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THE USE OF THE BOTTOM ASHES AND OF THE STEELMAKING SLAGS IN THE MANUFACTURING TECHNOLOGIES OF THE BUILDING MATERIALS

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The energetic and metallurgy industries of Romania represent the main waste sources significant from the point of quantitative view: the bottom ashes and the blast furnace and secondary metallurgical slags. Starting from the knowledge of the main chemical-physical properties of these two types of industrial wastes, there were inquired the exploitation possibilities in the technological practice, by using in the manufacturing of some building materials, for which these wastes represent the exclusive raw material source. The experiments considered the granular aggregate properties of the bottom ash and of the blast furnace slag, completed by the hydraulic binder of the secondary metallurgical slag, after the fine crushing.

Key words: metallurgy, energy industry, steelmaking slags, building materials, bottom ashes

INTRODUCTION

The industrial wastes continue to represent important polluting factors of the environment, assertion valid both regarding the quantities resulted from the day-to-day activity, and those accumulated up to the present in historical storages. From this point of view, in Romania is pointed out the wastes resulted from the energetics and metallurgical industry activities, respectively, the ashes resulted from the energetic coals burning and the blast furnace and treatment slags of the liquid steel.

In the case of the ashes resulted from the coals burning into the steam generator burners, the light ash (known as „flying ash”) is exploited 100 % on the industrial flows of Portland cement manufacturing, and the heavy ash or the burning slag (named „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. The speciality literature presents solutions of using this waste as raw material in the manufacturing technologies of the building materials [1-7], but the exploited quantity represents below 10% of that produced.

On the industrial flows of steelmaking, the metallurgical slags appears, also, in two distinguishing varieties: the blast furnace slag (resulted from the primary processes of BOF- Blast Oxygen Furnace or of EAF-Electric Arc Furnace) and the secondary metallurgical slag (resulted of the advanced processing of the liquid steel into the LF-Ladle Furnace treatment). The two slag varieties are totally different, regarding both the aspect and the chemical-physical characteristics: the blast furnace slag is a hard material, resulted by the recrystallization from the melting of some compounds with pheritic oxide base, while the secondary metallurgical slag represents a preponderant spraying waste, with calcium compositional base (about 60 % CaO). The blast furnace slag is partially used as thick aggregate, as substitute of the materials obtained by fragmentation of the natural rocks [8-9], while the secondary metallurgical slag has not yet defined a specific exploitation framework.

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THE USING POTENTIAL OF THE STUDIED WASTES

The heavy ash (the bottom ash) is considered to represent a source of light granular aggregate (density class

Table 1 **The main chemical-physical characteristics of the bottom ash[10]**

Characteristic		Specific value	Variation limits
Chemical composition / %	SiO_2	47,5	40 - 50
	Al_2O_3	17,4	16 - 21
	Fe_2O_3	8,6	8 - 9
	CaO	11,2	9 - 14
	Na_2O+K_2O	2,7	1,5 - 3
	LI	8,9	5 - 12
Humidity / %		22,8	20 - 28
Bulk density / g/cm³		0,9	0,85 - 1,05
Granulometer class / mm		0 - 4	0 - 8
Mineralogical composition		α – SiO_2 (quartz) $CaO.Al_2O_3.2SiO_2$ – Anorthite $2CaO.Al_2O_3.SiO_2$ – Gehlenite Fe_2O_3 – Hematite	

according to ASTM C330), the main characteristics being presented in Table 1 [10], where*) LI - Loose on ignition

The bottom ash evacuated in the low area of the burning installations and transported in the storehouses (after granulation) using the hydro-mixture process, does not present the pozzolanic properties and is inactive, in the mentioned state, at the contact with the water in the mixtures of concrete charges type. The chemically inert property of the bottom ash is considered to be given by the moulding thermal regime (1 000 – 1 200 ^oC) and the initial state of „compact slag" (sintered oxydic material).

The blast furnace slag (EOS) represents an oxydic material with a complex composition, dependant of the steel charge composition, by the same that, besides the basic oxydic compounds (Fe_2O_3, CaO, SiO_2, Al_2O_3, MgO) resulted from the usual additions of generated mineral compounds, it contains also compounds decantated after the oxidation of the metal elements (ferroalloys) added to the melting charges, depending of the produced steel mark (Cr, Ni, Co, Mn, W, V). The formation conditions of these slags, respectively the recrystallization from the melting process at over 1500 ^oC, give them a high thermodynamic stability, respectively the total inertia in the interaction with whatever compound from a normally concrete charge or from the ramming mass for buildings, including at the contact with the hydration formations generated by the Portland cements (pH basic medium). The formation condition also represents the argument for the fact that, even in the conditions of the presence with high weight of the heavy metals in the composition, these are not marked out in the laboratory tests made to determine the levigable elements, resulting the conclusion that the use of the blast furnace slags as granular aggregates for buildings do not involve risks of ecological contamination from this point of view [11].

The secondary metallurgical slag (LFS) derives from the specific processes of the melting steel processing in the Ladle Furnace. After the evacuation and the cooling, it presents the characteristics of the preponderant spraying material and which, from the point of chemical composition view, it could be considered nonspecific for the ferrous metallurgy technologies: SiO_2 12 - 25 %; Al_2O_3 4 - 8 %; Fe_2O_3 0,5 - 2 %; MgO 7 -15 %; CaO 50 - 65 %; MnO 0,3 - 3 %; Cr_2O_3 0,1 - 0,3 %; SO_3 0,5 – 1,8 % [12].

The precise nature of the secondary treatment slag is also shown by the mineralogical composition, determined by X-rays diffraction, where the preponderance of the calcical compounds is thrown out into relief again: CaO (calcium oxyde), $2CaO.SiO_2$ (calciumsilicate), $Ca_2(Mg_{0,5}Al_{0,5})(Si_{1,5}Al_{0,5}O_7)$ (melilite), $MgO.SiO_2$ (clinoenstatite).

This compositional nature of the secondary metallurgical slags suggests properties of hydraulic binder material, as long as the laboratory investigations attest the presence of the calcium oxyde in free form and bind with silicate compounds specific to the Portland cements, properties which can be intensified by simple grinding up to a comparable fineness with those of the usual building cements (maximum 2 % remainder on the sieve with the mesh of 0,09 mm).

PERFORMED WORKS

According to the SR 3910-2 of 1998 normative, the lime reactivity is defined by the volume of the 4N hydrocloric acid which neutralizes by titration in a definite period of time, a lime suspension in the water, in the presence of standard basic-acide indicator (phenolphthalein). During the works, the trying method was done in the similar conditions on the industrial lime samples and on the secondary metallurgical slag, the results being presented in Table 2.

Table 2 **Comparative test of reactivity lime/LF slag**

Material	Quantity	Water volume	HCl 4N consumed volume
Dried lime	5 g	200 ml	16,3
LF slag	5 g	200 ml	5,4

Calculating the ratio between the consumed hydrocloric acid volumes consumed in similar work conditions, it is estimated that the secondary metallurgical slag subject to test contains 33,13% CaO, equivalent as reactivity with the industrial lime.

To demonstrate the hydraulic binder aptitude of the secondary metallurgical slag, by mechanical-physical test laboratory carried out in university's laboratories, were made trying tests similar to the EN 196 norm specific to the classic hydraulic binder (cements), on a mixture made of 1350 g poligranular sand and fine grinding 450 g LF slag. The test results are shown in Table 3.

Applying the procedure of the same cement normative, comparative tests were also made for the setting time, using as reference materials two types of Portland cement the results being shown in the Table 4.

Table 3 **The mechanical-physical characteristics of the concrete hardened on the secondary metallurgical slag base**

Characteristic	Water / binding ratio	Compression resistance / MPa		
		After 2 days	After 7 days	After 28 days
Value	0,56	14,35	17,25	19,62

Table 4 **The determination of the setting time for the hydraulic binder**

Tested material	Used quantity / g	Water of normally consistency		Setting time	
		Volume / cm^3	/ %	Beginning	End
Cement 42,5N	300	131	43,6	4 h 20 min.	6 h 30 min.
Cement 52,5R	300	117	39,0	3 h 45 min.	4 h 45 min.
LF Slag	300	105	35,0	1 h 5 min.	4 h 20 min.

Starting from the premise that the secondary metallurgical slag (the LF slag) could play the role of hydraulic binder, it was tested the possibility to obtain some building materials of the strengthened ramming masses type, designed to the manufacturing of the equalization or filling layers, in the preparation works for the foundations or for the road buildings, the industrial wastes have to represent the exclusive components of those composition. For experimentally use, the aim wastes were obtained and manufactured, as follows:

- the bottom ash was sampled and used as itself, from the Valea Ceplea deposit of the Turceni Energetical Complex (52,5 ha, about 20 millions tones);
- the blast furnace slag was taken from the steelmaking flow in the SMR Balș and primary worked, by crushing and calibre graining in the dimensional class of 0 – 10 mm;
- the secondary metallurgical slag was taken on the production flow of the SRM Balș and primary worked, by advanced crushing in ball mill, up to the fineness characteristics to a remainder of maximum 2 % on the sieve with the mesh dimension of 0,09 mm.

According to the aim, during the experimental works were made four different mixtures of bottom ash, blast furnace slag (EOS) and secondary metallurgical slag (LFS), from which, after the damping with water, were manufactured by ramming test pieces for laboratory tests in the forms of cubes with the dimensions of 100x100x100 mm. The rammed pieces were immediately striking after the manufacturing, then stored in the conditions of avoidance of the natural drying (polyethylene packing) at the environment temperature (20 – 25 ^{o}C) and subject to the crushing strength test after 2, 7, 28 days from the manufacturing moment. To determine the density, rammed pieces were used maintained 3 days in free air at the environment temperature, then dried in the laboratory drying chamber 12 hours at the 105 ^{o}C temperature. The results of the laboratory tests are shown in Table 5.

Table 5 **The mechanical-physical characteristics of the masses obtained on the base of industrial wastes**

Sample	Composition / % mass			Density, dried at 105°C / g/cm^3	Crushing strength / MPa		
	Ash	EOS	LFS		2 days	7 days	28 days
1	60	-	40	1,08	2,86	4,12	4,62
2	40	20	40	1,22	3,16	4,85	5,11
3	20	40	40	1,68	4,22	5,15	5,72
4	10	50	40	1,96	5,08	6,12	6,84

DISCUTIONS

The heavy ash (bottom ash) and the steelmaking slags resulted on the technological flows of making and treatment of the steel can be included in the category of industrial wastes with a exploitation potential:

- the bottom ash and the blast furnace slag have the aptitude of granular aggregates and can replace or substitute the natural raw materials used with this technological purpose;
- secondary metallurgical slag presents characteristics of hydraulic binder, given by the free calcium oxide content and by the calcium silicates exactly like for the classic Portland cements.

To assure the practical possibilities of exploitation of the technological potential, the studied industries wastes (the bottom ash, the steelmaking slags) require plain primary works, of type of crushing, graining or fine crushing, technological operations which apply also in the case of the use of the natural raw materials.

The moulding mixtures obtained by exclusive use of these three types of the industrial wastes present hydraulic hardening properties, which can be exploited in the practice of the building materials manufacturing. From the point of view of the mechanical-physical characteristics after the hardening, these type of mixtures can not compete the classic concretes, but can be as attractive alternatives to the making of consolidate earth works, because the costs regarding the use of the habitual hydraulic bindings (lime, cement) are eliminated and the deteriorating impact of the environment by exploitation of the classic granular aggregates (sand, mineral rocks) is reduced.

From the point of view of environment protection, the exploitation of the bottom ashes and of the steelmaking slags by manufacturing technologies of the building materials assures two main advantages:

- the elimination of some important polluting factors of the environment with industrial wastes significant from the point of quantitative view;
- the protection and the preservation of the environment, by reducing the natural raw materials consumption (sands, mineral rocks).

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Note: The responsible translator for English language is the engineer certified English Patrascu Gheorghe Cristian, graduate Faculty of Metallurgy, Polytechnic University of Bucharest, Romania