

NEW RECYCLING DIRECTIONS FOR ASH RESULTING FROM LOW-GRADE COAL DEPOSITED IN ASH DUMP SITE

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ABSTRACT: Low-grade coal (lignite or brown coal) produces a significant impact upon the environment through multiple vectors (during mining, combustion and disposal and treatment of combustion by-products). With a power generation industry in which coal has still a significant weight a lot of research effort has been dedicated to identifying solutions to mitigate the impact upon the environment and place coal on the roadmap of circular economy. The paper discusses comparatively and present research data on two directions of recycling ash resulting from lignite combustion in Romania: (i) re-burning in mixture with coal in adequate proportions (due to the high content of unburned carbon, this has been proven to be possible) and (ii) obtaining highly valued raw materials for various industrial uses, such as graphite. Although completely different, each of the two recycling directions has particular advantages over the other one. The key property of the ash that both technologies exploit is the content of organic matter in the form of unburned carbon. The paper describes the two technologies, particular conditions for their applicability supported by experimental data and presents, comparatively, the advantages and disadvantages. A multi-criteria analysis is performed in order to point out the main differences between the two technologies. It is emphasized that a general solution does not exist and the most advantageous recycling direction depends on particular factors.

KEY WORDS: ash, unburned carbon, recycling, lignite, graphite

1. INTRODUCTION

Coal-based power generation has currently reached a critical point in its long existence. Although industrial revolution and the economic development of mankind over the last 200 years is closely related to coal, nowadays it is blamed for climate change effects observed over the last decades. While a cause-effect relationship between coal utilization caused emissions and climate change effects is difficult to establish, it is beyond doubt that CO₂ emissions increase constantly [1] with a variable rate and some fluctuations caused by natural economic cycles. However, the overall positive balance of carbon emissions is structured unevenly: while Europe has put significant effort and investment into carbon mitigation, Asia and America continue to develop facilities based on coal, constantly increasing their carbon

footprint. The development of renewables, which become increasingly competitive in terms of economic efficiency, seem though to curb the growth trend of coal industry [2].

The effort to reduce coal usage is considerably suppressed by increased demand for electricity in regions like South East Asia [3]. A comprehensive study on the coal future in the context of carbon footprint mitigation has been carried out by Pudasainee et al [4]. It has been shown that it simply not possible to go carbon-free in a time horizon of ten years or less.

One of the most impacting issues related to use of low-grade coal such as lignite is disposal of ash. The ash content of low-grade coal varies from 10 to 50%. In the context of the low content of carbon, it follows that large amounts of lignite must be burned in order to obtain the same amount of energy compared to high-grade coal, resulting in much higher

amounts of ash generated from coal compared to high-grade coal or hydro-carbons. Ash resulting from coal combustion has been until not long ago a waste material. Coal ash is a complex mixture consisting mainly of silica, aluminium, iron and calcium oxides. Several ash classes have been defined based on the CaO content, which is a key component in integrating ash into construction materials. In fact, recycling ash for construction material industry has been the first direction of use. Ash properties are heterogeneous and depend considerably on the ash type. In power generation industry, the most important categorizing criteria for ash, is the source: fly ash (FA) retained mostly by the electrostatic precipitators and bottom ash (BA) collected from the inferior part of the furnace. Cruceru et al [5] presented a comprehensive differential analysis of the two ash types. It was shown that FA has multiple recycling directions (however, far from 100% recyclability). According to the American Coal Ash Association (ACAA) the 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 [6]. The key property that differentiates BA from FA is the content of organic matter. The presence of organic matter has as the main cause incomplete combustion of coal particles in the furnace. Combustion dynamics is a complex process with many factors influencing it and not completely understood. However, several key factors that influence the content and the chemical composition of the unburned matter:

I. Coal quality. By this several properties are considered:

- a. the coal type
- b. the contamination with sterile material during the mining process
- c. the content of humidity.

II. The wear of the coal mills and the number of coal mills in operation. If coal mills do not produce coal particles small enough to undergo complete combustion in the furnace, incomplete combustion will occur as these particles do not spend enough time to ignite and burn completely. These

particles fall in the furnace ash-removal system and are mixed with the BA

III. The load of the boiler. Operation at partial loads results in lower temperatures in the furnace and throughout the flue gas ducts. As a result, drying of coal in the coal mills (performed with the help of exhaust gas) is incomplete and coal particles, even if they have appropriate size, burn only partially before they fall in the furnace ash-removal system

IV. In case of ash dumps where FA mixed with BA was deposited for very long time contamination of ash from vegetation occur

BA has a rather narrow range of recycling directions [7]. The main reasons that limit the possibilities of recycling are the content of unburned (or partially burned) coal, content of slag (molten ash due to the high temperature in the furnace) and a non-uniform particle size distribution (PSD). Trifunovic et al [8], evaluated the potential of recyclability of BA for road pavement materials. Four material samples with different contents of unburned carbon were studied as follows: raw bottom ash, two size fractions obtained from it (2–5 and <2mm) and bottom ash treated by the “float–sink” method. The content of unburned carbon was determined by simultaneous DTA/TGA. It was found that ash sorts with low carbon content and particle size less than 2 mm had adequate properties for road pavement materials.

Although BA is inferior quantitatively to FA, the absolute quantity is however, large, due to the large amount of coal. The most problematic type of ash is the one collected over time in ash dumps. It consists of a mixture of FA and BA with varying humidity content.

CASE STUDY – VALEA CEPLEA ASH DUMP

Valea Ceplea (Romania) ash dump is an artificial ash collection pond built in the Oltenia lignite basin (South-West of Romania) approximately 40 years ago. The ash dump has reached its maximum capacity several years ago and has been closed. The total surface area of the ash dump at the moment of closure was approximately 52.64

hectares with an estimate volume of 13 mil cubic meters. Valea Ceplea ash dump has been used to deposit the total ash (BA+FA) from a neighbouring coal-fired power plant (Turceni). The transportation method was pumping in a diluted solution with water using an ash/water ratio 10/1.

The first attempt to recycle the ash contained in Valea Ceplea ash dump was a traditional direction, which is raw material for fabrication of construction materials [9]. It was found that inadequate properties for the construction materials obtained resulted, rendering them commercially unsuitable. Preliminary studies demonstrated that a high content of organic matter was present in the ash contained in the Valea Ceplea ash dump, being the main cause of causing deterioration of the mechanical properties of the finite products. A complex bi-directional study attempted to identify and validate possible recycling directions for the ash deposited in the Valea Ceplea ash dump.

I. Ash re-burning in mixture with coal in the power plant boilers.

This requires several operations:

- a. Collecting ash from the ash dump
- b. Transportation of the ash to the power plant
- c. Mixing of ash and coal, followed by injection in the furnace

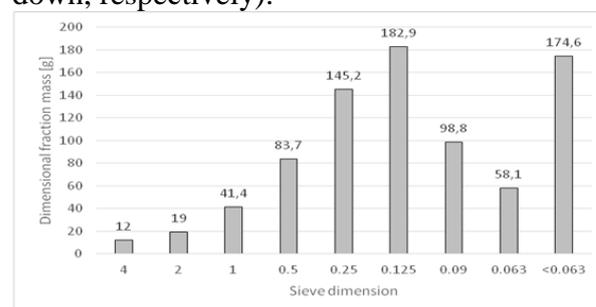
This technology has the advantage that coal particles contained in ash will undergo complete combustion. The advantage of the supplementary heat released by combustion of such particles is less important than the fact that the resulting ash will have a content of unburned carbon much lower, rendering it feasible for recycling in the traditional directions (such as construction materials).

These operations pose however, several problems. The most important is the energy consumption required to transport large amounts of ash from the ash dump to the power plant. Most of the ash, however, consists of FA with no content of organic matter. It follows that a significant amount of energy is spent to transport sterile material. The next question the study had to answer

was how would it be possible to separate the ash fraction containing unburned carbon from the rest of the ash. Given the combustion mechanisms that result in the presence of unburned carbon in the ash, it was hypothesized that the unburned carbon could be concentrated in large ash particles. Consequently, a dimensional analysis of the ash particles was carried out in order to identify the PSD function. The procedure applied was as follows:

- a. Ash samples were allowed to dry for 24 h at the room temperature in order to release natural humidity absorbed in the ash dump
- b. Complete removal of humidity was carried out in a drying chamber at 105 °C for 24 h. This was required in order to eliminate the superficial tension between ash particles that could result in adhesion of small particles to large ones
- c. Mechanical sieving was carried out employing a sieve shaker (Retsch AS200) with a sieving time of 5 minutes. The maximum number of sieves (nine) were used, with the following dimensions: 4 mm and higher, 2-4mm, 1-2 mm, 0.500-1 mm, 0.250-0.500 mm, 0.125-0.250 mm, 0.090-0.125 mm, 0.063-0.090 mm and 0.063 mm and less.

The raw ash PSD and the cumulative PSD function are presented in Figure 1 (top and down, respectively).



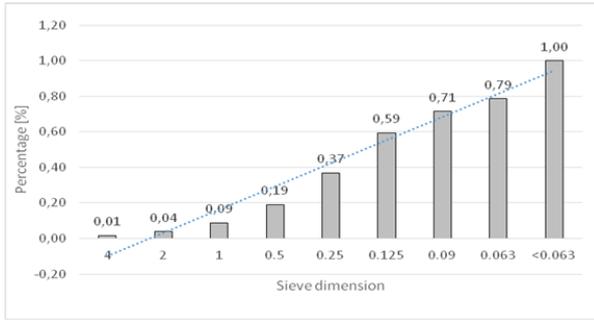


Figure 1. Ash particles PSD function (top) and cumulative PSD (bottom)

Several conclusions can be drawn from the plot presented in Figure 1:

- The probability function is not a uniform one, however from 4 mm down to 0.125 mm a uniform trend resembling a normal distribution can be observed. From 0.125 mm to 0.063 mm the trend is disrupted by the large value of the <0.063 mm percentage.
- The percentage of particles with size less than 0.063 mm is approximately 21%. This dimensional sort is specific to FA and is unlikely to contain unburned carbon
- Approximately 52% of the particles fall into the size range 0.09 – 0.25 mm.

The next phase of the study was to investigate the combustion characteristics of various ash dimensional sorts. While the content of unburned carbon in the ash is a good metric of combustion quality, it has little relevance when it comes to re-burning. Even though some ash dimensional sorts could contain carbon they may not have adequate combustion characteristics to ignite and burn completely once re-introduced in the boiler furnace. Consequently, another method to estimate the combustion capacity has been considered, which is determination of the calorific value using a calorimetric bomb. The device used in this study was an E2K Oxygen Bomb Calorimetric System, presented in Figure 2.



Figure 2. E2K Oxygen Bomb Calorimetric System

The E2K Oxygen Bomb Calorimetric System works on the basic principle: the sample is placed in a calorimetric vessel in a highly oxygen concentrated atmosphere at 30 bars. The system ignites the sample by means of a textile wick then it monitors the temperature increase caused by the combustion of the sample. The whole process is automated and computerized and the final calorific value is displayed on the bomb monitor. In case of a sample that does not ignite (due to its own incapacity to burn or inappropriate contact with the wick) the bomb monitor displays a message indicating that no combustion process was detected.

All nine dimensional sorts were subject to calorific value determination in order not only to determine the calorific value but most importantly, to estimate the ignition characteristics. The results are presented in Figure 3.

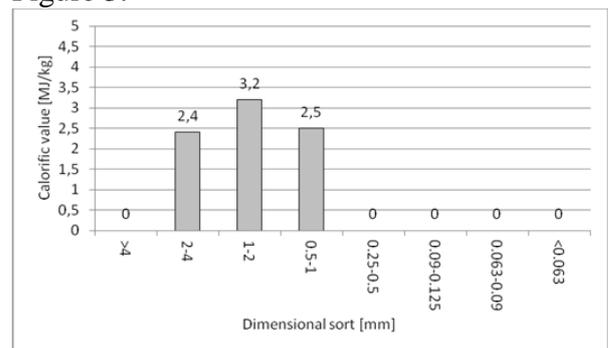


Figure 3. Ash calorific value by dimensional sorts

It was found that only three dimensional sorts have ignition and combustion properties with calorific values indicated in Figure 3. No ignition occurred in case of the other dimensional sorts.

The calorific values presented in Figure 3 are relatively low (compared to lignite, for which calorific value ranges from 6 to 10 MJ/kg).

However, in mixture with lignite it can burn properly eliminating completely the unburned carbon. In fact, re-burning of ash is applied at the coal-fired power plant CET Govora (Romania) with the difference that bottom ash is directly re-directed to the burners. This has a significant advantage, saving the expenditures associated to the transportation to and from the ash dump (which is not the case of the present study). Commercial implementation of the technology described requires the following phases:

- I. Raw ash drying
- II. Separation of ash particles by size (only 0.5 – 2 mm sorts are of interest, accounting for roughly 18% of the total ash)
- III. Transport to the power plant

The overall efficiency economic efficiency of the process is considerably reduced by the energy consumption required for phases I and III.

A secondary positive effect results from separation of particles is that the fractions excluded from re-burning can be used in other recycling directions.

Although no major economic benefit can be expected from ash re-burning, it can be the only feasible way to close the ash dump site and reclaim the area currently occupied

- II. Separation of unburned carbon and complex processing in order to obtain synthetic graphite followed by other separation procedures aiming at complete recycling of the ash contained in the ash dump

Graphite (Figure 4) – the hexagonal crystalline form of carbon - is a natural resource with usage in many industries. However, the crystalline morphology of natural graphite is that of a tri-dimensional granular structure, which limits considerably its applicability. Naturally occurring graphite is frequently associated with other minerals, such as quartz, calcite, micas and tourmaline.



Figure 4. Open-pit graphite mine

Obtaining synthetic graphite from coal ash is much more ambitious and complex and requires more phases, significant cost for equipment and energy consumption. A full economic analysis is required in order to establish the economic potential. A complex multi-objective study aimed to identifying technical feasibility and economic performance of obtaining graphite from ash with high content of unburned carbon (from Valea Ceplea ash dump) has been presented in [10]. Preliminary theoretical studies indicated that processing of ash by means of several physical and chemical processes can result in rising the carbon concentration in ash to 50% or more. However, strict regulations regarding environmental impact were set, which limited the applicable sorting and concentrating procedures to the following types: (i) dimensional sorting (mechanical sieving), (ii) magnetic separation, (iii) gravimetric separation by means of water floatability characteristics and (iv) mechanical grinding.

Obtaining synthetic graphite requires as a prerequisite a high concentration of residual carbon. The study [10] considered a number of eight stages of concentration in order to achieve the desired carbon concentration:

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

The main product for each procedure is the concentrated carbon graphitization precursor (CCGP), which represents the raw material for the actual graphitization procedure.

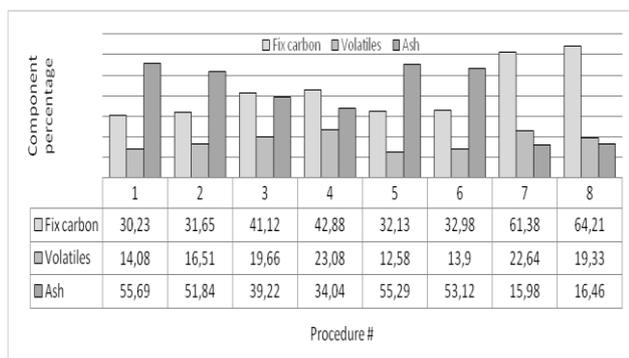


Figure 5. Fixed carbon content and the other components resulting from the eight procedures described above

Procedures 7 and 8 produced CCGP with fixed carbon concentration higher than 60%. In order to increase even further this value, volatile matter was removed from samples prior to application of the same set of procedures as described above. The results are presented in Figure 6 and demonstrate that same procedures, 7 and 8, have the highest

efficiency in terms of fixed carbon concentration.

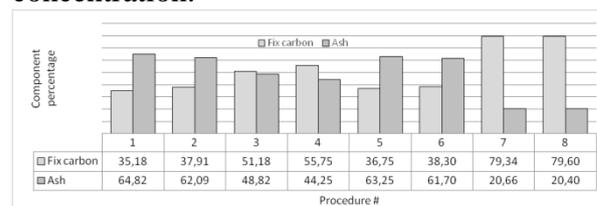


Figure 6. Fixed carbon and ash content in CCGP resulting from the eight procedures, after volatile matter removal

Elemental analysis demonstrated that the highest carbon content was found in the range 0.25 -4 mm (29.31% fixed carbon content), which is consistent with the results obtained in the case of the first recycling direction (re-burning), which showed that the only fraction with combustion characteristics is 0.5 - 4 mm. As a result, a pre-processing phase was introduced before the actual graphitization process in order to separate this particular ash sort for further processing. Separation was carried out by conventional mechanical sieving and the resulting concentrated sort (2-4 mm, with 29.31% fixed carbon content) was further subject to flotation in water. Separation based on floatability characteristics resulted in a concentrated fraction with 41.87% fixed carbon content (floating fraction). The next stage was removal of the fraction containing ferromagnetic material obtaining the final product, highly concentrated fixed carbon fraction (61.38% fixed carbon content), shown in Figure 7.



Figure 7. Highly concentrated fraction (61.38% fixed carbon content)

2. MULTI-CRITERIA DIFFERENTIAL ANALYSIS OF THE TWO RECYCLING DIRECTIONS

Both ash recycling technologies described in this paper rely on the same key property of ash, which is the content of unburned carbon. They are complimentary though (cannot be applied simultaneously), completely different in terms of objectives, complexity and implementation. A multi-criteria analysis is therefore necessary in order to offer a more general picture of the problem and facilitate the selection of one over the other. For each criteria a score from 1 (very unfavourable) to 5 (highly favourable) was assigned.

Criteria	Recycling direction		Observations
	Re-burnin g (I)	Graphitizati on (II)	
Overall degree of recyclability	2 (*)	5 (**)	(*) A relatively small fraction (18%) has combustion properties. Low unburned carbon fractions isolated through sieving have a reasonable recyclability potential. (**) Maximum score is awarded if recyclability directions are identified for secondary fractions.
Technology and process flow easy to implement	5	2 (*)	(*) If complete recyclability is aimed (see the criterion above), a very complex process flow must be designed in such way that recycling directions are identified for all secondary fractions.
Chemical reactants or additives with environmental impact	5	4 (*)	(*) Water is required for flotation phase. Waste water treatment must be considered, which counts as a penalty. No other reactants

			required to obtain the prime material for the actual graphitization process for any of the two procedures.
Energy efficiency	1 (*)	5 (**)	(*) Transport from the ash dump site to the power plant and humidity removal are energy-intensive processes resulting in a heavy penalty. (**) The whole process can be implemented in the vicinity of the ash dump site, eliminating the necessity of transportation.
Economic efficiency	1 (*)	5 (**)	(*) A relatively small fraction of ash can be processed by means of re-burning, removing the unburned carbon and rendering it appropriate for conventional recycling directions. Heavy penalty is applied. (**) Graphite is a prime material with high

			economic value. Maximum score is awarded.
Logistic and implementation effort and expenditures	5(*)	2(**)	(*) Drying and dimensional separation are the main processes. Simplicity of the process results in maximum score awarded. (**) Complex processes requiring special equipment and automation required. 3 points penalty applied.
Potential for standardization and applicability to other similar ash dump sites	4(*)	2(**)	(*) After determining combustion characteristics of ash deposited in any ash dump site the modifications to the process flow can be easily adapted. (**) The whole process flow must be designed for the particular value of the unburned carbon found in the raw ash. Difficult to adapt to new sites.
Flexibility and sensitivity to the key property – unburned	1(*)	4(**)	(*) Unburned carbon content is not enough to confer

carbon content			ignition properties. Although unburned carbon is present in several dimensional sorts, only three present ignition characteristics. Heavy penalty applied. (**) The process is capable to extract and concentrate carbon even from ash fractions with very low unburned carbon content. However, the efficiency of the process drops, resulting in a one point penalty.
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CONCLUSIONS

Two non-conventional recycling directions for ash deposited in ash dumps were proposed and analysed comparatively. Ash deposited in the ash dumps has special characteristics compared to FA and BA collected directly from the electrostatic precipitators and bottom of the furnace, respectively. Due to the high variability of physical and chemical properties, recycling this kind of ash is a complex challenge and on the other hand, no complete recycling can be achieved. The main characteristics that render ash deposited in ash dumps unsuitable for recycling are the content of unburned carbon and the non-uniform particle size distribution. There are few studies aiming at complete recycling and neutralizing closed ash dumps, which pose

serious environmental threats [11]. The present study offers two alternative approaches: (I) re-burning the fraction that has ignition characteristics and (II) successive separation and concentration in order to obtain raw material for obtaining synthetic graphite. The key factor that influences considerably implementation of both procedures is that the unburned carbon is concentrated in a narrow band of the PSD. However, procedure II can exploit a wider particle size range than procedure I (only three dimensional sorts have ignition characteristics).

A comprehensive multi-criteria comparative analysis was performed for the two procedures aiming to identify strengths and weak points of each procedure. A number of seven criteria were selected for the analysis and a score from 1 to 5 was assigned for each criterion. Since unburned carbon content and its distribution over the particle size range is a key element for both technologies, it was demonstrated that any of this technology does not have the potential to become an industrial standard, instead customized solutions must be tailored in each case.

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