SUITABILITY OF GRANULATED LEAD SLAG FOR VALORISATION

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ABSTRACT

The granulated slag resulting from the pyrometallurgical processing of lead-rich concentrates was chemically analysed quantitatively by X-ray fluorescent spectometry, microstructurally by scanning electron microscopy (SEM), and microcompositionally by energy dispersive X-ray analysis (EDAX).The compositional phases were determined using the qualitative analysis by X-ray diffraction (XRD). A leachate test was carried out in order to asses the constituents which can be leached from the slag and to determine if these are in accordance with the specific reference figures. The preliminary assessment of the acid draining of slag was carried out using the modified static ABA test by acid-base analysis.

In order to determine the possibility of valorisation of slag as a construction material for embankments, road foundations, and sub-base and base layers, the granulated lead slag was analysed by determining the chemical, physico-mechanical (granulometric analysis, compaction characteristics, California bearing capacity index, permeability) and geotechnical (direct undrained, unconsolidated shearing strength) characteristics and comparing these characteristics with those of sand.

1. INTRODUCTION

Sustainable development is the type of economic development in which people's present needs are met without compromising the future generations' possibility of meeting their own needs. In order to reach the aim of sustainable development we must promote the durable use of natural resources by valorising the wastes generated by industrial processes into products able to replace such resources.

In the Reference Document on Best Available Technique in the non ferrous metals processing industry (BREF-NMF) issued in December 2001 by the European IPPC Bureau, lead slag is deemed suitable for use in constructions (concrete manufacturing and road construction).

This paper investigates the slag obtained after the rapid cooling of the liquid slag resulting from processing lead-rich concentrates in a Water-Jacket hearth furnace in order to recycle the rapidly cooled slag as a construction material for road construction.

Since the primary slag resulting from the pyrometallurgical processing or lead-rich concentrates is included in category 10 – Wastes resulting from thermal processes, as hazardous waste code 10 04 01[1], in order to valorise it for road construction, in compliance with art. 6 of Law 211 of 2011 on the regime of wastes, we must determine the conditions under which this material ceases to be considered waste and obtains the statute of a construction material (*end of waste*)[2,3].

In order to determine the possibility of using these slags as construction materials for roads, one must know their chemical composition, leachability, and their acid draining, physico-mechanical and geotechnical characteristics [4,5,6,7].

2. THE EXPERIMENTAL PART

2.1. Investigating the slag's chemical composition

The slag's chemical composiiton was investigated quantitatively by X-ray fluorescent spectometry, using a sequential wavelength dispersive X-ray fluorescent (WDXRF) spectometer type S8 Tiger and the working method provided by Standard SR EN 15309:2007 Characterisation of wastes and soils. Determining the elementary composition by X-ray fluorescence. The results obtained using X-ray fluorescence (WDXRF) are shown in Table 1.

Table 1 Elementary and oxidic composition found by XRF analysis

Elements	Si	Fe	Ca	Mg	Al	Zn	Cu	Pb	K	Ti	S
%	0.86	32.15	8.68	0.61	1.65	5.34	0.24	2.36	0.23	0.18	1.35
Oxides	SiO_2	Fe_2O_3	CaO	MgO	Al_2O_3	ZnO	CuO	PbO			
%	11.14	45.93	12.15	1.02	1.45	6.65	0.3	2.54			

The intensity of the spectral lines for the analysed samples whose values are to be found in Table 1 is shown below, as follows:

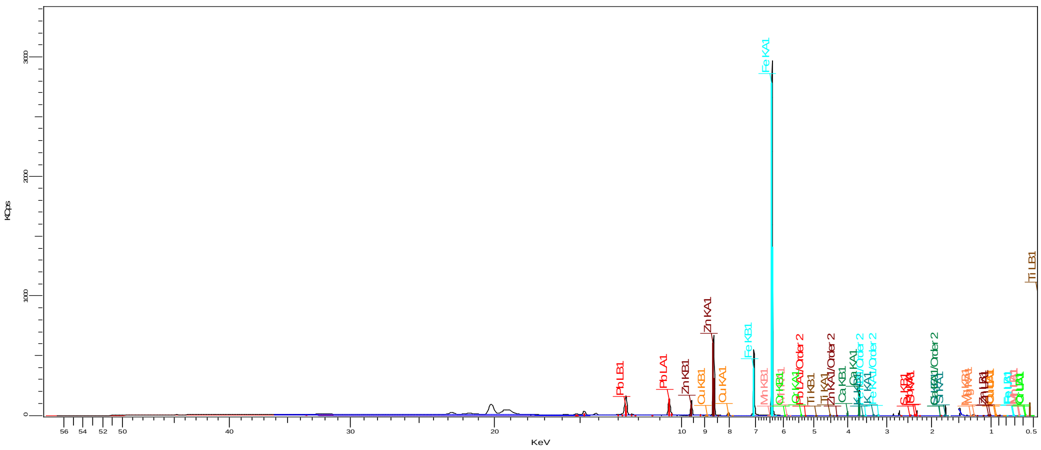

Fig. 1. Intensity of spectral lines for granulated slag

2.2. Microstructural and microcompositional investigation, and determination of the compositional phases for granulated slag

The slag samples were investigated microstructurally and microcompositionally by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) using a Quanta Inspect F scanning electron microscope.

The compositional phases were determined by X-ray diffraction (XRD) qualitative analysis, using a Panalytical X’Pert PRO MPD X-ray diffractometer, with a characteristic monocromatic CuKα X-ray beam with a Ni filter.

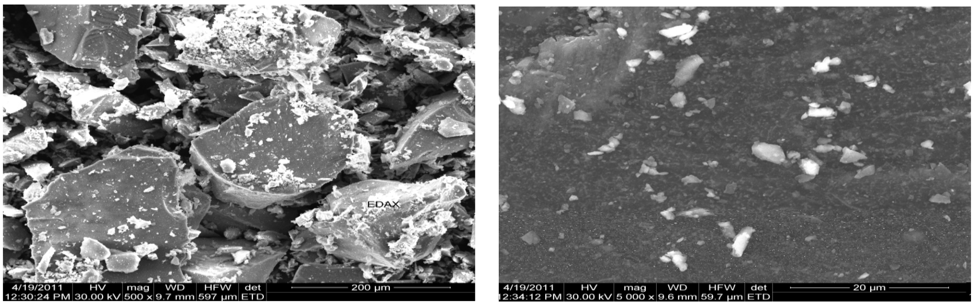

Fig. 2. Scanning electrone microscope (SEM) image of a granulated slag sample magnified 400x, 5000x

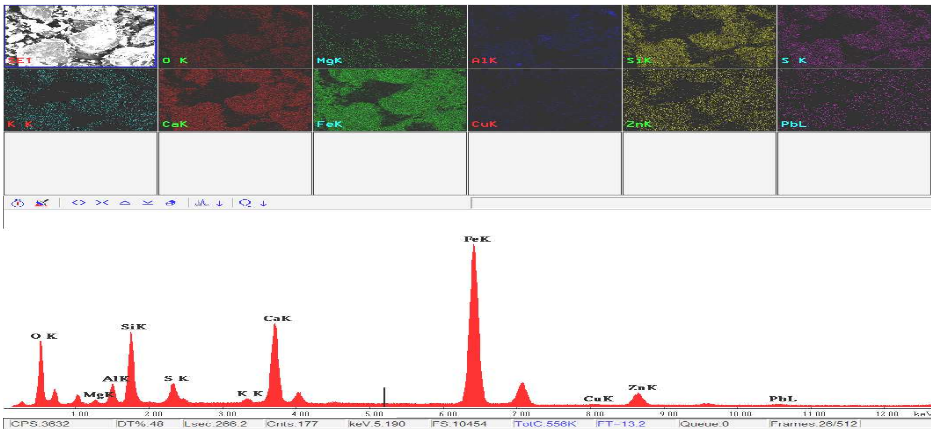

Fig. 3. Microcompositional image of granulated slag

a) at the bottom of the picture is shown the energy dispersive x-ray (EDAX spectre obtained for the micro-area in Figure 2. Note the presence in this micro-area of the following elements: O, Mg, Al, Si, S, K, Ca, Ti, Fe, Cu, Zn, Pb; b) in the upper left corner of the image is shown the aspect of the analysed micro-area; c) the other frames of the image show the distribution of the characteristic X-rays (for the elements specified in each frame) in the micro-area in the upper left frame of the image (this image is present in Figure 2 as well).

The figure below shows the diffractogram obtained for the granulated slag sample.

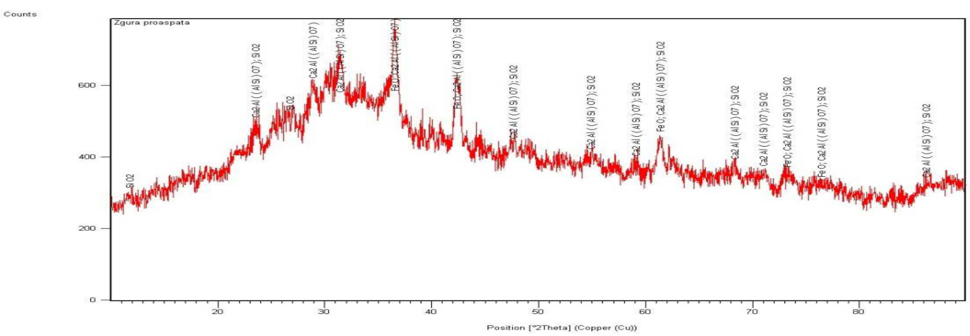

Fig. 4. (Indexed) x-ray diffractogram obtained for the granulated slag sample

The indexation of the obtained diffractogram reveals the presence as majoritary phases of FeO with a cubic crystalline network with centred facets, with a main maximum at angle $2\theta = 41.989^0$, and $Ca_2Al((AlSi)O_7)$ with a tetragonal crystalline network, with the main maximum at angle $2\theta = 31.415^0$, and as minority phase the compound SiO_2 with a romboedral crystalline network with the main maximum at angle $2\theta = 11.177^0$.

2.3. Leachability

In order to assess its leaching conformity, the slag sample was tested by batch leaching tests in compliance with the provisions of SR EN 12457/2003 – Leaching compliance test for granular wastes and sludges, Part 2 – One-stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction).

The quality indicators of the leachate were determined experimentally using a plasma emission spectometer - ICP - Mass Spectrometer Perkin Elmer tip Ealan DRC II.

Order 95/2005 issued by MAPM [the Romanian Ministry of Waters and Environmental Protection] on defining the criteria to be met by wastes so as to be included in the specific list of a storage facility and the national list of accepted wastes for each storing class, are provided the maximum admissible values for the specific leachated indicators for the determination of the characteristics of wastes which can be accepted for each waste storing class (inert, hazardous, non-hazardous).

Table 2 Contrastive analysis of the acceptable indicators specific for leachates

No.	Indicator		Maximum admissible values (mg/kg s.u) L/S-10 l/kg conform Ord.95/2005[8]		
		Granulated slags	Inert	Non-hazardous	Hazardous
1	TDS	36	4000	60000	100000
2	Chlorides	2.0	800	15000	25000
3	Sulphates	88.2	1000	20000	50000
4	Cadmium	< 0.08	0.04	1	5
5	Total chrome	0.1	0.5	10	70
6	Copper	0.11	2	50	100
7	Lead	2.6	0.5	10	50
8	Zinc	2.76	4	50	200
9	pH	6.65	Minimum 6		

2.4. Acid draining

The preliminary assessment of the slag's acid draining was carried out by ABA static test modified by the acid-base analysis, aiming at the analytical assessment of the minerals capable of generating acids and those with a natural potential of consuming acid when subjected to weather conditions.

The acid-base analysis includes two separate measurements:
- calculating the acid potential (AP) by total sulphur analysis, with the following equation:

$$AP = \text{Percentage of total sulphur} * 31.25$$

- determining the neutralisation potential (NP) by treating a small quantity of the finely ground sample with standardised hydrochloric acid and heating it to assure a complete reaction. To make sure that the quantity of acid added is enough to react with all the acid-consuming minerals present, an effervescence test ("fizz test") is carried out. The quantity of acid consumed by the base for neutralisation is used to calculate the neutralisation potential (NP), as follows:

$$NP = 50 * (a * x - b * y)/c$$

where:

a –HCl normality;

b – NaOH normality;

c – sample weight, in grams;

x – volume of added HCl, in ml;

y – volume of added NaOH at pH 8.3, in ml.

Table 3 Acid draining results

No.	Elements	Granulated slag
1	Sulphur	1.35
2	AP	42
3	NP	55
4	NNP=NP-AP	13
5	NNP criteria	0 < NNP < 20 uncertain
6	NPR(NP/AP)	1.30
7	NPR criteria	1-2 possibly generating acid draining

2.5. Chemical characteristics

The specific gravity or the density of the mineral skeleton of the granulated slag and sand were assessed according to STAS 6200/10-73. The value measured for sand was 2.65, whereas for lead slag it was 3.79. The high specific gravity of lead slag in comparison with that of sand is due to the presence in the slag of a high content of iron oxide. Lead slag is a granular blackish material similar to sand. The specific weight of these materials ranges between 2.8 and 3.8 [9].

2.6. Physical and mechanical characteristics

A sieve grain size analysis was performed in order to classify granulated slag in a class of non-cohesive earth, based on the predominance of certain grain fractions, as well as its non-uniformity and plasticity coefficients. For comparison the grain size analysis of the sand from the Tur river was performed as well.

Based on the grain size curves obtained, the non-uniformity coefficient U_n or the uniformity coefficient C_u were calculated, with a curving factor of 2.78 respectively 1.31 for slag, and 2.7 respectively 1.13 for sand.

According to STAS 1243-1983 – Identification and classification of earths, and SR EN 14688-2:2005 – Geotechnical research and tests. Identification and classification of earths, the grain size distribution of both granulated slag and sand is very uniform and the shape of the curves is well-graded.

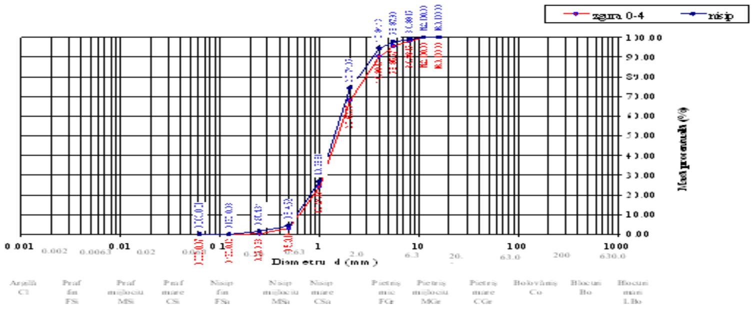

Fig. 5. Grain size curves for slag and sand

According to Tables 1, 2 and 3 of STAS 1243-1983 – Identification and classification of earths, based on the predominance of certain grain fractions, the non-uniformity, plasticity and grain-size coefficients, granulated slag can be classified as fine sand.

Compaction characteristics

The compaction characteristics were assessed by Proctor test according to STAS 1913/13-83, and consisted of compacting the granulated slag and sand samples using the same specific compaction mechanical work, so as to determine the maximum values of their dry density and volumic weight corresponding to the optimum dry and wet moisture contents.

The compaction characteristics were assessed by normal and modified Proctor test on eight granulated slag samples and eight sand samples.

During each compaction test the density (ρ) and dry density (dρ) of granulated slag and sand were calculated so that the Proctor dry density variation curves could be drawn based on the compaction moisture content.

The results obtained for the normal Proctor curve and the saturation for granulated slag and sand are summarised in Tables 4.

Table 4 Experimental data - normal PROCTOR, modified PROCTOR test

Compaction characteristics	Normal PROCTOR test		Modified PROCTOR test	
	Granulated slag	Sand	Granulated slag	Sand
Critical moisture content, w_{cr}, %	3.22	1.5	4.51	1.73
Optimum moisture content in wet domain, w_{opt}, %	5.86	3.0	5.86	3.69
Maximum dry density in wet domain, ρ_{dmax}, g/cm^3	2.21	1.71	2.24	1.76
Maximum dry volumic weight, γ_{dmax}, kN/m^3	21.68	16.78	21.97	17.27

Determining the Californian bearing capacity index (CBR)

A penetration force of 44.450 N was applied on the eight granulated slag and sand samples compacted by normal and modified Proctor test at different moisture contents and densities, using a piston with an area of 1935 mm^2 and a penetration speed of 1.269 mm/min. The force applied on the piston and the penetration speed were measured. Based on the measured values the penetration force variation graphs were drawn and the CBR index values were calculated for penetrations of 2.5 and 5 mm. The relative bearing capacity characteristics or the CBR index were determined by the CBR test using a CBR press connected to a computer to process the information obtained with the help of the GEOLAB programme.

Table 5 Values of CBR index at optimum moisture content

Characteristics	Normal Proctor test		Modified Proctor test	
	Granulated slag	Sand	Granulated slag	Sand
CBR index $I_{2,5}$	22.8	32.0	39.4	47.8
CBR index $I_{5,0}$	25.5	36.0	42.2	59.1

Determining the permeability

Permeability was determined by variable gradient permeameter method, according to STAS 1913/6-76. This method consists of a water current flowing in constant gradient (constant level difference, constant length of sample) through the samples of granulated slag and sand type 0-4 sand at a dry maximum density according to normal and modified Proctor test. The permeability coefficient for the granulated slag by normal and modified Proctor test is 3.10^{-3} cm/s, and for sand is 10^{-4} cm/s.

2.7. Geotechnical characteristics

In order to compare the shear strength of the granulated slag and sand samples compacted by normal and modified PROCTOR test at optimum compaction moisture content and maximum density, the shear strength of these samples was assessed by unconsolidated undrained (UU) direct shear test according to STAS 8942/2-82. The UU shear test was performed using a shearing device connected to a computer and the information obtained was processed using the GEOLAB programme.

The values of the angles of internal friction obtained for the granulated slag and sand compacted by normal and modified Proctor test are shown in the table below.

Table 8 Angles of internal friction

Shear strength parameters	Normal Proctor test		Modified Proctor test	
	Granulated slag	Sand	Granulated slag	Sand
Angle of internal friction, Φ, (degrees)	38.2	32.5	33.7	35.7

3. RESULTS AND DISCUSSIONS

The microstructural and microcompositional analysis, as well as the x-ray diffraction qualitative analysis prove the presence in the fresh granulated slag sample of the following chemical compounds: FeO (wüstite), $Ca_2Al((AlSi)O_7)$ (gehlenite), SiO_2 (silica).

The quality indicators of the leachate – TDS, sulphates, chlorides, Cr_{total}, Cu and Zn – meet the admissible values for the inert deposits, whereas the indicator Pb, Cd meets the admissible values for non-hazardous deposits.

The results of the modified ABA tests prove that the granulated slag does uncertain.

The compaction curves for dry granulated slag and sand do not have an inflexion point, which indicates the lack of sensitivity of the dry maximum density to the variation of humidity. The maximum dry volumic weight is 21.97 kN/m^3 for granulated slag and 17.27 kN/m^3 for sand, whereas the optimum humidity ranges between 5.86% and 3.69%.

The California bearing capacity index values (CBR) for the slag compacted by normal Proctor test, ranging between 22.84% and 25.55%, suggest that the slag can be used for embankment works, and those by modified Proctor test, ranging between 39.39% and 42.22%, suggest that the slag can be used in the foundation and sub-base layers for road pavements.

The results of the permeability test indicate good draining properties and prove the slag’s suitability for use for the construction of embankments and natural road foundations.

The internal friction angles determined ranged between 33.7^o and 38.2^o, which indicates a good shearing strength.

4. CONCLUSIONS

With a view to using the lead slag for road construction, one must specify the end-of-waste criteria indicating when the slag ceases to be a waste and obtains the status of a product.

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