METABK 54(1) 297-300 (2015)
UDC – UDK 669.011.004.8:620.91:624.016=111

# ASPECTS REGARDING THE USE OF THE INDUSTRIAL WASTES AS RAW MATERIALS FOR THE MANUFACTURE OF BUILDING MATERIALS

Received – Primljeno: 2014-04-15
Accepted – Prihvaćeno: 2014-08-20
Professional paper – Strukovni rad

In this article are present the results of physical and chemical characterisation activities, of industrial wastes: ash and slag, drilling sludge, metallurgical slag. Also, were established the conditions in which these industrial waste types could be used as raw materials for manufacture some building materials. The ash can be assimilated with a lightweight aggregate similar to the natural sands, the oil-well drilling sludge presents an advanced similarity with the suspensions of fine particles of sand clays, the steel melting slag in electric furnace has the characteristics of a dense granular aggregate and the secondary treatment steel slag is characterized by the high content of calcium oxide.

*Key words*: wastes, metallurgy, energy industry, building materials

## INTRODUCTION

The activities in the energetics, oil-well and metallurgy domains are widely recognized as the main generators of the industrial wastes and emissions of pollutants, the undeniable economic value of the products being continuosly associated to these negative aspects of the impact on the environment. Thus, it is easy to understand the special attention given to the problems relating to the possibility of the quantitative reduction, especially to the use of the wastes generated by these industries, respectively the reduction of the negative ecological impact, including their placing on the industrial flows of exploitation, by which will be reduced as much as possible the effects generated by the classical methods of storage directly on the ground.

For Romania, the problem generated by the wastes of the above mentioned industries is more than real and devolve upon two distinguishing main aspects: the production by the currently industrial practice and the existance of the historical deposits. It may seem difficult to accept, but the storage on the ground of these wastes, especially of those of the energetics and metallurgy sectors was and is further to modify the geographical relief.

In the speciality literature appear reffers of frequent reccurence on this genre of using the wastes. Thus, the bottom ash is presented to be interest for use as lightweight aggregate in the production of concrete masonry units, either as such or in the form of pellets [1] or extrused semi-manufactured goods [2]. There are also, reffers regarding the use in the manufacturing technologies of the bricks [3 - 5], tiles [6] and of the pavement elements [7].

R. G. Popa, L. G. Popescu, T. A. Abagiu, C. Popescu, R. Cazalbasu, Engineering Faculty, Constantin Brancusi University of Targu Jiu, Romania

The steelmaking slag resulted in the steel making process in the electric-arc furnace presents similarity with dense natural aggregates (crashed rocks). The literature shows the solutions of this kind of waste by reusing on the making flows [8], but in most of the cases reffers at the use as granular aggregate in the asphalt mixture or in the bottom compacted layers for the road way construction [9 - 10].

The sludge of the oil-well drilling differs from the point of compositional view, depending on the structure of the geological layers from the areas where are carried out the drilling works. By investigating and establishing the compositional characteristics (the oxidical and mineralogical chemical analyse) and the basic physical caracteristics (the dimensional distribution of the granules, the density in bulk, the humidity) of the bottom ash, of the drilling sludge (cuttings), from the Dacian and Ponţian geological layers, of the steelmaking slag of the steel making in the electric furnace (the CE slag) and of the steelmaking slag of the secondary treatment of the liquid steel in the furnace-ladle (the LF slag), it could be established the conditionns in which these industrial waste types could be used as raw materials for manufacture some building materials, exclusively or in combination with the consecrated raw materials, characteristics for this domain of production and for the industrial technical applications.

## MATERIAL AND METHOD

To establish in how many percentages and what is the technology in which the four types of the industrial wastes could be sources of alternative raw materials, there were analised, physical and chemical, representative samples of each type of waste.

*The bottom ash (the heavy ash)* was sampled from the historical deposit of slag and ash Valea Ceplea (place in Romania), where the slag and the ash are evacuated by hydromixture transport method (1:10). For the representativity of the characteristics, but, also, for the establishing of the variation way of the chemical and physical characteristics on the whole area of the deposit and on depth, to sample the ash elementary samples, it was established a methodology which provides the drilling in 120 points located at the intersections of a grid in forms of squares with the side of 100 m, at the deposit surface [11 - 12]. From every drilling point, the samples were taken out from the depths of 5 m, 10 m, 15 m and 20 m, plus other 20 samples taken out at approximately equal distances from the surface layer of the deposit, resulting thus, a number of 500 elementary samples. On the surface map of the Compartment no. 1 of the Valea Ceplea Deposit, there were delimited 5 areas, marked with E, F, G, H and I, which encompass an equal number of drilling points. For each area of the deposit, the representative samples, corresponding to the drilling depth of 5 m, 10 m, 15 m and 20 m, were obtained by cumulation of the elementary drilling samples, resulting thus, a number of 20 representative drilling samples, each of 60 - 80 kg, and a representative sample cumulated of all the elementary samples taken out at the 0 level. The cumulated samples were obtained by homogenizing of the elementary samples in the mixer, with free falling, the homogenizing time being of 3 minutes and were marked depending on the position from the deposit and on depth.

Of the representative bottom ash samples, laboratory samples were taken out, which were analised from the physical-mechanical point of view (the humidity, the granulometric composition and the density – the volumetric weight in settled and unsettled state) and from the chemical point of view, being determinated the oxidical composition.

The total humidity of the ash samples was deter minated using the thermobalance, and the humidity, by drying in the drying chamber at $105^0$ C, according to STAS 1913/I-82. The volumetric density was determinated using the laboratory balance, according to STAS 1913/3-76 [11 - 12].

The determination of the granulometric composition was made according to STAS 1913/5-85 by the help of the sieving device AS 200 Basic.

*The oil-well drilling sludge (sludge cuttings)* resulted from the extractions of 600 – 1 400 m depth, from the Dacian and Ponţian geological layers. The chemical and physical characterization of the oil-well drilling sludge was done on two samples, differenced by the two types of material used as densification addition:

- The drilling sludge sample with addition of calcium carbonate (limestone flour) – was obtained by cummulation of the elementary samples taken out from the drilling in the Dacian layer of the areas Oprişeneşti (Braila) and Valcele (Arges), resulting a representative sample of 120 kg.
- The drilling sludge with addition of barium sulphate - was taken out 10 samples, each of 70 – 80 kg, during the drilling operation at the Well 594 of the Boldesti-Scaieni (Prahova) area, from the drilling depth of 540 m, 650 m, 680 m, 710 m, 760 m, 850 m, 870 m, 890 m, 940 m and 960 m [13].

*The electric furnace slag* was sampled from the storage waste-dumps in gross form, thus how results after the decrepitation at the sudden cooling from the melting and the partial fragmentation during the handling, transport and storage operations. In the Institute of Metallurgical Researches, the CE slag was subject to the primary processing, by crushing and graining, obtaining the minced material which can be used as dense granular aggregate in the obtaining technologies of the building materials.

*The secondary treatment slag* as sampled after the evacuation from the furnace and cooling, in the form of a heterogeneous mixture, made by the hard melting fragments, crumbly fragments and spraying material. The representative samples form this waste were obtained after the separation of the hard meltings and the fine crushing of the backlogs.

From the point of view of the building material manufacturing technologies, where the studied industrial wastes was to form alternative raw materials, two categories were taken into account, from the point of view of the developing device of the resistance structure in the finished ceramic composite:

- the manufacturing of the shaping products (bricks) by half-dry, half-plastic and plastic pressing and extrusion processes, followed by dry heat treatment and burning at high temperature (mechanisms of ceramic binding);
- the obtaining of monolithic products (concretes, ramming masses) intended to be placed at the service place (pouring of the copings, injection) or to the prefabricated execution, having in composition usual cements for buildings (mechanisms of hydraulic binding).

## RESULTS AND DISCUSSIONS

The physical characteristics of the bottom ash are shown in Table 1. Of the listed data in the table it observes that the ash could be assimilated to a lightweight aggregate, which could replace the natural sand as ungreasing in the manufacturing technologies of bricks or concretes for the buildings. Given the quantity in bulk lower than the sand, it is expected that in case of the use of the ash to be obtained low density products, fact which in some conditions can be an advantage, first, by increasing of the phonic and thermal isolation.

From the point of view of the chemical composition, the bottom ash from the Valea Ceplea Deposit, can be classified in the oxidic class $SiO_2 – Al_2O_3 – Fe_2O_3 – CaO$, being from this point of view relively similar to the partial burnt feldspar calcareous clays (low burnt chamottes):

Table 1 **The physical characteristics of the bottom ash**

| Humidity | Granulatometric composition | | | | | | | | | | The volumetric mass in bulk / g/cm$^3$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Rest / %, mass on the sieve with the mashes / mm | | | | | | | | | | | |
| % | 4 | 3 | 2 | 1 | 0,5 | 0,2 | 0,09 | 0,06 | <0,06 | Unsettled | Settled |
| 29,46 | 2,55 | 1,23 | 2,10 | 5,11 | 7,75 | 18,66 | 25,55 | 9,13 | 27,91 | 0,77 | 0,97 |
| 29,53 | 3,24 | 1,35 | 2,25 | 5,57 | 8,10 | 19,22 | 25,86 | 8,50 | 25,92 | 0,79 | 0,97 |
| 25,04 | 3,37 | 1,86 | 2,93 | 5,96 | 7,95 | 19,07 | 25,53 | 7,99 | 25,33 | 0,76 | 0,96 |
| 28,68 | 5,43 | 1,80 | 2,44 | 5,81 | 7,80 | 18,56 | 25,36 | 8,03 | 24,76 | 0,79 | 0,98 |
| 28,72 | 3,17 | 1,68 | 2,28 | 5,58 | 8,12 | 19,41 | 26,70 | 8,62 | 24,44 | 0,76 | 0,96 |

$SiO_2$ 40 – 50 %; CaO 9 – 14 %; $Al_2O_3$ 16 – 21 %; $Na_2O$ + $K_2O$ 1,5 – 3 %; $Fe_2O_3$ 8 – 9 %; P.C. 5 – 12 % [11 - 12].

The membership of this class of materials is shown by the results of the mineralogic compositio n determinations made by the X-rays diffraction method, which attests the majority presence of α-quarz ($SiO_2$), Anorthite ($CaAl_2(SiO_4)_2$) and Hematite ($Fe_2O_3$) [13].

The physical characteristics of the drilling sludges of the representative samples are shown in Table 2. It observes that the presence of the barium sulphate causes a significant increase of the density of the driling sludge, both in the initial state and after the removing of the humidity excess, important aspect if the same effect will be observed in the case of the building materials obtained with the use of such kind of waste, too. To obtain the ecosustainable building materials, it concerns the sludge cuttings from the drillings at which as densify element is used the calcium carbonate (limestone flour), characterised by the oxidical chemical composition 50 - 55 % $SiO_2$, 8 - 12 % $Al_2O_3$, 3 - 5 % $Fe_2O_3$, 7 - 10 % CaO, 2 - 3 % MgO, 3,5 - 5,5 % $Na_2O$ + $K_2O$ and loss at calcination of 13 - 15% [11 - 12].

The physical characteristics of the representative samples of the slag of the electric furnace are shown in Table 3. The oxidical chemical composition resulted due to the laboratory determinations shows variations in much broader limits than those observed at the processed bottom ashes, as follows: $SiO_2$ 12 – 20 %; $Al_3O_3$ 3 – 7 %; $Fe_2O_3$ 25 – 38 %; MgO 3 – 6 %; CaO 32 – 42 %; MnO 5 – 8 %; $Cr_2O_3$ 0,5 – 1,4 %; $SO_3$ 0,5 – 1 %.

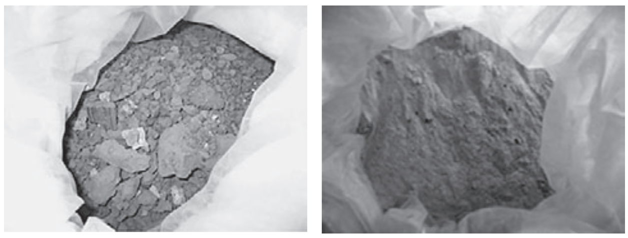
The physical characteristics of the secondary treatment slag are shown in Table 4. The chemical composition presents relatively broad limits of variation, being mentioned the fact that at this type of slag a special importance presents the CaO content, taking account of the fact that in the technological applications it is followed the exploitation of the aptitude of the hydraulic binder which this gives it: $SiO_2$ 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 % (Figure 1).

Table 2 **The physical characteristics of the oil-well drilling sludge**

| Sample | Marker | Litric density / g/cm$^3$ | Humidity / % | Finess (humid) Rest / %, mass on the sieve of 0,06 mm | Density after drying / g/cm$^3$ |
|---|---|---|---|---|---|
| Sludge $CaCOO_3$ | SDCa | 1,69 | 32,73 | 4,3 | 1,37 |
| Sludge $BaSO_4$ | SDBa1 | 1,86 | 15,85 | 2,3 | 1,65 |
| | SDBa2 | 1,79 | 16,99 | 2,1 | 1,68 |
| | SDBa3 | 1,84 | 16,52 | 2,2 | 1,66 |
| | SDBa4 | 1,85 | 16,27 | 2,1 | 1,66 |
| | SDBa5 | 1,84 | 16,92 | 2,1 | 1,65 |
| | SDBa6 | 1,86 | 18,95 | 2,5 | 1,68 |
| | SDBa7 | 1,82 | 16,46 | 3,4 | 1,64 |
| | SDBa8 | 1,81 | 16,69 | 4,5 | 1,68 |
| | SDBa9 | 1,88 | 16,66 | 2,6 | 1,67 |
| | SDBa10 | 1,87 | 16,14 | 1,8 | 1,67 |

## CONCLUSIONS

From the point of view of the chemical-physical characteristics, the studied wastes can be taken into account as alternative raw material sources to the manufacture of building materials:



a b

**Figure 1** Steelmaking slags (a - slag of electric furnace; b - slag of secondary treatment)

Table 3 **The physical characteristics of the slag of electric furnace**

| Source | Granulatometric composition | | | | | | | | | | Volumetric weight / g/cm$^3$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Rest / %, mass on the sieve with the mashes / mm | | | | | | | | | | | |
| | 5 | 4 | 3 | 2 | 1 | 0,5 | 0,2 | 0,09 | 0,06 | <0,06 | Unsettled | Settled |
| SMR Bals | 0 | 0,6 | 2,1 | 14,0 | 29,6 | 19,6 | 16,0 | 8,4 | 2,6 | 7,1 | 1,84 | 2,35 |
| Doosan IMGB | 0 | 1,9 | 0,8 | 10,6 | 35,0 | 25,2 | 14,8 | 5,6 | 1,2 | 1,9 | 1,78 | 2,23 |
| MECHEL | 0 | 2,1 | 3,2 | 16,5 | 33,3 | 18,5 | 15,6 | 8,1 | 2,0 | 0,7 | 1,87 | 2,34 |

Table 4 **The physical characteristics of the representative samples of the secondary treatment slag**

| Source | Humidity | Granulatometric composition Rest / %, mass on the sieve with the mashes / mm | | | | Volumetric weight / g/cm$^3$ | |
|---|---|---|---|---|---|---|---|
| | / % | 0,2 | 0,09 | 0,06 | <0,06 | Unsettled | Settled |
| SMR Bals | 0 | 0,9 | 1,8 | 2,9 | 94,4 | 1,08 | 1,79 |
| Doosan IMGB | 0 | 1,6 | 1,3 | 3,3 | 93,8 | 1,04 | 1,58 |
| MECHEL | 0 | 1,3 | 0,9 | 2,1 | 95,7 | 0,95 | 1,40 |

- the heavy bottom ash (the hearth ash), can be assimilated with a lightweight aggregate similar to the natural sands currently used, showing in addition the advantage of a lower density in bulk,
- the oil-well drilling sludge extract in the drilling area in Romania presents an advanced similarity with the suspensions of fine particles of sand clays which can replace them in the role of plasticizer addition to obtain the shaping mixtures,
- the steel melting slag in electric furnace, after the processing by crushing and granulation, has the characteristics of a dense granular aggregate and can be used with this role to obtain the concrete mixtures and the filling mass,
- the secondary treatment steel slag is characterized by the high content of calcium oxide and, after the fine crushing, can be taken account as addition with hydraulic binder effect.

## Acknowledgements

The present research has been carried out with the financial support given through LIFE10 ENV/RO/729 Project.

## REFERENCES

[1] Benjamin L. P., Groppo J., Perrone R., Evaluation of processed bottom ash for use as lightweight aggregate in the production of concrete masonry units, World of Coal Ash Conference, Lexington, USA, (2005).

[2] Steven H., Kosmatka W. C., Special types of concretes - Design and Control of Concrete Mixtures, 13th edition, EB-001, chapter 18, (1988), 315-333.

[3] Tayler G. V., Daidone W., The use of bottom ash in the manufacture of clay face brick, World of Coal Ash Conference, Denver, Colorado, USA (2011).

[4] Braganca S.R., Zimmer A., Bergmann C.P., Use of mineral coal ashes in insulating refractory brick, Refractories and Industrial Ceramics, 49 (2008) 4, 320-326.

[5] Zimmer A., Bergmann C.P., Fly ash of mineral coal as ceramic tiles raw material. Waste Management, 27 (2007), 1, 59-68.

[6] Neamtu I., Rujenescu N., Lazau I., Becherescu D., The use of bottom ash in the manufacture of concrete tiles, 8th International Conference The Days of the „Constantin Brâncuşi" University, Tg-Jiu (2002).

[7] Triches G., Silva A.D., Andrade Caldas PintoR., Incorporating bottom ash in roller compacted concrete for composite pavements, Proceedings of The Asean Federation of Cement Manufacturers Concret Road Symposium, Kuala Lumpur, (2007), 54-74.

[8] Dippenaar R., Industrial uses of slag. The use and re-use of iron and steelmaking slags, VII International Conference on Molten Slags Fluxes and Salt, Cape Town, South Africa, (2004), 57-70.

[9] www.nationalslag.org/appmatrix.htm, National Slag Association - Common uses for slag

[10] www.intechopen.com, Branca T. A., Colla V., Possible Uses of Steelmaking Slag in Agriculture

[11] Annex 4.1.a Characterization of the representative waste samples provided to the end-user LIFE Project New building materials by eco-sustainable recycling of industrial wastes, Mid Term Report, 2013.

[12] Annex 3.4 a: Characterization of the ash samples at provider site, LIFE Project New building materials by eco-sustainable recycling of industrial wastes, Mid Term Report, 2013.

[13] Predeanu G., Volceanov E., Abagiu T. A., Cruceru M., Slăvescu V., Racoceanu C., Coal ash characteristics to assess its possible uses, 13th International Multidisciplinary Scientific GeoConference SGEM 2013, 2013, Albena, Bulgaria Energy and Energy and Clean Technologies Proceedings, (2013) 309-317.

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