňová [3]. The main factors that influence the particle size and PSD were pointed out. Demir et al [8] 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 Obtaining Synthetic Graphite by Means of BA Recycling

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 [9], 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 [10] 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 [11] 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.

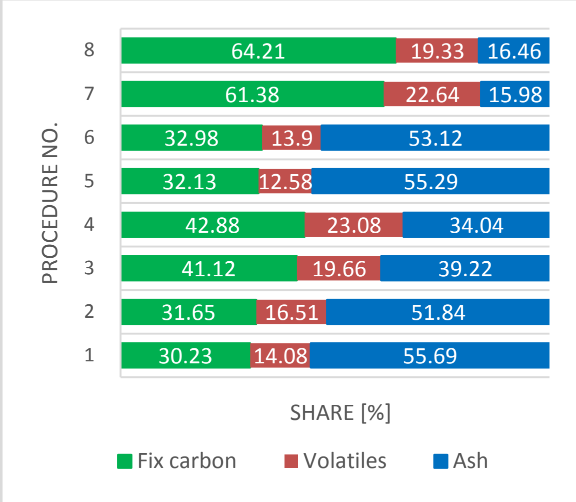

Figure 1. FCC percentage in CCGP

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 under according to the Romanian standards.

3 Complete Recycling Process Flow Description

A process flow has been defined in order to achieve complete recycling of BA The ash enters the process flow after the evacuation from the boiler into the main collector. The most significant part of the unburned carbon is present in the grain size fractions larger than 0.5 mm, as the elemental analysis of the raw BA revealed. Consequently, the primary separation process will extract the fraction with grain size >0.5 mm. Although the content of unburned carbon is high in this fraction, it accounts for 16.75 % only from the total amount of raw BA in terms of mass. The separation mechanism employed is the difference between water floatability properties of the two fractions. The efficiency of the separation process is defined in terms of mass percentage that fall in the desired grain size range:

- For grain size fraction >0.5 mm, 16,75 %
- For grain size fraction <0.5 mm, 83.25 %

The process flow will split from this point as shown in Figure 2 and described in detail in the next sections.

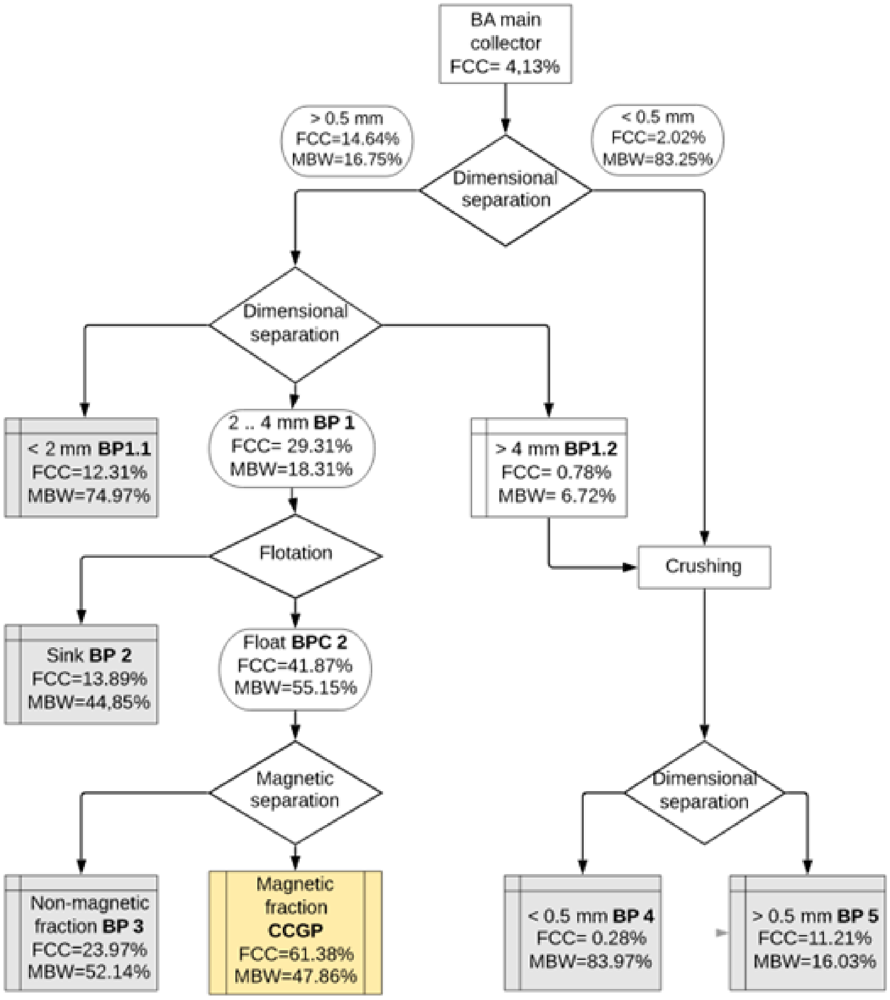

Figure 2. Overall process flow for complete BA recycling

3.1 Graphitization Process Flow

3.1.1 Dimensional Separation

Pre-processing stage of the graphitization process flow requires dimensional sorting of the BA particles using the conventional sieving procedure. This stage is required since elemental analysis reveals that the highest carbon content can be found in particles in the range 2-4 mm. The sieving process will separate the fraction 2-4 mm denoted BP1 (1^{st} stage concentrated) and will produce two by-products denoted BP1.1 and BP1.2, as shown in Table 2.

Table 2. By-products resulting from dimensional separation

Size range	< 2.0 mm	2.0 – 4.0 mm	>4.0 mm
FCC [%]	12.31	**29.31**	0.78
MBW [%]	74.97	18.31	6.72
Notation	BP1.1	BP 1	BP 1.2

3.1.2 Flotation

BP1 fraction will undergo further concentration being subject to water flotation. Significant density difference of the particles with high carbon content makes this stage possible. Flotation will produce the by-products presented in Table 3.

Table 3. Float/sink separation

Floatability	Float	Sink
FCC [%]	**41.87**	13.89
MBW [%]	55.15	44.85
Notation	BPC.2	BP 2

3.1.3.Magnetic Separation

By-product BP.C.2 will be subject to magnetic separation in order to screen out the fraction containing ferromagnetic material. Ferromagnetic material absence in the CCGP is a critical property for the graphitization process. The final results are presented in Table 4.

The graphitization process flow will thus produce the final concentrated fraction CCGP which will be used in the actual graphitization process and four by-products, BP 1.1, BP 1.2, BP 2 and BP 3.

Table 4. Magnetic separation: CCGP

Magnetic properties	Non-magnetic	Magnetic
FCC [%]	61.38	23.97
MBW [%]	47.86	52.14
Notation	CCGP	BP3

3.2 By-Products Recycling

The separation process - aiming to obtain CCGP - will produce the dominant fraction (<0.5 mm) in terms of mass representing a by-product of the main graphitization process. Values of the unburned carbon content suggest that this fraction can be mixed with BP 1.2 and further processed. The main difference between the two by-products is the PSD. In order to level out the PSD difference, BP 1.2 requires processing by milling. The non-uniform carbon distribution by particle size in this new mix allows separation of the fraction with high unburned carbon content. Thus, a relatively high unburned carbon content by-product with grain size >0.5 mm denoted BP 5 will be separated from the mix, as shown in Table 5.

Table 5. Dimensional separation

Dimensional separation	<0.5 mm	>0.5 mm
FCC [%]	0.28	11.21
MBW [%]	83.97	16.03
Notation	BP4	BP5

4 Recycling Options for the By-Products

The objective of the study was to obtain CCGP - a precursor for the graphitization process. A number of five by-products will result. The by-products differ in the PSD and the unburned carbon content.

The by-products can be categorized based on the unburned carbon content, as follows:

- A. High unburned carbon content: BP 3
- B. Average unburned carbon content: BP 1.1, BP 2 and BP 5
- C. Low unburned carbon content: BP 4

As ash is traditionally used in the construction materials industry, the first consideration is given to this usage. Due to the high organic matter content, A type by-products are not suitable for construction materials. B-type by-products can be used for refractory, thermo-insulating materials. In this case, unburned carbon can replace other conventional pore-former materials such as perlite, diatomite, haydite, lightweight chamotte, lightweight mullite, bubble alumina [12].

Pores presence in thermally insulating material is a key condition for achieving the desired thermo-physical properties of the finite product. Pore-formation results in a low thermal conductivity for thermally insulating materials. Pore-former agents must have characteristics adequate to the application.

Currently, the following techniques are employed to achieve thermal insulation properties through pore formation for construction elements:

- sawdust addition [13] for refractory construction elements with high thermal insulation
- expandable polystyrene [12] for insulating bricks

Another pore-forming agent is wood ash. It creates a more complex reaction during the heat treatment of the element with several factors influencing the pore density [14]. The presence of unburned carbon in the secondary waste BP1.1, BP2 and BP4 suggest that the unburned carbon can be employed as pore-formation agent in manufacturing of lightweight insulating construction elements [15]. High temperature heat treatment of the construction element will cause combustion and pyrolysis of the unburned carbon and will create a porous structure, which will contribute to increasing significantly the thermal insulation properties. On the other hand, a porous structure will lead to less satisfactory mechanical strength properties. The directions of use for recycling the by products resulting during various stages of the process flow are presented in Table 6.

Table 6. By-products recycling options

SW	FCC [%]	Recycling options
BP1.1	12.31	Additive for lightweight construction materials [15]
BP 2	13.89	
BP 5	11.21	
BP 3	23.97	Briquettes [14], [12] Co-combustion [2]
BP 4	0.28	Substituent for concrete aggregates [16]

5 Conclusions

Complete recycling of BA is a challenging process due to the inconstant nature of the physical and chemical properties. Existing recycling technologies employ usually one specific property of the BA resulting in a small recycling percentage.

A complex recycling process flow targeted on several recycling directions with the purpose of achieving complete recycling of BA deposited in ash landfills is presented. The principle on which the process flow is based is fractions separation with the purpose of obtaining uniform properties (either physical or chemical). Uniform distribution of properties renders each fraction suitable for a specific recycling direction and use.

The primary purpose of the process flow presented is obtaining synthetic graphite from unburned carbon present in the BA. The by-products resulting from various phases are further processed, sorted and mixed based on similarity of chemical and physical properties. A number of five by-products fractions with little dispersion of the chemical and physical properties are finally obtained and three recycling directions are identified for each, thus achieving full recycling of BA.

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