The Influence of Partial Substitution of Raw Materials with Heavy Ash on the Main Properties of Portland Cements

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The use of wastes in cement industry have impact both from economic and environmental point of views. Wastes can be used in clinker manufacture (to substitute raw materials or as alternative fuel) as well as supplementary cementitious materials in cement. This paper presents results regarding the use of heavy ash (bottom ash) as component of raw mix used for the clinker manufacture. Two types of cements were obtained by the milling of clinker produced with/without heavy ash (HA) as component of raw mix and gypsum (2%). The compressive strengths of these cements was assessed on plastic mortars (water:binder = 1:2 ratio and binder:aggregate = 1:3 ratio), cast in prismatic moulds (14x14x160 mm^3), hardened different periods of time comprised between 1 to 28 days. The hydration and hardening processes which occur in the cementitious systems with/without waste content were assessed on pastes with water to binder ratio of 0.5, hardened for 1 up to 90 days. X-ray diffraction (XRD) and complex thermal analysis (DTA-TG) were used for pastes' characterization. The composition of clinker was assessed by XRD and microstructure by scanning electron microscopy (SEM). The results obtained in the framework of this research do not show any important difference between the clinkers' characteristics produced with alternative raw material (heavy ash) as compared with the ones produced with natural raw materials. Also, the properties of cements produced of these clinkers are similar.

Keywords: bottom ash, clinker; cement Portland, properties

The use of wastes in cement industry have impact both from economic and environmental point of views. Wastes can be used:

-in clinker manufacture as substitute of raw materials [1 - 7] - such as silica sand, fly ash, ceramic wastes, or as alternative fuels [2, 8 - 15] - tyres, plastics, wood, paper, waste oils, sewage sludge;

-supplementary cementitious materials in blended cement [2, 16 - 20]- fly ash, blast furnace slag, silica fume, tuff, limestone fines, vegetable ashes and shale.

During the coal burning in a furnace the non-combustible parts forms ash which is generally stacked on the bottom of the coal-burning furnace; this ash is called bottom ash or heavy ash. A part of the finer ash particles can be also entrained by the hot gasses and collected in dust separators and is called fly ash. Coal combustion ashes (bottom and fly ashes) contain as main oxides calcium oxide (CaO), silica (SiO_2) and alumina (Al_2O_3) and can be used as a substitute for conventional raw materials in cement production. Due to the small specific surface area of bottom ashes the grinding is required. According to their properties, bottom ashes are put generally at the stage of grinding raw materials as part of mixed raw materials.

In our study heavy ash was used as alternative raw material in the production of Portland clinker. The main characteristics of this clinker were assessed and compared with those of a clinker obtained by the burning in the same conditions of a regular raw material mixture with the same composition.

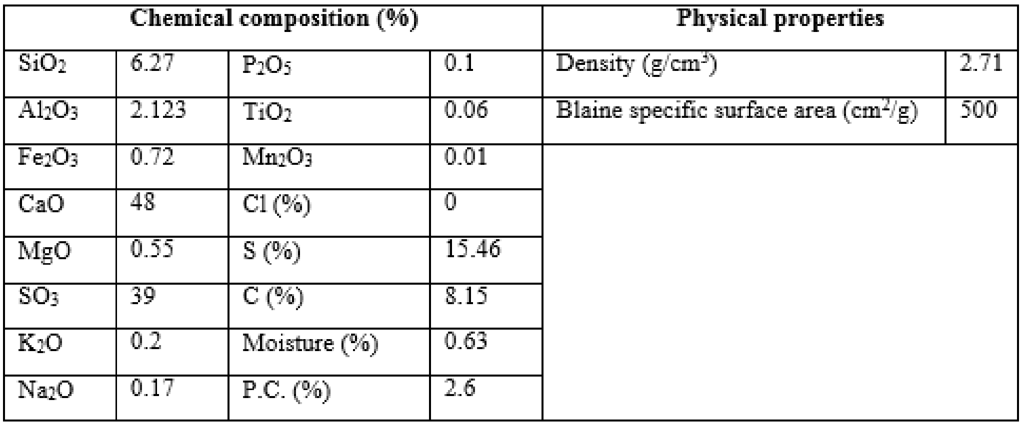
Experimental part

Materials and methods

Heavy (bottom) ash (HA), resulted in a power plant by the burning of solid fuel, mostly petroleum coke. The chemical composition of HA is shown in table 1.

The Portland clinkers were obtained by burning at 1450°C of a homogenous mix consisting of marl and limestone with/without HA addition. Because the sulphate content in HA is high (table 1), the substitution degree in the raw mix was limited at 4%.

To characterize the HA and the clinkers with/without HA addition, as well as the resulting cements, the following



Chemical composition (%)				Physical properties	
SiO_2	6.27	P_2O_5	0.1	Density (g/cm^3)	2.71
Al_2O_3	2.123	TiO_2	0.06	Blaine specific surface area (cm^2/g)	500
Fe_2O_3	0.72	Mn_2O_3	0.01		
CaO	48	Cl (%)	0		
MgO	0.55	S (%)	15.46		
SO_3	39	C (%)	8.15		
K_2O	0.2	Moisture (%)	0.63		
Na_2O	0.17	P.C. (%)	2.6		

Table 1
CHARACTERISTICS OF FLY ASH

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Table 2
OXIDE COMPOSITION OF CLINKERS

Clinker* / Oxide composition (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
A	22.10	5.19	3.08	65.90	1.24	1.04	0.81	0.55
B	22.17	5.18	3.07	65.90	1.25	1.05	0.82	0.56

**A- clinker obtained by burning a regular raw mix; B - clinker obtained by burning a raw mix with HA content.*

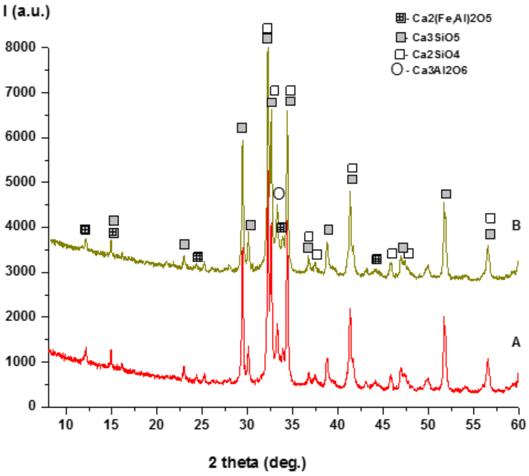

Fig. 1. X-ray patterns for clinkers A and B

methods were used:

- The chemical and mineralogical compositions were assessed by: i) X-ray diffraction (XRD) coupled with Rietveld analysis; XRD analyses were performed in the range 2θ= 5-65 degrees, using two diffractometers: Shimadzu XRD 6000 (λ = 1.5406 Å) and PANalytical Cubix (λ = 1.5418 Å); ii) X ray fluorescence spectrometry (Axios) was used for the assessment of oxide composition; iii) thermal analysis was performed using a DTG-TA-51H equipment, in oxidative atmosphere, in the 30-1000°C temperature range, with a heating rate of 10°C/min..
- The morphological and structural assessment of clinkers was performed by scanning electron microscopy (SEM) by means of Quanta Inspect F scanning electron microscope (1.2 nm resolution) with EDX.

The cement hydration and hardening processes were assessed on pastes with water to binder ratio of 0.5, hardened for 1 up to 90 days.

The normal consistency water and setting times of cements were determined according to European and corresponding Romanian standard norm [21].

Compressive strength was assessed on mortar specimens prepared with binder:sand=1:3 and water to binder ratio of 0.5, using as aggregates siliceous sand which fulfilled the requirements of European and corresponding Romanian norm [22]. The mortar specimens were cast in rectangular moulds (40x40x160mm), vibrated for 2 min and cured for 1 up to 28 days in humid air (R.H. 90%). The compressive strengths were assessed using a Matest machine, and the values represent the average of least four strength values assessed on specimens cured in similar conditions.

The quantitative mineralogical composition of clinkers was estimated by Rietveld refinement method – table 3. It can be noticed the high amount of alite (C_3S) in both clinkers therefore it can be classified as alite type clinkers.

The amount of free lime (assessed by the chemical method) fulfils the requirement of specific norms i.e. are below the 2% limit.

The data presented in tables 3 and 4 confirms , that in case of clinker B, in which 4% HA was used, the free-lime content is similar to clinker A, and the alite content is approximately equal to of clinker A. These results, corroborated with the similar amount of belite, confirm the same adequate kinetics of chemical processes that occur during burning treatment, and especially the conversion of belite in to alite.

Results and discussions

Characterisation of clinkers

The oxide composition of clinkers, assessed by fluorescence X-ray diffraction is presented in table 2. The results show no significant difference between the two clinkers from the point of view of oxide composition.

Figure 1 shows the diffraction patterns of clinkers; one can assess the peaks specific for calcium silicates i.e. 3CaO SiO_2 (C_3S) - JCPDS 42-0551 and 2CaO SiO_2 (C_2S) -

Table 3
QUANTITATIVE MINERALOGICAL COMPOSTION OF CLIKERS (ASSESSED BY RIETVELD METHOD)

Main Phase (%)	C_3S/ Alite	C_2S/ Belite	Tricalcium aluminate			C_4AF/ Ferrite
			cC_3A/ cubic	oC_3A/ orthohedric	C_3A Total	
A	67.25	12.07	4.44	4.49	8.90	8.45
B	67.26	12.16	4.39	4.71	9.11	8.27
Secondary Phase (%)	**Periclaz**	**Portlandite**	**Anhidrite**	**Aftalite**	**Arcanite**	**CaO_{free}**
A	0.14	0.34	0.00	0.69	0.88	1.27
B	0.17	0.28	0.74	0.71	0.80	1.30

Table 4
MAIN CHARACTERISTICS OF CEMENTS

	Residue (%):			Blaine specific surface area (cm^2/g)	Water for normal consistency (%)	Setting time (min.)	
	R_{045}	R_{090}	R_{200}			Initial	Final
Cement A	11.85	1.75	0.575	3400	30.2	215	295
Cement B	12.2	1.6	0.58	3340	30.2	211	271

JCPDS 24-0034, tricalcium aluminate - 3CaO Al$_2$O$_3$ (C$_3$A) JCPDS 33-0251 and brownmillerite - C$_2$(A,F) - JCPDS 30-0226). No significant changes are noticed from the point of view of the crystallinity of mineralogical phases, assessed by this method for the two studied clinkers.

The scanning electron microscopy images (fig. 2), show the presence of the XRD identified mineralogical phases: the prismatic alite crystals, round belite crystals and ferrite aluminate phase as an interstitial phase in characteristic *honeycomb* form [10, 23 - 25]. One can assess also some areas where belite crystals are present on the alite crystals surface or as inclusions in the alite crystals (see arrows). Alite crystals are locked in the vitreous interstitial phase, which smoothness their edges.

Based on the results presented so far one can state that the quality of clinker with HA addition is similar with the one obtained from regular raw materials.

Characterisation of cements

CEM I 52,5R type cements were prepared by the clinkers A and B milling with a 2% gypsum admixture. Their fineness (Blaine specific surfaces and residue on sieves with various opening sizes), normal water consistency and setting time are presented in table 4.

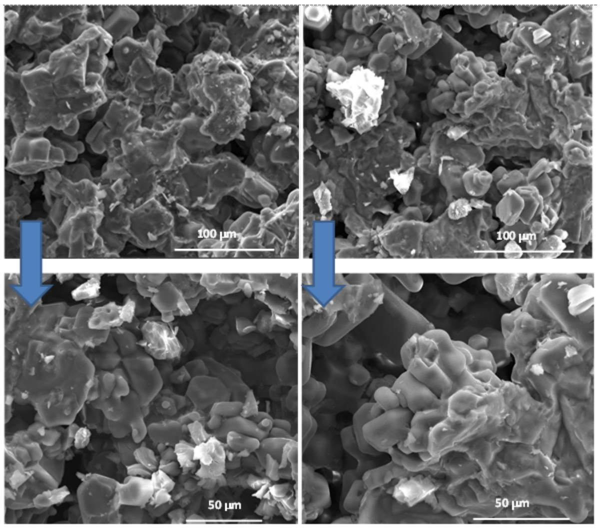

Fig. 2. Scanning electron microscopy images of clinkers A and B

Both clinkers exhibit the same grinding ability; the Blaine specific surface area and the granulometric distribution for both cements is approximately the same.

The value of water for normal consistency is approximately the same for both cements. The setting times of cement A and B are slightly different; the slightly shorter setting time for cement B may be due to the isomorphic addition of sulphur in calcium silicates lattice, thus leading to an important distortion of C$_2$S lattice [26 - 28].

In figure 3 are assessed mechanical properties for both cements (cement A - on based A clinker; cement B - on based A clinker).

The flexural and compressive strengths of cements A and B (fig. 3) are similar.

From point of view of cement hydration processes, the XRD patterns (fig. 4) and thermal analysis (TG and DTA) data (fig. 5), show similar kinetics for the hydration process for the studied cements, regardless of the hardening period.

On the diffraction patterns (fig. 4) of both cements A and B, it can be noticed that the intensity of anhydrous phases (C$_3$S, C$_2$S) peaks decrease with the increase of the hardening period; one can also notice the presence of peaks characteristic for the hydrates i.e. calcium hydroxide (JCPDS 04-0733) and ettringite (JCPDS 41-1451). The

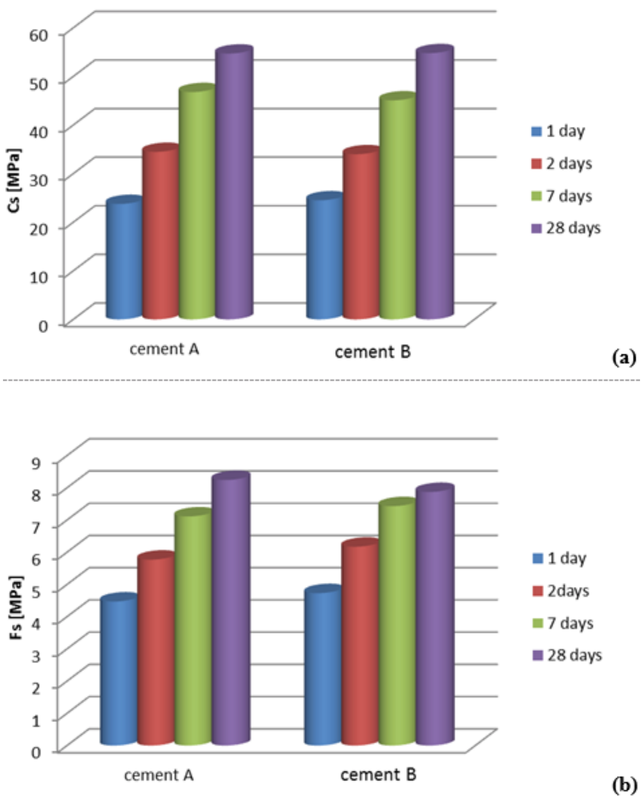

Fig. 3. Mechanical strengths *vs.* hardening time: a- compressive strength (Cs); b- flexural strength (Fs)

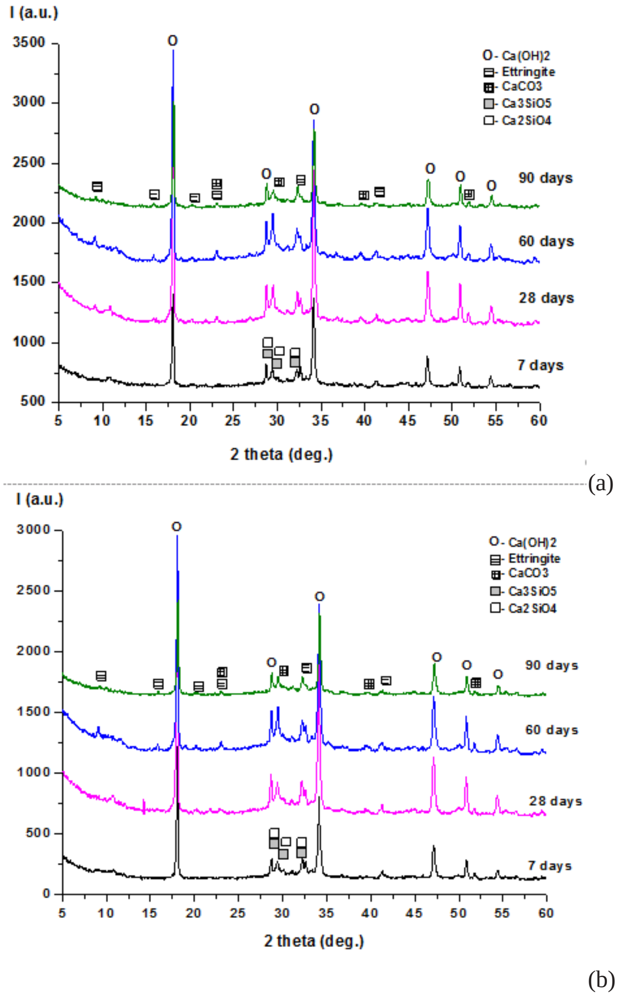

Fig. 4. Diffraction patterns of cements for different hardening period: a - cement A; b - cement B

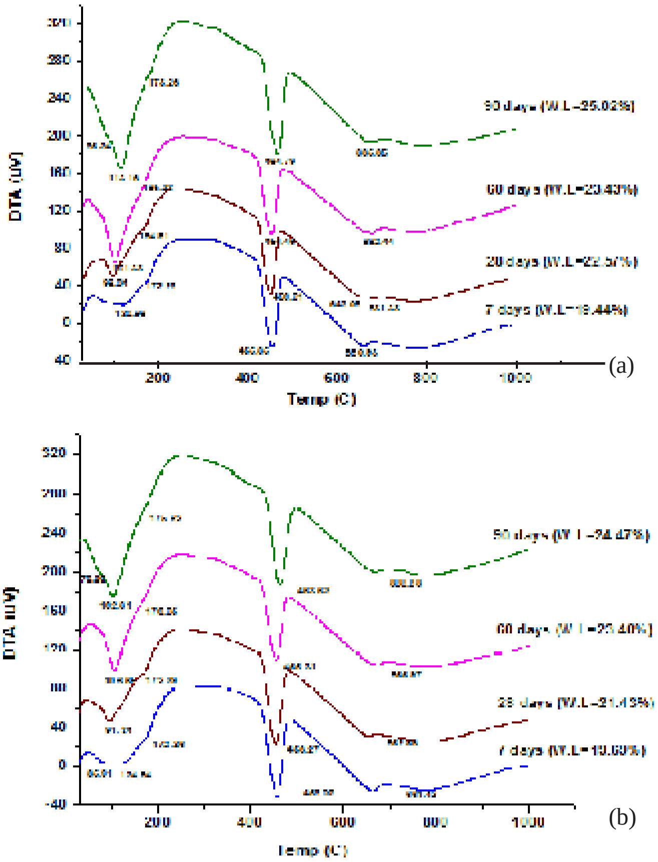

Fig. 5. Differential thermal analysis curves of cements after different hardening periods: a- cement A; b - cement B

presence of calcium carbonate (JCPDS 24-0027) is explained by the partial carbonation of Ca $(OH)_2$ with atmospheric CO_2 during specimens' preparation and curing.

Additional data on the nature of phases resulting from hydration-hydrolysis process were obtained by complex thermal analysis (fig. 5). On the DTA curves are present three main endothermic effects [23, 24, 29], as:

- the endothermic effect from 70 - 180°C can be attributed to the dehydration of ettringite (the effect with maxim at 80 - 90° C) and calcium silicate hydrates with a lower crystallinity degree (the shoulder at 110-180 ° C);
- the endothermic effect from 450 - 465°C is attributed to calcium hydroxide dehydration;
- the endothermic effect from 650 - 667°C is attributed to decarbonation of calcium carbonate.

Based on the above presented results one can say that the using of this type heavy ash as addition to the raw mix used for the manufacture of Portland clinker do not have a major influence of the quality of cement.

Conclusions

Based on the results obtained in this study, one can affirm that there are no significant differences from the point of view of amount and crystallinity of mineralogical phases, formed in the clinker obtained by the thermal treatment of raw mix with heavy (bottom) ash addition and the clinker obtained from a regular raw mixture. These results, corroborated with the lower amount of belite (C_2S) in these clinkers, confirm a good kinetics of the chemical processes that occur during thermal treatment, and especially the conversion of C_2S to C_3S. Therefore, the quality of both clinkers can be considered similar.

No major differences were found with respect to the oxide and mineralogical compositions of the two studied clinkers. Therefore, no significant differences in hardening processes and specific binding properties have been identified for the cements obtained by the clinkers grinding with gypsum.

Thus, it can be stated that the use of this heavy (bottom) ash, with a high SO_3 content, in small quantity in the raw mix has no negative influence on the quality of resulted clinker or cement. Also, the sulphur isomorphic addition in calcium silicates lattice, which determine an important distortion of C_2S lattice.

Acknowledgements: The electron microscopy analyses/images obtained on the samples were possible due to EU-funding project POSCCE-A2-O2.2.1-2013-1/Prioritary Axe 2, Project No. 638/12.03.2014, ID 1970, SMIS-CSNR code 48652.

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Manuscript received: 13.09. 2017