Increasing the residual carbon content from bottom ash by particle size separation

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Abstract: - In response to recent demand increases caused by emerging technologies, the European Commission (EC) established the Raw Materials Initiative to limit the impact that material supply shortages may have on the European economy. Natural graphite was identified as exhibiting a high supply risk and high economic importance. The paper presents the first stage of a research project which aims to demonstrate, by a detailed fundamental and applied investigation, the technical feasibility to utilize the bottom ash solid carbonaceous residue (char) as a substitute for graphite based materials. The experimental results highlight that the char from bottom ash can be concentrated using simple physical technologies.

Key-Words: - bottom ash, carbonaceous solid residue, char, graphite, size analysis

1 Introduction

Worldwide efforts are continuing to trace various effective ways of recovery coal combustion by-products (CCP), such as fly ash, bottom ash, boiler slag, gypsum from desulfurization, and fluidized bed combustion spent bed material. Countries like the US, England, Poland, Spain and more recently China, being the most eloquent examples in this regards [1].

Using coal as primary fuel it is recognized to be one of the most economically advantageous methods for the production of electricity, especially for the large capacity power plants, as long as the coal is extracted from power units neighboring areas that significantly reduce transportation costs. In Oltenia region (Romania) this goal is achieved due to the huge lignite deposits, and the coal being mined in open pits, the Energy Complex Oltenia (CEO) holding in Oltenia Basin two of the largest Romanian power plants operating on coal.

The major drawback, also widely recognized, is the generation of large amounts of CPP which storage raises concerns in terms of economy and environment (e.g. a 330 MW pulverized fuel unit consumes around 1,000 ton/h of coal and generates ca. 400 tones of ash and slag at the same time). It is true that a part of these CPP include fly ash that may be reintroduced into the economic circuit by using it in cement industry. However, only 5-8% of the coal ash generated is used currently in Romania, the rest being stored in large landfills, usually built through major changes of the natural landscape and containing tens or even hundreds of millions tones of ash [2-6]. Therefore, several actions are being made in Romania in order to decrease the amount of CPP landfilled, and to raise awareness concerning the need to revise legal provisions (e.g. actually the use of ash in road construction is still banned, without distinguishing between fly ash (chemically active ash that can generate important secondary phenomena by hydration processes) and bottom ash (chemically inert and with physical-chemical properties very close to those of natural granular aggregates, like sand) [4-8].

2 Problem Formulation

The University "Constantin Brancusi " of Targu Jiu (UCB) is actively involved since 2011 in an research effort to detect efficient directions to recover the bottom ashes generated by thermal power plants, prevalent in the Oltenia industrial area, particularly for using them as alternative raw material in the construction industry [2-5]. Therefore, UCB continue and diversify the efforts to recover this CPP through its participation in the European Project CHARPHITE consortium under the scope of the "Third ERA-MIN Joint Call (2015) on Sustainable Supply of Raw Materials in Europe", and represents a natural continuation of the above research direction [9, 10].

The project's main goal is to use the carbonaceous solid residue (char) from Oltenia bottom ash as substitution material for natural graphite in cutting-edge energy technologies, such as catalysts for electrochemical reactions in cell batteries or hydrogen and oxygen production by water electrolysis [9].

The UCB's research team contribution in this project mainly aims the separation of the char from fresh and landfilled bottom ash, and further assessment and utilization of the "char-free" bottom ash.

3 Problem Solution

3.1. The Oltenia lignite

The most important lignite deposits in Romania are located in Oltenia region, across three counties: Gorj, Mehedinti and Valcea. The thickness of the lignite layers ranges from a few centimeters to several meters, either continuous or intercalated by other rocks.

In recent years, almost 90% of Romanian lignite was mined from the 16 large open pits from Oltenia by excavators with large rotor that, in the case of thin lignite layers, also excavate the tailings bordering of the respective layers, increasing the content of ash from lignite, and the amount of CPP generated [4, 5, 7].

The lignite mined from Oltenia region contains a relative high percentage of xylite formations with a specific configuration of woody fiber structure, having a soft and elastic consistency that is a "fingerprint" of the original plant tissue [4-6]. For these reasons, the coal mills cannot grind the entire flow of lignite to the required size, and large size particles pass the mills. These particles do not entirely burn in the combustion chamber and fall to the bottom, being found in the composition of bottom ash and slag discharged from the steam generator, in coke or semi-coke state [2, 3].

Depending on the efficiency of combustion installations from large power plants, carbonaceous solid residue (char) is found in the bottom ash generated by the coal fired boiler. Under certain conditions, the char with high recovery potential can be considered as a residual organic material source [9].

In this study landfilled bottom ash samples from Oltenia lignite burned at Turceni and Govora power plants (PPT, and PPG, respectively) were sieved in order to assess the size fractions to be used for char concentration. Complementary analysis (proximate, elemental and calorific value) of Oltenia lignite and respective bottom ash samples were also conducted for a better understanding of the bottom ash properties.

3.2 Oltenia lignite samples

For this study lignite samples were collected from three open pits: Jilt Nord, Berbesti and Rosia, and have been analyzed in terms of proximate, elemental and calorific value:

- The proximate analysis of the individual coal samples, including bottom ash size fractions, was determined following ISO and ASTM standards. The equipment used for these tests included: mechanical agate mortar, sieve shaker with a set metal sieves ranging from 0.063 to 4.0 mm, analytical balance to ensure accuracy in weighing 0.0002 g, heating laboratory oven with a precision of 1 °C and horizontal electric muffle oven (1000±20°C).
- The elemental analysis was performed on the basis of thermal conductivity detection using a VARIO model MICRO CUBE for determination of the content of carbon, hydrogen, nitrogen, sulfur (C, H, N, S).
- The calorific value was carried out in a calorimetric bomb MINIMUM SYSTEM e2k model, according to ASTM D5468-02, ISO 1928, DIN 51900 and BS1016 105 standards.

3.3 Oltenia lignite bottom ash samples

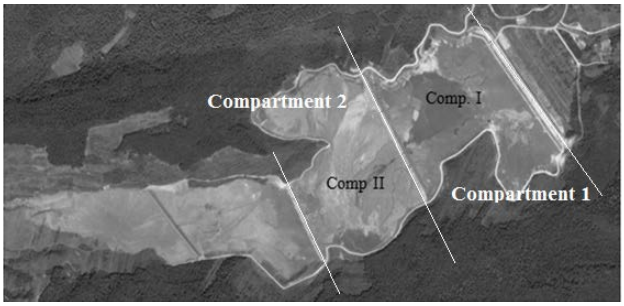
3.3.1 Studied area

The bottom ash samples studied where collected from the Ceplea Valley and Govora landfills (Fig.

1), and were generated in two distinct power plants Turceni (TPP) and Govora (GPP), respectively. The TPP is a conventional pulverized fuel PP, and is composed by four units, and each unit is equipped with six coal mills of 100 t/h of lignite and generating 1035 MW of steam; the GPP is a Combined Heat PP composed by three coal fired boilers, and each boiler is equipped with six coal mills of 44 t/h of lignite and generating 420 MW of steam.

3.3.2 Bottom ash sampling and characterization

Under the scope of project CHARPHITE 350 samples of bottom ash were collected from the Ceplea Valley and Govora landfills, and to have a wide coverage and thus a larger sample representativeness of each investigated deposit, the landfills were divided into areas with almost the same surface (Fig. 1), resulting in: 100 samples from Ceplea Valley compartment no. 1; 100 samples from Ceplea Valley compartment no. 2; 75 samples from Govora.



A

B

Fig. 1 Oltenia lignite bottom ash landfills:
(A) Ceplea Valley (Turceni PP);
(B) Govora (Govora PP).

Once collected the ash samples were immediately closed in plastic boxes, to preserve their original properties until the laboratory testing to determine the moisture concentration, bulk density and granulometry. Moisture was determined by drying the sample in an electric oven (150 liters capacity) at a temperature of 110 ^{o} C ± 2 ^{o} C by holding the maximum temperature for 10 hours.

Bulk densities (freely settled and tapped) and granulometry were determined after samples drying. The bulk density was determined following gravimetric method of STAS 1913/3-76 by weighting a known volume of bottom ash sample and using a gradated cylinder and an analytical balance.

To determine the bottom ash samples granulometry on a mass basis, a mechanical sieving trial was conducted using a set of standard R20 sieves with the following nominal sieve opening in mm: 4, 2; 1, 0.5, 0.25, 0.125, 0.09, and 0.063.

In order to assess the char characteristics of the samples from the Ceplea Valley – compartment 1 – the partner research team of University Politehnica Bucharest (UPB) [10] conducted a preliminary observation of the char under reflected light optical microscopy using glycerin immersion objectives with a combined magnification of ×350. In addition, the samples were sieved using a set of sieves (nominal sieve opening in mm: 3, 2; 1, 0.4, 0.2, 0.1), and conducted a proximate analysis (moisture, ash, volatile matter), which included also the Fixed carbon as a proxy to assess the char amount in these samples.

Preliminary trials were also conducted on one bottom ash sample from Ceplea Valley and another from Govora landfills to separate the char from 0.3 – 4 mm composite bottom ash through specific processes of dimensional selection (screening), blowing air jet (gravity separation) and floating in an aqueous medium.

4. Results and discussion

As expected the proximate analysis results of the Oltenia lignite samples (Table 1) show that these correspond to a high ash low rank-C coal (or Lignite C; according to ISO 11760-2005).

The average results of the bottom ash samples characterization are shown in Table 2. The bulk density values are relatively low, which is related with the inherent porosity and composition of several bottom ash components (e.g. the char in Fig. 2). However, the moisture content of the samples is very high, taking into account that they result from a combustion process, and that is explained by the fact that these bottom ashes are transported to the landfill as a slurry, and are exposed to rainfall.

Table 1. Results of the proximate, elemental, and calorific value of Oltenia lignite.

	Oltenia lignite open pits samples		
	Jilt Nord	Berbesti	Rosia
Proximate analysis (%)			
$M_{t, ar}$	42.10	42.48	44.51
Ash_{a}	22.95	24.96	17.52
Ash_{db}	39.59	43.38	31.58
Ultimate analysis (%)			
C	22.22	20.19	24.62
H	2.17	2.05	2.45
N	0.61	0.62	0.69
S_{t}	0.83	0.80	0.97
$O_{diff.}$	9.12	8.90	9.24
Calorific value (kcal/kg)			
HCV	2197	1987	2445
LCV	1859	1655	2080

M - moisture; t - total; ar - as received; db - dry basis; diff. - by difference; HCV - higher calorific value; LCV - lower heating value.

Table 2. Average results of moisture, bulk density and granulometry determination of bottom ash from Ceplea Valley and Govora landfils.

	Ceplea Valley		Govora
	Compart. 1	Compart. 2	
Moisture (%)	28.30	26.89	35.20
Bulk density [g/cm^3]			
Freely settled	0.66	0.75	0.52
Tapped	1.03	1.03	0.55
SNO (mm)	Mechanical sieving (wt.%)		
4	1.26	1.29	7.72
2	2.28	2.45	16.09
1	4.03	4.27	28.35
0.5	8.22	8.91	24.85
0.25	15.08	16.96	7.98
0.125	21.90	23.23	3.65
0.09	11.65	10.94	1.07
0.063	9.95	8.79	9.20
<0.063	25.64	22.46	1.08

SNO - Sieve nominal opening.

Meantime, the differences between the bottom ashes of Turceni and Govora are evident with regard to bulk density since the values for the bottom ash supplied by Govora PP are lower than the ones from Turceni PP.

The sieving trials (Table 2) show that the Ceplea Valley bottom ash is finer than the Govora's bottom ash (Fig. 2). The former has ca. 84 % of the mass passing the 0.5 mm sieve, while the latter only ca. 30% and presents a size distribution of the particles that is relatively close to a linear one (Fig. 2).

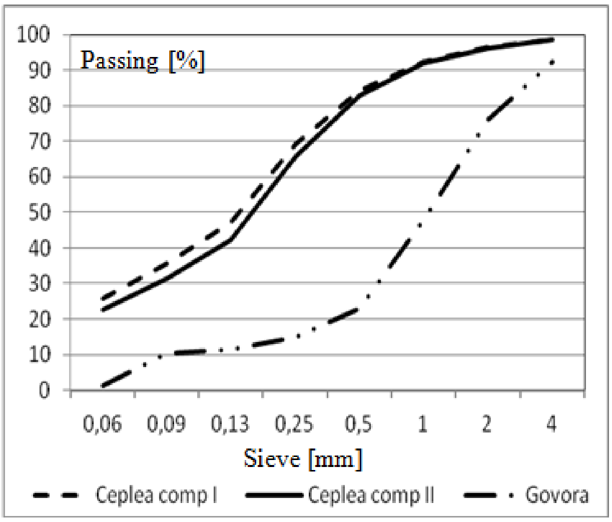


Fig. 2. Granulometric curves of the investigated ash samples

Therefore, it is clear that the characteristics of the bottom ash samples from Ceplea Valley compatment 1 and 2 are similar, while the Govora's bottom ash is different, which is attributed to the operating conditions since Turceni is a p.f. PP and Govora a CHPP, and these size differences have a major impact on further common applications of these bottom ashes.

The proximate analysis average results of 100 samples of bottom ash and size fractions from Ceplea Valley – compartment 1 – are shown in Table 3. The Fixed carbon (FC) results range from 0.06% to 11.75 % for the size fractions analyzed, and it is clear that the char must be concentrated in the > 0.4 mm size fractions since the FC concentration is much higher than in the lower size fractions and also in relation to the average value.

The explanation for this is due to the xylite fragments that, in the power plants boilers, are subjected only to a partial combustion due to their higher weight (caused by low milling capacity). Therefore, xylite remains in the coal powder suspension too short time for complete combustion, and end up in the bottom ashes.

Table 3. Proximate analysis: Ceplea Valley - compartment 1 - bottom ash: 100 samples average, and size fractions; bottom ash concentrated char samples from Turceni PP and Govora PP.

Grain size [mm]	Proximate analysis (%)			
	M_a	A_{db}	V_{db}	FC
2-3	3.57	74.66	9.65	11.75
1-2	4.26	72.76	8.52	15.18
0.4-1	3.13	81.42	6.59	8.16
0.2-0.4	1.63	90.78	4.03	1.31
0.1-0.2	1.47	93.34	2.68	0.14
< 0.1	1.62	92.66	3.43	0.06
100 samples average	4.08	93.49	4.89	1.63
Concentrated char samples				
Turceni	3.34	84.26	6.87	8.87
Govora	1.92	85.56	4.62	9.82

M_a moisture as received basis; db dry basis; A - ash;
V - volatile matter; FC – fixed carbon.

Examples of char and unburnt xylite identified in bottom ash samples of Turceni PP and Govora PP are shown in figure 3 micrographs.

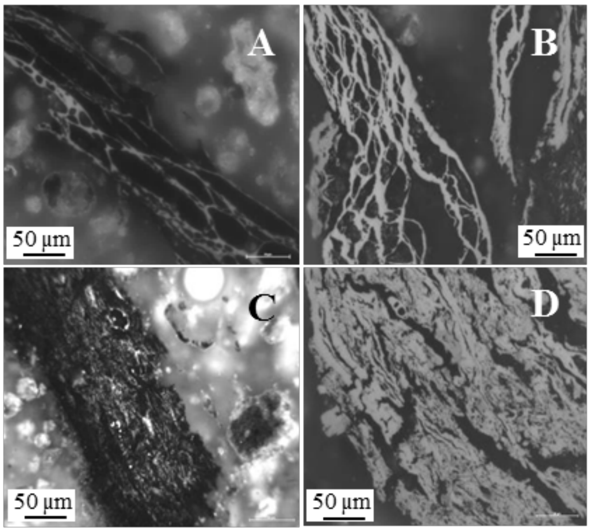


Fig. 3. Photomicrographs of carbonaceous residual carbon in Turceni (A, B, and D) and Govora (C) samples (reflected light microscopy, glycerin immersion ×350): A, B) degassed char particles originating in xylite cellular textinite; C) partially degassed char particle originating in huminite; D) non-degassed unburned coal particle originating in ulminite [10].

In terms of the overall purpose of the project, the 0.5- 4 mm category is interesting for char recovery. Nevertheless, the fraction between 0 – 0.4 mm will be used for the secondary purpose of the project, i.e. to find solutions of recycling the remaining bottom ash as granular aggregate – ceramic binder - for manufacturing construction materials. With this purpose, laboratory tests have been carried out to obtain fired clay throughout this industrial waste.

Meantime, preliminary char concentration trials using simple and easy procedures are effective to increase the rate of char from 0.4-3 mm size fractions of ash, as shown in table 3.

5 Conclusions

The ash samples collected from Ceplea Valley (Turceni PP) and Govora landfills slightly differ in terms of physical characteristics with respect to moisture (dependent on the release of the wet quenching or storage conditions).

The differences are evident with regard to bulk density, with the values for the bottom ash supplied by Govora PP being lower than the values for the ash from Turceni PP.

Differences also appear in size distribution (granulometry). It is noted that the ash collected in Ceplea Valley landfill is formed mainly of very small particles, below 0.4 mm, while the Govora bottom is coarser and the size distribution of the particles is relatively close to a linear one (Fig. 2).

In both samples from Ceplea Valley and Govora landfills, the unburnt is mostly present in fractions greater than 0.4 mm, and is composed by degassed char particles fromxylite and textinite and unburned ulminite.

Related to mineral residue obtained after the organic component separation, a major attention should be paid to dimensional fractions of less than 0.4 mm, net majority, since they may be used as an alternative source of raw material for construction materials.

Effective separation of carbonaceous solid residue from bottom ash can be achieved by physical methods based on the determined characteristics: size distribution and density differences.

Preliminary results obtained in this stage will become the guidance elements in future stages of application research.

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