Coal ash inorganic residue as raw material for construction elements

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Abstract: - The paper presents synthetically the results of an extensive experimental study on the extent to which bottom ash resulting from coal-fired power plants has the potential to be recycled and used in the building materials industry. Unlike fly ash collected mainly from the electrostatic precipitators, the bottom ash and slag consists of large articles and incorporates unburned organic matter resulted from incomplete oxidation of combustible compounds of the coal or even unburned coal. The presence of organic matter renders such ash unsuitable to be used as raw material in construction material industry. In this paper, a number of recipes based on bottom ash were developed in order to obtain construction material samples. The samples were tested for mechanical properties and their suitability to be used in the construction materials industry was assessed.

Key-Words: - Recycling, Coal-fired power plant ash, Bottom ash, Construction materials, Unburned carbon

1 Introduction and Literature Survey

Coal combustion in high capacity coal-fired power plants results in large amounts of ash and slag, which pose significant environment threats. The amount of ash resulting from coal combustion depends on the quality and composition of the raw coal and it can reach up to 50% (w) from the initial coal mass. In addition to the environment problems it causes the coal ash requires storage, thus occupying large areas. These large amounts of ash generated continuously led to researches aiming to identify possible usage or recycling technologies.

Coal ash consists mostly of flying ash, for which technologies exist to use it for Portland cement fabrication. However, heavy ash (slag and bottom ash) hardly reaches 10% in terms of recycling. Although the amount of such ash type is significantly smaller than fly ash, the fact that it is recycled only in small amounts contributes to a continuous increase of the accumulated amounts. The main reason that makes bottom ash difficult to recycle is the high content of unburned organic matter in various forms: mechanically unburned or partially burned coal particles, solid particles resulting from incomplete coal burning. The average content of residual coal found in bottom ash ranges from 3 to 5%. Considering the world coal consumption for electricity generation this percentage of unburned coal is equivalent to 10^7 tons/year.

Maroto-Valer et al [1] developed activated fly ash derived sorbents for CO_2 capture. Absorption capacity values of the activated amine impregnated samples of approximately 68 g CO_2/g sorbent were reported.

The amount of unburned organic matter in the bottom ash varies considerably, depending mainly on the initial composition of the coal. The combustion technology and combustion installation influence also to a significant extent the percentage of unburned coal found in the bottom ash and slag. Šyc et al [2] conducted a material analysis of bottom ash from waste to energy plants. The percentage of unburned organic matter found was approximately 1%. Wagner et al [3] conducted studies on the unburned organic matter present in coarse gasification ash. The unburned carbon particles were further macroscopically subdivided into remnant ''coal'' particles, solid carbon, layered carbon, and porous carbon.

The limitation of bottom ash usage and recyclability due to the content of unburned organic matter has been reported in several studies. Trifunovic et al [4] investigated the effect of unburned coal content in the bottom ash on its applicability to road construction. Four samples were investigated with different contents of unburned carbon, i.e. 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. When these materials were used as a component in the mixture: fly ash–Portland cement–bottom ash–water for road construction, it was found that only mixtures containing bottom ash with a lower carbon content (size fraction <2mmand treated) were employable.

The issue of presence of unburned coal in the bottom ash and the problem it poses when it comes to recyclability are well known and investigated. Pallarés et al [5] developed an algorithm based on a neural network model to predict the amount of unburned coal present in the bottom ash. Development of such an algorithm was necessary based on the observation that boiler condition and load influence significantly the amount of unburned coal present in the bottom ash.

The mechanism of unburned coal retention in the ash evacuated from the boiler has also been studied extensively. Zyrkowski et al [6] investigated the fly ash cenospheres from a coal-fired power plant unit. Physical, structural and chemical analysis was performed in order to identify the conditions leading to their formation. cenospheres have been collected and characterized by techniques such as SEM, EDS, XRD, XRF and Raman spectroscopy.

2. Methods and materials

Two classes of methods were employed in order to establish possible recycling technologies:

- Pressing followed by hot binding
- Compaction by means of vibrated casting of the mixtures based on hydraulic binder

2.1. Materials

The material consisted of mineral residue hereinafter known as secondary waste, categorized in four classes depending on the coal separation process that generates that particular product (secondary waste):

- DS1: secondary waste resulting from dimensional sieving of the raw bottom ash and slag, representing dimensional fraction under 2 mm;
- DS2: secondary waste resulting from water flotation of the fraction larger than 4 mm (from the raw bottom ash) representing the component that precipitates;
- DS3: secondary waste resulting from magnetic separation of the bottom ash fraction previously subject to flotation process;
- DS4: secondary waste resulting from fragmentation and dimensional sorting of the non-magnetic component, representing the fraction with grain size larger than 0.125 mm.

The visual appearance of the four wastes is presented in Figure 1.

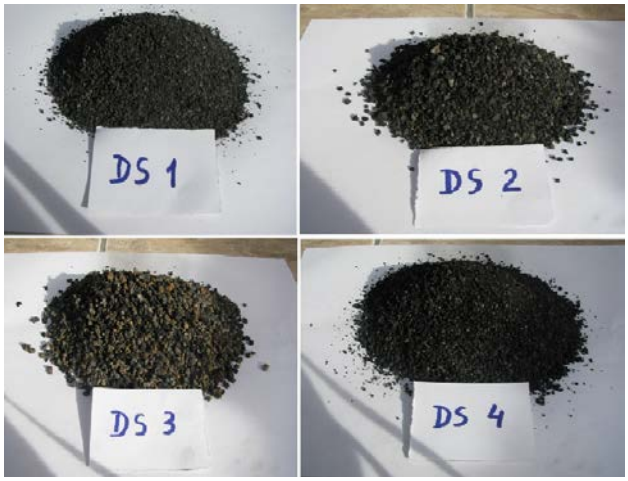

Figure 1. Appearance of the secondary waste from preliminary processing of the raw bottom ash

Physical characteristics of the secondary waste used in the experiments are presented in Table 1. Technical analysis was performed in order to identify other important physical characteristics. The results are presented in Table 2.

Table 1. Physical characteristics of the secondary waste samples

Sample	Rest (%) on sieve with gauge (mm)								Bulk density (g/cm3)	
	4	2.5	2	1	0.5	0.09	0.063	<0.63	Unsettled	Settled
DS1	0.0	0.0	0.1	29.9	34.5	3.6	2.3	2.9	0.55	0.61
DS2	0.0	0.0	80.3	15.1	1.9	0.4	0.3	0.5	0.52	0.58
DS3	0.0	1.5	87.5	8.6	0.6	0.4	0.3	0.4	0.25	0.29
DS4	0.0	0.0	16.7	37.2	18.1	0.6	0.0	0.0	0.30	0.35

Table 2. Results of the technical analysis performed on the four secondary waste samples

Sample	Humidity %	Ash, anhydrous %	Volatiles, anhydrous %	Fixed carbon, anhydrous %
DS1	3,55	83,26	4,79	11,95
DS2	3,26	71,64	12,22	16,14
DS3	2,06	83,06	3,46	13,48
DS4	8,02	12,44	25,85	61,71

Other materials used in the experiments are as follows:

Ceramic binder. As ceramic binder gray clay originating from sterile produced during lignite mining at Roşia de Jiu – Rovinari (Romania) was used, with main characteristics presented in Table 3.

Table 3. Characteristic of the ceramic binder

Characteristic		Value
Oxidic chemical composition (%)	Al2O3	12 – 18
	SiO2	60 – 70
	Fe2O3	4 – 8
	CaO+MgO	2 – 5
	Na2O+K2O	2 – 5
	P.C.	10 - 12
Melting point (0C)		1210 - 1240
Plasticity (Ip), (%)		25 - 30
Humidity, max. (%)		30 - 35

Hydraulic binder. Portland cement CEM II/B-M(S-LL)42.5R (HOLCIM Romania) and refractory cement ISTRA 50 (produced Heidelberg - Croatia) with main characteristics presented in Table 4.

Light granular aggregates. Expanded perlite and lightweight precast concrete (LPC) fragments (waste) were used.

Lignite (particles under 0.5 mm) collected from the process flow coal mill – boiler burner from Govora combined coal-fired power plant. It was used in order to optimize the dimensional distribution of the particles.

2.2. Manufacturing and thermal treatment of the experimental product samples.

The samples for ceramic binding products were obtained by means of pressing in a metallic moulds as cylinders with 50 mm diameter and 50 mm height. Nine samples were prepared as presented in Table 5.

Table 4. Characteristics of the hydraulic binder

Characteristic		Value	
		CEM II/B-M 42.5R	ISTRA 50
Hardening time	Beginning	4 h 15 min.	4 h 30 min.
	End	5 h 30 min.	6 h 30 min.
Compressive strength (MPa)	3 days	26.19	46.14
	7 dayse	36.85	58.16
	28 days	43.40	63.24

Compaction has been realized by means of pressing at the maximum pressure 25.5 MPa with one air removal stage at 5-10 MPa. After compaction the samples were maintained for 24 h at room temperature and then they were subject to drying and thermal treatment at high temperature. The cold bonded samples were obtained by means of vibrated casting in metallic moulds through manual compaction and mechanical vibration for a short period (5-8 sec) at 50 Hz and 0.5 mm amplitude. The dosage recipes are presented in Tables 5a and 5b.

Table 5a. Components dosage for concrete based on Portland cement. 1st series

Sample	Component dosage (%, w)				
	DS1	Ash <0.5 mm	LPC waste	Portland cement	Water dm^3/kg
T1	70			30	40.3
T2	60	10		30	40.7
T3	50	20		30	39.6
T4	35	20	15	30	44.1

Table 5b. Components dosage for concrete based on Portland cement. 2nd series

Sample	Component (% gravimetric)			Water %
	DS1	Fine ash <0.5 mm	Aluminium cement	
T5	70	-	30	43.2
T6	50	20	30	42.4

Table 5. Recipes (in %) used to prepare the experimental product samples

Sample	Component (%, gravimetric)								Water %
	DS1	DS2	DS3	DS4	Ash <0,5mm	Expanded perlite	Fine lignite	Clay Rovinari	
PØ								100	15.2
P1	27		23					50	13.1
P2	55					5		40	20.0
P3	60							40	15.9
P4	50					10		40	20.0
P5	60				5			35	16.1
P6	60				10			30	16.7
P7	17.5	17.5	17.5	17.5				30	18.1
P8	50			10				40	24.1
P9	40			10			10	40	22.1

The appearance of the finite product is shown in Figure 2.

Figure 2. Samples obtained through semi-dry pressing

After maintaining the samples in the moulds for 24 hours they were removed and deposited in a acclimatizing enclosure (20 ^{0}C ± 1 ^{0}C, humidity > 95 %) until thermal treatment of mechanical strength tests were performed.

Thermal treatment of the product samples was performed by drying at 110 °C in an electric oven with adjustable temperature programe. The samples were maintained for 8 hours at the maximum temperature

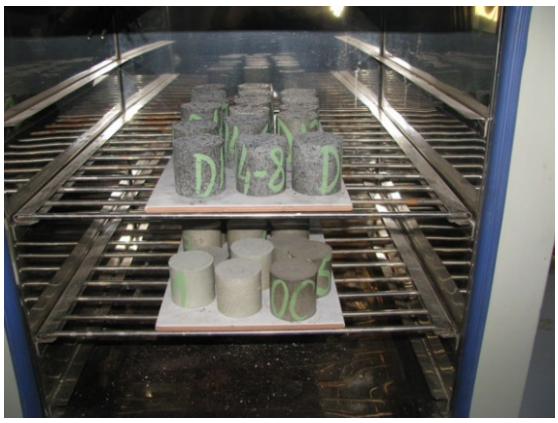

Figure 3a. Thermal treatment. Drying

Figure 3a. Thermal treatment. Burning

3. Results and discussion

The finite product samples were subject to specific laboratory tests in order to determine the main physical and material strength parameters, which are presented in Table 6

Table 6. Physical and mechanical characterisics of the samples

Sample	Density (g/cm^3) 110 °C	Density (g/cm^3) 1000 °C	Linear variation (%)	Compression strength MPa	Apparent density g/cm3	Absorption capacity %	Open porosity %
PØ	1.92	1.91	-0.75	16.49	1.93	13.50	26.12
P1	1.25	1.12	-0.98	5.12	1.17	41.64	48.60
P2	1.16	1.08	-2.93	4.18	1.12	45.50	50.91
P3	1.21	1.07	-2.73	3.20	1.03	53.23	54.78
P4	1.18	1.06	-2.09	3.77	1.09	47.97	52.07
P5	1.15	1.00	-2.36	3.06	1.02	54.32	55.39
P6	1.11	0.98	-3.03	3.06	1.00	56.15	55.88
P7	0.97	0.74	-2.84	0.23	0.78	82.17	64.16
P8	1.19	0.97	-1.09	14.74	1.00	55.58	55.44
P9	1.21	0.96	-1.51	14.92	0.99	57.94	57.22

It can be observed that regardless of the sample, using secondary waste resulted in a significant decrease of the density (39-60%) compared to the reference sample PØ (fabricated with clay only. Series PØ simulates the technology currently employed by a construction bricks manufacturer (MACOFIL S.A., Romania). Considering the high value of the gray clay melting point (more than 1200 °) the technology can be implemented in manufacturing refractory bricks with thermal insulation properties which can be used at temperatures up to 1000-1050 °C replacing the classic technology with combustible additives (sawdust).

On the other hand it can be noticed that density drop comes with a drop in mechanical strength, which can be explained by the fact that combustible content influences negatively the developing mechanism of the ceramic binding stage during the burning phase, which is equivalent to say that limits formation of the structure. As the combustible component is removed by burning it is expected that the open porosity will increase, which will positively influence the thermal and phonic insulation capacity.

The complete absence of the combustible components from the final product can be noticed analyzing the appearance of the section performed by breaking the sample. The appearance of a sample after being subject to mechanical compression test is shown in Figure 4. It can be noticed that the carbon content has been completely removed through burning at 1000 °C.

Figure 4. Appearance of a broken sample showing no carbon traces

The results of the tests performed on the product samples obtained by means of cold hydraulic hardening are presented in Tables 7a and 7b. The date presented demonstrates that such waste materials can be used as an alternative raw material in obtaining lightweight concrete for constructions. An important detail is the fact that size distribution in the cast mixture induces discontinuity effects in the grain size distribution. This can be easily controlled by adding fine ash (grain size under 0.5 mm). Grain size correction allows conditions for developing the structure.

Table 7a. Portland cement samples physical and mechanical characteristics

Sample	Density (g/cm3)		Compressive strength after 7 days (MPa)
	Raw	Dry	
T1	0.94	0.84	4.54
T2	1.07	0.93	6.45
T3	1.21	1.02	9.33
T4	1.27	1.02	6.73

Table 7a. Portland cement samples physical and mechanical characteristics

Characteristic		Samples	
		T5	T6
Density, g/cm^3	110 °C	1.42	1.42
	1100 °C	0.63	0.81
Compressive strength, MPa	110 °C	3.22	4.98
	1000 °C	1.35	1.84
Apparent density, g/cm3	1000 °C	0.71	0.89
Absorption capacity, %	1000 °C	93.00	71.75
Open porosity, %	1000 °C	65.79	63.51

4. Conclusion

Mineral residue obtained after separation of the unburned content in bottom ash can be used as alternative raw material for construction materials. Due to the remaining coal content the mineral residue can be used in fabrication of lightweight construction materials with coal content replacing the traditionally used combustible materials, such as sawdust. The high value of the thermal resistance of the coal ash makes it suitable for fabrication of insulation elements for high temperatures (up to 1000 °C). Grain size distribution from the mineral residue allows its usage as granular aggregate in concrete mixtures based on hydraulic binder. Both for ceramic and hydraulically binded products using the mineral residue as component in mixtures results in a lower value of the density.

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