EVALUAREA CARACTERISTICILOR ZGURILOR LF ÎN VEDEREA OBȚINERII DE MATERIALE PENTRU AMELIORAREA SOLURILOR ACIDE DIN AGRICULTURĂ
ASSESSMENT ON LF SLAGS CHARACTERISTICS USED FOR AGRICULTURAL ACIDIC SOILS IMPROVEMENT

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The development of an analysis methodology with embedded identification of significant issues regarding the use of steelmaking slags from secondary metallurgy in agriculture for acidic soils improvement leads to "elimination" of "waste" term assigned for Ladle Furnace (LF) slag and determines its conversion into useful by-product and environmentally friendly. This paper analyzes comparatively three Romanian sources of LF slag:

1) a steel manufacturer for power industry equipments fabrication (Source 1) ,

2) an alloyed steel manufacturer for the obtaining of rolling stocks (Source 2),

3) a steel manufacturer as long semi-finished forms (Source 3).

Each of these sources (companies) have particular characteristics of the steel manufacturing and LF slags storage which have been investigated in the paper in the attempt to exploit them as secondary resources to obtain materials for acidic soils amelioration.

Elaborarea unei metodologii de analiză care să cuprindă identificarea aspectelor semnificative privind utilizarea zgurii provenite de la elaborarea oțelului prin metalurgia secundară în agricultură pentru ameliorarea solurilor acide, conduce la „eliminarea" termenului de „deșeu", pus asupra zgurii LF și transformarea acestuia într-un subprodus util și prietenos cu mediul. Lucrarea analizează comparativ trei surse generatoare de zguri LF:

1) un producător de oțel destinat fabricației de material pentru industria energetică (sursa 1);

2) un producător de oțel mediu aliat destinat fabricației de material rulant feroviar (sursa 2);

3) un producător de oțel sub formă de semifabricate lungi (sursa 3).

Fiecare din aceste surse (companii) prezintă caracteristici specifice de fabricație a oțelului și de depozitare a zgurilor LF, care au fost investigate în lucrare în încercarea de valorificare a lor ca resurse secundare pentru obținerea unor materiale destinate ameliorării solurilor acide.

Keywords: environmental management, recycling, ladle furnace, white slag, acid soil amelioration, lime

1. Introduction

Changing global ecosystems, due to the consumption and production, showing how important is the process of rethinking the use of natural resources by the economy and society. Ensuring the sustainable development requires compliance with legal regulations based on principles such as precaution in decision-making, prevention of environmental risks and damage occurrence, biodiversity conservation and natural bio-geographically framework of specific ecosystems, removing with priority of the pollutants that affect human health directly and seriously. An important strategy for achieving this goal consists in developing the economy in a closed circuit, the transformation of matter and energy (flow-circular economy) without impinge the ecological balance by dumping waste outside the circuit, to close their flow. Recycling in our country means to reintroduce in the production flow, maximum 2/3 of waste; while 1/3 of waste remains temporary land filled with an unexploited potential.

LF slag occurs in ladle furnace (LF) processing of steel. This idea has been launched for the first time, in 1957 by ASEA-SKF company and implemented as ASEA-SKF process (1965) and as Finkl-Mohr process (1967). Both methods have the merit of using the arc heating unit in a different vessel than the base unit (electric arc furnace EAF), which thus remains only as scrap melting aggregate (devoted to decarburization and dephosphorising). The new unit, referred as ladle furnace (LF) provides a method for deoxidation / desulphurization processes, purification of the inclusions, control of thermal and chemical composition in principal steel making aggregate (EAF). In such way, the productivity of this main steelmaking aggregate (EAF) has increased from about 0.33 t / min.

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to about 1t/min (for a furnace of about 60 t, with duration of 1 hour per charge in case of high grade steels). The first ladle furnace units were equipped with vacuum and liquid steel stirring system (electromagnetic or pneumatic with argon). From this point we can consider that steel metallurgy has been splitted into:

- *Primary metallurgy*: development of iron (blast furnace slag by-product) and steel making (by-product of electric furnace slag or converter slag);

- *Secondary metallurgy*: refined steel (by-product secondary slag or LF slag).

The ladle furnace from this period, equipped with steel vacuuming device was obviously intended to low gas content steel, meaning high-quality steel. Further in 1971 the company Daido Steel Co. Ltd. Japan [1], launched the idea and the process, so called LF - ladle furnace, where no vacuum oven facility is attached and the stirring of the liquid steel is made by argon blowing through the bottom of the ladle furnace. According to the classification of the slag producers and users association "Euroslag" [2], the ladle furnace slag is classified as "secondary metallurgical slag" - SECS, but is also called as ladle furnace slag (LFS).

In such way the ladle-furnace process (LF) became more cheaper and could be applied to high mass production steel and on the other hand, the vacuuming operation of liquid steel was transferred to another unit, thus solving the problem of vacuum sealing in the area of heating electrodes.

The ladle furnace (LF) is known as smaller versions of electric arc furnaces [3], having all three graphite electrodes coupled to a transformer for liquid steel heating. The bottom of the ladle furnace is equipped with an argon injection system through porous plug for liquid steel stirring and mixing. The ladle furnace can also be equipped with injection lance for desulfurizing agents (Ca, Mg, CaSi, CaC_2, CaF_2, CaO) and / or supply system for deoxidizing additives or chemical composition adjustment. The addition of silicon and aluminum during the deoxidation stage leads to the formation of silica (SiO_2) and alumina (Al_2O_3), these oxides being absorbed by the slag generated as a result of ladle furnace processes.

The LF slag compared with the slag generated in the primary unit (EAF) has a lower content of FeO and higher of Al_2O_3. Most significant components of LF slag are: CaO (typically 40-60%), Al_2O_3, SiO_2 and MgO). A decreased content of FeO of this slag and their appearance earned them the name of the *white slag.* The most common applications of LF slag and of dusty steelworks slag are currently focused on the following areas:

1.Reintroduction into the steelmaking units:

for instance, in EAF furnace for slag foaming, as well as in basic oxygen converter or desulfurization ladle-furnace;
2. as a substitute for clinker or cement in mortar in the cement industry;
3. for acid mine water treatment;
4. as a fertilizer in the agriculture, because the trace elements in slag can act as micronutrients, or neutralizer for the acidic soils [4-6];
5. as a possible chemical trap for CO_2 sequestration, for example: the LF slag proving a better potential (14 times) than the EAF slag [4].

In this context, the paper investigated comparatively, three sources of LF slag from Romanian steel plants. Each of these sources (companies) with their particular characteristics of the steel manufacturing and storage of LF slag were considered in the attempt to exploit them as environmentally friendly secondary resources to obtain materials for improving acidic soils.

2. Experimental

2.1. The collecting and preparing process of samples for preliminary LF slag characterization

LF slag (slag from secondary treatment) 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 three possible sources of LF slag [7]:

- Source 1 - manufacturer of steel fabrication equipment for the energy industry.
- Source 2 - alloyed steel manufacturer for the production of rolling stock.
- Source 3 - manufacturer of long semi-finished steel product.

All these companies have efficient LF installations, commissioned or upgraded after 2000. Each of these sources (company) owning specific characteristics of the steel product and the storage of the slag LF.

LF slag collecting samples was done by establishing uniform sample size (8-12, average 10 kg); their removal is being carried during a working day, the specific manufacturing source.

It has been collected 6 samples for each LF slag sources of the specific storage unit any LF installations.

The objectives of the preparation procedures LF slags were considered to achieve the characteristics of those slags which make them useful in the acid soils amelioration process. According to the type of acid soils, amendments it must have specific properties, as well as the

properties, such as:

- Higher LF slag homogeneous to ensure equal treatment of cultivated area as large and thus a correct assessment of the effects of the amendment.

- Appropriate content (CaO_{free} and even CaO_{total}) as high to ensure a superior effect of amendment expressed as improved soil area / tonne of LF slag.

- Optimal grain size, having regard to the objective of high reactivity at acidic soil, and aim to reduce dust emissions into the atmosphere and limiting washing with rain water.

- Low content of potentially harmful elements for cultivated plants as well as leachate waters (leachable elements, $Fe_{metalic}$ and Fe_{oxidic}).

Based on these considerations, we designed a procedure of preparation of LF slags in six stages:

I. Crushing big lumps, eventually agglomerated during transport and storage, in order to bring the material to a convenient size at the grinding machine feeder (equipment: jaw crusher).

II. Ground grinding to a first separation of very hard particle size fractions followed by fine grinding (equipment: hammer mill).

III. Separation of hard fraction (> 3mm) for entry into the fine grinding stage (equipment: vibrating screen).

IV. To obtain a fine grain size under < 0.09 mm (machine: ball mill).

V. Homogenization to achieve the LF slag sample (equipment: paddle stirrer).

VI. Obtaining the non-ferrous LF slag sample (equipment: drum magnetic separator).

2.2. Physical-chemical characterization of samples of LF slag samples

Physical-chemical analysis of samples of slag samples were: bulk density and particle size distribution, chemical composition of non-metallic fraction, metallic fraction, leachability and mineralogical composition.

Bulk density was determined unsettled and compacted version according to the procedure SR EN ISO 3953: 2011. For the investigated LF slags, the volumetric weight was between 0.95 - 1.04 g/cm^3.

The size analysis performed according to the procedure of SREN 196-6: 2010, came out the following: LF slag analyzed dusty character with fraction <0.06 mm from 93.8 to 95.6%.

Chemical composition analyzes were performed by X-ray fluorescence method on PaNalytical Axios Advanced apparatus.

3. Results and discussion

3.1. Chemical composition

Preliminary tests of chemical analysis performed on XRF device for calibration related to LF slag samples showed a high variability of iron content. This fact has shown that the slag samples contain thin layer of metallic iron which affects the homogeneity of the sample, leading to variable results even for the same kind of sample. In order to avoid such a phenomenon has been performed particles sizing and manual magnetic separation, including the brushing of samples on 0.125 mm sieve to separate the metal fraction, and then the slag was investigated by XRF according to ASTM E 1621-05. The results of analyzes on slag samples are shown in Table 1.

Recalculation of chemical composition taking into account the amount of metallic Fe (% by weights) determined by manual magnetic separation, leads to the results as given in Table 2, which basically represent the chemical composition of slag samples including the metallic fraction.

The conclusion resulted from the chemical analyzes the of LF slags performed by XRF highlighted at this stage, the need for estimation of the proportion of *metal fraction* ($Fe_{metallic}$) in *LF slags* and the possibility to decrease $Fe_{metallic}$ amount by preparation operations of slags through magnetic separation.

In order to achieve magnetic separation test of slag it was prepared a sample of about 4 kg

Table 1

Chemical composition of non-ferrous fraction (%) - ASTM E 1621-05
Compoziția chimică a fracției nemetalice (%) - ASTM E 1621-05 /

Sample mark /*Marcaj probă*	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO
P1	17.76	0.23	7.06	1.27	1.34	15.47
P2	24.74	0.24	5.30	1.50	0.37	8.04
P3	23.35	0.28	8.72	1.26	0.39	9.00
Average value / *Valoarea medie*	**21.95**	**0.25**	**7.03**	**1.34**	**0.70**	**10.84**
Standard Deviation / *Abaterea medie standard*	3.6946	0.0265	1.7102	0.1358	0.5543	4.0412

Table 1 (cont.)

Sample mark /*Marcaj probă*	CaO	Na_2O	K_2O	P_2O_5	SO_3	F
P1	51.70	0.03	0.03	0.05	0.73	4.53
P2	56.15	0.05	0.01	0.01	2.21	1.60
P3	53.67	0.08	0.05	0.02	1.70	1.80
Average value / *Valoarea medie*	**53.84**	**0.05**	**0.03**	**0.03**	**1.55**	**2.64**
Standard Deviation / *Abaterea medie standard*	2.2299	0.0252	0.0200	0.0208	0.7518	1.6370

Table 2

The chemical composition of the non-ferrous fraction (%) -weighted by metallic iron content
Compoziţia chimică a fracţiei nemetalice (%) – ponderată cu conţinutul de fier metalic

Sample mark /*Marcaj probă*	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO
P1	17.50	0.23	6.96	1.25	1.32	15.24
P2	22.70	0.22	4.86	1.38	0.34	7.38
P3	23.08	0.28	8.62	1.25	0.39	8.90
Average value / *Valoarea medie*	**21.10**	**0.24**	**6.81**	**1.29**	**0.68**	**10.51**
Standard Deviation / *Abaterea medie standard*	3.1197	0.0310	1.8827	0.0739	0.5535	4.1725

Table. 2 (cont.)

Sample mark /*Marcaj probă*	CaO	Na_2O	K_2O	P_2O_5	SO_3	F	Fe met.
P1	50.95	0.03	0.03	0.05	0.72	4.46	1.45
P2	51.53	0.05	0.01	0.01	2.03	1.47	8.19
P3	53.06	0.08	0.05	0.02	1.68	1.78	1.13
Average value / *Valoarea medie*	**51.84**	**0.05**	**0.03**	**0.03**	**1.48**	**2.57**	**3.59**
Standard Deviation / *Abaterea medie standard*	1.0925	0.0252	0.0201	0.0208	0.6779	1.6470	3.9867

Table 3

The amount of non-magnetic fraction (deferrized LF slag) separated in each stage and in the whole process of magnetic separation
Ponderea fracţiei nemagnetice (zgura LF deferetizată) separată în fiecare etapă şi pentru întregul proces de separare magnetică

	Non-ferrous LF slag removal *Scoaterea de zgură LF deferetizată* %	Magnetic fraction *Fracţie magnetică* %	Loss *Pierderi* %
Phase I Magnetic separation *Etapa I Separare magnetică*	82.5	17.5	0
Phase II Magnetic separation of magnetic fraction *Etapa II Separare magnetică a fracţiei magnetice*	42.85	51.95	5.2
Phase II Magnetic separation of non-magnetic fraction *Etapa II Separare magnetică a fracţiei nemagnetice*	87.88	12.12	0
Global stage magnetic separation *Etapa globală separare magnetică*	80	19.1	0.9

Table 4

The amount of magnetic fraction of LF slags obtained after manual separation
Ponderea fractiei magnetice a zgurilor LF in urma separării manuale

Sample *Proba*	Sample quantity *Cantitate probă*, g	Quantity of Fe, after magnetic separation *Cantitate Fe, separat magnetic,* g	Magnetic fraction *Fracţia magnetică* %
P1	125.51	1.86	1.48
P2	102.44	9.19	8.97
P3	91.35	1.05	1.15
		Average value *Valoare medie*	3,86

(source 2) that has been passed through a magnetic separator with a rotating drum with a diameter of 400 mm, speed of 10 rpm and a feeding oscillating chute tilt at 5°. Maximum productivity of the separator was about 200 kg / h powdery material. The magnetic field is generated by a set of electromagnets placed eccentric in the drum and a magnetic field of 4000 Oe.

The non-magnetic fractions (deferized LF slag) separated in each stage and as whole process of magnetic separation are shown in Table 3.

The conclusion of this test revealed that the deferized LF slag fraction which can be obtained after a two stages magnetic separation is about 80%. This test will be useful in the designing stage of the technological process for LF slags preparation devoted to the investigation of plants vegetation in acidic soils ameliorate with LF slag in terms of leachability in plants.

Another characterization of $Fe_{metalic}$ content can be based on the results from the manual separation made in determining the chemical composition of slag LF - Table 4.

However, there are differences regarding the separated metal fraction in the two tests (first in pilot and second in the laboratory), the values are comparable and they will help us in the preparation of homogeneous lots of LF slag, either for sizing the requirements for material preparation and machinery for processing technology, or for

the procedure of quantitative determination of the chemical composition by XRF method.

The higher values recorded for "metal fraction" obtained in a pilot test is due to the fact that by this process are retained non-magnetic fraction around separating drum, as evidenced by the existence of a secondary stage of magnetic separation, when the magnetic fraction contains about 50% non-magnetic material. On can suppose that during this magnetic separation test, a certain amount of non-magnetic phase will passes and mixed with magnetic phase, and consequently a higher probability to found smaller content of $Fe_{metallic}$ in non-magnetic slag (useful for acidic soils improvement).

At the same time, during the laboratory scale test it was preferred the method of manual grinding and screening on 0.125 mm sieve, which can lead to a safe passing process of all loose fractions, excepting the plastic type of $Fe_{metallic}$. From this point of view it would be more correct to consider that while the magnetic drum method we separate a "magnetic fraction" encompassing even magnetic metallic compounds, the secondary method of grinding and fine sizing by sieving lead to a separation of a "metal fraction "in which only $Fe_{metalic}$ is included, consequently meaning a smaller fraction than of magnetic fraction. In addition, it was performed ultrasonically washing of the amount of Fe separated by grinding of sample P3 (1.05 g), in order to see how far reached magnetic separation using an ultrasonic bath.

After ultrasonically washing, it resulted an amount of 1.0467 g Fe containing about 95.9% Fe and we can conclude that for an accurate determination of chemical composition of LF slag, the best method for sample preparation and separation remains the manually grinding (in a mortar) followed by sizing on 0.125 mm sieve, while for up-scalling to pilot lots, the best processing method remains: crushing - sieving - magnetic separation on the magnetic drums.

3.2. Preliminary determination on LF slag leachability were interpreted according to Ministerial Order no. 95/2005 and shows that this type of slag waste does not fall in the category of "inert" waste, with a contents of Cd > 0.04 and Pb

content > 0.5 in leachate, but fall into the category of "hazardous" waste; additional measurements were made for the determination of leached Fe. The iron is an important element in fixing the vegetal tissues, but no presence of Fe in the slag leachate was detected.

3.3. Comparative analysis of the main LF slag indicators

Final tests for selected land lots for experiments included chemical analysis on which indicators were identified from the Table 5.

The reason for choosing only the chemical composition of this comparative analysis is due to the fact that the main objective is to neutralize acidic soils, which is done mainly by the chemical composition of LF slag as well as the slag grain-size distribution that is related to the speed and effectiveness of the neutralization. The data used in the analysis are compared in Table 5, including the characteristic data of the LF slag on the calcium carbonate equivalent (based on the CaO and MgO) to the all three production flows.

The data presented in the Table 5 shows that:

- LF slag corresponding to the three production flows has an average content of CaO, relatively equal.
- LF slag corresponding to the source 1 manufacturing cycle has reduced SiO_2 content and on that basis the LF slag basicity is higher than that corresponding to the other two slag sources.
- LF slag from the source 1 manufacturing cycle has the highest calcium carbonate equivalent.

Following the first analysis the corresponding to the manufacturing cycle LF slag of source 1 are more effective in treating acidic soil than the other two types of slag. However, in the frame of this analysis should be taken into account the variation range of chemical composition as well as of grain size of LF slag. The analysis showed that the range of variation for chemical composition and corresponding to the LF slag grain size distribution from source 1 of manufacturing cycle is about double than the corresponding LF slag from the other two production flows. Consequently, from this point

Table 5

The comparative analysis of basicity of LF slags versus their occurrence
Analiza comparativă a bazicității zgurilor LF în funcție de proveniență

Indicator of analysis *Indicator de analiză*	source 1 *sursa 1*	source 2 *sursa 2*	source 3 *sursa 3*
CaO mediu, %	55.27	56.71	55.68
SiO_2 mediu, %	14.67	23.04	23.68
Al_2O_3 mediu, %	5.18	5.28	7.37
Basicity index / Modul de bazicitate CaO/SiO_2	3.82	2.46	2.36
Basicity / Bazicitate, $(CaO+Al_2O_3)/SiO_2$	4.18	2.69	2.67
Calcium carbonate equivalent of LF slag (CCE) *Echivalentul în carbonat de calciu al zgurii LF (CCE)*	130.47	121.85	118.11

of view the chemical homogeneity and particle size of the slag is a weak point of the LF slag corresponding to the source 1.

4. Conclusion

Based on data obtained from particle size distribution analysis, specific gravity determination and LF slag chemical composition are characterized by:

I.A strong dusty character, meaning   an average of 85% -98% of particles bellow 0.06 mm and   2% - 12%   fraction over 0.09 mm for all investigated slags from three production sources.

II.The LF slags occurred from source 1 manufacturing cycle have in average of only 85% fraction of particles size bellow 0.06 mm, while the LF slag obtained at source 2 and source 3 have on average over 95% fraction bellow 0.06 mm.

III.The LF slags have an average bulk density in the range between 1.00 - 1.08 g/cm^3 in uncompacted condition, and between 1.60 -1.63 g/cm^3 in compacted condition, without significant differences among the three production sources.

IV. The LF slags have a high basicity: CaO = 50-53%, SiO$_2$ = 17-23% and black oxides content (Fe, Mn) < 3%.

V. The LF slags interpreted according to Ministerial Order no. 95/2005 show that the waste does not fall in the category of "inert" waste, with a content of Cd > 0.04 and Pb > 0.5 in leachate, but fall into the category of "non-hazardous" waste.

VI. The analyzed LF slags have had a calcium carbonate equivalent of 118 -130 and the highest value being recorded at source 1 manufacturing flow.

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