CHEMICAL AND STRUCTURAL ASSAYS AND ANALYSIS OF THE LEACHING BEHAVIOUR AND ACID DRAINING POTENTIAL OF GRANULATED LEAD SLAG

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The chemical assay of the granulated lead slag resulting from the pyrometallurgical processing of lead-rich concentrates was performed quantitatively by x-ray fluorescent spectrometry, then micro-structurally using a scanning electronic microscope (SEM), and micro-compositionally by energy dispersive x-ray analysis (EDAX). The compositional phases were determined by qualitative X-ray analysis (XRD). A leaching test was carried out in order to evaluate the constituents which can be leached from the slag and determine if these are in accordance with the specific reference values. The preliminary assessment of the acid draining potential of granulated lead slag was carried out by a static ABA test modified through acid-base accounting.

Keywords: granulated lead slag, characterisation, leaching behaviour, acid draining

1. Introduction

The sustainable development is the type of economic development which can satisfy people's current needs without compromising the future generations' capacity of meeting their own needs. In order to attain the purpose of sustainable development we must promote the sustainable use of the natural resources by using the wastes resulting from the industrial processes to manufacture products which can replace such resources.

The EU Framework Direction 2008/98/EC on wastes, transposed into the Romanian legislation through Law no. 211 of 2011 on the regime of wastes, provides the necessary steps towards environmental protection and the protection of population's health by preventing or reducing the negative effects produced by the generation and management of wastes, as well as the reduction of the general effects of using the natural resources and the increase of the efficiency of using such resources. According to the a.m. law, any substance originally classified as

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waste shall no longer be considered a waste after it has been recycled and valorized and when it meets the criteria established in accordance with the basic concepts provided in the four conditions of the same law.

Taking into consideration the variety of wastes and the environmental effects associates with these materials, different criteria should be established for each type of waste and such criteria must be defined for each side product and application of wastes.

In order to determine the potential of slags as road construction materials, the chemical and mineralogical composition, as well as the leachability and the acid draining potential of these slags must be assessed [1,2,3,4].

This paper investigates the fresh slag obtained after the fast cooling of the liquid slag resulting from smelting lead-rich concentrates in a Water-Jacket hearth furnace at SC Romplumb SA company, which was deposited in dumps for further use in road construction, and determining the conditions under which this slag can no longer be considered an „end-of-waste" material.

2. Results and discussions

2.1. Investigation of the chemical composition of granulated lead slag

The quantitative investigation of the chemical composition of fresh and aged granulated slag was carried out by x-ray fluorescent spectometry, with the help of a sequential wavelength-dispersive X-ray fluorescence spectometer (WDXRF), S8 Tiger. The working method was the one provided by Standard SR EN 15309:2007. Characterisation of wastes and earths. Determination of the elementary composition by x-ray fluorescence.

The results obtained by x-ray fluorescence (WDXRF) are shown in Table 1.

Table 1

The elementary composition of granulated lead slag identified by XRF analysis

Elements, %	Fresh granulated slag	Aged granulated slag	Elements, %	Fresh granulated slag	Aged granulated slag
Si	0.86	6.76	Cu	0.24	3.43
Al	-	1.75	S	0.49	2.96
Na	-	-	Pb	2.36	8.03
Fe	32.15	27.89	Ba	-	0.37
Ca	8.68	9.05	Cr	0.06	0.22
Mg	0.61	0.49	Sn	-	0.05
K	0.23	0.30	P	-	0.04
Cl	-	0.05	Sr	-	0.03
Ti	0.18	0.19	As	-	0.03
Mn	0.10	0.29	Ag	-	0.02
Zn	5.34	6.51	Ni	-	0.02

Below is illustrated the intensity of the spectral lines for the analysed samples, whose values are shown in Table 1:

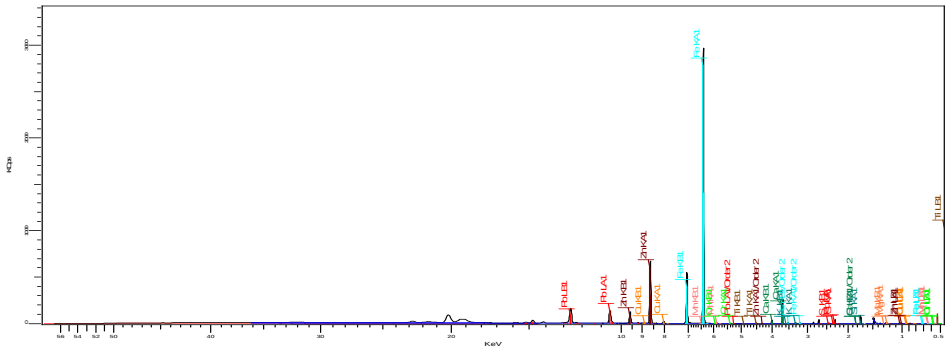

Fig. 1. The intensity of the spectral lines for the fresh granulated slag

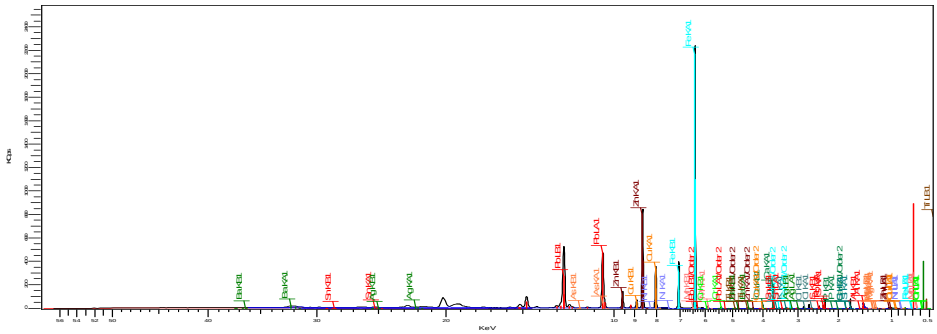

Fig. 2. The intensity of the spectral lines for the aged granulated slag

2.2. Micro-structural and micro-compositional investigation and determination of the compositional phases for the fresh and the aged granulated slags

The micro-structural and micro-compositional investigation of the slag samples was carried out using a scanning electronic microscope (SEM) and by the energy-dispersive x-ray microanalysis (EDAX) using a scanning electronic microscope Quanta Inspect F.

The compositional phases were determined by x-ray diffraction (XRD) qualitative analysis, using the x-ray diffractometer Panalytical X'Pert PRO MPD with a X-ray fascicle characteristic for CuK_{α} monochromatised by a Ni filter.

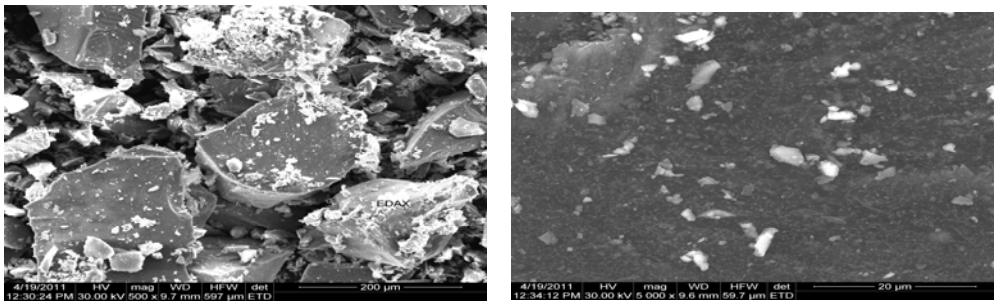

Fig. 3. Scanning electronic microscope (SEM) image of the fresh granulated slag sample, magnified 400x, 5000x

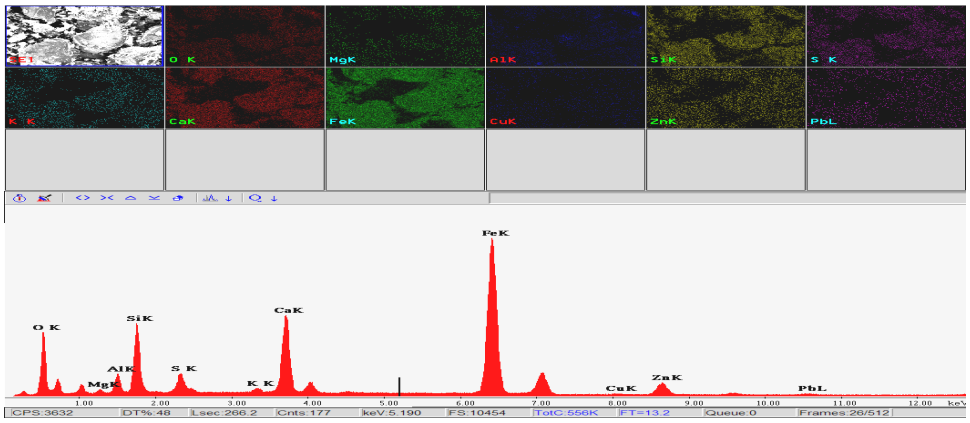

Fig. 4. Micro-compositional image of fresh granulated slag

a) at the bottom of the image is shown the spectrum of x-rays dispersive in energy (EDAX) obtained for the micro-area in Fig. 3. We can notice the presence in this micro-area of the following chemical elements: O, Mg, Al, Si, S, K, Ca, Ti, Fe, Cu, Zn and 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 shown in the upper left frame of the image (the same image is shown in Fig. 3).

The image above shows the presence in the analysed micro-area mainly of the following chemical elements: oxygen (O), silicon, (Si), aluminium (Al), magnesium (Mg), calcium (Ca), potassium (K), iron (Fe), zinc (Zn), sulphur (S), as majority elements, as well as traces of copper (Cu) and lead (Pb).

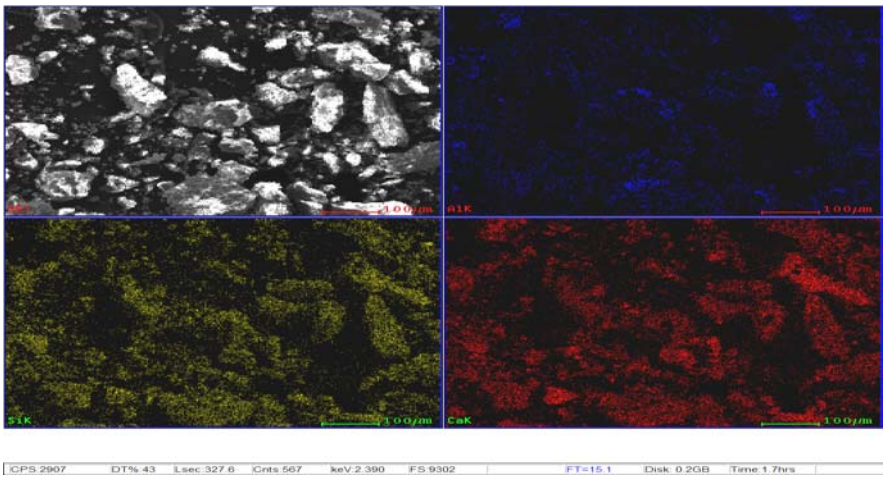

Fig. 5. Image of the distribution of the x rays characteristic for OK_{α}, SiK_{α}, CaK_{α} and FeK_{α} in the micro-area in the upper left frame of the image for the chemical elements oxygen (O), silicon (Si), calcium (Ca) and iron (Fe) (detailed from Fig. 4).

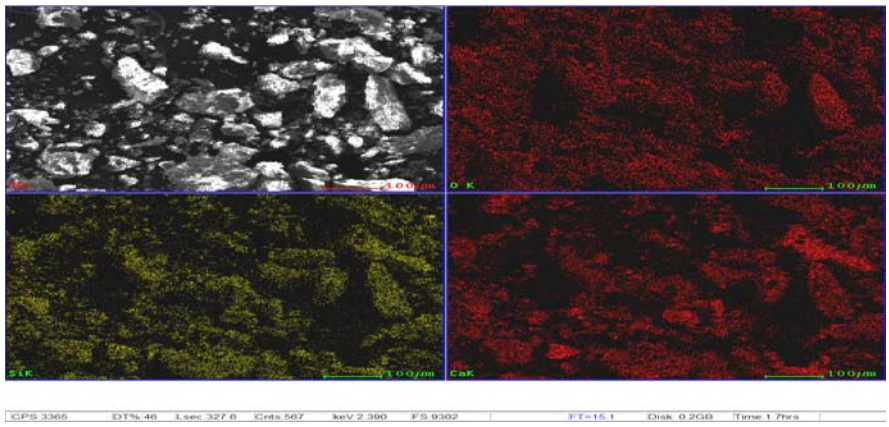

Fig. 6. Imagine of the distribution of the x rays characteristic for OKα, SiKα, CaKα in the micro-area in the upper left frame of the image for the chemical elements oxygen (O), silicon (Si) and calcium (Ca) (detail from Fig. 4).

From Figs. 4, 5 and 6 we can note the existence in the sample (powder) of a number of groups of elements, such as:

- the coexistence in certain areas of oxygen (O), calcium (Ca), silicon (Si) and aluminium (Al);
- the coexistence in certain areas of oxygen (O) and silicon (Si);
- the coexistence in certain areas of iron (Fe) and oxygen (O).

Fig. 7 shows the diffractogram obtained for the fresh granulated slag sample (powder).

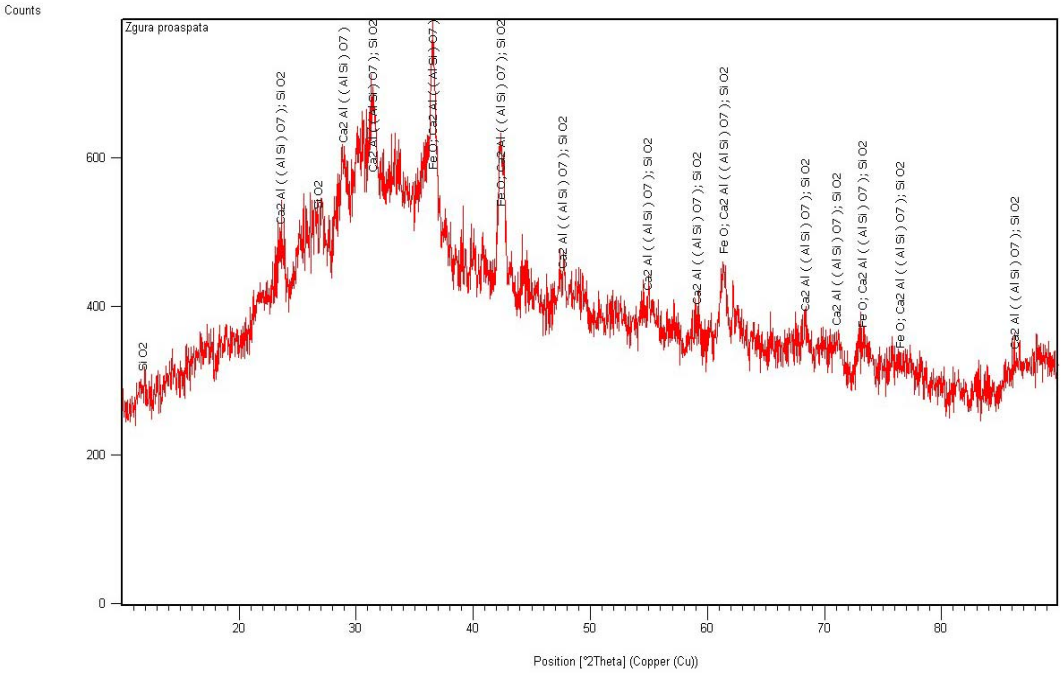

Fig. 7. X-ray diffractogram (indexed) obtained for the fresh granulated slag sample

The indexation of the diffractogram obtained reveals the following:

- The **majority phases** present in the sample are: **FeO**, with a cubic crystalline network with centred facets and a main maximum at the angle $2\theta = 41{,}989^0$, and **$Ca_2Al((AlSi)O_7)$**, with a tetragonal crystalline network and the main maximum at the angle $2\theta = 31.415^0$.
- The **minority phase** is the **SiO_2** compound. The **SiO_2** compound has a rhomboedhral crystalline network and the main maximum at angle $2\theta = 11.177^0$.

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

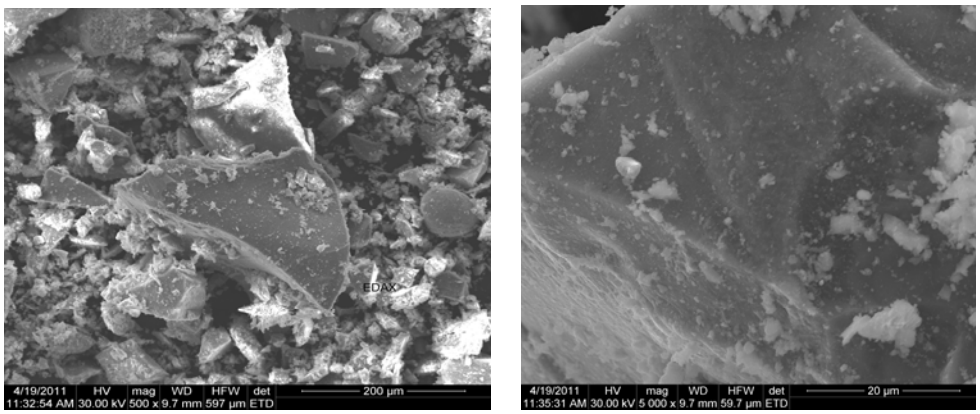

Fig. 8. Scanning electronic microscope (SEM) image of the aged granulated slag sample, magnified 500x, 5000x

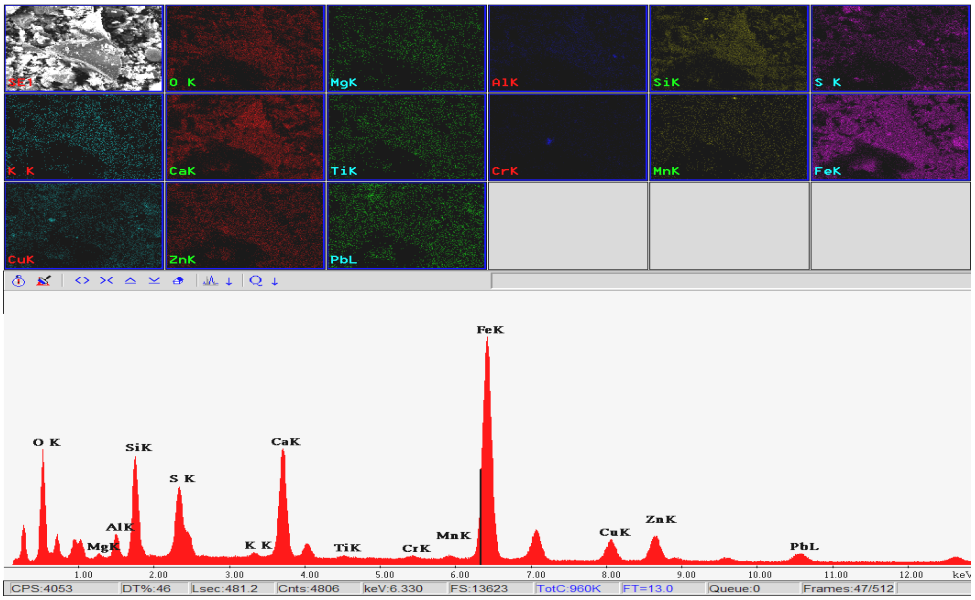

Fig. 9. Micro-compositional image of aged granulated slag:
a) at the bottom of the image is shown the energy-dispersive x-ray spectrum (EDAX) obtained for the micro-area in Fig. 8. We can note the presence in this micro-area of the following chemical elements**:** O, Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn and 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 typical x rays (for the elements specified in each frame) in the micro-area shown in the upper left frame of the image (the same image is shown in Fig. 8.)

The image above indicates the presence in the analysed micro-area chiefly of the following chemical elements, as majority elements: oxygen(O), silicon(Si), aluminium(Al),magnesium(Mg), calcium(Ca), potassium(K), iron(Fe), manganese

(Mn), copper(Cu), zinc(Zn), lead(Pb), sulphur(S), as well as traces of titanium (Ti) and chrome(Cr).

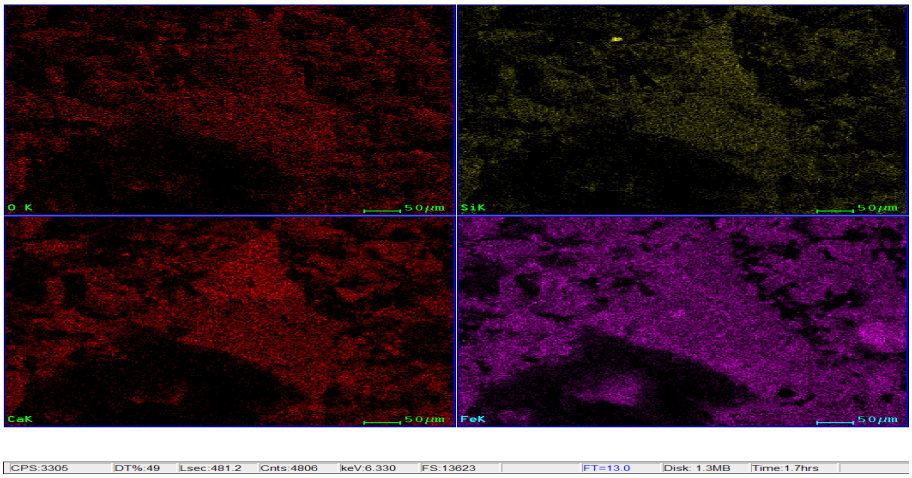

Fig. 10. Image of the distribution of the x rays characteristic for OK_α, SiK_α, CaK_α and FeK_α within the micro-area shown in the upper left frame of the image for the following chemical elements: oxygen (O), silicon (Si), calcium (Ca) and iron (Fe) (detailed from Fig. 9).

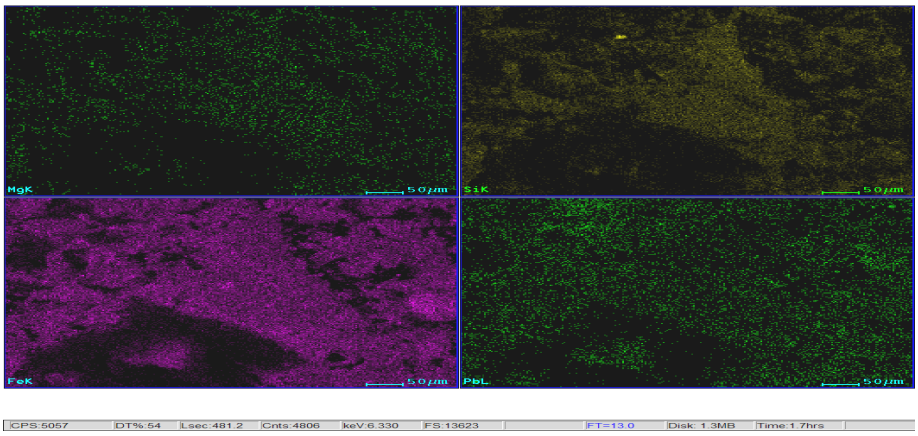

Fig. 11. Image of the distribution of the x rays characteristic for MgK_α, SiK_α , FeK_α and PbK_α within the micro-area shown in the upper left frame for the following chemical elements: magnesium (Mg), silicon (Si), iron (Fe) and lead (Pb) (detailed from Fig. 9.)

We can note in the majority of the powder particles (in the analysed micro-area) the existence of oxygen (O), silicon (Si), calcium (Ca) and iron (Fe), but as observed from Fig. 10, in some areas silicon (Si), calcium (Ca) and oxygen (O) coexist, whereas in others there are only iron (Fe) and oxygen (O) present.

Fig. 12 shows the diffractogram obtained for the aged granulated slag sample (powder).

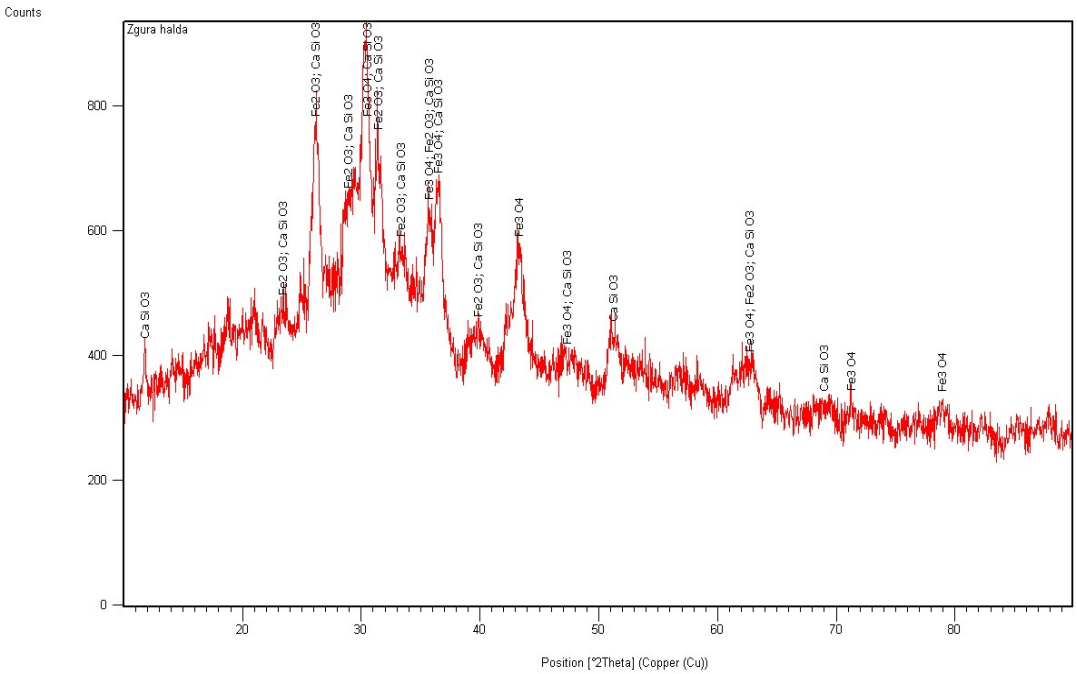

Fig. 12. X-ray diffractogram (indexed) obtained for the aged granulated slag sample (powder) The indexation of the diffractogram obtained reveals the following:

- The following are present in the sample as majority phases: Fe_2O_3, with a main maximum at angle $2\theta = 25{,}826^0$, and $CaSiO_3$, with a monoclinical crystalline network and a main maximum at angle $2\theta = 29{,}992^0$.
- The minority phase is represented of the Fe_3O_4 compound. The Fe_3O_4 compound is crystallised in a face-centred cubic structure and has the main maximum at angle $2\theta = 35{,}677^0$.

The micro-structural and micro-compositional analysis, as well as the x-ray diffraction qualitative analysis prove the existence in the aged granulated slag sample of the following chemical compounds: Fe_2O_3 (hematite), $CaSiO_3$ (wollastonite) and Fe_3O_4(magnetite).

2.3. Leaching behaviour

A leaching test was carried out in order to evaluate the constituents which can be leached from the slag and to determine if these are in accordance with the specific reference values.

In order to determine the compliance of the sample was tested by a batch leaching test with the provisions of SR EN 12457/2003 - Compliance checking test for leaching of granulated wastes and sludges, Part 2 - One-stage batch test at a liquid-solid ratio of 10 l/kg for materials with a high content of solids and particle sizes of up to 4 mm (with or without reduction of size)[5].

The quality indicators of the leachate for the granulated slag were determined experimentally using a plasma emission spectrometer - ICP - Mass Spectrometer Perkin Elmer type Ealan DRC II.

MAPN (the Romanian Ministry of Waters and Environmental Protection) Order 95/2005 on defining the criteria to be met by wastes so as to be included in the specific list of a storing facility and the national list of the wastes accepted for each storing class, provides the maximum values admissible for the characteristic indicators for each leachate in order to determine the characteristics of the wastes which can be accepted within each waste storing class (inert, non-hazardous, hazardous)[6].

Table 2

Contrastive analysis of the admissible indicators specific for a leachates

No.	Indicators	Maximum admissible values (mg/kg s.u) L/S-10 l/kg According to Ord.95/2005				
		Fresh granulated slag	Aged granulated slag	Inert	Non-hazardous	Hazardous
1	TDS	36	76	4000	60000	100000
2	Chlorides	2.0	3.5	800	15000	25000
3	Sulphates	88.2	354	1000	20000	50000
4	Cadmium	< 0.08	0.41	0.04	1	5
5	Total chrome	0.1	0.05	0.5	10	70
6	Copper	0.11	52	2	50	100
7	Lead	2.6	8.49	0.5	10	50
8	Zinc	2.76	53.6	4	50	200
9	pH	6.65	6.32	Minimum 6		

2.4. Acid draining potential

The preliminary assessment of the acid draining in slags was carried out by the modified ABA STATIC test through acid-base accounting.

The purpose of the test is to estimate analytically the quantities of acid-generating minerals and the minerals which have a natural potential for consuming acid when weathered.

The acid-base accounting includes two separate steps:

- calculating the acid-generating potential (AP) by analysing the total sulphur, using the following equation:

$$AP = \text{Total sulphur, percent} * 31{,}25$$

- determining the neutralising potential (NP) by treating a small quantity of the finely ground sample with standardised hydrochloric acid and heating the sample so as to assure a complete reaction. To make sure that the acid quantity added is enough to react with all the acid-consuming minerals in the sample, the effervescence test (the "fizz test") was used. The acid consumed by the base for neutralization is used to calculate the neutralising 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 HCl added, in ml;
y – volume of NaOH added, at pH 8,3, in ml.

Table 3

Acid draining test results

No.	Elements	Fresh granulated slag	Aged granulated slag
1	Sulphur	1.35	2.48
2	AP	42	78
3	NP	55	44
4	NNP=NP-AP	13	-34
5	NNP criteria	0 < NNP < 20 uncertain	NNP < 0 generates acid
6	NPR(NP/AP)	1.30	0.56
7	NPR criteria	1-2 possibly generating acid draining	<1 probably generates acid draining

3. Conclusions

The micro-structural and micro-compositional analysis and the x-ray diffraction qualitative analysis proved the presence in the analysed slag samples of the following compounds:
- oxides: FeO (wüstite), Fe_2O_3 (hematite), Fe_3O_4 (magnetite);
- silicates: $CaSiO_3$ (wollastonite), $Ca_2Al_2SiO_7$ (gehlenite), SiO_2 (silica).

The analysis of the quality of the leachate and the comparison of the determined quality indicators with the values provided by MAPM Order 95/2005 on defining the criteria to be met by wastes for storage and the national list of the wastes accepted for each storing class, revealed that quality indicators for the leachate obtained from granulated slag the (i.e., TDS, sulphates, chlorides, Cd, and total Cr) meet the admissible values for inert deposits, whereas for the Pb, Cu and Zn indicators they meet the values admitted for non-hazardous deposits.

The modified static ABA test results indicate that the fresh granulated slag is uncertain, whereas the aged slag generates acid.

The aged granulated slag from dump generates acid since it was subjected to oxidising conditions (oxygen, water), which leads to the oxidation of the Fe^{2+} and S^{2-} ions from pyrite, generating solid hydroxides and oxy-hydroxides (precipitate), sulphate ions and hydrogen ions in solution. The oxygen and the Fe^{3+} ion are the main oxidisers of pyrite and the oxidation of pyrite continues over indefinite periods of time, except when the Fe^{3+} ion, the oxygen or the pyrite are removed, or when the pH of the solution increases significantly.

R E F E R E N C E S

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[5] ******* SR EN 12457/2003 - Test de verificare a conformității pentru levigarea deşeurilor granulare şi a nămolurilor Partea 2 - Test cu o etapă pe şarjă la un raport lichid-solid de 10 l/kg pentru materiale cu conținut ridicat de solid şi cu dimensiunea particulei sub 4 mm (fără sau cu reducerea dimensiunii).

[6] ******* Ordinul MAPM nr.95/2005 privind definirea criteriilor care trebuie îndeplinite de deşeuri pentru a se regăsi pe lista specifică unui depozit şi lista națională de deşeuri acceptate în fiecare clasă de depozit de deşeuri.