New possibilities for conservation of natural resources by high capitalization of energy industry wastes

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Abstract: Power plants from Oltenia's region represent a major source of industrial wastes. Ash is the most important waste produced by power plants from coal combustion. The physical-chemical properties of ash vary substantially between producers and depend on the quality and the composition of fossil fuels that are used in modern power plants, as well as on combustion conditions. The diverse chemical, mineralogical and morphological properties of ash offer an opportunity to process it and recover various fractions with particular attributes. The main constituents are Al_2O_3, Fe_2O_3, CaO, MgO and in smaller quantities Na_2O and K_2O. Also, ash resulting from burning lignite from Oltenia Mining Basin has an important content of heavy and rare metals, carbonaceous solid residue, which may be recovered properly through extraction technologies.

Key-words: thermal power plant, bottom ash, reuse, carbonaceous solid residue

1 Introduction

The fuel used in large capacity power plants from Complexul Energetic Oltenia SA (CEO) consists of lignite extracted from open pits in Gorj County. During the production of electricity by lignite combustion occur secondary products, among which the most important is the ash, classified in two main types: fly ash (collected from flue gases through electrostatic systems) and heavy ash, or bottom ash, which are collected at the bottom of the combustion boilers and transported in the form of hydro-mixtures or dense slurry in specially designated deposits, known as ash and slag deposits [1,2].

Fly ash contains fine particles with diameters less than 0.25 mm (easily driven by wind). It leaves the burning chamber in the same time with the combustion gases, being partially retained and collected in the funnels, which are located under the air pre-heaters, and in the funnels of the flue. From the funnels, the ash is driven by free falling through large pipes (400 mm or 600 mm diameter), with high slope to the ground level, where it is mixed with water and then sent to pumps station.

Bottom ash consists of particles of 0.25 – 1mm or more. The slag is crushed and hydraulically transported, by channels to pumps station. The Bagger pumps stations ensure the transport of the ash and slag hydraulic mixture (ash/water 1:8...1:10) to the deposit. In case of thermal power plants from Oltenia, significant amounts of ash are produced due to relatively large mineral content in burned lignite (20 - 30 ash residues) [1,3].

The average characteristics of lignite from Oltenia Region are indicated in Table 1 [2]. In case of the ashes resulted from the coals burning into the steam generator burners, the light ash (known as „fly ash”) is exploited more than 80% on the industrial flows of Portland cement manufacturing, and the bottom ash continue to represent a poor exploited industrial waste, which generates a significant ecological impact by the soil clogging effects, source of the air dust or ecosystem modifier, by the huge stored quantities which contain, each, tens of million of tones and which cover tens of hectares of natural land [3].

Table 1. The average physical-chemical characteristics of lignite.

	Lignite average samples
Proximate analysis (%)	
$M_{t, ar}$	41.0 - 46.2
Ma	10.5 - 13.1
Ash_{db}	23.0 - 25.2
Ultimate analysis (%)	
C	21.0 - 25.8
H	2.0 - 2.1
N	0.5 - 0.65
S_t	0.8 - 1.1
$O_{diff.}$	7.0 - 8.85
Calorific value (MJ/kg)	
LCV	6.92 - 9.06

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

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2 Problem Formulation

Given the complex analyzes made during the LIFE 10 ENV/RO/729 Project, *New building materials by eco-sustainable recycling of industrial wastes - EcoWASTES*, was established that bottom ash of thermal power plant is an alternative solution for replacing of natural granular aggregates. Similar in terms of particle size distribution (0-3 mm) with medium sand and having the advantage of a much lower bulk density (0.7 - 0.9 g/cm^3), bottom ash contains maximum 25% moisture and up to 8% organic matter (residual carbon) [11-13].

The amount of historic deposits that store ash was estimated to more than 150 million tons. These amouts are stored in stable decanted deposits, with access to sampling, loading and transportation equipments. They belong to the same geographical area: Gorj (Turceni, Rovinari), Dolj (Craiova, Işalniţa), Hunedoara (Paroşeni), Valcea (Govora). Such deposits can be assimilated to natural deposits of light sand.

Lignite ash from Oltenia mining Basin emphasizes occurrence and content of a few heavy and rare metals [14,15]. Coal ashes already contain a quantity of concentrated valuable metals hosted in fine grained mineral relics, neo-formed minerals and glassy phases whose recovery is environment friendly, fast and low-cost process that saves metal resources [14,16].
Within the project *Assesment of possible recycling directions of heavy & rare metals recovered from combustion waste products* - RAREASH [14] implemented by an international consortium, are foreseen new directions for recovery of valuable metals from coal ashes. The project aims to demonstrate the technically feasible alternative to utilize fresh and reuse landfilled fly ash and bottom ash as a source soft (pulverized) rock for strategic metals production as Heavy and Rare Metals (HRM) consisting of 21 metals of which: Lanthanides (15 metals) plus Scandium and Yttrium, and Gallium, Strontium, Rubidium, and Wolfram [14,16].

Table 2. Physical-chemical characteristics of power plant ash [11]

Efficiency separation (%) on fractions (mm)									
5	4	2	1	0.5	0.25	0.125	0.09	0.063	< 0.063
0	1.4	4.0	3.9	5.4	9.1	19.5	15.8	14.6	26.4

Moisture (%)	Bulk density (g/cm^3)			
	Wet		Dry	
	Uncompacted	Compacted	Uncompacted	Compacted
23.8	0.86	0.89	0.78	0.80

Chemical composition (%)												
SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	$S_{pyritic}$	L.O.I.*
48.02	0.97	20.21	9.02	0.05	3.21	9.10	0.31	1.77	0.18	0.34	0.94	6.78

*LOI – Loss on Ignition

3 Problem Solution

3.1. Bottom ash– possible substitute for natural resources (lightweight sand) in building materials industry

Within *EcoWASTES project,* was identified the possibility of using ash as a substitute (70-100%) of natural light granular aggregates (perlite, diatomite ash, expanded vermiculite). Bottom ash may be assimilated to mild granular class aggregates according to ASTM C 330 classification and used to form the concrete or press molding mixtures and extrusion mixture (bricks). Bottom ash from thermal plants and scraping gray clay (resulting from lignite quarries) have heat resistant properties and can be used as raw materials in the manufacture of refractory products with the maximum working temperature up to 1150 °C [11, 12].

The following products were obtained through exclusive the use of this waste:

i*) bricks with a high ash content* (over 60%) and building blocks (concrete blocks) containing minimum 15% ash (fig. 1). Technologies from this category, known as cold bonding technologies, require various compacting mixtures methods applied according to the shape and size of obtained products, and also depending on the provided productivity:

- static pressing in mold
- vibropressing
- casting-vibrating in mold.

ii) *heat-insulator refractory concrete for lining industrial thermal aggregates,* where the use of ashes as light granular aggregate shows a high degree of specificity, by making use of its secondary characteristic - heat resistance (melting point of approximately 1200ºC).

Depending on the nature of hydraulic binder (silicate cement or aluminous cement), the ash can be used as light granular aggregate for heat-insulator concrete manufacture with maximum working temperature up to 800 - 1150 °C. For industrial testing phase, has been selected a batch of heat-insulator concrete with a density range of 0.8 to 0.9 g/cm^3 and a maximum working temperature of 800^0C, which was used for making, by spraying, the outer layer of refractory brick wall of a boiler of 420 tonnes/hour in the thermo-electric power plant Govora (fig. 2).

Fig. 1. Concrete blocks and building bricks, vibropressed and hydraulic strengthened, obtained from bottom ash and cement

a)
b)

Fig. 2. Heat insulator concrete applications
a) Area lining repair
b) Spraying concrete

3.2. Bottom ash – a secondary resource of Heavy and Rare Metals (HRM)

Presence of HRM in coal ash, most often in higher concentrations than in normal soils, can be explained by the known fact that plants and animals have the feature to accumulate during life these metals in living tissues. From this point, two advanced concentration stages have continued, the carbonization process of fossil fuels and subsequent combustion in industrial furnaces [16].

The HRM concentrations in coal bottom ashes – close to their occurrence in the Earth's crust which varies up to about 220 ppm - are available in interesting amounts due to their original concentration in coal forming basins (Fig. 3), and further concentration during combustion. The preliminary investigation of landfilled bottom ash demonstrated that they contain an interesting quantity of concentrated valuable metals (Table 3) [16].

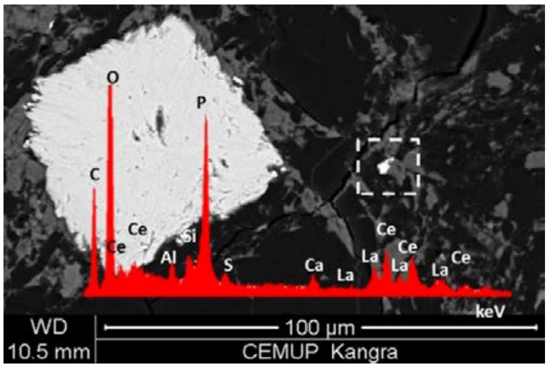

Fig. 3. Lanthanides in coal (SEM, BSE mode) [16]

Table 3. Chemical composition (major oxides (%), and trace elements (ppm) of coal combustion bottom ash [16]

Sample	Major oxides (%)											
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	MnO	P_2O_5	Na_2O	K_2O	SO_3	C.L.
1	49.7	0.77	20.95	8.96	2.48	9.25	0.08	0.2	0.21	1.55	0.59	5.06
2	40.8	0.67	15.7	8.4	2.36	13.75	0.08	0.21	0.19	1.35	4.6	11.69
3	45.24	0.76	19.15	8.65	2.35	9.45	0.07	0.24	0.2	1.44	1.52	10.73
4	46.8	0.68	19.4	8.9	2.42	9.35	0.08	0.24	0.25	1.42	1.38	8.88
5	48.15	0.7	21.7	10.1	3.05	9.05	0.05	0.18	0.28	2.18	0.84	3.75

	Trace elements (ppm)													
Average sample*	La	Ce	Pr	Nd	Sm	Eu	Gd	Yb	Sc	Ga	Rb	Sr	Y	W
	70	134	17	55	13	2	8	10	13	32	109	288	37	33

*by ICP-MS

Physical, chemical and mineralogical properties of coal ashes influence the opportunities for their use and disposal and affect the recovery of metals. A wide range of characterization techniques were performed, including: major and minor elements determination, petrographic and mineralogic characterization, particle size and size distribution, and morphology by scanning electron microscopy. Consecutively, extracting heavy and rare metals from thermal power plants ash can generate new opportunities for the use of the remained mineral residue as alternative raw material for building materials, being well known that in many cases there is skepticism regarding such applications, due to risks related to the presence of these metals in the composition.

4 Conclusion

In this study we demonstrated that bottom ash can be efficiently reused as a possible replacement for natural light granular aggregate for the production of building materials.

Results indicate that coal ashes are promising secondary raw materials that can be used to obtain HRM concentrates, high purity reactive, metals and metallic salts.

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