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RESEARCH ON THE USE OF SLAG FROM THE STEEL INDUSTRY IN AGRICULTURE AND FOR AMELIORATION ACIDIC SOILS

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Abstract. *The quantities of slag obtained world wide are increasing, which can lead to the removal of agricultural lands from the agricultural use and even to their pollution with various heavy metals. In accordance to statistical data, over 400 million tonnes of iron and steel slag are produced every year. Over the past 20 years, the recovery rate of these by-products from the steel industry has increased significantly. Innovative technological developments and the cooperation with other industries have brought the steel industry closer to reaching its Zero Waste goal. The slag obtained from the steel industry is a mixture of silica, calcium oxide, magnesium oxide and aluminium and iron oxides. Due to the characteristics of these secondary materials, respectively due to the high content of calcium oxide, they can be used on agricultural lands in order to neutralize the soil acidity and implicitly, for a better valorization of nutrients by the crop plants. Currently, the forecast given for the evolution of soils, both internationally and in our country, shows a continuous tendency of degradation of agricultural soils, agriculture being both a factor of degradation and a victim of the degradation caused by other socio-economic activities and also by agriculture itsel. In the last period, as a result of the application of agricultural technologies and due to the long-term fertilization with mineral Nitrogen fertilizers, a decrease in the soil's reaction has been recorded. The efficient use of these by-products of the steel industry as an amendment in agriculture in order to neutralize the soil's acidity, for improving crop productivity, for mitigating greenhouse gas emissions and for stabilizing heavy metals from contaminated soils, turns them into a value-added product in sustainable agriculture. This paper aims to present the influence of these materials resulted from the steel industry in improving the reaction of acidic soils, the influence they have on the main chemical properties of the soils and the influence on the production and quality of agricultural crops.*

Keywords*: steel industry residue, steel slag, soil fertility, recycling, soil amendaments, acid soil*

INTRODUCTION

With the rapid growth of industrialization, the increasing volume of by-products (slag), generated by the production of iron/steel, draws more attention to the need to recycle them more efficiently. The increasing quantities of slag that are deposited on the land cause the removal of more and more lands from the agricultural circuit and an increse in the costs of recycling them. As the population increases, the land available to dispose large quantities of slag in landfills is reduced, and the cost of disposal becomes higher. Moreover, soil filled with slag has become an important source of air, water and soil pollution, which adversely affects vegetation and human health (Branca and Colla, 2012).

In recent years, new technologies have been expanded, and some of them are under development in order to improve slag recovery rates. Recent research carried for increasing the use and valorization of slags in different fields of application, such as agriculture, has allowed the reduction of slag landfills and the conservation of natural resources (worldsteel.org).

Increasing the recovery and usage of slag in different fields of application, such as agriculture, is an imperative way for sustainable development (Ito,2015). Slags can be considered as oxide melts consisting mainly of oxides: CaO, SiO_2, Al_2O_3, MgO and FeO. In addition to those, slags may contain oxides of Mn, Na, Ti and Zi.

Depending on the concentration of the oxides, the steel slags are divided into basic and acidic. Most are the basic slags are classified according to the ratio of CaO : SiO_2, and in the case of acidic slags, they can be characterized by the ratio of SiO_2 : (FeO + MnO).

Table 1 presents the characteristics of the slags from the steel industry in different countries and in Romania.

Table 1

The characteristics of the slags from the steel industry in different countries and in Romania

Country	CaO	SiO_2	Al_2O_3	MgO	MnO	P_2O_5	Fe t	S
Turcia (Alanyali et al, 2006)	38,62	19,28	2,71	8,05	7,52	-	22,61	0,28
Japonia (Gao et al, 2015)	45,80	11,00	1,90	6,50	5,30	1,70	17,40	0,06
Brazilia (Oliviera et al, 2004)	45,20	12,20	0,80	5,50	7,10	-	18,80	0,07
Elveția (Tossavainen et al, 2007)	45	11,10	1,90	9,60	3,10	0,23	23,90	-
Franța (Waligora et al, 2010)	47,71	13,25	3,04	6,37	2,64	1,47	24,36	-
China (Rao et al, 2014)	42,92	11,51	1,40	4,36	4,04	0,83	23,74	0,07
România (ArcelorMittal, 2019)	40,90	34,70	14,10	7,70	0,14	-	-	0,01

INTERNATIONAL RESEARCH ON SLAG USE

The traditional use of slag, as a storage material, after the increse in steel production that started since the mid-1970s, has now reached maximum values, and pressure for natural resources and energy saving has led the steel industry to increase the recycling of this material, in order to enrich its application in different sectors (Nippon Slag Association, 2006).

In order to evaluate the possibility of using steel slag for soil improvement, research studies have been initiated in different countries.

In Japan, according to Nippon Slag Association statistics on slag use from 2012, slag consumption in the steel industry was of 1.390.000 tonnes for civil construction and 18.220.000 tonnes for cement production. The use of slag, as a raw material for the manufacture of fertilizers or for soil improvement, remains relatively low – 260.000 tonnes. However, slag fertilizers and the changes in soil that appear, as a result of their application can be considered as an ecological application method, in which the advantageous chemical properties of slags can be used to promote the growth of plants and yields of agricultural products as well as the decrease of the soil's acidic reaction. In Japan, in an experiment with rice cultivation where slag was applied with a high content of SiO_2, a yield of 6 tonnes/ha was obtained, with the absorption of N in rice of 100-120 kg/ha, while the amount of silicic acid required for rice is 10 times higher, respectively 1,000 - 1,200 kg/ha. The silicic acid absorbed by the roots of the rice plant is consumed to form glass cells called silica cells in the layers on the surface of the stems and leaves of the plant. "Silicate provides beneficial effects on plant health and soil structure, increases the phosphate mobility in the soil and the efficiency of phosphate fertilization" (Rex, 2002).

A field experiment conducted in China for two rice paddies (early and late paddy) to determine the individual and combined effects of steel slag and biochar amendments on CO_2,

CH_4, and N_2O emission, and rice productivity in a subtropical paddy field of China. The amendments did not significantly affect rice yield. It was observed that CO_2 was the main greenhouse gas emitted from all treatments of both paddies. Steel slag decreased the cumulative CO_2 flux in the late paddy. Biochar as well as steel slag + biochar treatment decreased the cumulative CO_2 flux in the late paddy and for the complete year (early and late paddy), while steel slag + biochar treatment also decreased the cumulative CH_4 flux in the early paddy. The biochar, and steel slag + biochar amendments decreased the global warming potential (GWP). Interestingly, the cumulative annual GWP was lower for the biochar (55,422 kg CO_2-eq ha^{-1}), and steel slag + biochar (53,965 kg CO_2-eq ha^{-1}) treatments than the control (68,962 kg CO_2-eq ha^{-1}). Total GWP per unit yield was lower for the combined application of steel slag + biochar (8951 kg CO_2-eq Mg^{-1} yield) compared to the control (12,805 kg CO_2-eq Mg^{-1} yield). This study suggested that the combined application of steel slag and biochar could be an effective long-term strategy to reduce greenhouse gases emission from paddies without any detrimental effect on the yield (Wang et al, 2019).

In Spain, a few studies have been carried out - a three-year research being carried out in the north of Spain on the use of steel slags on grazing lands, the results obtained being significant (Besga et al, 1996). The comparative study analyzed the soil changes induced by steel slag and those induced by traditional amendments. In this study, the influence on the soil's pH, on the Ca and Mg content in soil, on the saturation percentage of Al and on yields was taken into consideration. The increase in slag application rates linearly increased soil pH, which consequently led to a decreased Al solubility; this allowed the absorption of P, due to the change of insoluble forms in soluble ones. In addition, the soil content in Ca and Mg increased, resulting in an increased yield. On the other hand, the monitoring of Cd, Cr and Ni showed that, after applying the slag, there was no accumulation of heavy metals in the soil.

Currently, in India, the use of waste on agricultural land and not only the ones sourced from the steel industry, has gained attention due to a lack of adequate soil and due to the increased problems of industrial waste management. Annual slag production in India is of approximately 10 million tonnes. The use of these wastes in treating or improving the soil properties is of great interest as the black cotton soil covers an area of about 20% of the total area of land, with black cotton soil being considered a problematic soil due to the volume changes occurring with the variation of the moisture content. In this case, research was carried out by collecting samples and mixing with different percentages of slag in otder to create different mixtures.

Laboratory tests performed after applying different percentages of slag (5%, 10%, 15%, 20%, 25%) showed that with the increase of the percentage of slag used, the liquid limit decreased from 51 in the control variant to 39 in the variant where 25% slag was applied, the plastic limit increased gradually from 29.63% to 35.35% and the shrinkage limit increased from 14.56 in the control variant, to 28.5 when applying 25% furnace slag.

A preliminary laboratory study revealed that compared to blast furnace slag, electric arc furnace slag and ladle furnace slag, the Linz-Donawitz converter (LD) slag markedly decreased CH_4 production rate and increased microbial activity. In the greenhouse experiment, the LD slag amendment (2.0 Mg ha^{-1}) significantly ($p < 0.05$) increased grain yield by 10.3-15.2%, reduced CH_4 emissions by 17.8-24.0%, and decreased inorganic As concentrations in grain by 18.3-19.6%, compared to the unamended control. The increase in yield is attributed to the increased photosynthetic rates and increased availability of nutrients to the rice plant. Whereas, the decrease in CH_4 emissions could be due to the higher Fe availability in the slag amended soil, which acted as an alternate electron acceptor, thereby, suppressed CH_4 emissions. The more Fe-plaque formation which could adsorb more As and the competitive inhibition of As uptake with higher availability of Si could be the reason for the decrease in As uptake by rice cultivated with LD slag amendment (Gwon et al, 2018).

Contamination of rice (Oryza sativa) by Cd is of great concern. Steel slag could be used to amend Cd-contaminated soils and make them safe for cereal production. This work was conducted to study the effects of steel slag on Cd uptake and growth of rice plants in acidic and Cd-contaminated paddy soils and to determine the possible mechanisms behind these effects. Pot (rhizobag) experiments were conducted using rice plants grown on two acidic and Cd-contaminated paddy soils with or without steel slag amendment. Steel slag amendment significantly increased grain yield by 36-45% and root catalase activity, and decreased Cd concentrations in brown rice by 66-77% compared with the control, in both soils. Steel slag amendment also markedly decreased extractable soil Cd, Cd concentrations in pore-water and Cd translocation from roots to above-ground parts. It also significantly increased soil pH, extractable Si and Ca in soils and Ca concentrations in roots. Significant positive correlations were found between extractable soil Cd and Cd concentrations in rice tissues, but it was negatively correlated with soil pH and extractable Si. Calcium in root tissues significantly and negatively correlated with Cd translocation factors from roots to straw. Overall, steel slag amendment not only significantly promoted rice growth but decreased Cd accumulation in brown rice. These benefits appear to be related to improvements in soil conditions (e.g. increasing pH, extractable Si and Ca), a reduction in extractable soil Cd, and suppression of Cd translocation from roots to above-ground parts (He et al, 2017).

Iron- and steelmaking slag contains abundant Ca, Mg, and Fe, which are important elements in plant growth. It suggests that the slag could amend the soil which has elements Ca, Mg, and Fe in shortage. Researchers added steelmaking slag to Fe-deficient calcareous soils and planted corn with the modified soil and found that available Fe for plant growth was increased in soil (Zhang et al, 2020). The slag application in soil is a promising way to amend soil properties in the area where soil is not suitable for farming, which can be also considered slag as fertilizer (Li and Dai, 2018).

NATIONAL RESEARCH ON THE USE OF METALLURGICAL SLAG IN AGRICULTURE

The Romanian metallurgy sector currently has technological deficiencies in terms of collection, transport, storage and especially in terms of the exploitation of all categories of waste. Worldwide, about 80% of the residual steel is recovered, while in Romania, at present, only a maximum of around 48% of it is recovered, the rest being deposited.

Currently, the slag dumps from the metallurgical industry occupy an area of 300 hectares and contain over 100 million tonnes of waste, especially slags. In this context, the management of metallurgical waste, of slag in particular, plays an important role, as this waste is not only a source of pollution, but can also be a source of secondary raw materials. Therefore, efforts are being made to encourage the increased use of slag in areas where its efectiveness has been demonstrated, which would lead to a more efficient exploitation of natural resources.

In Romania, research has been carried out regarding the influence of metallurgical slags on the chemical properties of soils, especially on their pH, on the cation exchange capacity and on the degree of saturation bases. The experiments were carried out on several soil types by mixing 10 parts soil and one part slag and led to increases in the soil's reaction as following: in variant no.1 (*Frasin*) the reaction increased from 5.58 to 6.58, in variant no.2 (*Seaca*) the reaction increased from 6.19 to 6.79, in variant no.3 (*Piatra*) the reaction increased from 5.6 to 6.47 and in variant no.4 (*Drumul Mănăstirii*) the reaction increased from 5.47 to 6.41. The values obtained after the laboratory determinations show that applying steel slag as an amendment for acidic soils has a positive effect on the soil's pH. (Maria Cioroi, Licuta Nistor-Cristea, 2006).

Another research, where slag from the steel industry was used, with the aim was to capitalize on the basic potential of calcium oxide present in these slags and in order to verify if this can be an active amendment in the technologies used for the treatment of acidic soils. The experiment took place at the Moara Domnească Research and Development Farm located in the south est pert from Romania, where, in the last years, a decrease in the pH reaction of the chromic luvisols, from 6.4 to 5-5.5, was recorded.

Determination of the soil's pH reaction for the 0-20 cm depth, following the application of different doses of slag, showed an increase of the soil's pH value from 5.67 in the control variant to 6.12, when applying a dose of 5 tonnes/ha. For the depth of 20-40 cm, the increase of the soil's pH value was significant, determining the increase with one unit of pH, starting with the first year of application, respectively from 5.7 in the control variant to 6.72 in the variant with 5 t/ha of slag.

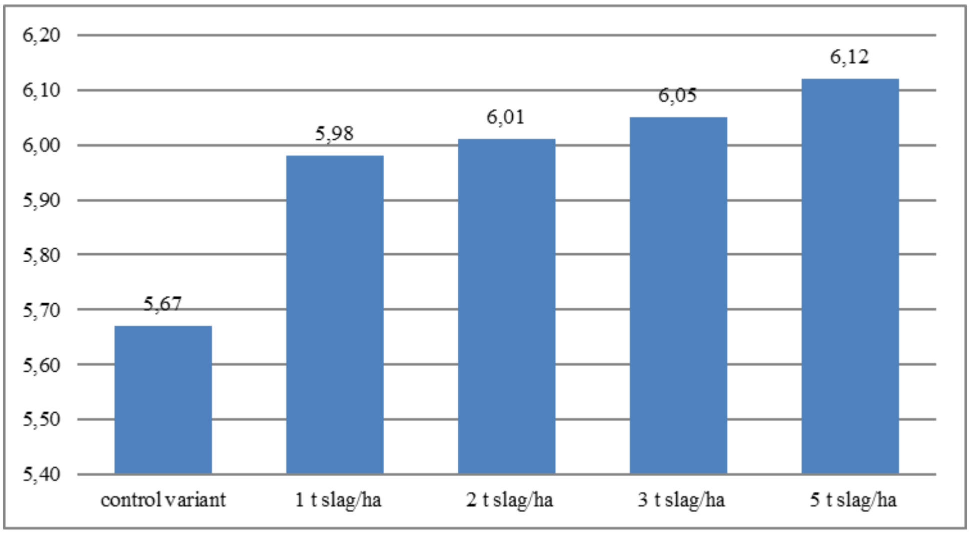

Figure 1-The effect of slag on the soil reaction (depth 0-20 cm)
(Mihalache.M. et al., 2016)

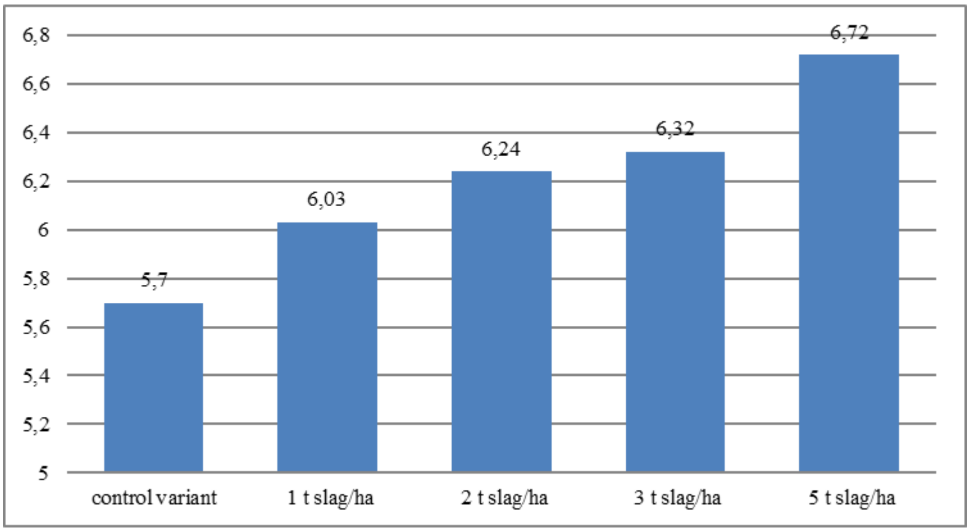

Figure 2-The effect of slag on the soil reaction (depth 20-40 cm)
(Mihalache.M. et al., 2016)

The application of the slag did not lead to a significant increase of the total nitrogen content in the soil, on the 0-20 cm depth the increse registered being from 0.147 to 0.157, when applying a dose of 1t/ha. Significant increases in potassium content and soil organic carbon content were recorded. The heavy metal determinations made after the application of the slag in the experimental field recorded a content below the maximum permissible limits.

The application of the slag in the experiments from Moara Domnească on the chromic luvisols resulted in significant and very significant increases on the productions of the cultivated plants (Mihalache et al, 2016).

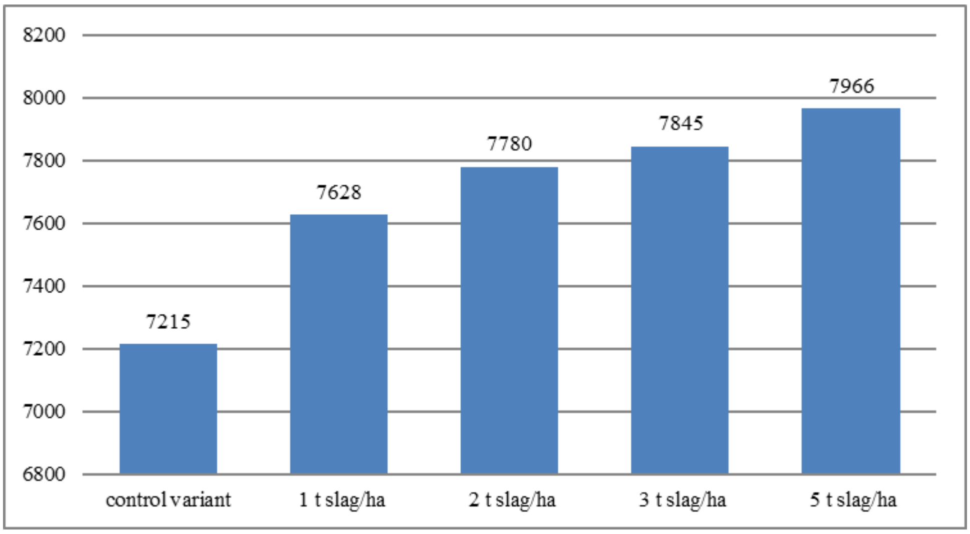

Figure 3-The influence of slag on the maise yield (Mihalache. M. et al., 2016)

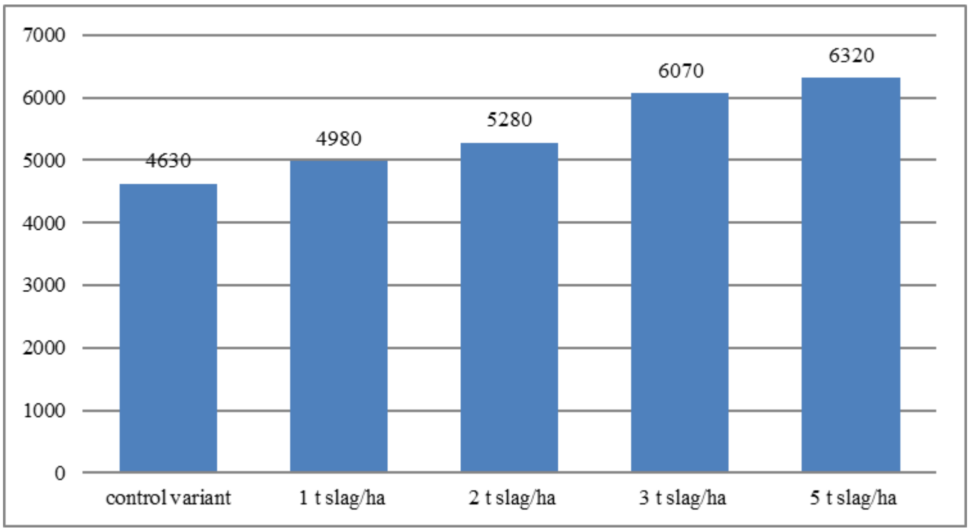

Figure 4-The influence of slag on the wheat yield –

(Mihalache. M. et al., 2016)

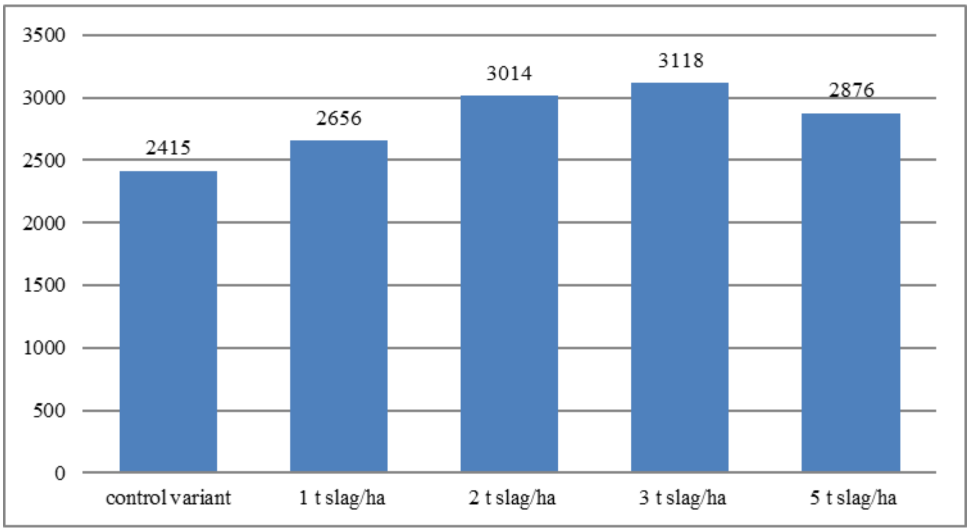

Figure 5-The influence of slag on the soybean yield

(Mihalache. M. et al., 2016)

CONCLUSIONS

The presence of a high content of calcium carbonate in the soils and the use of these residues from the steel industry is recommended in order to correct the soil's acidity.

Steel slag has a positive effect that is given by it's influence in changing the soil's pH, but especially by the changes that occur in the soil as a result of acidity correction.

Research conducted worldwide and in Romania has shown that the application of slags from the steel industry on agricultural lands has led to an increase in the soil's reaction, the soil's organic matter content, while also leading to a better utilization of nutrients by crop plants.

The use of slags from the steel industry in agriculture produces not only economic but also environmental benefits. A more efficient exploitation of natural resources can be achieved both in the steelmaking process and in agriculture.

Obviously, fertilizers applied to the soil should provide nutrients, and should not have adverse effects on the environment and on human, animal and plant health. Therefore, many studies have focused in particular on the behavior and immobilization of the main heavy metals (eg. Cr, Cd, Cu, Pb) in the soil, in order to obtain a more efficient and sustainable use of the slag from the steel industry in agriculture, while also improving the recycling methods for these by-products.

By applying different doses of slag, significant increases of production were observed in the case of the experimental crops - maise, wheat and soybean.

Recovery of valuable substances from slag is another suitable way of management. In fact, the current usage of the slag is still in the initial stage. Its application in soil treatment has great potential, and great efforts are demanded in the field.

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