IN MEMORIAM Prof Dr. Ing. PETRU BALTĂ

O NOUĂ ABORDARE A PROCEDURII DE RECUPERARE A UNUI MATERIAL NECONVENŢIONAL – ZGURA LF – CA AMENDAMENT PENTRU SOLURILE ACIDE
A NEW APPROACH FOR RECOVERY PROCEDURE OF THE UNCONVENTIONAL MATERIAL -LF SLAG- FOR ACID SOIL AMENDMENTS

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This approach is dealing with the recovery procedure of LF slags in agriculture as acid soils amendments. LF slag (slag from secondary treatment of steel) occurs in the form of a powdery material.

By using these slags in improving of acid soils seeks the calcium oxide high basicity from the slag, so this type of slags can be an active amendment in acidic soil treatment technologies.

We have identified various sources of LF slag, such as: 1) steel manufacturer for fabrication of equipments for energy industry, 2) alloyed steel manufacturer for the production of rolling stocks and 3) manufacturer of long semi-finished steel products.

LF slag collected samples was done in order to establish uniform sample batches.

The replacement of natural materials used to relieve acid soil with an unconventional material, like waste - slag LF was effective and leads to positive environmental effects.

Această abordare se referă la elaborarea unei proceduri de recuperare a zgurilor LF în agricultură ca amendamente pentru soluri acide. Zgura LF (zgură de tratament secundar al oţelului) se prezintă sub forma unui material pulverulent.

Prin utilizarea acestor zguri pentru ameliorarea solurilor acide se urmăreşte valorificarea potenţialului bazic al oxidului de calciu prezent în aceste zguri, astfel încât acest tip de zgură poate constitui un amendament activ în tehnologiile de tratare a solurilor acide.

Am identificat mai multe surse de zgură LF, precum: 1) producător de echipamente de fabricaţie oţel pentru industria energetică, 2) producător de oţel aliat pentru producerea de material rulant şi 3) producător de produse din oţel lung semifinite.

Colectarea de probe de zgură LF a fost făcută în scopul de a stabili loturi uniforme de probă.

Înlocuirea materialelor naturale utilizate pentru ameliorarea solurilor acide cu un material neconvenţional, gen deşeu - zgură LF - a fost eficace şi conduce la efecte pozitive asupra mediului.

Keywords: *ladle furnace, LF slag, amendent, acid soil*

1. Introduction

Metallurgical slag generated in the primary unit is used in various fields of economy, such us: cement production, road construction, hydraulic engineering as well as fertilizer.

In Romania, according to the official data, there are 1.8 million ha of acid agricultural fields which represent around 12% from the all agricultural surface. On the other hand in Romania are generated yearly about 25000 t of LF slag. The total amount of LF slag generated in the technological process depends on the activity of specialized companies (production cycle of each specific sources of LF slag). The total elimination of this waste dumps in Romania is not yet possible.

The LF (ladle furnace) slag is a secondary metallurgy slag resulting from the refining of steel and it is a different slag than that generated in primary steelmaking operation units (electric arc furnace). In a lot of steelmaking plants the possibility to operate the slag recycling process has been carefully evaluated in order to decrease the environmental impact and to avoid the use of dumping ground for special wastes. The most significant LF slag components are CaO (usually 40 - 60%), Al_2O_3, SiO_2, and MgO. Due its high CaO content, the LF slag is predominantly dusty and is not suitable for many applications in construction, but seems to be appropriate as acid soil amendment.

The main applications of current dusty steelworks slag are currently focused on the following areas:

- used as addition of the clinker or in cement mortar [1-6];

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• used for acid mine water treatment [7];
• used as a fertilizer in the agriculture because of trace elements in slag, which may act as a micronutrient [8, 9], or a neutralizer for the acid soil [1 - 3];
• used as a possible trap for chemical sequestration of CO_2, the LF slag having the potential of 14 times greater than the classical slag [10, 11].

White dust slag character (as it is called LF slag) makes this eco-product to have limitations on emissions of dust, more restrictive, both in the production hall and storage stockpiles.

Usually the amendment of acidic soils is performed by using natural raw materials such as: lime and dolomite; the consumption arising up to 20 t/ha according to the solid acidity level and the type of cultivated plants.

The present paper assess the possibility of LF slag recycling by developing a new technology for preparation of such waste material in order to lead to a high homogeneity of particle size and chemical composition, followed by preliminary testing on agricultural acid soil. Consequently, it is expected the conversion of an industrial waste (slag LF) into a byproduct applicable in a new area.

2. Collection and preparation of LF slags to be tested for acid soil amendment

LF slag batches were collected from three different locations, as follows:
- Source 1- steel producer for the energy industry.
- Source 2- medium-alloy steel manufacturer for rolling stocks.
- Source 3 - steel producer for long semi-finished (moldings) steel products.

Individual characterization of the three above mentioned groups showed differences in chemical composition and particle size, as follows:
- LF slags volumetric weight was 0.95 - 1.04 g / cm^3.
- LF slag dusty character is confirmed by their fine fraction (rest of 93.8 to 95.6% on < 0.06 mm sieve).
- LF slag has a white dusty character due its high content of CaO, ranging from 50.9 to 53.0%, low content of black oxides (Fe, Mn between 1.25 - 1.38% and 0,34 - 1.32, respectively).
- Metallic (Fe) content of LF slag was between 1.4 to 8.1%; and through drum magnetic separation, the "magnetic fraction" was even 20%.

Because steel makers want to avoid to

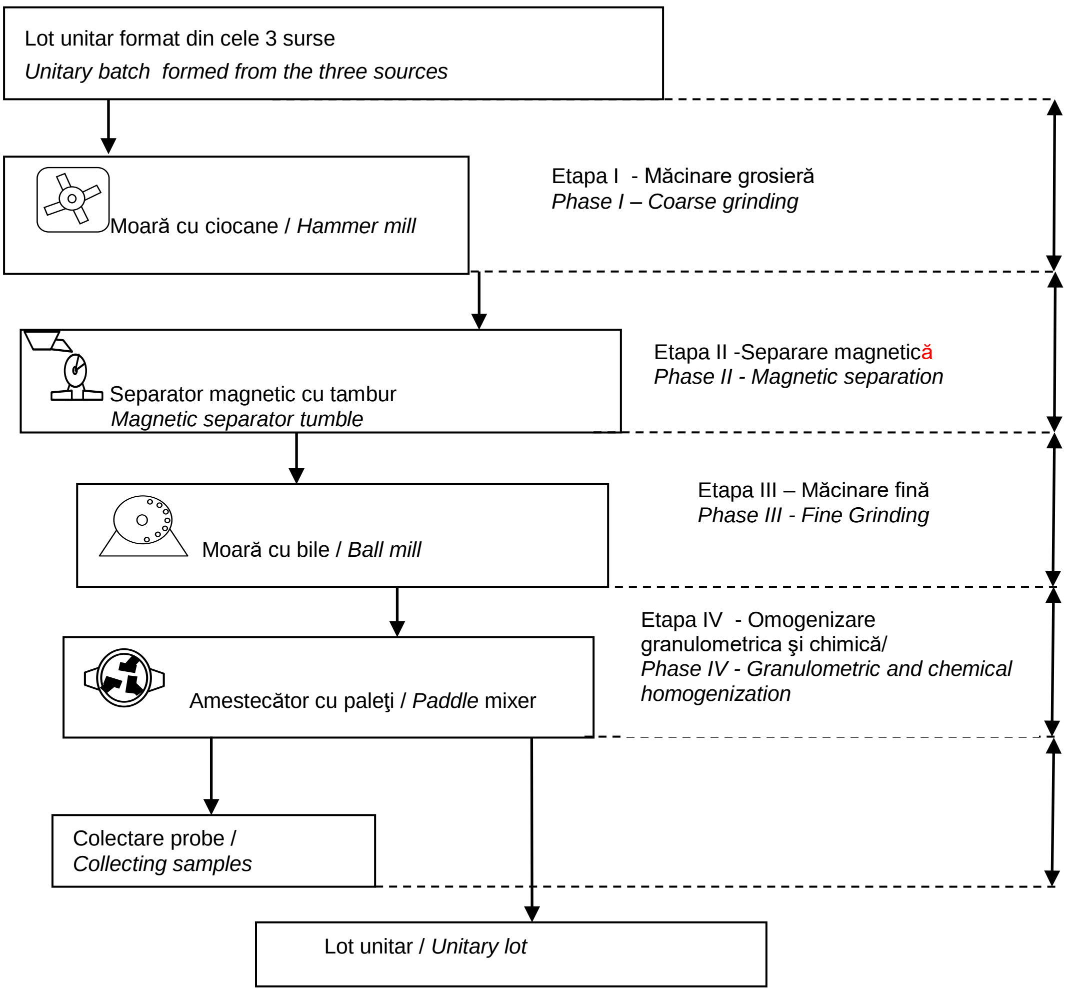


Fig. 1 - The technological flow for the LF slag preparation / *Fluxul tehnologic de pregătire a zgurii LF* .

manage and prepare their own slag, it can be notices worldwide, the development of companies that collect the slags from several sources, prepare and sell them as marketable product.

Our method of preparation the multiple sources collection of slag was carried on with establishing a technology training to ensure the necessary qualities breeder.

LF slag preparation procedure comprises the following steps (Figure 1):

I. Bringing the LF slag particles dimensions through coarse grinding, bellow 5 mm (equipment: hammer mill);

II. Iron separation from the LF slag (equipment: drum magnetic separator);

III. Pulverization to obtain a grain size bellow 0.06 mm (equipment: ball mill);

IV. Particle size and chemical homogeneity (equipment: paddle mixer).

3. Characterisation prepared LF slag

The unitary batch of LF slag was prepared according to the above technological process was characterized physically and chemically. In order to achieve this objective were taken and characterized three samples from different areas of the unitary batch.

The physical-chemical analyses of samples collected from the consignment of slag were:
- bulk density and particle size,
- chemical composition.

3.1. Uniformity of the unitary lot size LF slag

Size composition was determined by using the method of SR EN 24497: 1994 "Metal powders - Determination of grain size by dry sieving " and sieving analysis according to the procedure SR EN 196-6: 2010 and volumetric weight was determined by the procedure of SR EN ISO 3953 : 2011 "Metal powders - Determination of density in tamped state".

The obtained results are shown in Table 1.

Uniformity of particles size, expressed as average sample value is compared to the extreme values and can be remark:

- more than 99.9% for the fraction < 0.06mm;
- 96% for the bulk weight.

The grain size distribution of unitary batch of LF slag based on average samples is given in Table 2.

Table 2

Grain size distribution of unitary batch of LF slag
Compoziţia granulometrică a lotului unitar de zgură LF

Grain size fraction *Fracţia granulometrică*	%	Deviation *Abaterea*
> 0,09mm	6.2	±0.3
> 0,06mm	3.0	±0.3
< 0,06mm	90.8	±0.5

3.2. Chemical uniformity of the LF slag average sample

The chemical composition was determined by X-ray fluorescence analysis by using a PANalytical Axios Advanced device.

The results are shown in Table 3.

The uniformity of the chemical composition expressed as average sample value is compared to the extreme values and on can conclude that:

- about 99.5% for the SiO_2 compound;
- more than 99.2% for Al_2O_3 compound;
- more than 99.8% for the compound of CaO;
- 99.3% over the simple basicity, reckoned as CaO / SiO_2 index.

The chemical composition of LF slag unitary batch based on average samples is given in Table 4.

Table 1

The grain size distribution of the unitary batch
Caracteristicile granulometrice ale lotului unitar

Characteristics of the unitary batch *Caracteristici lot unitar*	Granulometric composition *Compoziţie granulometrică* — Rest (%) on sieve with mesh size (mm) *Rest (%) pe sita cu ochiurile (mm)*			Bulk density *Greutate volumetrică* — g/cm^3	
	0.09	0.06	<0.06	Untamped *Netasat*	Tamped *Tasat*
Maximum / *Maxim*	6.3	3.1	91.2	1.1	1.72
Minimum / *Minim*	6.0	2.8	90.7	1.0	1.65
Average / *Media*	6.17	2.97	90.87	1.05	1.69
Mediana / *Mediana*	6.20	3.00	90.70	1.06	1.70
Average standard deviation *Abaterea medie*	0.11	0.11	0.22	0.04	0.03
Standard deviation *Abaterea standard*	0.15	0.15	0.25	0.06	0.04

Table 3

Chemical composition of the unitary samples batch / *Compozitia chimică a lotului de probe unitar*

Characteristics unitary lot Caracteristici lot unitar	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	MnO	K_2O	P_2O_5	V_2O_5	Cr_2O_3	F	SO_3
Maximum / *Maxim*	20.46	0.23	6.07	1.25	10.02	55.78	0.98	0.045	0.041	0.065	0.064	4.89	1.16
Minimum / *Minim*	19.05	0.21	5.85	1.07	8.78	53.96	0.86	0.022	0.027	0.058	0.045	3.52	0.94
Average / *Media*	19.95	0.22	5.96	1.16	9.55	55.04	0.93	0.034	0.033	0.062	0.057	4.15	1.08
Median / *Mediana*	20.33	0.22	5.97	1.15	9.86	55.38	0.94	0.035	0.032	0.062	0.062	4.04	1.13
Average standard deviation *Abaterea medie*	0.60	0.01	0.08	0.06	0.52	0.72	0.04	0.008	0.005	0.002	0.008	0.49	0.09
Standard deviation *Abaterea standard*	0.78	0.01	0.11	0.09	0.67	0.96	0.06	0.012	0.007	0.004	0.010	0.69	0.12

Table 4

Chemical composition of unitary LF slag batch
Compoziţia chimică a lotului unitar de zgură LF

Component *Componentul*	%	Deviation *Abaterea*
SiO_2	19.85	±0.60
TiO_2	0.22	±0.01
Al_2O_3	6.01	±0.07
Fe_2O_3	1.18	±0.06
MgO	9.42	±0.51
CaO	55.12	±0.72
MnO	0.89	±0.04
K_2O	0.031	±0.008
P_2O_5	0.034	±0.005
V_2O_5	0.062	±0.002
Cr_2O_3	0.055	±0.008
F	4.13	±0.49
SO_3	1.11	±0.09

4. Preliminary results on acid soil amendment

The unitary batch of LF slag was used for preliminary laboratory tests for the pH improvement of an acid soil from Moara Domneasca location. It was considered 3 admixture amounts of LF slag such as: 1, 4 and 8 % (by weight) and investigated the variation of soil pH, every 5, 10 and 30 days [12, 13].The results of the evolution of pH on farm plots treated with slag, relative to the untreated reference farm plot is presented in Figure 2.

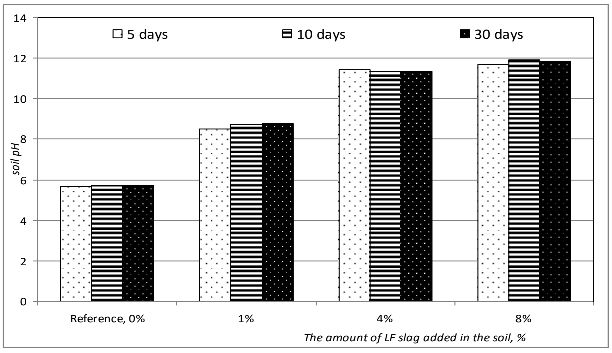


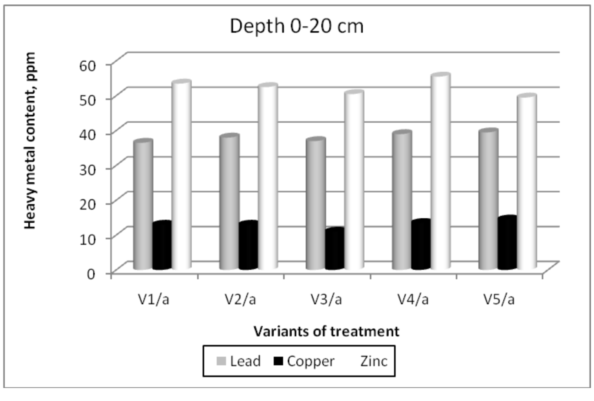
Fig. 2 - Influence of treatment with LF slag on pH soil / *Influenţa tratării cu zgură LF asupra pH-ului din sol.*

The presented results show that is enough 1% LF slag admixture for the soil treatment to get an increase of pH from about 5 to more than 8. Moreover, while it is observed that even after 30 days, the pH of the soil treated with LF slag, it does not change significantly.

The soil samples were used to determine the content of heavy metals, especially Pb, Cu, Zn, Cr, Cd to investigate the influence of LF slag addition on experimental field.

Determination of heavy metals in soil, was carried out with a portable XRF device, type Oxford Instruments X-MET 3000TX, using "Measurement of heavy metals in soils" PL-14-01 / 10.16.2013 procedure, developed under the Quality Management System implemented and applied in INCDMNR-IMNR as required by ISO 9001: 2008. According to the above-mentioned procedure, the soil samples collected were dried, milled and sieved through the sieve of 200 μm mesh. Such processing may be considered to offer both qualitative and quantitative results. The LF slag was added in soil in different quantities, assigned as follows: V1- blank; V2 – 1 t slag/ ha; V3 - 2 t slag/ ha; V4 - 3 t slag/ ha and V5 - 5 t slag/ ha. It could be assumed that one hectare of arable land, of a thickness of 40 cm, has around 3.000t. Consequently, the V5 version -5t / ha, it means about 0.17% slag. The soil samples were collected from two depths, respectively: 0-20 cm coded “a” and 20-40 cm coded “b”.

The graphical representation of heavy metals content (Pb, Cu, Zn) versus the 5 imposed investigated options, for the two depths, are shown in Figures 3a and 3b. It should be noticed that in soil samples we did not detect cadmium.



Figures 3a

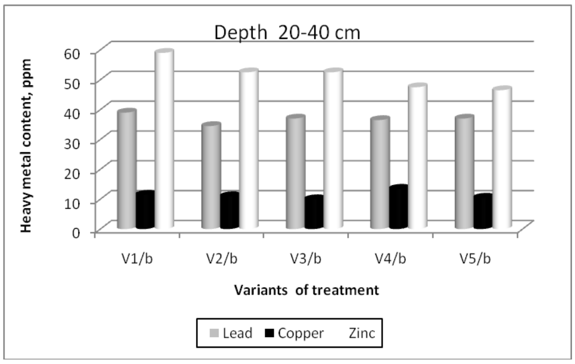


Fig. 3 b

Comparing the experimental data presented in Figures 3a and 3b in conjunction with Table 1 of the Annex to the Order no. 756 of 3 November 1997 approving the rules on assessment of environmental pollution (with changes in OM 592/2002, OM 1144/2002) - given bellow- it should be noticed that *the values are below the alert threshold* for traces of chemical elements existing in soils. Therefore, we can conclude that the heavy metal content in soil is not influenced dramatically by the presence of slag in the used concentration and has no negative effect on soil and plants. Moreover, the corn and wheat crops exhibit an enhanced productivity with the increasing of LF slag content added in the soil.

The choice of material for the relief of acid soils brings unconventional and natural resources saving advantages of limestone or dolomite, which are used in some cases to treat acidic soil. In this way it contributes to environmental protection in two ways: by harnessing of waste and saving natural resources with a beneficial impact on sustainable development. The use of LF slag - a metallurgical waste as amendment for acidic soils is 25 - 40% is more advantageous, being cheaper than the conventional use of lime and dolomite. Also, it should be notices a decrease of LF slag dumps in metallurgical industry.

5. Conclusions

- LF slag is generated in secondary metallurgy, resulting from the refining of steel, with a profound dusty feature, that has no applications in Romania in the construction industry, are generally deposited in landfills, but has a high potential for improvement of acid soils.
- Our investigation shows that the recycling of LF metallurgical slag is effective for relieve acid soil and a flow sheet in four stages in order obtain grain size distribution and chemical homogeneity was developed.
- The preparation process of LF slag can lead to advanced degrees of particle size and chemical homogeneity, of over 99%.
- Preliminary tests on LF slag addition on farm plots have shown that it can raise soil pH from 5 to over 8, by using up to 1% LF slag.

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Extract from Table 1 of the Annex to the Order no. 756 of November 3, 1997
Extras din Tabelul nr. 1 din Anexa la Ordinul nr. 756 din 3 noiembrie 1997

Traces of element *Urme de element*	Normal values *Valori normale*	Alert thresholds *Praguri de alertă* Types of use *Tipuri de folosinţe*		Intervention thresholds *Praguri de intervenţie* Types of use *Tipuri de folosinţe*	
		Sensibile *Sensitive*	Less sensitive *Mai puţin sensibile*	Sensibile *Sensitive*	Less sensitive *Mai puţin sensibile*
I. Metals / *Metale* :					
Cadmium / *Cadmiu* (Cd)	1	3	5	5	10
Chromium / *Crom* (Cr):					
Cr total	30	100	300	300	600
Cr hexavalent	1	4	10	10	20
Copper / *Cupru* (Cu)	20	100	250	200	500
Lead / *Plumb* (Pb)	20	50	250	100	1.000
Zinc (Zn)	100	300	700	600	1.500

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