International Journal of Environmental Science
http://www.iaras.org/iaras/journals/ijes

Utilization of coal-fired ash waste in the production of heat-resistant refractory products

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Abstract: Studying the possibilities of capitalizing the ash residue resulting from the separation of the unburned coal, the main idea is not to elaborate, as a whole, a recovery technology that generates another unused waste.

Key words: coal, bottom ash, waste

1.Introduction

It is known that coal provides roughly 30% of global primary energy needs, with global coal production reaching 7830 Mt in 1912/1 /, and current reserves are thought to last at least 100 years of operation at the same level / 2 /. Under these conditions, it is imperative to consider coal as an important natural resource for obtaining primary energy in all medium- and even long-term development strategies.

It is also known that the burning of fossil fuels is the main greenhouse gas generator process but without being able to demonstrate that, from this point of view, coal would outweigh the potential of natural gas or oil-derived fuels, each intervening a number of collateral factors related to exploitation, transport, storage, primary processing, etc., each generating the same or less significant effect.

In the case of the burning of coal for power generation, the inconvenience of the slag and ash residue generation is important, which obviously creates critic ecologic problems. Depending on the quality of the burned coal, ash can account for over 50% of the fuel used. From this point of view, it is justified the continuous effort made in the field of research towards the recovery of this type of industrial energy waste, namely to avoid the traditional storage procedure in large-scale deposits which, irrespective of the constructive method, is a continuous source of disturbance of the natural environment.

The major weight of the ashes resulting from the burning of coal for power generation is represented by fly ash, for which long-term recovery technology has been implemented for use in the production of Portland cement additions (over 80% of this type of ash). However, the problem remains unresolved with regard to heavy ash (slag and ash), the recovery of which does not exceed the 10% threshold of the generated quantity. Even if the share of generation is low, this state of non-use generates continuously the growth of stocks stored with tens of millions of tons annually.

One of the seemingly "paradoxical" aspects is that the relatively low potential for the recovery of heavy ashes derives from their unburnt coal content, namely that the very process that generates them determines this situation by the yield of the initial coal firing process. On average, the residual coal content of the ash waste is 3-5%, which at current consumption represents a tier of tons of millions of tons of unpleasant coal per year worldwide (3), easy to compare even with Annual production level of a carbonate pool.

2. Thematic frame

Starting from the above-mentioned aspects, "Constantin Brâncuşi" University of Târgu Jiu (UCB) directed the scientific research efforts towards investigating the possibilities of re-introducing the thermal power of the ash through the recovery of the residual coal. In this respect, UCB joined the international consortium engaged in the research project "Coal Char as a Substitute Material of Natural Graphite in Green Energy Technologies - CHARPHITE". This work was funded under the "3rd ERA-MIN Joint Call (2015) on Sustainable Supply of Raw Materials in Europe" by a grant from the Romanian National Authority for Scientific Research and Innovation, CCCDI - UEFISCDI, project CHARPHITE, Contract No.14 and 15/2016.

Within the framework of the partnership, UCB is also responsible for studying the possibilities for the recovery of the ash residues resulting from the separation of the unburned coal. The main idea is obviously not to elaborate as a whole a recovery technology that generates other unused waste. In this respect, at the present stage of the research, it has been determined that in some working variants, after the application of the processes of concentration of the unbound carbon residue, a residue of power plant slag and ash with a predominantly mineral composition, however characterized by the presence of carbon with weight with a mass of 10-20%, and the total separation of which would require a technological effort likely to determine the economic inefficiency of the overall technology. At the same time, the presence with such a share of the carbonaceous component cancels the possibility of using such waste as an alternative source of raw materials for the manufacture of conventional building materials. The technological solution for the recovery of this waste residue started from the fact that the slag and ash from the hearth resulted after the combustion of the coal-fired lignite basins Oltenia in the hearths of the thermal power plants also has a thermosetting vocation (melting point above 1150 0C), simultaneously with density in (Less than 1.0 g / cm^3), which leads them to a certain potential for capitalizing in relatively high temperature (1000 - 1150 ° C) thermal insulation products. For these product categories, the production variant is known by using mixtures of raw materials with combustible admixtures (usually wood sawdust), removing them by burning on the production stream generating pores to increase thermal insulation capacity. The final ash residue described above has both advantages: light granular aggregate content + fuel content.

3. Experimental works carried out

3.1. Selection of the raw material

The series of reference experimental works started from the use as primary waste of slag and ash separated by specific process at the base of the lignite combustion installations which equip the burners of the steam boilers of CET Govora. Within this Energy Complex in Romania, there is a constant concern for the capitalization of the ashes of thermal power, manifested also by the establishment and the support of ROMCEN, an association of generators and users of ash from the thermal power plant in Romania and affiliated to the European Organization ECOBA / 4 /. The aforesaid ash was separated by sieving into the dimensional fractions of 4 mm, 3.15 - 4 mm, 2.5 - 3.15 mm, 2 - 2.5 mm and less than 2 mm (Figure 1), for which the technical analysis was performed. The results obtained are shown in Table 1.

Figure 1. Heavy ash size fractions

Table 1. Elemental analysis

Grain size fraction	Elemental analysis			
	W, %	A, %	V, %	Cfix, %
>4 mm	9.55	34.51	35.58	29.91
3.15-4 mm	9.46	32.41	28.77	38.82
2.5-3.15 mm	9.79	42.05	21.1	36.85
2-2.5 mm	7.79	53.84	14.89	31.27
<2 mm	3.21	79.55	79.55	14.42

Experiments were carried out using the grain size les than 2 mm.

For correction of the grain size composition of the mixtures for casting, the coal ash with grain size less than 0.5 mm was used, with no unburnt carbon content. As ceramic binder gray clay from Roşia de Jiu (Rovinari) was used, which resulted as mining mineral waste, in the scraping works related to the exploitation of lignite in surface pits. Also, in the parallel series of experimental samples, the addition of expanded perlite, the ultra-light granular aggregate commonly used in industrial applications, was also used. The main characteristics of these raw materials are presented in Tables 2,3 and 4.

Table 2. Oxidic chemical composition of Rosia de Jiu clay /5/

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI
65.80	0.68	15.97	5.40	0.11	1.64	0.85	1.86	2.37	0.12	5.35

LOI - Loss on ignition

Table 3. Chemical composition of expanded perlite /6/

Base oxidic compounds (%, weight)								LOI
SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	
74.78	0.09	12.73	1.35	0.13	0.81	2.76	4.70	2.60

Table 4. Main physical characteristics of expanded perlite /6/

Grain size distribution									Bulk density g/cm^3	
The rest (%, masic) on the sieve size (mm)										
4	3	2	1	0,5	0,2	0,09	0,06	<0.06	Tamped	Untamped
5.68	19.8	36.1	23.7	9.5	4.2	1.0	-	-	0.10	0.12

The possibility of using the selected ash to obtain thermally resistant products (relatively high melting point) is also suggested by the results of advanced compositional investigations carried out on samples taken at CET Govora, presented in Tables 5 and 6.

Table 5. Govora Bottom ash (Chemical analysis by XRF spectrometry)

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Mn_3O_4	Fe_2O_3	LOI	Total
0.49	1.74	18.68	49.82	0.09	0.35	1.80	3.47	0.67	0.06	6.03	17.21	100.41

Tabelul 6. Mineralogy of Govora bottom ash (wt%) by XRD and Siroquant analysis

Component	Wt%
Quartz	13.6
Calcite	0.4
Mullite	5.2
Hematite	0.6
Maghemite	0.7
Anortite	4.5
Amorphous	75.0

By correlating the data in Tables 5 and 6, the high melting temperature is explained by the fact that, following high temperature transformations in the furnace, the calcium oxide (fuser) is fixed to the anorthetes by interaction with silico-silicone formations. In turn, they (mostly kaolinite) are thermally stabilized by mullite formation. The major part of the amorphous phase obviously derives from the formation of vitreous components (typical of the thermal coke slag) at the high temperature of the furnace and with the major intervention of all strong oxidizing components (Na_2O, K_2O, Fe_2O_3).

3.2. Composition and processing of the casting mixtures

By using the raw materials described above, 5 series of experimental samples were made, the (gravimetric) dosing of the components in the molding mixtures is shown in Table 7.

Table 7. Dosage receipe (wt%)

Sample ID	Ash with residual carbon <2 mm	Ash without residual carbon <0,5 mm	Ash Roșia de Jiu	Expanded perlite
K1	60		40	
K2	60	10	30	
K3	60	5	35	
K4	50		40	10
K5	55		40	5

Casting mixtures were moistened with water (15-20%) until it reached the specific half-hardness workability. Experimental specimens (cylinders Ø50 mm, h 35-55 mm) were made by pressing in a metal die at a maximum nominal pressure of 25 MPa with a de-aeration step at the 2-4 MPa threshold. After making the specimens, the specimens were kept for 24 hours at ambient temperature, then subjected to thermal drying treatments at 110 ° C ± 2 ° C (8 hours maximum temperature range) and laboratory electrical furnace burning at 1000 ° C ± 5 ° C Gradient 3 ° C / minute, 3 hours maximum temperature, free cooling with the closed door) - Figure 2. The variation in the height of the specimens was selected from the desire to determine the possible differences between the combustion removal rates of the fuel additive residual coal from ash).

Figure 2. Test specimens (a – after casting, b – after drying and calcination)

4. Results and discussion

The first finding was that the carbonate residue in the experimental specimens was completely removed from combustion (Figure 3), valid for all the processed specimens, and found after the destructive mechanical compression test.

The specimens, both after drying at 110 ° C and after firing at 1000 ° C and cooling, were subjected to laboratory tests to determine the main physical and mechanical characteristics: apparent geometric density, density - absorption - open porosity (water-borne method)), dimensional variation after burning, mechanical compressive strength.

The results obtained are presented in Table 8 (mean values for compositional series). As a reference element (indicative sample K0), a product obtained (under the same laboratory conditions) from a mixture of Roşia de Jiu clay (40%) and unselected coal ash (about 5% Residual coal) / 7 /.

Figure 3. Appearance of the broken test specimen

Table 8. Test results

Sample		Geometric density g/cm^3	Hydrostatic tests g/cm^3, %			Linear variation 110-1000 ^{0}C %	Compressive strength MPa
			Dens.	Abs.	Por.		
K0	110 ^{0}C	1.51				- 1.94	11.82
	1000 ^{0}C	1.40	1.39	30.9	43.0		15.51
K1	110 ^{0}C	1.21				- 1.88	1.26
	1000 ^{0}C	1.07	1.03	53.23	54.78		3.21
K2	110 ^{0}C	1.11				- 2.50	1.18
	1000 ^{0}C	0.98	1.00	56.15	55.88		3.11
K3	110 ^{0}C	1.15				- 1.96	1.06
	1000 ^{0}C	1.00	1.02	54.32	55.39		3.07
K4	110 ^{0}C	1.16				- 2.69	2.04
	1000 ^{0}C	1.08	1.11	45.93	51.17		4.24
K5	110 ^{0}C	1.18				- 1.70	1.98
	1000 ^{0}C	1.06	1.08	48.33	52.35		3.88

By correlating the data entered in Tables 7 and 8, the following main conclusions can be drawn:

- the use as a component of ash containing residual coal leads to a decrease in the density of the burned products by approx. 30%, obviously due to increased porosity by approx. 30%;
- In the series of fuel additive samples, the density decreases with the reduction of the clay content;
- in terms of mechanical strengths, there is a clear reduction (up to 80% relative to the characteristic K0 product), a natural phenomenon, since thermal insulation products do not usually have mechanical vocations;
- the use of expanded perlite ensures a relative increase in mechanical strength, due to the achievement of a better compaction to the shaping (better dimensional distribution of the granules in the mixture).

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