Obtaining thermal insulating refractory products using ash from coal-fired thermal power plants containing residual coal

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Abstract: - In this paper, we present new Development of technologies for the recovery of ash waste resulting from burning of coal without the generation of other wastes. The experimental works have made it possible to define the practical conditions for the use of the industrial waste studied in obtaining ceramic composites belonging to the category of building materials.

Key-Words: - fossil fuels, energy coals, combustion, slag and ash.

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.

The use of power plant ash for the production of brazing mixtures for pressed building materials is mentioned in the literature at the world level, where positive results obtained by incorporating the ash raw material in the plastic cutting mixtures with a mass of 15-20% [3,4,5]. Internally, S.C. FIBROCIM S.A. in collaboration with the Polytechnic University of Timisoara, studies the possibility of using ash aggregates as aggregates in the tile manufacturing recipes, presenting the results obtained in the variants where the ash replaces 5%, 10% and 15% of the sand in the classical recipes as a degreaser [6]. Also, the use of ash is successfully tested by SC MACOFIL SA in Targu Jiu, as a recipe in situations where the basic raw material was a clay with a low content of degreasing component [3].

In all the cited cases, the conclusion of the specialists is unanimous: heavy hearths (hearth ashes) are a raw material of great interest to the building materials industry and which, in the case of a rigorous approach to the exploitation problem, can constitute a mineral resource at least at as valuable as fly ash (filter ash), which they currently have the "disadvantage", but perhaps in the future the "advantage" of evacuation from the combustion streams of energy coals in a mass ratio of 10: 1.

In the case of the thermal power plants, one of the important compositional parameters determined is the fixed carbon content, a parameter which is able to classify this type of industrial waste in terms of the efficiency of the combustion equipment and of the residual coal remaining in the ash evacuated.

For technical uses of ash, the retention of unburnt coal may be an inconvenience, both in terms of being a totally different component from the compositional point of view of the rest of the oxidizing components, and in that it may sometimes cause undesirable side effects. For example, in the case of ash use as a raw material in the manufacture of building materials, it can cause gray tints of finished products.

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 Brancusi" University of Targu 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 ^{o}C), 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 [9]. 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

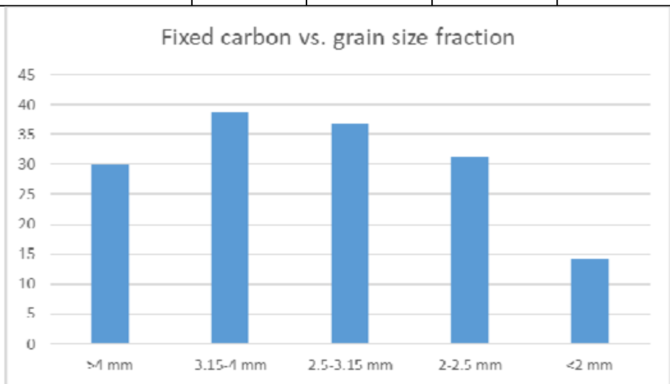

Figure 2.

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 Rosia 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 expanded pearlite used as an auxiliary granular aggregate came from a current production batch of SC PROCEMA PERLIT SRL Jilava, similar to the batches used in lightweight thermosetting concrete on the industrial flows of the profile producers.

The main characteristics of these raw materials are presented in Tables 2, 3, 4, 5 and 6.

Table 2. Oxidic chemical composition of Rosia de Jiu clay [10]

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. Ash grain size

Grain size distribution				
Remaining (%, weight) on the sieve (mm)				
4	3,15	2,5	2	<0.63
2,6	3,1	4,0	5,8	84,4

Table 4. Bulk density

Fraction	Bulk density (g/cm^3)	
	Tampped	Untampped
>4	0,31	0,35
3.15 - 4	0,31	0,36
2.5 - 3.15	0,29	0,34
2 - 2.5	0,31	0,36
<2	0,46	0,54

Table 5. Chemical composition of expanded perlite [11]

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 6. Main physical characteristics of expanded perlite [11]

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 7 and 8.

Table 7. 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

Table 8. 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 7 and 8, 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 9.

Table 9. 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 3. 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 4.

Figure 3. Test specimens after casting

Figure 4. Test specimens after drying and calcination

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).

4. Results and discussion

The first finding was that the carbonate residue in the experimental specimens was completely removed from combustion (Figure 5), valid for all the processed specimens, and found after the destructive mechanical compression test.

For the determination of density, absorption capacity and porosity, the samples were weighed dry, boiled in water for 2.5 hours to completely replace the open air pores with water, then weighed immersed in water and wet, in air, obtaining the parameters required for calculation:

- ms - mass of the sample in dry state, g
- mu - mass of the wet sample (pores filled with water), g
- mh - mass of wet sample immersed in water (hydrostatic weighing), g

Using the measured parameters, the sample properties are calculated:

$$d = \frac{m_s}{m_u - m_h} \times \rho \qquad (1)$$

$$P = \frac{(m_u - m_s) \times 100}{m_u - m_h} \qquad (2)$$

$$A = \frac{(m_u - m_s) \times 100}{m_s} \qquad (3)$$

where: d - sample density, g / cm^3

ρ - density of the immersion fluid (water), g / cm^3

P - open sample porosity,%

A - sample absorption capacity,%

For this determination, mass measurements were made with an accuracy of 0.1 g.

The results obtained are presented in Table 10 (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) [12].

Figure 5. Appearance of the broken test specimen

Table 10. 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 9 and 10, 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% (Figure 6);
- 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 (Figure 7);
-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).

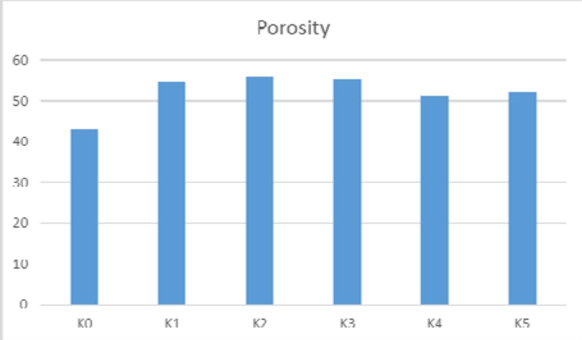

Figure 6.

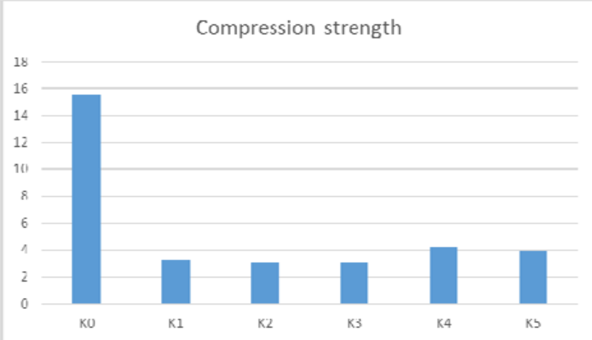

Figure 7.

5. Conclusion

The experimental works have made it possible to define the practical conditions for the use of the industrial waste studied in obtaining ceramic composites belonging to the category of building materials:
- thermal power ash presents the characteristics of a light granular aggregate, which on this basis can become an alternative raw material, both for the manufacture of pressed products and high-temperature casting (bricks).
- from the point of view of the chemical composition, the use of ash from the thermal power plant does not involve major changes given the similarity with many of the natural granular aggregates (limestone sands).
- the use of ash as an alternative source of raw materials can also give the advantage of obtaining products with lower manufacturing costs compared to classic variants.

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